PART - II

SALTS OF SUBSTITUTED MALONIC ACIDS

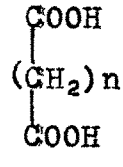
INTRODUCTION

(SALTS)

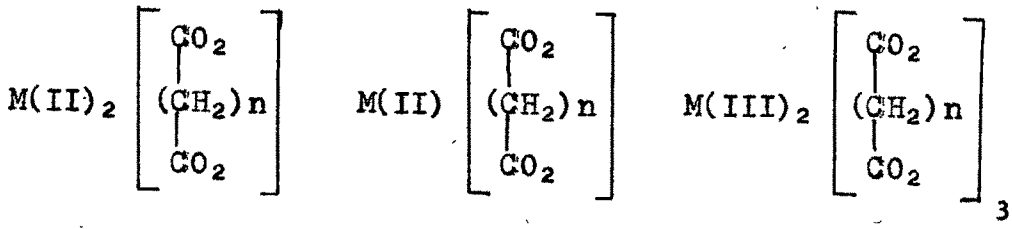
INTRODUCTION

I.1. General :

Many studies have been reported in the literature on the aliphatic dicarboxylic acids (I) and their salts (II) and complexes (III).



(I)



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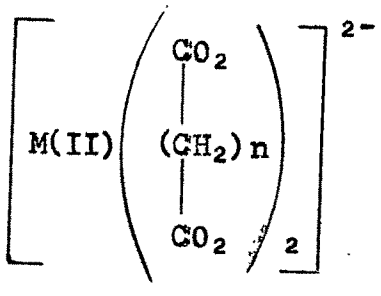
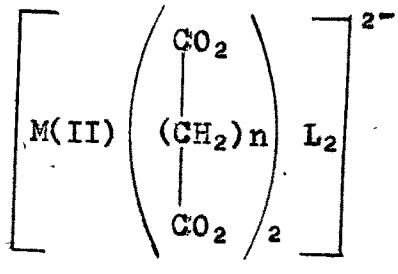
(II)



(a)



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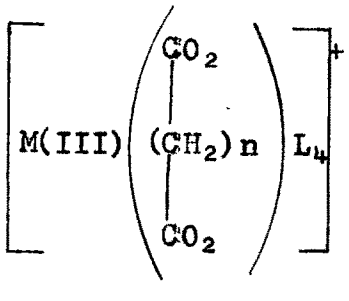

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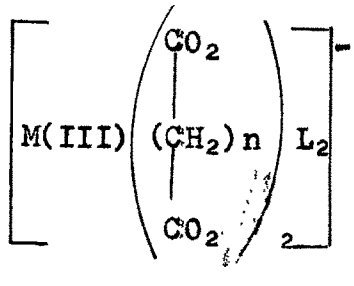

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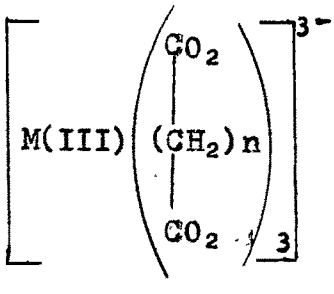

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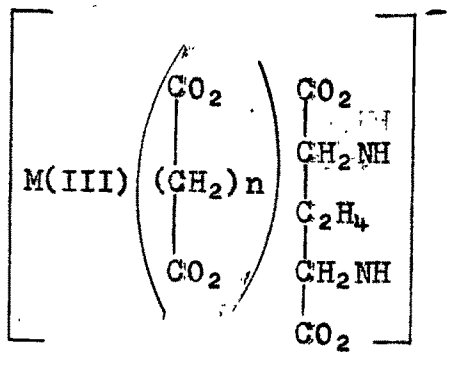
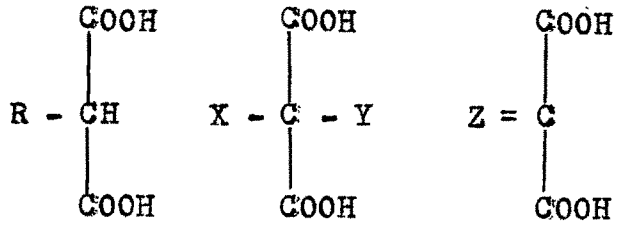


(f)

(III)

These include investigations on malonic acid (I,II,III ; n = 1) in relation to oxalic acid (I,II,III ; n = 0), succinic acid (I,II,III ; n = 2), etc. Many substituted malonic acids (IV) are also reported in the literature. These are tabulated in table A.

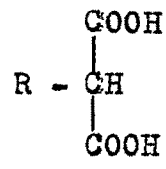


(a) (b) (c)

(IV)

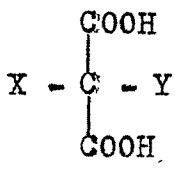
Table A

(I)



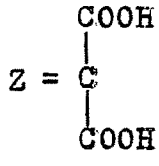
R =	References
CH_3	1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18.
C_2H_5	19,20,21,22,23,24,25,26,27,28,29.
$n\text{-}C_3H_7$	30,31.
$i\text{-}C_4H_9$	32,33,34,35.
$n\text{-}C_5H_{11}$	36.
$i\text{-}C_5H_{11}$	37,38.
$i\text{-}C_6H_{13}$	39,40.
$n\text{-}C_7H_{15}$	41.
$n\text{-}C_{11}H_{23}$	42.
$n\text{-}C_{18}H_{37}$	43,44.
$n\text{-}C_{22}H_{45}$	42,43.
$n\text{-}C_{28}H_{57}$	45.
$n\text{-}C_{30}H_{61}$	45.
$n\text{-}C_{32}H_{65}$	45.
$n\text{-}C_{34}H_{69}$	45.
$n\text{-}C_{36}H_{73}$	45.
Cl	46,47,48,49,50.
Br	47,51,52,53.
C_6H_5	54.
$(C_6H_5)_2CH$	55.
$C_6H_5CH_2$-	56,57,58,59,60,61,62,63.
$C_6H_5CH_2CH{=}CH$-	64,65.

(II)

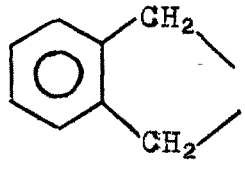


X =	Y =	References
CH_3	CH_3	22,66,67,68,69,70,71,72,73, 74,75,76,77.
C_2H_5	C_2H_5	78,79,80,81,82,83.
C_2H_5	n-C_3H_7	84.
n-C_3H_7	n-C_3H_7	30.
$C_{18}H_{37}$	$C_{18}H_{37}$	85.
C_2H_5	Cl	86.
C_2H_5	Br	87.
Cl	Cl	47,88.
Br	Br	47,88,89,90.
I	I	90.
F	F	91.
Cl	Br	92.
CH_3	C_6H_5	93,94.
CH_3	$C_6H_5CH_2$-	95.
C_6H_5	$C_6H_5CH_2$-	93.
C_6H_5	CH_2=$CHCH_2$-	93,96,97.
$C_6H_5CH_2$	$C_6H_5CH_2$	57,58,98,99,100.

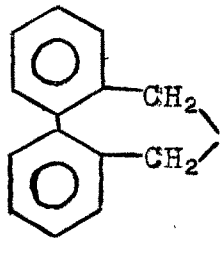
(III)



Z =	References
C_6H_5CH	60,101,102,103,104,105,106.
$2\text{-}ClC_6H_4CH$	107.
$2\text{-}BrC_6H_4CH$	107.
$2\text{-}IC_6H_4CH$	107.
$2\text{-}NO_2C_6H_4CH$	108.
$3\text{-}NO_2C_6H_4CH$	104,108.
$4\text{-}NO_2C_6H_4CH$	103,104,108.
$2,4\text{-}(NO_2)_2C_6H_3CH$	109.
$C_6H_5CH_2CH_2CH$	64,65.
$C_6H_5CH{=}CHCH$	65,104,110,111,112,113,114.
$2\text{-}NO_2C_6H_4CH{=}CHCH$	115.
$4\text{-}NO_2C_6H_4CH{=}CHCH$	115.



116,117,118.



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Although many substituted malonic acids are known, only few references are found in the literature on their salts and complexes. A brief review on the malonic and substituted malonic acids and their salts and complexes is presented below.

I.2. Malonic and substituted malonic acids :

Various mono and di-substituted derivatives of malonic acids are presented in table A. Besides, polymeric substances from malonic ester[120,121] and polymeric amino malonic acid[122] are also known.

Infra red spectra of the esters, amides and sodium or potassium salts of malonic and other dicarboxylic acids have been widely studied.[123,124,125,126,127,128,129,130,131,132,133] Frequencies were assigned to the > C=O, >C-O- and -OH groups and the influences of chelation and of sodium/potassium atom on the spectrum were discussed. Infra red spectra of the substituted malonic acids and their esters (substituent = alkyl, chloro, bromo, phenyl, nitro, benzylidene etc.) were also investigated.[134,135,136,137,138] Hadzi and Sheppard[139] studied the infra red and proton magnetic resonance spectra of the malonic and other dicarboxylic acids and their deuterated derivatives and discussed the dimeric nature of the acids. Edsall and Ghazanfar,[140] Edsall and Myers[141] investigated the Raman spectra

of malonic and other dicarboxylic acids, their sodium salts and their deuterated products and discussed the influence of substituents, ionisation and deuteration on the Raman lines.

Baly and Schaefer[142] studied the absorption spectra of substituted malonic acids in aqueous, alcoholic, alcoholic HCl and alcoholic NaOEt solutions. Graham and Macbeth[143] studied the absorption spectra of the esters and amides of the substituted bromo malonic acids in aqueous, alcoholic and alkali solutions, compared them with those of the bromo and nitro paraffins and discussed the labile nature of bromine in these compounds.

Other studies on malonic and substituted malonic acids and their derivatives include thermal decomposition,[144] viscosity,[145] electrical conductivity,[146,147,148] catalytic activity[149] etc. From the measurements of the electrical conductivity of the solutions and potentiometric titrations were derived the dissociation constants of substituted malonic acids.[150,151,152,153,154,155]

I.3. Salts and complexes of cobalt with malonic and substituted malonic acids :

Raymond et al.[156] prepared hydrated cobalt malonate. Thomas[157] observed that the double salt of malonic acid with potassium and cobalt (III) was unstable. Krebbs et al.[158] found that although the double salt of oxalic acid with potassium and cobalt (III) could be

partially resolved with starch, such resolution could not be achieved with the corresponding malonate. Kapadia[159] attempted to prepare the coordination polymer from potassium cobalt (II) malonate and formaldehyde.

Complex cations containing cobalt (III), malonate and a coordinating ligand such as ethylene diamine, diethylene triamine, 1,10-phenanthroline etc. have been prepared.[160,161,162,163] Similarly complex anions containing cobalt (III), malonate and nitrite or ethylene diamine diacetate were obtained.[164,165] Salts of cobalt (III) with malonic (or oxalic) acid and glycine were also obtained.[166,167]

Dwyer, Reid and Garvan[168] prepared the complex anion containing cobalt (III), malonate and ethylene diamine and studied its resolution into its opical isomers. Percival and Wardlaw[169] prepared the oxy-complex anion containing oxy-cobalt and malonate and carried out cryoscopic and conductivity measurements to study its dissociation. Formation of intermediates in the reaction between cobalt and malonic acid were studied by the temperature jump method by Cavasino.[170]

van Saun and Douglas[171] resolved the complex anion of cobalt (III) with ethylenediamine diacetate and malonate and studied their circular dichroism and proton magnetic resonance spectra. Yoneda and Morimoto[172,173] prepared the complex ions of cobalt with malonic acid and ethylene diamine and studied their PMR spectra. They observed a quartet and attributed it to CH_2 group.

They observed that the proton signal disappeared on keeping the sample in D_2O overnight. Buckingham[174] studied the PMR spectra of such complexes and used them to differentiate between cis and trans isomers. PMR spectra of cobalt malonates were also discussed by Milner and Pratt.[175] Absorption spectra, circular dichroism and optical retatory dispersion of the anionic cobalt malonate complex were studied by Hidaka et al.[176] and Douglas et al.[177] Ranadae and Subba Rao[178] determined the magnetic moment of cobalt malonate. Ion exchange studies using ^{60}Co were carried out by Monk,[179] Manning and Monk[180] and Suzuki.[181] The dissociation constants of cobalt malonates have been determined by potentiometric, spectrophotometric and conductometric methods.[182,183,184,185] Calorimetric studies[186] led to the evaluation of the enthalpy of formation of cobalt malonate.

Kopple and Miller[187] studied the reduction of cobalt (III) malonate cation with bivalent chromium.

Cobalt salts of the substituted malonic acids have been prepared recently[188] and their relative stabilities are considered.

I. 4. <u>Salts and complexes of copper with malonic and substituted malonic acids</u> :

Wendt[189] studied the formation of copper malonate by the relaxation method using a sound tube. Suzuki[190,191] determined the dissociation constant of copper malonate from EMF measurements. Riley[192] and Ives and Riley[193,194]

prepared copper salts of malonic and alkyl malonic acids, determined their electrical conductivity in solution and discussed the effect of alkyl substitution on the stability of the anionic copper malonate complex. Ives[195] also studied the effect of pyridine on the conductivity of copper malonate in solution. Kapadia[159] attempted to prepare the coordination polymer from potassium copper malonate and formaldehyde.

The dissociation constants of copper malonates in solution were investigated by spectrophotometric, potentiometric, polarographic, conductometric and kinetic methods.[182,185,196,197,198,199,200] The dissociation constants of the salts and complexes of copper with substituted malonic acids were studied by potentiometric and polarographic methods.[188,201,202]

From the calorimetric studies of copper malonate and oxalate, their enthalpy of formation was calculated.[186,20

Rajan[204] investigated ESR spectra of the salts of copper with malonic and other dicarboxylic acids and discussed the pairing of copper atoms. Graddon[205] studied the absorption spectra of the salts of copper with malonic and substituted malonic acids.

Many studies[178,206,207,208,209,210,211] were made on the magnetic moment of the salts and complexes of malonic and other dicarboxylic acids. Low values were obtained in many cases and were related to the spin-pairing resulting from the dimeric and polymeric chains.

I.5. Salts and complexes of nickel with malonic and substituted malonic acids :

The formation of nickel malonate has been investigated by pressure jump, temperature jump and relaxation methods.[212,213,214,215] Kapadia[159] attempted to prepare the coordination polymer from potassium nickel malonate and formaldehyde.

Products of the thermal decomposition of nickel malonate have been considered by thermogravimetry.[216] Calorimetric studies[186,203] of nickel malonate led to the determination of its enthalpy of formation.

The dissociation constants of nickel malonates have been determined by spectrophotometric and potentiometric methods.[184,185,198,217,218] The dissociation constants of the nickel salts of the substituted malonic acids were studied by potentiometric, conductometric and polarographic methods.[188,194,201] The stability constants of the complexes of nickel with dithio malonic, dithio oxalic and dithio carbonic acids were determined by spectrophotometric method[219] and their relative stability was considered.

The magnetic moment of the nickel salts of malonic and other dicarboxylic acids were determined by Ranadae and Subba Rao[178] and by Ploquin and Vergneau[211]. PMR spectra were discussed by Milner and Pratt.[175]

I.6. Salts and complexes of iron with malonic and substituted malonic acids :

Weinland and Loebich[220] observed that iron in complex iron (III) malonates could be in the cation or the anion. Jaeger and Gromingen[221] found that the complexes of alkali metal and iron (III) with malonic acid could be obtained in racemic form only. Complex-forming ability of malonic acid with iron was investigated in relation to the catalytic oxidation of iron.[222,223]

The formation of iron malonates and their stability constants were determined by spectrophotometric, potentiometric, polarographic and solubility methods.[224,225,226,227,228]

The absorption spectra of the anionic iron (II) malonate complexes were studied by Hatfield[229] and ligand field parameters were determined.

Magnetic moments and Mossbauer spectra of the complex iron malonates have been widely studied in recent years.[230,231,232,233,234,235] The magnetic, X-ray and thermogravimetric studies on the hydrated iron (II) malonate[236] are also reported.

I.7. Salts and complexes of manganese with malonic and substituted malonic acids :

Formation of the complex manganese (III) malonates was studied by various workers.[237,238,239,240] Conductometric, spectrophotometric and pH studies[241]

showed the presence of 1:1 salt in the solution of manganese (II) malonate.

The dissociation of manganese malonates in solution was studied by ion exchange and kinetic methods[242,243] and by spectrophotometric and potentiometric methods.[184,185]

Dingle[244] observed d-d and charge-tranfer transitions in the absorption spectrum of manganese malonate and Cohn and Townsend[245] studied its ESR spectrum. Gray(Jr.)[246] and Ranadae and Subba Rao[178] determined the magnetic moment of the malonate and oxalate complexes of manganese.

I. 8. Salts and complexes of zinc with malonic and substituted malonic acids :

Rowlands and Monk[247] studied the solvent extraction of the zinc salts of malonic and other dicarboxylic acids and proposed two stages of association.

The dissociation constants of the zinc salts of malonic and substituted malonic acids were determined by conductometric and potentiometric methods.[188,190,194,198,201]

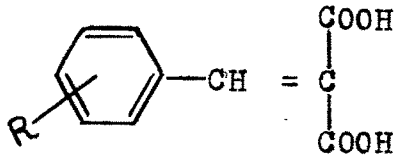
Investigations were carried out on the thermal decomposition of the zinc salts of malonic and other decarboxylic acids in the pure state and as a deposit on coal.[248]

Thermodynamic calculations have been made by Nair[249] on the zinc salts of malonic and other dicarboxylic acids and by George[250] on the salts of first transition series metals with various ligands.

Mata Prasad et al.[251] studied the diamagnetism of the salts of zinc,magnesium etc. of malonic acid.

1.10. Present work :

Kapadia investigated in our laboratories the possibility of polymerising the anionic malonate complexes containing bivalent transition metal ions such as copper, nickel or cobalt, using formaldehyde solutions. Many difficulties were encountered in establishing the reaction and identifying the products. It was considered essential to know the nature of the salts and complexes of substituted malonic acids. The literature survey showed that only a few compounds were known. Hence it was suggested that salts and complexes of substituted malonic acids be prepared and studied. For that purpose benzylidene malonic acid and its derivatives can be selected. The acids decompose on heating into cinnamic acid and its derivatives.



Therefore the salts of these acids should be prepared under different conditions. It would provide comparison for the different methods adopted.

The phenyl group in the acid would cause steric hindrance and would result in disturbing the coplanarity of the molecular system. It was believed that the present investigations would help in assessing the deflection due to the steric factor.

Further the preparation of salts and complexes of these acids should assist in correlating the behaviour of malonic and substituted malonic acids in their salts and complexes.

With these considerations inview, it was proposed

1. to prepare benzylidene and substituted benzylidene malonic acids;
2. to prepare their salts with transition metal ions of the first transition series, by different methods;
3. to prepare their double salts (complexes) with potassium and transition metal ions ;
4. to evaluate the effect of steric hindrance on the planarity of the acid molecule ;
5. to determine the electrical conductivity, magnetic susceptibility and absorption spectra of the salts and complexes prepared.

The investigations carried out as above and the results obtained are presented and discussed in the following pages.

EXPERIMENTAL

(SALTS)

II. EXPERIMENTAL

II. 1. General :

1 (i) . Reagents and solvents :

All reagents and solvents used were of C.P. grade or better.

1 (ii). Analysis of new products :

Analysis of new products were obtained for metal, nitrogen, carbon and hydrogen as required (by micro methods).

1 (iii). Melting point :

All melting points recorded herein are uncorrected.

1 (iv). UV Spectra :

The ultra-violet absorption spectra of the compounds in solution were prepared from the readings of the Beckman Spectrophotometer model DU using 10 mm matched quartz cells.

1 (v) . Visible spectra :

Absorption spectra in the visible region of some compounds in nujol mull were obtained for us on a

recording spectrophotometer.

1 (vi). Electrical conductivity :

Electrical conductivity of some compounds in solution was measured on Toshniwal's conductivity bridge model CL-01 using platinum electrodes.

1 (vii) Magnetic susceptibility :

Magnetic susceptibility of the transition metal compounds was determined at room temperature on Gouy's magnetic balance using calibrated pyrex glass tubes.

1 (viii) Paper chromatography :

An attempt was made to fractionate a few of the "basic " and "acidic " salts by ascending paper chromatographic technique, using filter paper strips (1.5 " x 10 ").

1 (ix) Thin-layer chromatography :

TLC technique was adopted in studying the nature of some "acidic " and "basic " salts using silica gel.

The observations and results of the various determinations for different compounds are given at appropriate places in the following pages.

II.2. Substituted malonic acids (benzylidene malonic acids) :

(i) Benzylidene malonic acid :

The method of Fujiwara and Naruse[252] was adopted for its preparation.

Benzaldehyde (1 mole), malonic acid (1 mole) and piperidine (0.1 mole) were mixed and heated on a water bath for about 1 1/2 hours. The mixture changed into a homogeneous liquid in about fifteen minutes and after twenty minutes a white solid began to separate. At the end the whole reaction mixture became solid. It was dissolved in sodium bicarbonate solution and extracted with ether for removing unreacted benzaldehyde. On acidification of the aqueous solution white solid was obtained, which was washed with water, dried and recrystallised from hot water as white needles, m.p. 195-6°.

It is soluble in hot water, acetone, alcohol, chloroform and ether and sparingly soluble in benzene and petroleum ether.

E-values of the compound in methanol and alkali solutions in the ultraviolet region of the spectrum are presented in table 1.

(ii) Ortho-chlorobenzylidene malonic acid :

It was prepared according to the method of Pandya and Pandya[253].

Table 1

E-Value of the benzylidene malonic acid in different solvents in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-value	
	in methanol	in alkali
360	13.15	0.00
352	15.79	0.00
344	15.79	0.00
336	23.68	0.00
328	36.84	0.00
320	85.51	0.00
312	181.6	0.00
304	355.2	77.66
296	545.9	334.9
288	710.4	601.9
280	787.9	864.0
272	747.1	957.9
264	618.3	854.3
256	460.7	659.9
248	322.3	475.6
240	226.1	359.1
232	230.2	

Ortho-chlorobenzaldehyde (1 mole), malonic acid (1 mole) were heated on a water bath for 4 hours. After about 2 hours, a white solid began to separate. At the end the whole reaction mixture was taken in sodium bicarbonate solution. It was extracted with ether for removing unreacted ortho-chlorobenzaldehyde. The aldehyde-free filtrate was acidified with hydrochloric acid and left overnight. The precipitates were filtered, washed with cold water and dried. The product was recrystallised from ether + petroleum ether as white crystals, m.p.192°.

It is soluble in hot water, acetone, alcohol and ether and insoluble in benzene, chloroform and petroleum ether.

E-values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 2.

(iii) Para-chlorobenzylidene malonic acid :

It was prepared by the method of Pandya and Pandya.[253]

Para-chlorobenzaldehyde (1mole), malonic acid (1 mole) and alcohol (15 ml.) were heated on a water bath for about 4 hours. After about 2 hours, a white solid began to separate. At the end the whole reaction mixture was taken in sodium bicarbonate solution. It was extracted with ether for removing unreacted para-chlorobenzaldehyde. The aldehyde-free filtrate was acidified with hydrochloric acid and left overnight. The precipitates were filtered,

Table 2

E-Values of the substituted benzylidene malonic acid in different solvents in the ultra-violet region (360- 220 mμ)

Wave-length (mμ)	E-value			
	o-chlorobenzylidene malonic acid		p-chlorobenzylidene malonic acid	
	in methanol	in alkali	in methanol	in alkali
360	0.00	0.00	8.06	0.00
352	0.88	0.00	14.51	0.00
344	2.20	0.00	29.02	11.27
336	9.42	0.00	40.31	14.08
328	16.73	0.00	80.63	18.31
320	46.22	0.00	161.3	28.16
312	99.47	45.11	319.3	129.4
304	165.9	121.9	499.9	309.8
296	259.7	243.9	640.6	521.1
288	376.3	414.6	728.8	746.4
280	484.2	579.2	730.5	926.6
272	541.4	657.2	661.2	922.2
264	506.1	597.4	540.1	802.8
256	405.0	475.5	414.4	631.0
248	290.5	366.6	314.5	471.8
240	220.1	292.6	258.0	401.4
232	345.5	426.9	322.5	

washed with cold water and dried. The product was recrystallised from dilute alcohol as white crystals, m.p.197-8^{0}(decomp.)

It is soluble in hot water,alcohol,ether and acetone and insoluble in benzene and chloroform.

E-values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 2.

(iv) Para-methoxybenzylidene malonic acid :

It was prepared by the method of Pandya and Vahidya[254].

Anisaldehyde (1 mole),malonic acid (1 mole) and few drops of piperidine were heated on a water bath for 4 hours. The mixture changed into a homogeneous liquid in 1 1/2 hours and in another 1/2 hour yellow solid began to separate and at the end the whole reaction mixture became solid. It was dissolved in sodium bicarbonate solution and extracted with ether for removing unreacted anisaldehyde. On acidification yellow solid was obtained. It was filtered,washed with cold water,dried and recrystallised from dilute alcohol as yellow crystals, m.p. 195-6^{0}.

It is soluble in hot water,alcohol,acetone and insoluble in benzene,petroleum ether,ether and chloroform.

E-values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 3.

Table 3

E-Values of the substituted benzylidene malonic acid in different solvents in the ultra-violet region (360 - 220 mμ)

Wave-length (mμ)	E-value			
	p-methoxybenzylidene malonic acid		p-nitrobenzylidene malonic acid	
	in methanol	in alkali	in methanol	in alkali
360	50.29	0.00	52.38	235.3
352	96.27	0.00	89.30	358.8
344	175.3	0.00	148.8	482.2
336	310.6	0.00	232.1	576.8
328	510.1	22.61	308.5	637.5
320	732.8	134.2	398.7	658.8
312	862.2	427.6	458.3	623.4
304	826.2	631.4	488.1	566.6
296	751.3	852.5	488.1	447.0
288	653.7	1013.0	466.7	358.8
280	520.8	999.7	429.7	285.9
272	360.7	815.6	386.9	262.3
264	229.9	532.8	341.7	270.5
256	143.6	296.0	300.0	317.7
248	125.0	164.4	271.4	382.3
240	237.1	124.9	264.3	470.6
232	458.3	263.1	276.2	

(v) Para-nitrobenzylidene malonic acid :

The method of Marckwald[255] was adopted for its preparation.

Para-nitrobenzaldehyde (1.2 g.), malonic acid (1.4 g.), ammonia (1.2 g.) were mixed and alcohol(2.5 ml.) was added to it. The whole reaction mixture was heated to 60-70° for 2 hours. In first 1/2 hour, the mixture remained clear and then suddenly became turbid. The reaction mixture was taken into dilute sodium hydroxide solution and unreacted para-nitrobenzaldehyde was removed by filtration. On acidification of the filtrate with dilute sulphuric acid, a yellow solid was obtained. It was filtered, washed with water and dried. The product was recrystallised from dilute alcohol as yellow crystals melting at 227° with decomposition.

It is sparingly soluble in hot water and soluble in all common organic solvents except benzene and chloroform.

E-values of the compound in methanol and alkali solutions in the ultra-violet region of the spectrum are presented in table 3.

II.3. Co-salt of substituted malonic acids :

(i) Partition method :

Substituted malonic acid dissolved in ether was added to the solution of cobalt acetate dissolved in water (ligand: metal:: 1.5 : 1). The solution was

stirred at low speed for two hours at low temperature and left overnight. The ether layer was separated and the precipitates were filtered,washed with water,acetone and ether and dried.

(ii) Acetate method :

The alcoholic solution of substituted malonic acid and aqueous solution of cobalt acetate were mixed (ligand:metal:: 1.2 : 1) and refluxed for about 6 hours. They were filtered,washed with water,alcohol and ether and dried.

(iii) Carbonate method :

To a dilute solution of the substituted malonic acid in water, cobalt carbonate was added (ligand:metal:: 1.2 : 1). The solution was boiled for half an hour and filtered hot to remove unreacted cobalt carbonate. The filtrate was taken in an evaporating dish and concentrated on a water bath. The precipitates were filtered,washed with water,acetone and ether and dried.

(iv) Hydroxide method :

The aqueous solution of substituted malonic acid and suspension of cobalt hydroxide in water were mixed (ligand: metal:: 1.2 : 1). The resulting solution was boiled for half an hour and filtered hot for removing unreacted residue. The filtrate was concentrated in an evaporating dish on a water bath. The precipitates were filtered,washed with water,alcohol and ether and dried.

The cobalt hydroxide used was made by adding hot solution of sodium hydroxide to a boiling solution

of cobalt sulphate. The precipitates were filtered, washed several times with hot water and used without drying.

They are slightly soluble in water, alcohol, pyridine and dimethyl formamide and insoluble in all other common organic solvents. The colour, m.p., analysis etc. of these complexes are presented in tables 4 to 8. E-values of the compounds in methanol in the ultra-violet region of the spectrum are presented in tables 9 to 13. The mass magnetic susceptibilities and diamagnetic corrections of these complexes are given in tables 14 to 18.

II.4. Cu-salts of substituted malonic acids :

(i) Partition method :

Substituted malonic acid dissolved in ether was added to the solution of copper acetate dissolved in water (ligand:metal:: 1.5 : 1). The solution was stirred at low speed for two hours at low temperature and left overnight. The ether layer was separated and the precipitates were filtered, washed with water, acetone and ether and dried.

(ii) Acetate method :

The alcoholic solution of substituted malonic acid and aqueous solution of copper acetate were mixed (ligand: metal :: 1.2 : 1) and refluxed for about six hours. They were filtered, washed with water, alcohol and ether and dried.

(iii) Carbonate method :

To a dilute solution of substituted malonic acid

Table 4

Cobalt salts of benzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Co found	% C reqd.	% Co reqd.
1.	Co BM (PA)	Partition	Pink	> 300	$C_{10}H_{14}O_8Co$	37.57	18.61	37.41	18.35
2.	Co BM (CA)	Carbonate	Pink	> 300	$C_{23}H_{38}O_{30}Co_5$	25.11	27.20	25.36	27.06
3.	Co BM (HY)	Hydroxide	Pink	> 300	$C_{10}H_{24}O_{15}Co_3$	20.78	32.58	21.40	31.52

Table 5

Cobalt salts of ortho-chlorobenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Co found	% C reqd.	% Co reqd.
1.	Co ClM(PA)	Partition	Pink	>300	$C_{10}H_{12}O_{7.5}ClCo$	36.21	16.20	34.64	17.00
2.	Co ClM(HS)	Acetate	Pink	>300	$C_{10}H_{14}O_{8.5}ClCo$	33.66	15.15	32.94	16.16
3.	Co ClM(CA)	Carbonate	Pink	>300	$C_{10}H_{12}O_{7.5}ClCo$	35.68	16.04	34.64	17.00
4.	Co ClM(HY)	Hydroxide	Pink	>300	$C_{10}H_{10}O_{6.5}ClCo$	36.14	18.09	36.55	17.94

Table 6

Cobalt salts of para-chlorobenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Co found	% C reqd.	% Co reqd.
1.	Co ChM (PA)	Partition	Pink	> 300	$C_{10}H_{14}O_{8.5}ClCo$	33.41	15.55	32.94	16.16
2.	Co ChM (HS)	Acetate	Pink	> 300	$C_{10}H_9O_6ClCo$	38.78	18.45	37.57	18.44
3.	Co ChM (CA)	Carbonate	Pink	> 300	$C_{10}H_9O_6ClCo$	39.05	17.70	37.57	18.44
4.	Co ChM (HY)	Hydroxide	Pink	> 300	$C_{10}H_{16}O_{10.5}ClCo_2$	26.74	25.50	26.24	25.76

Table 7

Cobalt salts of para-methoxybenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Co found	% C reqd.	% Co reqd.
1.	Co MM (PA)	Partition	Pink	> 300	$C_{11}H_{12}O_7Co$	41.58	17.58	41.93	18.71
2.	Co MM (HS)	Acetate	red pink shinnggg plates	> 300	$C_{11}H_{12}O_7Co$	42.03	17.96	41.93	18.71
3.	Co MM (CA)	Carbonate	red pink plates	> 300	$C_{11}H_{12}O_7Co$	41.90	18.39	41.93	18.71
4.	Co MM (HY)	Hydroxide	Pink	> 300	$C_{22}H_{54}O_{32}Co_5$	24.12	26.23	23.49	26.20

Table 8

Cobalt salts of para-nitrobenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Co found	% C reqd.	% Co reqd.
1.	Co NM (PA)	Partition	Pink	≫ 300	$C_{10}H_{13}O_{10}NCo$	32.48	15.92	32.79	16.10
2.	Co NM (HS)	Acetate	Pink	> 300	$C_{10}H_{11}O_9NCo$	34.85	15.80	34.49	16.93
3.	Co NM (CA)	Carbonate	Pink	> 300	$C_{10}H_{13}O_{10}NCo$	32.81	15.86	32.79	16.10
4.	Co NM (HY)	Hydroxide	Pink	≫ 300	$C_{30}H_{27}O_{25}N_3Co_4$	33.90	21.69	33.83	22.14

Table 9

E-Values of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E- Value		
	Co BM (PA)	Co BM (CA)	Co BM (HY)
360	6.25	4.63	9.67
352	8.33	4.63	9.67
344	10.42	5.55	14.67
336	15.63	6.48	20.66
328	20.83	12.03	26.67
320	36.46	19.45	36.34
312	83.33	35.19	57.99
304	189.5	74.08	85.00
296	333.3	120.3	117.3
288	445.8	159.2	149.4
280	512.5	182.4	188.7
272	518.7	178.7	196.2
264	477.1	175.0	216.0
256	406.2	180.5	237.3
248	307.3	161.1	220.0
240	255.2	151.1	223.4
232	302.1	183.3	306.7

Table 10

E-values of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-value			
	Co C1M(PA)	Co C1M(HS)	Co C1M(CA)	Co C1M(HY)
360	10.97	15.53	5.15	9.00
352	6.10	18.49	5.15	9.00
344	9.76	22.29	5.15	9.00
336	13.42	26.35	8.82	12.67
328	20.73	35.14	14.71	19.00
320	39.64	58.64	29.42	41.01
312	79.27	98.65	67.66	91.66
304	132.30	158.80	117.70	131.70
296	201.20	231.10	182.40	176.00
288	271.90	310.90	247.80	226.70
280	333.00	375.00	305.90	274.00
272	365.30	406.10	332.40	323.30
264	366.50	398.70	322.10	306.00
256	330.60	371.00	272.00	265.10
248	263.40	306.80	213.20	213.30
240	235.40	281.00	181.70	185.00
232	359.80	437.80	275.70	260.00

Table 11

Optical density of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	Optical density			
	Co ChM(PA)	Co ChM(HS)	Co ChM(CA)	Co ChM(HY)
360	0.017	0.010	0.012	0.023
352	0.020	0.013	0.012	0.023
344	0.025	0.020	0.014	0.023
336	0.037	0.032	0.023	0.024
328	0.062	0.056	0.038	0.036
320	0.117	0.102	0.080	0.058
312	0.245	0.220	0.180	0.120
304	0.430	0.402	0.335	0.225
296	0.590	0.570	0.478	0.320
288	0.718	0.708	0.600	0.402
280	0.749	0.775	0.651	0.447
272	0.718	0.740	0.639	0.432
264	0.622	0.695	0.590	0.395
256	0.520	0.618	0.512	0.340
248	0.395	0.478	0.400	0.260
240	0.344	0.428	0.329	0.210
232	0.482	0.602	0.418	0.245

Table 12

E-Values of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-value			
	Co MM(PA)	Co MM(HS)	Co MM(CA)	Co MM(HY)
360	25.00	11.11	12.79	9.72
352	38.16	20.64	23.13	16.66
344	69.15	45.24	50.00	30.56
336	129.6	100.8	106.3	58.33
328	227.0	203.1	203.2	105.4
320	354.0	347.6	340.0	170.1
312	483.7	498.4	471.9	234.7
304	538.3	569.8	535.7	252.1
296	563.9	610.2	561.3	268.0
288	552.7	593.6	539.4	258.3
280	490.4	514.2	465.7	229.2
272	406.6	396.8	351.3	180.5
264	342.2	295.2	250.0	140.9
256	302.7	223.8	182.5	113.2
248	261.9	174.6	140.6	89.58
240	317.1	212.6	182.5	107.6
232	539.5	403.2	346.9	194.5

Table 13

E-Values of the compounds in methanol in the ultraviolet region (360-220 mμ)

Wavelength (mμ)	E-value			
	Co NM(PA)	Co NM(HS)	Co NM(CA)	Co NM(HY)
360	64.18	69.69	78.68	72.01
352	111.5	115.2	135.3	122.0
344	179.0	183.3	212.0	196.0
336	253.3	261.3	301.5	276.0
328	322.9	333.4	382.3	354.0
320	369.9	378.7	439.7	412.0
312	383.7	394.7	464.7	432.0
304	368.2	378.7	450.1	416.0
296	327.4	344.0	411.8	368.1
288	273.6	300.0	349.3	304.0
280	214.8	250.0	295.6	242.0
272	174.3	206.1	261.7	200.8
264	153.3	196.2	244.1	179.3
256	164.2	204.6	264.0	180.8
248	178.3	213.6	279.5	198.0
240	212.1	244.0	328.1	232.0
232	267.5	312.9	426.5	284.1

Table 14

Magnetic susceptibility of cobalt salts of benzylidene malonic acid

No.	Complex	Mass Magnetic susceptibility $\chi_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Co-atom) $\chi \times 10^6$
1.	Co BM (PA)	35.00	34.9	- 143
2.	Co BM (CA)	48.55	34.6	- 86
3.	Co BM (HY)	50.56	34.7	- 76

Table 15

Magnetic susceptibility of cobalt salts of ortho-chlorobenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. ($^\circ$C)	Diamagnetic corrections (per Co-atom) $\chi \times 10^6$
1.	Co ClM (PA)	30.07	32.8	- 155
2.	Co ClM (HS)	28.97	32.5	- 165
3.	Co ClM (CA)	31.78	32.2	- 155
4.	Co ClM (HY)	35.75	30.4	- 144

Table 16

Magnetic susceptibility of cobalt salts of para-chlorobenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{o}C)	Diamagnetic corrections (per Co-atom) $\chi \times 10^6$
1.	Co ChM (PA)	29.33	32.2	- 165
2.	Co ChM (HS)	32.87	33.7	- 139
3.	Co ChM (CA)	32.52	33.7	- 139
4.	Co ChM (HY)	40.85	33.8	- 96

Table 17

Magnetic susceptibility of cobalt salts of para-methoxybenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{o}C)	Diamagnetic corrections (per Co-atom) $\chi \times 10^6$
1.	Co MM (PA)	34.79	33.9	- 138
2.	Co MM (HS)	37.20	32.0	- 138
3.	Co MM (CA)	33.51	32.5	- 138
4.	Co MM (HY)	47.03	30.2	- 96

Table 18

Magnetic susceptibility of cobalt salts of para-nitrobenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{0}C)	Diamagnetic corrections (per Co-atom) $\chi \times 10^6$
1.	Co NM (PA)	30.64	33.7	- 148
2.	Co NM (HS)	33.75	33.8	- 138
3.	Co NM (CA)	32.03	33.7	- 148
4.	Co NM (HY)	35.74	33.6	- 100

in water,copper carbonate was added (ligand:metal:: 1.2 :1). The solution was boiled for half an hour and filtered hot to remove unreacted copper carbonate. The filtrate was taken in an evaporating dish and concentrated on a water bath. The precipitates were filtered,washed with water,acetone and ether and dried.

(iv) Hydroxide method :

The aqueous solution of substituted malonic acid and suspension of copper hydroxide in water were mixed (ligand:metal:: 1.2 : 1). The resulting solution was boiled for half an hour and filtered hot for removing unreacted residue. The filtrate was concentrated in an evaporating dish on a water bath. The precipitates were filtered,washed with water,alcohol and ether and dried.

The copper hydroxide used was made by adding cold solution of sodium hydroxide to a cold solution of copper sulphate. The precipitates were filtered,washed several times with cold water and used without drying.

Besides the usual blue coloured products, green coloured products were obtained in a few cases.

They are slightly soluble in water,alcohol and dimethyl formamide and insoluble in all other common organic solvents (Grass green coloured salts are also insoluble in water).

The colour,m.p.,analysis etc. of these complexes are presented in tables 19 to 23. E-values of the compounds in methanol in the ultra-violet region of

Table 19

Copper salts of benzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Cu found	% C reqd.	% Cu reqd.
1.	Cu BM (HS)	Acetate	Grass green	280 (decomp)	$C_{10}H_8O_5Cu$	45.07	22.68	44.20	23.39
2.	Cu BM (CA) (Green)	Carbonate	Grass green	291 (decomp)	$C_{10}H_7O_{4.5}Cu$	46.48	23.00	45.72	24.19
3.	Cu BM (CA) (Blue)	Carbonate	Blue	> 300	$C_{12}H_{30}O_{22}Cu_3$	19.61	27.25	20.10	26.59
4.	Cu BM (HY) (Green)	Hydroxide	Grass green	280 (decomp)	$C_{10}H_7O_{4.5}Cu$	46.34	23.38	45.72	24.19
5.	Cu BM (HY) (Blue)	Hydroxide	Blue	> 300	$C_{10}H_{32}O_{19}Cu_3$	18.44	29.28	18.57	29.47

Table 20

Copper salts of ortho-chlorobenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Cu found	% C reqd.	% Cu reqd.
1.	Cu ClM (PA)	Partition	Blue	244 (decomp)	$C_{30}H_{37}O_{22}Cl_3Cu_2$	36.66	13.21	36.64	12.93
2.	Cu ClM (HS)	Acetate	Light blue	256 (decomp)	$C_{30}H_{32}O_{19.5}Cl_3Cu_2$	39.98	12.99	38.41	13.55
3.	Cu ClM (CA)	Carbonate	Greenish blue	243 (decomp)	$C_{30}H_{39}O_{23}Cl_3Cu_2$	35.41	13.13	35.99	12.70
4.	Cu ClM (HY)	Hydroxide	Blue	235 (decomp)	$C_{20}H_{37}O_{22.5}Cl_2Cu_3$	27.42	20.73	26.71	21.20

Table 21

Copper salts of para-chlorobenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Cu found	% C reqd.	% Cu reqd.
1.	Cu ChM (PA)	Partition	Grass green	298 (decomp)	$C_{15}H_{11.5}O_{7.5}Cl_{1.5}Cu$	41.77	14.43	42.05	14.84
2.	Cu ChM (HS)	Acetate	Grass green	278 (decomp)	$C_{15}H_{11.5}O_{7.5}Cl_{1.5}Cu$	41.50	14.52	42.05	14.84
3.	Cu ChM (HY)	Hydroxide	Green	295 (decomp)	$C_{15}H_{11.5}O_{7.5}Cl_{1.5}Cu$	42.58	14.47	42.05	14.84

Table 22

Copper salts of para-methoxybenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Cu found	% C reqd.	% Cu reqd.
1.	Cu MM (PA)	Partition	Grass green	246 (d)	$C_{11}H_{13}O_{7.5}Cu$	39.72	18.90	40.18	19.33
2.	Cu MM (HS)	Acetate	Grass green	271 (d)	$C_{77}H_{64}O_{38}Cu_6$	46.57	19.83	46.73	19.27
3.	Cu MM (CA)	Carbonate	Grass green	279 (d)	$C_{66}H_{54}O_{32}Cu_5$	47.45	18.92	47.34	18.98
4.	Cu MM (HY)	Hydroxide	Grass green	267 (d)	$C_{44}H_{40}O_{23}Cu_3$	46.76	17.00	46.89	16.92

Table 23

Copper salts of para-nitrobenzylidene malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Cu found	% C reqd.	% Cu reqd.
1.	Cu NM (PA)	Partition	Blue	251 (decomp)	$C_{10}H_{11}O_9NCu$	34.75	16.90	34.05	18.02
2.	Cu NM (HS) (Green)	Acetate	Grass green	280 (decomp)	$C_{10}H_7O_7NCu$	38.19	19.17	37.91	20.06
3.	Cu NM (HS) (Blue)	Acetate	Blue	254 (decomp)	$C_{10}H_{11}O_9NCu$	34.77	17.65	34.05	18.02
4.	Cu NM (CA)	Carbonate	Blue	248 (decomp)	$C_{10}H_{12}O_{9.5}NCu$	33.10	16.97	33.20	17.57
5.	Cu NM (HY)	Hydroxide	Blue	253 (decomp)	$C_{10}H_{10}O_{8.5}NCu$	34.61	19.00	34.93	18.48

the spectrum are presented in tables 24 to 26. The mass magnetic susceptibilities and diamagnetic corrections of these complexes are given in tables 27 to 31.

II.5. Ni-salts of substituted malonic acids :

Attempts to prepare salts of nickel by partition or acetate method were unsuccessful.

(i) Carbonate method :

To a dilute solution of substituted malonic acid in water, nickel carbonate was added (ligand:metal:: 1.2 : 1). The solution was boiled for half an hour and filtered hot to remove unreacted nickel carbonate. The filtrate was taken in an evaporating dish and concentrated on a water bath. The precipitates were filtered, washed with water, acetone and ether and dried.

(ii) Hydroxide method :

The aqueous solution of substituted malonic acid and suspension of nickel hydroxide in water were mixed (ligand :metal:: 1.2 :1). The resulting solution was boiled for half an hour and filtered hot for removing unreacted residue. The filtrate was concentrated in an evaporating dish on a water bath. The precipitates were filtered, washed with water, alcohol and ether and dried.

The nickel hydroxide used was made by adding hot solution of sodium hydroxide to a boiling solution of nickel sulphate. The precipitates were filtered, washed several times with hot water and used without drying.

Table 24

E-Values of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-value	
	Cu BM(CA) (Blue)	Cu BM(HY) (Blue)
360	3.41	3.20
352	4.92	3.90
344	6.06	4.96
336	8.71	5.67
328	13.63	9.57
320	16.66	12.76
312	25.00	19.51
304	38.64	30.50
296	55.31	48.22
288	78.41	73.07
280	109.8	105.0
272	152.3	152.5
264	207.6	201.8
256	246.9	236.9
248	242.4	236.9
240	234.5	223.5
232	246.2	227.0

Table 25

E-Values of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-Value			
	Cu ClM(PA)	Cu ClM(HS)	Cu ClM(CA)	Cu ClM(HY)
360	3.33	9.48	7.00	6.25
352	3.33	11.20	13.00	6.25
344	3.33	11.20	15.00	8.75
336	13.33	20.68	19.00	10.80
328	28.00	28.44	32.00	16.88
320	58.66	49.14	60.00	31.25
312	120.00	84.47	107.00	54.38
304	193.3	137.9	172.0	87.50
296	283.3	193.9	245.0	131.2
288	385.3	256.8	320.0	179.4
280	459.9	314.7	380.0	225.0
272	492.6	349.1	411.0	261.3
264	479.3	356.9	410.0	272.6
256	411.3	334.4	371.0	261.3
248	341.4	288.7	308.0	234.4
240	314.7	277.6	288.0	210.6
232	439.9	372.4	410.0	243.8

Table 26

E-Values of the compounds in methanol in the ultra-violet region (360 - 220 mμ)

Wave-length (mμ)	E- Value				
	Cu NM(PA)	Cu NM(HS) (Green)	Cu NM(HS) (Blue)	Cu NM(CA)	Cu NM(HY)
360	45.00	43.05	49.99	49.99	50.00
352	84.37	76.38	79.86	84.72	95.00
344	145.6	135.4	138.9	147.9	170.0
336	234.4	216.6	216.6	231.2	272.0
328	330.0	311.1	298.6	319.5	385.0
320	412.5	381.9	375.0	401.4	482.0
312	467.6	429.1	436.1	450.0	548.0
304	482.5	459.7	454.7	472.2	560.0
296	457.5	461.7	447.9	450.6	533.0
288	412.5	438.8	424.2	409.8	478.0
280	364.4	424.2	388.2	364.6	416.0
272	314.5	406.9	376.3	322.9	360.0
264	288.1	408.3	381.9	306.9	323.0
256	286.3	404.1	409.8	313.8	316.0
248	288.7	388.9	401.4	315.3	324.0
240	308.1	396.5	430.5	340.4	339.0
232	356.3	465.2	555.5	409.8	370.0

Table 27

Magnetic susceptibility of copper salts of benzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{o}C)	Diamagnetic corrections (per Cu-atom) $\chi \times 10^6$
1.	Cu BM (HS)	4.18	34.7	- 111
2.	Cu BM (CA) (Green)	4.18	34.7	- 106
3.	Cu BM (CA) (Blue)	7.74	34.5	- 96
4.	Cu BM (HY) (Green)	5.55	31.9	- 106
5.	Cu BM (HY) (Blue)	8.14	34.0	- 90

Table 28

Magnetic susceptibility of copper salts of ortho-chlorobenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^0C)	Diamagnetic corrections (per Cu-atom) $\chi \times 10^6$
1.	Cu ClM (PA)	4.27	31.9	- 227
2.	Cu ClM (HS)	4.47	33.9	- 214
3.	Cu ClM (CA)	4.38	32.0	- 232
4.	Cu ClM (HY)	5.52	30.6	- 138

Table 29

Magnetic susceptibility of copper salts of para-chlorobenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Cu-atom) $\chi \times 10^6$
1.	Cu ChM (PA)	3.42	31.1	- 190
2.	Cu ChM (HS)	3.46	33.9	- 190
3.	Cu ChM (HY)	3.51	34.1	- 190

Table 30

Magnetic susceptibility of copper salts of para-methoxybenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $X_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Cu -atom) $X \times 10^6$
1.	Cu MM (PA)	3.60	32.5	- 138
2.	Cu MM (HS)	6.11	32.0	- 142
3.	Cu MM (CA)	5.98	32.5	- 144
4.	Cu MM (HY)	5.45	30.3	- 165

Table 31

Magnetic susceptibility of copper salts of para-nitrobenzylidene malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Cu-atom) $\chi \times 10^6$
1.	Cu NM (PA)	5.06	33.8	- 138
2.	Cu NM (HS) (Green)	5.14	33.6	- 117
3.	Cu NM (HS) (Blue)	4.84	33.6	- 138
4.	Cu NM (CA)	5.02	33.7	- 143
5.	Cu NM (HY)	5.73	33.8	- 133

They are slightly soluble in water, alcohol and dimethyl formamide and insoluble in all other common organic solvents.

The colour, m.p., analysis etc. of these complexes are presented in tables 32 and 33. Optical densities of the compounds in methanol in the ultra-violet region of the spectrum are presented in tables 34 and 35. The mass magnetic susceptibilities and diamagnetic corrections of these complexes are given in tables 36 and 37.

II.6. Zn-salts of substituted malonic acids :

Partition method :

Substituted malonic acid dissolved in ether was added to the solution of zinc acetate dissolved in water (ligand :metal:: 1.5:1). The solution was stirred at low speed for two hours at low temperature and left overnight. The etherial layer was separated and the precipitates were filtered, washed with water, acetone and ether and dried.

They are slightly soluble in dimethyl formamide and pyridine, insoluble in water and all other common organic solvents (Zn NM is sparingly soluble in water).

The colour, m.p., analysis etc. of these complexes are presented in table 38.

II.7. Mn-salts of substituted malonic acids :

Partition method :

Substituted malonic acid dissolved in ether was

Table 32

Nickel salts of substituted malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Ni found	% C reqd.	% Ni reqd.
1.	Ni BM (HY)	Hydroxide	Light green	> 300	$C_{10}H_{32}O_{19}Ni_3$	18.97	27.94	18.99	27.86
2.	Ni ClM (CA)	Carbonate	Light green	> 300	$C_{10}H_{17}O_{10}ClNi$	31.55	14.60	30.68	15.01
3.	Ni ClM (HY)	Hydroxide	Light green	> 300	$C_{10}H_{12}O_{7\cdot5}ClNi$	32.71	17.80	34.65	16.95
4.	Ni ChM (HY)	Hydroxide	Light green	> 300	$C_{10}H_{10}O_{6\cdot5}ClNi$	35.17	18.51	36.56	17.88
5.	Ni ChM (CA)	Carbonate	Light green	> 300	$C_{12}H_{21}O_{18}ClNi_3$	22.04	26.83	21.67	26.50

Table 33

Nickel salts of substituted malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Ni found	% C reqd.	% Ni reqd.
1.	Ni MM (CA)	Carbonate	Pale green	> 300	$C_{12}H_{20}O_{14}Ni_2$	28.30	23.38	28.49	23.24
2.	Ni MM (HY)	Hydroxide	Pale green	> 300	$C_{33}H_{64}O_{37}Ni_5$	29.22	21.43	29.44	21.83
3.	Ni NM (CA)	Carbonate	Light green	>> 300	$C_{40}H_{68}O_{47}N_4Ni_3$	30.87	11.84	31.32	11.49
4.	Ni NM (HY)	Hydroxide	Light green	> 300	$C_{10}H_{13}O_{10}NNi$	32.91	15.58	32.82	16.05

Table 34

Optical density of the compounds in methanol in the ultra-violet region (360- 220 mμ)

Wave-length (mμ)	Optical density				
	Ni BM(HY)	Ni ClM(CA)	Ni ClM(HY)	Ni ChM(HY)	Ni ChM(CA)
360	0.014	0.029	0.007	0.014	0.007
352	0.015	0.033	0.007	0.017	0.010
344	0.020	0.036	0.007	0.020	0.014
336	0.030	0.043	0.007	0.028	0.018
328	0.043	0.056	0.014	0.043	0.027
320	0.062	0.085	0.038	0.090	0.040
312	0.104	0.155	0.100	0.210	0.070
304	0.204	0.240	0.185	0.390	0.127
296	0.320	0.345	0.300	0.560	0.175
288	0.432	0.455	0.420	0.705	0.225
280	0.498	0.548	0.520	0.788	0.251
272	0.507	0.580	0.569	0.790	0.268
264	0.520	0.565	0.555	0.805	0.306
256	0.560	0.530	0.505	0.800	0.334
248	0.530	0.450	0.418	0.660	0.292
240	0.518	0.440	0.349	0.590	0.284
232	0.645	0.680	0.490	0.735	

Table 35

Optical density of the compounds in methanol in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	Optical density			
	N1 MM(CA)	N1 MM(HY)	N1 NM(CA)	N1 NM(HY)
360	0.026	0.025	0.082	0.115
352	0.038	0.040	0.134	0.205
344	0.072	0.075	0.212	0.340
336	0.132	0.140	0.305	0.495
328	0.248	0.270	0.395	0.635
320	0.395	0.435	0.455	0.740
312	0.551	0.595	0.478	0.782
304	0.625	0.680	0.460	0.748
296	0.669	0.782	0.419	0.660
288	0.682	0.850	0.356	0.545
280	0.622	0.810	0.300	0.428
272	0.511	0.702	0.256	0.342
264	0.418	0.532	0.235	0.290
256	0.350	0.412	0.244	0.302
248	0.302	0.317	0.260	0.331
240	0.357	0.370	0.304	0.387
232	0.595	0.618	0.390	0.478

Table 36

Magnetic susceptibility of nickel salts of substituted malonic acid

No.	Complex	Mass magnetic susceptibility $X_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Ni-atom) $X \times 10^6$
1.	Ni BM (HY)	23.42	35.0	- 90
2.	Ni ClM (CA)	11.48	31.9	- 181
3.	Ni ClM (HY)	13.99	30.9	- 155
4.	Ni ChM (HY)	13.57	35.1	- 144
5.	Ni ChM (CA)	20.95	34.7	- 88

Table 37

Magnetic susceptibility of nickel salts of substituted malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{0}C)	Diamagnetic corrections (per Ni-atom) $\chi \times 10^6$
1.	Ni MM(CA)	18.45	35.1	- 106
2.	Ni MM(HY)	16.60	34.9	- 119
3.	Ni NM(CA)	9.70	33.9	- 220
4.	Ni NM(HY)	14.05	33.9	- 148

Table 38

Zinc salts of substituted malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Zn found	% C reqd.	% Zn reqd.
1.	Zn BM (PA)	Partition	White	> 300	$C_{10}H_{11}O_{6.5}Zn$	41.11	21.11	39.95	21.77
2.	Zn ClM (PA)	Partition	White	294 (d)	$C_{10}H_9O_6ClZn$	37.69	19.75	36.82	20.06
3.	Zn MM (PA)	Partition	White	> 300	$C_{11}H_{11}O_{6.5}Zn$	43.32	20.09	42.25	20.93
4.	Zn NM (PA)	Partition	Pale yellow	> 300	$C_{10}H_{11}O_9NZn$	33.82	18.46	33.86	18.45

added to the solution of manganese acetate dissolved in water (ligand :metal:: 1.5:1). The solution was stirred at low speed for two hours at low temperature and left overnight. The etherial layer was separated and the precipitates were filtered,washed with water,acetone and ether and dried.

They are slightly soluble in water,alcohol, pyridine and dimethyl formamide and insoluble in all other common organic solvents.

The colour,m.p., analysis etc. of these complexes are presented in table 39. E-values of the compounds in methanol in the ultra-violet region of the spectrum are presented in table 40. The mass magnetic susceptibilities and diamagnetic corrections of these complexes are given in table 41.

II.8. Complex salts :

(a) K-Co-salts of substituted malonic acids :

To a solution of the substituted malonic acid (3 g.) in water (100 ml.), potassium carbonate (0.915 g.) was added slowly,followed by cobalt carbonate(0.786 g.) with heating and stirring. The mixture was boiled for half an hour and filtered hot for removing unreacted residue. The filtrate was concentrated in an evaporating dish on a water bath. The mother liquor was decanted off and the crystalline mass was carefully washed with water, acetone and ether and dried. Further crops were recovered

Table 39

Manganese salts of substituted malonic acid

No.	Complex	Method	Colour	M.P. (°C)	Formula	Analysis			
						% C found	% Mn found	% C regd.	% Mn regd.
1.	Mn BM (PA)	Partition	Pale yellow	>300	$C_{10}H_{10}O_6Mn$	42.61	19.63	42.72	19.54
2.	Mn ClM (PA)	Partition	White	296 (decomp)	$C_{10}H_9O_6ClMn$	38.04	18.22	38.05	17.41
3.	Mn ChM (PA)	Partition	Pale yellow	>300	$C_{10}H_7O_5ClMn$	40.21	18.74	40.34	18.46
4.	Mn MM (PA)	Partition	Pale yellow	>300	$C_{11}H_{12}O_7Mn$	42.35	18.44	42.46	17.66
5.	Mn NM (PA)	Partition	Pale yellow	> 300	$C_{10}H_{12}O_{9.5}NMn$	33.28	16.11	34.01	15.56

Table 40

E-Values of the compounds in methanol in the ultra-violet region (360- 220 mμ)

Wave-length (mμ)	E- Value				
	Mn BM(PA)	Mn ClM(PA)	Mn ChM(PA)	Mn MM(PA)	Mn NM(PA)
360	0.00	2.10	0.0000	1.1181	156.3
352	0.00	2.10	0.00	1.81	229.2
344	0.00	2.10	0.00	5.44	302.1
336	0.00	6.17	0.00	22.75	369.8
328	0.00	8.23	0.00	67.94	411.4
320	0.00	15.43	0.84	185.7	429.1
312	0.00	47.32	48.14	380.4	397.9
304	69.21	90.51	249.1	507.2	348.9
296	245.1	164.5	401.2	596.0	285.4
288	418.2	272.6	565.8	647.6	211.4
280	567.2	376.4	669.7	593.2	151.0
272	599.9	437.1	643.6	466.5	113.5
264	528.8	423.7	511.0	303.4	111.4
256	392.2	356.9	356.3	176.6	138.6
248	254.8	272.6	228.0	99.63	176.0
240	158.6	211.8	152.0	86.04	213.5
232	129.8	303.4	164.6	194.7	245.8

Table 41

Magnetic susceptibility of manganese salts of substituted malonic acid

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{0}C)	Diamagnetic corrections (per Mn-atom) $\chi \times 10^6$
1.	Mn BM (PA)	54.11	30.0	- 122
2.	Mn ClM (PA)	47.79	30.2	- 139
3.	Mn ChM (PA)	50.29	31.8	- 129
4.	Mn MM (PA)	48.87	30.9	- 138
5.	Mn NM (PA)	42.86	30.2	- 143

from the mother liquor. It was recrystallised from dilute alcohol.

They are soluble in water and alcohol and insoluble in all other common organic solvents.

The colour, m.p., analysis etc. of these compounds are presented in table 42. E-values of the compounds in water in the ultra-violet region of the spectrum are presented in table 43. The mass magnetic susceptibilities and diamagnetic corrections of these compounds are given in table 44. Electrical resistances of the compounds in water are presented in table 45.

(b) K-Cu-salts of substituted malonic acids :

To a solution of substituted malonic acid (3 g.) in water (100 ml.), potassium carbonate (0.915 g.) was added slowly, followed by copper carbonate (0.819 g.) with heating and stirring. The mixture was boiled for half an hour and filtered hot for removing unreacted residue. The filtrate was concentrated in an evaporating dish on a water bath. The mother liquor was decanted off and the crystalline mass was carefully washed with water, acetone and ether and dried. It was recrystallised from dilute alcohol.

In the preparation of KCu ChM two products were obtained. One is coloured grass green and the other one blue. The blue one on boiling with water for about 10 minutes, changed into grass green one.

Table 42

Complex salts of substituted malonic acid with potassium and cobalt

No.	Complex	Colour	M.P. (°C)	Formula	Analysis			
					% C found	% Co found	% C reqd.	% Co reqd.
1.	KCo BM	Pink	> 300	$K_2CoC_{20}H_{18}O_{11}$	42.02	10.56	42.03	10.31
2.	KCo ClM	Pink	271 (decomp)	$K_2CoC_{20}H_{16}O_{11}Cl_2$	37.71	9.43	37.49	9.20
3.	KCo ChM	Pink	> 300	$K_2CoC_{20}H_{12}O_9Cl_2$	39.41	9.67	39.73	9.75
4.	KCo MM	Pink	> 300	$K_2CoC_{22}H_{22}O_{13}$	41.68	9.64	41.83	9.33
5.	KCo NM	Pink	> 300	$K_2CoC_{20}H_{20}O_{17}N_2$	34.41	8.49	34.43	8.45

Table 43

E-Values of the compounds in water in the ultra-violet region (360- 220 mμ)

Wave-length (mμ)	E- value				
	KCo BM	KCo ClM	KCo ChM	KCo MM	KCo NM
360	4.81	5.21	2.23	3.26	164.3
352	4.81	5.21	2.23	3.26	236.3
344	4.81	5.21	2.23	5.86	316.4
336	5.77	6.94	2.23	17.58	384.5
328	5.77	8.68	2.23	58.59	432.6
320	5.77	15.63	5.58	175.8	450.2
312	19.23	53.81	50.21	371.1	432.6
304	96.16	104.2	234.3	494.8	384.5
296	283.6	182.3	373.8	559.9	324.5
288	471.2	299.4	524.4	598.9	256.4
280	623.2	401.0	622.6	536.9	196.3
272	658.8	464.4	597.0	416.9	161.8
264	586.5	444.4	474.2	263.7	161.8
256	452.0	377.6	329.2	146.5	189.9
248	317.4	286.4	217.6	76.83	228.3
240	223.1	219.6	156.3	63.8	272.4
232	199.1	308.1	161.4	162.8	308.4
224	384.7	468.7			314.1

Table 44

Magnetic susceptibility of complex salts of substituted malonic acid with potassium and cobalt.

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Co-atom) $\chi \times 10^6$
1.	KCo BM	20.70	31.9	- 259
2.	KCo ClM	22.32	31.3	- 293
3.	KCo ChM	25.05	29.8	- 272
4.	KCo MM	21.18	29.9	- 292
5.	KCo NM	21.64	31.2	- 291

Table 45

Electrical resistance of the complex salts in solution

No.	Complex	Concentration g/l	Resistance (ohms) x 10^{-4}
1.	KCo BM	0.286	0.315
2.	KCo ClM	0.272	0.465
3.	KCo ChM	0.240	0.435
4.	KCo MM	0.258	0.375
5.	KCo NM	0.222	0.485

They are soluble in water, alcohol and dimethyl formamide and insoluble in all other common organic solvents.

The colour, m.p., analysis etc. of these compounds are presented in table 46. E-values of the compounds in water in the ultra-violet region of the spectrum are presented in table 47. The mass magnetic susceptibilities and diamagnetic corrections of these compounds are given in table 48. Electrical conductances of the compounds in water are presented in table 49.

(c) K-Ni-salts of substituted malonic acids :

To a solution of the substituted malonic acid (3 g.) in water (100 ml.), potassium carbonate (0.915 g.) was added slowly, followed by nickel carbonate (0.786 g.) with heating and stirring. The mixture was boiled for half an hour and filtered hot for removing unreacted residue. The filtrate was concentrated in an evaporating dish on a water bath. The mother liquor was decanted off and the crystalline mass was carefully washed with water, acetone and ether and dried. Further crops were recovered from the mother liquor. It was recrystallised from dilute alcohol.

They are soluble in water and alcohol and insoluble in all other common organic solvents.

The colour, m.p., analysis etc. of these compounds are presented in table 50. E-values of the compounds in water in the ultra-violet region of the

Table 46

Complex salts of substituted malonic acid with potassium and copper

No.	Complex	Colour	M.P. (°C)	Formula	Analysis			
					% C found	% Cu found	% C reqd.	% Cu reqd.
1.	KCu BM	Blue	241 (decomp)	$K_2CuC_{20}H_{20}O_{12}$	39.99	10.64	40.42	10.69
2.	KCu ClM	Blue	257 (decomp)	$K_2CuC_{20}H_{16}O_{11}Cl_2$	37.73	9.72	37.22	9.85
3.	KCu ChM	Blue	250 (decomp)	$K_2CuC_{20}H_{14}O_{10}Cl_2$	38.13	10.06	38.29	10.14
4.	KCu NM	Blue	275 (decomp)	$K_2CuC_{20}H_{20}O_{17}N_2$	34.80	8.77	34.21	9.05

Table 47

E-Values of the compounds in water in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E-value			
	KCu BM I	KCu ClM	KCu ChM	KCu NM
360	2.31	0.00	4.87	163.0
352	2.31	0.00	6.49	240.0
344	2.31	0.00	7.52	317.0
336	4.63	2.27	10.04	382.1
328	9.26	7.79	17.94	434.6
320	19.29	20.78	38.15	456.3
312	42.44	54.45	95.76	439.1
304	121.2	103.9	275.9	398.5
296	273.9	175.3	409.9	344.2
288	424.4	266.2	551.8	276.2
280	540.1	350.5	626.5	217.3
272	559.4	396.1	600.5	181.1
264	497.7	383.1	487.0	181.1
256	389.6	321.4	353.0	206.5
248	281.6	253.2	247.5	244.4
240	208.4	211.0	190.7	285.2
232	196.7	293.8	215.0	321.5
224	351.1	422.0	355.5	327.8

Table 48

Magnetic susceptibility of complex salts of substituted malonic acid with potassium and copper

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^{0}C)	Diamagnetic corrections (per Cu-atom) $\chi \times 10^6$
1.	KCu BM	2.80	29.5	- 269
2.	KCu ClM	3.12	31.6	- 293
3.	KCu NM	2.74	30.3	- 291

Table 49

Electrical resistance of the complex salts in solution

No.	Complex	Concentration g/l	Resistance (ohms) x 10^{-4}
1.	KCu BM	0.252	0.475
2.	KCu ClM	0.280	0.445
3.	KCu ChM	0.292	0.485
4.	KCu NM	0.232	0.595

Table 50

Complex salts of substituted malonic acid with potassium and nickel

No.	Complex	Colour	M.P. (°C)	Formula	Analysis			
					% C found	% Ni found	% C reqd.	% Ni reqd.
1.	KNi BM	Green	304-5 (decomp)	$K_2NiC_{20}H_{18}O_{11}$	42.27	10.47	42.04	10.28
2.	KNi ClM	Green	307 (decomp)	$K_2NiC_{20}H_{18}O_{12}Cl_2$	37.07	8.54	36.48	8.92
3.	KNi ChM	Green	297 (decomp)	$K_2NiC_{20}H_{22}O_{14}Cl_2$	34.23	8.59	34.58	8.46
4.	KNi MM	Green	309 (decomp)	$K_2NiC_{22}H_{22}O_{13}$	41.51	9.29	41.85	9.30
5.	KNi NM	Green	273 (decomp)	$K_2NiC_{20}H_{24}O_{19}N_2$	32.29	8.69	32.75	8.01

spectrum are presented in Table 51. The mass magnetic susceptibilities and diamagnetic corrections of these compounds are given in Table 52. Electrical resistances of the compounds in aqueous solution are presented in Table 53. Further the electrical resistance of KNi NM in aqueous solution is studied at different dilutions as shown in table 54.

Table 51

E-Values of the compounds in water in the ultra-violet region (360-220 mμ)

Wave-length (mμ)	E- value				
	KNi BM	KNi ClM	KNi ChM	KNi MM	KNi NM
360	2.12	0.00	0.00	0.00	133.2
352	2.12	0.00	0.00	0.00	197.5
344	2.12	0.00	0.00	7.94	261.9
336	2.12	3.55	0.00	21.15	317.1
328	2.12	5.32	1.64	66.43	358.4
320	4.24	10.64	8.22	198.4	373.1
312	10.59	39.88	53.44	416.6	358.4
304	95.32	79.77	230.2	568.3	323.4
296	259.5	150.7	370.0	666.5	271.1
288	439.5	249.4	509.8	724.7	216.0
280	569.9	341.3	590.3	670.5	172.8
272	599.5	394.5	565.7	535.7	144.3
264	527.4	382.9	452.8	370.3	143.3
256	401.6	323.5	320.7	224.8	165.4
248	275.4	245.6	213.8	142.9	195.7
240	180.1	186.1	148.0	129.6	230.7
232	150.4	257.8	160.3	257.8	266.5
224		398.8			273.0

Table 52

Magnetic susceptibility of complex salts of substituted malonic acid with potassium and nickel

No.	Complex	Mass magnetic susceptibility $\chi_g \times 10^6$	Temp. (^oC)	Diamagnetic corrections (per Ni-atom) $\chi \times 10^6$
1.	KNi BM	8.37	32.2	- 259
2.	KNi ClM	7.79	29.9	- 303
3.	KNi ChM	7.68	29.8	- 324
4.	KNi MM	8.35	30.0	- 292
5.	KNi NM	7.27	29.8	- 306

Table 53

Electrical resistance of the complex salts in solution

No.	Complex	Concentration g/l	Resistance (ohms) x 10^{-4}
1.	KNi BM	0.230	0.395
2.	KNi ClM	0.282	0.480
3.	KNi ChM	0.312	0.390
4.	KNi MM	0.260	0.410
5.	KNi NM	0.236	0.490

Table 54

Electrical resistance of KNi NM in aqueous solution at different concentrations

No.	Concentration (M)	Resistance (ohms) x 10^{-4}
1.	1 / 500	0.095
2.	1 / 1000	0.175
3.	1 / 5000	0.695
4.	1 / 10000	1.20

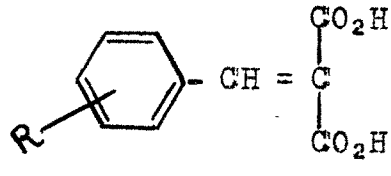
RESULTS AND DISCUSSION

(SALTS)

III. Results and Discussion :

III. I. Ligands :

The ligands selected for the present investigations were benzylidene malonic acid and its derivatives having substituents on the phenyl ring. They are represented as (I)



(I)

R =

a = H

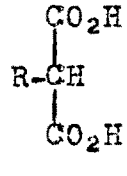
b = o-Cl

c = p-Cl

d = p-OCH_3

e = p-NO_2

They are related to other substituted malonic acids (II and III) and β-diketones(IV-i) and their triketone-type derivatives (IV-ii)



(II)

R =

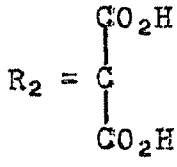
a = alkyl

b = aryl

c = NO_2

d = NH_2

e = NO



(III)

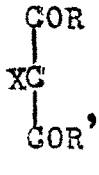
R_2 =

a = $(alkyl)_2$

b = $(aryl)_2$

c = alkyl, aryl

d = CH_2



(IV)

	R	R'
a =	Me	Me
b =	Ph	Ph
c =	Me	Ph
d =	Me	OEt
e =	Ph	OEt
f =	Me	NHPh
g =	Ph	NHPh

X =

(i) H_2

(ii) NOH

The acids are soluble in water, alcohol, acetone etc. but insoluble in benzene, chloroform, petroleum ether etc.[256] The ionisation constants[257] of the acid (Ia) in water are

$$K_1 = 4.08 \times 10^{-3}$$

$$K_2 = 3.15 \times 10^{-6}$$

The corresponding values for malonic acid[258] are

$$K_1 = 1.41 \times 10^{-3}$$

$$K_2 = 2.08 \times 10^{-6}$$

Ammonium, silver and barium salts of the acid (I-a) are known.[259] The acid is also known to decompose on heating into cinnamic acid. Hence the preparation of salts was carried out at room temperature and whenever heating was required it was done in solution on water bath.

-X- -X- -X-

The ultra-violet absorption spectra of the acids in alcoholic and alkali solutions are presented in figures 1, 2 and 3 and the wavelengths for maximum absorption (λ max) and their corresponding E-values are presented in table 56.

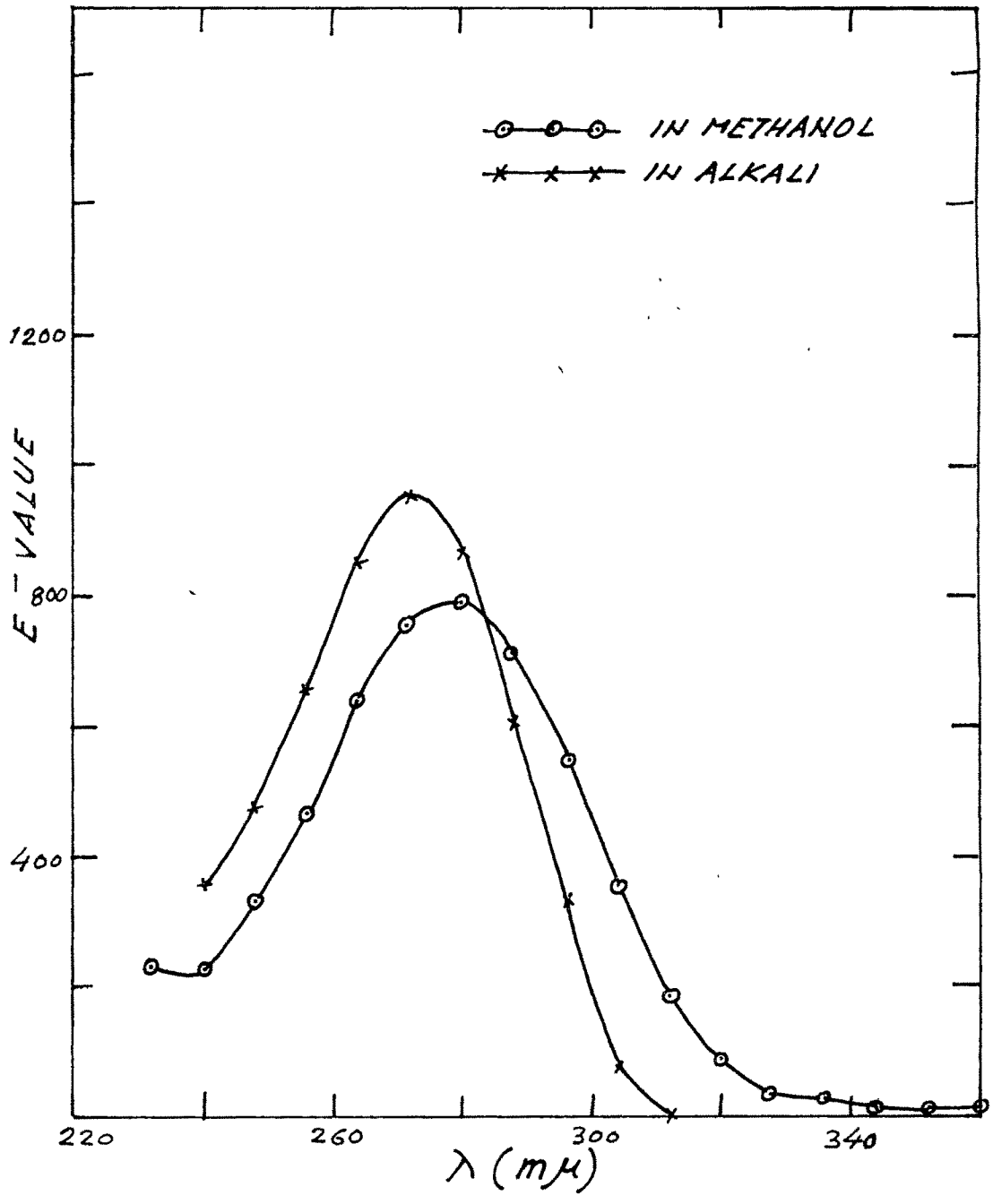


FIG. 1 UV ABSORPTION SPECTRA OF THE BENZYLIDENE MALONIC ACID.

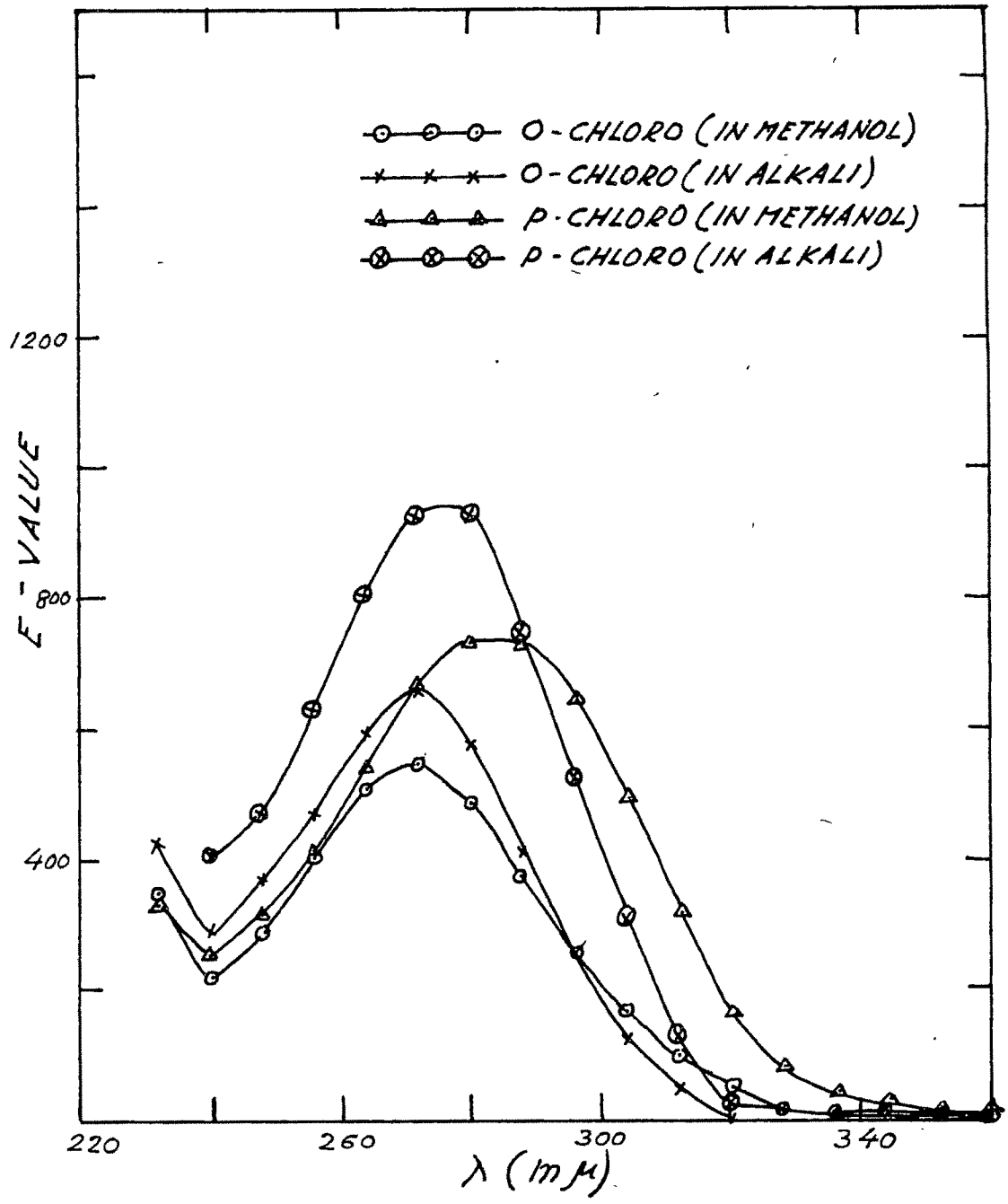


FIG. 2 UV ABSORPTION SPECTRA OF THE CHLORO BENZYLIDENE MALONIC ACIDS.

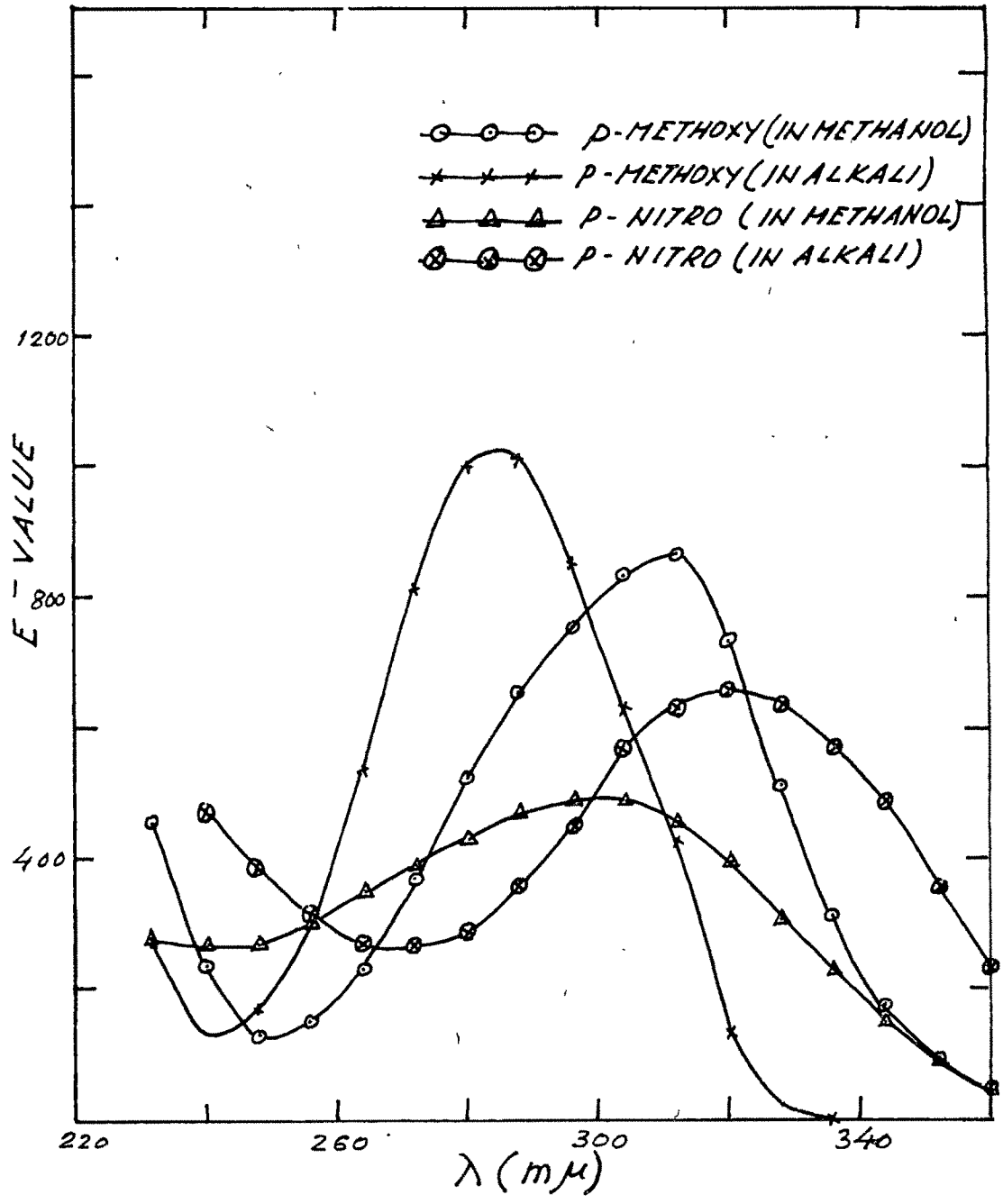


FIG. 3 UV ABSORPTION SPECTRA OF THE P-METHOXY AND P-NITRO-BENZYLIDENE MALONIC ACIDS.

Table 56

Ultra-violet absorption spectra of benzylidene malonic acid and substituted benzylidene malonic acid.

No.	Substance	in methanol		in alkali	
		λmax (mμ)	E-value	λmax (max)	E-value
1.	BM	280	787.9	272	957.9
2.	ClM	272	541.4	270-72	657.2
3.	ChM	284	736.9	276	943.6
4.	MM	308	876.6	284	1041.0
5.	NM	300	494.0	318-20	658.8 +

+ Ppts formed after one hour.

The absorption band of the unsubstituted acid in alcoholic solution is at 280 mμ . It is considered to be a conjugation band ($\pi - \pi^*$ band). Since the absorption band of styrene is at 248 mμ (in alcoholic solution), the conjugation is considered to be extended through the molecule. The value of the band is intermediate between those for cinnamaldehyde (289 mμ) and trans-cinnamic acid (273 mμ). Thus the extension of conjugation caused by two carboxylic groups in a crossed manner along the conjugated system is even less than that caused by a carbonyl group and may be attributed to the steric effect.

The substituents on the phenyl ring cause a well marked shift in the absorption band. Thus in the alcoholic solutions, the ortho substituent causes a blue shift whereas the para substituent causes a red shift. The red shift in alcoholic solution is increasing in order

H < p-chloro < p-nitro < p-methoxy

Similar red shifts of the absorption band are also observed in the spectra of para-substituted derivatives in alkali solution. However, the red shift increases in order

H < p-chloro < p-methoxy < p-nitro

All these substituents contain lone pair of electrons on the substituent atom linked to the ring and hence can effectively increase the length of

conjugation, when placed at the para position, thereby leading to a red-shift of the band.

The shift attributed to hetero atoms (groups) may be related to their electrostatic and resonance effects. Thus the electronegativity[260] of these atoms increases in order

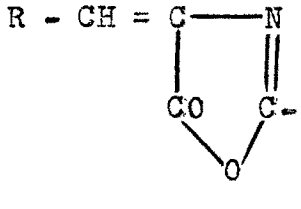
$$Cl \sim N < O$$

and the resonance parameter[260] (k) of these atoms in combination with carbon atoms increases in order

$$C\text{-}Cl < C - N \sim C - O$$

The shift is greater for the nitro derivative than for the methoxy derivative in alkali solution. It may be due to increased resonance stabilisation of the nitro compound in alkali solution.

Bassi, Deulofeu and Ortega[261] observed that in the case of the spectra of



the substituent R shifts the absorption band of the unsubstituted molecule. The shift increases in order

$$H < \text{nitro} < \text{methoxy}$$

They suggested that groups such as nitro and methoxy with high mesomeric effect, when placed at the

para position where this effect can work through the conjugated system, would have the highest shift.

-X- -X- -X-

Absorption spectra are useful in studying the distortion of the molecule from planarity. Thus, in the case of biphenyl derivatives,[262] the replacement of some or all of the hydrogen atoms at 2,2',6,6' positions in biphenyl by other atoms or groups increases greatly the steric interference. It results in the hypsochromic and hypochromic shifts of the absorption band of biphenyl as shown below for methyl substituent. The shift can be related to the twist angle θ of the co-annular bond in the biphenyls, and quantitative calculations can be made by HMO method.

Biphenyl	λmax (mμ)	ϵ-max
unsubstituted	248	16600
2-methyl	235	10500
2,6-dimethyl	231 (sh)	5600
2,2'-dimethyl	227 (sh)	6800
2,2'-dichloro	230 (sh)	6600

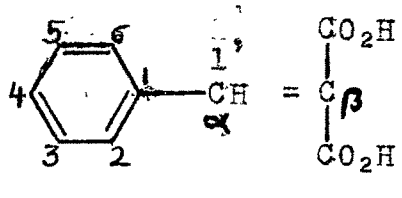
Similarly in the case of styrene derivatives,[263] introduction of substituents at the ortho, alpha and cis beta positions in the styrene molecule causes steric interference. It is reflected in the hypsochromic and hypochromic effect of the absorption band of styrene as shown below for methyl substituent. The shift is

related to the twist angle θ of the essential single bond. The angle θ, calculated by HMO method,[263] is also presented below.

Styrene	λmax (mμ)	ε-max	θ°
unsubstituted	248	14600	0
o,p-dimethyl	251		30.7
o,o-dimethyl	238		54
α-methyl	241.5	11400	33
cis-β-methyl	240.6	13800	35
α-β-dimethyl	244	8700	31.5

The acid (I-a) used in the present investigation can be considered to be a β,β-dicarboxylic acid derivative of styrene. Hence calculations are made for the steric effect of these substituents and the resultant distortion of the molecule from planarity is evaluated.

The hypsochromic shift of the band is used to calculate the twist angle θ of 1,1' bond as follows :



In a linear conjugated system, steric hindrance to the planarity of the system is considered, to a first approximation, to be releived only by the twist of the essential single bond or bonds. In general, twist of a

bond does not affect the σ-bond energy. Since an essential single bond has a relatively low π-bond order, the decrease in the delocalisation energy of π-electrons caused by the twist of such a bond will be relatively small. Furthermore, in most cases it is expected that twist of such a bond will rapidly reduce the steric repulsion between atoms not directly bonded together.

The observed absorption band may be considered to be due to the one-electron transition from the highest occupied π MO to the lowest vacant π MO. Hence the wave number at the absorption maximum of the band should correspond to the energy difference between the two π MO's (ψ_{+1} and ψ_{-1}) or two electronic states calculated with the most probable or equilibrium nuclear configurations in the ground electronic state. Similarly the observed intensity of each band can be related to the oscillator strength calculated with ground state equilibrium nuclear configuration.

The resonance parameter k for a twisted bond can be related to the angle of twist θ . Hence if the position of this band of related systems can be correlated well with the MO calculations, the position of the bands can be related to the angle of twist by calculating π MO's and their energies as functions of the parameter k for the twisted bond.

Adopting Whelands assumptions,[264] one can write that

$$k_{ij} = S_{ij} / S$$

where k_{ij} and S_{ij} are the resonance parameter and overlap integral for the i-j double bond of the length R_{ij} and S is the standard π-π overlap integral for the standard C-C bond in the benzene.

Using Mulliken's values[265] for the π-π overlap integrals for C-C bond at various interatomic distances , one can obtain K_{ij} values as shown below.

R_{ij}	S_{ij}	k_{ij}
1.39	0.249	1.000
1.48	0.214	0.858
1.50	0.206	0.827
1.54	0.192	0.771

When the overlap integral S_{ij} between two p orbitals of C-atoms with interatomic distance R_{ij} and the angle of twist θ_{ij} is expressed as S (R,θ), we can write as follows :

$$S(R,\theta) = S(R,0^{0}) \cos\theta$$

Similarly

$$k(R,\theta) = k(R,0^{0}) \cos\theta$$
$$= k(R_{90},0^{0}) \cos\theta + \left[k(R_{0},0^{0}) - k(R_{90},0^{0})\right] \cos^{2}\theta$$

$$= k(R_0,0^\circ)\cos\theta - \left[k(R_{90},0^\circ) - k(R_{90},0^\circ)\right] \times \cos\theta\,(1-\cos\theta)$$

R_0 and R_{90} are the lengths of the bond C-C when $\theta = 0^\circ$ and when $\theta = 90^\circ$ respectively. If R_0 and R_{90} are assumed to be $1.48^\circ A$ and $1.54^\circ A$ respectively, we find that

(a) $$R = R_{90} - (R_{90} - R_0)\cos\theta$$
$$= 1.54^\circ A - (1.54^\circ A - 1.48^\circ A)\cos\theta$$
$$= 1.54^\circ A - 0.06^\circ A \cos\theta$$

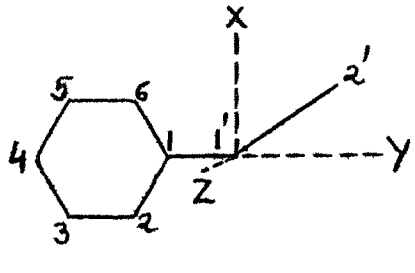
(b) $$k\,(R_{90},0^\circ) = 0.771$$

(c) $$k\,(R_0,0^\circ) - k(R_{90},0^\circ) = 1.446\,(R_{90}-R_0)$$
$$= 1.446\,(0.06)$$
$$= 0.0867$$

and

(d) $$k\,(R,\theta) = 0.771\cos\theta + 0.0867\cos^2\theta$$
$$= 0.858\cos\theta - 0.0867\cos\theta(1-\cos\theta)$$

The skeleton of the styrene π-system is illustrated below :



The plane of the ethylenic bond has been taken as the XY plane and the direction of the 1-1' bond as the direction of the Y-axis.

In application of the simple LCAOMO method to this system, the following assumptions are made.

The length of the ethylenic bond (1-2' bond) is 1.34° A and a value of 1.08 is used for the resonance parameter k for this bond. The length of the essential single bond (1-1' bond) is 1.48° A, the interplanar angle θ between the benzene ring and the ethylenic bond is 0°, and the value of the resonance parameter k for 1-1' bond is 0.858.

The resonance parameter k for a twisted bond is related to the angle of twist θ and bond length R by the following equation :

$$k\,(R,\theta) = 0.858\cos\theta - 0.0867\cos\theta(1-\cos\theta)$$

The value of the second term is relatively small and is neglected as a rough approximation. Hence

$$k\,(R,\theta) = 0.858\cos\theta$$

The band at 248 mμ as mentioned earlier, is due to the one electron transition from $\psi_4 + 1$ to $\psi_4 - 1$. The calculated values[263] of the energy of transition ΔE as a function of the parameter k for 1-1' bond are presented below :

k	0.858	0.700	0.500	0.300	0.100	0.0
θ(deg)	0	33.9	52.6	68.1	82.7	90
R(^{o}A)	1.480	1.490	1.504	1.518	1.532	1.540
$\Delta E(-\beta)$	1.474	1.568	1.697	1.834	1.967	2.000

As a first approximation, ψ_4+1 can be considered as arising from a mixture of $\varphi+1$ of benzene and $\varphi+1$ of ethylene and ψ_4-1 can be considered as arising from a mixture of $\varphi-1$ of benzene and $\varphi-1$ of ethylene. When the interplanar angle θ becomes 90^{o}, ψ_4+1 and ψ_4-1 of styrene reduce to $\varphi+1$ and $\varphi-1$ of benzene respectively, and the styrene band reduces to the benzene p-band.

The twist angle θ for benzylidene malonic acid can be estimated as follows :

The transition energy ΔE calculated for the planar conformation of the acid ($\theta=0^{o}$) is denoted by ΔE_s and the corresponding wave number ν is denoted by ν_s and wave length by λ_s.

The bathochromic effect of β- carboxylic group is assumed to be approximately equivalent in trans and cis positions. Its magnitude is found to be 25 mμ and allowance for it is to be made for cis position in correcting λ_s.

The value of ΔE for k = 0 is denoted by ΔE_L and the corresponding wave number by ν_L and wave length

by λL. λL for benzene is taken as 208.3 mμ. Hence the value of ΔE corresponding to the observed value of ν of compound can be calculated by the use of the following relation :

$$\Delta E = \Delta E_L - (\Delta E_L - \Delta E_S) \frac{(\nu_L - \nu)}{(\nu_L + \nu_S)}$$

From the value of ΔE, the corresponding value of k and hence the values of θ and R are obtained and are presented below :

Styrene	λ (mμ)	λ_S (mμ)	λ_L (mμ)	E ($-\beta$)	k	θ (^{o})	R (^o_A)
unsubstituted	248	-	-	1.474	0.858	0	1.480
trans β CO_2H	273	-	-	-	→	-	-
$\beta,\beta(CO_2H)_2$	280	298	208.3	1.552	0.73	30	1.489

Additional steric interference will be caused by the introduction of an ortho substituent (chlorine) on the phenyl ring. Calculations can be made as suggested above, assuming the bathochromic shift due to chlorine in the o- or p-position to be about 4 mμ. The results for o-chloro derivative will be obtained as follows :

Styrene	λ	λ_s	λ_L	ΔE ($-\beta$)	k	θ ($^\circ$dg)	R ($^\circ$A)
unsubstituted	248	-	-	1.474	0.858	0	1.480
o-chloro, $\beta,\beta(CO_2H)_2$	272	302	212.3	1.611	0.635	40	1.494

- ✕ - - ✕ - - ✕ -

III.2. Salts of benzylidene malonic acids :

The above acids have been investigated for their ability to form salts with different metals, under different conditions. For that purpose four different methods have been studied with three metal ions. The methods adopted were (a) partition method (b) solution method (c) carbonate suspension method and (d) hydroxide suspension method. The acids would usually be expected to give normal salts as represented by equation (i)

$$M + H_2L \longrightarrow (ML) + 2H \quad \text{.....(i)}$$

Such products would be obtained if the ion displacement can be complete, as expected in the solution or partition method. Different products would be formed by the partial ion displacement ; basic or mixed ligand products would be obtained in such cases as in equation(ii)

$$(X+1)\ MCO_3 + H_2L \longrightarrow (MCO_3)_X\ ML + H_2O + CO_2 \quad \text{.....(iia)}$$

$$(X+1)\ M(OH)_2 + H_2L \longrightarrow \left[M(OH)_2\right]_x ML + 2H_2O \ldots\ldots\ldots (iib)$$

$$(X+1)\ MR_2 + H_2L \longrightarrow \left[MR\right)_x\Big] ML + 2HR \ldots\ldots\ldots\ldots (iic)$$

The formation of the basic product may be co-precipitation or may involve complex formation and will be dependent on the nature of the metal and the ligand.

Besides, the salts may contain additional acid as shown in (iii)

$$ML + H_2L \longrightarrow H_2(ML_2) \ldots\ldots\ldots\ldots (iiia)$$

$$Z\ ML + H_2L \longrightarrow H_2L\ (ML)_z \ldots\ldots\ldots (iiib)$$

The formation of such products will depend primarily on the nature of the metal for the same ligand while using different methods.

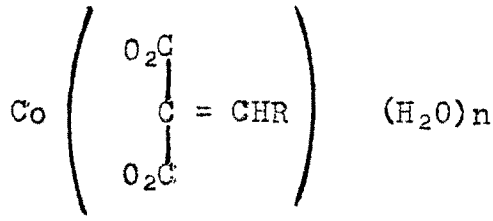
Studies on the formation of the cobalt, copper and nickel salts by the above methods and their properties are presented first, in the following pages.

III. 3. Cobalt (II) salts of benzylidene malonic acids :

Cobalt salts of benzylidene malonic acid and its derivatives (I) were prepared by four different methods : (a) partition method (b) solution method (c) carbonate method and (d) hydroxide method. The analysis of the products is given in tables 4 to 8.

We find that the salts prepared by the Partition method are quite similar and may be represented

on the basis of analysis, as (V).



(V)

R =

a = C_6H_5-

b = o-ClC_6H_4-

c = p-ClC_6H_4-

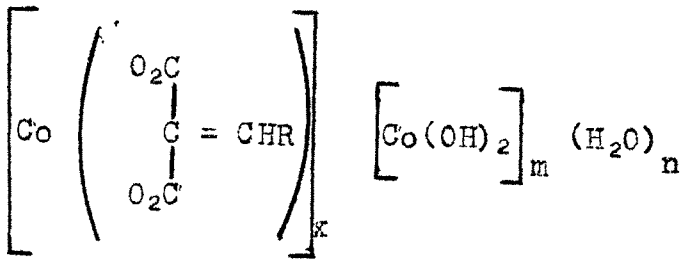
d = p-$CH_3OC_6H_4$-

e = p-$NO_2C_6H_4$-

where the value of n depends on the ligand used.

The products obtained by the solution method are also quite similar and can be represented by (V) ; however, the amount of the product obtained is less than that of the product in the partition method. Hence the partition method would be preferable to the solution method for the preparation of these salts.

The products obtained by the hydroxide method are all basic except in the case of the salt of the o-chloro derivative and may be represented as (VI).



(VI)

R =

a = C_6H_5-

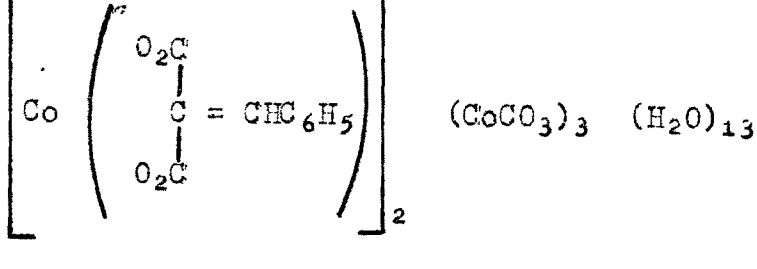
b = p-ClC_6H_4-

c = p-$CH_3OC_6H_4$-

d = p-$NO_2C_6H_4$-

where the values of x, n and m depend on the nature of the ligand. The salt obtained with o-chloro derivative can be represented by (V).

The products obtained by the carbonate method can be represented by (V) except in the case of the salt of benzylidene malonic acid which is represented as (VII).

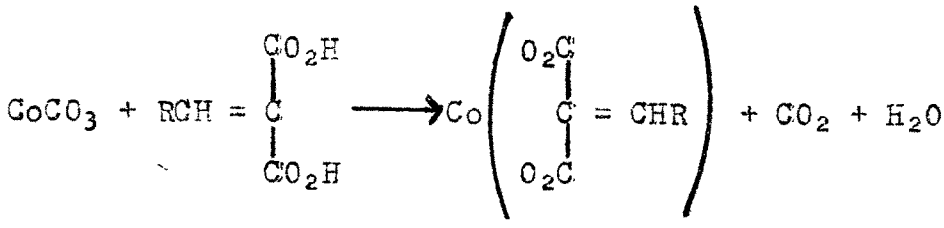


(VII)

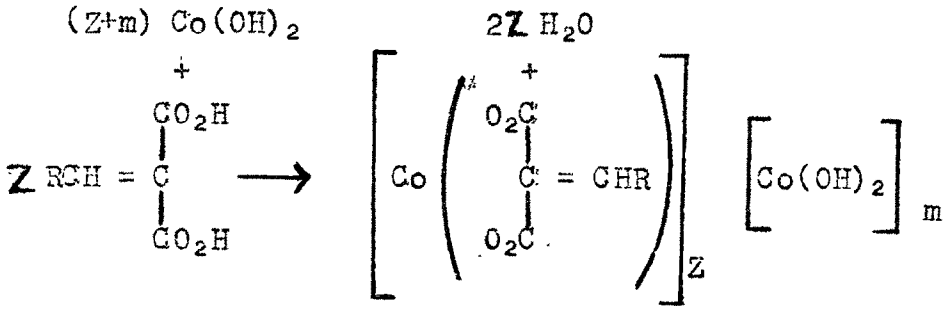
It may be possible that the "basic" salts may contain cobalt hydroxide or cobalt carbonate in the

adsorbed or occluded form. This possibility is excluded on the basis of the observations that only a single spot was obtained with these basic salts on a paper chromatograph.

The results indicate that the replacement of the carbonate ion by the acid anion is complete in case of the o-or p-substituted benzylidene malonic acids.



However, the replacement of the hydroxide ion by those acid anions is partial only, as



It may be noted that no salt of the type H_2L.CoL is formed in any case. Hence only two types of salts are formed by cobalt with these acids. And the type of the salt obtained depends more on the method of preparation adopted rather than on the nature of the acid used.

-X- -X- -X-

The absorption spectra of these salts in the ultra violet region are given in figures 4 to 8 and their absorption bands are given in tables 57 to 61. The absorption band of the salt is intermediate between those of the acid in alcohol and alkali. The replacement of the acid proton by the metal ion causes perturbation in the electronic energy levels of the acid. It results in the shift of the band which is greatest for the sodium ion.

It is also seen that an additional band at 256-58 mμ is observed in the case of the basic salts of cobalt with benzylidene malonic acid. The blue shift of the additional band suggests increased energy of transition and may be attributed to the decreased conjugation. It may arise from the additional steric hindrance caused to a part of the ligand by the basic component of the molecule.

-X- -X- -X-

The magnetic moments of these salts are presented in tables 62 to 66. The magnetic moments of the normal salts prepared by different methods are very similar within the limits as shown below :

Salt	μ(B.M.)
Co BM	5.31
Co ClM	5.22 ± 0.17
Co ChM	5.13 ± 0.04
Co MM	5.25 ± 0.15
Co NM	5.35 ± 0.07

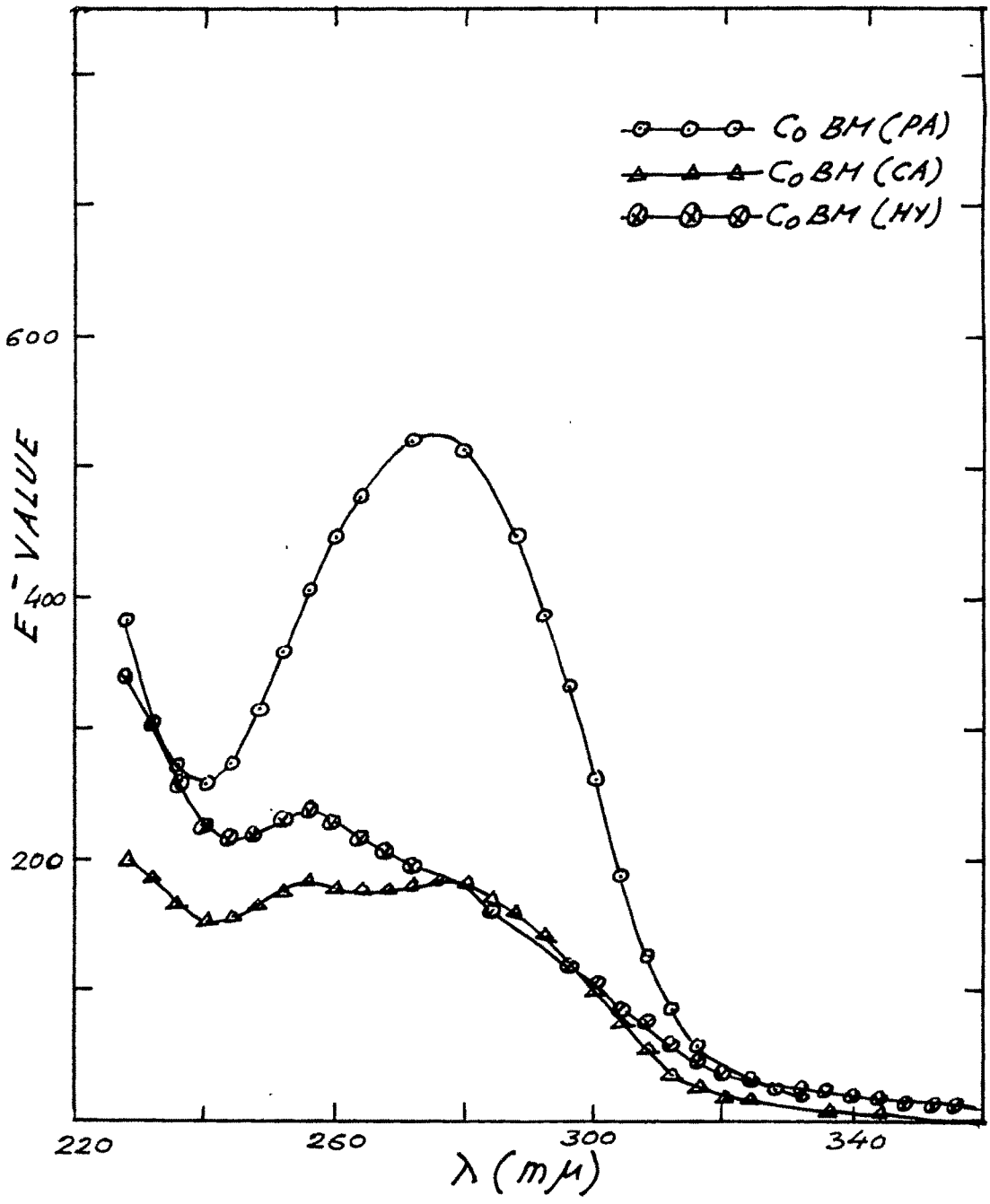


FIG. 4 UV ABSORPTION SPECTRA OF THE COBALT SALTS OF THE BENZYLIDENE MALONIC ACID.

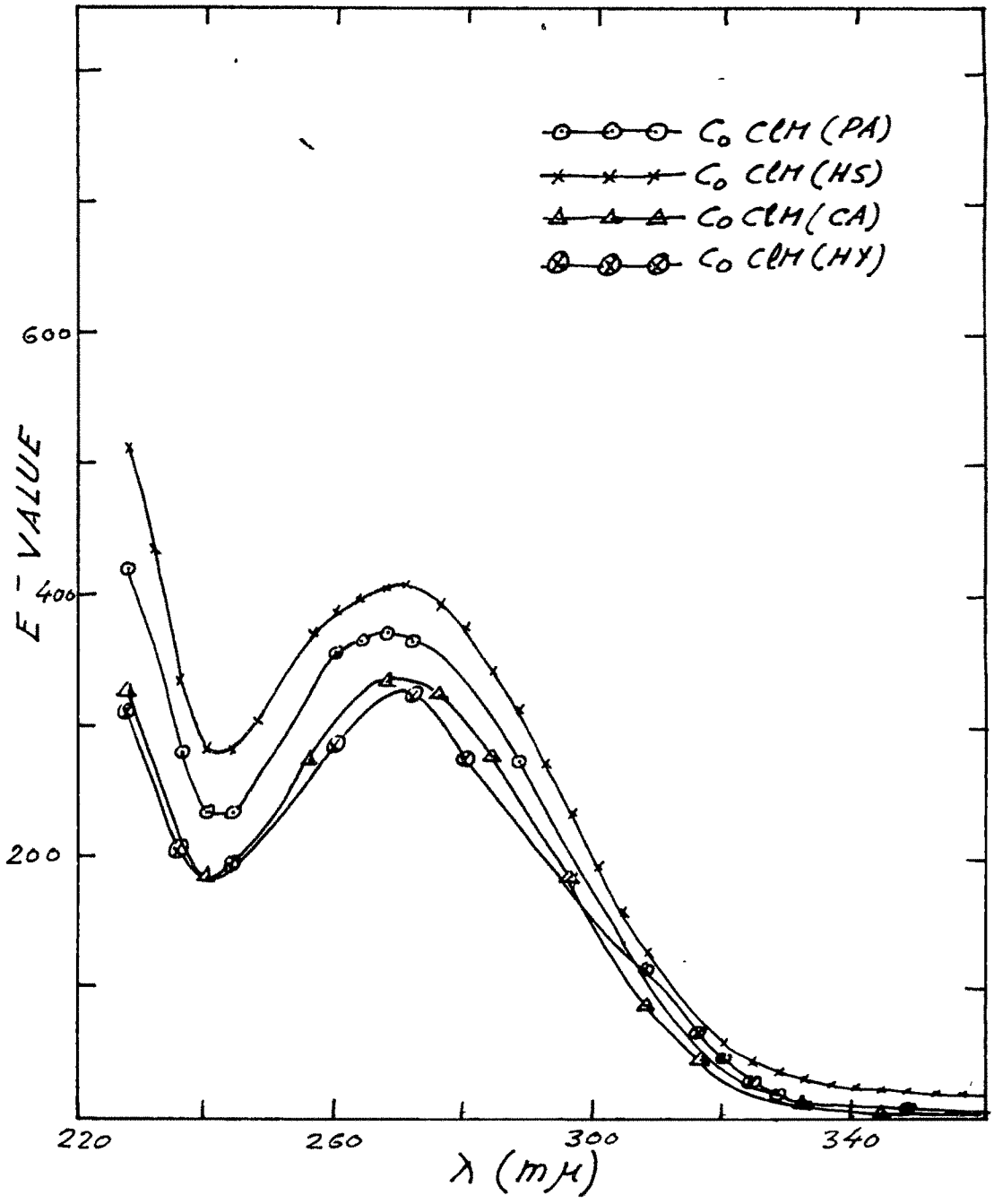


FIG. 5 UV ABSORPTION SPECTRA OF THE COBALT SALTS OF THE ORTHO-CHLOROBENZYLIDENE MALONIC ACID.

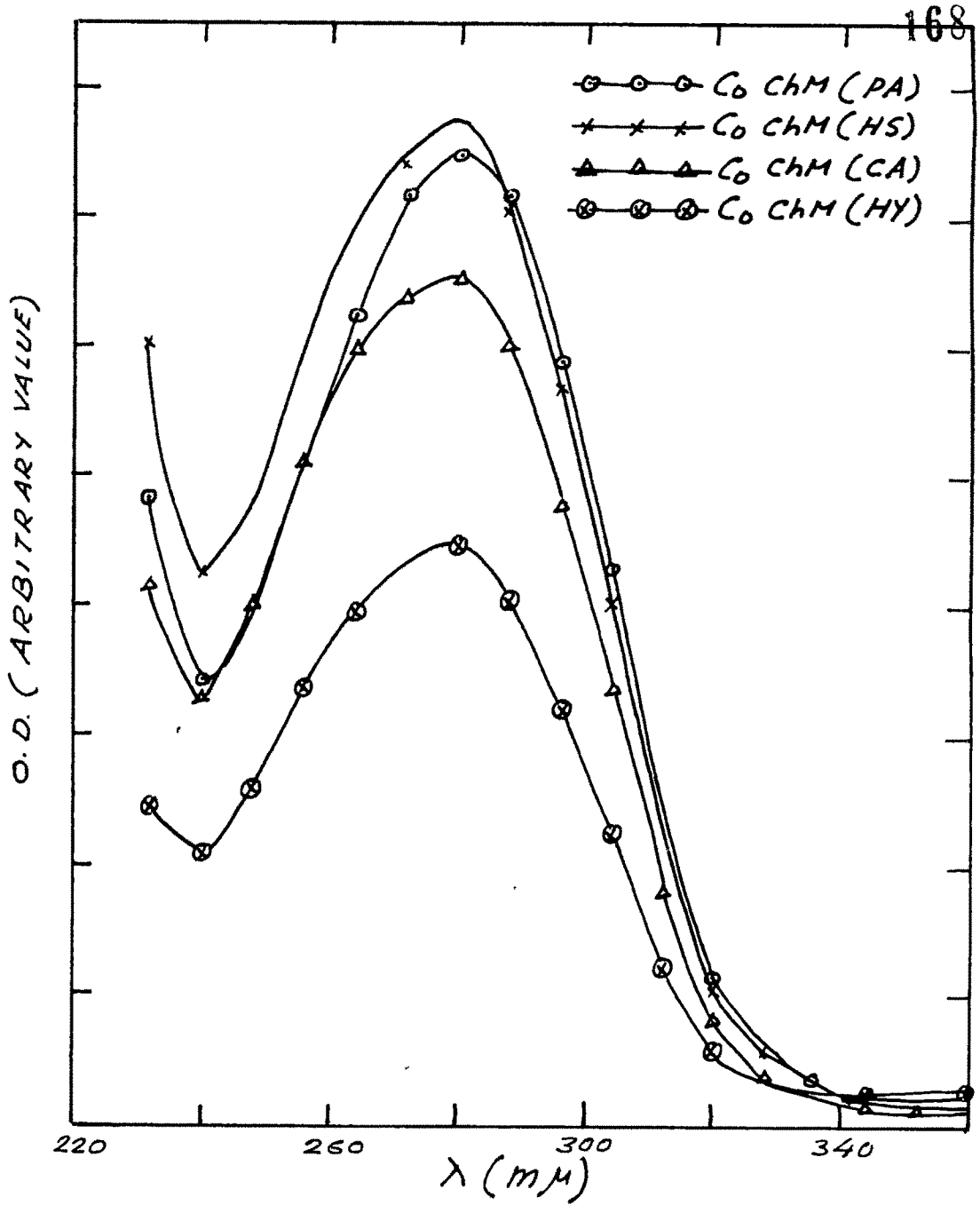


FIG. 6 UV ABSORPTION SPECTRA OF THE COBALT SALTS OF THE PARA-CHLOROBENZYLIDENE MALONIC ACID.

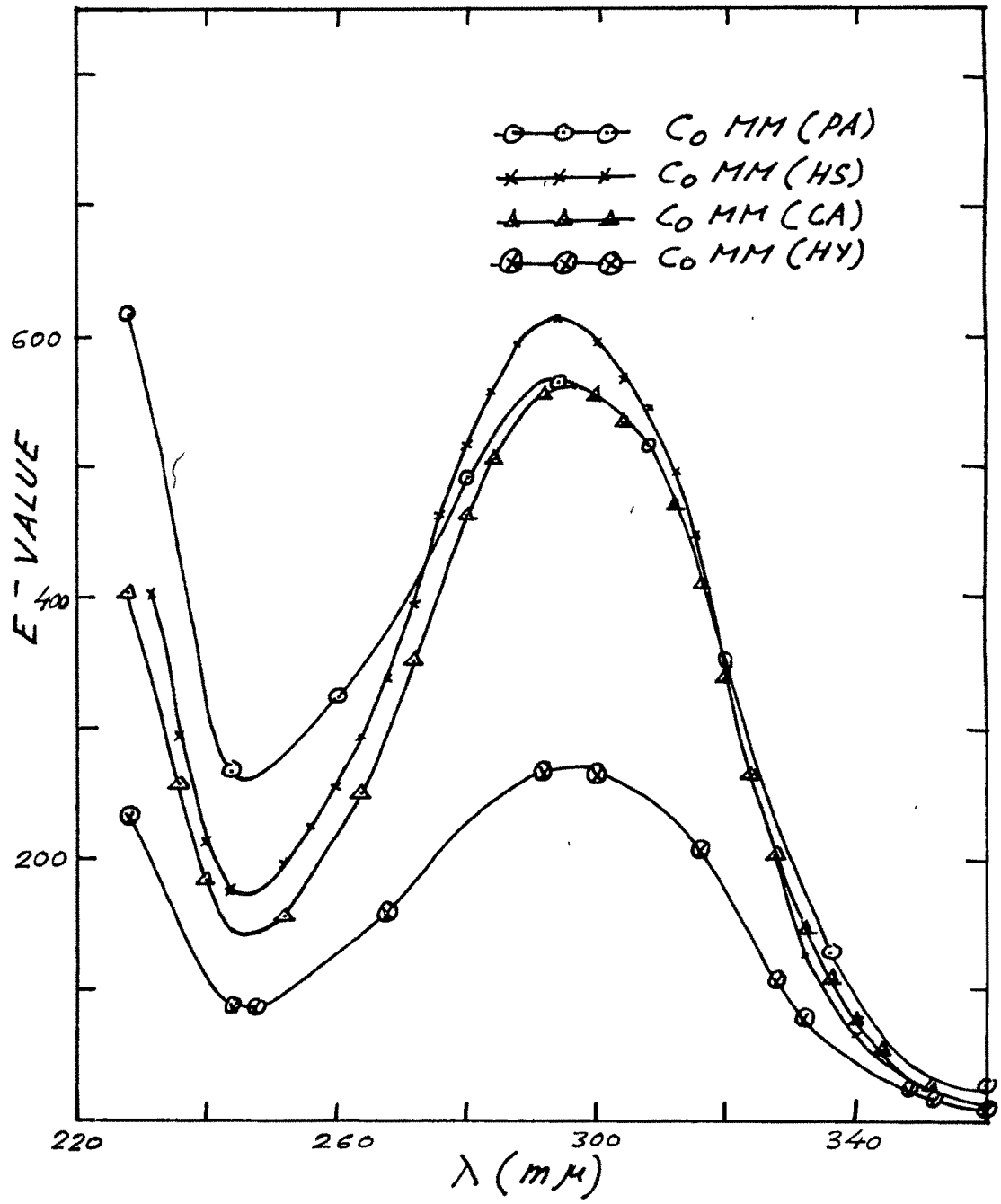


FIG.7 UV ABSORPTION SPECTRA OF THE COBALT SALTS OF THE PARA-METHOXY BENZYLIDENE MALONIC ACID.

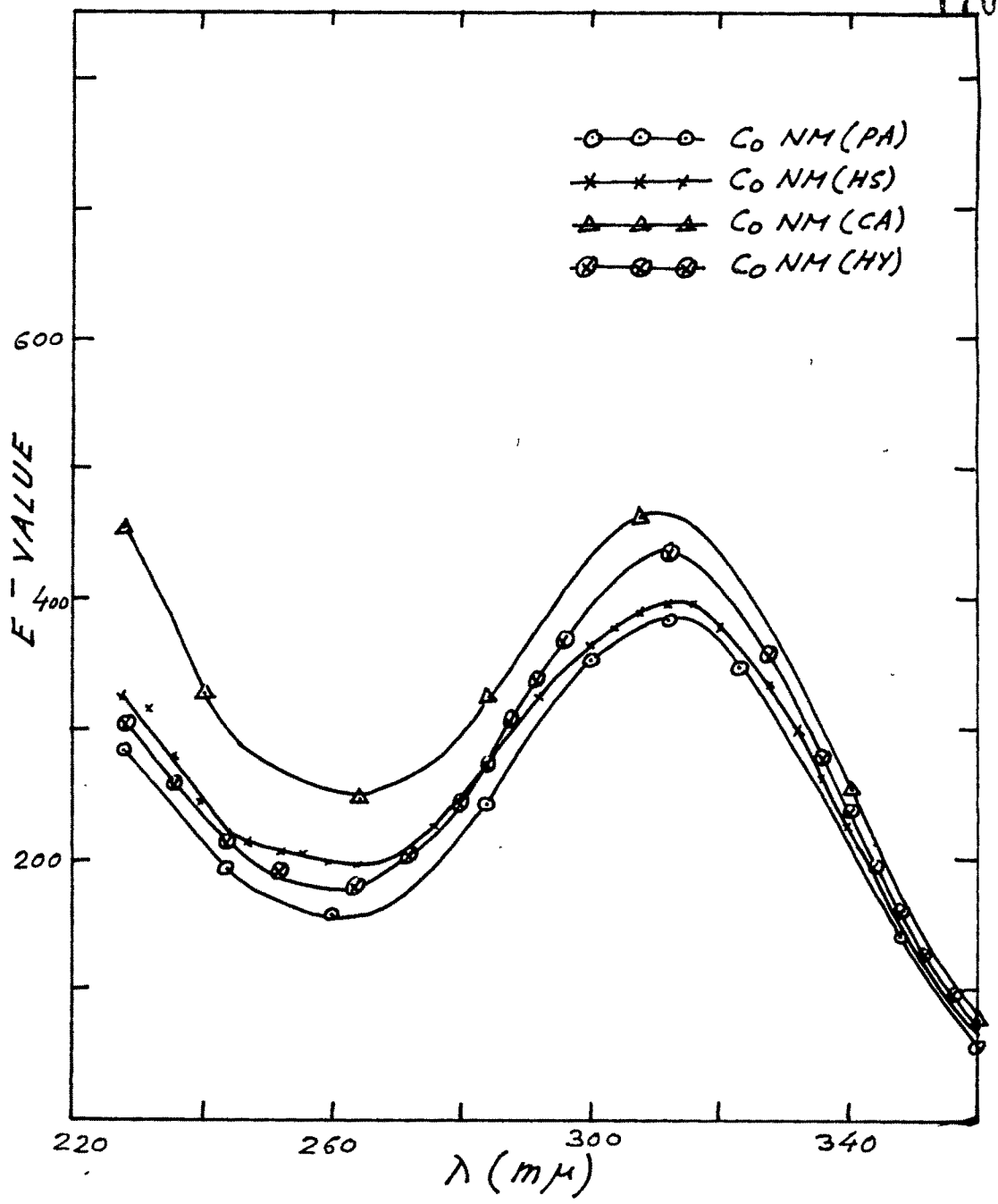


FIG. 8 UV ABSORPTION SPECTRA OF THE COBALT SALTS OF THE PARA-NITROBENZYLIDENE MALONIC ACID.

Table 57

Ultra-violet absorption spectra of cobalt salts of benzylidene malonic acid in metharol.

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-value
1.	Co BM (PA)	$C_{10}H_{14}O_8Co$	274-76	521.8
2.	Co BM (CA)	$C_{23}H_{38}O_{30}Co_5$	278	184.3
			256-58	180.5
3.	Co BM (HY)	$C_{10}H_{24}O_{15}Co_3$	278 (sh)	177.3
			256	237.3

Table 58

Ultraviolet absorption spectra of cobalt salts of ortho-chlorobenzylidene malonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-value
1.	Co ClM (PA)	$C_{10}H_{12}O_{7.5}ClCo$	268-70	370.8
2.	Co ClM (HS)	$C_{10}H_{14}O_{8.5}ClCo$	270	406.7
3.	Co ClM (CA)	$C_{10}H_{12}O_{7.5}ClCo$	270	333.9
4.	Co ClM (HY)	$C_{10}H_{10}O_{6.5}ClCo$	270	325.0

Table 59

Ultra-violet absorption spectra of cobalt salts of para-chlorobenzylidene malonic acid in methanol

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	O.D.
1.	Co ChM (PA)	$C_{10}H_{14}O_{8.5}ClCo$	282	0.755
2.	Co ChM (HS)	$C_{10}H_9O_6ClCo$	280	0.775
3.	Co ChM (CA)	$C_{10}H_9O_6ClCo$	278	0.656
4.	Co ChM (HY)	$C_{10}H_{16}O_{10,5}ClCo_2$	280	0.447

Table 60

Ultra-violet absorption spectra of cobalt salts of para-methoxybenzylidene malonic acid in methanol

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-Value
1.	Co MM (PA)	$C_{11}H_{12}O_7Co$	294-96	565.2
2.	Co MM (HS)	$C_{11}H_{12}O_7Co$	294	611.9
3.	Co MM (CA)	$C_{11}H_{12}O_7Co$	296	561.3
4.	Co MM (HY)	$C_{22}H_{54}O_{32}Co_5$	296	268.0

Table 61

Ultra-violet absorption spectra of cobalt salts of para-nitrobenzylidene malonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-Value
1.	Co NM (PA)	$C_{10}H_{13}O_{10}NCo$	314	385.8
2.	Co NM (HS)	$C_{10}H_{11}O_{9}NCo$	312	394.7
3.	Co NM (CA)	$C_{10}H_{13}O_{10}NCo$	312	464.7
4.	Co NM (HY)	$C_{30}H_{27}O_{25}N_{3}Co_{4}$	312	432.0

Table 62

Magnetic moments of cobalt salts of benzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Co BM(PA)	11230	11373	5.31
2.	Co BM(CA)	10562	10648	5.14
3.	Co BM(HY)	9446	9522	4.86

Table 63

Magnetic moments of cobalt salts of ortho-chlorobenzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $X'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Co ClM(PA)	10420	10575	5.11
2.	Co ClM(HS)	10550	10715	5.14
3.	Co ClM(CA)	11010	11165	5.24
4.	Co ClM(HY)	11740	11884	5.39

Table 64

Magnetic moments of cobalt salts of para-chlorobenzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Co ChM(PA)	10690	10855	5.17
2.	Co ChM(HS)	10500	10639	5.13
3.	Co ChM(CA)	10390	10529	5.10
4.	Co ChM(HY)	9340	9436	4.83

Table 65

Magnetic moments of cobalt salts of para-methoxybenzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Co MM(PA)	10950	11088	5.24
2.	Co MM(HS)	11710	11848	5.40
3.	Co MM(CA)	10540	10678	5.13
4.	Co MM(HY)	10570	10666	5.10

Table 66

Magnetic moments of cobalt salts of para-nitrobenzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Co NM(PA)	11190	11338	5.29
2.	Co NM(HS)	11740	11878	5.42
3.	Co NM(CA)	11690	11838	5.41
4.	Co NM(HY)	9507	9607	4.87

Cobalt atoms in these salts are considered to have octahedral stereochemistry.

The magnetic moments of the basic salts of cobalt fall in two groups (a) $\mu \sim 5.1$ B.M. and (b) $\mu \sim 4.8$ B.M. The first group of compounds include Co BM (CA) and Co MM (HY). In these cases the ratio of normal salt to cobalt hydroxide or carbonate is 2:3. It is considered that in these cases there is no magnetic interaction between different cobalt atoms nor is there a change in the stereochemistry of these atoms due to chemical interactions.

The second group of compounds include Co BM(HY), Co ChM(HY) and Co NM(HY). In these cases the ratio of normal salt to cobalt hydroxide is varying (1:2, 1:1 and 3:1 respectively). The low value of the magnetic moment in these cases may be attributed to (a) the magnetic interaction of cobalt atoms or (b) the changes in stereochemistry of cobalt atoms. Thus in a basic salt of ratio 1:1, one cobalt atom may remain octahedral but the other one may become tetrahedral. Thus the expected value of magnetic moment will be about 4.8 B.M. Alternatively, magnetic interaction between cobalt atoms may take place through bridge atoms, resulting in some spin-pairing and hence in the lowering of the magnetic moment. Similar arguments can be made for basic salts of other ratios.

-X- - X - - X -

These cobalt salts may be compared with those of other related ligands (IV). β-Diketones (IV-i) form complexes with cobalt of the type CoL_2. Of these complexes, $Co(acac)_2$ is shown to be tetrameric,[266,267,268] while $Co(dpm)_2$ is considered to be essentially tetrahedral.[269] It is suggested that in non-coordinating solvents as in the solid state, cobalt attains a coordination number of six through polymerisation, while in coordinating solvents, the solvent occupies the two available positions.[267,270] Triketone-type ligands (IV-ii) form complexes with cobalt of the type $HCoL_3$.[271,272] Thus bivalent cobalt has a preference for coordination number six in these complexes and attains it either through normal bond formation or through polymerisation. Further, the acid salts similar to those formed by the oxime-ketone ligands (IV-ii) are not formed by cobalt with the acids under investigation.

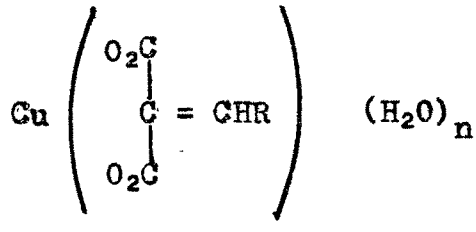
- X - - X - - X -

III. 4. Copper salts of benzylidene malonic acids :

Copper (II) salts of benzylidene malonic acid and its derivatives (I) were prepared by four different methods : (a) partition method (b) solution method (c) carbonate method and (d) hydroxide method. The analysis of the products are given in tables 19 to 23.

We find that the type of the salts obtained depends more on the nature of the ligand rather than on the method of preparation. Thus copper salts of benzylidene malonic acid and p-nitrobenzylidene malonic acid, prepared

by different methods are quite similar and may be represented as (VIII).



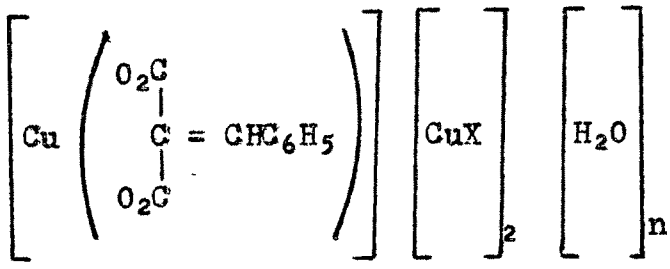
(VIII)

R =

a = C_6H_5-

b = p-$NO_2C_6H_4$-

Besides, like the cobalt salts, basic copper salts of benzylidene malonic acid are also obtained by the carbonate and hydroxide methods and may be represented as (IX)



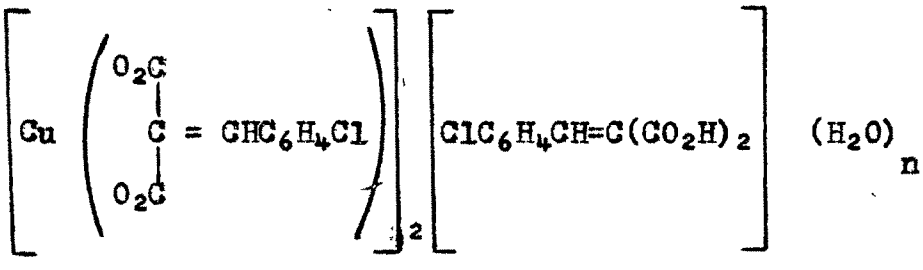
(IX)

X =

a = CO_3

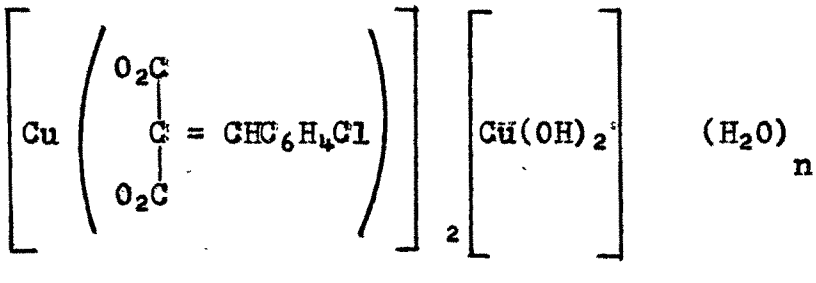
b = $(OH)_2$

On the other hand, Cu-salts of o-and p-chlorobenzylidene malonic acids are generally acidic and may be represented as (X) except



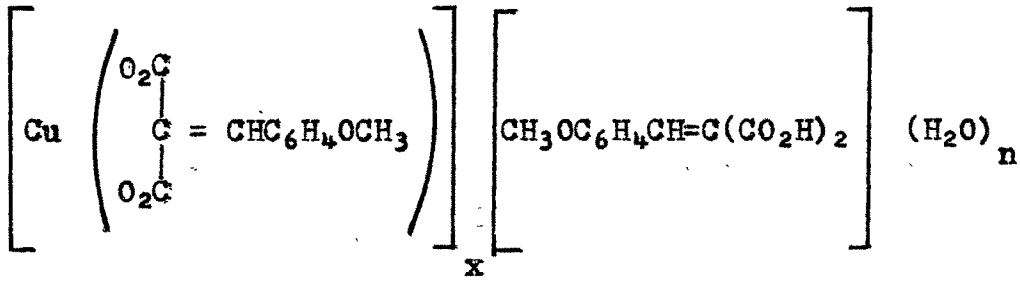
(X)

the copper salt of o-chlorobenzylidene malonic acid prepared by the hydroxide method which is basic and may be represented as (XI)



(XI)

The copper salt of p-methoxybenzylidene malonic acid obtained by the partition method may be represented as VIII (R=p-$OCH_3C_6H_4$) and those obtained by other methods are acidic , and are represented as (XII)



(XII)

where the value of x depends on the method of preparation. It may be possible that the acidic salts may contain acid in the adsorbed or occluded form. This possibility is excluded on the basis of the observations that (i) the products were carefully washed with various solvents and (ii) no separation of the acidic copper salts of, say, o-chlorobenzylidene malonic acid into two or more fractions could be achieved by thin layer chromatographic separation.

The results show that three types of salts, normal, acidic and basic are obtained in this case, and there is a greater tendency for the formation of acidic salts than that for the formation of basic salts.

- X - - X - - X -

The absorption spectra of these salts in the ultra-violet region are given in figures 9 to 11 and the absorption bands are presented in tables 67 to 69.

A new band at 256 mμ was observed in the case of basic cobalt salts of benzylidene malonic acid. Similarly, a band at 252-54 mμ is observed in the case of the basic copper salts of benzylidene malonic acid. It may arise from the additional steric hindrance caused to the ligand by the basic component of the molecule. The band at 254-56 mμ is also observed for the normal copper salt of p-nitrobenzylidene malonic acid prepared by the solution method but not for the normal salts

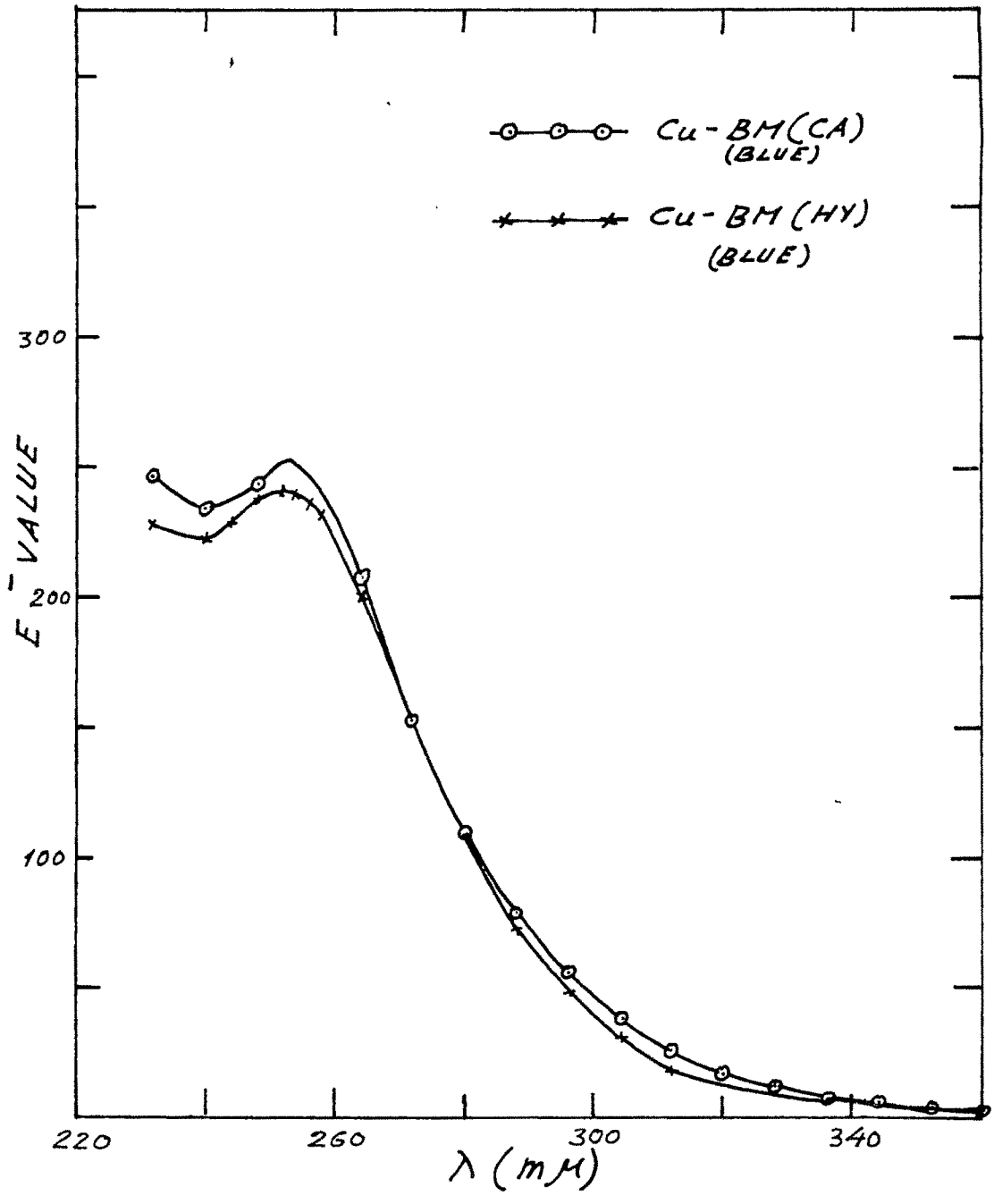


FIG. 9 UV ABSORPTION SPECTRA OF THE COPPER SALTS OF THE BENZYLIDENE MALONIC ACID.

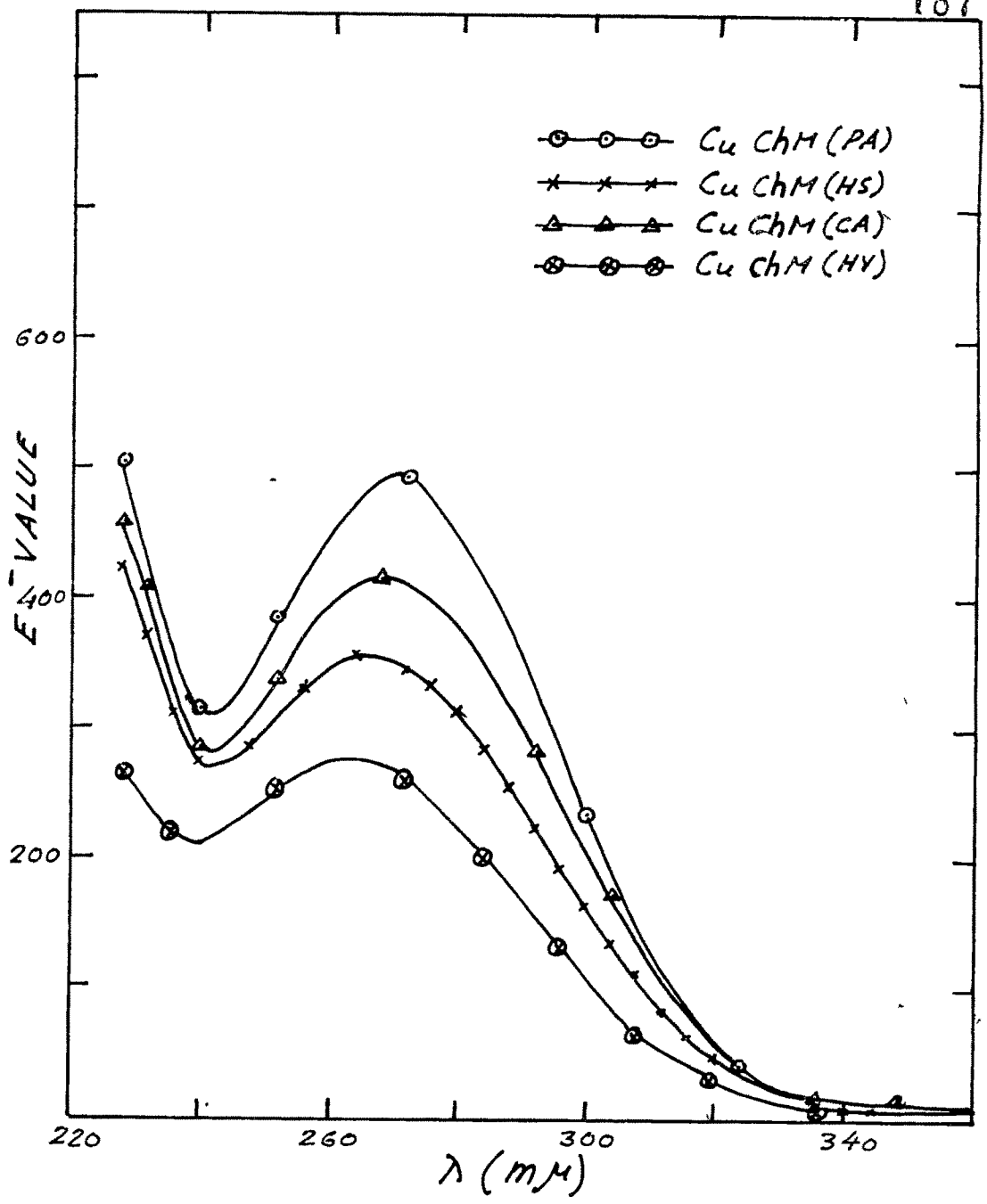


FIG. 10 UV ABSORPTION SPECTRA OF THE COPPER SALTS OF THE PARA-CHLOROBENZYLIDENE MALONIC ACID.

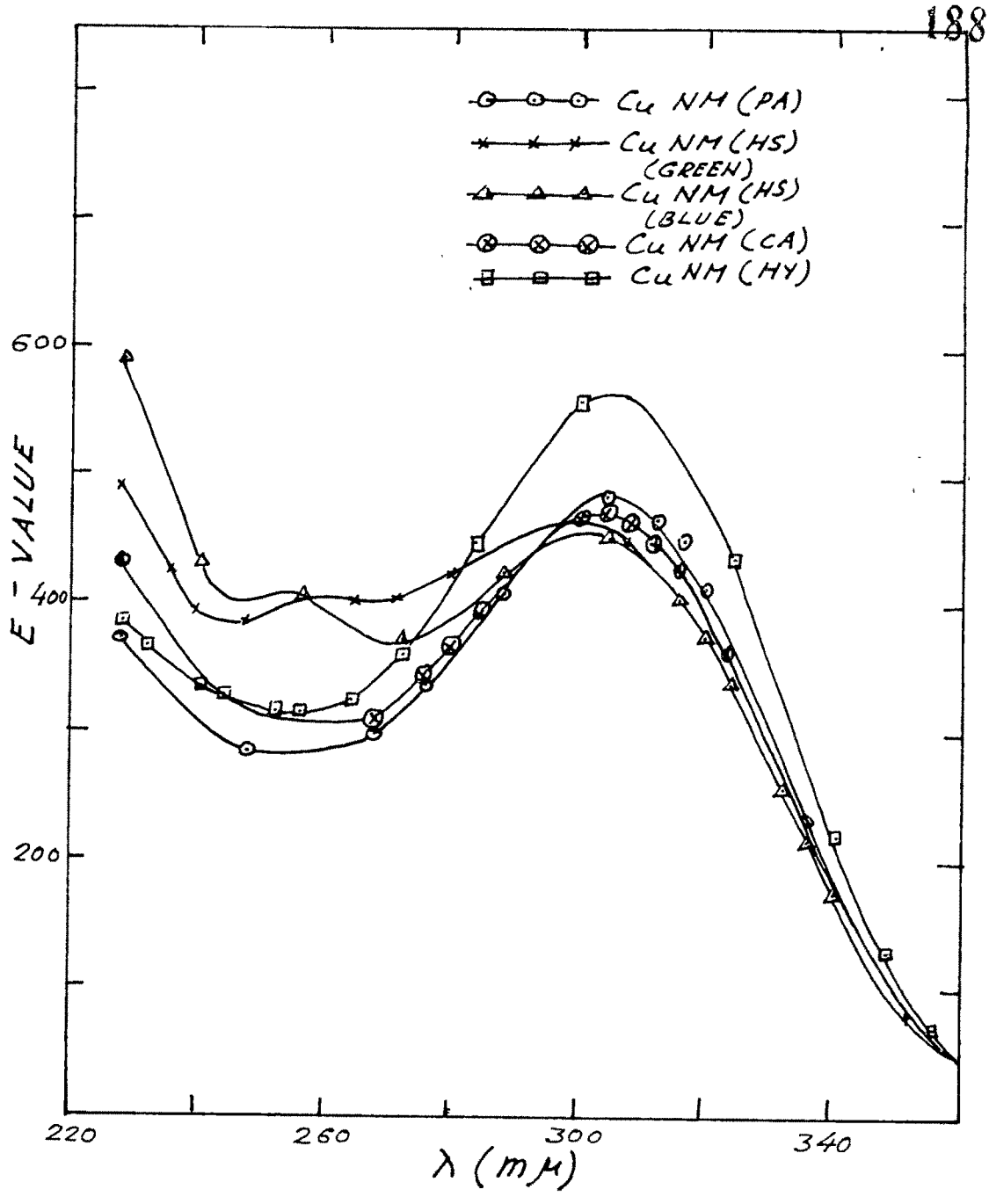


FIG. 11 UV ABSORPTION SPECTRA OF THE COPPER SALTS OF THE PARA-NITROBENZYLIDENE MALONIC ACID.

Table 67

Ultra-violet absorption spectra of copper salts of benzylidene malonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-Value
1.	Cu BM (CA) (Blue)	$C_{12}H_{30}O_{22}Cu_3$	252	251.1
2.	Cu BM (HY) (Blue)	$C_{10}H_{32}O_{19}Cu_3$	252-54	241.2

Table 68

Ultra-violet absorption spectra of copper salts of ortho-chlorobenzylidene malonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-Value
1.	Cu ClM (PA)	$C_{30}H_{37}O_{22}Cl_3Cu_2$	270	496.7
2.	Cu ClM (HS)	$C_{30}H_{32}O_{19.5}Cl_3Cu_2$	266	358.6
3.	Cu ClM (CA)	$C_{30}H_{39}O_{23}Cl_3Cu_2$	268	416.0
4.	Cu ClM (HY)	$C_{20}H_{37}O_{22.5}Cl_2Cu_3$	262	273.8

Table 69

Ultra-violet absorption spectra of copper salts of para-nitrobenzylidene mallonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λmax (mμ)	E-Value
1.	Cu NM(PA)	$C_{10}H_{11}O_9NCu$	304	482.5
2.	Cu NM(HS)	$C_{10}H_7O_7NCu$	298	465.2
	(Green)		256	404.1
3.	Cu NM(HS)	$C_{10}H_{11}O_9NCu$	300	456.8
	(Blue)		254	410.2
4.	Cu NM(CA)	$C_{10}H_{12}O_{9.5}NCu$	304	472.2
5.	Cu NM(HY)	$C_{10}H_{10}O_{8.5}NCu$	306-08	561.0

prepared by other methods. This difference in behaviour remains unexplained.

- X - - X - - X -

The magnetic moments of these salts are presented in tables 70 to 74. The magnetic moments of the salts prepared by different methods are :

μ (B.M.)

	normal salt	acidic salt	basic salt
Cu BM	1.85 ± 0.12	-	2.17 + 0.03
Cu ClM	-	2.41 ± 0.03	2.09
Cu ChM	-	2.03 ± 0.02	-
Cu MM	1.80	2.31 ± 0.01	-
Cu NM	2.18 ± 0.10	-	-

The results show that the values of the magnetic moment of these salts are not low. Low values of the magnetic moment are observed for the copper salts of oxalic acid and other α,ω dicarboxylic acids but not of malonic acid.[206-211] Thus the copper salts of substituted malonic acids resemble that of unsubstituted malonic acid. Further the values can be divided in two groups : (a) $\mu \sim 1.8$ B.M. and (b) $\mu \sim 2.2$ B.M. The first set of values is observed for the normal salts (except Cu NM). The second set of values is observed for acidic and basic salts and also for Cu NM and may indicate similar nature of these compounds. Both the acidic and basic salts may

Table 70

Magnetic moments of copper salts of benzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Cu BM(HS)	1135	1246	1.76
2.	Cu BM(CA) (Green)	1097	1203	1.73
3.	Cu BM(CA) (Blue)	1848	1944	2.20
4.	Cu BM(HY) (Green)	1456	1562	1.96
5.	Cu BM(HY) (Blue)	1753	1843	2.14

Table 71

Magnetic moments of copper salts of ortho-chlorobenzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Cu ClM (PA)	2097	2324	2.39
2.	Cu ClM (HS)	2095	2309	2.39
3.	Cu ClM (CA)	2190	2422	2.44
4.	Cu ClM (HY)	1653	1791	2.09

Table 72

Magnetic moments of copper salts of para-chlorobenzylidene malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Cu ChM(PA)	1464	1654	2.01
2.	Cu ChM(HS)	1481	1671	2.03
3.	Cu ChM(HY)	1503	1693	2.05

Table 73

Magnetic moments of copper salts of para-methoxybenzylidene malonic acid

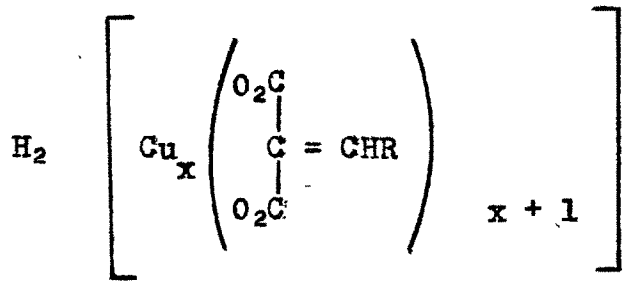
No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Cu MM (PA)	1182	1320	1.80
2.	Cu MM (HS)	2013	2155	2.31
3.	Cu MM (CA)	2004	2148	2.30
4.	Cu MM (HY)	2045	2210	2.32

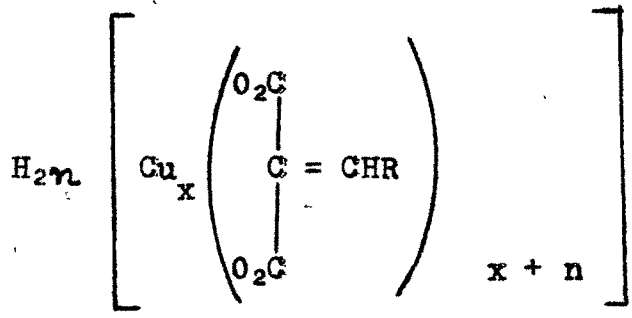
Table 74

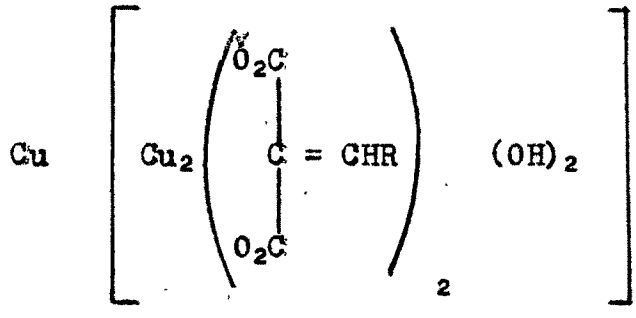
Magnetic moments of copper salts of para-nitrobenzylidene malonic acid

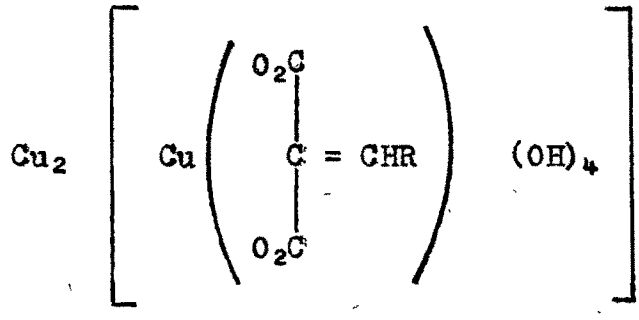
No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Cu NM (PA)	1783	1921	2.18
2.	Cu NM (HS) (Green)	1628	1745	2.08
3.	Cu NM (HS) (Blue)	1706	1844	2.13
4.	Cu NM (CA)	1814	1957	2.20
5.	Cu NM (HY)	1968	2101	2.28

be considered to contain copper in the complex anion, at least partly as represented below :

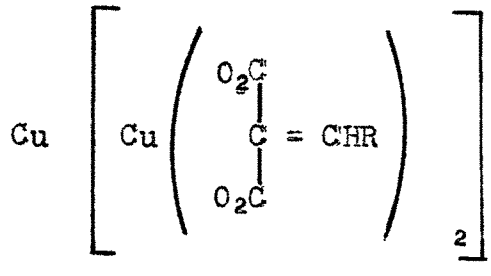








The normal salt Cu NM is also believed to be a complex one.



In the case of Cu NM two hydrates are obtained by the solution method, one is coloured green and contains one water molecule while the other is coloured blue and contains three water molecules. Other Cu NM salts prepared by different methods are hydrated, contain more than two water molecules and are coloured blue.

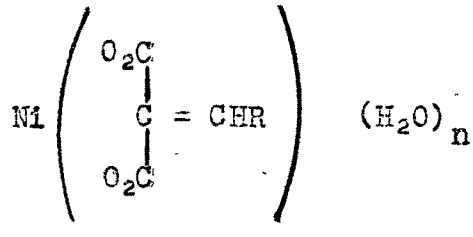
The copper complexes formed by β-diketones (IV-i) and oxime-ketones (IV-ii) may be represented as CuL_2 or $CuL(OH)$.[271,273,274] No acid salts of these ligands are known. We find that the acids under investigation form three types of salts : CuL, $(CuL)x\ Cu(OH)_2$ and $(CuL)x\ H_2L$.

- X - - X - - X -

III. 5. Nickel salts of benzylidene malonic acids :

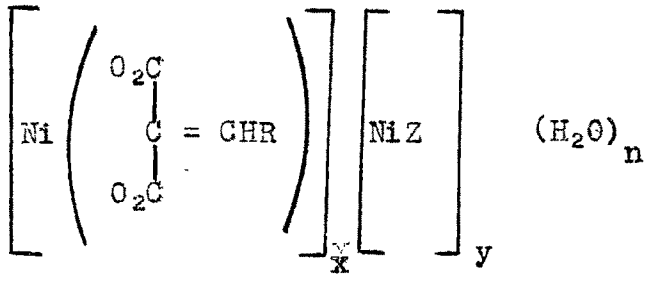
Nickel (II) salts of benzylidene malonic acid and its derivatives (I) were prepared by two methods : (a) carbonate method and (b) hydroxide method. Attempts to prepare the salts by partition and solution methods were unsuccessful. The analysis of the products obtained

are presented in tables 32 and 33. The type of the salts obtained depends both on the nature of the ligand and the method of preparation. The three types of salts obtained may be represented as (XIII), (XIV) and (XV)



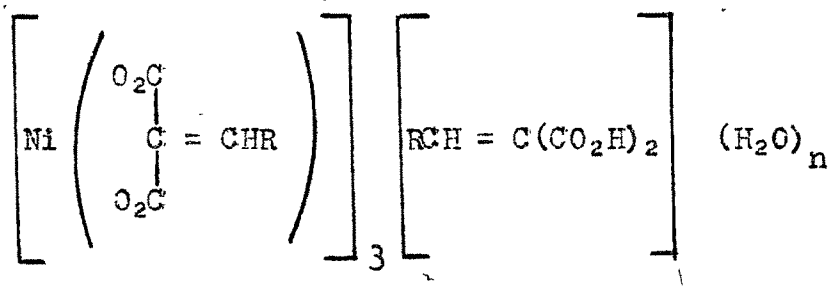
(XIII)

R =	Method
a = o-ClC_6H_4	CA ; HY
b = p-ClC_6H_4	HY
c = p-$NO_2C_6H_4$	HY



(XIV)

	R =	Z =	Method	x =	y =
a	p-ClC_6H_4	CO_3	CA	1	2
b	p-$CH_3OC_6H_4$	CO_3	CA	1	1
c	p-$CH_3OC_6H_4$	$(OH)_2$	HY	3	2
d	C_6H_5	$(OH)_2$	HY	1	2



(XV)

R =	Method
$p\text{-}NO_2C_6H_4$	CA

The absorption spectra of these salts are presented in figures 12 and 13 and the absorption bands are given in tables 75 and 76. The results show that a band is observed at 256 mμ in case of the basic nickel salts of benzylidene malonic acid as in the case of the basic salts of cobalt and copper with the same acid. Similar behaviour is observed in case of the nickel salts of p-chlorobenzylidene malonic acid (band at 258-60 mμ).

The magnetic moments of these salts are presented in tables 77 and 78. The magnetic moments of the salts prepared by different methods are :

	μ (B.M.)		
	normal salt	acidic salt	basic salt
Ni BM	-	-	3.53
Ni ClM	3.44 ± 0.06	-	-
Ni ChM	3.38	-	3.43
Ni MM	-	-	3.40 ± 0.04
Ni NM	3.62	3.58	-

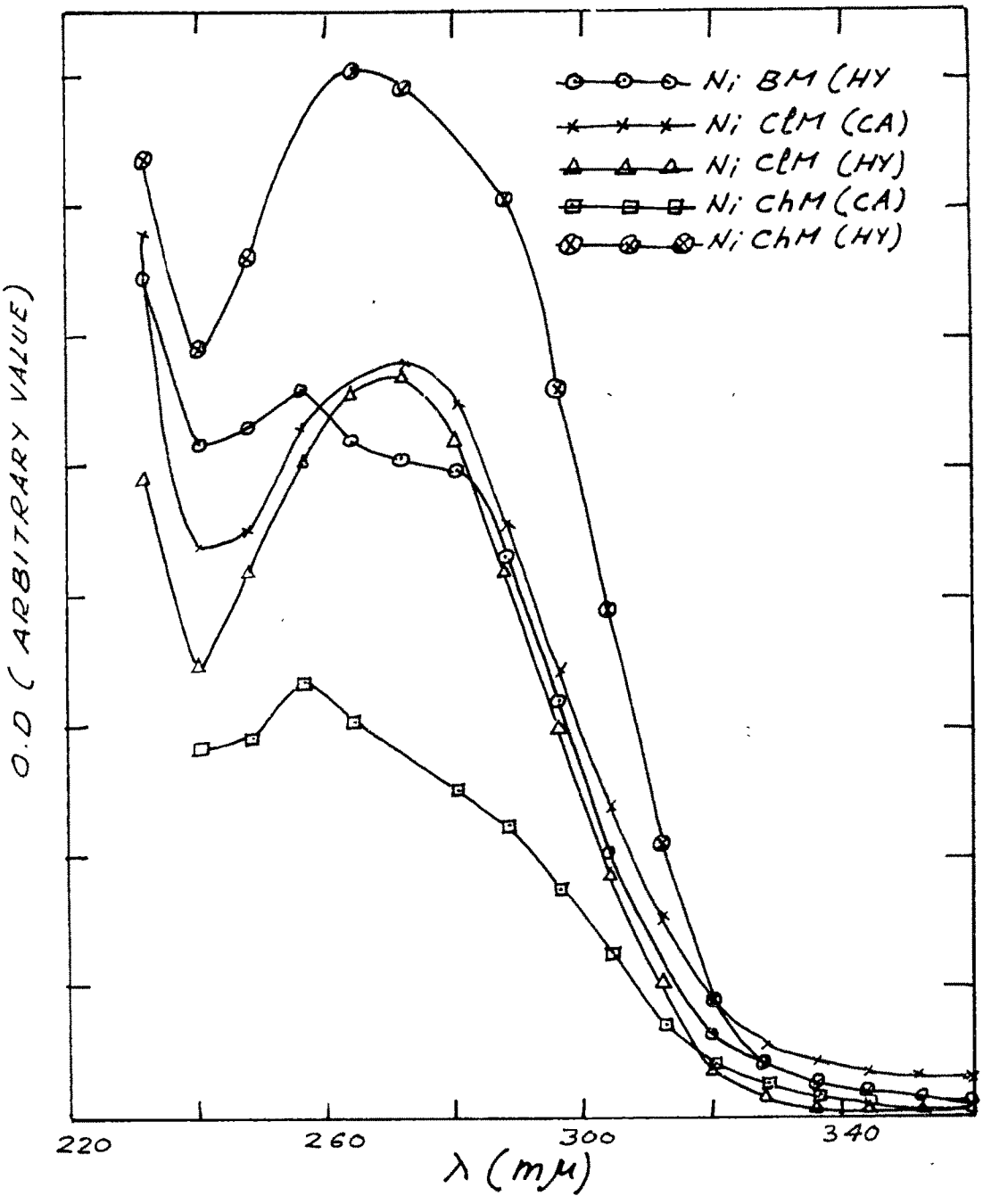


FIG. 12 UV ABSORPTION SPECTRA OF THE NICKEL SALTS OF THE SUBSTITUTED BENZYLIDENE MALONIC ACIDS.

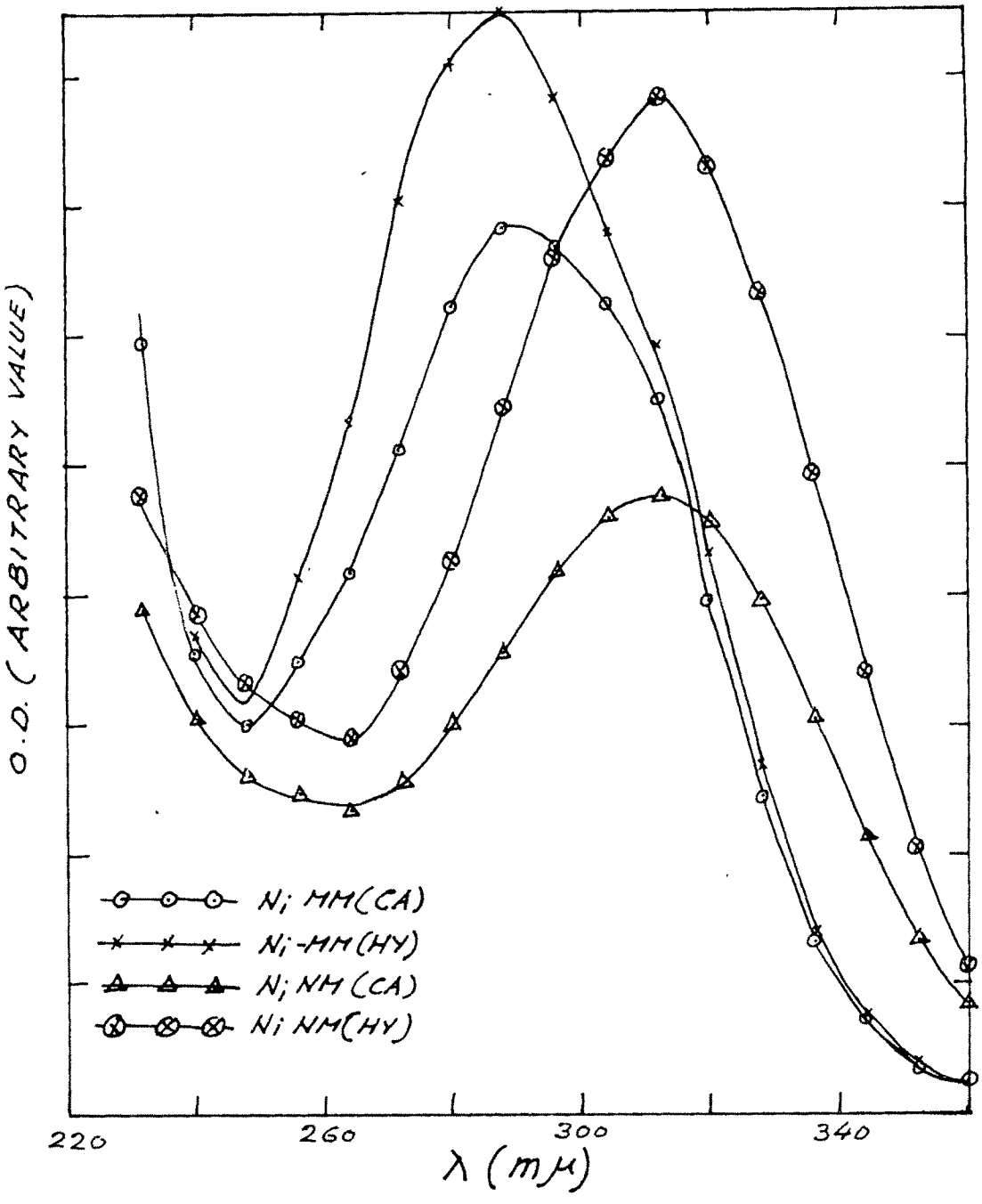


FIG. 13 UV ABSORPTION SPECTRA OF THE NICKEL SALTS OF THE P-METHOXY (AND P-NITRO) BENZYLIDENE MALONIC ACIDS.

Table 75

Ultra-violet absorption spectra of nickel salts of substituted malonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λ_{max} (mμ)	O.D.
1.	Ni BM (HY)	$C_{10}H_{32}O_{19}Ni_3$	256	0.560
2.	Ni ClM(CA)	$C_{10}H_{17}O_{10}ClNi$	272	0.580
3.	Ni ClM(HY)	$C_{10}H_{12}O_{7.5}ClNi$	270	0.571
4.	Ni ChM(HY)	$C_{10}H_{10}O_{6.5}ClNi$	260	0.825
5.	Ni ChM(CA)	$C_{12}H_{21}O_{18}ClNi_3$	258	0.335

Table 76

Ultra-violet absorption spectra of nickel salts of substituted malonic acid in methanol.

No.	Complex	Formula of the complex	in methanol	
			λ_{max} (mμ)	O.D.
1.	Ni MN (CA)	$C_{12}H_{20}O_{14}Ni_2$	290	0.690
2.	Ni MM (HY)	$C_{33}H_{64}O_{37}Ni_5$	288	0.850
3.	Ni NM (CA)	$C_{40}H_{68}O_{47}N_4Ni_3$	312	0.478
4.	Ni NM (HY)	$C_{10}H_{13}O_{10}NNi$	312	0.782

Table 77

Magnetic moments of nickel salts of substituted malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi'_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Ni BM (HY)	4933	5023	3.53
2.	Ni ClM (CA)	4491	4672	3.39
3.	Ni ClM (HY)	4845	5000	3.50
4.	Ni ChM (HY)	4453	4597	3.38
5.	Ni ChM (CA)	4643	4731	3.43

Table 78

Magnetic moments of nickel salts of substituted malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Ni MM (CA)	4662	4768	3.44
2.	Ni MM (HY)	4465	4584	3.37
3.	Ni NM (CA)	4953	5173	3.58
4.	Ni NM (HY)	5137	5285	3.62

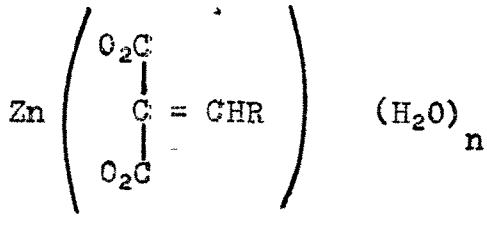
The results show that nickel salts are octahedral, and that no distinction can be made between the acidic (or basic) salts and normal salts as is possible in the case of the copper and cobalt salts. Ranade and SubbaRao[178] observed the magnetic moment of nickel malonate as 3.27 B.M. and suggested octahedral configuration for it.

Nickel complexes of β-diketones in the hydrated form are monomeric and octahedral[275] while anhydrous complexes are trimeric containing 6-coordinate nickel.[276] Nickel complexes of oxime-ketones are likely to be dimeric.[271]

- X - - X - - X -

III. 6. Zinc salts of benzylidene malonic acids :

The studies on the cobalt, copper and nickel salts of benzylidene malonic acids showed that the partition method of preparing the salts was a better method wherever feasible. Hence the zinc (II) salts of benzylidene malonic acid and its derivatives were prepared by the partition method. The analyses of the salts are presented in table 38. The results show that they are all normal salts and may be represented as (XVI)



(XVI)

R =

a C_6H_5 -

b o-ClC_6H_4-

c p-$CH_3OC_6H_4$-

d p-$NO_2C_6H_4$-

They are insoluble in various solvents and are believed to be tetrahedral.

The absorption spectrum of Zn NM is presented in fig. 14. Its absorption band is at 320 mμ with E-value of 426.7.

- X - - X - - X -

III.7. Manganese salts of benzylidene malonic acids :

Manganese (II) salts of benzylidene malonic acid and its derivatives (I) were prepared by the partition method. The analyses of the products are given in table 39. The results show that they are all normal salts and may be represented as (XVII)

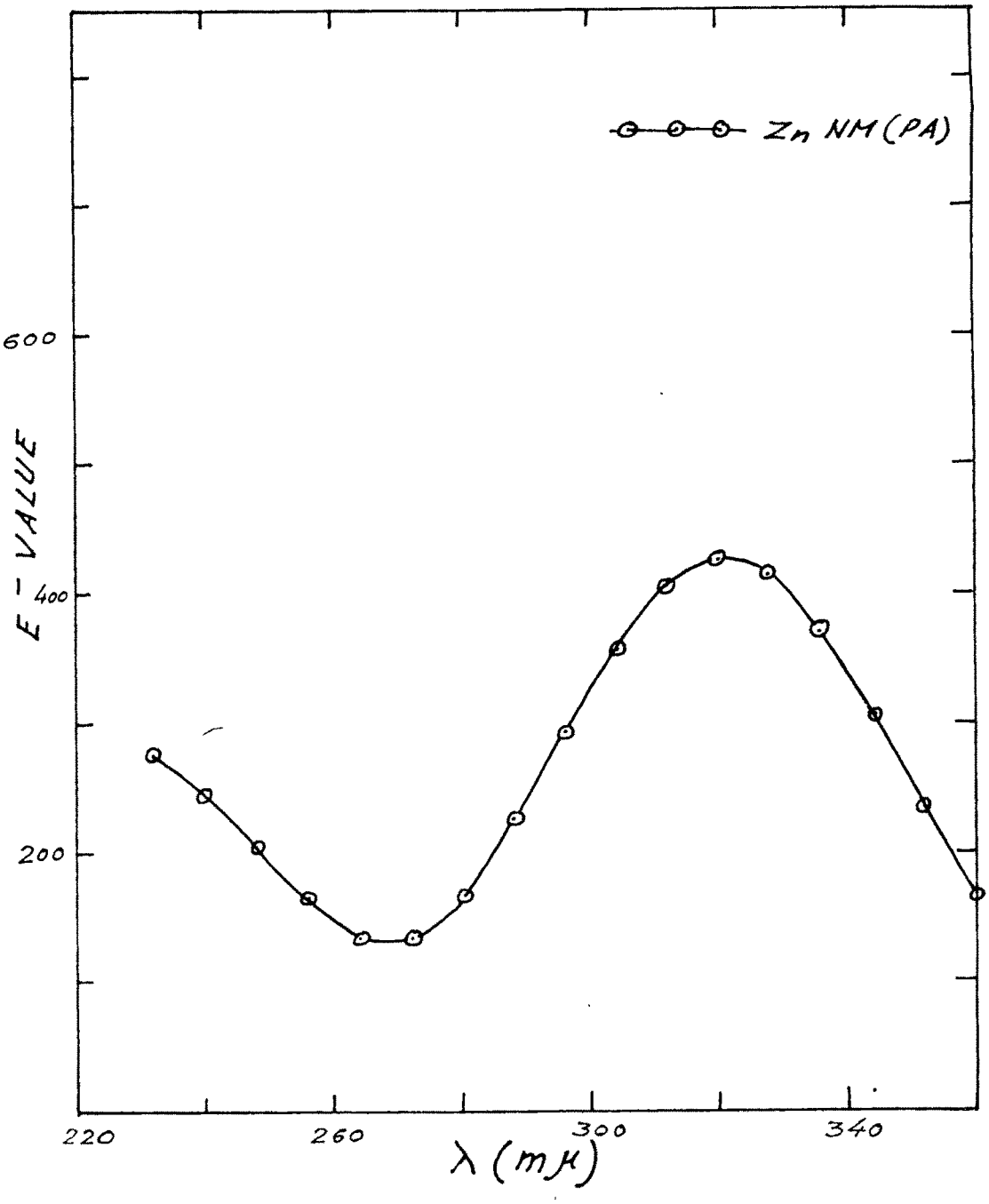
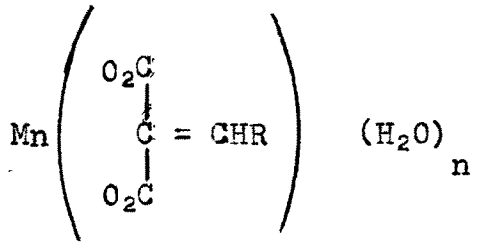


FIG. 14 UV ABSORPTION SPECTRA OF THE ZINC SALT OF THE P-NITROBENZYLIDENE MALONIC ACID.



(XVII)

R =

a = C_6H_5-

b = o-ClC_6H_4-

c = p-ClC_6H_4-

d = p-$CH_3OC_6H_4$-

e = p-$NO_2C_6H_4$-

Their absorption spectra are given in figure 15 and their absorption bands are presented in table 79.

The magnetic moments of the salts are presented in table 80. The average value of the moment is 6.11 B.M.

III.8. Copper, nickel and cobalt salts of chlorobenzylidene malonic acids - further studies :

8(a) Visible absorption spectra :

The copper, nickel and cobalt salts of o-or p-chlorobenzylidene malonic acid were selected for the study of their visible absorption spectra. These spectra are presented in fig. 16. The absorption bands are presented

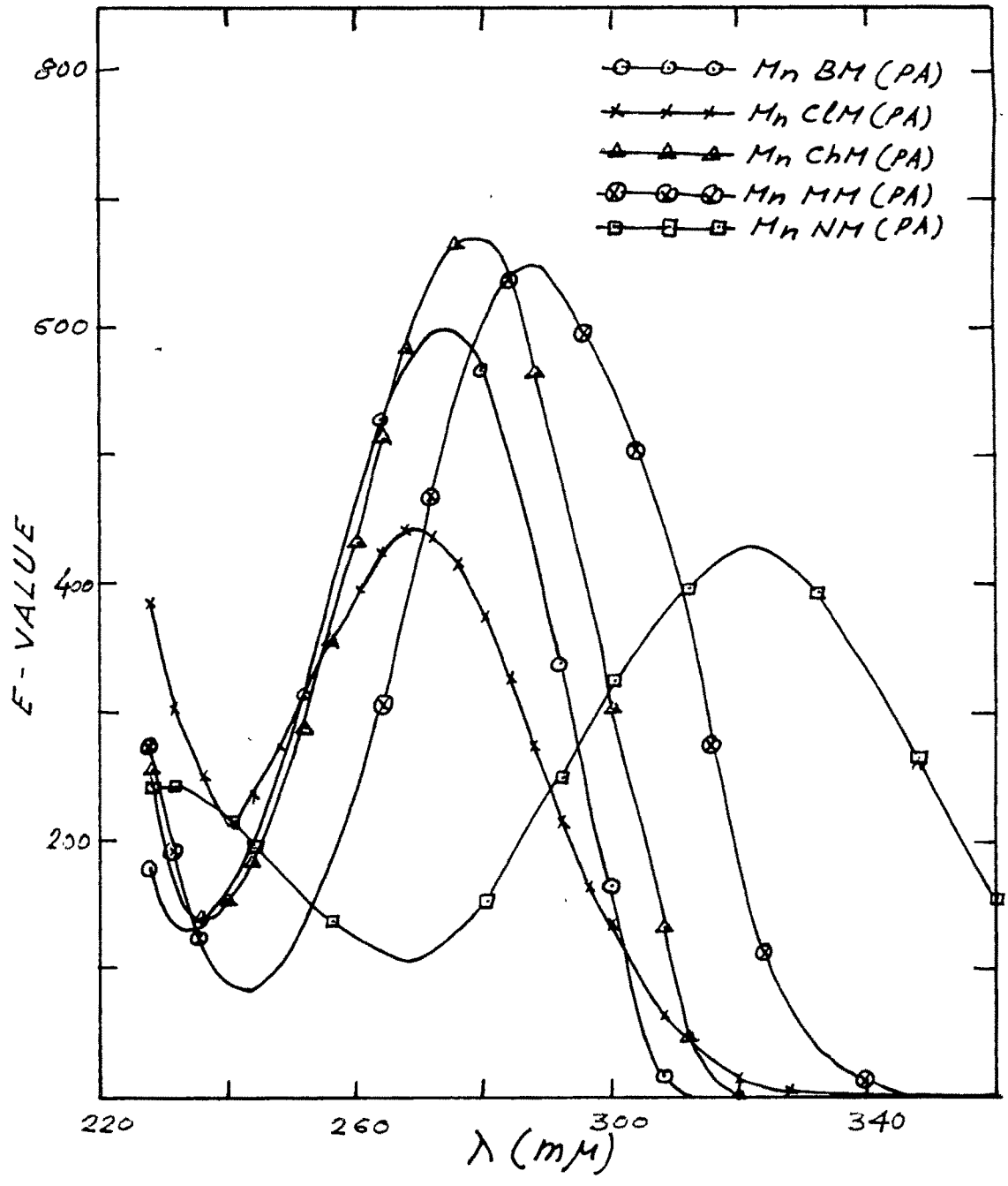


FIG. 15 UV ABSORPTION SPECTRA OF THE MANGANESE SALTS OF THE SUBSTITUTED BENZYLIDENE MALONIC ACIDS.

Table 79

Ultra-violet absorption spectra of manganese salts of substituted malonic acid in methanol.

No.	Complex	Formula of the complex	in metharol	
			λ_{max} (mμ)	E-Value
1.	Mn BM (PA)	$C_{10}H_{10}O_6Mn$	274	603.9
2.	Mn ClM (PA)	$C_{10}H_9O_6ClMn$	268	440.1
3.	Mn ChM (PA)	$C_{10}H_7O_5ClMn$	278	673.9
4.	Mn MM (PA)	$C_{11}H_{12}O_7Mn$	288	647.6
5.	Mn NM (PA)	$C_{10}H_{12}O_{9.5}NMn$	320	429.1

Table 80

Magnetic moments of manganese salts of substituted malonic acid

No.	Compound	Molar magnetic susceptibility (per metal atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $\chi_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	Mn BM (PA)	15200	15322	6.12
2.	Mn ClM (PA)	15080	15219	6.10
3.	Mn ChM (PA)	14960	15089	6.09
4.	Mn MM (PA)	15190	15328	6.13
5.	Mn NM (PA)	15120	15263	6.11

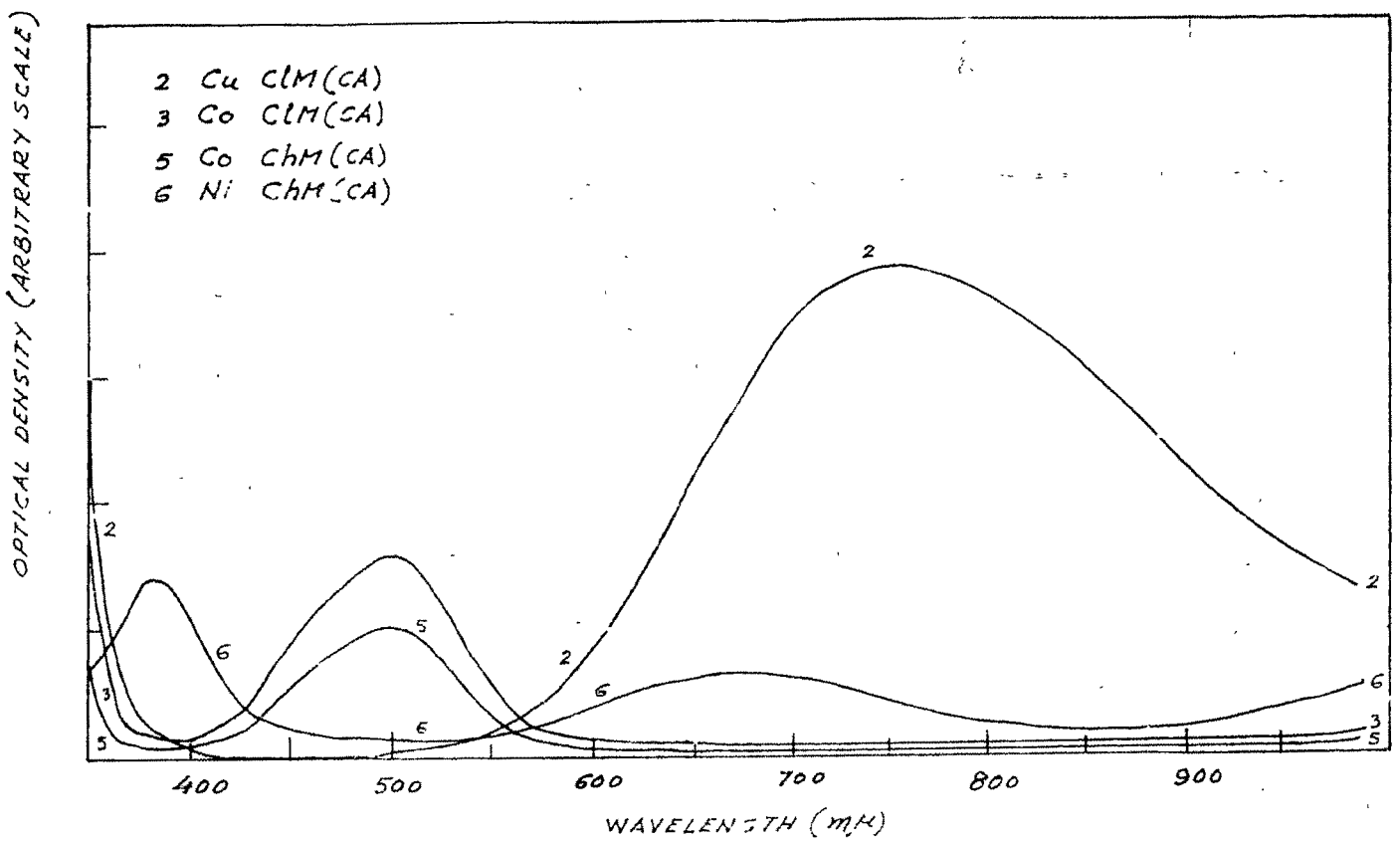


FIG. 16 VISIBLE ABSORPTION SPECTRA OF THE COPPER, NICKEL AND COBALT SALTS OF CHLOROBENZYLIDENE MALONIC ACIDS.

below:

Salt	band frequency (cm^{-1})
Ni ChM(CA)	14820, 26170
Co ClM (CA)	19920
Co ChM (CA)	18810
Cu ClM (CA)	13320

We may consider the spectrum of the nickel salt first. The absorption bands are the d-d bands and be attributed to the transitions due to the weak octahedral crystal field around nickel. The splitting of the terms due to the octahedral crystal field[277] is shown in fig. 17. Three absorption bands should be observed corresponding to the following three spin-allowed transitions.

$$^3A_{2g} \longrightarrow {}^3T_{2g}$$

$$^3A_{2g} \longrightarrow {}^3T_{1g} \text{ (F), and}$$

$$^3A_{2g} \longrightarrow {}^3T_{1g} \text{ (P).}$$

The first band would be outside the range of investigation and hence is not observed.

The two bands observed at 14820 cm^{-1} and

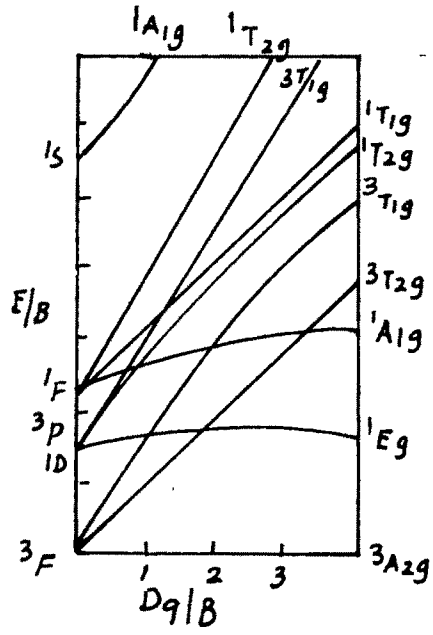


FIG. 17 (a) TANABE-SUGANO DIAGRAM FOR d^8 (Ni^{2+} - OCTAHEDRAL SYMMETRY)

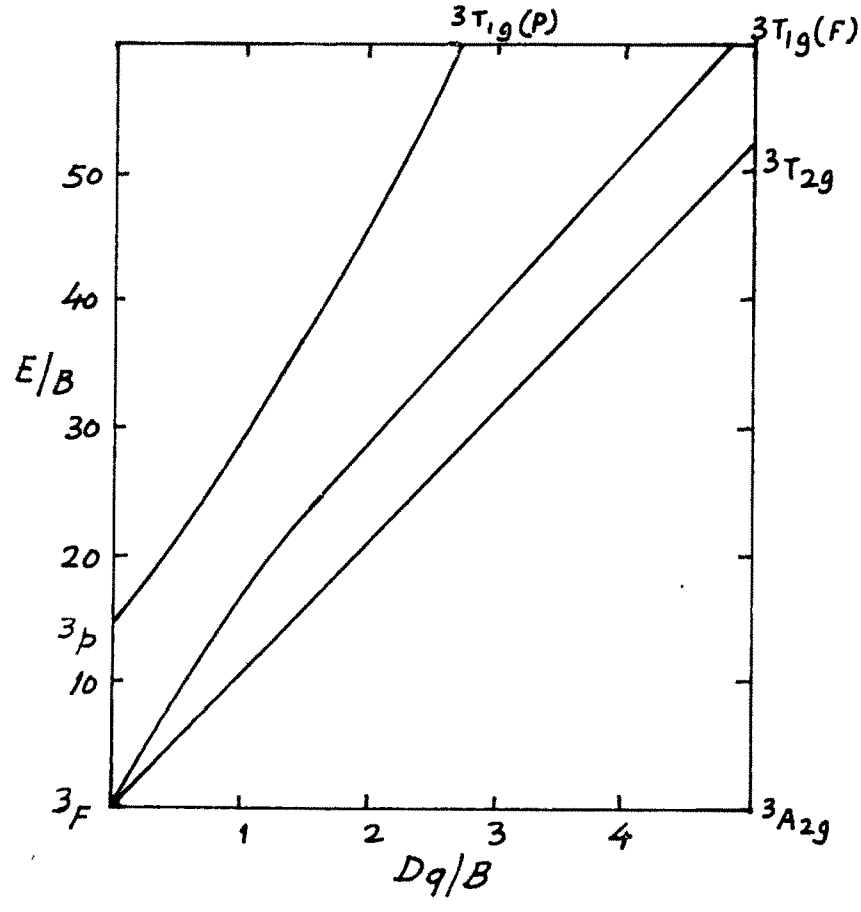


FIG. 17 (b) ENERGY DIAGRAM FOR d^8 (TRIPLET TERMS)

26170 cm^{-1} are attributed to the

$$^3A_{2g} \longrightarrow {}^3T_{1g}\ (F) \quad \text{and} \quad {}^3A_{2g} \longrightarrow {}^3T_{1g}\ (P)$$

transitions.

These observations can be used together with fig. 17(b) to evaluate various crystal field parameters. We observe that

$$\frac{E\left[{}^3A_{2g} \longrightarrow {}^3T_{1g}\ (P)\right]}{E\left[{}^3A_{2g} \longrightarrow {}^3T_{1g}\ (F)\right]} = 1.77$$

From the figure, we find that the ratio fits well for

$$Dq / B = 0.945$$

and that

$$\frac{E\left[{}^3A_{2g} \longrightarrow {}^3T_{1g}\ (F)\right]}{B} = 15.7$$

Hence for the Ni^{2+} in the salt

$$B = 945\ cm^{-1}$$

$$Dq = 893\ cm^{-1}$$

and $$\Delta = 8930\ cm^{-1}$$

Since the value of B for the free Ni^{2+} ion is 1080 cm^{-1}, the ratio

$$\beta = \frac{\text{B for } Ni^{2+} \text{ ion in the salt}}{\text{B for } Ni^{2+} \text{ ion in free state}}$$

is 0.875.

Further

$$E\left({}^{3}A_{2g}\right) = -10716 \text{ cm}^{-1}$$

and $$E\left({}^{3}T_{2g}\right) = -1786 \text{ cm}^{-1}$$

Since

$$\Delta = f \times g \times 10^{3}$$

(Where f and g are constants[279] for the ligand and metal ion respectively)

$$8930 = f \times 8.9 \times 10^{3}$$

or $$f = 1.00$$

Similarly

$$\beta = 1-hk$$

(Where h and k are constants[279] for the ligand and the metal ion respectively)

$$0.875 = 1-h \times .12$$

or $$h = 1.04$$

The value of p for Ni^{2+} in the salt is

$$p = 15B = 14175 \text{ cm}^{-1}$$

The values of $E\left[{}^3T_{1g}(F)\right]$ and $E\left[{}^3T_{1g}(P)\right]$ can be evaluated from the following secular determinant:

$$\begin{vmatrix} -6\,Dq - E & 4Dq \\ 4\,Dq & p - E \end{vmatrix} = 0$$

On expansion, we obtain the equation

$$E^2 + (6Dq - p)\,E - 16(Dq)^2 - 6\,Dqp = 0$$

The roots of this equation are the energies of the two ${}^3T_{1g}$ terms --- ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$.

The values are obtained as 4080 cm^{-1} and 15450 cm^{-1}.

Hence

$$E\left[{}^3T_{1g}(F)\right] = 4080 \text{ cm}^{-1}$$

and

$$E\left[{}^3T_{1g}(P)\right] = 15450 \text{ cm}^{-1}$$

We calculate the energies of transitions as

$$E\left[{}^3A_{2g} \longrightarrow {}^3T_{1g}(F)\right] = 14796 \text{ cm}^{-1}$$

and $$E\left[{}^3A_{2g} \longrightarrow {}^3T_{1g}(P)\right] = 26166 \text{ cm}^{-1}$$

The close aggrement between the observed and calculated values indicates the correctness of the assignments.

-X- -X- -X-

If the values of f and h derived for the ligand from the study of the crystal field bands for the nickel salts are considered applicable for the cobalt salts also, we find that

$$\Delta = 1.00 \times 9.3 \times 10^3$$

$$= 9300 \text{ cm}^{-1}$$

$$\text{or } Dq = 930 \text{ cm}^{-1}$$

$$\text{and } \beta = 1 - 1.04 \times .24$$

$$= .75$$

hence B for cobalt in the salt = $.75 \times 1120$

$$= 840 \text{ cm}^{-1}$$

Further

$$Dq / B = 1.107$$

and $$E/B = \frac{19920}{840} = 23.7 \text{ for Co ClM (CA)}$$

$\frac{19810}{840}$ = 23.6 for Co ChM(CA)

By referring to the fig. 18 which shows the splitting of terms for the octahedral crystal field for cobalt (II) complexes, we find that these values fit to the

$$^4T_{1g}\ (F) \longrightarrow {}^4T_{1g}\ (P) \text{ transition}$$

Using the secular determinant and the values of Dq and B as suggested above we calculate the energies of the $^4T_{1g}$ terms. These values are

$$E\left[{}^4T_{1g}\ (F)\right] = -6310\ cm^{-1}$$

$$E\left[{}^4T_{1g}\ (P)\right] = +13330\ cm^{-1}$$

and

$$E\left({}^4A_{2g}\right) = +11160\ cm^{-1} \text{ and}$$

$$E\left({}^4T_{2g}\right) = +1860\ cm^{-1}.$$

- X - - X - - X -

The absorption band for Cu ClM(CA) is observed at 13320 cm^{-1}. It may be related to the octahedral

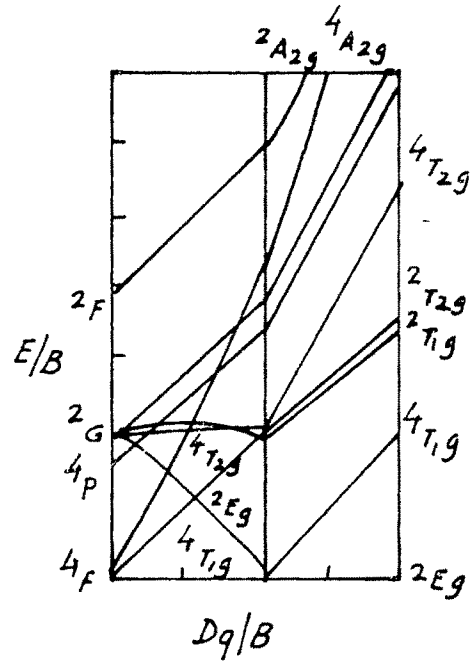


FIG. 18 (a) TANABE-SUGANO DIAGRAM FOR d^7
(Co^{2+} - OCTAHEDRAL SYMMETRY)

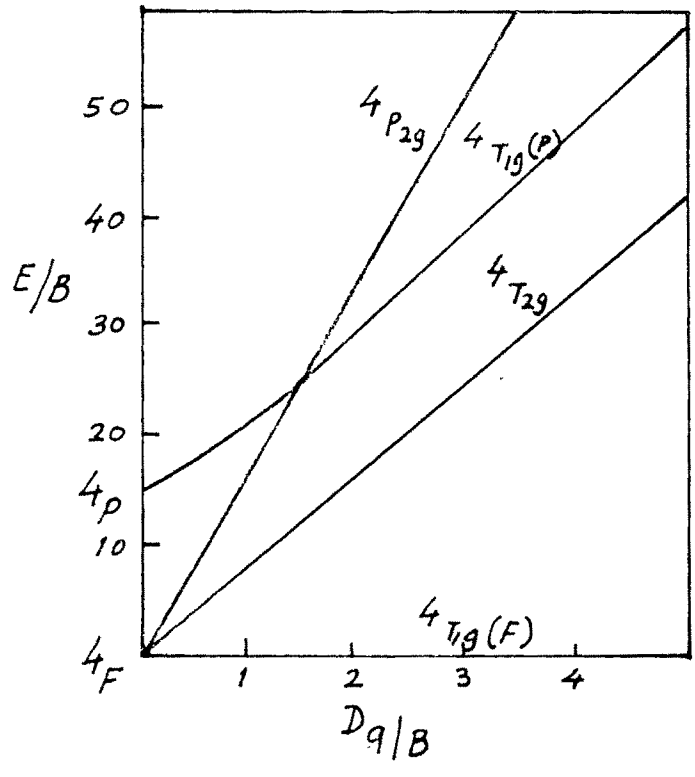


FIG. 18 (b) ENERGY DIAGRAM FOR d^7
(QUARTET TERMS)

crystal field around copper (II) (Fig. 19) and be attributed to the

$$^2E_g \longrightarrow {}^2T_{2g}$$ transition.

Hence,

$$\Delta = 13320 \text{ cm}^{-1}$$

and $$Dq = 1332 \text{ cm}^{-1}$$

We compile the crystal field parameters as follows :

	Dq (cm^{-1})	B (cm^{-1})
Ni (II)	893	945
Co (II)	930	840
Cu (II)	1320	

The results show that the value of Dq for the metal ion increases in order

$$Ni^{2+} < Co^{2+} < Cu^{2+}$$

as expected for the spectrochemical series.

The value of f observed for the ligand is the same as that suggested for water and greater than that for oxalic acid. Further the value of h for the ligand

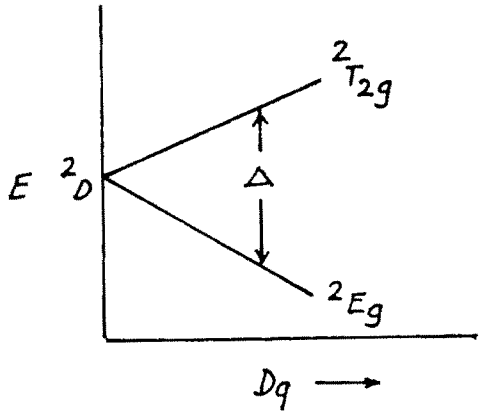


FIG. 19 ENERGY DIAGRAM FOR d^9 SYSTEM (Cu^{2+} - OCTAHEDRAL SYMMETRY)

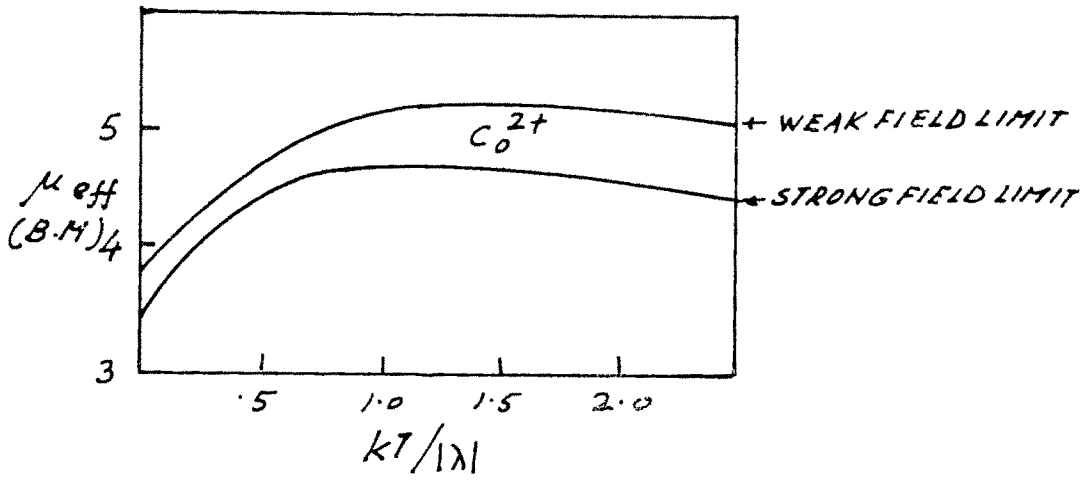


FIG. 20 MAGNETIC MOMENT AS A FUNCTION OF TEMPERATURE FOR $^4T_{1g}$ GROUND TERM IN CUBIC STEREOCHEMISTRY.

is also comparable to that for water and is much smaller than that for oxalic acid. It would imply that oxalic acid reduces the free ion value of B to a much greater extent than water or the ligand under consideration and that it causes the splitting of terms to a small extent than water or the ligand.

-X- -X- -X-

8(b) Magnetic susceptibility :

Bivalent nickel ion in the octahedral crystal field will have $^3A_{2g}$ ground term. Hence the magnetic moment and magnetic susceptibility for the nickel ion from the first order Zeeman effect terms[280] will be

$$\mu = (1 + \lambda / \Delta)\sqrt{4S(S+1)}$$

$$= \mu^{\text{spin only}} (1 + \lambda / \Delta).$$

and $$\chi_A = \chi_A^{\text{spin only}} (1 - 8\lambda / \Delta).$$

where λ is the spin-orbit coupling constant. Since the values of $\chi_A^{\text{spin only}}$, λ and Δ are known as 3333×10^{-6} CGS / mole, $-315\ cm^{-1}$ and $8930\ cm^{-1}$, we find the value of χ_A as 4273×10^{-6} CGS/ mole. It is

smaller than the observed value and the difference to a large extent be attributed to the susceptibility due to the second order Zeeman effect.

For bivalent cobalt in the weak octahedral crystal field, $^4T_{1g}$ (F) is the ground term. For the T ground terms the magnetic moment will be dependent upon $kT/|\lambda|$. This dependence is shown in fig. 20, in which the two curves indicate the values for two extremes of the ligand field strength. For $kT/|\lambda| = 1.24$, the range of the magnetic moment will be 4.64 to 5.24 B.M. The observed values are close to the higher value and correspond to the weak field limit.

For bivalent copper in the octahedral crystal field, ^2E_g is the ground term. Hence, the magnetic susceptibility of the copper ion from the first order Zeeman effect terms will be

$$\chi_A = \chi_A^{\text{spin only}} (1 - 4\lambda / \Delta)$$

Since $\chi_A^{\text{spin only}}$, λ and Δ for copper (II) ion are known as 1250×10^{-6} CGS / mole, $-830\ cm^{-1}$ and $13320\ cm^{-1}$ respectively, we calculate the value of χ_A as 1562×10^{-6} CGS / mole. The value is much smaller than the observed one. The large difference cannot be accounted for in terms of the second order Zeeman effect

terms. It may arise from distortions caused by anisotropy and low symmetry crystal fields.

The ratio χ_A (obs) / χ_A (calc) has a value greater than one for nickel and copper salts ; it cannot be explained in usual terms.

- X - - X - - X -

III.9. Salts of substituted benzylidene malonic acids-general

9 (a) Ultra-violet absorption spectra :

The absorption bands (in cm^{-1}) of benzylidene malonic acid and its salts are

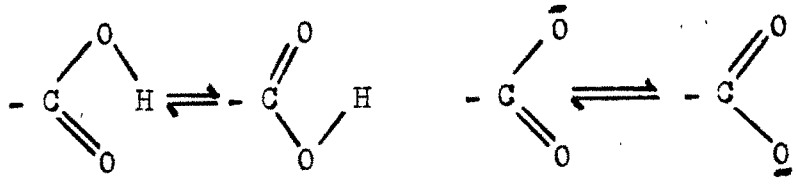
BM(alc) 35710 BM(alk) 36770

Co BM (PA) 36230-500Mn BM(PA) 36500

A large difference in the values of the absorption bands for the acid in alcohol and alkali is observed. One of the possible reasons for this can be the change in the distortion of the molecule from coplanarity. Calculations show, however, that the angle θ is quite comparable in the two cases and hence it cannot be the main cause for the shift of the band.

The alternative suggestion can be the change in the effective length of the conjugated system. A blue shift will be observed if a linearly conjugated system

modifies so that a part of its π-electron system branches out. In the present case, the carboxylic group can be represented as follows :



(a) (b)

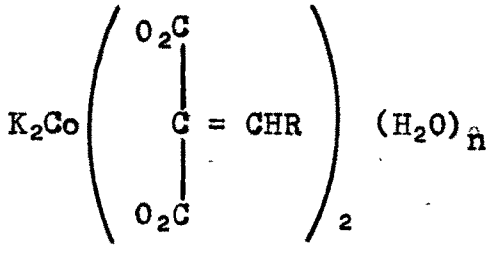
If it is assumed that the delocalisation of π- electrons is less for (a) than for (b) , it would explain the branching out of the π-electron system in case of ions and hence a blue shift.

The absorption band for the salts of the acid with cobalt (II), manganese (II) etc. has an intermediate value. It can be related to (i) the metal-ligand bond and (ii) the nature of the metal. Since the effect of the nature of the metal ion on the band position is not well understood as yet, we can explain it grossly as the effect of the metal-ligand bond. Since a weak crystal field is detected in the salts investigated, metal-ligand π-bonding is absent in the salts. It is suggested that the effect of the metal is to decrease the delocalisation of π-electrons so that (b) would approach (a).

The pattern of observations of the absorption bands is the same for p-chloro and p-methoxy benzylidene malonic acids and their salts and can similarly be explained.

III. 10. Complex salts of potassium and cobalt with benzylidene malonic acids :

The complex salts of potassium and cobalt with benzylidene malonic acid and its derivatives (I) were prepared by treating the carbonates of potassium and cobalt with the acid. The analyses of the salts are given in table 42. The results show that they can be represented as (XVIII).



(XVIII)

R =

a = C_6H_5-

b = o-ClC_6H_4-

c = p-ClC_6H_4-

d = p-$CH_3OC_6H_4$-

e = p-$NO_2C_6H_4$-

Their absorption spectra in the ultra-violet region are presented in fig. 21 and their absorption bands are given in table 81. The absorption band of the salt containing K and Co is nearer to the absorption band of the acid in alkali solution than that of the corresponding normal salt of Co alone.

The absorption spectra of two salts in the visible region are presented in fig. 22. They have an absorption

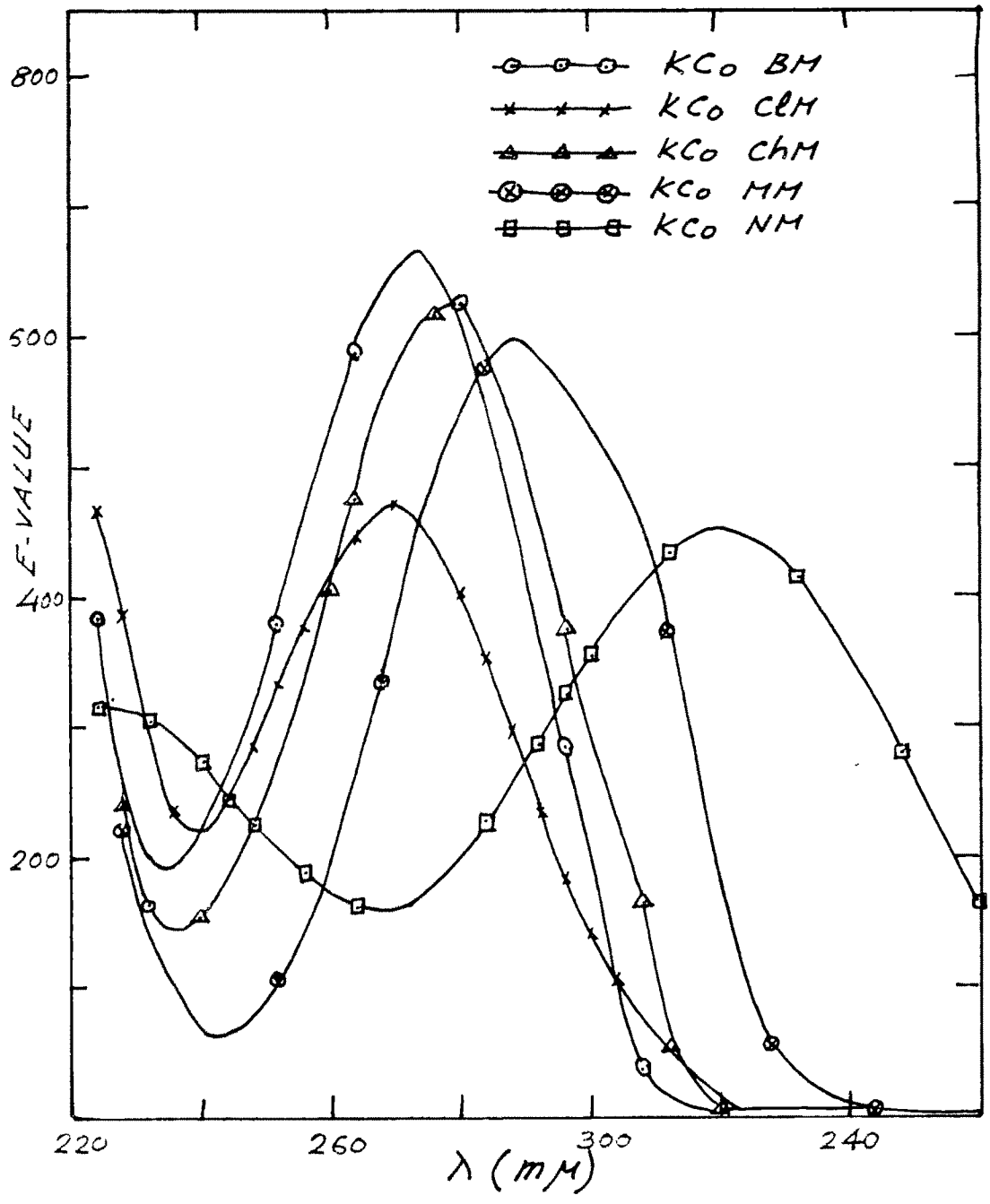


FIG. 21 UV ABSORPTION SPECTRA OF THE COMPLEX SALTS OF COBALT AND POTASSIUM WITH THE SUBSTITUTED BENZYLIDENE MALONIC ACIDS.

Table 81

Ultra-violet absorption spectra of complex salts of substituted malonic acid with potassium and cobalt in water.

No.	Complex	Formula of the complex	in water	
			λ max (mμ)	E-Value
1.	KCo BM	$K_2CoC_{20}H_{18}O_{11}$	274	661.6
2.	KCo ClM	$K_2CoC_{20}H_{16}O_{11}Cl_2$	270	470.0
3.	KCo ChM	$K_2CoC_{20}H_{12}O_9Cl_2$	278	627.0
4.	KCo MM	$K_2CoC_{22}H_{22}O_{13}$	288	598.9
5.	KCo NM	$K_2CoC_{20}H_{20}O_{17}N_2$	320	450.2

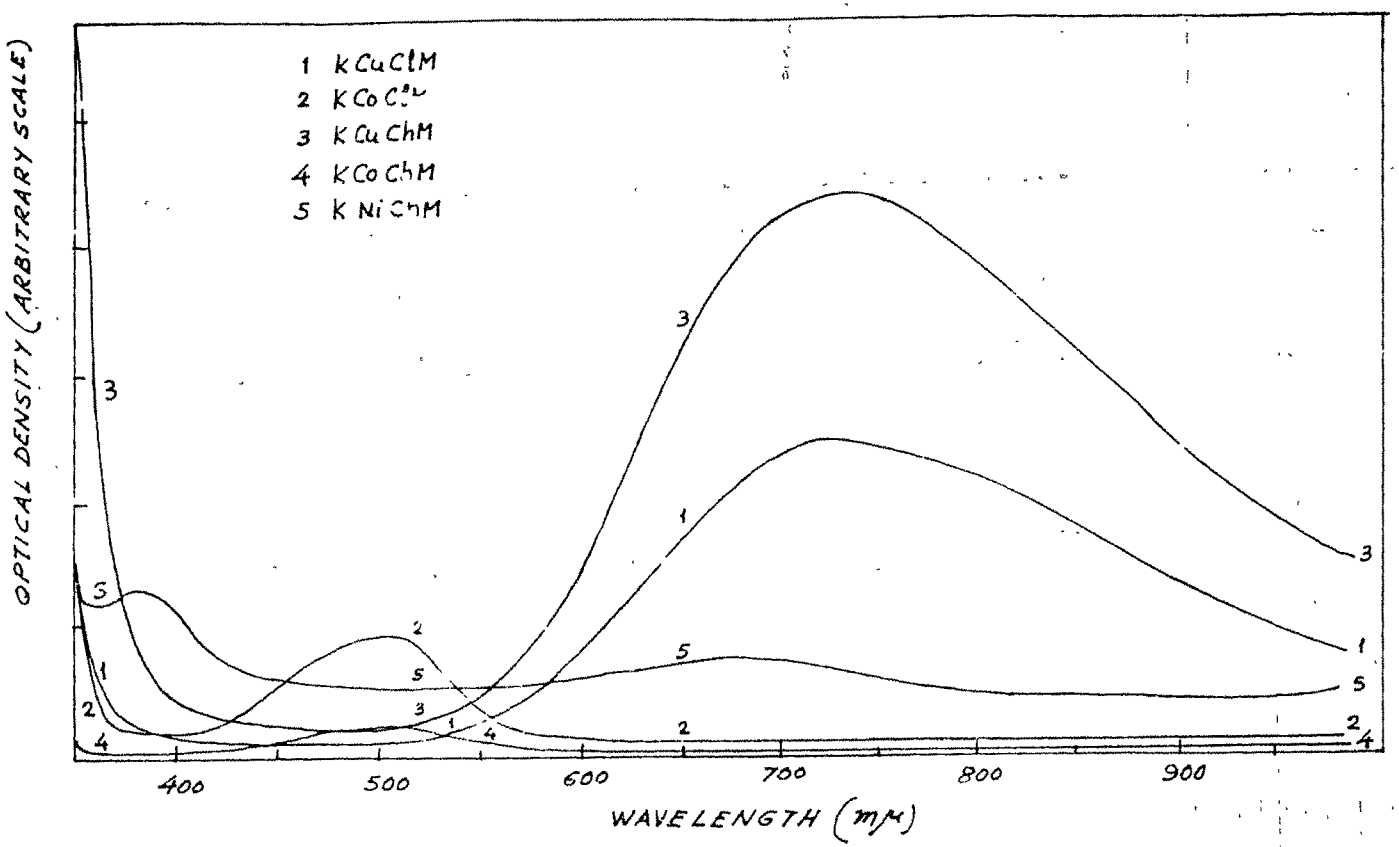


FIG. 22 VISIBLE ABSORPTION SPECTRA OF THE COMPLEX SALTS OF SUBSTITUTED BENZYLIDENE MALONIC ACIDS.

band at 19920 cm^{-1}. In continuation of our studies on Co ClM, we can suggest that for the weak octahedral crystal field

$$Dq = 930\ cm^{-1}$$

and $$B = 840\ cm^{-1}.$$

Further $$Dq/B = 1.107$$

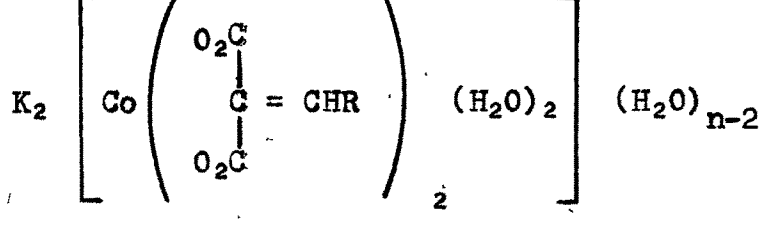
and $$E/B = 23.7$$

The band can be attributed to the

$$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$$ transition.

The magnetic moments of these salts are presented in table 82. The values are anomalous ; they are very high for weak octahedral crystal field.

The molar conductivity of these salts is presented in table 83. The range of the values indicates the presence of complex ions in solution. Hence the salts are represented as (XIX)



(XIX)

Table 82

Magnetic moments of complex salts of substituted malonic acid with potassium and cobalt

No.	Compound	Molar magnetic susceptibility (per Co-atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per Co-atom) $\chi'_m \times 10^6$	Magnetic moment (per Co-atom) (μ) B.M.
1.	KCo BM	11820	12079	5.45
2.	KCo ClM	14290	14583	5.98
3.	KCo ChM	15130	15402	6.13
4.	KCo MM	13370	13662	5.78
5.	KCo NM	15090	15381	6.14

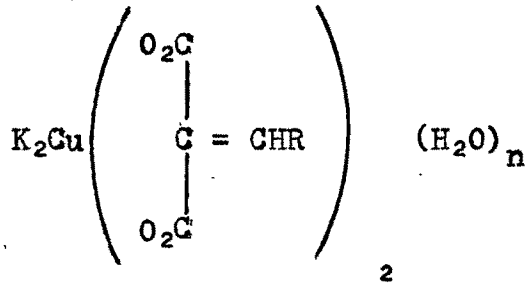
Table 83

Molar conductivities of the complex salts in solution

No.	Complex	Specific resistivity (ohm-cm) x 10^{-4}	Molar conductivity (cm^{2} ohm^{-1} $mole^{-1}$)
1.	KCo BM	0.583	342
2.	KCo ClM	0.861	273
3.	KCo ChM	0.806	312
4.	KCo MM	0.700	352
5.	KCo NM	0.900	349

III. 11. Complex salts of potassium and copper with benzylidene malonic acids :

The complex salts of potassium and copper with benzylidene malonic acid and its derivatives (I) were prepared by treating the carbonates of potassium and copper with the acid. The analysis of the products is given in table 46. The results show that they can be represented as (XX).



(XX)

R =

a = C_6H_5-

b = o-ClC_6H_4-

c = p-ClC_6H_4-

d = p-$NO_2C_6H_4$-

Their ultra-violet absorption spectra are given in fig. 23 and their absorption bands are presented in table 84.

The absorption band of the salt containing K and Cu is nearer to the absorption band of the acid in alkali solution than that of the corresponding salt of Cu alone.

The absorption spectra of two salts in the visible region are presented in fig. 22. The absorption

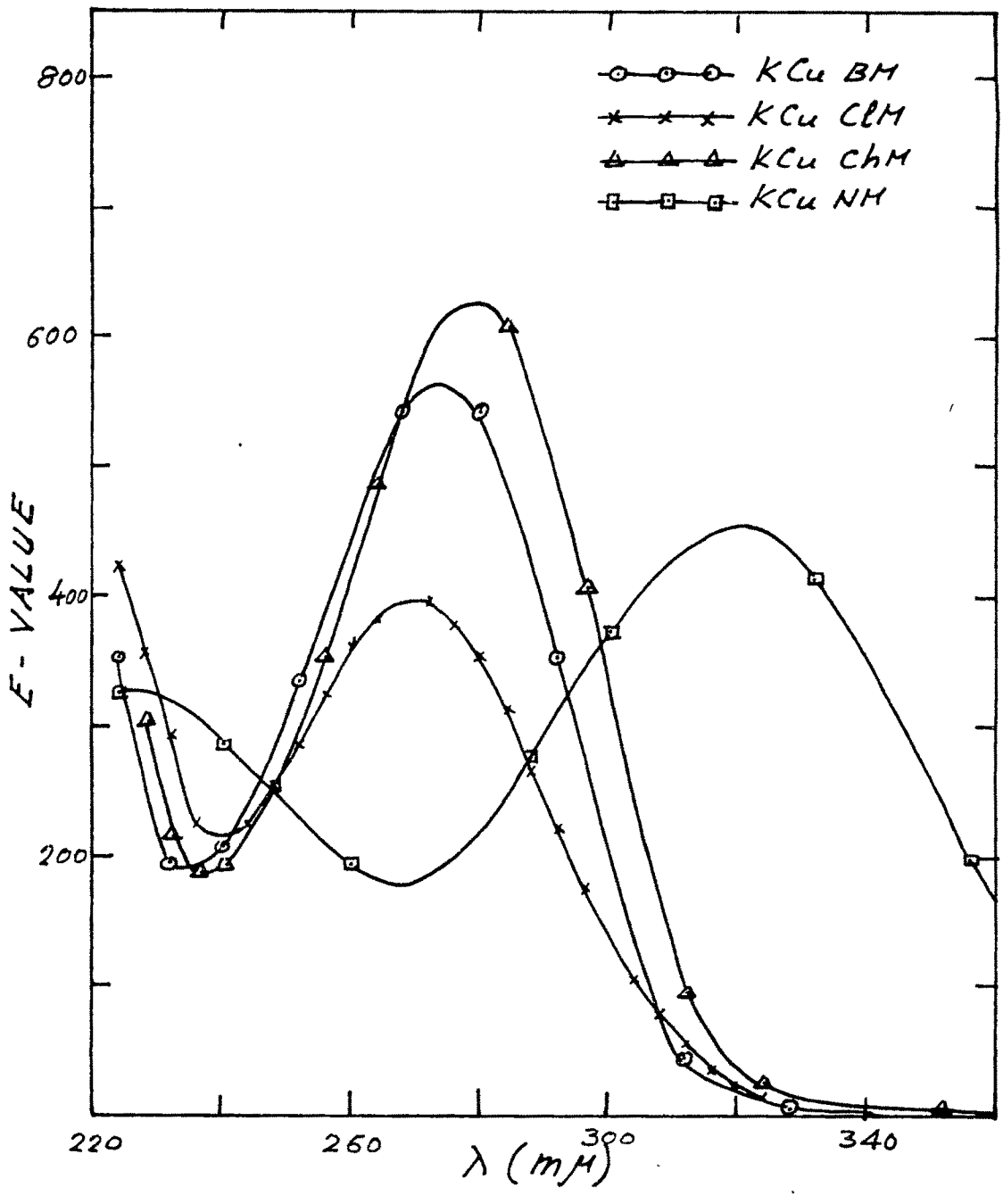


FIG.23 UV ABSORPTION SPECTRA OF THE COMPLEX SALTS OF COPPER AND POTASSIUM WITH THE SUBSTITUTED BENZYLIDENE MALONIC ACIDS.

Table 84

Ultra-violet absorption spectra of complex salts of substituted malonic acid with potassium and copper in water.

No.	Complex	Formula of the complex	in water	
			λmax (mμ)	E-Value
1.	KCu BM	$K_2CuC_{20}H_{20}O_{12}$	274	563.2
2.	KCu ClM	$K_2CuC_{20}H_{16}O_{11}Cl_2$	270	399.3
3.	KCu ChM	$K_2CuC_{20}H_{14}O_{10}Cl_2$	280	626.5
4.	KCu NM	$K_2CuC_{20}H_{20}O_{17}N_2$	320	456.3

band is at 13600 cm^{-1} for KCu ClM and at 13700 cm^{-1} for KCu ChM . In continuation of our studies on Cu ClM, we suggest that the band be related to the octahedral crystal field around copper and be attributed to the

$$^2E_g \longrightarrow {}^2T_{2g} \quad \text{transition}$$

Hence,

Δ = 13600 cm^{-1} for KCu ClM

= 13700 cm^{-1} for KCu ChM

and Dq = 1360 cm^{-1} for KCu ClM

= 1370 cm^{-1} for KCu ChM.

The magnetic moments of these salts are presented in table 85. The values are varying from 2.17 B.M. to 2.38 B.M. As observed earlier, the magnetic moment of the copper salts may be about 1.8 B.M. if the salt is a normal one and about 2.2 B.M. if it is a complex one. It is confirmed by our present observation that the value of the magnetic moment for copper complex is about 2.2 B.M.

The molar conductivity of these salts is presented in table 86. The range of the values indicate the presence of complex ions in solution. Hence the salts are represented as (XXI).

Table 85

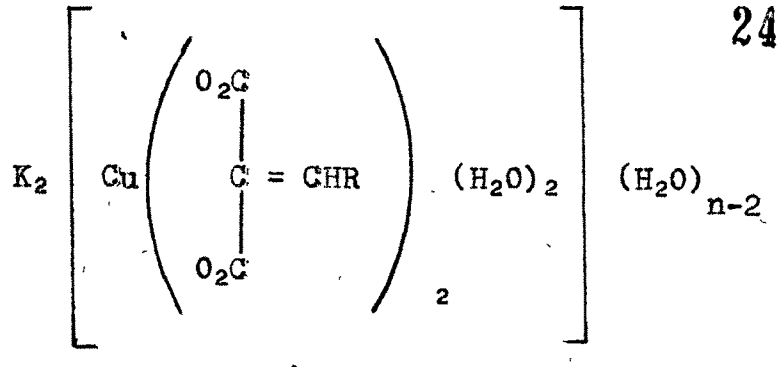
Magnetic moments of complex salts of substituted malonic acid with potassium and copper

No.	Compound	Molar magnetic susceptibility (per Cu-atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per Cu-atom) $\chi_m' \times 10^6$	Magnetic moment (per Cu-atom) (μ) B.M.
1.	KCu BM	1663	1932	2.17
2.	KCu ClM	2012	2305	2.38
3.	KCu NM	1923	2214	2.33

Table 86

Molar conductivities of the complex salts in solution

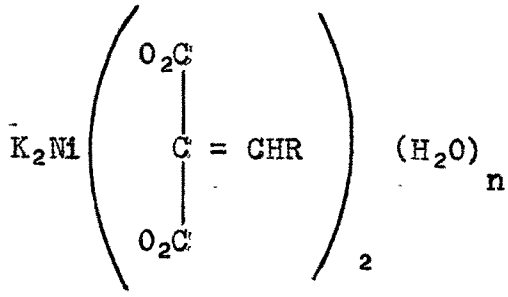
No.	Complex	Specific resistivity (ohm-cm) x 10^{-4}	Molar conductivity (cm^{2} ohm^{-1} . $mole^{-1}$)
1.	KCu BM	0.880	268
2.	KCu ClM	0.824	282
3.	KCu ChM	0.900	239
4.	KCu NM	1.10	267



(XXI)

III. 12. Complex salts of potassium and nickel with benzylidène malonic acids :

The complex salts of potassium and nickel with benzylidene malonic acid and its derivatives (I) were prepared by treating the carbonates of potassium and nickel with the acids. The analysis of the products is presented in table 50. The results show that they may be represented as (XXII).



(XXII)

R =

a = C_6H_5-

b = o-ClC_6H_4-

c = p-ClC_6H_4-

d = p-$CH_3OC_6H_4$-

e = p-$NO_2C_6H_4$-

Their absorption spectra are given in fig. 24 and their absorption bands are presented in table 87.

The absorption band of the salt containing K and Ni is nearer to the absorption band of the acid in alkali solution than that of the corresponding salt of Ni alone.

The absorption spectrum of a salt in the visible region is presented in fig. 22. The absorption bands are at 14600 cm^{-1} and 26320 cm^{-1} (for KNi ChM). In continuation of our studies on Ni ChM, we suggest that weak octahedral crystal field exists around nickel and that the absorption bands at 14600 cm^{-1} and 26320 cm^{-1} be attributed to the

$$^3A_{2g} \longrightarrow {}^3T_{1g}\ (F) \quad \text{and} \quad {}^3A_{2g} \longrightarrow {}^3T_{1g}\ (P)$$

transitions.

Further,

$$Dq / B = 0.896,$$

$$B = 978\ cm^{-1}$$

$$Dq = 876\ cm^{-1}$$

and $$\Delta = 8760\ cm^{-1}.$$

Their magnetic moments are presented in table 88. The values indicate the octahedral nature of nickel in the complex.

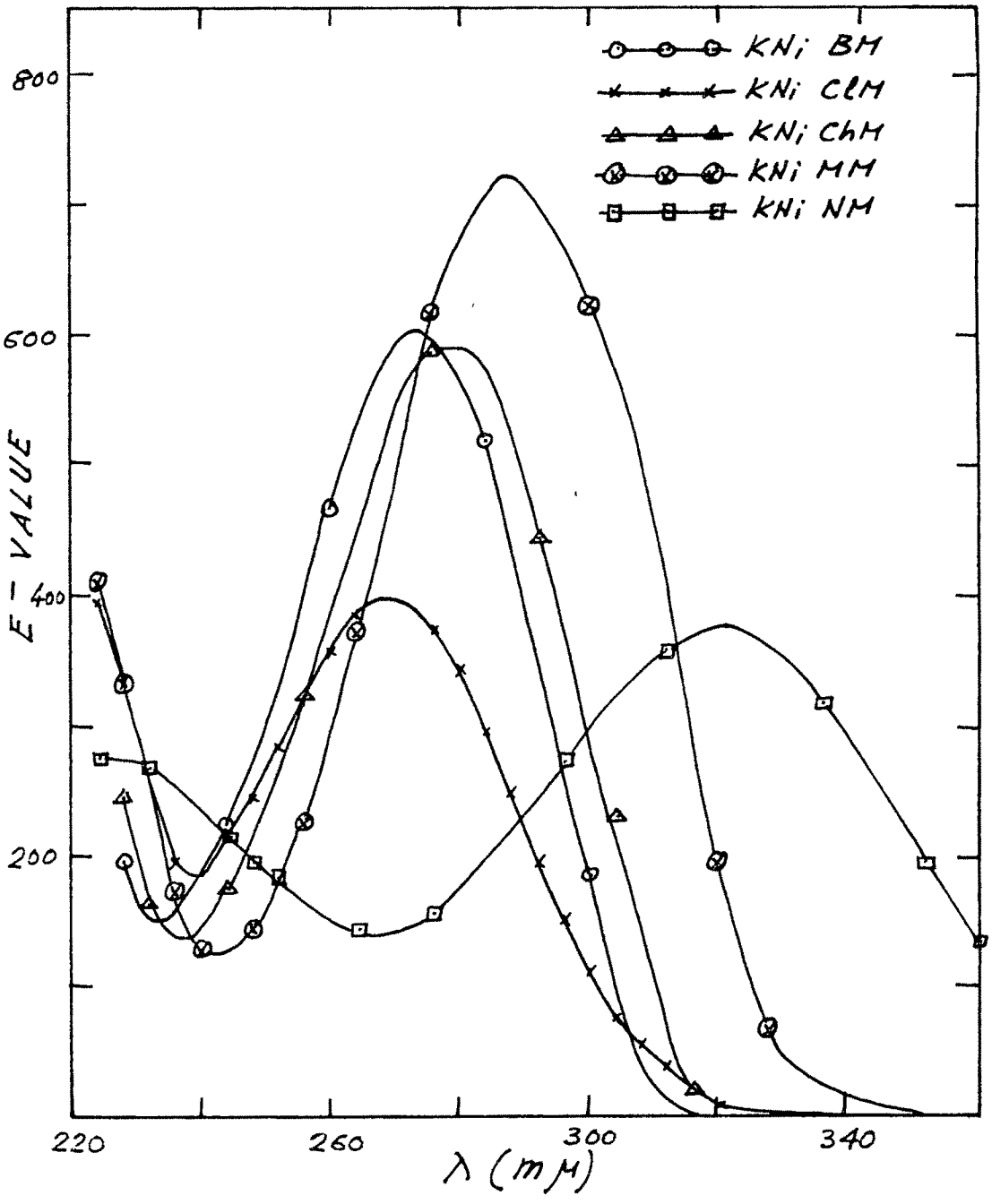


FIG. 24 UV ABSORPTION SPECTRA OF THE COMPLEX SALTS OF NICKEL AND POTASSIUM WITH THE SUBSTITUTED BENZYLIDENE MALONIC ACIDS.

Table 87

Ultra-violet absorption spectra of complex salts of substituted malonic acid with potassium and nickel in water.

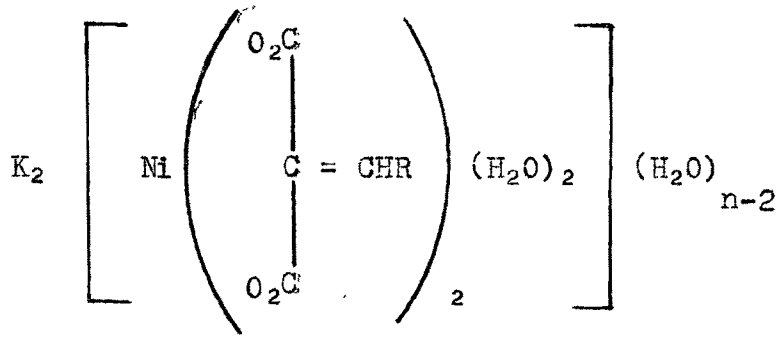
No.	Complex	Formula of the complex	in water	
			λmax (mμ)	E-Value
1.	KNi BM	$K_2NiC_{20}H_{18}O_{11}$	274	601.6
2.	KNi ClM	$K_2NiC_{20}H_{18}O_{12}Cl_2$	268-70	397.1
3.	KNi ChM	$K_2NiC_{20}H_{22}O_{14}Cl_2$	278-80	590.3
4.	KNi MM	$K_2NiC_{22}H_{22}O_{13}$	288	724.7
5.	KNi NM	$K_2NiC_{20}H_{24}O_{19}N_2$	320	373.1

Table 88

Magnetic moments of complex salts of substituted malonic acid with potassium and nickel

No.	Compound	Molar magnetic susceptibility (per Ni-atom) $\chi_m \times 10^6$	Corrected molar magnetic susceptibility (per Ni-atom) $\chi'_m \times 10^6$	Magnetic moment (per Ni-atom) (μ) B.M.
1.	KNi BM	4778	5037	3.52
2.	KNi ClM	5125	5428	3.64
3.	KNi ChN	5330	5654	3.71
4.	KNi MM	5267	5559	3.68
5.	KNi NM	5261	5567	3.69

The molar conductivity of these salts is presented in table 89. The range of the values indicates the presence of complex ions in solution. Hence the salts are represented as (XXIII).



(XXIII)

The molar conductivity of KNi NM at various concentrations is presented in table 90. The results show that the dissociation of the complex ion increases with dilution.

III. 13. Complex salts of the substituted malonic acids-general :

The visible absorption spectrum, the ultra-violet absorption spectrum, the magnetic susceptibility and the electrical conductivity of the complex salts of copper, nickel and cobalt with benzylidene malonic acid and its derivatives have been studied.

From the study of the visible absorption spectra of some of these complexes, we find that the crystal field splitting (Δ) is 9300 cm^{-1} for the cobalt complex, 13600 and 13700 cm^{-1} for the copper complexes and

Table 89

Molar conductivities of the complex salts in solution

No.	Complex	Specific resistivity (ohm-cm) x 10^{-4}	Molar conductivity (cm^{2} ohm^{-1} $mole^{-1}$)
1.	KNi BM	0.731	339
2.	KNi ClM	0.888	262
3.	KNi ChM	0.722	308
4.	KNi MM	0.759	320
5.	KNi NM	0.907	342

Table 90

Molar conductivity of KNi NM at different dilutions

No.	Concentration (M)	Specific resistivity (ohm-cm) x 10^{-4}	Molar conductivity (cm^{2} ohm^{-1} $mole^{-1}$)
1.	1 / 500	0.176	284
2.	1 / 1000	0.324	309
3.	1 / 5000	1.30	388
4.	1 / 10000	2.22	450

8760 cm^{-1} for the nickel complex. The value increases in order

$$Ni^{2+} < Co^{2+} < Cu^{2+}$$

The order is the same as observed by us for the salts of these metal ions with the acids.

The value of the crystal field parameter B is also derived and is found to be 840 cm^{-1} for the cobalt complex and 978 cm^{-1} for the nickel complex.

The molar electrical conductivity of these complexes increases generally in order

$$Cu^{2+} < Ni^{2+} \sim Co^{2+}$$

Hence the copper complexes are much less dissociated than the corresponding nickel or cobalt complexes. However the molar conductivity of the copper, nickel and cobalt complexes of o-chlorobenzylidene malonic acid is very nearly the same. The results show that the relative dissociation is not only dependent on the nature of the metal ion but also on the nature and position of the substituent in the acid molecule.

The ultra-violet absorption spectra of these complexes show that the value of the absorption band is almost the same for the complexes of the same acid, irrespective of the nature of the metal ion. The value is closer to the one for the acid in alkali solution than to the one for the acid in alcoholic solution.

The magnetic moments of the cobalt, copper and nickel complexes are 5.45 - 6.14 B.M. ; 2.17 -2.38 B.M. and 3.52 - 3.71 B.M. respectively. These values correspond to weak octahedral crystal field with large orbital contribution. For some cobalt complexes, the values are anomalously high. It may be interpreted in terms of strengthening due to spin-spin interaction, but is not confirmed by other evidences.

- X - - X - - X -

Kapadia[159] attempted to prepare polymers from the complex salts of malonic acid. It became necessary to know for such studies if the complex ions of the unsubstituted malonic acid and its bis-derivatives would be sufficiently stable in solution for the polymerisation reactions to be observed. We now find that the complex ions of various substituted benzylidence malonic acids are fairly stable in solution as indicated by electrical conductivity and other measurements. Hence we believe that polymerisation reactions can be attempted with complex malonates possessing suitable stereochemical configurations so that fairly stable polymeric anions can be obtained.

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