RESULTS AND DISCUSSION

III Results and Discussion

III.1. vic-oxime-ketone and its complexes :

1 (a) 2,3-Dioxobutyranilide-2-oxime (OK) :

Acetoacetanilide was treated with nitrous acid in ice-cold solution to obtain the ligand 2,3-dioxobutyranilide-2-oxime (eq.a).

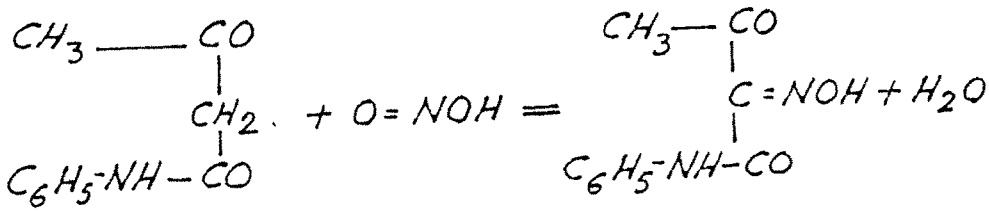
The reaction takes place at the CH_2 centre and not at the CH_3 centre or NH centre. It is in accord with the suggestions of Meyer (210,250) Knorr (251), Naik,et al. (223), Dave and Talati (231), Desai (233) and Patel (237).

The unsymmatrical oxime ketone would exhibit stereoisomerism. Thus the stereoisomers that might be obtained in the present case may be represented as(XXXI-a,b). However, attempts to obtain these isomers have failed; only one product is obtained. Hantzsch (252) suggested that only one isomeric form is obtained because of the relative instability of the other. The following evidence from literature may be considered to arrive at the decision regarding its isomeric nature.

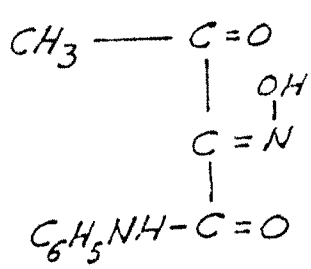
(i) Ethyl 2,3-dioxobutyrate-2-oxime gives reactions with metal ions which are similar to those of the ligand under consideration (237,253). It indicates that NH of the anilide group is not directly involved in the formation of the chelate ring.

(ii) Taylor (254) suggested that ethyl 2,3-dioxobutyrate-2-oxime has anti-acetyl configuration.

(iii) Talati (224) suggested that N-aryl-2,3-dioxobutyramide-2-oxime possesses syn-amide configuration, the oxime

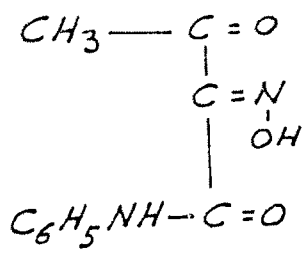


Eq. (a)



ANTI-AMIDE STRUCTURE

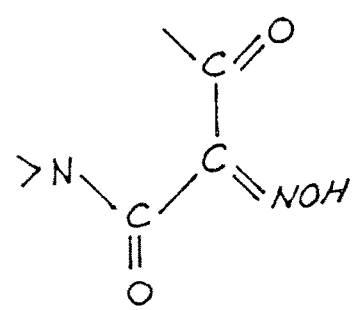
(a)



SYN-AMIDE STRUCTURE

(b)

(XXXI)



(XXXII)

hydrogen forming chelate ring with acetyl carbonyl.

(iv) Desai (233) observed that the stability of N-aryl-2,3-dioxobutyramide-2-oxime is greater than that of ethyl 2,3-dioxobutyrate-2-oxime and proposed that the amide NH may be involved in H-bonding with oxime-O.

(v) Patel (237) found that the stability of 2,3-dioxobutyranilide-2-oxime is greater than that of N-methyl-2,3-dioxobutyranilide-2-oxime. He attributed the decrease in stability on substitution at the amide group to the non-formation of chelate ring involving anilide NH group and to the steric effect of the methyl group.

Hence 2,3-dioxobutyranilide-2-oxime is believed to have syn-amide structure and the oxime group is believed to be involved in the formation of two chelate rings.

-x- -x- -x-

From the study of the ultra-violet absorption spectra of the ligand in different solvents (224,233), the wave length maxima were found at 236-8 mμ and 280-81 mμ in aqueous solution, 236-8 mμ in methanol solution and 245-7 mμ and 280-2 mμ in caustic soda solution.

The K band at 236 -8 mμ has been attributed by Dave and Talati (231) to the crossed conjugated system (XXXII).

The X band observed at 280-2 mμ has been attributed by Desai (233) to the ionic tautomer of the ligand. The band gets intensified in alkali due to the increased concentration of the ionic tautomer.

-x- -x- -x-

Kuster (226) and Taylor and Ewbank (227) prepared the iron, cobalt, nickel and copper complexes of ethyl 2,3-dioxobutyrate-2-oxime. Desai, Patel and Mankad (255) prepared copper, nickel and cobalt complexes and Desai (233) prepared iron complex of 2,3-dioxobutyranilide-2-oxime. We have prepared copper, nickel, cobalt, iron, manganese, zinc, strontium and magnesium complexes of 2,3-dioxobutyranilide-2-oxime and studied some of their properties. The absorption spectra of these complexes in the ultraviolet and visible region of the spectrum are presented in Figs.1 to 4. The absorption bands of the complexes in the ultraviolet spectra are presented in table 31. The magnetic moment of some of these complexes is presented in table 32 and the electrical conductivity of some complexes in solution is presented in table 33.

I (b) Nickel complex of 2,3-dioxobutyranilide-2-oxime (OK Ni) :

The complex was prepared at the ether-water interface and recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XXXIII).

Similar formulae were given by Taylor and Ewbank (227) and Desai, Patel and Mankad (255) to represent their products.

Okac and Simek (256) found that salts of diacetyl monoxime were too unstable to be prepared in pure state and that the nickel salt of α-benzilmonoxime was obtained as a basic one.

Malatesta (257) prepared the nickel complexes of isonitroso acetophenone and isonitroso benzoyl acetone and

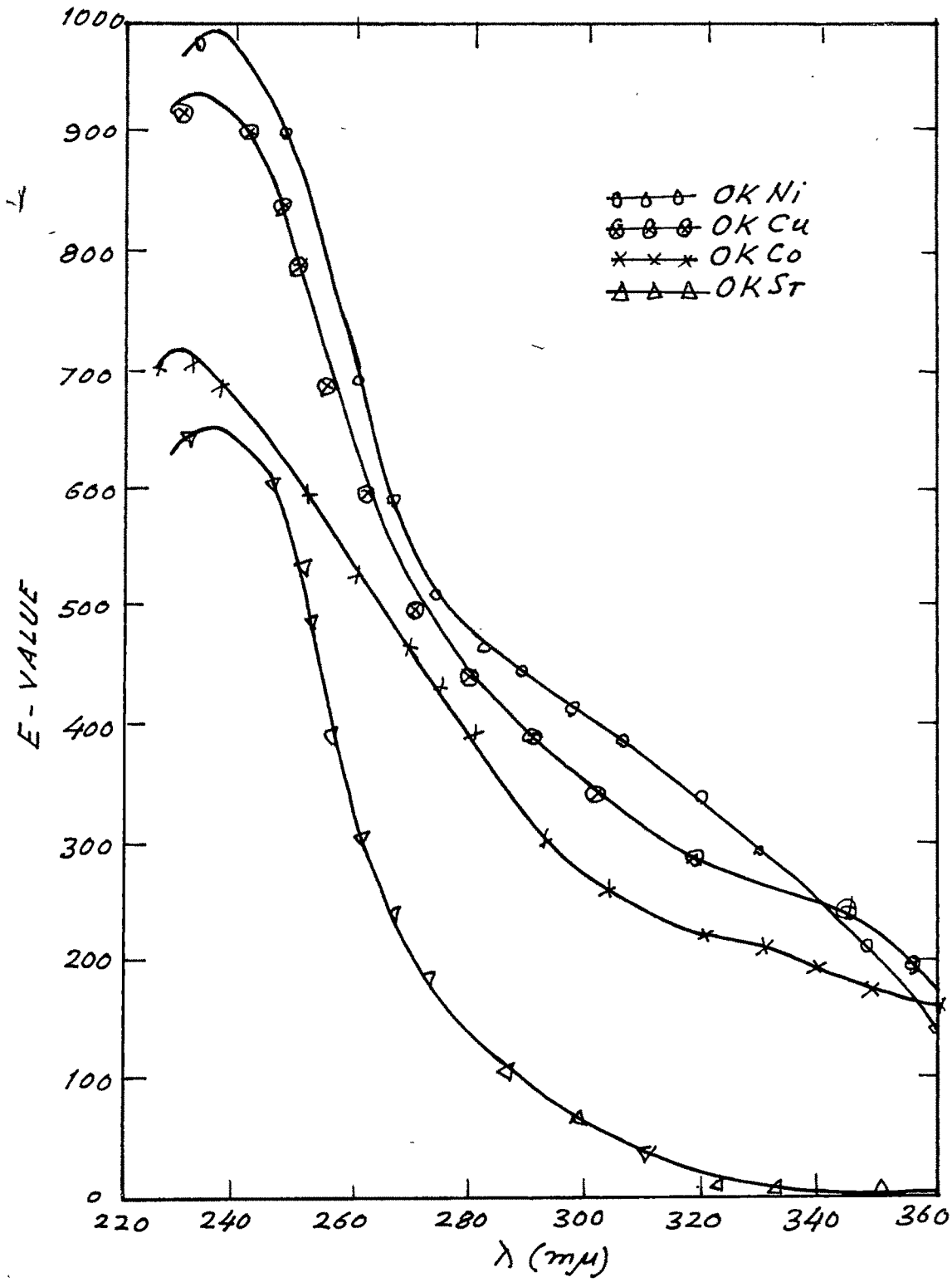


FIG. 1 UV ABSORPTION SPECTRA OF OK-Cu; OK-Ni; OK-Co; OK-Sr

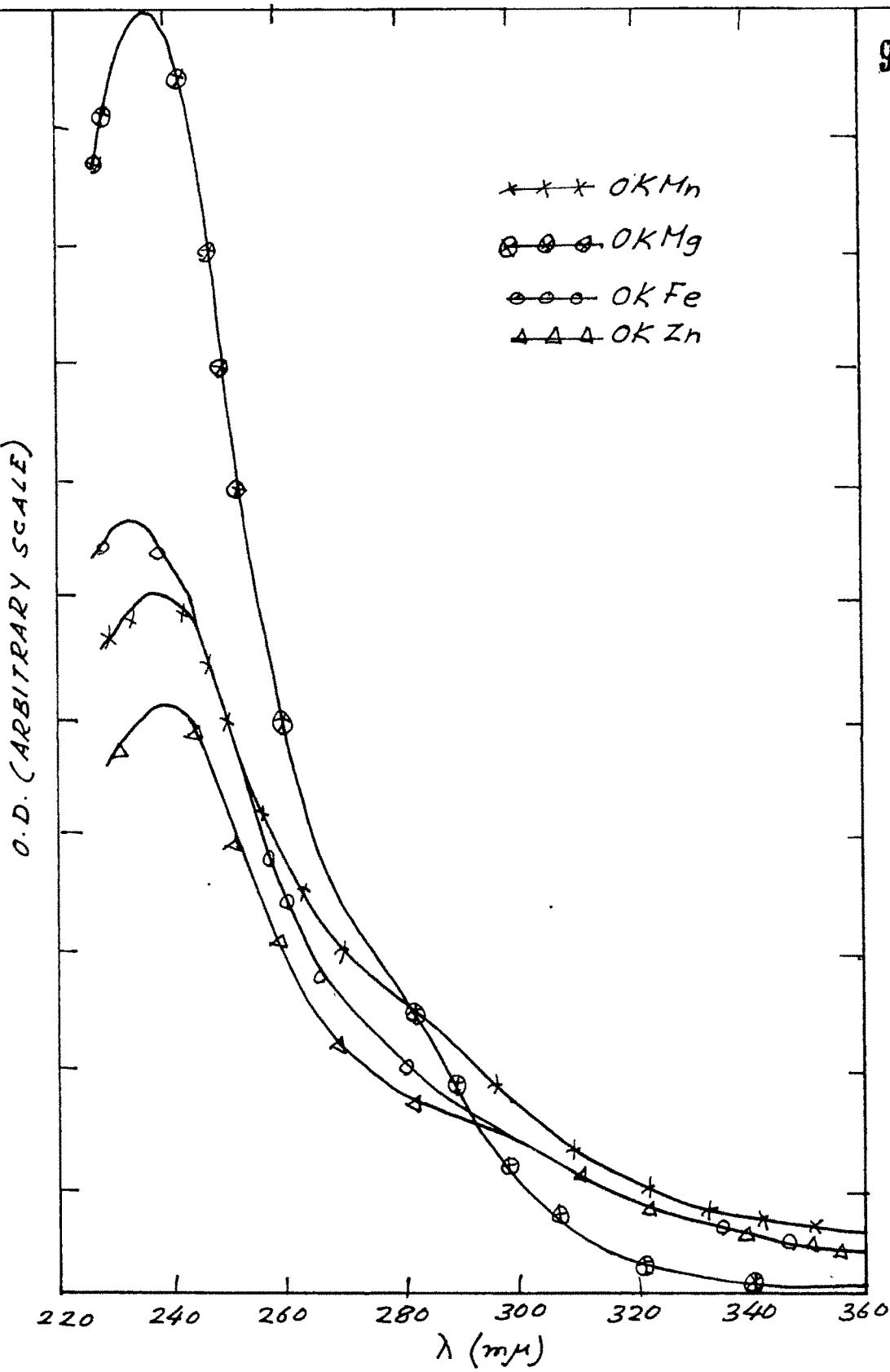


FIG. 2. UV ABSORPTION SPECTRA OF OK-Mg; OK-Fe; OK-Mn AND OK-Zn

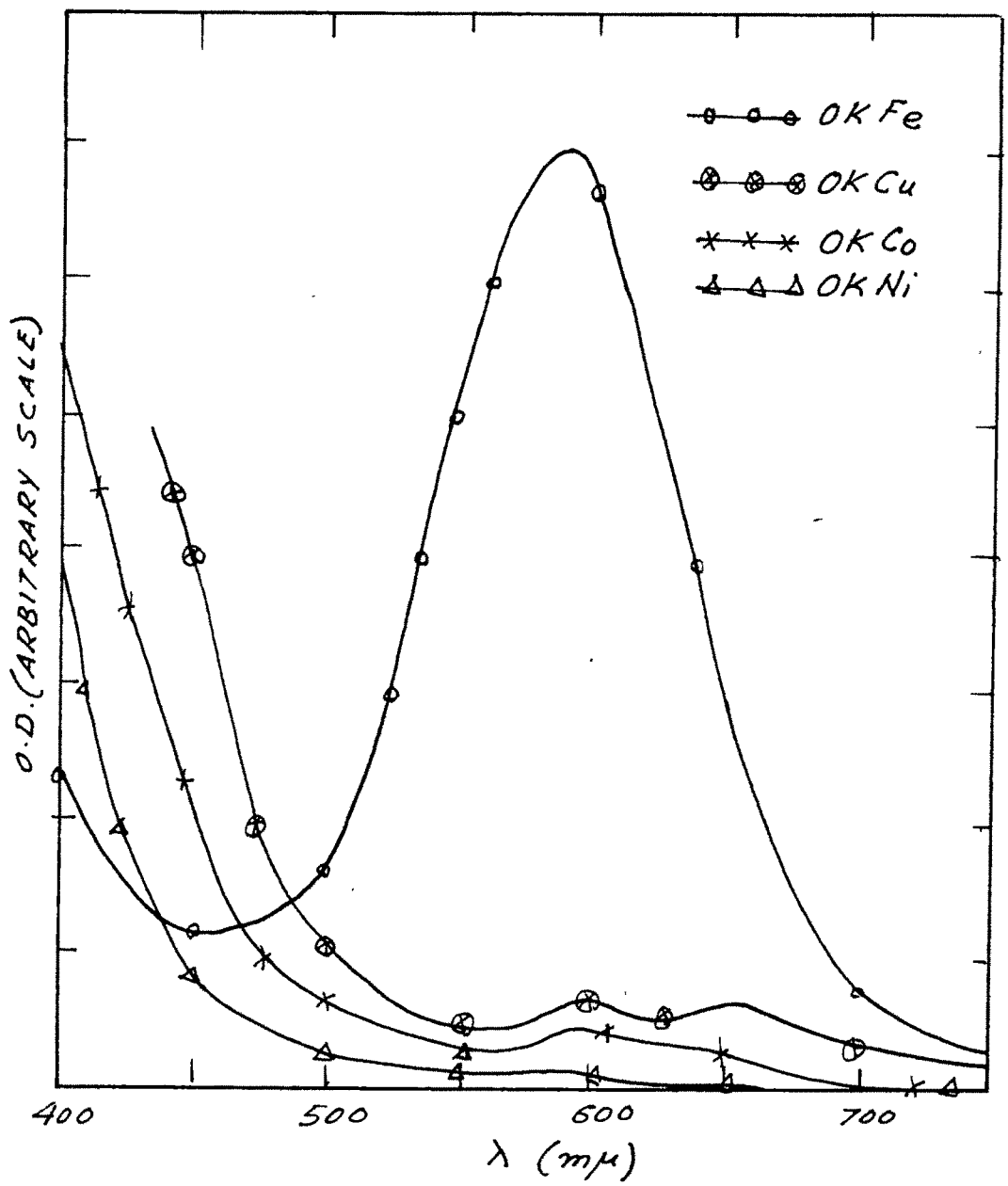


FIG. 3. VISIBLE ABSORPTION SPECTRA OF OK-Cu, Ok-Ni; OK-Co AND OK-Fe

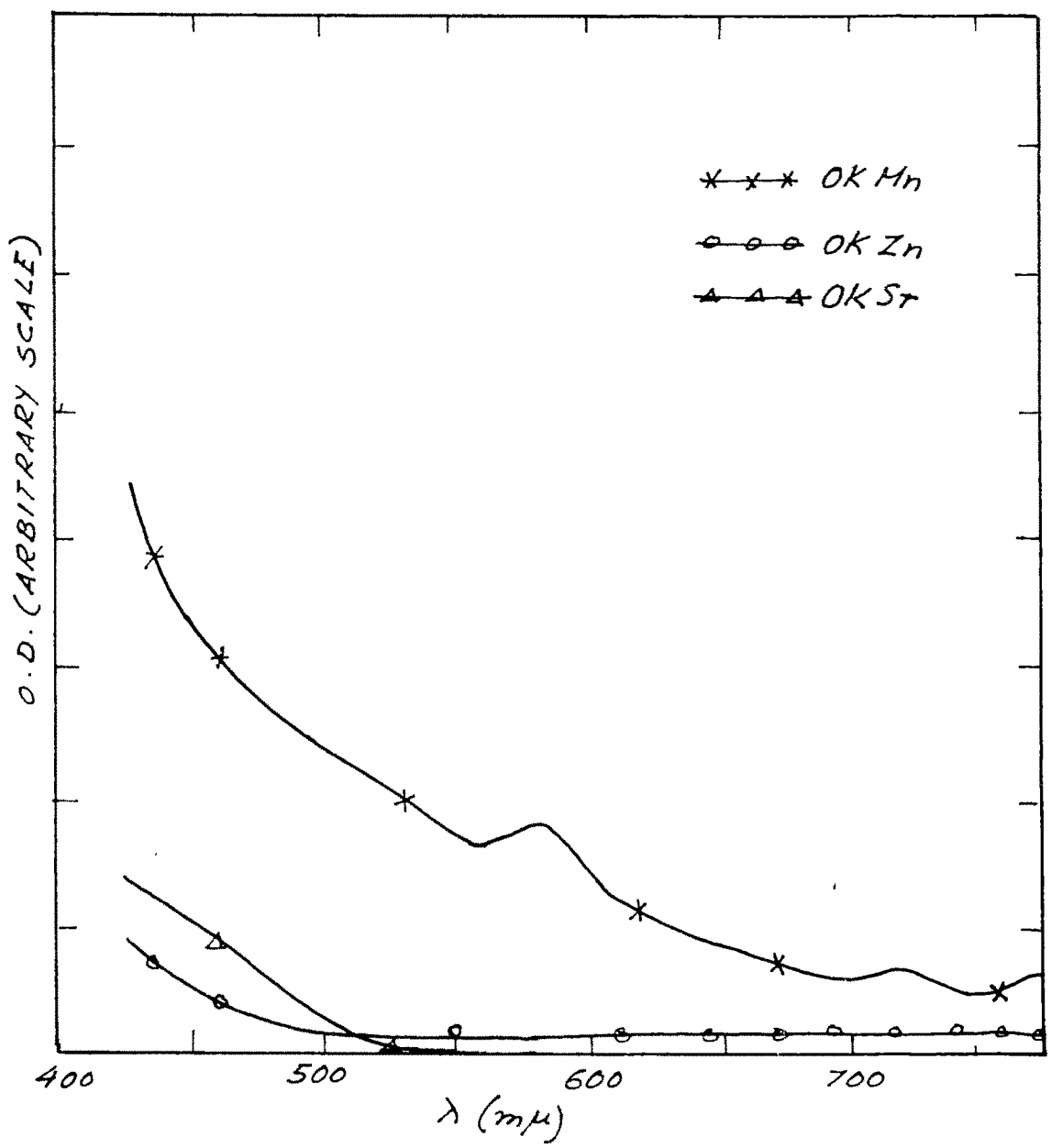


FIG.4. VISIBLE ABSORPTION SPECTRA OF OK-Mn; OK-Zn AND OK-Sr

Table-31.

Absorption bands of the complexes of 2,3-dioxobutyranilide-2-oxime.

No.	Complex	λ_{max} (mμ)	E-value	λ_{max} (mμ)
1.	OK Cu	234-6	925	600, 650
2.	OK Ni	236-8	985	580
3.	OK Co	231-2	715	590
4.	OK Fe	232-3		590
5.	OK Mn	236		580,720,780
6.	OK Zn	238		-
7.	OK Sr	236-8	645	-
8.	OK Mg	236		

Table 32

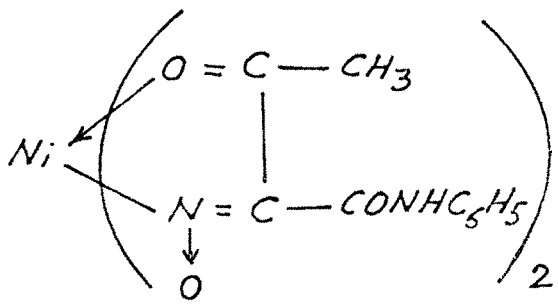
Magnetic moments of the complexes of 2,3-dioxobutyranilide-2-oxime.

No.	Complex	Molar magnetic susceptibility $X_m \times 10^6$	Corrected molar magnetic susceptibility $X'_m \times 10^6$	Magnetic moment μ (B.M.)
1.	OK Cu	1211	1401	1.84
2.	OK Ni	2969	3159	2.78
3.	OK Co	1148	1427	1.87
4.	OK Fe	9974	10301	5.02

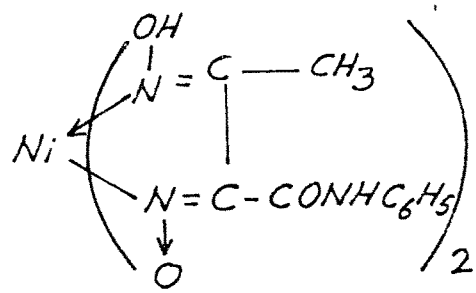
Table 33

Electrical conductivity of the complexes of 2,3-dioxobutyranilide-2-oxime in solution.

No.	Complex	Electrical resistivity (meg-ohm-cm)	Molar conductivity
1.	OK Cu	1.5	7.9
2.	OK Ni	0.73	16.0
3.	OK Co	0.34	39.0



(XXXIII)



(XXXIV)

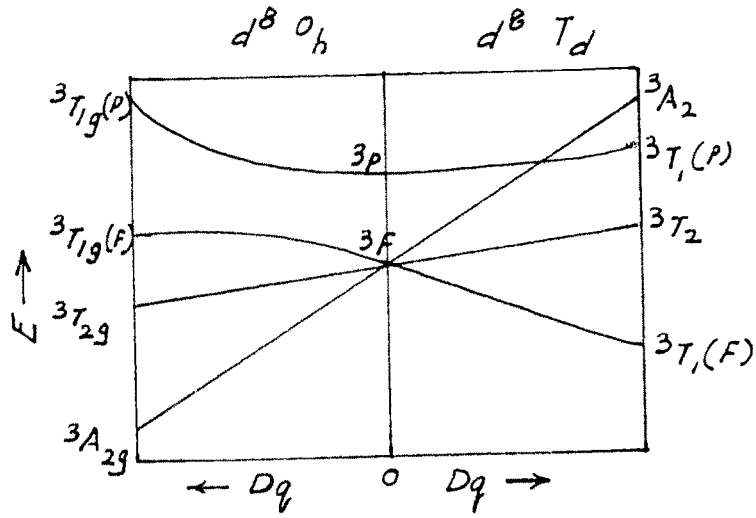


FIG. a. ORGEL DIAGRAM FOR d^8 - NICKEL (II) COMPLEXES

FOR NICKEL (II) IN WEAK OCTAHEDRAL FIELD,

$$E(^3A_{2g}) = -12\,Dq \quad \ldots\ldots\ldots (b\text{-}i)$$

$$E(^3T_{2g}) = -2\,Dq \quad \ldots\ldots\ldots (b\text{-}ii)$$

FOR $E(^3T_{1g}(F))$ AND $E(^3T_{1g}(P))$,

$$[6Dq \cdot P - 16(Dq)^2] + [-6Dq - P]E + E^2 = 0 \ldots\ldots (b\text{-}iii)$$

Eq. (b)

$$\beta = 1 - hk \ldots\ldots\ldots\ldots\ldots (c)$$

Eq. (c)

found their magnetic moment as about 2.72 B.M.

-x- -x- -x-

The complex (OK Ni) was converted into the nickel complex of 2,3-dioxobutyranilide dioxime (XXXIV) by treating the complex (OK Ni) with hydroxyl amine.

The results indicate that the complex (OK Ni) may have configuration comparable to that of (XXXIV). Talati (224) established that the complex (XXXIV) contains the two ligands along a square plane. Hance the complex OK Ni may also have the two ligands distributed along a square plane. (The difference is that (XXXIV) is a spin-paired complex, wheras OK Ni is a spin-free one.)

It has an absorption band in the ultraviolet region at 236-8 mμ ; band at 280-1 mμ is not observed. Hence the complex is not essentially ionic. Precipitation of nickel from the complex by hydrogen sulphide is not observed. The molar conductivity of the complex in alcoholic solution also suggests the non-electrolytic nature of the complex.

The magnetic moment of the complex is calculated as 2.78 B.M. It indicates the presence of two unpaired electrons per nickel atom in the complex. The complex is suggested to have an octahedral configuration. The value of the magnetic moment is closer to the spin-only value, indicating the quenching of the orbital angular momentum (Introduction of the Curie - Weiss constant θ might bring the value close to the spin-only value.).

A crystal field band is observed at 580 mμ in the absorption spectrum of the complex in the visible region. The splitting of the states as a function of Dq for the

octahedral and tetrahedral nickel(II) (d^8) complexes is described by the Orgel diagram (fig.a) (258). The band indicates the absence of the tetrahedral crystal field. (ϵ_m is less than 20.) Further, the tetrahedral or square planar nature of the complex can be ruled out on the basis of the magnetic measurements. If the weak octahedral crystal field is suggested, the band may be attributed to the

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

Comparison of the corresponding absorption band in the spectra of $(Ni\ am_6)^{++}$, $(Ni\ en_3)^{++}$ and OK Ni shows that the strength of the crystal field in OK Ni is comparable to that in $(Ni\ am_6)^{++}$. Hence the crystal field splitting (Δ or 10 Dq) for d^8 system in OK Ni is suggested as 10800 cm^{-1}(259).

We may calculate the energies of the triplet states - E ($^3A_{2g}$) , E ($^3T_{2g}$) and E ($^3T_{1g}$(F)) . The graphical information contained in the Orgel diagram is more accurately represented by the series of eq.(b) which relates the energies of these states to the Dq value of the ligand. (p is the energy of the ^3p state relative to that of the ^3F state and is found equal to 15 B for nickel (II) in the gaseous state, where B is the Racah parameter for inter-electronic repulsion.) Since Dq for OK Ni is suggested as 1080 cm^{-1}, we find from eq.(b -i) and eq.(b-ii) that

$$E\ (^3A_{2g}) = -\ 12960\ cm^{-1} \quad \ldots\ldots\ (E_o)$$

$$E\ (\ ^3T_{2g}) = -\ 2160\ \ cm^{-1} \quad \ldots\ldots\ (E_1)$$

We can solve eq. (b-iii), taking p = 12620 cm^{-1} and find that

$$E\ (\ ^3T_{1g}(F)\ ) = +\ 4250\ \ cm^{-1} \ldots\ldots\ (E_2)$$

(We calculate the energy of transition ($E_2 - E_o$) as 17210 cm^{-1} in agreement with our observed value of 17240 cm^{-1}.)

Since the value of p (i.e. 15 B) for nickel (II) in the gaseous state is known to be 15840 cm^{-1}, a low value of p (i.e. 15 B') is obtained for nickel (II) in OK Ni. The lowering of the ^3p state is mainly a measure of covalency and is expressed as β or β_0 (258)

$$\beta = B' / B$$

$$\beta_0 = (B-B')/ B \times 100$$

The value of β_0 for OK Ni is obtained as 20.3% . Hence for OK Ni

$$D_q = 1080\ \ cm^{-1}$$

$$B' = 840\ \ cm^{-1} \quad \text{and}$$

$$\beta = 0.797$$

Using Jorgenson's relation (eq.c) (260) and the value of K and β for nickel (II) as 0.12 and 0.797 respectively, we find that the value of h for the ligand is 1.69.(No crystal field band is observed below 480 mμ becasuee the ligand absorbs appreciably below 480 mμ.)

-x- -x- -x-

For the purpose of comparison, the complex was also prepared by another method using nickel carbonate. The analysis suggested the same composition of the complex. The solubility of the two complexes in different solvents is the same. The two phase method of preparation is, however, better than the carbonate method.

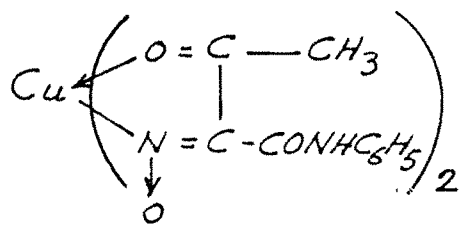
1 (c) Copper complex of 2,3-dioxobutyranilide-2-oxime (OK Cu) :

It was prepared at the ether-water interface and crystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XXXV).

Similar formula is given by Desai, Patel and Mankad (255) for their product. Taylor and Ewbank (227) obtained a product of copper with ethyl 2,3-dioxo-butyrate-2-oxime containing copper to ester ligand in the ration of 1 : 1 and represented it as a basic complex. Okac and Simek (256) prepared the copper complex of α-benzil monoxime and represented it as a basic complex.

The complex in alcoholic solution has an absorption band at 234-36 mμ in the ultraviolet absorption spectrum and X-band is absent in the spectrum, indicating essentially nonionic nature of the complex. The electrical conductivity of the complex in solution also indicates the non-electrolyte nature of the complex. Hydrogen sulphide does not precipitate copper sulphide from the solution of the complex.

The visible absorption spectrum of the complex in solution has two absorption bands at 600 mμ and 650 mμ .



(XXXV)

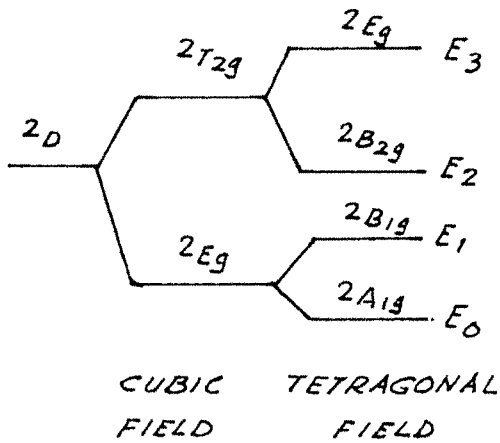


FIG. b CRYSTAL FIELD SPLITTING OF COPPER(II) - d^9 IN TETRAGONAL FIELD

$$E_3 = \frac{2}{5}\Delta + \frac{1}{3}\delta \quad \ldots\ldots\ldots (d\text{-}i)$$

$$E_2 = \frac{2}{5}\Delta - \frac{2}{3}\delta \quad \ldots\ldots\ldots (d\text{-}ii)$$

$$E_1 = -\frac{3}{5}\Delta + \frac{1}{2}\mu \quad \ldots\ldots\ldots (d\text{-}iii)$$

$$E_0 = -\frac{3}{5}\Delta - \frac{1}{2}\mu \quad \ldots\ldots\ldots (d\text{-}iv)$$

Eq. (d)

$$g_{11} = 2 - \frac{8\lambda}{E_2 - E_0} \quad \ldots\ldots\ldots (e\text{-}i)$$

$$g_{\perp} = 2 - \frac{2\lambda}{E_3 - E_0} \quad \ldots\ldots\ldots (e\text{-}ii)$$

Eq. (e)

The absorption bands may be attributed to the distorted octahedral crystal field and be related to the band observed in the type of complexes CuL_4S_2 where LH represents the ligand and S the solvent. The splitting of the bands is relatively large and may not be due to the spin-orbit coupling. If tetragonal distortion of the octahedral crystal field (fig.-b) (258) is suggested, the absorption bands may be attributed to the

$$^2A_{1g} \longrightarrow {}^2B_{2g} \quad \text{and} \quad {}^2A_{1g} \longrightarrow {}^2E_g \quad \text{transitions.}$$

It is possible to calculate the values of δ and μ using the equations (d) suggested for the various energy states and the two energies of transition. For OK Cu, these values are

$$\Delta = + 15890 \text{ cm}^{-1}$$
$$\delta = + 1270 \text{ cm}^{-1} \quad \text{and}$$
$$\mu = + 690 \text{ cm}^{-1}.$$

-x- -x- -x-

The magnetic moment of the complex is calculated as 1.86 B.M. It suggests the square planar distribution of the ligand groups around copper. Equations (e) show that anisotropy exists for g-values and hence for the magnetic moment of the complex.

-x- -x- -x-

The copper complexes were also prepared by using copper acetate in alcohol, copper carbonate and copper foil. On the basis of analysis, the compositions of these complex-es are suggested the same. The solubilities of these

complexes in different solvents are the same. Of the different methods of preparations attempted, the two phase method appears to be better than the other methods.

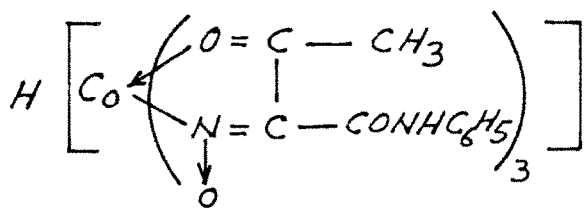
1. (d) Cobalt complex of 2,3-dioxobutyranilide-2-oxime (OK Co) :

It was prepared at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XXXVI).

Similar formula is given for the product by Kuster (226) who also obtained the ammonium salt of the complex.

It has an absorption band at 231-2 mμ and no band at 280-1 mμ. It indicates non-electrolyte nature of the complex anion. Further, hydrogen sulphide does not precipitate cobalt sulphide from the solution of the complex. The electrical conductivity of the complex is small and indicates weak electrolyte nature of the complex and non-electrolyte nature of the complex anion.

The magnetic moment of the complex is calculated as 1.86 B.M. It suggests low-spin octahedral nature of the complex. Few examples of low-spin octahedral cobalt (II) complexes are known. Burstall and Nyholm (261) prepared $[Co(diarsine)_3](ClO_4)_2$ and found μ_{eff} = 1.92 B.M. Figgis and Nyholm (262) prepared two complexes containing $[Co(NO_2)_6]^{4-}$ and observed μ_{eff}= 1.8-1.9 B.M. They suggested that the unpaired electron is in the d_z^2 orbital. A series of isonitrile complexes has been reported by Sacco and Cotton (263) to contain spin-paired (μ_{eff}= 1.89 B.M.) octahedral complexes of the type $[Co(MeNC)_4X_2]$ where X = Cl, Br or I.



(XXXVI)

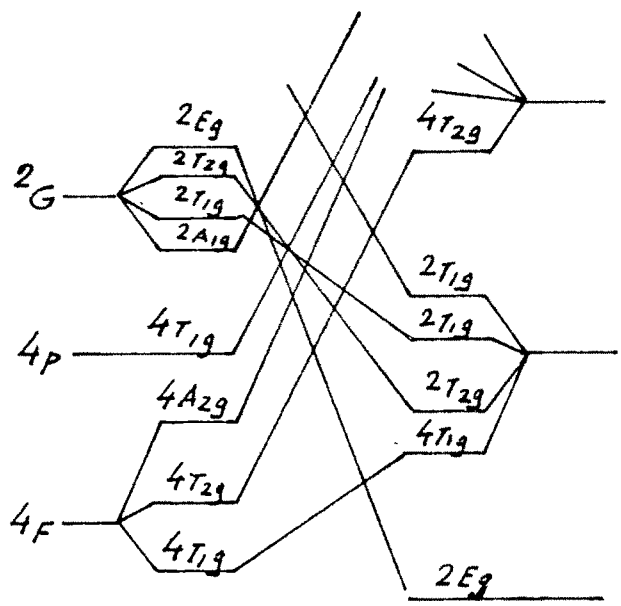


FIG.(C) CORRELATION DIAGRAM FOR FREE ION TERMS → STRONG FIELD CONFIGURATIONS FOR d^7 IN O_h (Co^{2+}, oct)

$$E(^4T_{1g}) = 21A - 40B + 14C \quad \ldots\ldots\ldots (f\text{-}i)$$

$$E(^2E_g) = 21A - 36B + 18C \quad \ldots\ldots\ldots (f\text{-}ii)$$

$$TT = 4B + 4C \quad \ldots\ldots\ldots\ldots\ldots (f\text{-}iii)$$

Eq. (f)

The visible absorption spectrum of the complex in solution has an absorption band at 590 mμ. The band is related to the octahedral crystal field. If we take into consideration the magnetic moment of the complex, we suggest that the strong octahedral crystal field exists (fig.C) (264) and that the band be attributed to the

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

In the weak octahedral crystal field, the ground state for cobalt (II) is $^4T_{1g}$ and its energy is represented by the equation (f - i), where A,B and C are Racah parameters. In the strong octahedral crystal field, the ground state is ^2E_g and its energy is represented by the equation (f-ii). From these, we obtain an expression (f-iii) for the energy at the cross-over point, termed as the spin-pairing energy(π).

When $\Delta < \pi$, the ground term will be $^4T_{1g}$ and when $\Delta > \pi$, the ground term will be ^2E_g. If the values of B and C/B for the free cobalt (II) ion are taken as 1120 cm^{-1} and 3.9 respectively (264), we find that the spin-pairing energy (π) for the free cobalt (II) ion required for the change-over from the spin-free state to the spin-paired state is 21950 cm^{-1}. In fact, cobalt (II) in the complex is not present in the free-ion state . Using Jorgenson's relation (eq.c) and the values of h and k as 1.69 and 0.24 respectively, we find that for cobalt (II)

$$\beta = 0.594$$
$$B' = 665 \ cm^{-1} \text{ and}$$
$$\pi = 12240 \ cm^{-1}.$$

Since $\Delta > \pi$, spin-paired complex is obtained. We further find that the value of D_q/B is 2.55. It is greater than the value of D_q/B required for the cross-over in the Tanabe-Sugano diagram (264) and confirms spin-pairing in the complex.

-x- -x- -x-

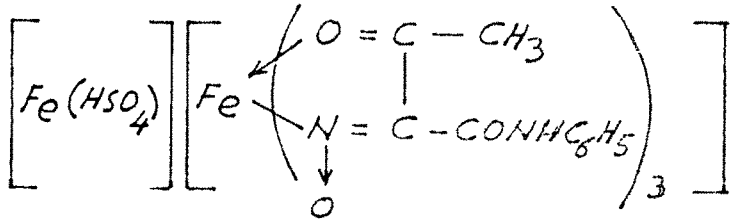
For the purpose of comparison, the complex was also prepared by the carbonate method. The analysis suggests the same composition of the complex. The solubility of the two complexes in different solvents is the same. The two phase method of preparation is, however, preferable to the carbonate method.

1.(e) Iron(II) complex of 2,3-dioxobutyranilide-2-oxime (OK Fe) :

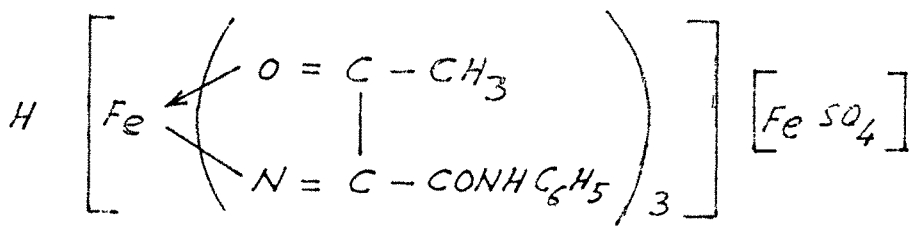
It was prepared at the ether-water interface in the presence of sulphate and acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in acetone, benzene, chloroform, pyridine and dimethyl formamide. It contains sulphate which can be precipitated from the solution by barium chloride. Iron sulphide is precipitated by hydrogen sulphide from the solution of the complex.

On the basis of analysis, it is formulated as (XXXVII). The alternative structures (XXXVIII) and (XXXIX) are considered less probable.

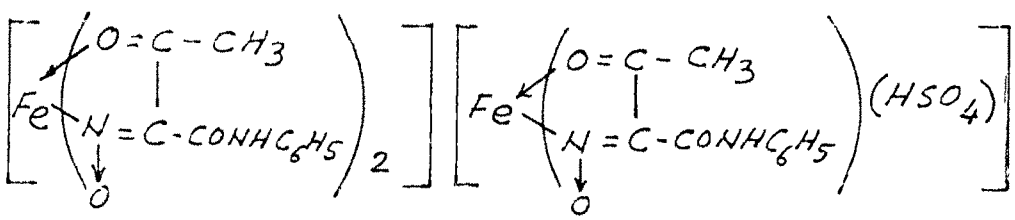
Formulae similar to (XXXVII) are given for the product obtained from ethyl 2,3-dioxobutyrate-2-oxime by Kuster (226) and for the products obtained from isonitroso diketones $(RCO)_2C = NOH$ by Giovanni (265). The octahedral



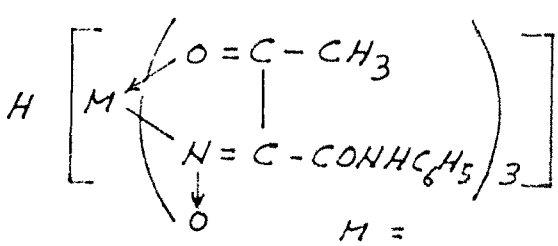
(XXXVII)



(XXXVIII)



(XXXIX)

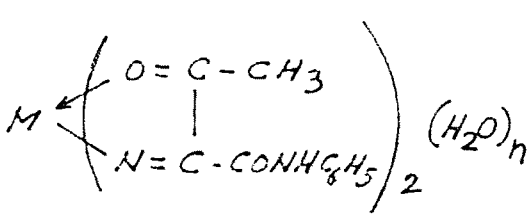


M =

a: Mn

b: Zn

(XL)



M =	n =
a: Sr	2
b: Mg	0

(XLI)

iron (II) complexes were diamagnetic.

It is considered that one of the two iron atoms is 6-coordinated and diamagnetic, and the other atom is paramagnetic. Hence the molar magnetic susceptibility is used in calculating the magnetic moment. The moment is obtained as 5.02 B.M. It indicates the ionic nature of the other iron atom in the complex.

It has an absorption band at 232-3 mμ and no band at 280-1 mμ in the UV spectrum in solution. The absorption band in the visible spectrum is at 590 mμ. It is a charge transfer band with ϵ_m of about 2000, and is attributed to the M⟶L charge transfer. We suggest that the crystal field band is masked by the charge transfer and ligand absorptions.

1. (f) Manganese complex of 2,3-dioxobutyranilide-2-oxime (OK Mn) :

It was prepared at the ether-water interface in the presence of sulphate and acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis it is formulated as (XL-a).

Hydrogen sulphide precipitates manganese sulphide fro the solution of the complex. It has an absorption band at 236 mμ and no band at 280-1 mμ. In the absorption spectrum in the visible region, the absorption bands are observed at 580 mμ, 720 mμ and 780 mμ, and may be related to the weak octahedral ligand field. Using Tanabe-Sugano diagram for d^5 complexes (fig.d), we suggest that the absorption bands he attributed to the $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$

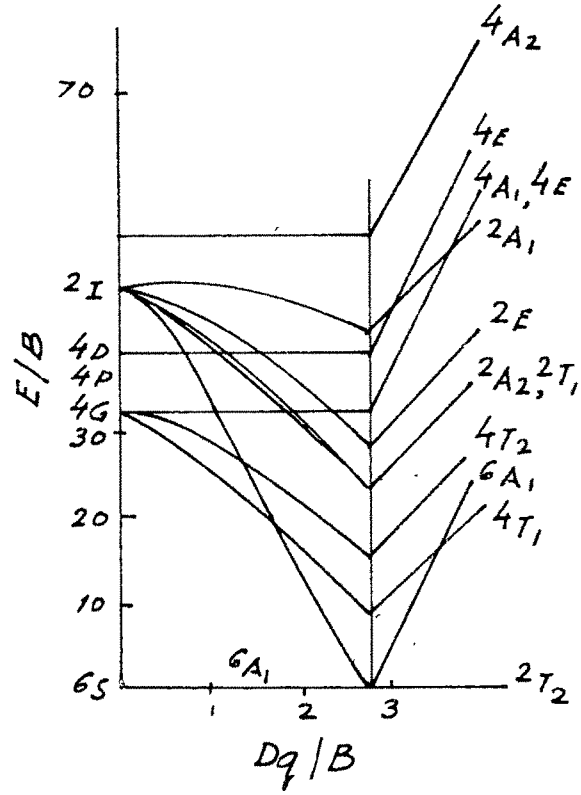
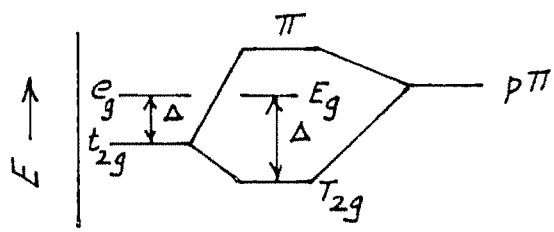


FIG. (d) THE ENERGY DIAGRAM FOR THE CONFIGURATION d^5 (Mn^{2+})



METAL	COMPLEX	LIGAND
d-ORBITALS	INCLUDING π-BONDING	EMPTY pπ-ORBITALS

FIG. (e) EFFECT OF π-BONDING ON THE ENERGY OF THE T_{2g} LEVEL AND ON Δ. (FILLED METAL ORBITALS AND EMPTY LIGAND ORBITALS)

transitions. Comparison of the ratios of the energies of these transitions with those of E/B for the corresponding transitions for a fixed value of D_q/B derived from the diagram helps in selecting the value of D_q/B as 1.2. Hence the average value of B (i.e. B') can be derived as 550 cm^{-1}, and that of D_q as 660 cm^{-1}. Taking the value of B for free manganese (II) ion as 960 cm^{-1}, we obtain the value of β as 0.573. Hence for OKMn

$$B' = 550\ cm^{-1}$$

$$\beta = 0.573 \quad \text{and}$$

$$D_q = 660\ cm^{-1}.$$

1. (g) Zinc complex of 2,3-dioxobutyranilide-2-oxime (OK-Zn).

It was prepared at the ether-water interface in the presence of sulphate and acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XL-b).

Hydrogen sulphide precipitates zinc sulphide from the solution of the complex. It is diamagnetic and has an absorption band at 238 mμ. It is considered to have octahedral configuration.

1. (h) Strontium complex of 2,3-dioxobutyranilide-2-oxime (OK-Sr) :

It was prepared at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XLI-a).

It is dimagnetic and has an absorption band at 236-8 mμ.

1. (j) Magnesium complex of 2,3-dioxobutyranilide-2-oxime (OK-Mg) :

It was prepared from the metal foil and the ligand. It is soluble in pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XLI-b)

It is diamagnetic and has an absorption band at 236 mμ.

1. (k) Complexes of 2,3-dioxobutyranilide-2-oxime : general :

Bivalent metal ions of the first transition series and alkaline earth metals are studied for their ability to form complexes with 2,3-dioxobutyranilide-2-oxime. (Complexes of alkali metals were attempted, but could not be prepared.).

In the first place, attempts were made to prepare the sodium, potassium, calcium and barium complexes from the homogeneous solution. These were unsucessful. Then the two phase method was adopted. Sodium, potassium, calcium, magnesium and barium complexes could not be obtained in the pure state. However, strontium complex was obtained in a pure, well-defined state and was studied further.

Later, another method was tried in the case of magnesium. Magnesium complex was obtained by using magnesium metal. This method can be adopted for other metals, but was not tried further.

Six transition metals of the first transition

series, namely manganese, iron, cobalt, nickel, copper and zinc were used. The two-phase method was found suitable for the preparation of their complexes. Some of these were also prepared by other methods, namely the carbonate and the metal-foil method. Two phase method of preparation is found better for their preparation.

-x- -x- -x-

These ions combine with (i) two ligand anions forming electrically neutral molecules ML_2 or (ii) three ligand anions forming complex anions $(ML_3)^-$. Accordingly, two series of complexes are obtained : (i) ML_2 series and (ii) ML_3 series. Copper, nickel, strontium and Magnesium fall under group (i), while manganese, iron, cobalt and zinc fall under group (ii).

-x- -x- -x-

Their magnetic and spectroscopic properties provide interesting observations. Strong octahedral ligand fields are present in the complexes of iron (d^6) and cobalt (d^7), as indicated by their magnetic moments.

The values of Δ and β_o obtained for these complexes are

	$\Delta(cm^{-1})$	β_o
OK Mn	6600	42.7 %
OK Co	17000	40.6 %
OK Ni	10800	20.3 %

The metals fall in the increasing order of Δ values as

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

It forms a part of the spectrochemical series of

metals observed with different ligands.(266).

If we compare the Δ values of the complexes of cobalt and nickel with the ligands such as water, ammonia, ethylenediamine,etc. we find that their Δ values for any particular ligand do not differ by more than 10 to 15 %. However, in the present case,the value for the cobalt complex is much higher than that for the nickel complex. Associated with this is the increase in the β_0 value for the cobalt complex compared with that for the nickel complex. Hence one can suggest that besides σ-bonding, there is π-bonding also in the cobalt complex. If t_{2g} electrons of cobalt are involved in π-bonding with the ligand, it would lead to the delocalisation of the metal d-electrons.It would results in the increased crystal-field splitting (fig.e), Spin-pairing is observed from the increased crystal field strength and ^2E_g becomes the ground state. Under these conditions, Jahn-Teller effect will be operative and will also lead to the increased crystal field splitting.

A rough estimate of the crystal field parameters can be obtained for OK Fe if it is assumed that the absoption band is a crystal field band superimposed by the charge transfer band, and that the values of β for iron (II) and cobalt (II) are the same. Since the value of B for the free iron (II) ion is 1060 cm^{-1},the value of B in the complex is obtained as 630 cm^{-1}. Using Tanabe-Sugano diagram (fig.f), we obtain the value of Dq/B as 3.0 and of Dq as 1890 cm^{-1}. The value of Dq/B at the cross-over point is 2.0.Hence a strong crystal field exists and the band is attributed to the

$$^1A_{1g} \longrightarrow {}^1T_{1g}$$ transition.

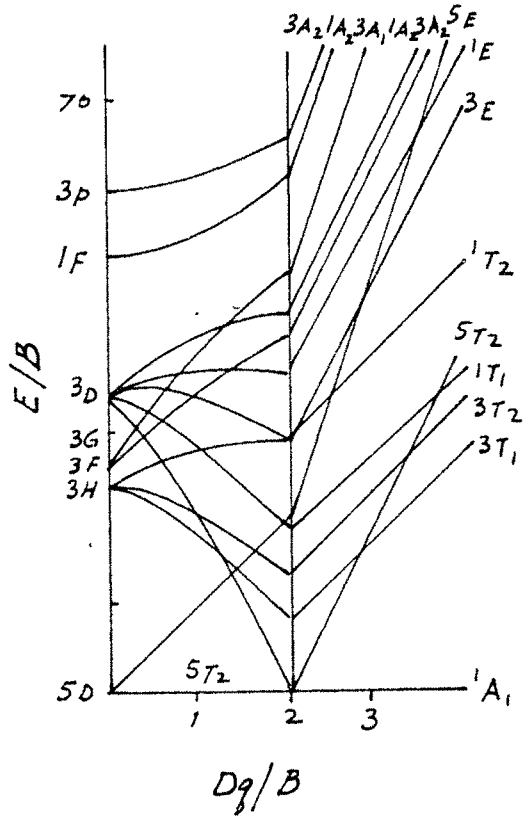


FIG.(f) ENERGY DIAGRAM FOR THE CONFIGURATION $d^6(Fe^{2+})$

$$\chi_{obs} = \chi_{SPIN\ ONLY}\left(1 - \frac{4\lambda k^2}{\Delta}\right) + \frac{4N\beta^2 k^2}{\Delta}$$

N = AVOGDRO'S NUMBER

β = BOHR MAGNETON

Eq. (9)

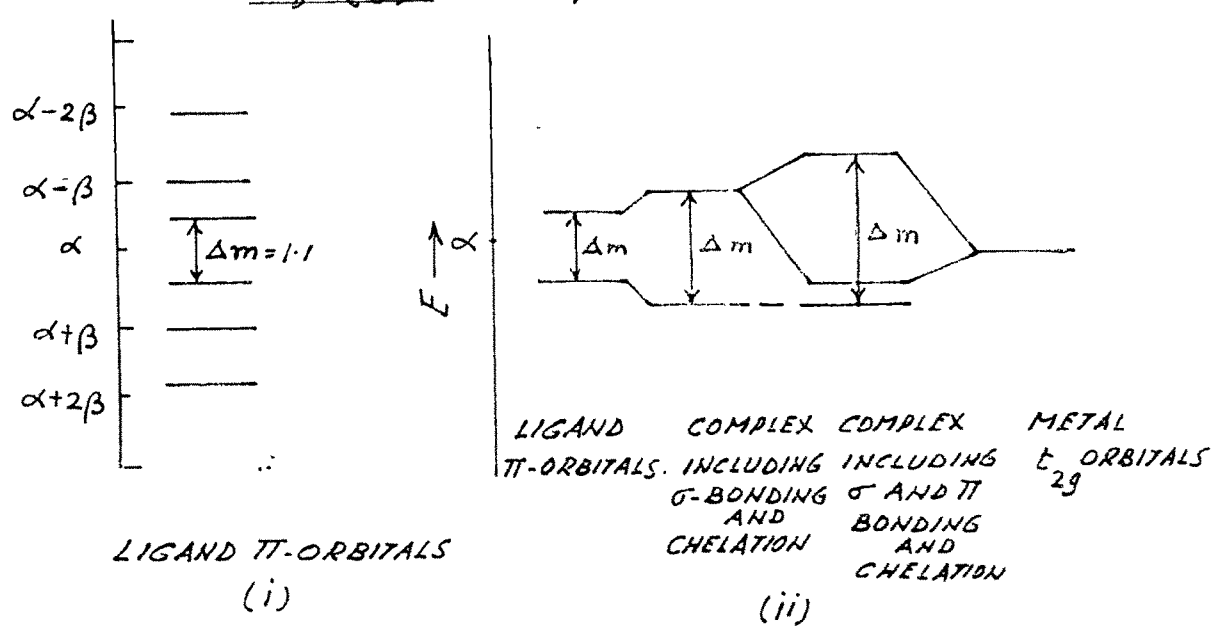


FIG.(g). EFFECT OF σ-BONDING AND π-BONDING ON THE HIGHEST OCCUPIED AND LOWEST VACANT LIGAND π-ORBITALS.

The approximate values of the crystal field parameters for the diamagnetic iron (II) in OK Fe are

$$B' = 630 \quad cm^{-1}$$

$$\beta = 0.594$$

$$Dq = 1890 \quad cm^{-1}.$$

The revised spectrochemical series becomes

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+}$.

The increased crystal field splitting may be associated with π-bonding in the complex. Both $M \longrightarrow L$ π-bonding and charge transfer will be involved.

-x- -x- -x-

The delocalisation of the t_{2g} electrons also influences the magnetic moment. It results in the reduction of the angular orbital momentum and the corresponding lowering of the magnetic moment. It is usually evaluated in terms of a constant k. The value of k is unity for no delocalisation and is somewhat less than unity when delocalisation has taken place.

The calculations can be made for for d^7 system-cobalt (II) in OK Co having ^2E_g ground state by using eq.(g-i).

$$1427 = 1250\ (1-0.121\ k^2) + 61\ k^2$$

Hence the value of k is obtained as 0.91. This evaluation of k is of limited accuracy, but there is a distinct indication of delocalisation of the t_{2g} electrons.

-x- -x- -x-

The UV absorption spectra of these compounds show absorption band at 231-46 mμ. The ligand in the anionic form has an absorption band at 245-46 mμ. The ligand chelated with a proton or a metal ion (e.g. Sr,Mg,Zn)

containing no incomplete shell of d-electrons has an absorption band at 236-38 mμ . The band observed at 231-33 mμ is attributed to the ligand chelated with a metal ion (e.g. Co, Fe) containing incomplete shall of d-electrons and involving stronger interaction of the metal with the ligand. This is confirmed by their β_e values.

We adopt the HMO method for evaluating the ii-energy levels of the crossed conjugated system

, using the values of $K_{O} = 0$ and $K_{C} = N$ as unity and neglecting h. The π-energy levels are represented in fig (g-i). We find that $\Delta m = 1.1$, and it corresponds to the absorption band at about 40800 cm^{-1} for the ligand anion. The effects of σ-bonding and π-bonding on the highest occupied and lowest vacant π-orbitals of the ligand are considered in fig.(g-ii). σ-Bonding with chelation results in the modification of those energy levels so that the value of Δm increases and an absorption band is observed at about 42000 cm^{-1}. Further, when M ⟶ L π-bond formation takes place through the utilisation of the metal t_{2g} electrons and empty ligand π orbitals, the energy levels modify further, resulting in the additional increase in the value of Δm. An absorption band is observed at about 43000 cm^{-1} in OK Co and OK Fe, confirming π-bonding in them.

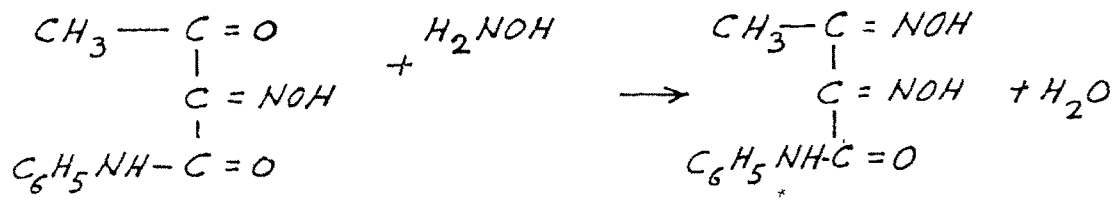
III. 2. Dioxime and its iron complex

2.(a) 2,3-Dioxobutyranilide dioxime :

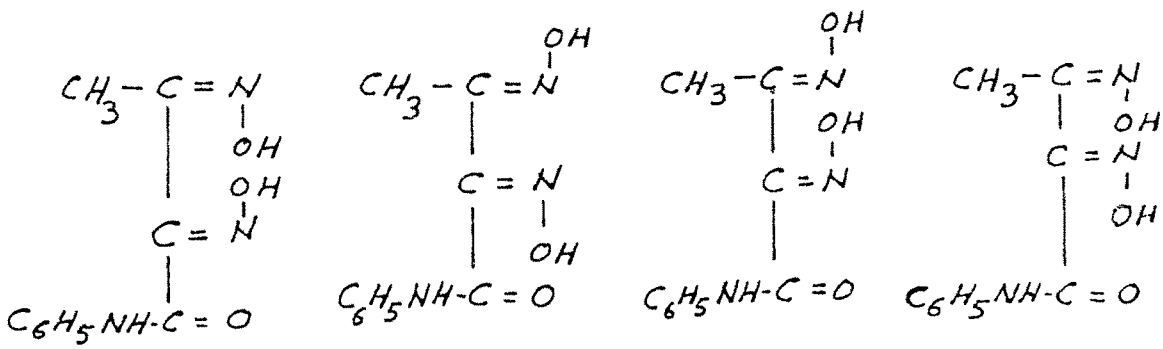
2,3-Dioxobutyranilide-2-oxime was treated with hydroxyl amine to obtain 2,3-dioxobutyranilide dioxime. (eq.h).

It is in agreement with the suggestions of Knorr and Reuter (230) and Talati (224). It would be capable of existing in four steroisomeric forms (XLII). However, only one product is isolated (224,230). The stereoisomeric nature of the product can be deduced on the basis of the chelating properties of the isomeric forms as follows :
Syn-dioxime would be incapable of forming metallic complexes. Amphi dioxime would form greenish yellow compounds with nickel in which the dioxime molecule would act as a dibasic acid. Anti-dioximes would form metal complexes with nickel in which the dioxime molecule would act as a monobasic acid. The dioxime under investigation is known to form the complex with nickel in which the dioxime molecule is found to act as a monobasic acid. Hence the dioxime is suggested to have anti-dioxime structure (224). This is also in accord with the observation of Ishidata (267) that the dioxime obtained from -CO-C(=NOH)- would have an anti-dioxime configuration.

It has absorption band at 233-34 mμ in aqueous solution, at 236-38 mμ in alcoholic solution and at 271-74 mμ in alkali solution. The K band observed at 233-38 mμ is attributed to the crossed conjugated system (XLIII) (224). The X band observed at 271-74 mμ is attributed to its ionic tautomer (233).

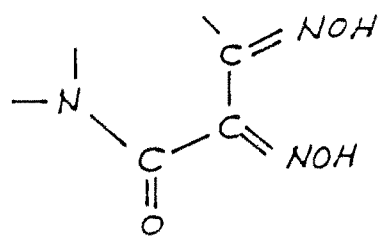


Eq. (h)

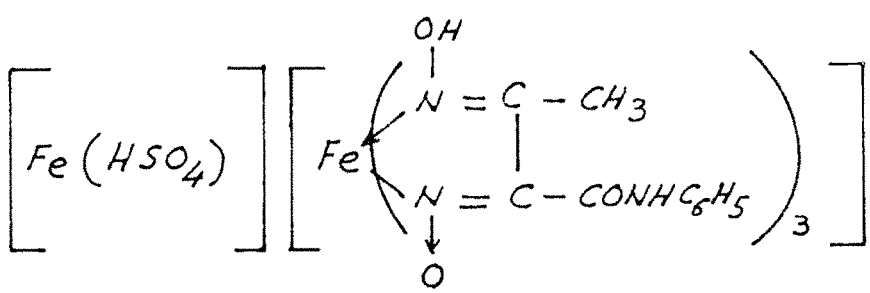


(a) SYN. (b) ANTI. (c-i) AMPHI. (c-ii) AMPHI

(XLII)



(XLIII)



(XLIV)

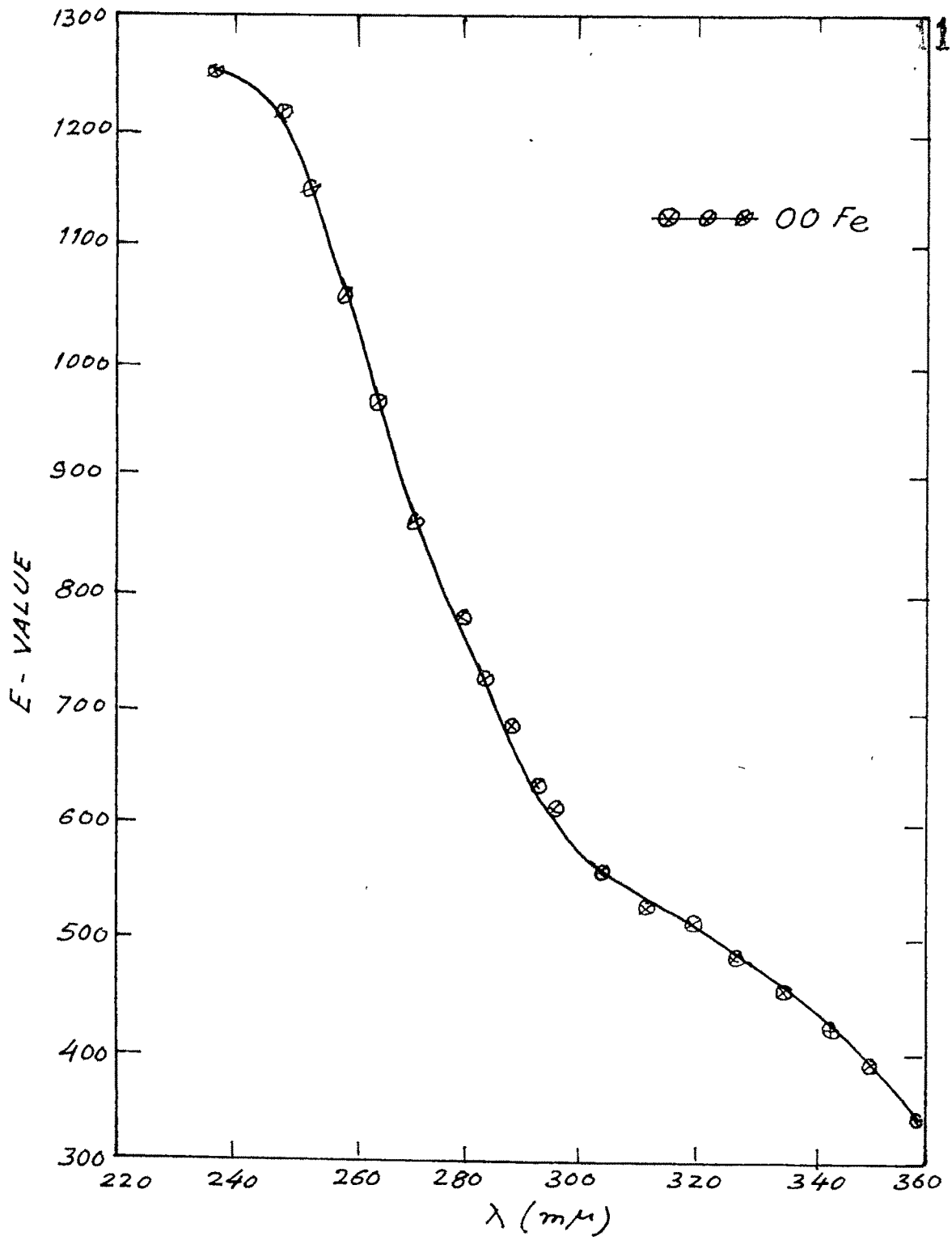


FIG. 5. UV ABSORPTION SPECTRUM OF OO-Fe

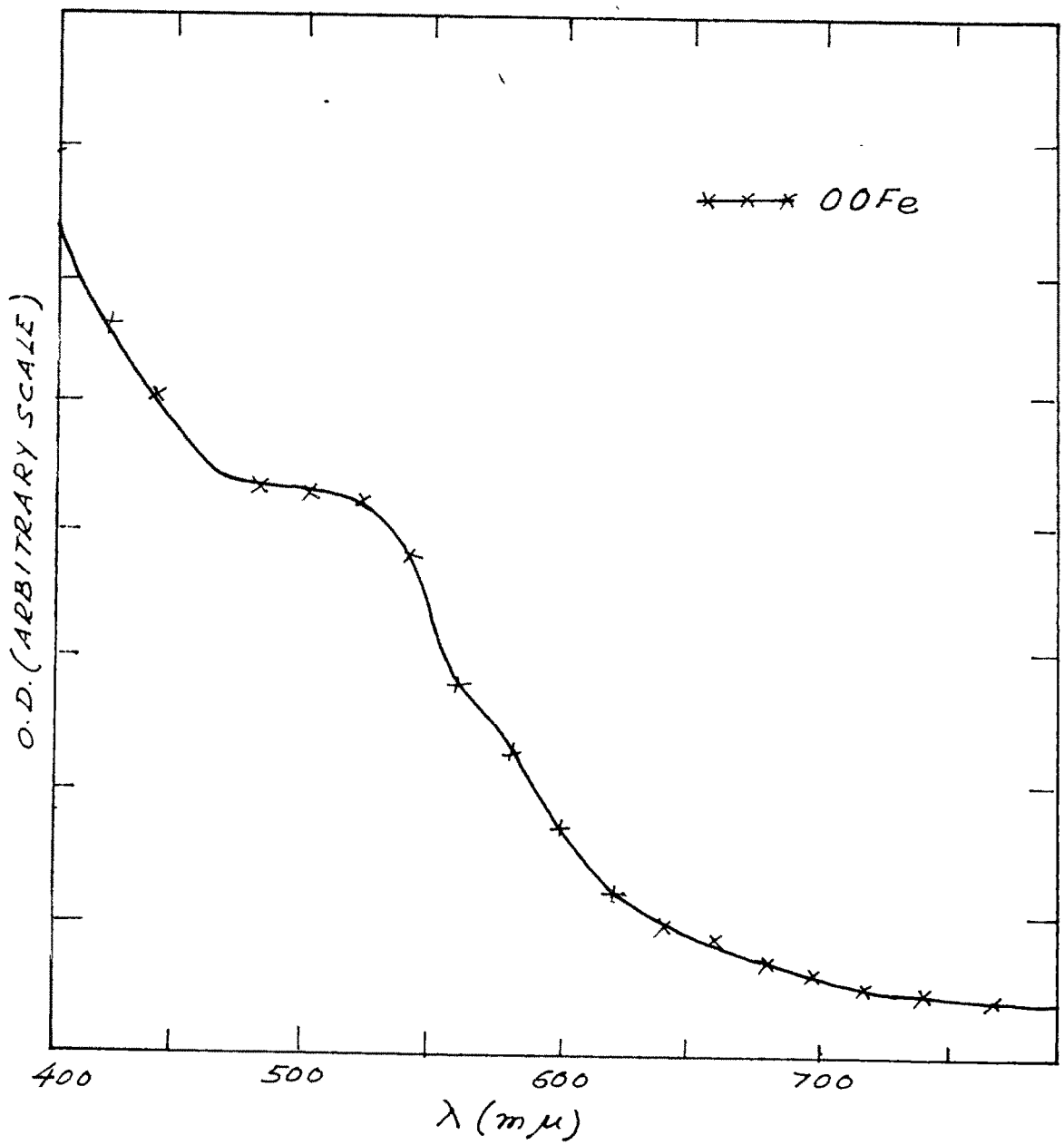


FIG. 6. VISIBLE ABSORPTION SPECTRA OF OO-Fe

Talati (224) investigated the complexes of 2,3-dioxobutyranilide dioxime. Desai (223) prepared the iron complex of the ligand. The product obtained by him was formulated as $Fe_2(L)_3$ (OH) $(H_2O)_5$. We have studied the preparation of the iron complex by another method. The absorption spectra of the complex are presented in figs.5 and 6.

2 (b) Iron (II) complex of 2,3-dioxobutyranilide dioxime :

It was prepared at the ether-water interface in the presence of sulphate and acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XLIV).

One of the two iron atoms in the complex is 6-coordinated and diamagnetic and the other atom is paramagnetic. Only one paramagnetic atom is present in the complex molecule. Hence the molar magnetic susceptibility is used in calculating the magnetic moment. The moment is obtained as 5.0 B.M. and indicates ionic nature of the atom.

The absorption band (K-band) in the UV spectrum is shifted to a shorter wavelength and hence is not observed. The absorption spectrum in the visible region contains shoulders at 560 mμ and 470 mμ. These are considered to be the charge transfer bands. The colour of the solution is unstable and fades on standing.

III.3. Phenyl hydrazone of 2,3-dioxobutyranilide -2-oxime and its metal complexes :

3.(a) Phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime (OZ) :

It was prepared from 2,3-dioxobutyranilide-2-oxime and phenyl hydrazine. The reaction is represented by the equation (i).

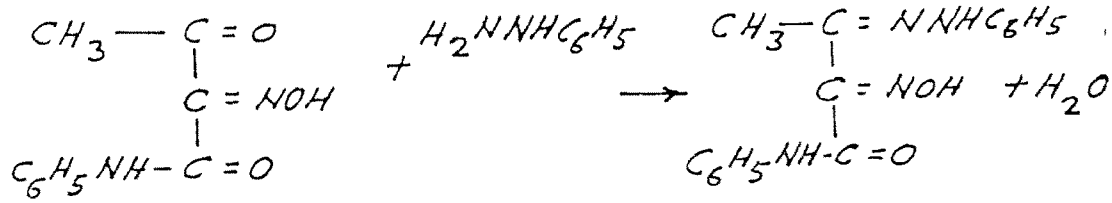
Desai (233) showed that it has an anti-configuration. He studied its absorption spectrum and showed that the absorption bands are at 240 mμ, 302 mμ (sh) and 324 mμ in methanol. He prepared its nickel and cobalt complexes and studied some of their properties.

We have prepared the complexes of the ligand (OZ) with barium, aluminium and zinc. Desai (233) could isolate the oxidation product of the ligand but no complex with copper. We have isolated a product containing copper. We have studied their absorption spectra (figs.7,8). Their absorption bands are presented in table 34.

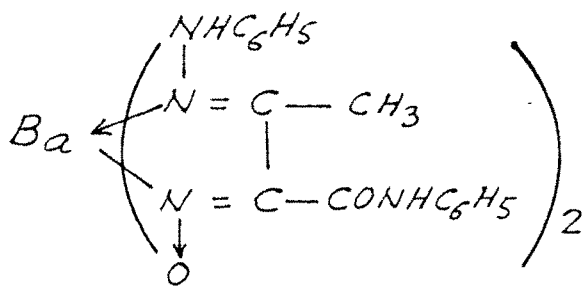
3 (b) Barium complex of the oxime-hydrazone (OZ-Ba)

The complex was prepared at the ether-water interface in the presence of ammonium hydroxide. It is soluble in alcohol, acetone, benzene, ether, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XLV).

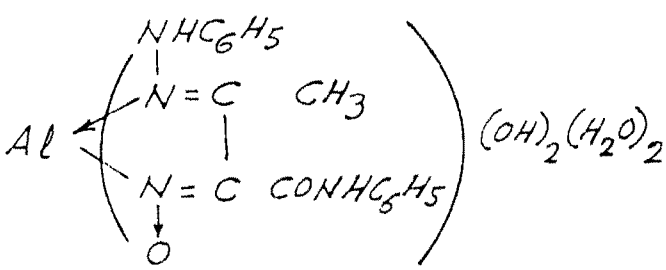
Its absorption bands are at 244 mμ, 304 mμ (sh) and 324 mμ. The ligand spectrum maintains its shape and bands in the spectrum of the barium complex of the



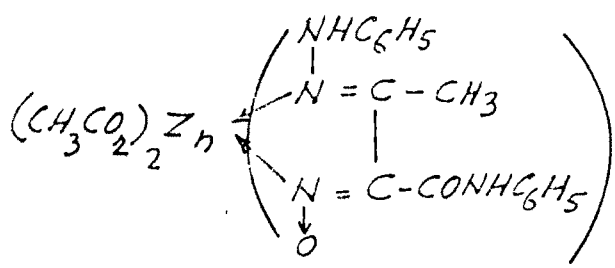
Eq. (i)



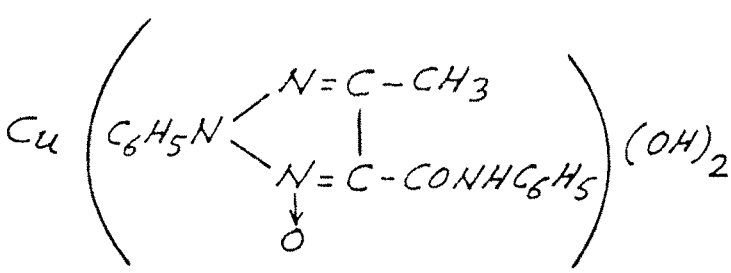
(XLV)



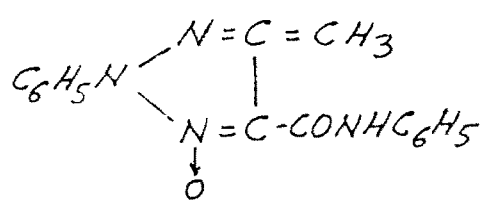
(XLVI)



(XLVII)



(a)



(b)

(XLVIII)

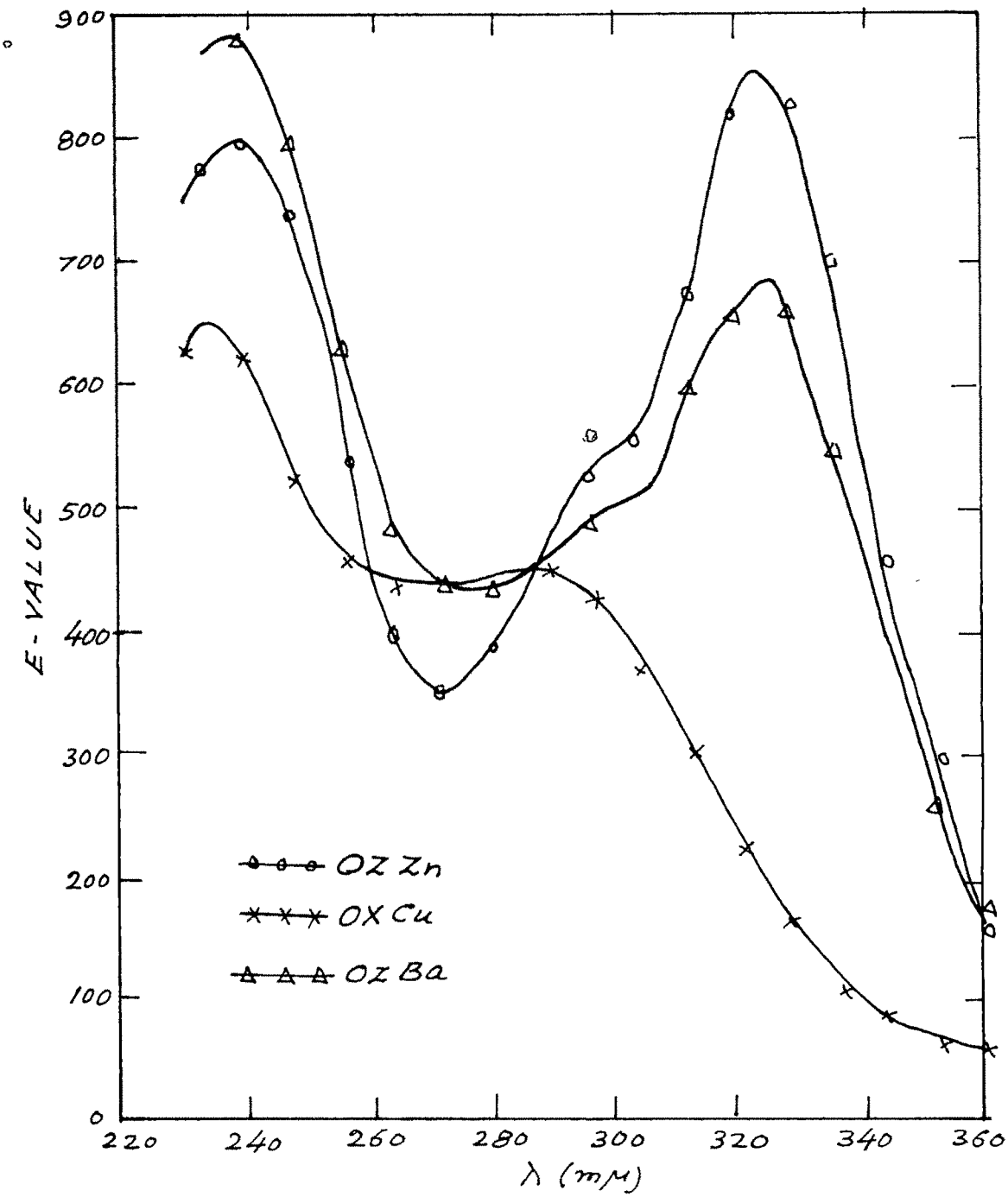


FIG. 7. UV ABSORPTION SPECTRA OF OZ-Zn, OX-Cu AND OZ-Ba.

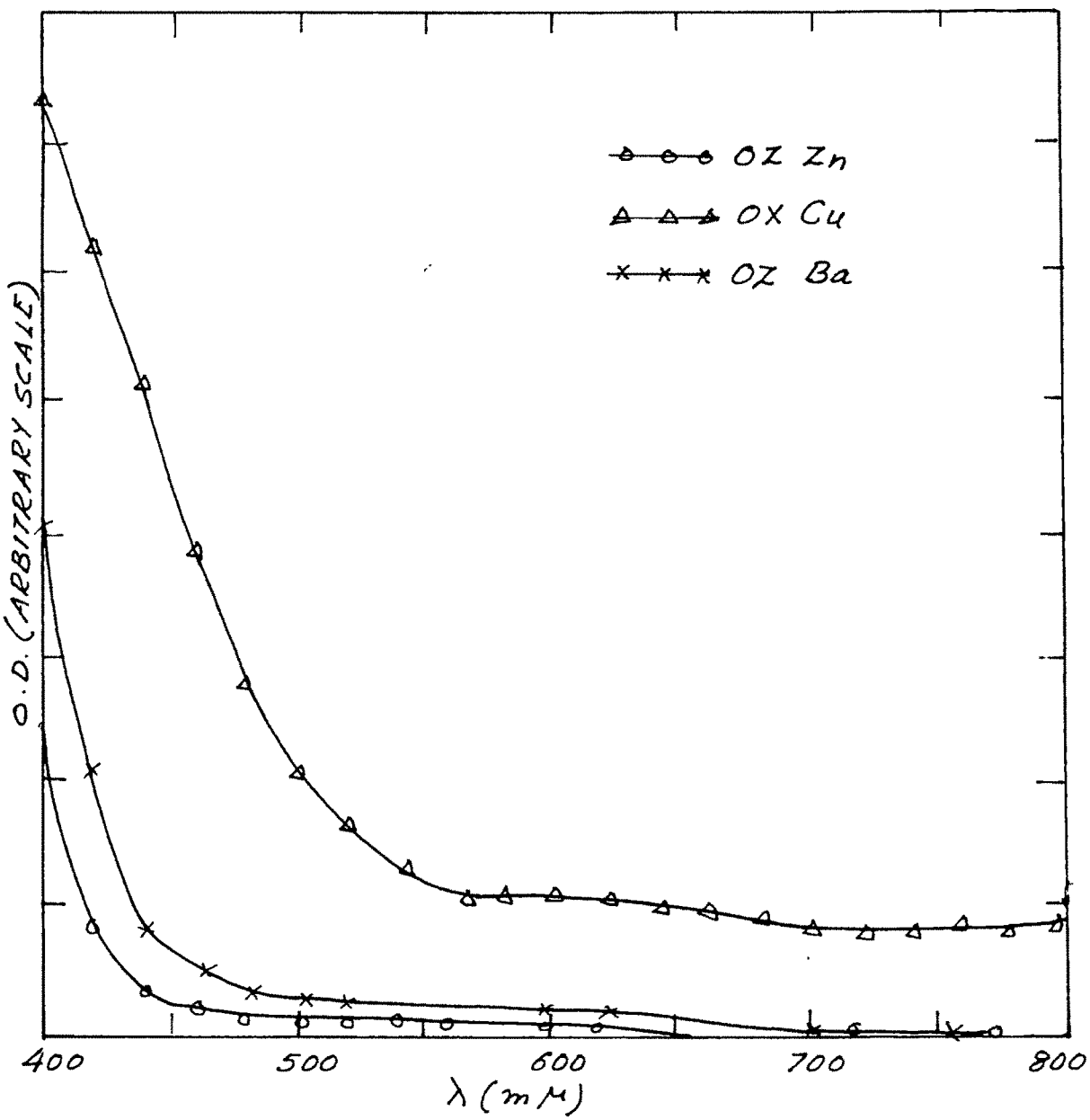


FIG. 8. VISIBLE ABSORPTION SPECTRA OF OZ-Zn, OX-Cu AND OZ-Ba

Table 34

Absorption bands of the complexes [illegible]

No.	Complex	UV Spectra λ-max (mμ)	E-value	Visible Spectra λ- max (mμ)
1.	OZBa	244	890	-
		304 (Sh)	495	
		324	690	
2.	OZZn	240	800	-
		304 (Sh)	560	
		324	840	
3.	OX Cu	236	635	-
		286	435	

ligand. The molar conductivity of the solution of the complex is calculated as 200. It indicates that the dilute solution contains barium in the ionic form.

3 (c) Aluminium complex of the oxime-hydrazone (OZ-Al)

Attempts were made to prepare aluminium complexes of the oxime-ketone, the dioxime and the oxime-hydrazone. Uniform products could not be isolated with the oxime-ketone and the dioxime. The complex was obtained with the oxime-hydrazone in the alcoholic solution in the presence of acetate ions and was recrystallised from methanol. On the basis of analysis, it is formulated as (XLVI).

It is insoluble in water but soluble in various organic solvents. It is assumed to have octahedral configuration.

3. (d) Zinc complex of the oxime-hydrazone (OZ-Zn)

The complex was obtained at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XLVII).

It gave a positive test for acetate ion. Its absorption spectrum contains bands at 240 mμ. 304 mμ (sh) and 324 mμ. Its molar electrical conductivity is calculated as 22. Hence it is considered to be a non-electrolyte and possibly having a tetrahedral structure.

3 (e) Copper complex obtained from the oxime-ketone (OX-Cu) :

The complex was obtained at the ether-water

interface and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XLVIII-a).

Desai (233) attempted to prepare the copper complex and was able to isolate the substance which was characterised by him as (XLVIII-b).

The copper complex obtained by us is of (XLVIII-b) Its absorption spectrum is different from that of the oxime-hydrazone but is similar to that of (XLVIII-b).

Its magnetic moment is calculated as 1.76 B.M.

3. (f) Complexes of the phenyl hydrazone of 2,3-dioxo-butyranilide-2-oxime : general :

We are successful in preparing the non-transition metal complexes of the oxime-hydrazone. Basic aluminium complex was obtained because of the use of the basic aluminium acetate in the preparation. Zinc complex is an addition product. It shows that the oxime-hydraxone can also act as a coordinating agent instead of as an acidic agent.

We have confirmed the observation of Desai that copper (II) catalyses the oxidation of the oxime-hydrazone.

III. 4. Schiff base from 2,3-dioxobutyranilide-2-oxime and methyl amine and its transition metal complexes :

4 (a) Oxime Schiff base :

It was obtained from the reactants (vic-oxime ketone and methyl amine) in ether as represented by the equation (j).

Since the oxime-ketone is shown to have the syn-amide structure, its Schiff base can have two isomeric forms (XLIX).

Anti-configuration is attributed to the product on the basis of the following observations :

(i) Oxime of 2,3-dioxobutyranilide-2-oxime is shown to have anti-configuration (224) ;

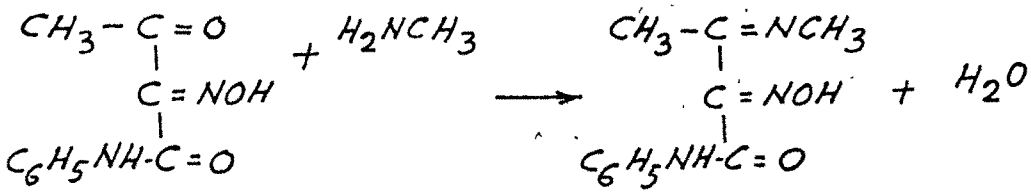
(ii) Phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime is shown to have anti-configuration (233).

(iii) Amphi-structure would not favour the formation of metal complexes with the transition metal ion due to the steric effect of the alkyl/aryl group (L) (237).

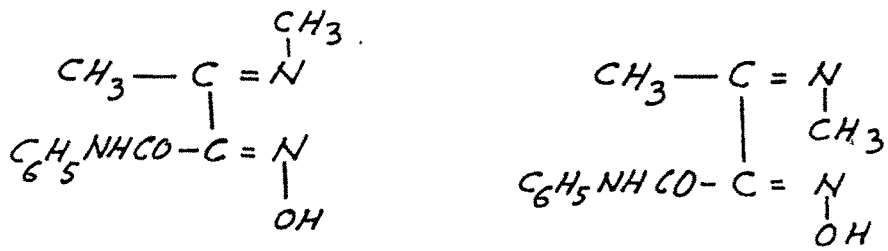
Anti-structure would favour the formation of the metal complexes. The ligand under investigation forms metal complexes and may be considered to have an anti-structure.

The ligand (OA) is soluble in various organic solvents. Its absorption spectra in alcoholic and alkali solutions are presented in fig.(9) and the absorption bands are presented in table 35.

Patel (237) observed that the absorption spec-

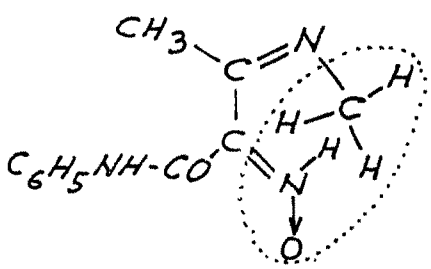


Eq. (j)

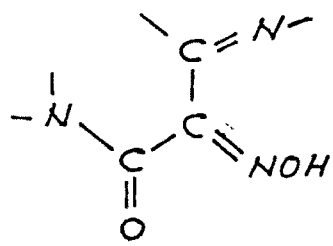


(a) ANTI (b) AMPHI

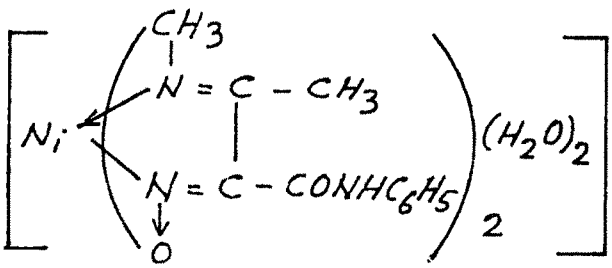
(XLIX)



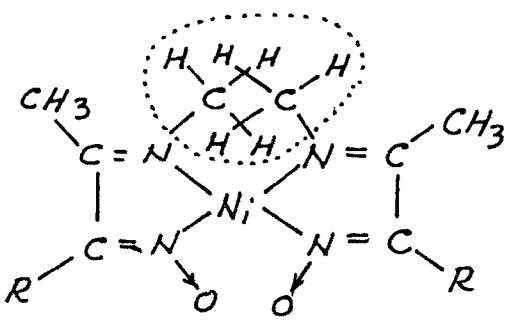
(L)



(LI)



(LII)



(LIII)

$$\chi_{obs} = \chi_{SPIN\ ONLY}\left(1 - \frac{8\lambda k^2}{\Delta}\right) + \frac{8N\beta^2 k^2}{\Delta}$$

Eq. (k)

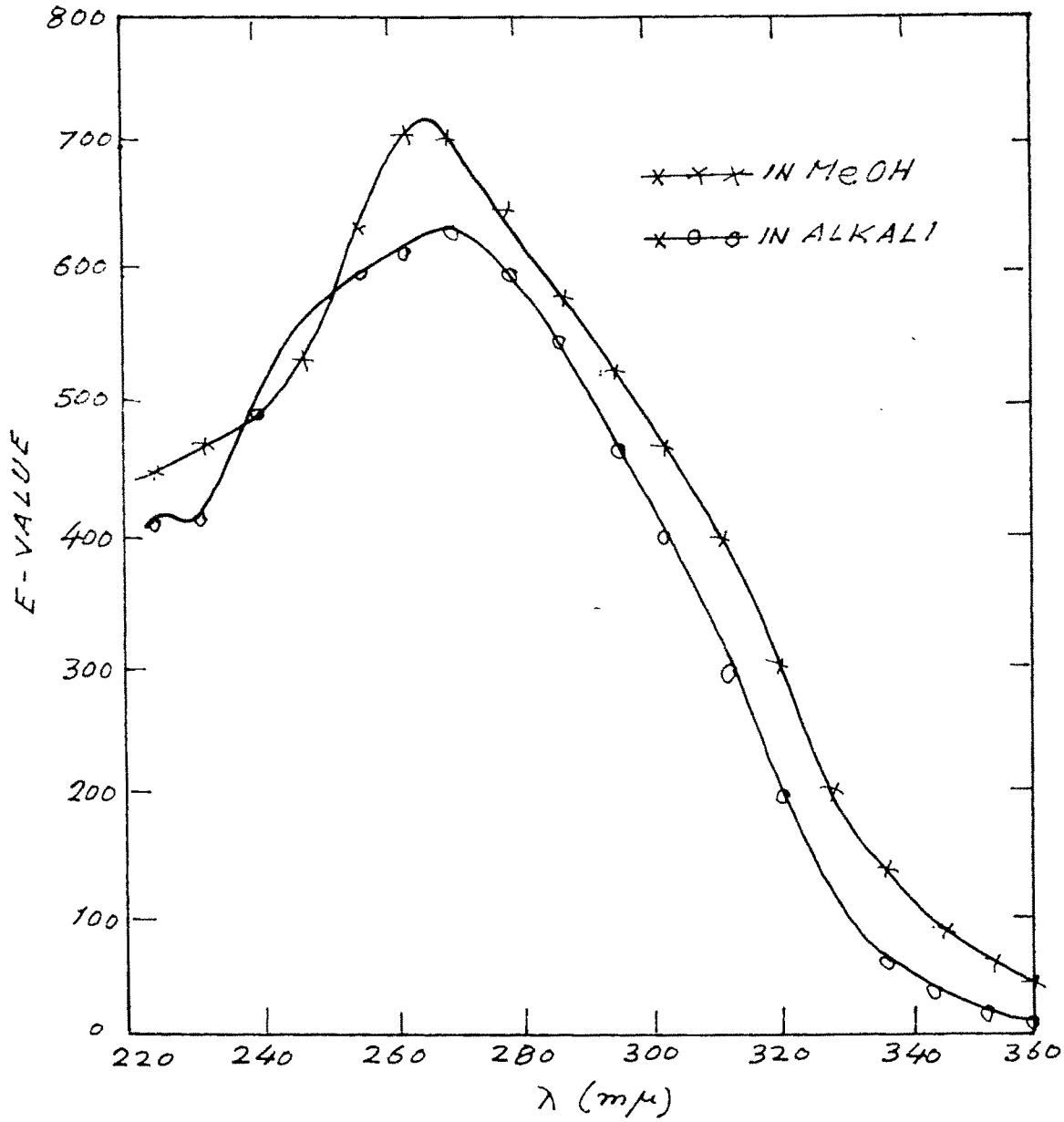


FIG.9. UV ABSORPTION SPECTRA OF OA

Table 35

Absorption bands of $CH_3 - \underset{\underset{C_6H_5NHCO-}{|}}{C} = NR$

$C_6H_5NHCO- C = NOH$

No.	ligand R =	in methanol		in alkali	
		λ max (mμ)	E-value	λmax (mμ)	E-value
1.	CH_3	266-8	710	232	410
				272	625
2.	C_6H_5	231-2	815	258	390
				290-2	450
3.	$C_6H_5CH_2$	226	490		
		270-2	420	268-70	490

ctrum of the Schiff base where R = C_6H_5 is different from that of the Schiff base where R = $C_6H_5CH_2$. He attributed it to the presence of the -CH_2-group inbetween the crossed conjugated system (LI) and the phenyl group.

The absorption bands of the oxime-Schiff bases (where R = C_6H_5- and $C_6H_5CH_2$-) are also presented in table 35. We find that the spectrum of the ligand (OA) where R =CH_3 is comparable to that of the ligand where R=C_6H_5-CH_2.

The ligand gives characteristic reactions with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), etc.These reactions are investigated further. The products are isolated and studied to elucidate their nature. Their magnetic moments are presented in table 36. Their absorption spectra are shown in figs.10 and 11 and their absorption bands are given in table 37.

4.(b) Nickel (II) complex of the oxime-Schiff base (OANI) :

The complex was obtained at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, chloroform,benzene, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LII).

Pfeiffer (239) prepared the nickel complex of the Schiff base from 2,3-butane dione monoxime and methyl amine and showed the similarity of its structure to that of nickel dimethylglyoximate.

Talati(224) prepared the nickel complex of the dioxime of 2,3-dioxobutyranilide. He found it to be diamagnetic and suggested a square planar structure for the

Table 36

Magnetic moments of the complexes of the Schiff base of 2,3-dioxobutyranilide-2-oxime and methyl amine or its hydrolysed product

no.	Complex	Molar magnetic susceptibility $X_m \times 10^6$	Corrected molar magnetic susceptibility $X_m' \times 10^6$	Magnetic moments μ (B.M.)
1.	OA- Ni	4446	4678	3.39
2.	OA- Co	1144	1457	1.90
3.	OA- Fe	5205	5449	3.65
4.	OK- Cu	1185	1375	1.84
5.	OA- Mn	14590	14759	6.04

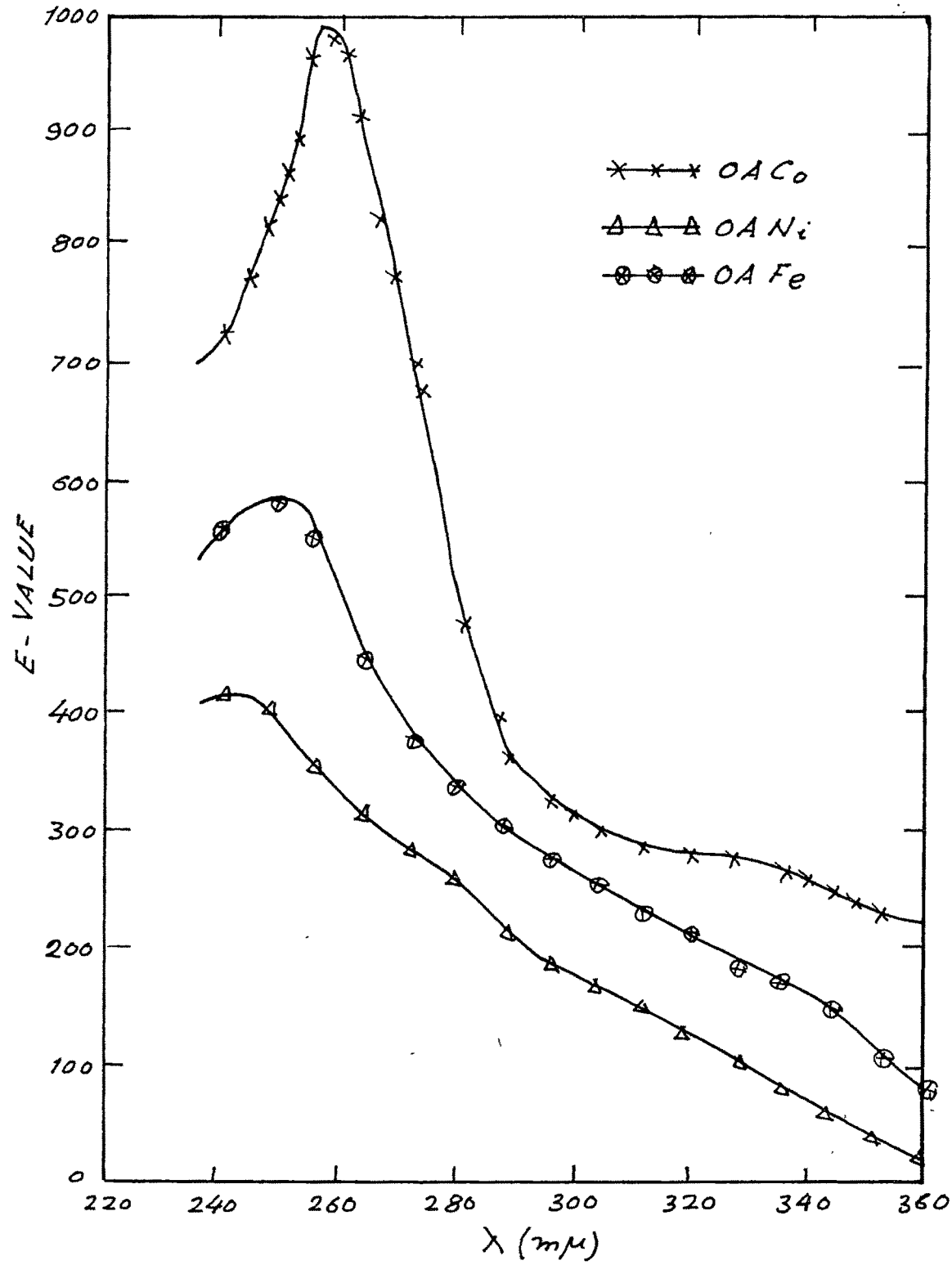


FIG. 10. UV ABSORPTION SPECTRA OF OA-Co; OA-Ni AND OA-Fe

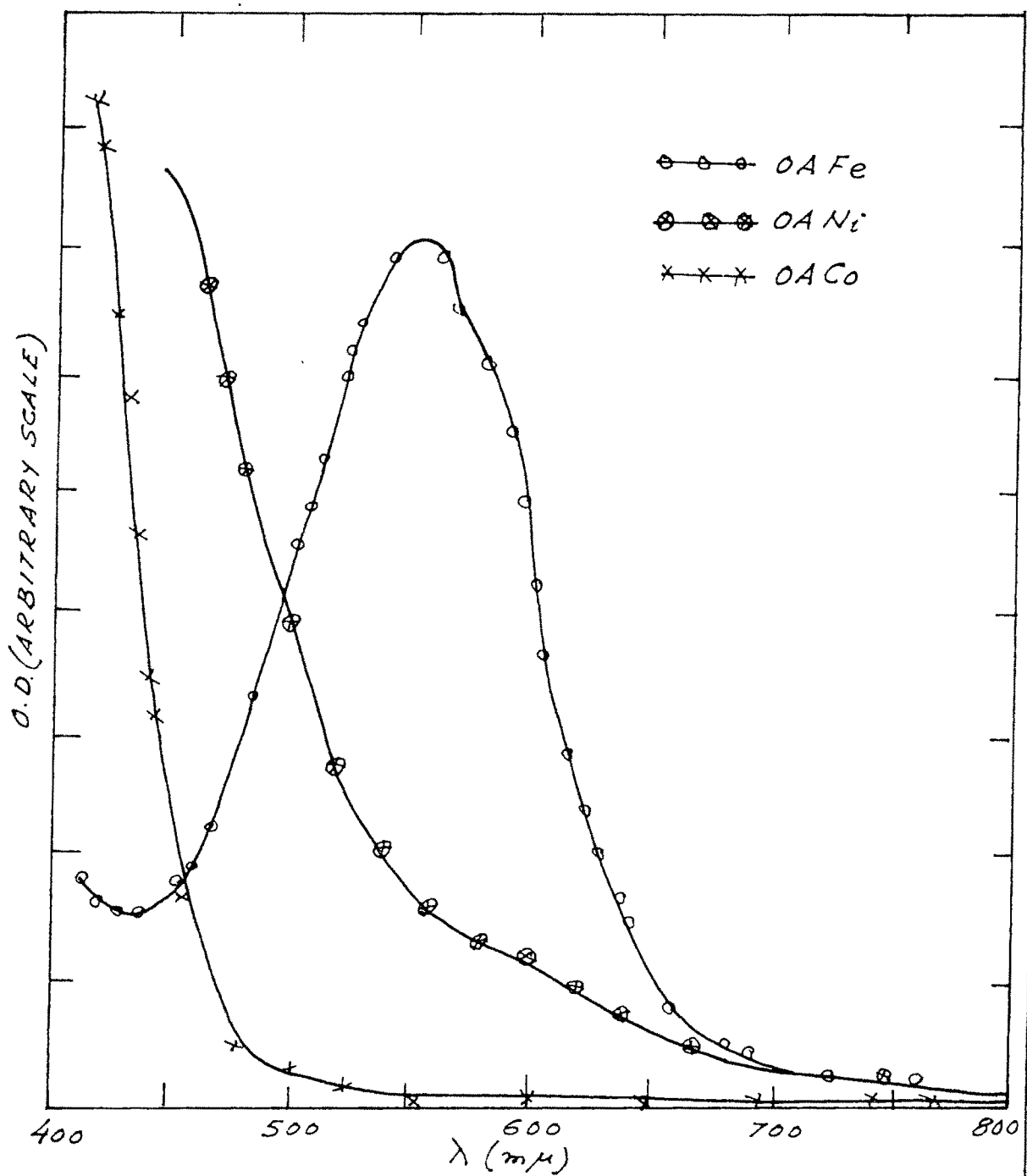


FIG. 11. VISIBLE ABSORPTION SPECTRA OF OA-Fe, OA-Co AND OA-Ni

Table 37

Absorption bands of the complexes of OA

No.	Complex	λ max (mμ)	E-value	λ max (mμ)
1	OA Ni	240-4	410	-
2	OA Co	258	980	-
3	OA Fe	248-52	580	550

complex comparable to that of the nickel dimethyl glyoximate.

Desai (233) prepared the nickel complex of the phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime. He found it to be diamagnetic and suggested a square planar structure for the complex comparable to that of the nickel dimethyl glyoximate.

Patel (237) prepared the nickel complexes of the Schiff bases of 2,3-dioxobutyr(aryl) amide-2-oxime. He found them to be paramagnetic and suggested that these were the first example of a series of paramagnetic nickel complexes with glyoxime-type ligands.

Magnetic moment of the complex is found to be 3.4 B. M., indicating the presence of two unpaired electrons.

Sellwood (268) writes : All complexes in which nickel is bonded to four nitrogen atoms, irrespective of whether these nitrogen atoms belong to the pyrrole ring, oxime or triazene ring have proved to be diamagnetic. But if for some reason, the chelate groups are prevented from assuming a coplanar configuration, it is to be expected that the resulting disturbances will be reflected in the magnetic moment of the metal ion.

If the complex is assumed to have a cis structure (LIII). Some distortion due to steric effect may occur and the complex would acquire tetrahedral configuration.

The complex can be obtained from OKNi and methylamine. It would indicate that the paramagnetic nature of OKNi is maintained in OANi. We suggest, that the strength of the ligand field is not enough to bring about spin-pairing. We say

that merely the presence of four nitrogen atoms bonded to a nickel atom without steric strain should not be considered enough criterion for the magnetic nature of the complex. The complex is suggested to have trans octahedral configuration. Using the equation (k), we calculate the value of Δ / k^2 as 7800 cm^{-1}.

The complex has an absorption band at 240-4 mμ in its UV spectrum. The $\pi \rightarrow \pi^*$ band of the complex is at a longer wave-length than that of the ligand. This would result from the extension of the conjugation of the ligand $\pi\pi$ -- system. Hence we suggest that the metal atom acts as a bridge between the two ligand groups and that the delocalisation of $\pi\pi$-electrons through the metal atom becomes possible. Thus the 5-membered ring system becomes completely conjugated. When a 4-membered linearly conjugated diene type or diketone type $\pi\pi$-system or a 5-membered ring system contain ing a diene type or diketone type $\pi\pi$-system changes to a 5-membered cyclic conjugated $\pi\pi$-system, the decrease in the energy of transition or the increase in the wave length of absorption is observed. It provides additional support for our contention that the nitrogen atoms of the ligand molecules which are bonded to the nickel atom are coplanar with the nickel atom.

No band is observed in the visible spectrum in the range investigated.

4. (c) Copper complex obtained from the oxime-Schiff base (OK-Cu) :

The complex was obtained at the ether-water inter-

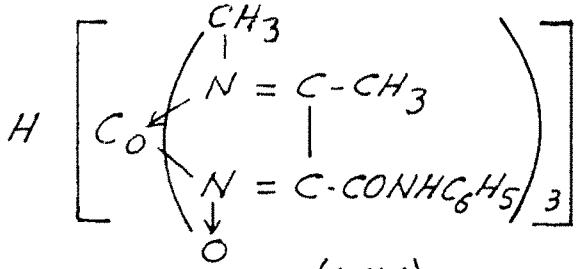
face and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (XXXV).

The ligand OK was obtained from the complex when it was dissolved in acid and extracted with ether. The magnetic moment and the absorption spectrum of the complex are the same as those for OK-Cu. The results show that the copper complex of OA would be very unstable and would get converted to the copper complex of OK, indicating the unstability of OA in presence of copper. Desai (233) observed that the phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime underwent oxidation in presence of copper. Patel (237) showed that when the Schiff bases are formed from aromatic amines, they could not form the copper complexes containing the ligand to metal ratio of 2:1. Thus the Schiff bases obtained from the aromatic amine and the aliphatic amine of small size differ in their behaviour towards copper.

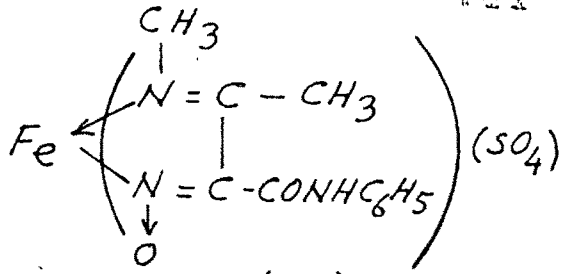
4. (d) Cobalt complex of the oxime-Schiff base (OA-Co) :

The complex was obtained at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LIV).

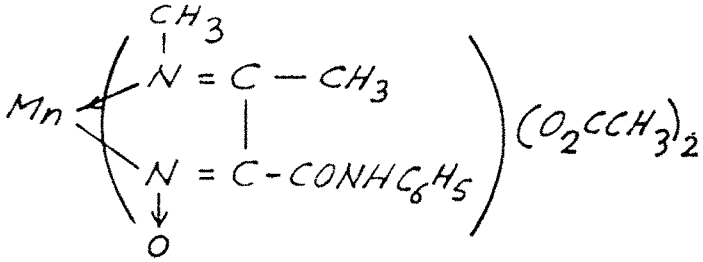
The structure is comparable to that of OK-Co. Its magnetic moment is calculated as 1.90 B.M. Hence low spin octahedral structure is suggested for the complex. Using the equation (g), we find that the value of Δ / k^2 is 17100 cm^{-1}.



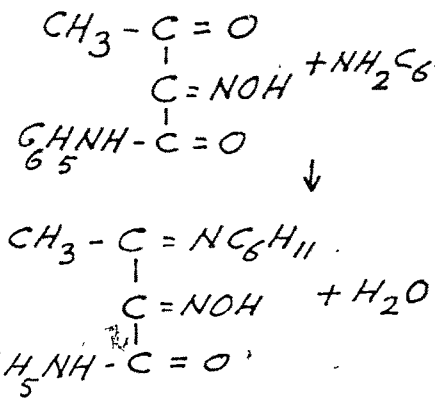
(LIV)



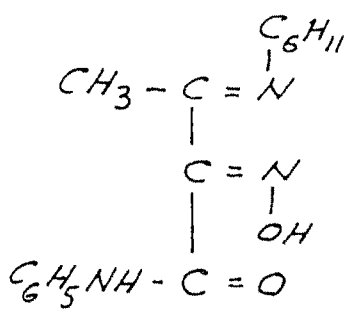
(LV)



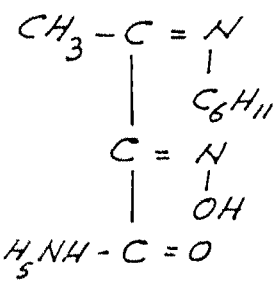
(LVI)



Eq. (l)

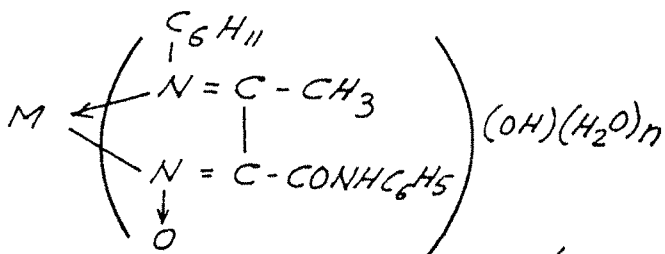


(a) ANTI.



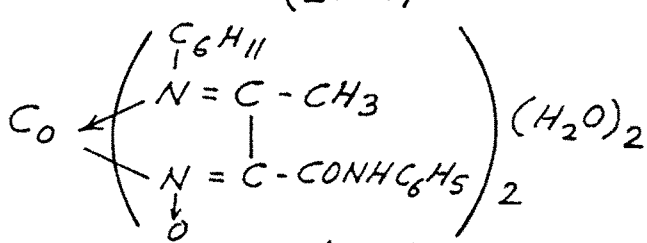
(b) AMPHI.

(LVII)



M =	n =
(a) Ni	1
(b) Fe	3

(LVIII)



(LIX)

It has an absorption band at 258 mμ . The $\pi \rightarrow \pi^*$ band of the ligand has shifted towards a longer wave length on complex formation with cobalt (II). As discussed in the case of the nickel complex, the conjugation of the ligand π-system is extended by the metal atom. The extension of conjugation is associated with the decrease in the energy of transition or the increase in the wave length of absorption.

No band is observed in the visible spectrum. In this respect, it resembles $[Co(NO_2)_6]^{4-}$.

4. (e) Iron complex of the oxime-Schiff-base (OA-Fe) :

The complex was prepared from the alcoholic solution in the presence of sulphate and acetate ions. It was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, alcohol, acetone, benzene, ether, pyridine and dimethyl formamide. Precipitates of barium sulphate are obtained when it is treated with barium chloride. On the basis of analysis, it is formulated as (LV).

It has an absorption band at 550 mμ in its visible spectrum. The band may be considered to be a weak charge transfer band.

Its absorption band in the UV spectrum is at 248-52 mμ . The ligand $\pi \rightarrow \pi^*$ band has shifted towards a longer wave length on complex formation. As suggested earlier, the conjugation of the ligand π- system, is extented by the metal atom. The extension of conjugation is associated with the decrease in the energy of transition or the increase in the wave length of absorption.

The magnetic moment of the complex is 3.65 B.M. It indicates the presence of two unpaired electrons. We suggest that the complex has a square planar structure. (It is known that the square planar ferrous phthalocyanine has the magnetic moment of 3.8 B.M. at room temperature.)

4. (f) Manganese complex of the oxime-Schiff-base (OA-Mn)

The complex was propared from the alcoholic solution in presence of acetate ions. It is soluble in pyridine, and dimethyl formamide. Manganese is precipitated from the solution as manganese sulphide by hydrogen sulphide. On the basis of analysis, it is formulated as (LVI).

It has the magnetic moment of 6.04 B.M. The spectra of the complex were not investigated.

4. (g) Metal complexes of the oxime-Schiff base (OA-M) :

general :

We can compare the relative nature of the complexes of OA and OK. We find that (i) the complexes of (a) cobalt and (b) nickel are similar in formula, and many properties, (ii) the complexes of (a) iron and (b) manganese are different in many respects, OA behaving as a coordinating agent and not as an acidic agent like OK, and (iii) the complexes of copper are the same, OA being converted into OK in presence of copper.

The extension of conjugation of the ligand π-system through complex formation, as suggested from the study of their UV spectra is

$$Ni^{2+} < Fe^{2+} < Co^{2+}.$$

We also find that the values of Δ / k^2 for nickel and cobalt complexes are 7800 cm^{-1} and 17100 cm^{-1} respectively. $\Delta / k^2 > \pi$ for the cobalt complex and hence spin-pairing would take place. Spin-pairing is found to take place in the complexes of cobalt and iron of both ligands from the magnetic measurements.

III.5. Schiff base from 2,3-dioxobutyranilide-2-oxime and cyclohexylamine and its transition metal complexes

5.(a) Oxime-Schiff base (OC) :

It was prepared from the reactants in ether as represented by the equation (1).

Since the oxime ketone is shown to have the syn-amide structure, its Schiff base can have two isomeric forms (LVII).

Anti-configuration is attributed to it on the basis of its similarity to OA.

Its absorption spectra in alcoholic and alkali solutions are presented in fig.12, and the absorption bands are presented in table 38. The absorption curves and the absorption bands of OC can be compared with those of other oxime Schiff bases (R=alkyl, $C_6H_5CH_2$-, aryl). It shows that the spectrum of OC in methanol in similar to that of the ligand when R = alkyl or $C_6H_5CH_2$-, and that the spectrum of OC in alkali resembles more to the ligand when R = aryl.

The ligand gives characteristic reactions with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). Their reactions were studied further and attempts were made to isolate the complexes. It was not possible to get Cu(II), Mn(II) and Zn(II) complexes of any definite composition. Complexes with Ni(II), Co(II), Fe(II) were isolated and studied. Their magnetic moments are presented in table 39. Their absorption spectra in the ultraviolet and visible regions are shown in figs. 13 and 14 and their absorption

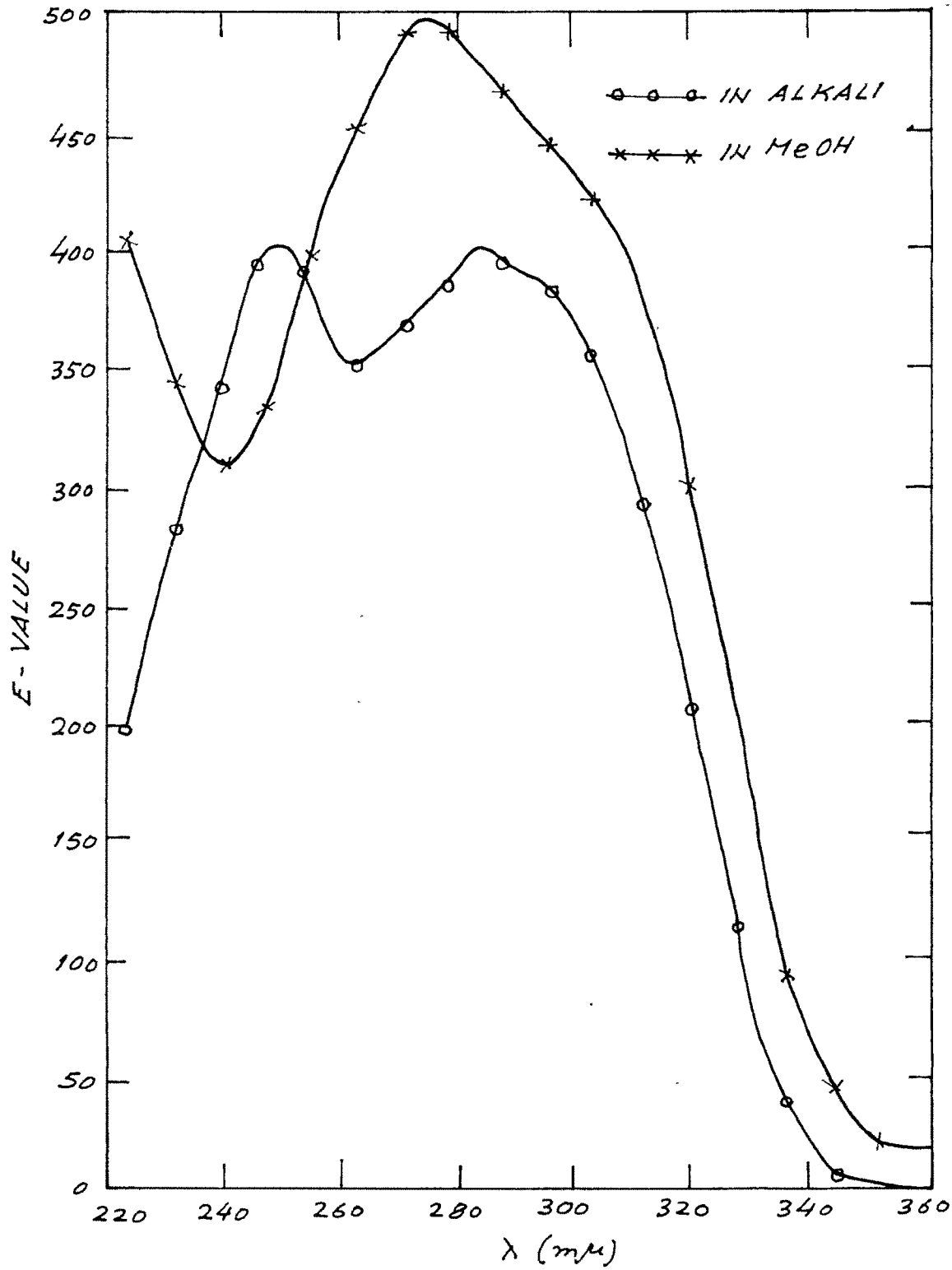


FIG. 12. UV ABSORPTION SPECTRA OF OC

Table 38

Absorption bands of OC and its complexes

No.	ligand / complex	λmax (mμ)	E-value	λmax (mμ)
1.	OC (in methanol)	272	490	
	OC (in alkali)	250	410	
		286	400	
2.	OK Co C	244-6	500	-
3.	OC Fe	240-4	440	
4.	OC Ni			590

Table 39

Magnetic moments of the complexes of the Schiff base of 2,3-dioxobutyranilide-2-oxime and cyclohexylamine or its hydrolysed product

No.	Complex	Molar magnetic susceptibility $X_m \times 10^6$	Corrected molar magnetic susceptibility $X_m' \times 10^6$	Magnetic moment μ (B.M.)
1.	OC- Ni	3535	3720	3.03
2.	OK- CO(c)	3030	3241	2.83
3.	OC- Fe	3552	3758	3.05

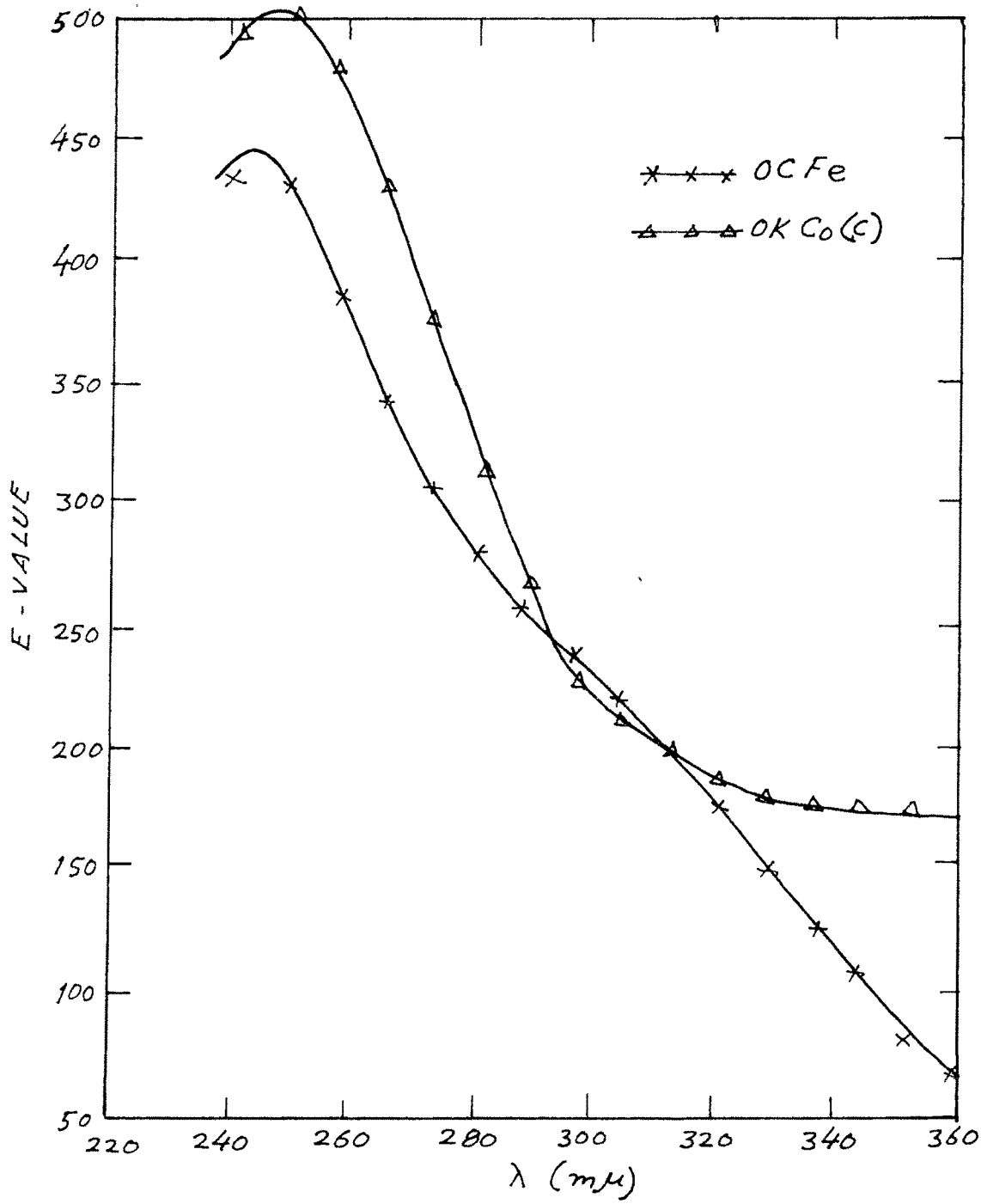


FIG. 13. UV ABSORPTION SPECTRA OF OC-Fe AND OK-Co(C)

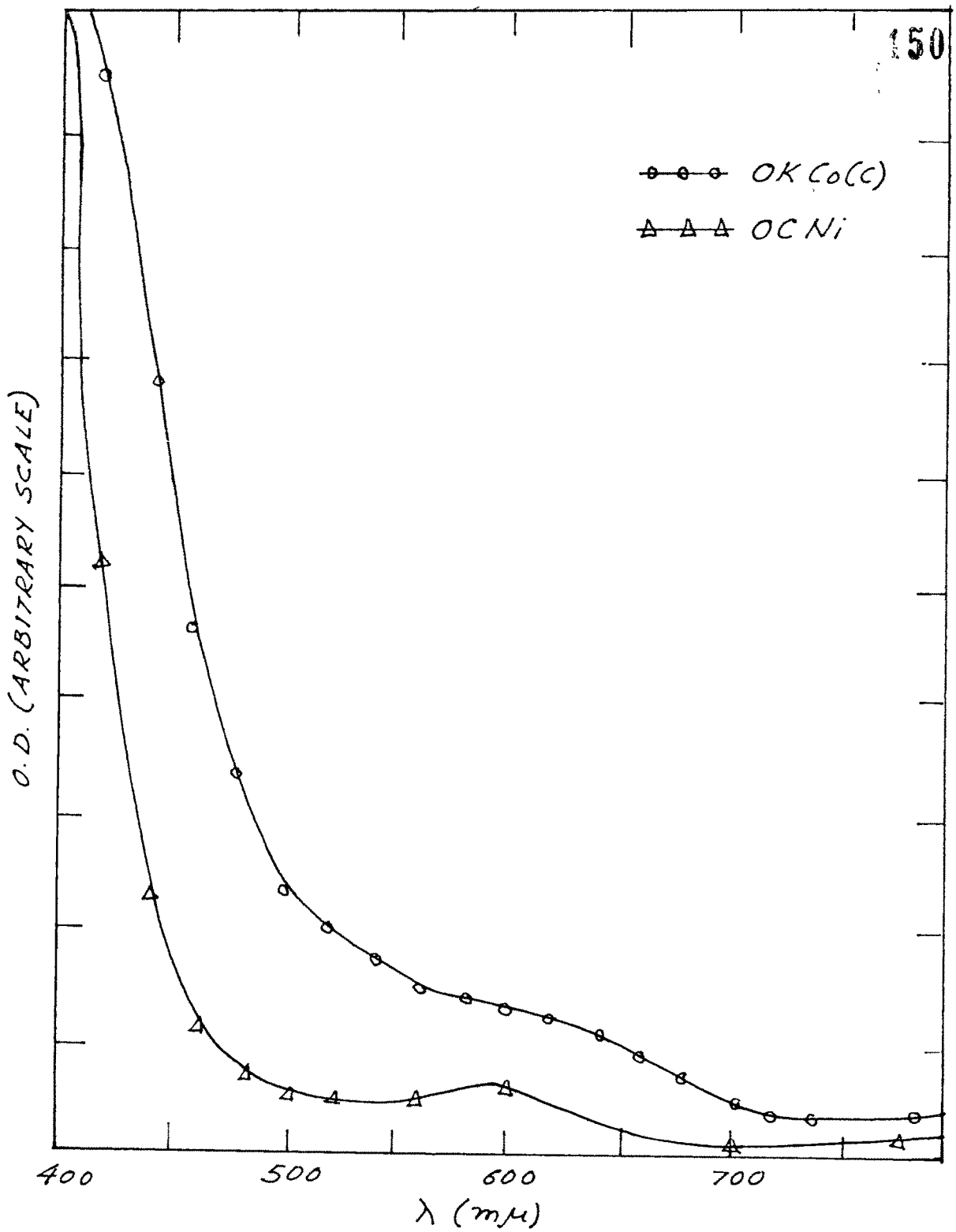


FIG. 14. VISIBLE ABSORPTION SPECTRA OF OK-Co(C) AND OC-Ni

bands are given in table 38.

5. (b) Nickel complex of the oxime-Schiff base (OC Ni) :

The complex was prepared from the alcoholic solution in the presence of acetate ions and was recrystallised from chloroform + Petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LVIII-a).

It shows that the two ligand molecules cannot combine with nickel atom. It may be attributed to the strong steric repulsion. Its magnetic moment is 3.03 B.M. It may be related to the distorted octahedral crystal field, resulting in the formation of a spin-free complex.

It has an absorption band at 590 mμ. in the visible spectrum. Since the distortion of the crystal field does not appear, simple, no attempt is made to decide the nature of transition.

5. (c) Cobalt complex obtained from the oxime-Schiff base (OK Co C) :

The complex was prepared from the alcoholic solution in the presence of acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, ether, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LIX).

The ligand OK was isolated from the complex by dissolving it in the acid and extracting with ether. It may be noted here that the ligand OK forms a complex $HCoL_3$.

Different nature of the complex obtained in the present case is the result of a different starting material. The ligand OC provides considerable steric repulsion when second and third ligand molecules would react with the cobalt atom. At the same time, the ligand attached to the cobalt gets converted into OK. In this process, only two ligand molecules converted into OK molecules remain linked to cobalt.

Its magnetic moment is found to be 2.83 B.M. It is related to the tetragonal nature of the complex.

5. (d) Iron complex of the oxime-Schiff base (OC Fe):

The complex was prepared from the alcoholic solution in the presence of Sulphate and acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, ether, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LVIII-b).

Its magnetic moment is found to be 3.05 B.M. It indicates the presence of two unpaired electrons. It is related to the distorted weak octahedral crystal field. It has an absorption band at 240 - 4 mμ in its UV spectrum in solution.

5. (e) Metal complexes of the oxime-Schiff base (OC-M)-general :

When we compare the ligand OA with the ligand OC, we find that the small methyl group is replaced by the bulky cyclohexyl group. The group is attached to the

coordinating imino group and hence would cause considerable steric interference to the formation of ■ square planar (ML_2) or octahedral $(ML_3)^-$ complexes. This is reflected in the complexes obtained. The nickel and iron complexes contain the metal to ligand ration of 1:1 as expected on steric considerations.

Further, the ligand OA is found converted into the ligand OK in its copper complex (OK Cu). Such a complex could not be isolated with the ligand OC, because the complex with copper to ligand ratio of 1:2 would not be formed. In the case of cobalt, metal to ligand ratio of 1:3 is expected. In that case, the ratio of 1:2 is found and the ligand OC is converted into the ligand OK.

III-6. Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diaminohexane and its transition metal complexes :

6. (a) Oxime Schiff base (OD) :

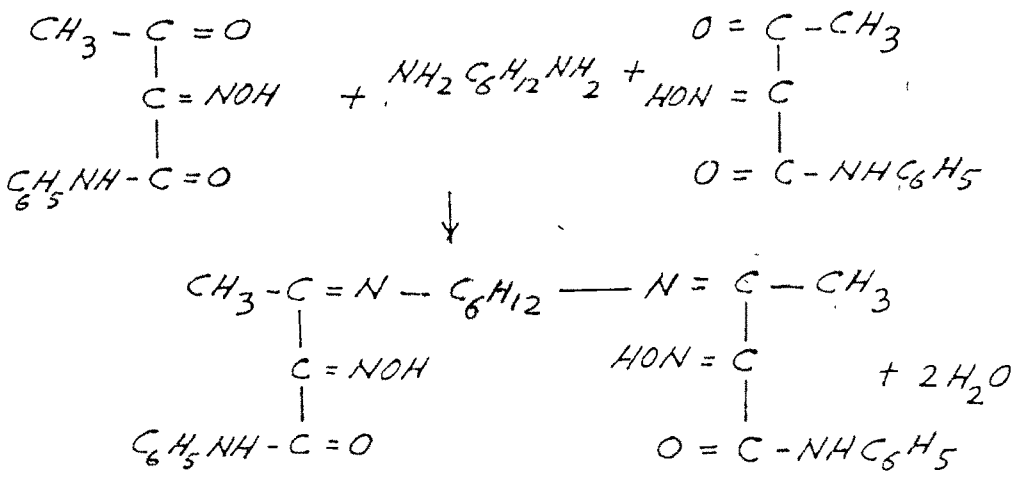
It was prepared from the reactants in ether as represented by the equation (m).

Thus a tetradentate (ie.bis-bidantate) ligand is formed. From its similarity to the other vic-oxime Schiff bases, OA and OC, its oxime-Schiff base grouping is considered to have an anti-configuration.

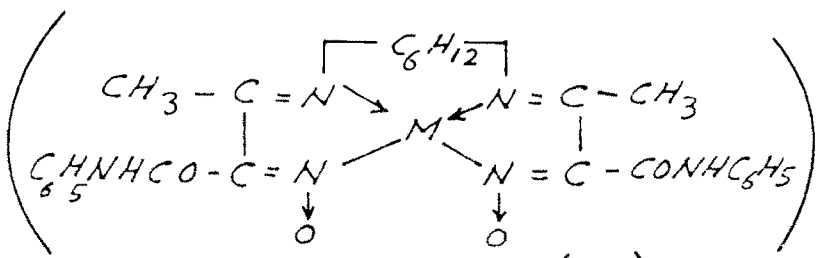
Its absorption spectra in the alcoholic and alkali solutions are presented in fig.15 and the absorption bands are presented in table 40. The absorption curves and the absorption bands of OD are similar to those of OC in both alcoholic and alkali solutions.

The ligand gives characteristic reactions with Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and Zn(II). Their reactions were a studied further. Products were isolated in each case and investigated for their different properties. Their magnectic moments are presented in table 41. Their absorption spectra in the ultraviolet and visible regions are shown in figs. 16 and 17 and their absorption bands are presented in table 40.

The tetradentate ligand can combine with the metal atom in the ratro of 1:1. The complexes formed will be monomeric if a single ligand molecule combines with the metal atom, dimeric if two ligand molecules combine with two

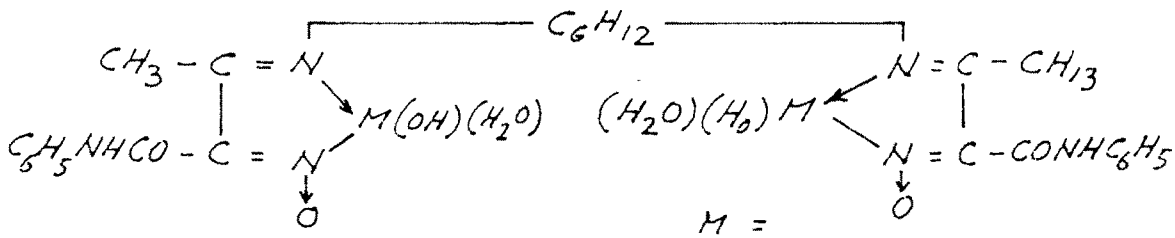


Eq. (m)



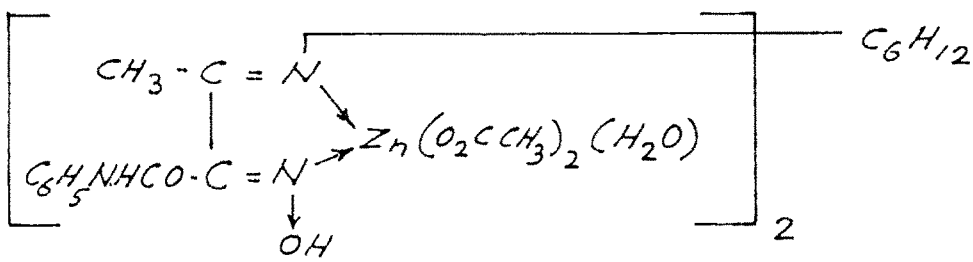
M =	n =
(a) Ni	5
(b) Co	4
(c) Mn	2

(LX)



M =
(a) Cu
(b) Fe

(LXI)



(LXII)

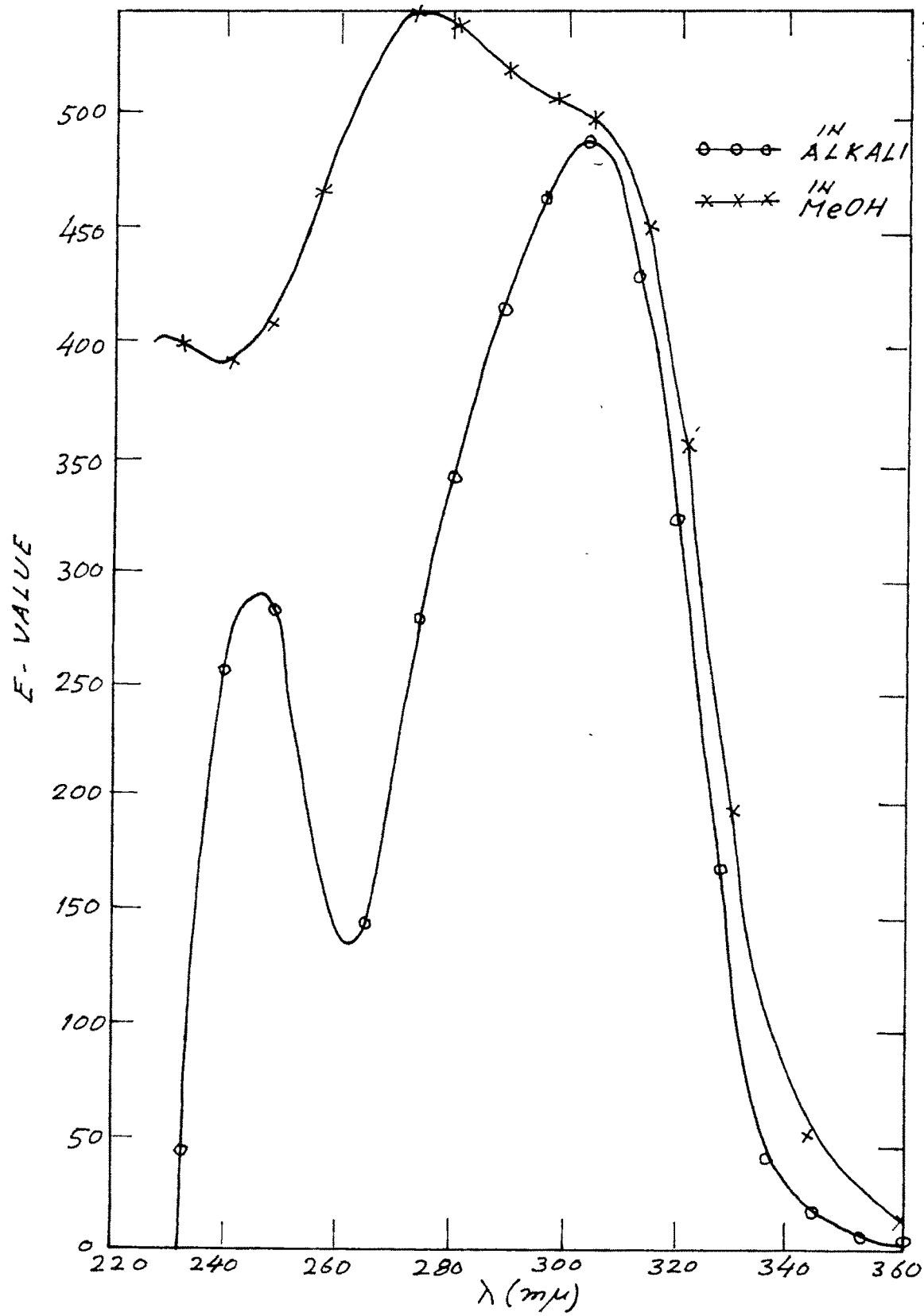


FIG. 15. UV ABSORPTION SPECTRA OF OD

Table 40

Absorption bands of OD and its complexes

No.	ligand / complex	λ max (mμ)	E-value	λ max (mμ)
1.	OD (in methamol)	230	400	-
		274	550	
	OD (in alkali)	248	290	
		304	490	
2.	ODNi	242	400	-
3.	ODCo	248	70	-
4.	ODFe	242-4	410	580
5.	ODCu	244-6	260	600

Table 41

Magnetic moments of the complexes of the Schiff base of 2,3-dioxobutyranilide-2-oxime and hexamethylene diamine

No.	Complex	Molar magnetic susceptibility $X_m \times 10^6$	Corrected molar magnetic susceptibility $X_m' \times 10^6$	Magnetic moment μ (B.M.)
1.	OD-Cu	859	1009	1.57
2.	OD-Ni	3517	3821	3.07
3.	OD-Co	1491	1784	2.10
4.	OD-Fe	3024	3174	2.80

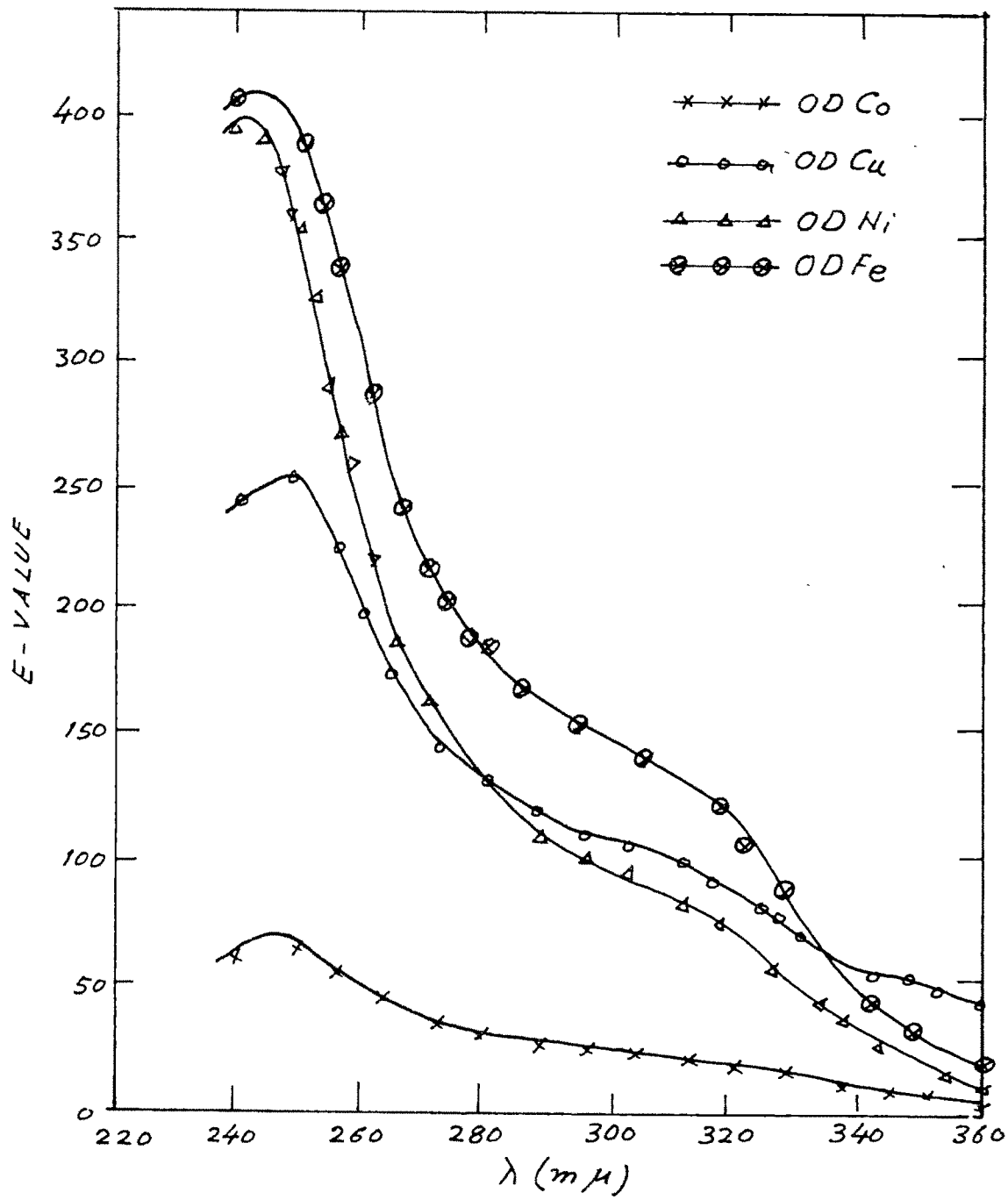


FIG. 16. UV ABSORPTION SPECTRA OF OD-Cu; OD-Co; OD-Ni AND OD-Fe

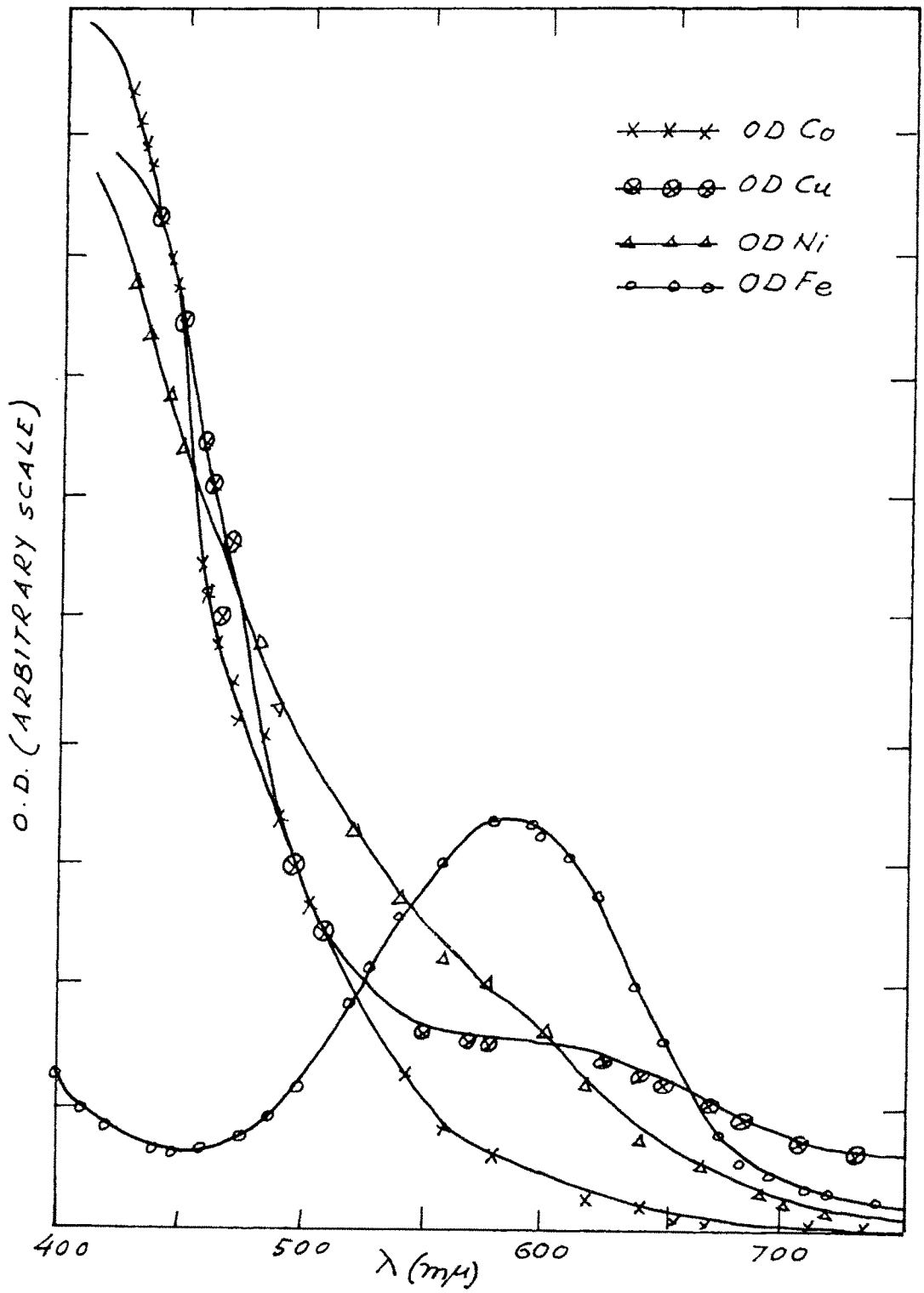


FIG. 17. VISIBLE ABSORPTION SPECTRA OF OD-Co; OD-Cu; OD-Ni AND OD-Fe

metal atoms and polymeric if the metal atom and the ligand molecule are present alternatively in the polymeric chain.

6. (b) Nickel complex of the bis-oxime-Schiff-base (ODNi)

The complex was prepared from the alcoholic solution in the presence of acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine, dimethyl formamide, etc. On the basis of analysis, it is represented as (LX-a).

Its magnetic moment is found to be 3.07 B.M. It indicates the presence of two unpaired electrons and may be related to the distorted octahedral crystal field.

It has an absorption band at 242 mμ in its UV spectrum. The ligand $\pi \rightarrow \pi^*$ band has shifted to a longer wave length on complex-formation with nickel. It indicates the extension of conjugation of the ligand π-system in the complex. A conjugated ring system is obtained. It has resulted in the lowering of the energy of transition or the increase in the wave-length of absorption.

6. (c) Copper complex of the bis-oxime-Schiff-base(ODCu)

The complex was prepared in the alcoholic solution in the presence of acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LXI-a).

It has an absorption band at 244-46 mμ in its UV spectrum. The $\pi \rightarrow \pi^*$ band of the ligand has shifted to a longer wave length. As discussed in the case of the

nickel complex, the conjugation of the ligand π-system is extended on complex formation and a conjugated ring system is formed. It has resulted in the lowering of the energy of transition or the increase in the wave length of absorption.

It has an absorption band at 600 mμ in its visible spectrum. It may be related to the distorted octahedral crystal field. The distortion is likely to be trigonal (fig.h). The band may be attributed to the

$$^2E_g \longrightarrow {}^2A_{1g} \text{ transition.}$$

The magnetic moment of the complex is found to be 1.57 B.M. The value is low and may be attributed to the spin-spin interaction leading to the antiferromagnetic behaviour. It is likely that the copper atoms are weakly bonded.

6. (d) Cobalt complex of the bis-oxime-Schiff-base (ODCo)

The complex was prepared in the alcoholic solution in the presence of acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LX-b).

It has an absorption band at 248 mμ in its UV spectrum. The ligand $\pi \longrightarrow \pi^*$ band has shifted to a longer wave-length on complex-formation. It indicates the extension of conjugation of the ligand π-system on complex-formation. It results in the lowering of the energy of transition or the increase in the wave-length of absorption.

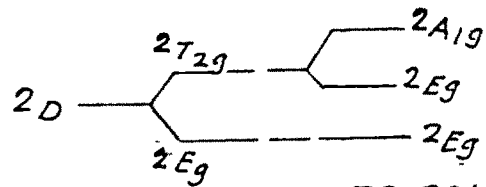
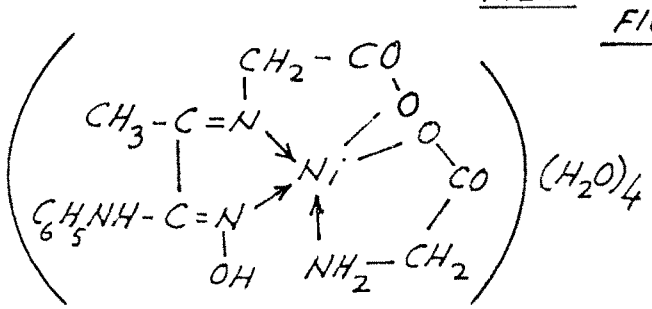
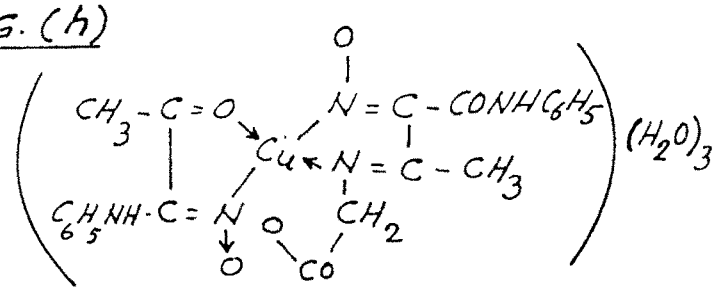


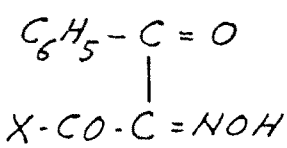
FIG. (h)



(LXVIII)

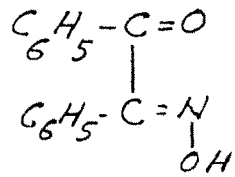


(LXIV)

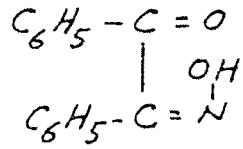


X =
(a) C_6H_5NH
(b) C_2H_5O

(LXV)

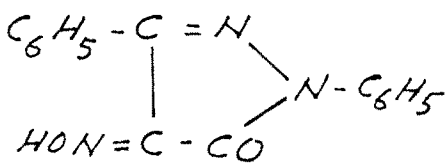


(a) α - ISOMER

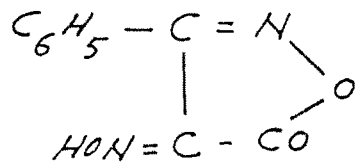


(b) β - ISOMER

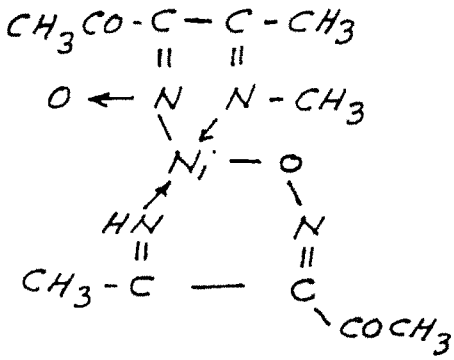
(LXVI)



(LXVII)



(LXVIII)



(LXIX)

Its magnetic moment is found to be 2.10 B.M. It is related to the strong octahedral crystal field, and indicates octahedral configuration for low-spin cobalt complex. Using the equation (g), we obtain the value of Δ / k^2 as 6780 cm^{-1}. Since spin-pairing has taken place, Δ should be large ($\Delta > \pi$) ; in other words, k should have a small value, indicating considerable delocalisation of the matel t_{2g} electrons.

6.(e) Iron complex of the bis-oxime-Schiff-base (ODFe)

The complex was prepared at the chloroform-water interface in the presence of sulphate and acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LXI-b).

It has an absorption band at 242-4 mμ in its UV spectrum. The ligand $\pi \longrightarrow \pi^*$ band has shifted to a longer wavelength on complex-formation. It indicates the extension of conjugation of the ligand π-system on complex-formation. It leads to the increase in the wave length of absorption on complex formation.

It has an absorption band at 580 mμ in its visible spectrum. It is a charge-transfer band.

Its magnetic moment is calculated as 2.80 B.M. It may be related to the distorted octahedral crystal field. The distortion is likely to be tetragonal.

6. (f) Manganese complex of the bis-oxime-Schiff-base (ODMn)

The complex was prepared in alcoholic solution in presence of acetate ions and was recrystallised from

chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LX-c).

It is considered to have an octahedral structure.

6. (g) Zinc complex of the bis-oxime-Schiff-base (ODZn) :

The complex was prepared in alcoholic solution in presence of acetate ions and was recrystallised from chloroform + petroleum ether. It is soluble in alcohol, acetone, benzene, chloroform, pyridine and dimethyl formamide. It gives test for acetate. On the basis of analysis, it is formulated as (LXII).

It may have an octahedral structure.

6. (h) Complexes of bis-oxime-Schiff-base (ODM): general

Kapadia (238) attempted to prepare the complexes of bis-oxime-Schiff bases. Complexes could not be isolated when he tried to prepare them from the metal salt and the ligand obtained from benzidine or p-phenylene diamine. However, complexes were prepared when the metal salt was treated with OK and the diamine. The generalisations from his studies are that (i) when the chlorides of copper and nickel and the sulphate of iron are used, the acid anions are not replaced and additive compounds of the ligands with metal salts are formed, and (ii) when the acetates of copper and cobalt are used, the acetate ions are replaced completely by the oxime ketone or its Schiff-base.

We used metal acetates for the preparation of the

complexes. We found that acetate ion is replaced completely in the case of manganese, cobalt, nickel and copper but not in the case of zinc. Further, the sulphate ion is replaced from iron sulphate when its complex is formed.

We find that normal complexes are formed with manganese, cobalt and nickel, while basic complexes are obtained with iron and copper.

If a comparison is made between OD and OA, we find that OD, unlike OA, is not converted into OK in the presence of copper ions.

Similarly if a comparison is made between OD and OC, we find that OD, unlike OC, is not converted into OK in the presence of cobalt ion. These results show that OD is more stable than OA or OC.

We have suggested that octahedral complexes are formed with cobalt, manganese and zinc, and distorted octahedral complexes are obtained with copper, nickel and iron.

Complexes of a few quadridentate ligands (Schiff bases) are known. Complexes of the Schiff bases obtained from a diamine and acetylacetone are studied by Morgan and Main-Smith (269), Ueno and Martell (270) Dudek and Holm(271), etc; Complexes of the Schiff bases obtained from the diamine and salicylaldehyde are studied by Hall and Waters (272), Tsu-maki (273), Hughes, Wilmarth and Calvin (274), Pfeiffer and Glaser (275) etc. We have presented here our magnetic and spectral studies on some complexes of OD.

III. 7. Transition metal complexes of tridentate ligand (oxime-Schiff-base-carboxylic acid)

7. (a) Tri-dentate ligand and its complexes

In continuation of our studies on bidentate and bis-bidentate ligands obtained from the oxime-ketone and mono-or di-amines, we attempted to prepare the tridentate ligand from the oxime-ketone and glycine(amino acetic acid); however, we could not isolate the product of the desired composition. Hence we tried to prepare the transition metal complexes of the suggested ligand by different methods. In the first place, we mixed the acetate of copper or nickel with the oxime-ketone and glycine. Product containing the tridentate ligand could not be obtained. We, then, prepared the copper and nickel complexes of the oxime-ketone and treated them with glycine. Once again, we failed to isolate the product of the tridentate ligand. In another attempt, be prepared the di-glycinates of copper and nickel and treated them with the oxime-ketone. The products were isolated and studied. Their absorption spectra in the visible region are presented in fig.(18). Their magnetic moments are presented in table 42.

7. (b) Nickel complex : (Gly)O-Ni:

It was prepared from the di-glycinato nickel and the oxime-ketone at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LXIII).

The formula indicates the mixed ligand nature of the complex. We find that the two glycinate

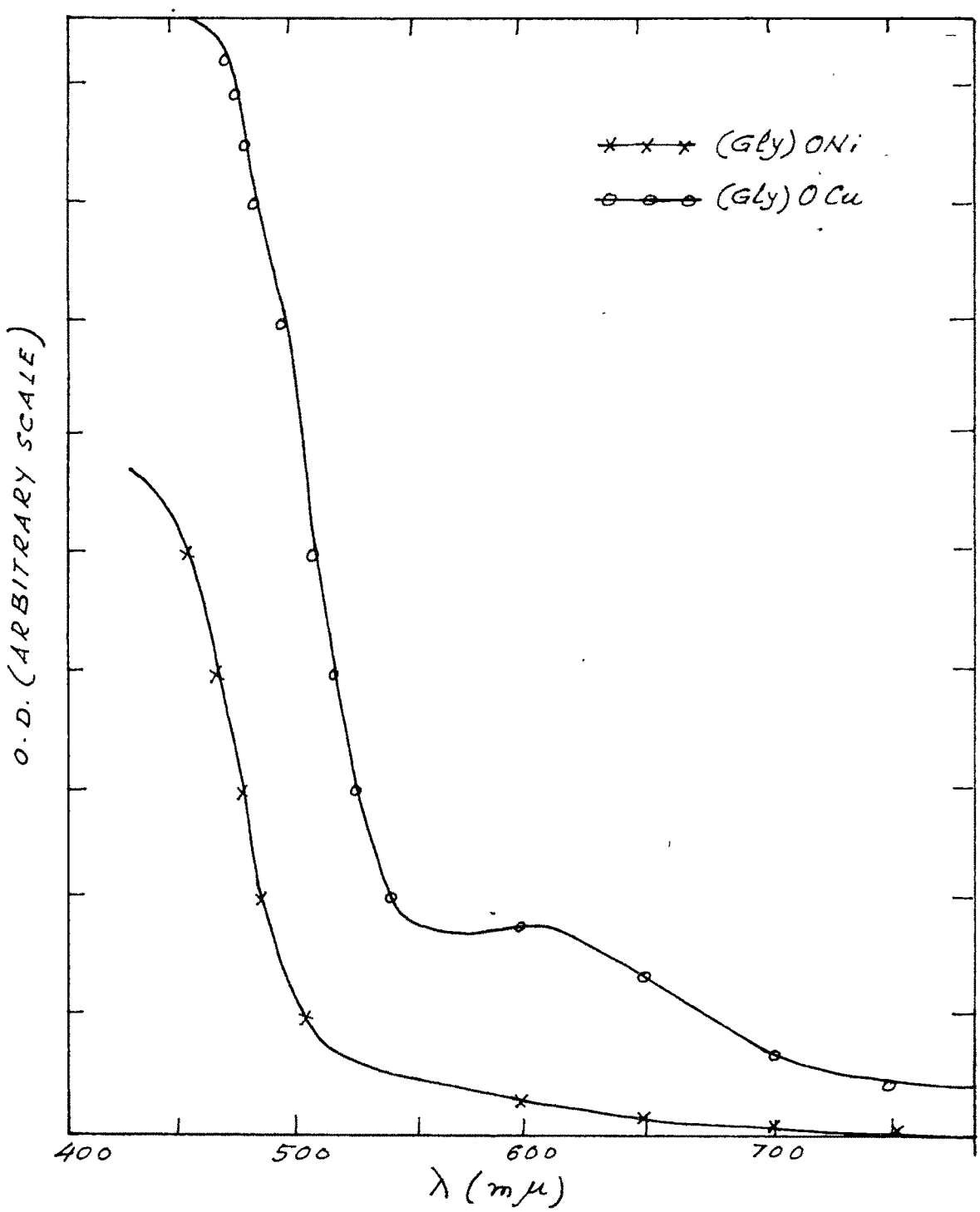


FIG. 18. VISIBLE ABSORPTION SPECTRA OF (GLY)O-Cu AND (GLY)O-Ni

Table 42

Magnetic moments of the diglycinato-metal and of the metal complexes obtained from (di-glycinato) metal and 2,3-dioxobutyranilide-2-oxime

No.	Complex	Molar magnetic susceptibility $\chi_m \times 10^6$	Corrected molar magnetic susceptibility $\chi_m' \times 10^6$	Magnetic moment μ (B.M.)
1.	(Gly)O-Cu	1402	1646	2.01
2.	(Gly)O-Ni	3031	3214	2.82
3.	(Gly) -Cu	1584	1669	2.03
4.	(Gly) -Ni	4394	4489	3.33

ions are not replaced from the complex by OK.However, one of the glycinate ions reacts with OK, forming a tridentate Schiff base.

Its magnetic moment is found to be 2.82 B.M. It indicates the presence of a distorted octahedral crystal field. The distortion is likely to be tetragonal.

7. (c) Copper complex :

It was prepared from the di-glycinato copper and the oxime-ketone (OK) at the ether-water interface and was recrystallised from chloroform + petroleum ether. It is soluble in chloroform, pyridine and dimethyl formamide. On the basis of analysis, it is formulated as (LXIV).

The formula indicates the mixed ligand nature of the complex. We suggest that the glycinate ion is replaced by OK and that one of the two OK anions reacts with glycinate ion forming a Schiff base, resulting in a tridentate ligand.

Its magnetic moment is found to be 2.01 B.M. It indicates the presence of the distorted octahedral crystal field.

The absorption band in the visible spectrum is at 590 mμ. It also indicates the presence of the distorted octahedral crystal field.

7. (d) Metal Complexes - general :

Although, theoretically it appears possible to prepare octahedral complexes of the tridentate ligands with

6-coordinate bivalent metals, we find it difficult to prepare such complexes. The complexes obtained by us apparently contain bidentate and tridentate ligands. Exact nature cannot be established from these studies.

III.8. Oximino ligands :

2,3-dioxobutyranilide-2-oxime and its derivatives such as dioxime, oxime-hydrazone, oxime-imine, etc. have been widely used in our laboratories for the preparation of their complexes and the study of their properties. We extend these studies to the preparation of 3-phenyl 2,3-dioxo propionanilide 2-oxime and its desivatives.

3-Phenyl 2,3-dioxopropionanilide-2-oxime was prepared from benzoyl acetanilide by a reaction similar to (a). Ethyl 3-phenyl 2,3-dioxopropionate-2-oxime was prepared from ethyl benzoyl acetate by a similar reaction. For the purpose of comparative studies, α and β benzil monoximes, 1,3-diphenyl 4-isonitroso pyrazol-5-one and 3-phenyl 4-isonitroso isoxazol-5-one were prepared. Their absorption spectra are presented in figs. 19 to 23 and their absorption bands are presented in table -43.

We find that the absorption band of the oxime-ketone (anilide)(LXV-a) is at 253-4 mμ in alcohol and at 256 mμ in alkali solution. similarly, the absorption band of the oxime-ketone ester (LXV-b) is at 249-50 mμ in alcohol and at 250 mμ in alkali solution. When the spectra of these compounds are compared with those of 2,3-dioxobutyranilide-2-oxime, we find that the new ligands do not show any shift in the band position with the change in medium from alcohol to alkali. Such a difference can be accounted for from the study of the spectra of benzil monoximes.

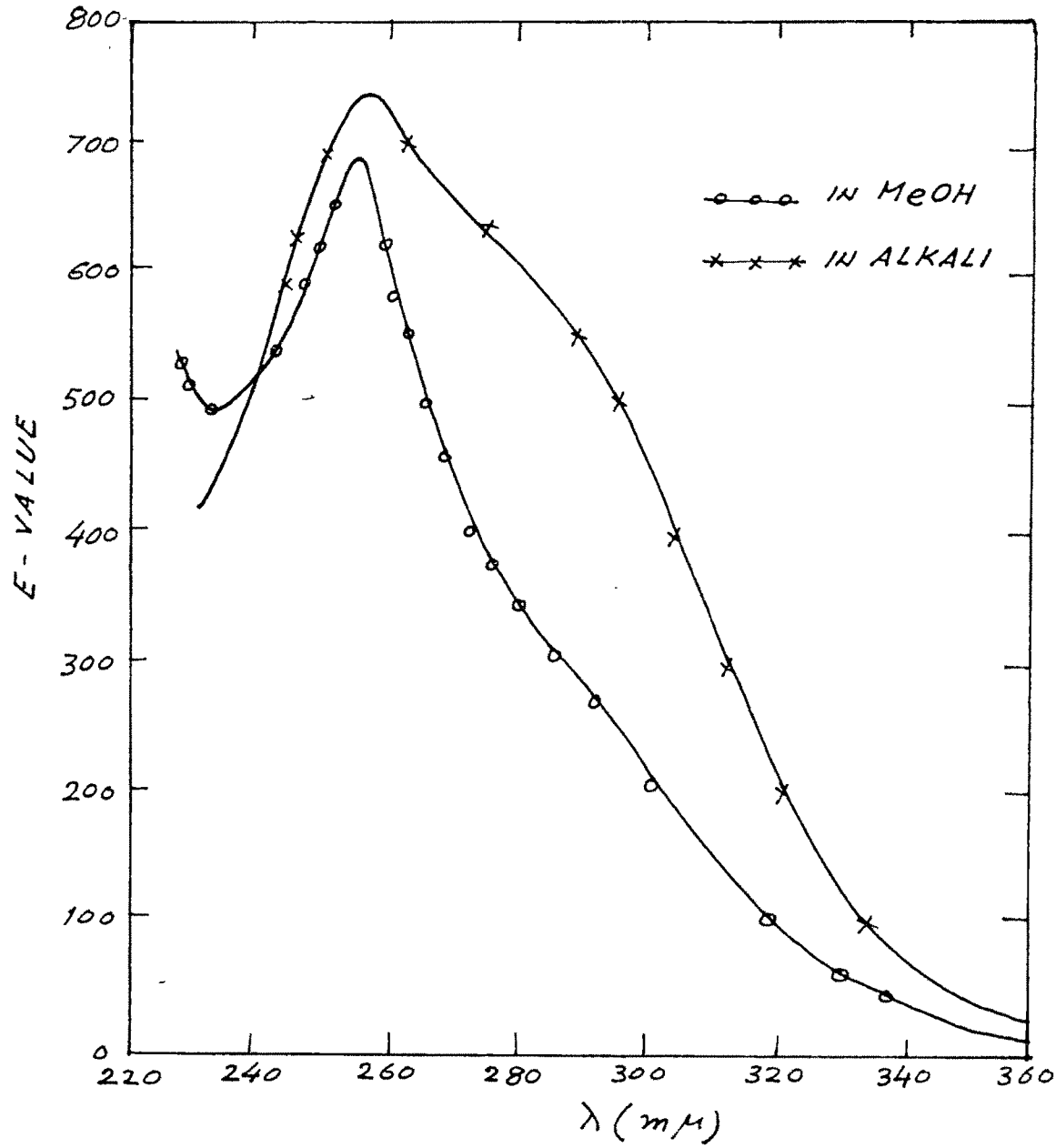


FIG. 19 UV ABSORPTION SPECTRA

OF 3-PHENYL 2,3-DIOXOPROPIONANILIDE 2-OXIME

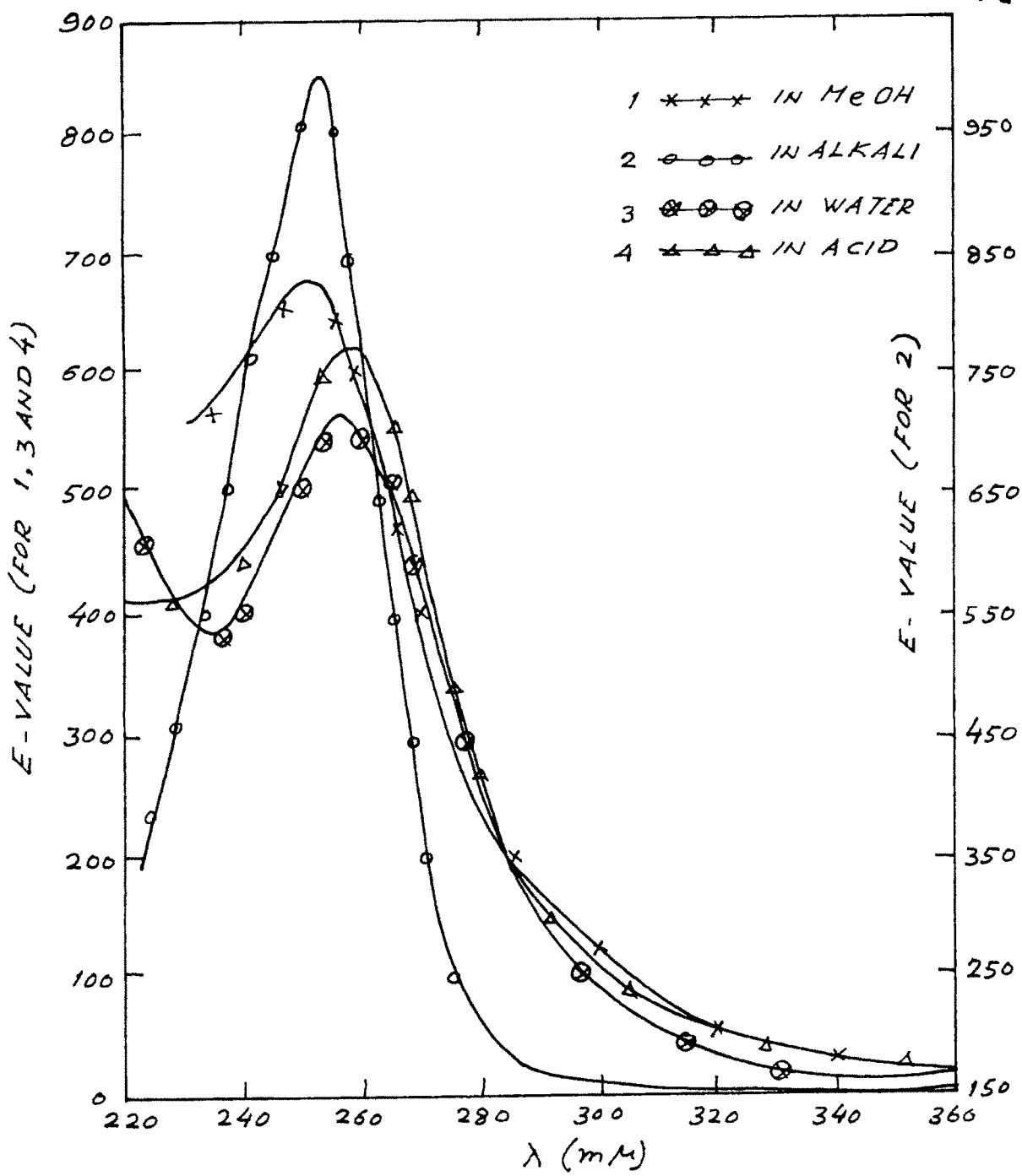


FIG.20. UV ABSORPTION SPECTRA OF ETHYL ESTER OF 3-PHENYL 2,3-DIOXO PROPIONIC ACID-2-OXIME

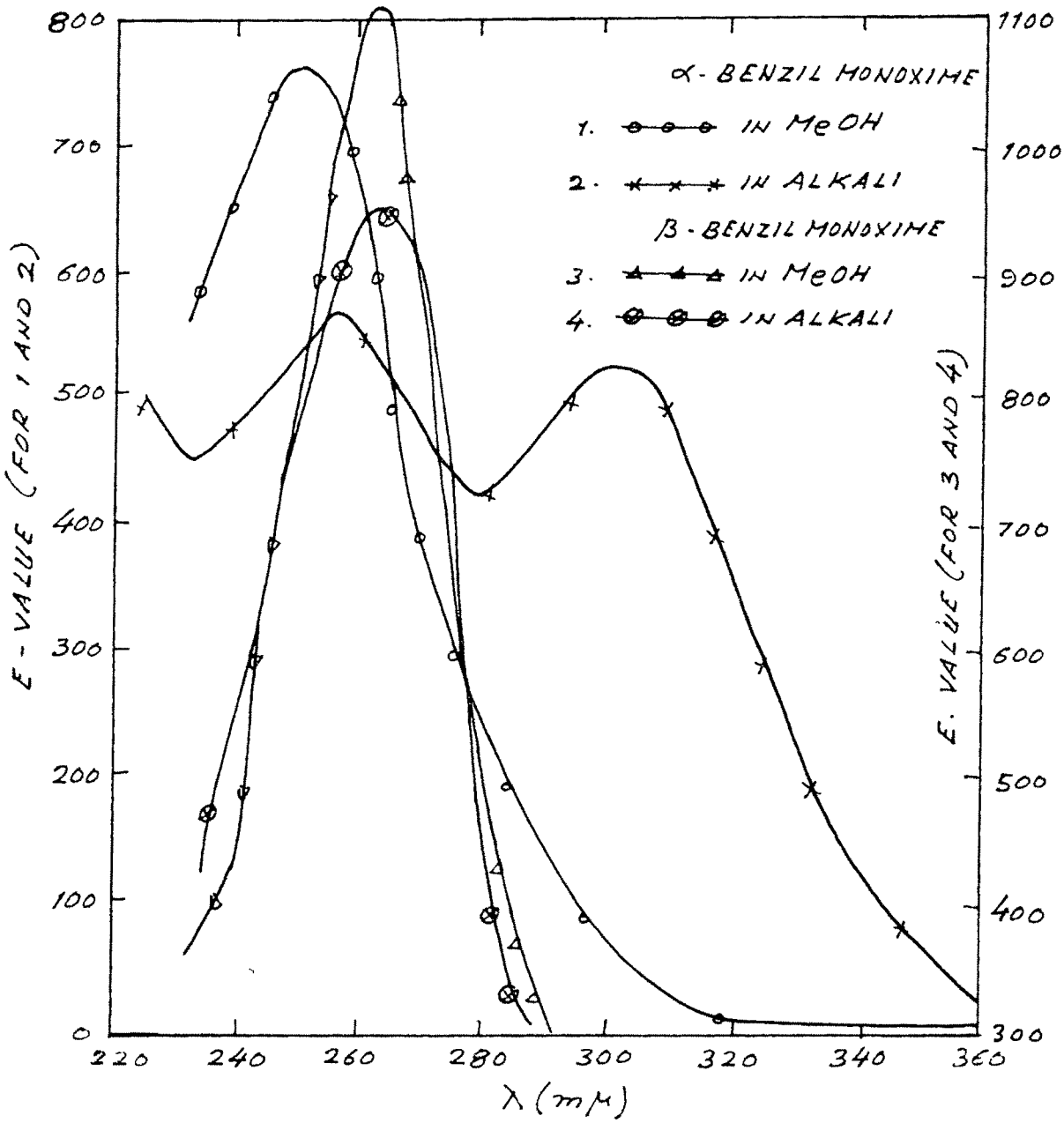


FIG. 21. UV ABSORPTION SPECTRA OF α - BENZIL MONOXIME AND β - BENZIL MONOXIME

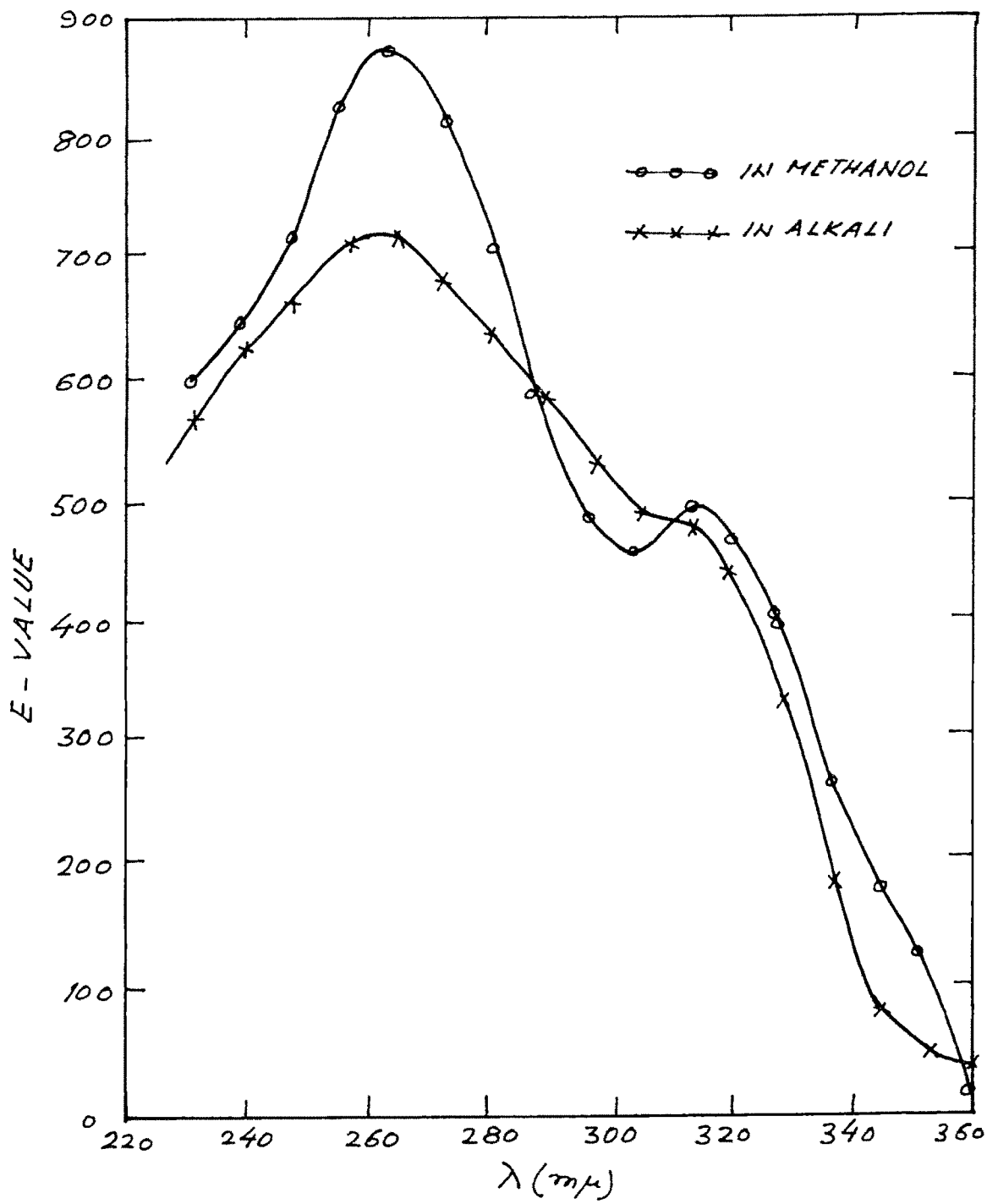


FIG. 22 UV ABSORPTION SPECTRA
OF 1.3 DIPHENYL - 4 ISONITROSO PYRAZOL - 5-ONE

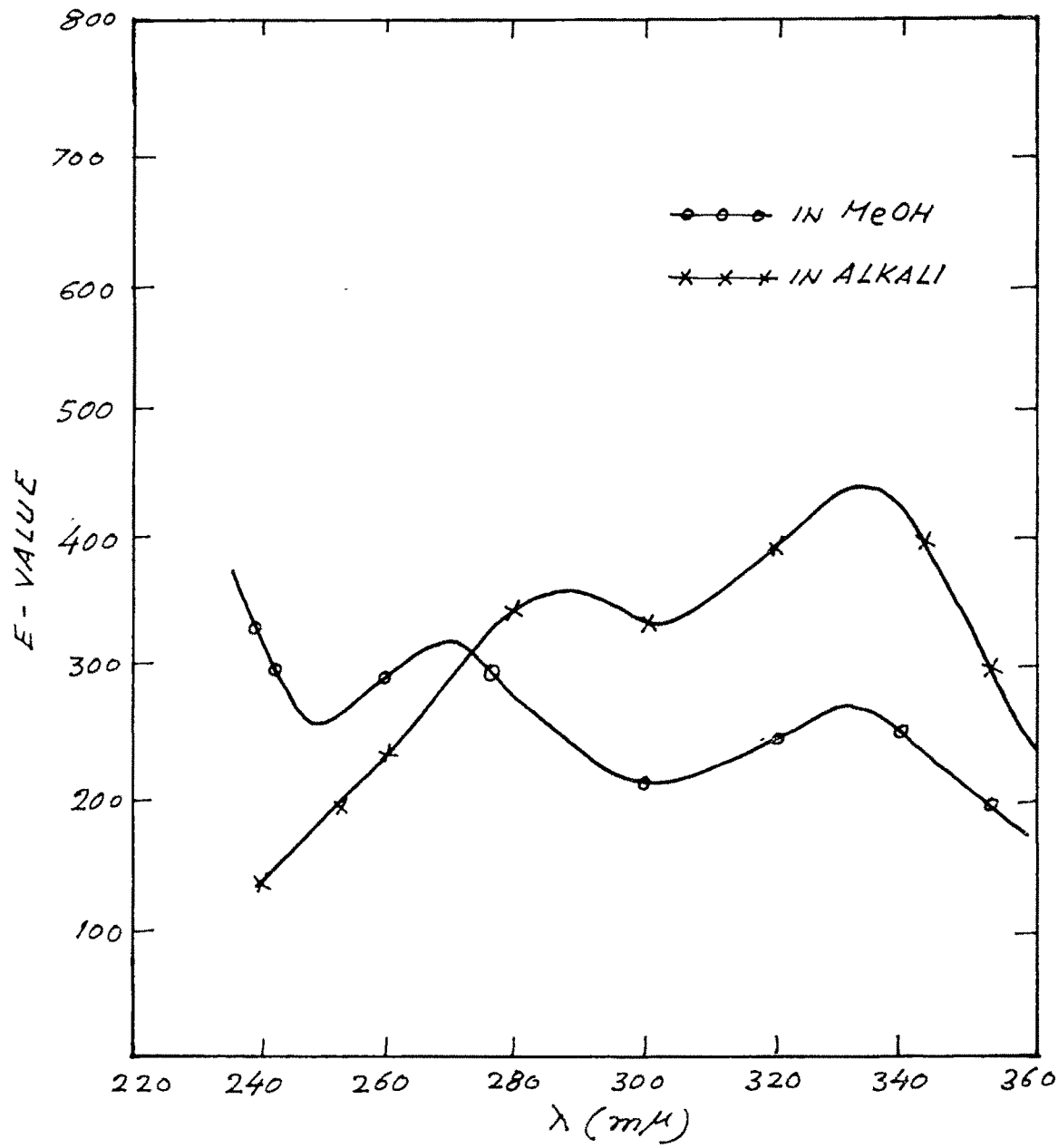


FIG. 23. UV ABSORPTION SPECTRA OF 3-PHENYL 4-ISONITROSO ISOXAZOL-5-ONE

Table 43

Absorption bands

No.	Ligand	in methanol		in alkali	
		λmax (mμ)	E-value	λmax (mμ)	E-value
1.	LXV-a	253-4	690	256	766
2.	LXV-b	249-50	670	250	990
3.	LXVI-a	248	760	266	540
4.	LXVI-b	260	1110	260	960
5.	LXVIII	270	320	-	-
		332	270	332	440
6.	LXVII	262	830	234	350
		312	490	280	1250

In the case of β-benzil monoxime, the band is not shifted in position with the change in solvent from alcohol to alkali; on the other hand, in the case of α-benzil monoxime, the band is shifted in position with the change in solvent from alcohol to alkali. Hence it is suggested that 2,3-dioxobutyranilide-2-oxime resembles α-benzil monoxime and confirms the anti-oxime-ketone nature (XXXI-b) for both of them, and that 3-phenyl 2,3-dioxopropionanilide-2-oxime resembles β-benzil monoxime and indicates syn-oxime-ketone nature (XXXI-a) for both of them.

The difference in the structure of these compounds is reflected in their properties. The aliphatic ligand (XXXI) could be readily converted into various derivatives by converting the ketone group into the oxime group, imine group, hydrazone group, etc. On the other hand, the reactivity of the aromatic ligand (LXV) is much reduced. We failed to convert the ketone group into the imine group, hydrazone group, etc.

We also observe that the aliphatic ligand (XXXI) gives a characteristic iron-blue reaction ; it is not given by the aromatic ligand.

We further note that the aliphatic ligand gives the X-band, particularly in alkali solution; it is not observed in the UV spectrum of the aromatic ligand, even in the alkali solution.

We suggest that all these properties are interrelated, and that the aromatic ligand can be much less

useful for the study of the complexes.

This spectral comparison can be extended to other oxime-ketone systems. Tus, the spectrum of 1,3-diphenyl 4-isonitroso pyrazol-5-one in alkali solution resembles those of 2,3-dioxobutyranilide-2-oxime and α-benzil monoxime in alkali solution in having two absorption bands. Similarly, the spectrum of 3-phenyl 4-isonitroso isoxazol-5-one in alkali soultion has two absorption bands and hence resembles those of 2,3-dioxobutyranilide-2-oxime and α-benzil monoxime.

III. 9. Addenda :

9. (a) Nickel complex of the oxime-imine:

While the thesis was being typed, we came across a recent publication of Lacey, MacDonald, McConnell and Shannon in chemical communications (19, 1206, (1971)). They prepared a nickel complex using acetyl acetone, sodium nitrite, methyl amine hydrochloride, nickel acetate and ammonia. From the X-ray crystal structure investigations, they formulated it as (LXIX). The study of its spectral and magnetic properties, when carried out, will help us in correlating our compounds with (LXIX). We believe, that it will provide interesting results.

9. (b) Iron (II) complexes:

The oxime-ketone, the dioxime and the oxime-imines, under investigation, give a characterestic iron-blue reaction. The reaction with the oxime-ketone and the dioxime gives rise to an intense blue colour. Different investigators in our laboratories were able to isolate products containing different ratios of metal to ligand. In all cases the formation of an octahedral complex of iron was suggested and some excess iron was left over. It has not been possible for us to isolate a pure octahedral iron (II) complex free from excess iron. One of the possibilities is that excess iron is taking part in the reaction and that the absorption band corresponding to the blue colouration and suggested to be a charge-transfer band may be attributed to the

intervalency charge-transfer absorption. In the complexes of oxime-imines with iron, the above explanation can be considered possible if dimeric or polymeric nature of the complex is assumed. In any case, Donor $\rightarrow$ Acceptor charge-transfer is taking place in these compounds. The study of their Mossbauer spectra will help us in suggesting the state of iron and the nature of charge-transfer.