CHAPTER 3

Synthesis of the ternary complexes of copper (II) with tertiary diimines and O^- - O coordinating ligands.

page

3.1 Introduction to the literature on the synthesis of ternary complexes and solid state studies.

The isolation of complex compounds in solid state enables the study of various spectral and magnetic properties. These can provide evidence for the formation of particular species in solution under the conditions of isolation and the studies in solution and solid state can prove to be complementary to each other. Also the synthesis of complexes becomes necessary while looking for their applications in the fields like catalysis [1] and medicine [2, 3] . They provide important paths for the synthesis of drugs with specific activity [4], macromolecules and also some important organic compounds like unsymmetrical Schiff bases [5]. Nucleophilic substitution reactions like nitration , bromination can be carried out with greater ease on the coordinated ligands [5] . It is well known that amine exchange over coordinated imines and Schiff base formation of coordinated aldehydes are facilitated and hence this provides easier method to synthesize various Schiff bases. As will be discussed later, these reactions can be carried out with still greater ease with some ternary complexes.

Ternary complexes with a variety of ligands have been synthesized and characterized by various workers [6-11]. Ternary complexes of copper (II) nickel (II) and oxovanadium (IV) containing 2-hydroxy aromatic aldehydes or ketones have been synthesized [12-22] and their reactions with various mono-and diamines have been carried out to get complexes of bi - or tetradentate Schiff base ligands [12-22] . Also the complexes containing 2-hydroxy aromatic aldehydes or ketones as one ligand and β-diketones like acetyl acetone, benzoyl acetone, dibenzoyl methide or β-naphthoyl acetone have been prepared and the products of their reactions with various amines have been isolated and characterized [23-25]. Electrophilic substitution reactions like nitration and bromination have also been carried out over some of these complexes [20, 21, 25-28]. Mixed ligand complexes of copper (II) containing N-alkylated ethylene diamine and pseudohalide anions have been synthesized and the effect of anion has been studied [29].

However, the survey of literature reveals that prime importance has been given to the ternary complexes containing tertiary diimines like 2,2'-bipyridyl. The compounds of the complex cations [Co L (bipy)]$^+$ or [Co L (phen)]$^+$, where L = dimethyl glyoxime were isolated [30]. Mixed ligand complexes containing Co^{III}, paludrine and bipy or phen have been described by Gheorghiu and coworkers [30 a]. Preparation and characterization of the mixed ligand complexes of Cu^{II} phthalimide with bipy or phen was reported by Narain [31]. Synthesis and characterization of [MAL $(H_2O)_2$] SO_4 where M is bivalent ion of Ni, Cu, Zn or Cd, A = bipy or phen and L = en or pn have been reported [32]. Dutta and coworkers observed that the reaction of cis-diamine cobalt (II) sulphate with en and bipy or phen results in the formation of mixed ligand complex, Co (en) (bipy) or Co (en) (phen) [33]. They have synthesized several heterochelates of oxovanadium (IV) [34] like [VO (C_2O_4) (bipy)] [35] and of cobalt (II) and copper (II) with bipy or phen and biguanide [36, 37]. They have also synthesized a number of mixed ligand chelates of the type [Cu (AA) (XY)] Z, where XY = glycine or α - (DL) -alanine, AA = bipy, phen or N-phen and Z = Cl^-, Br^-, I^- [38].

There have been several studies of mixed-ligand copper (II) bipy complexes with carboxylic or amino acids [39–43]. The mixed ligand complexes of the type [M bipy L] where, M = Cu^{II}, Ni^{II} and L = higher homologue of glycine have been reported by Chidambaram and Bhattacharya [44, 45]. Ternary complexes of UO_2^{VI} with bipy, phen and o-, m- and p-aminobenzoic acid were studied by Ripen and Saceben [46]. The mixed ligand complexes of the oxalate anion and bipy with copper (II) have been prepared by a number of groups [47–49]. Solid state reactivity has indicated polymorphism in this complex [50].

Reactions of bis acetylacetonate - or bis ethylacetoacetate copper (II) with apliphatic diamines or tertiary diimines like bipy or phen resulted in six coordinate Cu^{II} complexes [51]. Octahedral complexes of Co^{II} bis ethylacetoacetate with aromatic heterocyclic amine such as bipy or phen have been synthesized [52]. The Fluorescent properties of various Eu^{II} chelates of dibenzoyl methide, benzoylacetone, β - naphthoyl acetonate were observed to be enhanced on coordination with bipy or phen [53]. Mixed ligand chelates of Cr^{III} [54] and various rare earth metal ions [55] with acetylacetone and bipy or phen have been isolated and studied. Ternary copper (II) complexes with bipy or phen and acetylacetone, benzoylacetone or dibenzoyl methane have been isolated with nitrate [56], perchlorate [57] and sulphate [58] as outer ions. Electronic, IR, ESR and photoacoustic spectral studies of a series of mixed ligand copper complexes of the form [Cu A $(B)_n$] X, n = 1 or 2, A = acetylacetonate, B = morpholine, piperidine, bipy or phen, X = NO_3^- or ClO_4^- have indicated five coordinate structure with oxygen of ClO_4^- or NO_3^- at the fifth position [59].

Synthesis and redox and spectral properties of the complexes [(trpy) (bipy) M - OH_2 $]^{2+}$ (M = Ru, Os ; trpy = 2,2',2" - terpyridine) has been reported by Meyer et al [60]. The compounds of the type [Ru $(phen)_2$ en] I_2 and [Ru $(en)_2$ Phen] I_2 were synthesized and characterized by analysis, visible spectral and PMR studies [61]. Synthesis and electrochemical properties of [Ru $(bipy)_2$ L $]^{n+}$ (n = 2, L = 2 - (o - hydroxy phenyl) benzimidazole have been described [62, 63] and the oxidation potentials have been rationalized in terms of the donor property of L [63]. Ruthenium (II) trischelate complexes containing bipy and 2,2' - biisoquinoline have been prepared and their spectroelectrochemical properties have been investigated [64]. Also the spectroelectrochemical properties of [Ru $(bpz)_x$ $(bipy)_{3-x}$ $]^{2-n}$ (x = 1-3, n = 0-3, bpz = 2,2'-

bipyrazine) have been studied recently [65]. Preparation and electron transfer reactions of Ru^{II} trischelate complexes containing bipy and 2,2' - bipyridine - 4,4' - disulphonic acid or 2,2' - bipyridine - 4,4' dicarboxylic acid have been reported [66].

Mixed ligand complexes [Pt (bipy) L] , where L = phthalic acid, salicylic acid, thiosalicylic acid, catechol, 4 - tert - butylcatechol, 3, 4 - dimercapto toluene were prepared and characterized by various spectral methods [67]. Later four complexes have been shown to behave as potential photosensitizers. Ternary complexes of oxovanadium (IV) with bipy and pyrocatechol or 3, 5 di-tert - butyl catechol have been isolated [68]. Earlier reports include preparation and characterization of [M bipy catechol] where M = Cu^{II}, Ni^{II}, Zn^{II} and Cd^{II} [69]. Recently, preparation of [Cu N-phen L] complexes where L = catechol, 2,3-dihydroxy naphthalene and biologically important ligands like dopamine, phenylalanine, tyrosine and L - dopa has been reported from our laboratory [70]. Among the other studies involving biologically important ligands are the crystal structure determination of [Cu Inosine - 5' - monophosphate imidazole] [71], [copper (II)-2,2' - bipyridyl - pyridoxic acid] [72, 73] , [copper 2,2' bipyridyl pyridoxic acid - γ - lactone] [72-73], chloro (2,2' - bipyridyl) (pyridoxine) copper (II) perchlorate hydrate [74] and (pyridoxinato) bis (2,2' - bipyridyl) cobalt (III) perchlorate [74]. Crystal structure and physicochemical properties of the complexes formed between ATP, dpa and bivalent metal ions Ca, Mg, Sr, Mn, Co, Cu and Zn have been described by Cini et al [75]. Thermal and spectral properties and crystal and molecular structure of (N-tosylglycinato) (2,2' - bipyridine) copper (II) have been reported by Antolini and Menabue [76].

Synthesis and characterization of some ternary complexes with the O^{-}- O coordinating ligands of the present interest have also been reported. Mixed ligand complexes [Cu A L] $^{+}$, where A = bipy or phen and L = sal, naph or acph have been isolated with perchlorate [77] or tetrafluoroborate [78] as counter ions. Syamal and Ghanekar [79–81] have reported the synthesis of mixed ligand cobalt (III) complexes with tetradentate Schiff base ligands and acetoacetanilide or other bidentate ligands. Ternary complexes of oxovanadium (IV) with bipy or phen and β -diketones., β -ketoesters or β'-ketoanilides have been synthesized [82]. The complexes [Cu A L] ClO_4 with A = bipy, phen or 2-(2'pyridyl) benzimidazole and L = derivatives of salicylamide or β -ketoanilides have been reported from our laboratory [83–85].

In the present study an attempt is made to isolate the ternary complexes which have been studied, potentiometrically, in solutions (Ch. 2), in order to support their formation in solutions. The complexes [Cu A L] ClO_4 , where A = dpa or N - phen and L = L^1 - L^{12} have been isolated from aqueous alcohol solutions. The complexes have been characterized by analyses, conductivity and magnetic susceptibility measurements and electronic and IR spectral studies.

3.2 Methods of preparation and characterization.

Chemicals · All chemicals used were as mentioned earlier. Solvents were purified by distillation before use.

General preparation of the ternary complexes [Cu A L] ClO_4 *:

A warm solution containing equimolar amounts of the ligands A (5.0 mmol) and L (5.0 mmol) in 40 ml alcohol was added to a warm solution of 5.0 mmol copper acetate monohydrate in 20-30 ml water. The resulting solution was refluxed on water bath for about 10-15 mins. To this was added dropwise a concentrated solution of sodium perchlorate in water till the precipitation was complete. The resulting solid was filtered, washed with water-alcohol mixture followed by pure alcohol and dried in air.

The complexes were analysed for copper by acid decomposition, followed by iodometric titration and by complexometric titration with EDTA using pyrocatechol violet as indicator. N and C, H analyses were carried out in the micro analytical laboratory of the University.

Conductivity measurements were carried out using one millimolar solutions of the complexes in methanol on a Toshniwal conductivity bridge Type CL01/01 A.

*

Warning ! Although the perchlorate salts reported here seem to be stable to shock and heat, and we have worked with these compounds without incident, the unpredictable behaviour of perchlorate salts necessitates extreme caution in their handling.

Room temperature magnetic measurements were made by Gouy method using Hg [Co (CNS)$_4$] as calibrant. Magnetic moments per atom were calculated using the formula.

$$(\mu_{eff})^2 = 3kT\,\chi_M/N\beta^2$$

Where, χ_M = molar magnetic susceptibility per copper atom and the other terms have their usual meanings. The temperature independant paramagnetism, $N\alpha$, was considered to be 60 ppm per copper atom. Pascal corrections for the ligands and the counter ion (perchlorate) have been incorporated.

Electronic spectra were recorded in ethanolic or methanolic solutions or in dioxane - water mixtures (1:1 v/v) on a Carl - Zeiss SPECORD UV-VIS spectrophotometer or on shimadzu UV 240. Diffuse reflectance spectra (d.r.s), with barium sulphate as reference, were also recorded on shimadzu UV 240 equipped with an integrating sphere assembly. IR spectra of the complexes in the range 250 to 4000 cm^{-1} were recorded in KBr phase on a Perkin-Elmer IR spectrophotometer model no. 567 or on a shimadzu IR spectrophotometer.

The results of analyses and the spectral data are recorded in Table 3.2.1 to 3.2.3.

Table 3.2.1 : Elemental analyses, Magnetic moment and molar conductivity data of the complexes [Cu AL]. ClO_4

Complex	Analyses				μ	Λ
	% Cu	% C	% H	% N	B.M.	10^{-3}M.
1. [Cu A^1 L^1]. ClO_4	14.15	43.74	2.86	9.12	1.75	105
	(13.96)	(44.03)	(3.07)	(9.23)		
2. [Cu A^2L^1]. ClO_4	12.59	44.71	2.35	8.93	1.65	96
	(12.48)	(44.77)	(2.36)	(8.32)		
3. [Cu A^1 L^2]. ClO_4	11.84	38.70	2.63	8.09	1.71	110
	(11.90)	(38.21)	(2.44)	(7.87)		
4. [Cu A^2 L^2]. ClO_4	10.82	38.33	2.04	6.67	1.82	91
	(10.81)	(38.78)	(2.04)	(7.14)		
5. [Cu A^1 L^3]. ClO_4	12.53	40.33	2.74	10.84	1.78	94
	(12.70)	(40.79)	(2.56)	(11.18)		
6. [Cu A^2 L^3]. ClO_4	11.41	40.73	2.41	9.99	1.77	110
	(11.46)	(41.15)	(1.98)	(10.11)		
7. [Cu A^1 L^4]. ClO_4	12.66	50.02	3.02	8.16	1.79	100
	(12.58)	(49.88)	(3.16)	(8.31)		
8. [Cu A^2 L^4]. ClO_4	11.50	48.92	2.55	7.37	1.72	92
	(11.36)	(49.35)	(2.50)	(7.51)		
9. [Cu A^1 L^5]. ClO_4	13.07	45.77	3.88	8.77	1.70	110
	(13.57)	(46.15)	(3.42)	(8.97)		
10. [Cu A^2 L^5]. ClO_4	12.12	45.81	2.41	7.57	1.84	97
	(12.15)	(45.88)	(2.87)	(8.03)		

Table 3.2.1 Contd.

Complex	Analyses % Cu	% C	% H	% N	μ B.M.	Λ 10^{-3}M.
11. [Cu A^1 L^6]. ClO_4	12.34	46.70	3.45	10.64	1.81	110
	(12.46)	(47.05)	(3.72)	(10.98)		
12. [Cu A^2 L^6]. ClO_4	11.09	46.39	3.39	10.58	1.80	102
	(11.25)	(46.68)	(3.01)	(9.93)		
13. [Cu A^1 L^7]. ClO_4	12.12	47.67	3.71	9.98	1.75	101
	(12.12)	(48.09)	(3.82)	(10.69)		
14. [Cu A^2 L^7]. ClO_4	10.64	47.93	3.54	9.91	1.68	102
	(10.97)	(47.75)	(3.29)	(9.69)		
15. [Cu A^1 L^8]. ClO_4	11.72	46.42	4.02	10.74	1.88	102
	(11.77)	(46.66)	(3.89)	(10.37)		
16. [Cu A^2 L^8]. ClO_4	10.57	46.53	3.54	8.97	1.72	104
	(10.68)	(46.38)	(3.19)	(9.41)		
17. [Cu A^1 L^9]. ClO_4	10.95	52.19	3.72	9.54	1.78	101
	(11.11)	(52.44)	(3.67)	(9.79)		
18. [Cu A^2 L^9]. ClO_4	10.26	51.46	2.60	8.55	1.73	111
	(10.13)	(51.67)	(3.03)	(8.93)		
19. [Cu A^1 L^{10}]. ClO_4	13.29	43.00	3.65	11.75	1.75	88
	(13.52)	(43.40)	(3.19)	(11.91)		
20. [Cu A^2 L^{10}]. ClO_4	12.33	43.80	2.60	10.68	1.87	84
	(12.10)	(43.43)	(2.48)	(10.67)		
21. [Cu A^1 L^{11}]. ClO_4	12.06	50.10	3.25	9.98	1.78	102
	(11.64)	(50.54)	(3.48)	(10.26)		

Table 3.2.1 Contd.

	Complex	Analyses.				μ	Λ
		% Cu	% C	% H	% N	B.M.	10^{-3}M.
22.	$[Cu\ A^2\ L^{11}].\ ClO_4$	10.57	48.79	3.31	9.25	1.87	100
		(10.55)	(49.83)	(2.82)	(9.31)		
23.	$[Cu\ A^1 L^{12}].\ ClO_4$	11.46	37.70	2.76	10.70	1.79	100
		(11.60)	(37.23)	(2.55)	(10.22)		
24.	$[Cu\ A^2\ L^{12}].\ ClO_4$	10.39	38.10	2.19	9.35	1.81	92
		(10.52)	(37.70)	(1.99)	(9.29)		

a) Equivalent conductances measured for 10^{-3}M methanolic. solutions are reported in $\Omega^{-1}\ cm^2\ mol^{-1}$.

b) The values in parentheses are those calculated for the formula $[CuAL].\ ClO_4$.

Table 3.2.2 : Infrared absorption frequencies of the complexes [Cu AL] . ClO_4

	Complex	IR frequencies $\bar{\nu}$ in cm^{-1}
1.	$[Cu\ A^1\ L^1].\ ClO_4$	3320 (m), 3210 (m), 3140 (m), 3110 (w), 3040 (w) 1628 (s), 1600 (s), 1578 (s), 1550 (w), 1510 (s), 1470 (s), 1450 (m), 1425 (s), 1390 (s), 1320 (w), 1300 (s), 1260 (m), 1220 (s), 1200 (m), 1182 (m), 1155 (s), 1135 (s), 1115 (s), 1080 (s), 1050 (s), 1015 (m), 1000 (s), 985 (m), 915 (m), 900 (m), 890 (m), 850 (m), 825 (m), 775 (s), 755 (s), 725 (m), 655 (m), 640 (m), 610 (s), 580 (m), 535 (w), 510 (m), 445 (w), 425 (m-w), 410 (m), 390 (w), 370 (w), 335 (w), 315 (w), 295 (m-w).
2.	$[Cu\ A^2\ L^1].\ ClO_4$	3080 (m), 3000 (m), 2880 (w), 1615 (s), 1572 (m), 1535 (m), 1510 (s), 1505 (s), 1455 (w), 1425 (s), 1388 (m), 1360 (m), 1340 (s), 1325 (m), 1300 (w), 1210 (m), 1190 (s), 1150 (s), 1130 (s), 1110 (s), 1095 (s), 1070 (s), 970 (w), 905 (m), 875 (w), 840 (s), 815 (s), 795 (w), 780 (w), 770 (w) 760 (s), 740 (m), 720 (s), 700 (w), 665 (m), 625 (s), 605 (w), 550 (w), 535 (w), 450 (m), 435 (m), 410 (m), 350 (w).
3.	$[Cu\ A^1\ L^2].\ ClO_4$	3310 (m), 3240 (m), 3200 (m), 3140 (m), 1630 (s), 1605 (s), 1580 (s), 1510 (s), 1500 (s), 1470 (s), 1438 (m), 1425 (m), 1410 (w), 1370 (s), 1320 (w), 1290 (s), 1260 (w), 1235 (m), 1222 (s), 1170 (s), 1160 (s), 1120 (s) 1090 (s), 1070 (s), 1050 (s) 1010 (m), 990 (w), 955 (w), 902 (m), 880 (w), 860 (w), 828 (s), 770 (s), 725 (w), 710 (s), 690 (w), 640 (m), 615 (s), 540 (w), 525 (m), 445 (m), 420 (m), 400 (w), 380 (m), 350 (w), 330 (m), 300 (w).

4. [Cu A^2 L^2]. ClO_4 3070 (m), 2990 (w),
1615 (s), 1585 (m), 1530 (w), 1510 (w), 1440 (m),
1420 (m), 1380 (m), 1355 (w), 1340 , 1315 , 1240 (w),
1205 (w), 1180 (m), 1160 (m-s), 1140 (m), 1110 (s),
1090 (s), 1060 (s), 925 (w), 910 (w), 850 (s), 820 (m),
785 (m), 755 (m), 735 (m), 720 (s), 695 (w), 670 (w),
660 (w), 640 (m), 625 (m), 550 (w), 450 (w).

5. [Cu A^1 L^3]. ClO_4 3350 (w), 3050 (w),
1630 (s), 1600 (m), 1590 (s), 1545 (s), 1545 (s), 1530 (s),
1450 (m), 1440 (s), 1410 (s-m), 1375 (m), 1310 (s),
1250 (m), 1235 (s-m), 1200 (w), 1180 (m), 1165 (m),
1140 (w), 1090 (s), 1060 (s), 1020 (w), 940 (w), 905 (w),
865 (w), 840 (m), 770 (s), 720 (s), 690 (w), 650 (m).

6. [Cu A^2 L^3]. ClO_4 3500 (w), 3050 (w),
1610 (s), 1600 (s), 1570 (m), 1530 (m), 1525 (m),
1500 (m), 1480 (m), 1430 (m), 1410 (m), 1390 (m),
1330 (w), 1315 (s), 1300 (s), 1230 (w), 1190 (w),
1170 (m), 1120 (m), 1100 (s), 1080 (s), 1050 (m),
925 (m), 900 (w), 840 (w), 830 (m), 810 (w), 770 (w),
745 (m), 725 (m), 710 (s), 690 (w), 645 (w), 615 (m),
510 (w), 460 (w), 430 (w), 400 (w), 370 (w).

7. [Cu A^1 L^4]. ClO_4 3420 (w), 3340 (w), 3200 (w),
1640 (s), 1618 (s), 1605 (s), 1587 (s), 1530 (s), 1487 (s),
1432 (s), 1425 (s), 1390 (s), 1380 (s), 1340 (m), 1310 (w),
1280 (m), 1255 (w), 1240 (m), 1200 (s), 1180 (m),
1170 (m), 1145 (s), 1100 (s), 1070 (s), 1060 (s),1020 (m),
990 (m), 940 (w), 930 (w), 910 (w), 865 (w), 840 (s),

780 (s), 750 (s), 700 (w), 660 (m), 625 (s), 560 (w), 525 (m), 490 (w), 465 (m), 445 (w), 420 (m), 405 (w), 370 (m), 350 (w), 310 (w).

8. [Cu A^2 L^4]. ClO_4

3230 (w), 3060 (m),
1620 (s), 1610 (s), 1595 (s), 1575 (s), 1525 (s), 1510 (s), 1415 (s), 1380 (s), 1360 (s), 1335 (s), 1295 (w), 1250 (w), 1210 (w), 1200 (w), 1185 (m), 1160 (w), 1140 (m), 1100 (s), 1085 (s), 1055 (s), 970 (m), 835 (s), 810 (m), 760 (m), 750 (m), 725 (w), 715 (s), 650 (w), 620 (m), 565 (w), 460 (m).

9. [Cu A^1 L^5]. ClO_4

3340 (w),
1630 (s), 1593 (s), 1575 (s), 1512 (s), 1470 (s), 1420 (s), 1365 (m), 1323 (m), 1260 (w), 1245 (w), 1228 (s), 1155 (m), 1130 (s), 1105 (s), 1080 (s), 1055 (s), 1010 (m), 962 (w), 925 (w), 900 (w), 850 (m), 760 (s), 735 (w), 715 (w), 690 (w), 675 (w), 630 (m), 615 (s), 550 (w), 515 (m), 480 (w), 450 (w), 410 (m), 390 (w), 360 (w), 340 (w).

10. [Cu A^2 L^5]. ClO_4

3300-3600 (w,b), 3070 (w),
1620 (w), 1600 (s), 1580 (s), 1540 (w), 1510 (s), 1500 (s), 1450 (m), 1415 (s), 1365 (m), 1330 (s), 1295 (w), 1250 (w), 1225 (s), 1200 (w), 1175 (w), 1150 (m-s), 1135 (m-s), 1100 (s), 1065 (s), 1015 (w), 970 (w), 925 (w), 905 (w), 865 (w), 855 (w), 830 (s), 810 (m), 750 (s), 735 (m), 710 (s), 650 (w), 615 (s), 560 (w), 515 (w), 445 (w), 430 (m), 420 (w).

11. $[Cu\ A^1\ L^6].\ ClO_4$ 3360 (m), 3300 (m), 3200 (w), 3100 (w),

1635 (s), 1620 (s), 1585 (s), 1540 (s), 1500 (m),
1480 (s), 1440 (s), 1420 (m), 1370 (w), 1320 (s),
1300 (m), 1260 (m-s), 1235 (m-s), 1200 (w),
1180 (w), 1160 (w), 1100 (s), 1070 (s), 1020 (w),
975 (s-m), 900 (w), 870 (w), 850 (w), 760 (s),
690 (m), 650 (m).

12. $[Cu\ A^2\ L^6].\ ClO_4$ 3500 (w), 3000 (w),

1630 (m), 1610 (m), 1590 (s), 1540 (s), 1520 (s),
1490 (s), 1440 (s), 1425 (m), 1345 (m), 1320 (s),
1305 (m), 1260 (m), 1240 (m), 1200 (m), 1180 (m-w),
1160 (w), 1100 (s), 1060 (s), 975 (s), 930 (very w),
910 (w), 840 (s), 825 (w), 810 (w), 780 (m), 760 (s),
720 (s-m), 695 (m), 655 (w).

13. $[Cu\ A^1\ L^7].\ ClO_4$ 3350 (m),

1635 (s), 1610 (s), 1590 (s), 1580 (s), 1530-1550 (s,b),
1500 (s), 1480 (s), 1455 (s), 1440 (s), 1415 (s), 1370 (w),
1295 (m), 1265 (s), 1240 (s), 1185 (m) 1165 (m),
1160 (s-m), 1100-1080 (s,b), 1025 (m), 1015 (m),
975 (s), 950 (w), 905 (w), 860 (w), 845 (w), 760 (s),
740 (m), 680 (w).

14. $[Cu\ A^2\ L^7].\ ClO_4$ 3350 (w), 3000 (w),

1610 (s), 1585 (s), 1530 (s), 1480 (m), 1450 (s-m)
1425 (m), 1390 (w), 1350 (m), 1335 (s), 1300 (s),
1260 (s), 1190 (m), 1150 (w), 1080 (s), 1000 (w),
970 (m-s), 930 (w), 910 (w), 870 (w), 840 (s),
815 (m-w), 780 (m), 755 (s), 720 (s), 660 W.

15.	[Cu A^1 L^8]. ClO_4	3360 (s), 3300 (m), 3250 (w), 3200 (w), 1635 (s), 1610 (s), 1585 (s), 1530-1550 (s,b), 1480 (s), 1450 (s), 1430 (s), 1370 (m), 1340 (m-s), 1330 (m-s), 1290 (s), 1260 (s), 1250 (s), 1235 (m-s), 1220 (m), 1190 (w), 1180 (m), 1165 (m), 1110-1095 (s,b), 1070 (s), 1060 (s). 1025 (s), 970 (s), 930 (w), 905 (w), 875 (w), 850 (w), 770 (s), 750 (s), 650 (m).
16.	[Cu A^2 L^8]. ClO_4	3300 (m), 3050 (w), 1600 (s), 1580 (s), 1540 (s), 1520 (s), 1480 (s), 1460 (s), 1420 (s), 1330 (s), 1290 (s), 1250 (s), 1220 (m), 1180 (w), 1160 (w), 1150 (w), 1090 (s), 1020 (m), 960 (m), 910 (w), 840 (m-s), 820 (m), 800 (m), 760 (s), 720 (m-s), 650 (w).
17.	[Cu A^1 L^9]. ClO_4	3000-3350 (m,b), 1635 (s), 1615 (s), 1585 (s), 1575 (w), 1540 (s,b), 1500 (m-s), 1480 (s), 1440 (s), 1370 (w), 1320 (s), 1300 (m), 1270 (w), 1240 (s), 1205 (m), 1165 (m), 1160 (m), 1125 (s), 1090 (s), 1060 (s), 1010 (s-m), 905 (m), 845 (w), 770 (s), 740 (m), 690 (m).
18.	[Cu A^2 L^9]. ClO_4	3300 (w), 3050 (w), 1620 (m-s), 1590 (s), 1575 (w), 1550 (s), 1520 (s), 1505 (s), 1485 (s), 1440 (s), 1430 (m), 1350 (m-s), 1325 (s), 1300 (w), 1240 (m), 1220 (m), 1180 (w), 1150 (w), 1100 (s), 1070 (s), 1010 (m), 910 (m), 840 (m), 810 (w), 775 (m), 755 (s), 720 (m), 695 (m).

19.	$[Cu\ A^1\ L^{10}].\ ClO_4$	3470 (m), 3350 (m), 3200 (w), 3020 (m), 1655 (m), 1635 (s), 1600 (s), 1594 (m-s), 1570 (m), 1540 (s), 1485 (s), 1435 (m), 1315 (m), 1260 (m), 1235 (m), 1160 (m), 1145 (m), 1110 (s). 1100 (s), 1065 (s), 1010 (w), 905 (w), 860 (m), 760 (s), 715 (w), 650 (w).
20.	$[Cu\ A^2\ L^{10}].\ ClO_4$	3450 (m), 3350 (m), 1640 (s), 1600 (s), 1585 (w), 1570 (s),1535 (s),1520 (s). 1470 (s), 1450 (m), 1425 (m), 1390 (w), 1335 (s), 1250 (s), 1210 (w), 1180 (w), 1140 (m), 1100 (s), 910 (w), 870 (m), 840 (s), 820 (m), 755 (s), 720 (s), 660 (w).
21.	$[Cu\ A^1\ L^{11}].\ ClO_4$	3500 (w), 3300 (m), 3200 (w), 3100 (w), 1635 (s), 1610 (s), 1580 (s), 1540 (s), 1475 (s), 1450 (m), 1440 (s-m), 1370 (w), 1350 (m), 1320 (m). 1295 (w), 1270 (m), 1235 (m), 1165 (m), 1135 (s), 1100 (s), 1015 (m), 930 (w), 905 (w), 865 (w), 840 (w), 805 (w), 755 (s), 695 (m), 660 (w).
22.	$[Cu\ A^2 L^{11}].\ ClO_4$	3350 (m), 3050 (w), 1610 (s), 1580 (s), 1530 (s), 1495 (m-s), 1450 (s). 1435 (m),1425 (m), 1345 (s), 1330 (s), 1270 (m), 1240 (m), 1220 (w), 1180 (w), 1140 (s), 1100 (s), 910 (w), 870 (m), 840 (s-m), 820 (m), 755 (s), 720 (m), 695 (m), 660 (w).

23.	$[Cu A^1 L^{12}] . ClO_4$	3450 (m), 3350 (m), 3200 (w), 3100 (w), 1640 (s), 1595 (s), 1585 (s), 1570 (m), 1530 (s), 1480 (s), 1435 (s), 1390 (w), 1315 (m), 1250 (m), 1230 (m), 1165 (m), 1120 (s), 1100 (s), 1080 (s), 1070 (s), 1020 (m), 905 (w), 830 (m), 770 (s), 670 (w), 650 (w).
24.	$[Cu A^2 L^{12}] . ClO_4$	3430 (m), 3330 (m), 3220 (m), 3050 (w), 1640 (s), 1600 (s), 1560 (s), 1540 (s), 1520 (s), 1455 (s), 1440 (m), 1425 (m-s), 1390 (m), 1330 (s), 1250 (m-s), 1210 (w), 1180 (m), 1140 (m), 1100 (s), 930 (w), 910 (w), 880 (w), 840 (s), 815 (m), 775 (m), 755 (m), 720 (s), 680 (w), 650 (w).

Table 3.2.3 : Electronic spectra of the ternary complexes [Cu AL]. ClO_4

	Compound	$\bar{\nu}$ (cm^{-1}). In methanol	$\bar{\nu}$ (cm^{-1}). d.r.s.
1.	[Cu A^1 L^1]. ClO_4	45360,40880, 39000 (sh), 36320, 33200, 31520, 25440,15680.	15870
2.	[Cu A^2 L^1]. ClO_4	45400, 41960, 36300, 34000(sh) 32000 (sh), 25680, 21000 (sh) 15950.	16080
3.	[Cu A^1 L^2]. ClO_4	44800, 40400, 36320, 33280, 31520, 24720, 15920.	16450, 14080
4.	[Cu A^2 L^2]. ClO_4	44850, 41600, 36360, 34000 (sh) 32000 (sh), 24800, 15880.	16180
5.	[Cu A^1 L^3]. ClO_4	45200, 39840, 30880, 33200 (sh) , 26320 (sh), 15360.	16750, 14500
6.	[Cu A^2 L^3]. ClO_4	45400, 42650, 36480, 34000 (sh), 30500, 21500 (sh), 15920.	16890
7.	[Cu A^1 L^4]. ClO_4	44000, 40160, 39000 (sh), 37680 (sh), 33040, 31200, 25600, 24800, 15520.	16390
8.	[Cu A^2 L^4]. ClO_4	44000, 42000 (sh), 38880 (sh) 37520 (sh), 36080, 31200, 25600, 24720, 15950.	16670

Table 3.2.3 Contd.

	Compound	$\bar{\nu}$ (cm^{-1}). in methanol	$\bar{\nu}$ (cm^{-1}). d.r.s.
9.	$[Cu\ A^1\ L^5].ClO_4$	45520, 40160, 36640, 33200, 31440, 25920, 15760.	16450, 14080
10.	$[Cu\ A^2\ L^5].ClO_4$	45360, 42400, 36370, 32150(sh), 26400, 18800(sh), 16160.	18030, 15620(sh)
11.	$[Cu\ A^1\ L^6].ClO_4$	48300, 39900, 33250, 25280, 15700.	22250, 16550
12.	$[Cu\ A^2\ L^6].ClO_4$	49500, 41670, 35210, 32790, 20830, 15950.	16950
13.	$[Cu\ A^1\ L^7].ClO_4$	47650, 40150, 34200, 31600(sh), 25600, 15800.	16840
14.	$[Cu\ A^2\ L^7].ClO_4$	48540, 42920, 35340, 29410 19610, 16080.	17090
15.	$[Cu\ A^1\ L^8].ClO_4$	47900, 40000, 33100 25500, 15750.	22730, 17210
16.	$[Cu\ A^2\ L^8].ClO_4$	49020, 40980, 35210, 32700, 15970.	16920
17.	$[Cu\ A^1\ L^9].ClO_4$	48200, 40300, 31700, 28700(sh), 22000(sh), 15700.	16950
18.	$[Cu\ A^2\ L^9].ClO_4$	49260, 42500, 35090, 31000, 21700, 15720.	20830, 17240

Table 3.2.3 Contd.

	Compound	$\bar{\nu}$ (cm^{-1}). In methanol	$\bar{\nu}$ (cm^{-1}). d.r.s.
19.	$[Cu\ A^1\ L^{10}].ClO_4$	47700, 45800, 40150, 33000, 31700, 24200, 15600.	23580, 15500
20.	$[Cu\ A^2\ L^{10}].ClO_4$	47620, 36360, 29410, 23800, 15720.	16835
21.	$[Cu\ A^1\ L^{11}].ClO_4$	47680, 45700, 39850, 33150, 31680, 23650, 15500.	22990, 16150
22.	$[Cu\ A^2\ L^{11}].ClO_4$	48540, 45800, 35340. 29410 23700, 15670.	22220, 16660
23.	$[Cu\ A^1\ L^{12}].ClO_4$	47520, 45200, 39900, 33200 31550, 23800, 15350.	23260, 16180
24.	$[Cu\ A^2\ L^{12}].ClO_4$	46700, 34970, 29450, 23000, 15650.	22220, 16610

3.3 Characterization of the complexes and the spectral properties.

The species distribution curves (plots of concentration of different species versus pH) (Fig. 2.2.13 to 2.2.36) indicate that between the pH range ~ 6.0 to 7.5 only the ternary complex [Cu A L] exists ; concentration of the binary species CuA reduces to an insignificant level and the formation of another binary species CuL does not start at all. Hence, this is the ideal pH range for the isolation of the ternary complexes. Natural pH of the solution obtained by mixing equimolar amounts of copper acetate monohydrate, and the two ligands in alcohol-water mixture lies in this pH range and hence assures the formation of only $[\mathrm{Cu\ A\ L}]^{1+}$, which can be obtained in solid form by the addition of a neutral salt of suitable anion like sodium perchlorate.

The analyses of the complexes (Table 3.2.1) correspond to the general formula [Cu A L]. ClO_4 which can be shown, structurally, as in Fig. 3.3.1 to 3.3.3. Molar conductance values of the 1 millimolar solutions of the complexes in methanol are typical of 1:1 electrolytes indicating the ionic nature of the perchlorate binding.

Room temperature magnetic susceptibility measurements correspond to one unpaired electron except in some cases where a slight lowering in magnetic moment indicates a possibility of weak intermolecular spin-spin interaction between the copper (II) centres in the dimers, possibly formed by the linking of Cu^{II} of one molecule with O^- of the secondary ligand of the adjacent molecule in the solid state. According to a recent report [86] , crystal structure of (di-2-pyridyl-amine) salicylaldehydato copper (II) perchlorate exists as a dimeric unit with two large apical Cu —— O distances , one towards the O of the ClO_4 anion and the other one, linking two monomeric units, towards the O of the nearest salicylal-dehyde molecule .

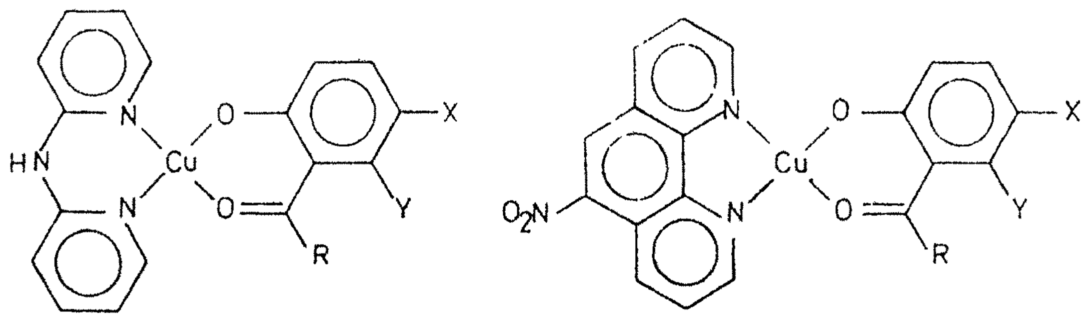

Fig. 3.3.1 R = H, X=H, Br, NO_2 , Y=H ; R=H, XY= $-(CH)_4$; R=CH_3, X=Y=H

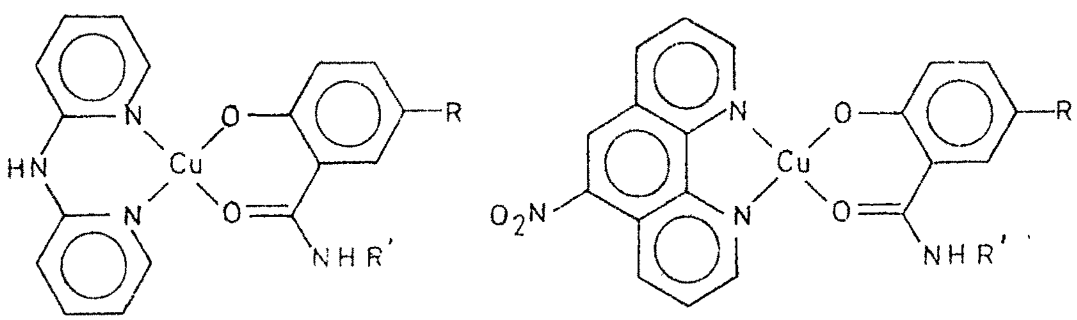

Fig. 3.3.2 R=H, Br , R'=H , R=H ; R'= C_6H_5

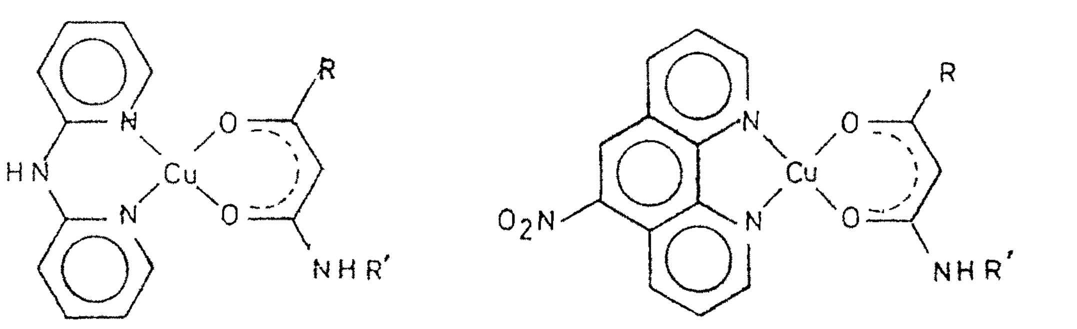

Fig. 3.3.3 R=CH_3, R'=C_6H_5, o-Me C_6H_4, o-MeO C_6H_4, R = R'=C_6H_5 .

IR spectra.

IR spectra of the complexes in KBr phase exhibit the bands at frequencies characteristic of the primary ligand and the aromatic part of the secondary ligands in the region between 600 cm^{-1} to 1700 cm^{-1} . A strong absorption band at ca. 1100 cm^{-1} is observed corresponding to the asymmetric ν_{Cl-O} of the perchlorate. This band and the absence of any absorption at 920 cm^{-1}, corresponding to the symmetric ν_{Cl-O}, support that the perchlorate anion is having T_d symmetry and is not coordinated with the metal ion [87].

Free o-hydroxy aromatic aldehydes, ketones and salicylamide ligands exhibit $\nu_{C=O}$ at 1695 - 1715 cm^{-1} , 1680 - 1700 cm^{-1} and 1670 - 1680 cm^{-1} , respectively. The β-ketoanilides exhibit two bands one corresponding to $\nu_{C=O}$ of the ketone and the other corresponding to the stretching of the amide $\rangle C=O$. However , in ternary complexes containing salicylaldehyde and salicylamide derivatives , $\nu_{C=O}$ is found to occur between 1600 and 1640 cm^{-1} . The shift towards the lower energy region is due to the coordination of oxygen with the metal ion. One of the two bands in β-ketoanilides corresponding to $\rangle C=O$ stretch disappears on complexation indicating enolization of the keto group.

In addition to the above bands, complexes involving dpa exhibit a band at ca. 3200 cm^{-1}, corresponding to the ν_{N-H} . Besides this, all the complexes with bidenate amides or anilides or as secondary ligands exhibit ν_{N-H} of the amide group at $\sim$3350 cm^{-1} and $\sim$3200 cm^{-1} and δ_{N-H} at ~1590 cm^{-1} . These are almost at the same place as in the free ligands, thus supporting the fact that these ligands coordinate through bidentate O-O sites.

Electronic Spectra

Electronic spectra of the complexes in 50% (v/v) aqueous dioxane (or methanol) and the diffuse reflectance spectra are almost identical. The complexes [Cu A L] . ClO_4 exhibit a low intensity (Emax ~ 100) broad band between 590 and 640 nm. This can be assigned to the three possible transitions, $A_{1g} \leftarrow B_{1g}$, $B_{2g} \leftarrow B_{1g}$ and $E_g \leftarrow B_{1g}$ in octahedral complexes with a d^9 metal centre. These are very close in energy and hence result in a broad band. However, in the complexes with A = N-phen and L = L^5 - L^7 and A = dpa or N-phen and L = L^9 L^{12} , an additional low intensity band appears in the region between 420 to 550 nm. In these complexes because of the metal $\longrightarrow$ ligand π bonding , the d_{zx} and d_{yz} (e_g) orbitals of the metal ion are lowered down. where as d_{xy} (b_{2g}) orbital is raised in energy. This results in the shift in the $E_g \leftarrow B_{1g}$ transition to higher energy and the other two tansitions $B_{2g} \leftarrow B_{1g}$ and $A_{1g} \leftarrow B_{1g}$ remain merged resulting in a broad band at ~ 620 nm. The latter can be considered to correspond, roughly to 10 Dq, and is slightly shifted towards higher energy (~ 590-600 nm) in the d.r.s indicating very weak intermolecular interaction in the axial direction. The energies of the bands also indicate slight distortion from planarity in the geometry around the metal ion.

The positions of the bands are recorded in Table 3.2.3. Bands in the UV region correspond to the transitions within the two ligand molecules. As discussed earlier in Ch. 2 the d-d transitions in all the complexes in methanol occur almost at the same positions as in 50% aq. dioxane. They are at higher energy than the positions estimated from the average of the energies of the corresponding binary complex. (Table 2.3.1) , supporting the stabilization of the ternary complexes compared to their binary analogues.

Tables [2.3.1] and [3.2.3] also reveal that the separation of $E_g \longleftarrow B_{1g}$ transition , from the other two transitions , takes place only in the case of 2-hydroxy acetophenone and the amide ligands , i.e. the ligands with electron releasing groups at the α carbon atom. The increase in electron density at the coordinating sites of the secondary ligand results in a stronger M-L σ interaction which simultaneously favours greater $M \longrightarrow A$ π interaction. This supports the observation made earlier on the basis of solution studies, that the substituents over the secondary ligands , which increase the basicity or electron density at the coordination sites , result in greater stabilization of the ternary complexes involving π - bonding tertiary diimines as a primary ligand.

3.4 References

1. A.E. Martell and M.M. Taquikhan, "Homogeneous Catalysis by Metal Complexes", Vol. II, Academic Press , New York , 1978.

2. H. Sigel , Ed : Metal ions in biological systems , Marcell Dekker , New York , Vol.14 , 1982 .

3. D.L. Banville , W.D. Wilson and L.G. Marzilli , Inorg. Chem. 1985 , **24,** 2479.

4. H. Elo and P. Lumme , Inorg. Chim. Acta 1987 , **136** , 149.

5. Literature involving these kind of reactions is cited in the following paragraph.

6. A.A. Schilt , J. Am. Chem. Soc. 1960 , **82** , 3000.

7. D.L. Alleston and A.G. Davies , J. Chem. Soc. 1962 , 2050.

8. G.E. Coates and S.I.E. Green , J. Chem. Soc. 1962 , 3340.

9. M. Tsutsui , Z. Chem. 1962 , **2** , 214.

10. M. Murakami , S. Sench . N. Matsusato , H. Hatani and J.W. Kang, Nippon Kagaku. Zashi. 1962 , **83** , 734.

11. B.K. Sen , N.N. Ghosh and P.B. Sarkar , Sci. Cult. 1963 , **29 (4)** , 201.

12. B.T. Thaker and P.K. Bhattacharya , J. Inorg. Nucl. Chem. 1975 , **37** , 615.

13. V.B. Mohankumar and P.K. Bhattacharya , J. Indian Chem. Soc. 1975, **LII** , 1041.

14. B.T. Thaker and P.K. Bhattacharya , Indian J. Chem. 1976 , **14A,** 619.

15. R.K. Kohli and P.K. Bhattacharya , Bull. Chem. Soc. Jpn. 1976 , **49(10)** , 2872.

16. V.B. Mohankumar and P.K. Bhattacharya , Indian J. Chem. 1977 , **15A** , 132.

17. R.K. Kohli and P.K. Bhattacharya , Indian J. Chem. 1977 , **15A,** 566.

18. V.B. Mohankumar , B.T. Thaker , R.K. Kohli and P.K. Bhattacharya , Bull. Chem. Soc. Jpn. 1977 , **50(6)** , 1482.

19. B.T. Thaker and P.K. Bhattacharya , Indian J. Chem. 1979 , **17A** , 371.

20. B.A. Jani , R.K. Kohli and P.K. Bhattacharya , J. Indian Chem. Soc., 1981 , **58** , 18.

21. B.A. Jani and P.K. Bhattacharya , J. Indian Chem. Soc. 1981 , **58** , 207.

22. B.J. Pandya and P.K. Bhattacharya , Indian J. Chem. 1985 , **24A** , 403.

23. Uma Doraswamy and P.K. Bhattacharya , J. Inorg. Nucl. Chem. 1975 **37** , 1665.

24. Uma Doraswamy and P.K. Bhattacharya , Indian J. Chem. 1977 , **15** A, 129.

25. Uma Doraswamy and P.K. Bhattacharya , Indian J. Chem. 1977 , **15** A, 828.

26. B.T. Thaker and P.K. Bhattacharya , Bull. Chem. Soc. Jpn. 1976 , **49(10)** , 2845.

27. V.B. Mohankumar , R.K. Kohli and P.K. Bhattacharya , Indian J. Chem. 1977 , **15A** , 1025.

28. B.A. Jani and P.K. Bhattacharya , Indian J. Chem. 1979 , **18A** , 80.

29. Y. Fukuda , N. Sato , N. Hoshino and K. Sone , Bull. Chem. Soc. Jpn. 1981 , **54** , 428.

30. C. Varhelyi , I. Ganesou and M. Preda ,
Rev. Roum. Chim. (Germany) 1973 , **18** , 823.

31. G. Narain , Indian J. Chem., 1966 , **4(15)** , 248.

32. P.C. Parikh and P.K. Bhattacharya , J. Indian Chem. Soc. 1976 , **LIII** , 776.

33. R.L. Dutta and S. Sarkar , Sci. Cult. 1960 , **30(II)** , 549.

34. R.L. Dutta and S. Ghosh , J. Inorg. Nucl. Chem. 1966 , **28(I)** , 247.

35. R.L. Dutta and S. Ghosh , J. Indian Chem. Soc. 1967 , **44(4)** , 306.

36. R.L. Dutta , D.De and A. Syamal , J. Indian Chem. Soc. 1968 , **45 (I)** , 663.

37. R.L. Dutta and S. Sarkar , J. Indian Chem. Soc. 1967 **44** , 832 , 842, 853.

38. R.L. Dutta and D. De , J. Indian Chem. Soc. 1969 , **46** , 74.

39. G. Arena, R.P. Bonomo , E. Rizzarelli and A. Seminara , Inorg. Chem. 1978 , **13** , 30.

40. D.P. Murtha and R.A. Walton , Inorg. Chim. Acta 1974 , **8** , 279.

41. J. Michel and R.A. Walton , J. Inorg. Nucl. Chem. 1975 , **37** , 71.

42. S. Gurrieri , S. Musameci , E. Rizzarelli and A. Seminova , J. Inorg. Nucl. Chem. 1976 , **38** , 1215.

43. W.L. Kwik , K. P. Ang and G. Chen , J. Inorg. Nucl. Chem., 1980 , **42** , 303.

44. M.V. Chidambaram and P.K. Bhattacharya , Inst. of Chemists (India) , 1972 , Vol. XLIV.

45. M.V. Chidambaram : "Formation and Stability of some amino acid chelates", Ph. D. thesis , M.S. University of Baroda , 1971.

46. R. Ripan and V. Saceban , Rev. Rounaine. Chim. , 1966 , 11, 321.

47. K. Sone , S. Utsuno and T. Ogura , J. Inorg. Nucl. Chem. 1969 , **31** , 117.

48. F.A. Walker , H. Sigel and D.B. Mc Cormick , Inorg. Chem. 1972 , **11**, 2756.

49. I.M. Proctor , B.J. Hathaway and P.G. Hodgson , J. Inorg. Nucl. Chem.. 1972 , **34** , 3689.

50. P.O' Brien , J. Chem. Soc. Dalton Trans. 1981 , 1540.

51. T. Karauchi , M. Matsui , Y. Nakamura and S. Ooi , Bull. Chem. Soc. Jpn. , 1974 , **47** , 12.

52. A. Syamal , J. Indian Chem. Soc. 1968 , **45(II)** , 74.

53. E. Butler and K. Kreber , Z. Naturforsch 1965 , **209** , 408.

54. E.A. Bayazitova , U.V. Zelentsov and V.I. Spitsyn , Zh. Neorg. Khim. 1968 , **13(2)** ,479.

55. L.I. Kononenko , UKr. Khim. Zh. 1965 , **31(10)** , 1031.

56. G.N. Rao and J.S. Thakur , Indian J. Chem. 1974 , **12** , 861.

57. Uma Doraswamy : "Studies in some mixed ligand complexes containing β-dicarbonyls" , M.S. University of Baroda , 1976.

58. Y. Yasuhiro , M. Miyazaki , S. Ikeda and N. Yauagi , Chem. Pharm. Bull. 1970 , **18(8)** , 158994.

59. Raghuvir Singh and L.V.K.N. Ramalingeshwara Rao , Polyhedron 1984 , **3(2)** , 137.

60. K.J. Takeuchi , M.S. Thompson , D.W. Pipes and T.J. Meyer , Inorg. Chem. 1984 , **23**(13) , 1845.

61. D.F. Mahoney and J.K. Beattie , Inorg. Chem. 1973 , **12(II)** , 2561.

62. M.A. Haga , Inorg. Chim. Acta. 1984 , **45**(5) , L183.

63. M.A. Haga , Inorg. Chim Acta 1983 , **75** (I) , 29.

64. A. Juris , F. Barigelletti , V. Balzani , P. Belser and A.V. Zelewsky, Inorg. Chem. 1985 , **24**(2) , 202.

65. C.T. Tait , R.J. Donohoe , M.K. De Armond and D.W. Wertz , Inorg. Chem. 1987 , **26** , 2754.

66. K.R. Seddon and M.J. Pilling , J. Chem. Soc. Dalton Trans. 1985 , **11** , 2247.

67. L. Kumar , K.H. Puthraya and T.S. Srivastava , Inorg. Chim. Acta 1984 , **86** (3) , 173.

68. B. Galetti and M. Postel , Nouveau J. Chim. 1984 , **8(7)** , 481.

69. I.P. Mavani , C.R. Jejurkar and P.K. Bhattacharya , Indian J. Chem. 1972 , **10** (9) , 948.

70. N.A. Emanuel and P.K. Bhattacharya , Polyhedron 1987 , **6(5)** , 845.

71. M. Damodara Poojary and H. Manohar , Inorg. Chem. 1985 , **24(7)** , 1065.

72. S.P. Sudhakara Rao , H. Manohar , K. Aoki , H. Yamazaki and R. Bau., J. Chem. Soc. Chem. Commun , 1986 , 4.

73. S.P. Sudhakara Rao , H. Manohar , K. Aoki and H. Yamazaki , J. Chem. Soc. Dalton Trans. 1987 , 1009.

74. S.P. Sudhakara Rao. K.I. Varughese and H. Manohar , Inorg. Chem. 1986 , **25** , 734.

75. R. Cini , M.C. Burla , A. Nunzi, G.P. Polidori and P.F. Zanazzi , J. Chem. Soc. Dalton Trans. 1984 **(II)** , 2467.

76. L. Antolini and L. Menabue , Inorg. Chem. 1984 , **23(10)** , 1418.

77. R.K. Kohli and P.K. Bhattacharya , J. Indian Chem. Soc. 1977 , **LIV** , 340.

78. P.J. Patel and P.K. Bhattacharya , J. Coord. Chem. 1984 , **13** , 113.

79. A. Syamal and V.D. Ghanekar , Curr. Sci. 1975 , **44** , 186.

80. A. Syamal and V.D. Ghanekar , Indian J. Chem. 1975 , **13** , 602.

81. A. Syamal and V.D. Ghanekar , J. Coord. Chem. 1975 , **5** , 39.

82. B.J. Pandya and P.K. Bhattacharya , Indian J. Chem. 1986 , **25A** , 776.

83. K. Gopalkrishnan , U.V. Chudasama and P.K. Bhattacharya , J. Indian Chem. Soc. 1979 , **56** , 445.

84. K. Gopalkrishnan and P.K. Bhattacharya , J. Chem. Soc. Dalton Trans., 1981 , 543.

85. K. Gopalkrishnan and P.K. Bhattacharya , J. Chem. Soc. Dalton Trans., 1982 , 353.

86. M.T. Garland , J. Y. Le Marouille , and E. Spondine , Acta. Crystallogr., Sect. C : Cryst.Struct. Commun. 1985 , **C41(6)** , 855 ; Chem. Abstr . 1985 , **103(6)** , 46247j.

87. K. Nakamoto in "Infrared and Raman Spectra of inorganic and Coordinate compounds" , 3rd ed. John Wiley and Sons Inc. 1978.