

Synthesis and characterization of Cr(III) and Cu(II) complexes of hexaazaphenH₂¹ Sulekh Chandra*, ¹ Rajavally Prem and ² Smriti Raizada.¹ Department of Chemistry, Zakhir Husain Delhi College, JLN-Marg, New Delhi, India.² Department of Chemistry, MMH College, Gaziabad, Uttar Pradesh, India.

*Corresponding Author: E-Mail: schandra_00@yahoo.com

ABSTRACT

A novel hexadentate nitrogen donor [N₆] macrocyclic ligand, i.e. hexaazaphen H₂ (L) has been synthesized. Cr(III) and Cu(II) complexes of this ligand have been prepared and characterized by elemental analyzes, molar conductance measurements, magnetic susceptibility measurements, mass, ¹H NMR (ligand), IR, electronic and EPR spectral studies. On the basis of molar conductance the Cr (III) complexes may be formulated as Cr(L)X₃ and Cu(II) complexes may be formulated as Cu(L)X₂, where X= Cl⁻, Br⁻, NO₃⁻, and CH₃COO⁻. On the basis of IR, electronic and EPR spectral studies an octahedral geometry has been designated to Cr(III), and tetragonal for Cu(II) complexes.

Keywords: Cr(III), Cu(II) complexes of hexaazaphenH₂, Elemental analyzes, Molar conductance.

1. INTRODUCTION

The design and study of metal containing macrocycle is one of the major current research interests in different fields of chemistry [1-4]. Transition metal complexes with azamacrocyclic ligands have received much attention as an active part of metalloenzymes [5], biomimic model compound [6], catalytic [7], biological [8], clinical, analytical and industrial fields [9-11]. These complexes are also significant for the development of new methodologies in separation science [12] or stable structure [13] and different other spectral characteristics [14]. Aza macrocycles are of interest for a number of biomedical applications, including MRI contrast enhancement, radiotracer conjugation and receptor antagonism [15]. Now days, preparation of coordination compounds on solid surfaces has made possible the development of nanoscale devices with novel properties. Construction of coordination compounds is also possible on metal oxides, nanotubes and graphite. These nano-materials have potential applications in a variety of functional systems or devices such as artificial photosynthesis and light harvesting [16]. In the case of azamacrocyclic ligands, the mode of metal incorporation is very much similar to that of metalloproteins in which the requisite metal is bound in a macrocyclic cavity or cleft produced by the conformational arrangement of the protein [17].

In the present paper we report the comparative determination of structure, function, relationship underlying metal ion binding by the ligand L (figure-1) with Cr(III) and Cu(II) metal ions.

2. EXPERIMENTAL

All the chemicals used were of AnalaR grade, and were procured from Aldrich. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard spectroscopic grade.

2.1. Synthesis of ligand

The ligand L₁ was prepared as per figure 1. 2-chloro-1, 10-phenanthroline was prepared according to the methods shown by B. E Halcrow and W. O Kermack [18]. 2-chloro-1,10-phenanthroline (Fig.1-I) (15.9 g) and dimethyl sulphate (50 mL) was heated at 120 °C for 1hr. Cooled and poured the mixture into dry ether (300 mL) with stirring, white precipitate obtained. Obtained white precipitate (20.1 g in 300 mL water) was treated with a solution of sodium hydroxide (80 g in 300 mL water). Now a solution of potassium ferricyanide (53 g in 150 mL water) was added. The pale yellow precipitate obtained was refluxed with benzene. Removal of benzene yielded needles of (Fig.1-II) 2-chloro-10-methyl-1, 10-phenanthroline-9-one (12.9 g). Mixtures of, yellow precipitate (2 g), phosphorous pentachloride (2.5 g) and phosphoryl chloride (15 mL) were refluxed for 8 hrs. Excess phosphoryl chloride was removed by distillation under reduced pressure. 100 mL of ice cool water was added and the solution was basified with ammonia. The precipitate crystallized from benzene as needles of 2, 9-dichloro-1, 10-phenanthroline (Fig.1-III). A mixture of 2, 9-dichloro-1, 10-phenanthroline (2.0 g), phenol (10 g) and acetamide (3.5 g) was maintained at 160 °C

and a stream of ammonia gas was bubbled through this solution for 8 hrs. Excess of phenol and acetamide were removed by distillation under reduced pressure and the residue was dissolved in acetic acid (10 mL). 4N-sodium hydroxide was added until the mixture was alkaline. Pale yellow precipitate was crystallized from ethanol as 2, 9-diamino-1, 10-phenanthroline (Fig.1-IV). A mixture of 2,9-dichloro-1,10-phenanthroline (125 mg), 2,9-diamino-1,10-phenanthroline (105 mg), potassium carbonate (138 mg) and nitrobenzene (10 mL) was maintained at 180 °C with stirring for 5 hrs. Excess nitrobenzene was removed by steam distillation and filtered the yellow residue, which was recrystallized from quinoline and yellow needles of ligand L (Fig.1-V) was obtained. Yield 65 %, m.p. 474 °C, [Found: C 74.28; H 4.02; N 21.68, C₂₄H₁₄N₆ (for atomic mass 386.44) calculated: C 74.59; H 3.66; N 21.75 %]

2.2. Synthesis of complexes

The complexes were prepared by using ligand L and salts of chromium and copper having anions Cl⁻, Br⁻, NO₃⁻, and CH₃COO⁻.

Hot nitrobenzene solution of the ligand and benzyl alcohol solution of corresponding metal salt was mixed and refluxed with

continuous stirring for 3hrs. The colored precipitates obtained were filtered washed with nitrobenzene, acetone and water and then dried at 100 °C. The complexes were recrystallized from quinoline and used for analysis.

2.3. Physical measurements

The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Guoy balance using CuSO₄.5H₂O as a calibrant. Electron impact mass spectra were recorded on JEOL, LMS, DX-303 mass spectrometer. ¹H NMR spectra were recorded on a Hitachi FT-NMR, model R-600 spectrometer using deuterated DMSO as a solvent. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra (KBr) were recorded on a Perkin Elmer FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini 1240 spectrophotometer. EPR spectra of the complexes were recorded as polycrystalline samples and in DMSO solution, at room temperature on an E4-EPR spectrometer using DPPH as the g-marker.

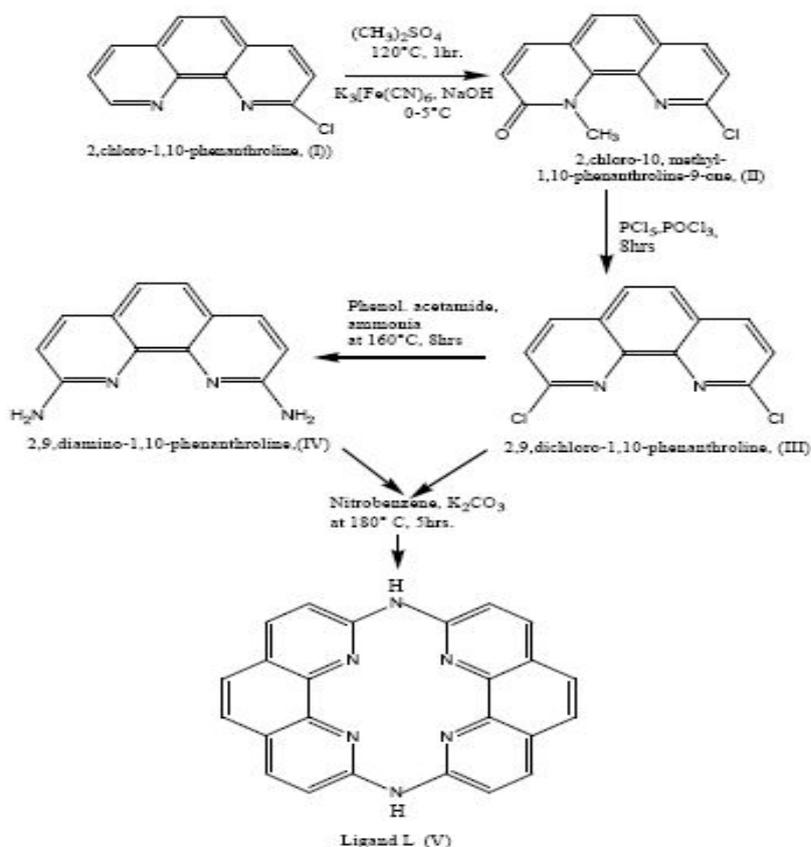


Figure - 1: Synthesis of ligand

3. RESULTS AND DISCUSSION

3.1. Ligand

Mass spectra confirm the proposed formulae of ligand. The structure of the product was verified by its mass spectrum: m/e 386(M^+) and 193 (M^{2+}). In contrast to the spectrum of 2, 9-diamino- 1, 10-phenanthroline, the M^+ and M^{2+} peaks were much more intense than those of the fragment ions ($< 2\%$ of M^+ and M^{2+}). This minor fragmentation seems to be due to aromatic stability.

IR spectrum of the ligand showed band at 2780 cm^{-1} and 900 cm^{-1} assigned to stretching and out-of-plane deformation N-H vibrations, which disappear on N-deuteriation. The ν_{NH} value is much lower than and δ_{NH} value is much higher than those of porphyrins. The values for porphyrins are near 3310 cm^{-1} and between 680 and 675 cm^{-1} , respectively [19]. It was found that the bands corresponding to N-H stretching are missing. This experimental observation suggested that imine was the prevailing form of the ligand (Fig. 2).

^1H NMR spectrum of the ligand supports its cyclic structure [$\delta(\text{CF}_3\text{CO})_2\text{H}$] 8.07 (4H, d), 8.35 (4H, s), and 9.00 (4H, d) ppm] and was similar to that of 2,9-disubstituted 1,10-phenanthroline. No N-H absorption was observed, presumably owing to exchange with the solvent.

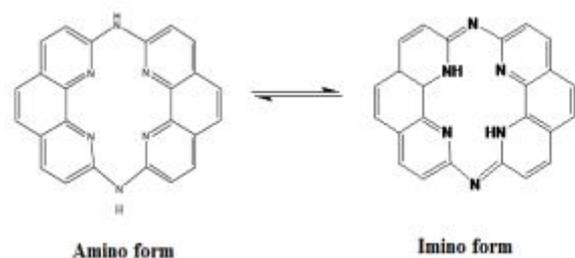


Figure - 2: Tautomeric forms of ligand L

3.2. Complexes

On the basis of elemental analysis the complexes were found to have general composition $M(\text{L})\text{X}_3$ and $M_1(\text{L})\text{X}_2$ (where $M = \text{Cr}$, $M_1 = \text{Cu}$ and $\text{X} = \text{Cl}^-$, Br^- , NO_3^- , CH_3COO^-) (Table-1). The molar conductance of chromium complexes in dimethyl sulphoxide (DMSO) indicates that they are 1:1 electrolyte in nature. Thus these complexes may be formulated as $[\text{Cr}(\text{L})\text{X}_2]\text{X}$. However copper complexes are non-electrolyte in nature. Thus these complexes may be formulated as $[\text{Cu}(\text{L})\text{X}_2]$.

3.3. Chromium (III) complexes

Magnetic moments of all Cr (III) complexes were recorded at room temperature. They show magnetic moments in the range 3.71 to

3.78 B.M. (Table 2) corresponding to three unpaired electrons [20]. The low value of magnetic moments may be due to low symmetry. On complexation, the position of IR spectral bands corresponds to $\nu_{\text{C}=\text{N}}$ is shifted towards lower side. This indicates that the coordination takes place through the nitrogen atoms of the imine group. Thus it is implied that the ligand behaves as hexadentate. The IR spectra of nitrate complexes show absorption bands in the region of 1464 - 1526 cm^{-1} (ν_5) ν_a (NO_2), 1167 - 1199 cm^{-1} (ν_1) ν_s (NO_2) and 778 - 806 cm^{-1} (ν_2) ν (NO). This indicates that the nitrate group coordinates in a unidentate manner [21-23]. A broad absorption band in the region of 1372 - 1384 cm^{-1} has also appeared which corresponds to uncoordinated nitrate group.

The electronic spectra of complexes display the transition in the range 18103 to 18865 cm^{-1} and 24376 to 28625 cm^{-1} , which may be assigned to the $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})(\nu_1)$ and $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{F})(\nu_2)$ spin allowed d-d transitions respectively. These transitions reveal that Cr(III) ion is in octahedral environment. The electronic spectra of the complexes also display the third transition in the range 33784 - 39063 cm^{-1} . In the octahedral environment Cr(III) complexes exhibits the third d-d transition corresponding to the $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})(\nu_3)$ above 30000 cm^{-1} but in this region the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand bands are also observed. Thus the third (ν_3) d-d transition is obscured by these transitions. Further, as the Cr(III) ion is a weak oxidizing agent as well as weak reducing agent, ligand-to-metal (LMCT) and metal-to-ligand (MLCT) charge transfer transitions are expected to appear only in the UV region of electronic spectra of Cr(III) complexes [24]. Thus, the charge transfer bands are also obscured by the high intensity intraligand bands. As a result, a broad band is appeared in the region 34364 - 37735 cm^{-1} .

The ligand field parameters like Racah inter-electronic repulsion parameter B, ligand field splitting stabilization energy 10 Dq , covalency factor β and ligand field stabilization energy (LFSE) have been calculated for the complexes. The energy associated with $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})(\nu_1)$ corresponds to the value of 10Dq . The value of B has been calculated by the transition energy ratio diagram. The complexes under study show the lower value of B than that of the free ion which indicates the orbital overlapping and delocalization of d-orbital. The covalency factor β is calculated by using the expression: $\beta = B_{\text{complex}}/B_{\text{free ion}}$, where value of B for Cr(III) ion is 1030 cm^{-1} [25]. The complexes show the value of β (0.58-0.82) (Table-3) less than unity which suggests the covalent nature of the metal ligand bond.

The spin Hamiltonian for chromium (III) complexes ($S = 3/2$) may be written as:

$$H = g\beta S.H. + D[S_z^2 - 5/4] + E[s_x^2 - S_y^2]$$

Table – 1: Molar conductance and elemental analysis data of the complexes.

Complexes	M.Wt	Color	Yield (%)	M.P. (°C)	Molar conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	Elemental analyses (%) Found (calculated)			
						Cr	C	H	N
[Cr(L)Cl ₂]Cl CrC ₂₄ H ₁₂ N ₆ Cl ₃	542.77	Green	65	286	82	9.38 (9.58)	52.89 (53.11)	2.35 (2.23)	15.21 (15.49)
[Cr(L)Br ₂]Br CrC ₂₄ H ₁₂ N ₆ Br ₃	676.12	Bluish green	60	288	79	7.72 (7.69)	42.72 (42.63)	2.00 (1.79)	12.59 (12.43)
[Cr(L)(NO ₃) ₂]NO ₃ CrC ₂₄ H ₁₂ N ₉ O ₉	622.45	Dark green	68	274	93	8.18 (8.35)	46.24 (46.31)	2.26 (1.95)	20.02 (20.26)
[Cr(L)CH ₃ COO] ₂ CH ₃ COO CrC ₃₀ H ₂₁ N ₆ O ₆	613.57	Light green	58	269	88	8.62 (8.47)	58.46 (58.72)	3.56 (3.46)	13.82 (13.70)
Cu(L)Cl ₂ CuC ₂₄ H ₁₂ N ₆ Cl ₂	518.87	Dark blue	60	258	13.4	12.16 (12.25)	55.79 (55.55)	2.75 (2.34)	16.21 (16.20)
Cu(L)Br ₂ CuC ₂₄ H ₁₂ N ₆ Br ₂	607.77	Blue	63	264	14.8	10.23 (10.46)	47.72 (47.43)	2.20 (1.99)	13.59 (13.83)
Cu(L)(NO ₃) ₂ CuC ₂₄ H ₁₂ N ₈ O ₆	571.99	Blue green	64	278	12.6	11.32 (11.11)	50.24 (50.39)	2.36 (2.12)	19.02 (19.59)
Cu(L)CH ₃ COO) ₂ CuC ₂₈ H ₁₈ N ₆ O ₆	566.07	Blue green	59	259	14.0	11.01 (11.23)	59.46 (59.41)	3.56 (3.21)	14.82 (14.85)

Table 2: Magnetic moment and electronic spectral data of the complexes

Complexes	μ_{eff} (B.M.)	λ_{max} (cm ⁻¹)
[Cr(L)Cl ₂]Cl	3.75	18521, 26240, 35555
[Cr(L)Br ₂]Br	3.78	18624, 25636, 33784
[Cr(L)(NO ₃) ₂]NO ₃	3.74	18865, 24376, 36914
[Cr(L)CH ₃ COO] ₂ CH ₃ COO	3.71	18103, 28625, 39063
Cu(L)Cl ₂	1.83	14203, 19658, 22502
Cu(L)Br ₂	1.86	14152, 19505, 22544
Cu(L)(NO ₃) ₂	1.95	14365, 19592, 22462
Cu(L)CH ₃ COO) ₂	1.92	14393, 19567, 22353

Table 3: Ligand field parameters of Cr(III) complexes

Complexes	Dq	B (cm ⁻¹)	B	LFSE (KJ mol ⁻¹)
[Cr(L)Cl ₂]Cl	1850	562	0.62	263.8
[Cr(L)Br ₂]Br	1864	649	0.58	268.2
[Cr(L)(NO ₃) ₂]NO ₃	1882	863	0.82	261.5
[Cr(L)CH ₃ COO) ₂ CH ₃ COO	1815	724	0.76	267.9

Table 4: EPR Spectral data of the complexes

Complexes	g_{\parallel}	g_{\perp}	g_{iso}	G
Cu(L)Cl ₂	2.211	2.0194	2.0838	10.88
Cu(L)Br ₂	2.204	2.0198	2.0804	10.53
Cu(L)(NO ₃) ₂	2.209	2.0190	2.0824	10.20
Cu(L)CH ₃ COO) ₂	2.207	2.0199	2.0845	10.45
[Cr(L)Cl ₂]Cl	-	-	1.96	-
[Cr(L)Br ₂]Br	-	-	1.99	-
[Cr(L)(NO ₃) ₂]NO ₃	-	-	1.98	-
[Cr(L)CH ₃ COO) ₂] CH ₃ COO	-	-	1.96	-

The ⁴F state of d³ ion in octahedral symmetry has the orbital singlet state lowest in energy with all excited state at much higher energies. The d³ ion has relatively long spin – lattice relaxation times and gives narrow EPR absorption line even at room temperature. In octahedral symmetry the ground state belongs to the ⁴A_{2g} irreducible representation and is connected through the spin orbit coupling to the excited ⁴T_{2g} states only for this reason the g and A terms are nearly isotropic even in highly distorted crystal fields. In d³ ions the symmetry of the crystal field is primarily exhibited through spin term D and E. In the crystal field theory the value of g is given by $g = 2.00023(1 - 4\lambda/10Dq)$.

The EPR spectra of the polycrystalline sample have been recorded at room temperature, values of g lies in the range 1.96–1.99 (Table-4). In the above expression 1 is the effective spin orbit coupling constant for the metal ion in the complex. Owen noted that the reduction of spin orbit coupling constant from the free ion value of 90 cm⁻¹ for Cr(III) can be employed as a measure of metal ligand covalency. It is possible to define the covalency parameters analogous to nephelauxtic parameter which is the ratio of the spin-orbit coupling constant for the complex and free ion. The spectra show a single broad line with peak to peak separation in the range 260-275 GHz.

3.4. Copper (II) complexes

Magnetic moment of all the Cu(II) complexes recorded at room temperature lie in the range 1.83-1.95 B.M. (Table 2) corresponding to one unpaired electron. Although the theory suggests that there should be some correlation between the magnitude of orbital contribution and the coordination geometry [26]. In practice it is not observed, presumably because of distortion and other variables like covalence. Only if there is an antiferromagnetic interaction between copper

pairs, in which case lower magnetic moments or even diamagnetic results. The data in the present complexes show absence of such interactions. All the complexes may be considered to have tetragonal geometries with planar coordination of the ligand around Cu²⁺ ion and the anions.

On complexation the position of IR bands corresponds to $\nu_{\text{C=N}}$ is shifted towards lower side. This indicates that the coordination takes place through the nitrogen atoms of the imine group. Thus it is implied that the ligands L behaves as hexadentate. The IR spectra of all the complexes show absorption bands in the region of 1382–1384 (ν_5), $\nu_a(\text{NO}_2)$, 1155–1198 (ν_1), $\nu_s(\text{NO}_2)$ and 792–825 cm⁻¹(ν_2) $\nu(\text{NO})$. This indicates that the nitrate group coordinates in a unidentate manner [27].

The electronic spectra of Cu(II) complexes show three bands in range of 14152-14393, 19505-19658 and 22353-22502 cm⁻¹ corresponding to tetragonal geometry which can be assigned to ²B_{1g}→²A_{1g}, and ²B_{1g}→²B_{2g} transitions, respectively. In all cases the transition ²B_{1g}→²B_{2g} is usually not observed as a separate band in the tetragonal field [28]. In some cases a band above 30000 cm⁻¹ has been observed. This may be due to charge transfer which could arise from the transfer of an electron from an orbital largely belonging to a central atom. The splitting of the ²E_g state is a measure of the planar and axial field.

The EPR spectra of the Cu (II) complexes were recorded as polycrystalline sample at room temperature. Spectra for polycrystalline sample exhibit absorptions typical for the mononuclear species with axial symmetry.

The absence of Cu-Cu interaction can be explained by proposing transitions, i.e. $\Delta M_s = \pm 2$ between two paramagnetic centers are negligible

[29]. The analysis of spectra gave $g_{\parallel} = 2.204-2.211$ and $g_{\perp} = 2.0190-2.0199$ (Table-4).

This supports that there is a considerable mixing of ground and excited state terms and also reflected in the magnetic moment values which are slightly greater than spin-only value for Cu(II), i.e. 1.83 to 1.95 B.M, which is indicating the formation of mononuclear Cu(II) complexes, the ratio $g_{\parallel} > g > g_{\perp} > 2.0023$ evaluated for all Cu(II) complexes, suggest that unpaired electron is localized in $d_{x^2-y^2}$ orbital and the spectral features are characteristics of tetragonally distorted octahedron.

In addition there is exchange-coupling interaction between the two copper centers explained by Hathaway^[30] expression $G = (g_{\parallel}-2)(g_{\perp}-2)$. According to Hathaway if the value of G is greater than four, the exchange interaction is negligible, where when the value of G is less than four a considerable interaction is indicated in solid complex. The calculated G values are given in Table-4, which is more than 4 that indicates that there is no metal-metal interaction.

4. CONCLUSION

Structure of the complexes on the basis of elemental analysis, molar conductance measurement, magnetic moment, IR, electronic and EPR spectral data, following structure may be proposed for the chromium (Fig.3) and copper (Fig.4) complexes.

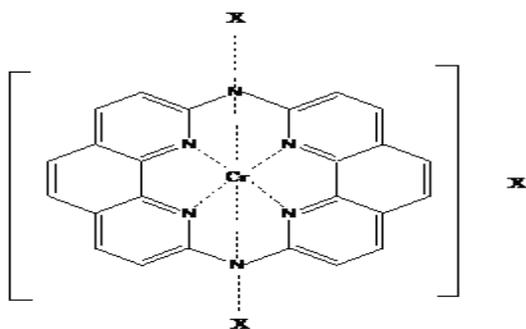


Figure - 3: Cr (III) complexes with ligand **L** (Where, **X** = Cl⁻, Br⁻, NO₃⁻, CH₃COO⁻)

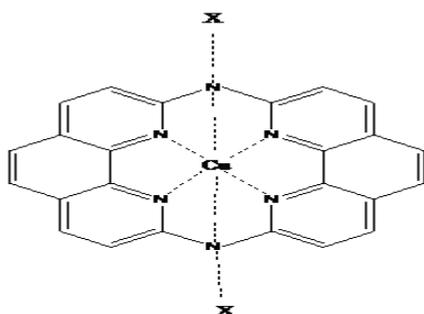


Figure - 3: Ca (II) complexes with ligand **L** (Where, **X** = Cl⁻, Br⁻, NO₃⁻, CH₃COO⁻)

Acknowledgements

The authors thank UGC for financial assistance and SAIF, IIT, Mumbai for recording EPR spectra.

5. REFERENCES

1. Fekner T, Gallucci J and Chan MK. J. Am. Chem. Soc., 2004; 126: 223.
2. Sessler JL, EKatayev E, Pantos GD and Ustynuk YA. Chem. Commun., 2004; 124: 1276,
3. Chandra S and Kumar R. Trans. Met. Chem., 2004; 29: 269.
4. Belanger S, JHup JT, Stem CL, Slone RV, Wastern DF and Carrell TG. J. Am. Chem. Soc., 1999; 121: 557.
5. Chandra S, Gupta LK and Gupta K. J. Ind. Chem. Soc., 2004; 81: 833.
6. Huzenkamp MF, Strucke AC, Cavolli E, Godel HU. J. Chem. Soc. Dalton Trans, 2000; 251.
7. Niasari MS and Amiri A. J. Mol. Cat., 2005; 235A: 114.
8. Singh DP, Kumar R and Tyagi P. Trans. Met. Chem., 2006; 31: 970.
9. Bhendkar AK, Vijay K and Raut AW. Acta Ciencia indica (chemistry), 2004; 30: 29.
10. Mohamed GG. Spectrochim Acta A, 2006; 64(1): 188.
11. Bibhesh KS and Devjani A. Inter. J. of Basic and App. Chem. Sci., 2012; 2(1): 84.
12. Karlin KD and Zubieta J. Biological and Inorganic Copper Chemistry, Adenine Press Guilderland, New York, 1986.
13. Fornica M, Fusi V, Micheloni M, Pontellini R and Romani P. Polyhedron, 2000; 19: 2501.
14. Lampeka YD and Gavrish SP. Polyhedron, 2000; 19: 2533.
15. Mewis RE and Archibald S. J. Coordination Chemistry Reviews, 2010; 254: 1686.
16. Rakesh Kumar and Sangeeta Oberai. Adv. Appl. Sci. Res., 2011; 2(5): 1.
17. GAO EQ, Sun HY, Liao DZ, Jiang ZH and Yan. Polyhedron, 2002; 21: 359.

18. Halcrow BE and Kermack WO. J. Chem. Soc., 1946; 156.
19. Caughey WC, Albewn JO, Fujimoto WY and York JL. J. Org. Chem., 1966; 31: 2631.
20. Lever ABP. Inorganic Electronic Spectroscopy", 1st ed. Elseiver, Amsterdam, 1968.
21. Chandra S, Gupta LK, Bansal U. *Spectrochim Acta A*, 2006; 65: 792.
22. Gerioch M and Mason R. J. Chem. Soc., 2007; 296.
23. Hathaway BI and Billing DE. Coord. Chem. Rev., 1970; 5: 143.
24. Chandra S. *Shewata, Spectrochim Acta A*, 2008; 71: 720.
25. Figgis BN. Introduction to Ligand Fields. 1st ed. Wiley Eastern Limited, New Delhi, 1966.
26. Swamy SJ and Pola S. *Spectrochim Acta A*, 2008; 70: 929.
27. Duce PM, Kingston BM, Lappert MF, Srivastava RC, Frazer MJ and Newton WE. J. Chem. Soc. A, 1969; 2814.
28. Hathaway BJ, Dudely RJ and Nichollas P. J. Chem. Soc., 1968; 1845.
29. Chandra S, Gupta LK and Sangeetika, *Spectrochim. Acta A*, 2005; 62:453.
30. Hathaway BJ. Essays in Chemistry, (Ed. J.N.Bardly and R. D. Gillard), Academic press, New York, 61, 1971.