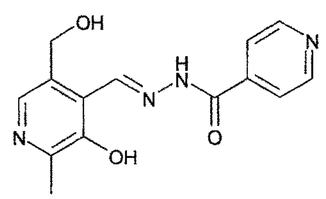
CHAPTER 4

Angular Trinuclear Complexes with bis(oxalo)dihydrazones of aromatic aldehydes: Effect of end Group variation.

4.1 Introduction

Hydrazine and its derivatives like acyl and aroyl hydrazines provide important building blocks for the design of polyfunctional chelating ligands. This is because of the ease of condensing hydrazine with various multidentate aldehydes, ketones, esters and acid chlorides. The interest in these compounds is also because of the interesting redox and, more importantly, the biological activity associated with them[1-5]. Acyl hydrazones of salicylaldehyde, pyridoxalisonicotinoylhydrazone (PIH), and their complexes with

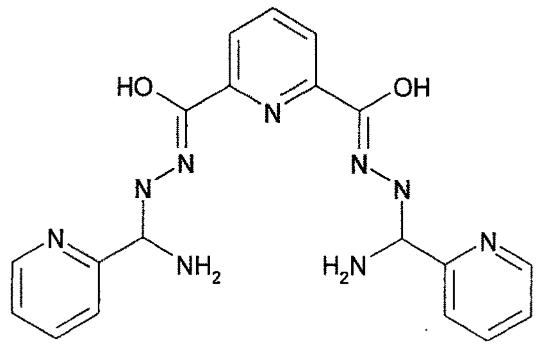


PIH

transition metal ions are some of the most studied.[1,2,4] The derivatives of pyridoxal and 2-hydroxy benzaldehyde with isonicotinichydrazide or benzhydrazide were found to mobilize iron significantly from ^{59}Fe-labeled reticulocytes. The effectiveness of the compounds tested decreases in the following order, PIH, pyridoxalbenzoylhydrazone, 2-hydroxy benzal benzoyl hydrazone, pyridoxal valine schiff base and pyridoxal.[4] The efficiency of these compounds exceeded the ability of common chelators such as desferrioxamine, bipy, nitrilotriacetic acid etc to mobilize iron from reticulocytes.[1] Because of the iron chelating ability, these compounds can be useful as antiproliferative, antineoplastic agents[6,7] for the treatment of cancers, which are sensitive to iron chelation therapy. A variety of acetyl, pyridyl, furoyl and several other acyl or aroyl hydrazones and their complexes involving pyridoxal, salicyldehyde and 2-hydroxy napthaldehyde benzoyl hydrazones with hydroxyl, methyl, nitro, amino, t-butyl, methoxy or halogen substitutions on the ring have been studied. They all have been found to be far better antiproliferative agents than classical drugs like DFO (Desferyoxamine)[8]. PIH being lipophilic can mobilize intracellular iron and replace transferrin.[9,10] Copper(II) and gadolinium(III) complexes with PIH have also been found to be cytotoxic.[11] A series of transition metal complexes of salicylaldehyde acyl hydrazone and their cytotoxicity has been reported. Extensive variation in the acyl group was made from acetic to dodecenoyl and oleic acid to the highly polar cyano- and fluoro acetic groups. The cytotoxicity of the complexes was found to decrease in the order Cu>Ni>Zn=Mn>Fe=Cr>Co.[12] In general, it was found that the more lipophilic complexes have greater cytotoxicity. Steric and electronic factors were found to play only minor role.[12] Salicyldehyde benzoyl hydrazone itself has bactereostatic and antitumor activity while its copper(II) complex is found to be hundred times more active than the ligand itself.[13,14] copper(II) complex of salicyldehyde and acetyl hydrazone has radioprotective and cytotoxic properties.[12,15] Binuclear complexes of di(pyridoxal)hydrazone and di(salicylaldehyde)hydrazones with variable length methylene linkers $-(CH_2-)_n$ were found to form oligomers with chain lengths >5.[16] SIH has also shown antioxidant effects and hence is useful in the prevention of H_2O_2 injury.[17]

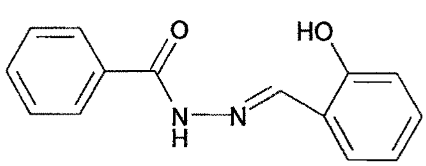
Because of the versatility associated with hydrazine derivatives their combinations with bi- or polynucealting ligands are thought to be more interesting since they can enable a lot of variations in the coordination geometry and electron density around metal ions. Oxalo dihydrazide is one such efficient binucleating building block.[18] Synthesis of number of oxalyl dihydrazines has been reported. However, hardly any of these have been explored so far as ligand for bi- or polynuclear complexes. Bis-(salicyldehyde) iminodiacetyl hydrazone has been used as trinucleating ligand occupying three coordination positions around each of the three copper ions.[19] The copper(II) centers were found to be weakly antiferromagnetically coupled. The complex used, belongs to a very similar family of extensively studied category of diazine bridged copper complexes. A series of diazine copper(II) complexes were studied earlier by Thomson *et al.* They could correlate the value of exchange coupling constant J with the torsion angle α between Cu-N-N-Cu centers and the diazine i.e. the bridge angle. The relation was shown to be $J = 2.233\ \alpha - 183.7$.[20]

Dinuclear transition metal complexes with symmetrical and unsymmetrical dihydrazones derived from various aldehydes like, derivates of pyridine aldehyde (pyridine-2-carbaldehyde), diacetyl pyridine, dipyridyl ketone with hydrazides of picolinic acid and pyridine-2,6-dicarboxylic acid[21] $(2poap)_2$ have been



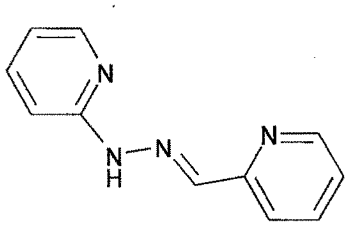
2poap

reported and their crystal structures have been studied.[21-27] Aroylhydrazones of pyridoxal and of salicyldehyde like, pysal and pypy, chelate transition metal ions in an analogous manner with Gly-His-Lys-copper(II) complexes and studied for growth inhibition of the cultured Fibrosarcoma cells.[5]



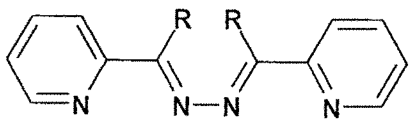
pysal

and



pypy

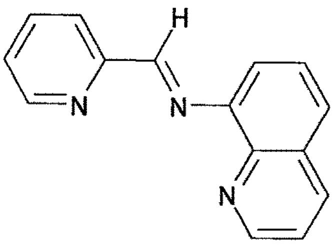
Similar complexes synthesized by condensation of oxalodihydrazides with various pyridyl aldehydes.[28-33], dipyridyl ketone to acetyl pyridine, picolylamide have also been reported.[34-42] All the polydentate ligands mentioned above have flexible linkers between terminal donor units and hence can lead to the formation of helicate structures[28-33] and can form self assembled clusters and grids.[22,34] The diazine group in these complexes acts as an efficient mediator of spin exchange. The open chain polydentate diazines based on N-N bond fragments with the following type, display several possible mononucleating and dinucleating modes due to flexibility of the ligand viz.



R
R
N
N
N
N

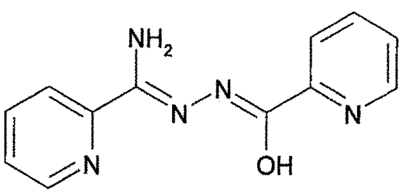
,

(a)



H
N
N
N

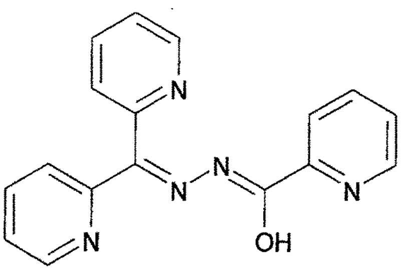
(b)



NH2
N
N
N
N
OH

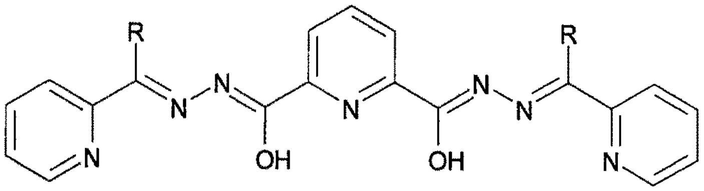
,

(c)



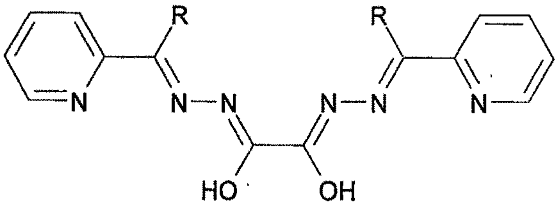
N
N
N
N
N
OH

(d)



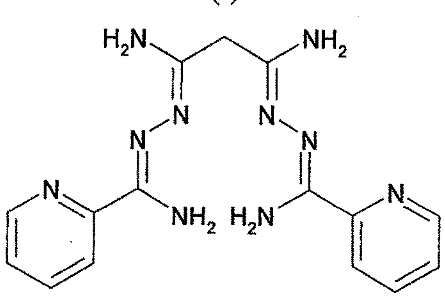
R
R
N
N
N
N
N
N
N
OH
OH

(e)



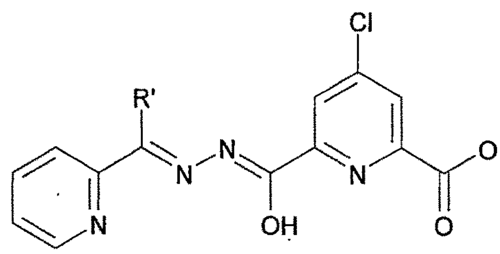
R
R
N
N
N
N
N
N
HO
OH

(f)



H2N
NH2
N
N
N
N
N
N
NH2
H2N

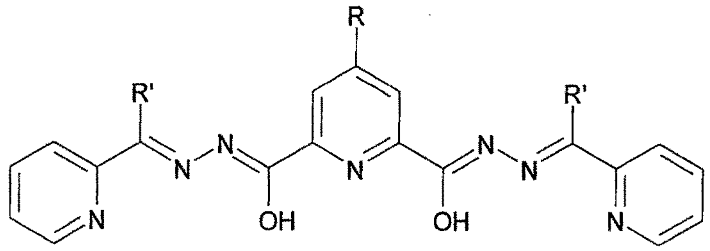
(g)



(h)

Above ligands, where R may be different substituents, can form mono nuclear[43-46], dinuclear[36,47-52], trinuclear[53] or tetranuclear[54,55] complexes.

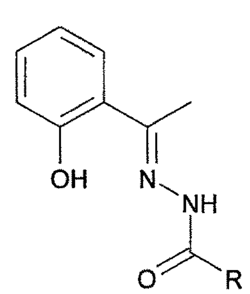
The tetradentate ligand (b), (poap) has been shown to organize Mn(II), cobalt(II), nickel(II) and copper(II) centers in to square homo tetranuclear clusters with just alkoxide bridges between the metal centers. These systems display dominant antiferromagnetic exchange, except the copper containing cluster, where ferromagnetic coupling prevails.[23] The heptadentate ligand (e), where R = NH_2, forms self assembled 3x3 nonamanganese grids involving oxygen bridges, shows very weak ferromagnetic property and five equivalent redox potentials in electrochemical studies.[22] The ligand po2p (d) has a linear arrangement of copper(II) centres linked by trans arrangement of N-N single bonds. A d_{x2-y2} magnetic ground state assigned to each metal and the trans diazine bridging leads to a strong antiferromagnetic coupling relating the twist of the copper magnetic planes around the N-N bond to the exchange integral.[21] The ligand (f), where R = NH_2 (pttp), R = CH_3 (mpttp), R = 2-pyridyl (ppttp) were also studied by Thomson et.al.[21] A disubstituted central 2,6-pyridine fragment represents a rigid fragment connecting the terminal hydrazone groups, and is responsible, in part for the grid formation in the complexes formed by the ligands mapttp (g) with manganese(II) and 2pyoap (h) with nickel(II). In these cases the paramagnetic metal centers are well separated and have a weak antiferromagnetic coupling or non-existent spin exchange.[28] The 4 and 2,6-disubstitued pyridine bridged ligands like (i)



(i)

were also studied. With R' = Cl and another ligand where R' = Ph and R = Cl, did not form the nonanuclear grids but with copper(II) form the Cu_8 pinwheels with moderately strong antiferromagnetic interactions. Copper(II) complex with ligand (h) was also studied. This typical copper trinuclear complex shows moderately strong antiferromagnetism. Direct bridging between copper ions occurs through μ_2-N-N diazine groups and longer O-C-N hydrazone connections, leading to moderately strong antiferromagnetic exchange between adjacent metal centers.[56] Studies on dinuclear copper(II) complexes of a series of open chain N_4 and N_5 diazine ligands have shown that a variety of geometrical confirmations can be created, which depend on co-ligands and reaction conditions and that a linear relationship exists between the rotation angle and the exchange integral over a 105° range with ferromagnetic coupling at angles less than 80° and antiferromagnetic coupling at >80°.[57-59]

The copper chelating reagent cuprizone i.e. bis(cyclohexaamine oxalyl dihydrazone) is found to inhibit benzylamine oxidase by binding with pyridoxal phosphate.[60] It is shown that complexation of the aroyl hydrazone increases their cytoxicity with copper than with iron.[61] Salicyldehyde benzoyl hydrazone (j),



(j)

and analogous complexes can behave as neutral, mononegative or dinegative tridentate ONO donors.[53,62,63] These complexes exist as dimers because of the bridging ability possessed by the oxygen atoms. Binuclear copper(II) complexes of these ligands have strong antiferromagnetic interaction with singlet-triplet gap between 172 to 276 cm^{-1}.[64] Salicyldehyde hydrazone of acid hydrazide of 5-naproxen forms infinite one dimensional chain with strong antiferromagnetically coupled intramolecular hydrogen bonds leading to an E-configuration.[65] Thus it can be seen that the diazine containing ligands can provide a variety of patterns in the structure and magnetic behaviour of the related complexes.

In the present work, use of oxalodihydrazide in the synthesis of twelve new trinucleating ligands, having three coordination pockets to hold the metal ion is demonstrated. By changing the end group coordination pocket, variation in the electrochemical and magnetic properties is expected to get modified at the molecular level. All of the ligands and complexes have been characterized and their magnetic and electrochemical properties have been studied.

4.2 Experimental

Materials

AR quality diethyl oxalate, hydrazine hydrate, sal, van, naph, brsal, 3m2hacph and cupric acetate monohydrate for the synthesis of trinucleating ligands and their copper complexes, and silver nitrate for cyclic voltammetry, were purchased from Merck. Methanol, DMF and DMSO used for conductivity measurements and voltammetric studies, respectively, were of AR or spectroscopic grade and purchased from Merck. AR quality tetrabutylammonium perchlorate (TBAP), used in voltammetric studies was obtained from Fluka. All reagents were used as received. All solvents used in the synthesis were distilled before use.

Synthesis of decadentate trinucleating ligands

Synthesis of oxalodihydrazide (oxd)

21.540g (20ml, 0.146mmol) diethyl oxalate was kept in 60ml of ethanol in 100ml flat bottom flask and heated to reflux. At reflux condition, 10ml ethanolic solution of 21.920g (21.28ml, 0.438mol) of hydrazine hydrate was added in the previous solution, slowly and drop wise. During the addition, white coloured solid product separated out. Addition was completed in half an hour and the reaction mixture was further allowed to reflux for 5hrs to ensure completion of the reaction. The product was filtered, washed several times with 10ml portions of ethanol and dried in air m. p. = 285°C (dec). m. p. = 285°C (dec).

Synthesis of oxalodihydrazide salicylhydrazone, (oxdsal)

1.888g (16mmol) of **oxd** was suspended in 20ml of ethanol and refluxed for 20min. In the reflux condition, 10ml ethanolic solution of **sal** 1.953g (1.674ml, 16mmol) was added slowly and drops wise from dropping funnel. Pure white colored **oxd** then turned to off white, as the reaction completed after 7hrs.

The hydrazones**, oxdvan**, **oxdnaph**, **oxdbrsal** and **oxd3m2hacph** have been prepared by following a similar procedure and taking equivalent amounts of van, naph, brsal and 3m2hacph in place of sal.

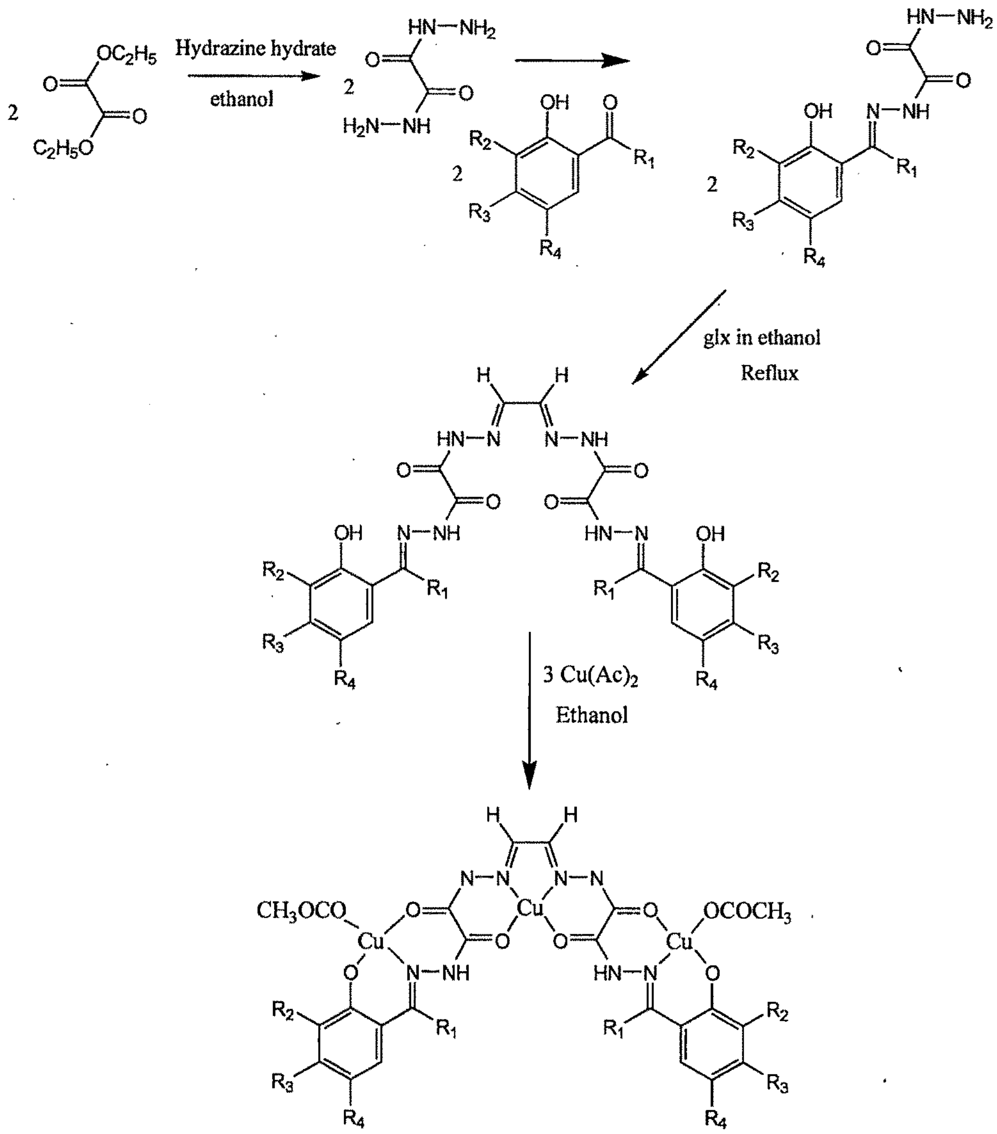
Synthesis of glyoxal dihydrazone of oxalodihydrazide salicylhydrazone, (oxdsalglx)

1.00g (4.500mmol) of **oxdsal** was suspended in 40ml of ethanol and was heated to reflux. At reflux condition 0.473g (2.252mmol) of glyoxal in 20ml ethanol, was added slowly and drop wise from a dropping funnel. The solution was allowed to reflux further for 1hr, while the progress of the reaction was monitored by TLC. A light yellow product was filtered, washed with ethanol and dried in air. Purity of the product was ensured by single spot on TLC. Similar procedure was followed for the synthesis of other five trinucleating ligands with equivalent quantities of **oxdvan**, **oxdnaph**, **oxdbrsal** and **oxd3m2hacph** in place of **oxdsal**, to synthesize, **oxdvanglx**, **oxdnaphglx**, **oxdbrsalglx** and **oxd3m2hacphglx**. Yields, elemental analyses and melting points of all the newly synthesized ligands are given in the Table 4.1.

Synthesis of trinuclear complexes

Trinucleating ligand **oxdsalglx,** 0.500g (1.073mmoles), was suspended in 15ml of ethanol in flat bottom flask and 30ml ethanolic solution of cupric acetate monohydrate 0.643g (3.2188mmol, 5% excess) was added from dropping funnel slowly and drop wise. During the addition of metal ion solution, the light yellow colored ligand dissolved and new green coloured microcrystalline solid started appearing. After completion of the addition of metal ion solution, the mixture was allowed to reflux for 6hrs to ensure completion of the reaction. The product was filtered, washed thoroughly with ethanol (10 x 10ml) and dried in air.

Scheme 4.1: Synthesis of oxdglx complexes.



Where the trinuclear complexes are,

[Cu_3oxdsalglx]$(Ac)_2$ **(M_1)**, R_1, R_2, R_3, R_4 = H.

[Cu_3oxdvanglx]$(Ac)_2$ **(M_2)**, R_2 = OCH_3, R_1, R_3, R_4 = H.

[Cu_3oxdnapglx]$(Ac)_2$ **(M_3)**, R_1, R_2 = H, R_3, R_4 = -CH=CH-.

[Cu_3oxdbrsalglx]$(Ac)_2$ **(M_4)**, R_1, R_2, R_3 = H, R_4 = Br.

[Cu_3oxdacphglx]$(Ac)_2$ **(M_5)**, R_1 = CH_3, R_2, R_3, R_4 = H.

[Cu_3oxd3m2hyacphglx]$(Ac)_2$ **(M_6)**, R_1, R_2 = CH_3, R_3, R_4 = H.

The reaction was repeated using equivalent amounts of the trinucleating ligands **oxdvanglx**, **oxdbrsalglx**, **oxdnaphglx**, **oxdacphglx** and **oxd3m2hyacphglx** in place of **oxdsalglx** and equimolar quantities of cupric acetate monohydrate. All six new trinuclear complexes were obtained in moderate to good yields.

Synthesis of ligands and complexes are summarized in Scheme 4.1.

Physical Measurements

All physical measurements, cyclic voltametric studies, FAB-Mass analysis were recorded using the instruments as mentioned earlier in chapter two. (page no.79)

4.3 Results and Discussion

Characterization of dioxamide ligands

The ligands were obtained in good yields. The elemental analysis of the ligands was found to be matching within appreciable range with the values calculated from the suggested formulae. In the FTIR spectrum of the ligands following important features have been observed which confirm their formation.

Table 4.1 Yield, elemental analysis and physical constants of oxdglx type ligands.

Sr. No.	Ligands	Yield (%)	Elemental Analysis (%) C	H	N	m.p. (°C)
1.	oxdsalglx $C_{20}H_{18}O_6N_8$	88	51.99 (51.50)	3.59 (3.86)	24.43 (24.03)	286 (dec)
2.	oxdvanglx $C_{22}H_{22}O_8N_8$	48	50.19 (50.51)	4.58 (4.18)	21.62 (21.29)	285 (dec)
3.	oxdnapglx $C_{28}H_{22}O_6N_8$	45	59.10 (59.36)	3.75 (3.80)	20.16 (19.78)	270 (dec)
4.	oxdbrsalglx $C_{20}H1_6O_6N_8Br_2$	32	38.02 (38.46)	2.63 (2.56)	17.96 (17.94)	266 (dec)
5.	oxdacphglx $C_{22}H_{22}O_6N_8$	50	53.20 (53.44)	4.30 (4.44)	22.62 (22.67)	276 (dec)
6.	oxd3m2hacphglx $C_{24}H_{26}O_6N_8$	54	55.02 (55.17)	5.48 (4.98)	21.59 (21.45)	272 (dec)

^{1}H NMR spectra of Ligands

The ^{1}H NMR spectra of ligands **oxdsalglx** and **oxdvanglx** were recorded in mixed d6-DMSO-$CDCl_3$ solvents.

The ligand **oxdsalglx** has C_2 symmetric structure. Both the aromatic protons (a) (**Fig.4.1**), show a triplet at 6.91ppm corresponding to two protons. The next double doublet has been observed at 7.3ppm corresponding to one ring protons (b). Aromatic proton (c) has been observed to resonate at 7.3ppm as a doublet corresponding to one proton. Protons in the imine group –CH=N- have been observed at 7.93ppm showing a sharp singlet corresponding to one proton (d). The imine proton (e), corresponding to Ar-CH=N-, was observed at 8.74ppm as a singlet. One of the proton corresponding to –NH (f), was observed at 11.31 ppm showing a sharp singlet and another –NH, i.e. proton (g), was observed at 12.69ppm with a sharp singlet. Thus the formation of **oxdsalglx** is confirmed.

In the ^{1}H NMR of **oxdvanglx** (**Fig.4.2**), a sharp singlet corresponding to six –OCH_3 (a) protons, has been observed at 3.87ppm, aromatic proton (b), was observed at 6.86ppm, giving a triplet corresponding to two protons. Both the aromatic protons (c) show double doublet at 7.0ppm corresponding to four protons. Protons corresponding to –CH=N- (d), have a sharp singlet at 7.99ppm, while another –CH=N (e) has a singlet at 8.75ppm. The two amide protons –NH (f) and -NH (h) have two singlets at 10.12 and 12.74ppm, respectively. The –OH protons shows a broad peak at 11.32ppm corresponding to two protons. All the values confirm the suggested structure of the trinucleating ligand, **oxdvanglx**.

All these values confirm the formation of ligand as per the suggested formula.

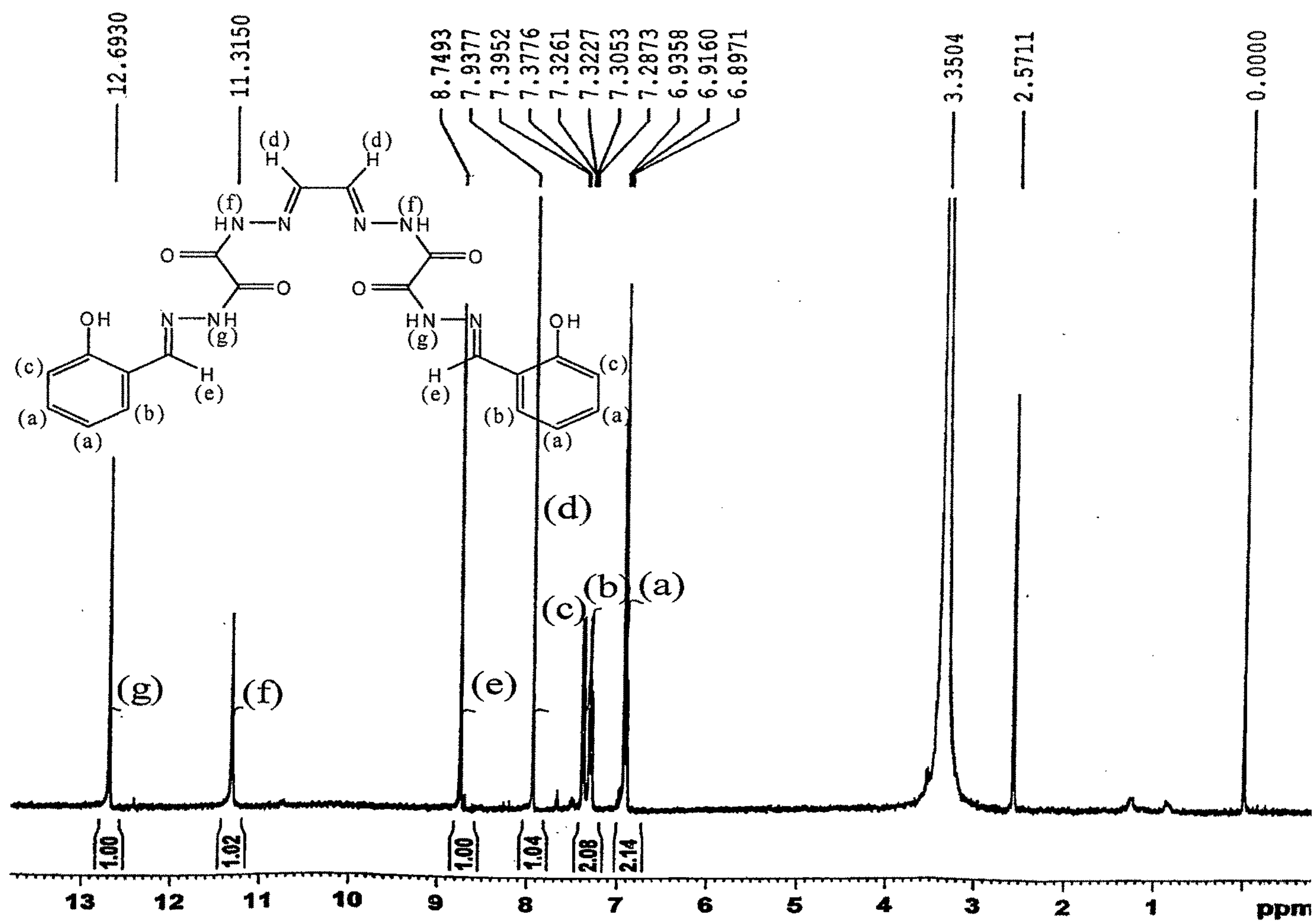


Fig.4.1 ^{1}H NMR spectrum of the ligand **oxdsalglx** in DMSO-$CDCl_3$.

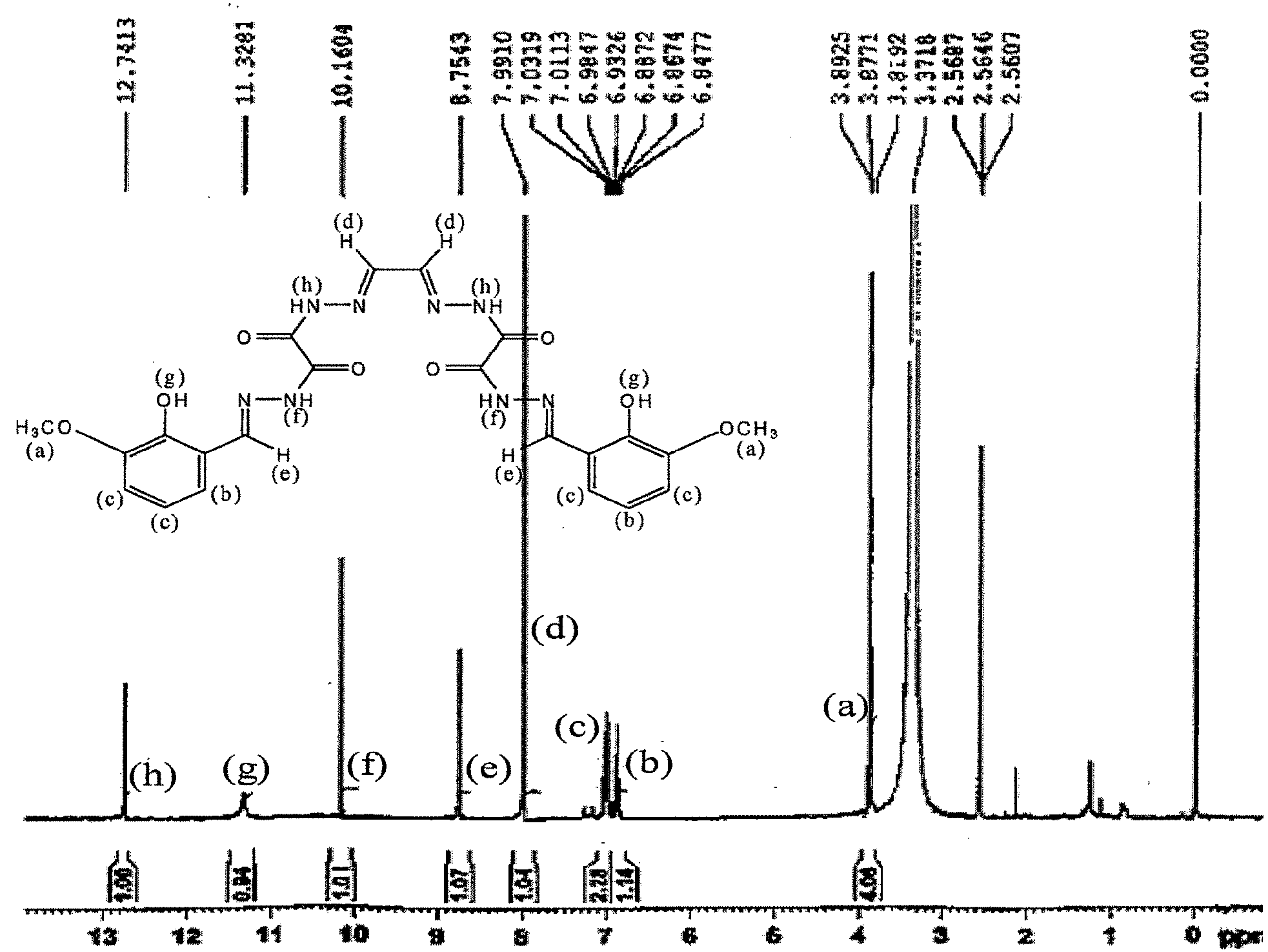


Fig.4.2 ^{1}H NMR spectrum of the ligand **oxdvanglx** in DMSO-$CDCl_3$.

Characterization of the trinuclear Complexes

The complexes were obtained in good yields. The elemental analyses of all the complexes are agreeable with the values calculated from the formulae suggested in Table 4.2.

Table 4.2 Yield and Elemental analysis of the **oxdglx** Complexes.

Sr. No.	Complex	Yield (%)	Elemental Analysis (%)		
			C	H	N
1.	**[Cu_3oxdsalglx]$(Ac)_2$** $C_{24}H_{20}O_{10}N_8Cu_3$	78	37.37 (37.46)	2.59 (2.66)	14.53 (14.37)
2.	**[Cu_3oxdvanglx]$(Ac)_2$** $C_{26}H_{24}O_{12}N_8Cu_3$	82	37.56 (38.02)	2.88 (3.29)	13.48 (13.67)
3.	**[Cu_3oxdnapglx] $(Ac)_2$** $C_{32}H_{24}O_{10}N_8Cu_3$	86.66	44.10 (44.49)	2.75 (3.24)	12.86 (13.07)
4.	**[Cu_3oxdbrsalglx]$(Ac)_2$** $C_{24}H_{18}O_{10}N_8Br_2Cu_3$	79.63	31.02 (31.49)	1.93 (2.35)	12.06 (12.46)
5.	**[Cu_3oxdacphglx]$(Ac)_2$** $C_{26}H_{24}O_{10}N_8Cu_3$	79.19	39.06 (39.49)	3.00 (3.23)	14.02 (14.38)
6.	**[Cu_3oxd3m2hacphglx]$(Ac)_2$** $C_{28}H_{28}O_{10}N_8Cu_3$	73.58	40.64 (41.13)	3.38 (3.71)	13.54 (14.00)

FAB mass spectra of the complexes **[Cu_3oxdsalglx]$(Ac)_2$**, **[Cu_3oxdvanglx]$(Ac)_2$** and **[Cu_3oxdnapglx]$(Ac)_2$** have been recorded using m-nitrobenzylalcohol as matrix. Though the complexes have limited solubility in this solvent, peaks corresponding to the parent ions and other important fragments could be identified.

The trinuclear complex **[Cu_3oxdsalglx]$(Ac)_2$** was analyzed by FAB-Mass spectrometry **(Fig.4.3)**. [Cu_3oxdsalglx]$^{2+}$/2 was found to be present at m/Z 328 for the calculated m/Z 327.12. The fragments like [Cu_3oxdsalglx]$^{2+}$+H^+/3 at m/Z 216 [Cu_3oxdsalglx]$(Ac^-)_2$+H^+ at m/Z 769 and [Cu_2H_2oxdsalglx].H_2O^{2+}/2 at m/Z 307 confirm the for formation of complex with the calculated m/Z 769.12. The next fragment [Cu_3oxdsalglx]Ac^- was observed to be at m/Z 710, which was calculated to be m/Z 710.12. The fragment [Cuoxdsalglx], was observed at m/Z 527 which was found to be at m/Z 527.

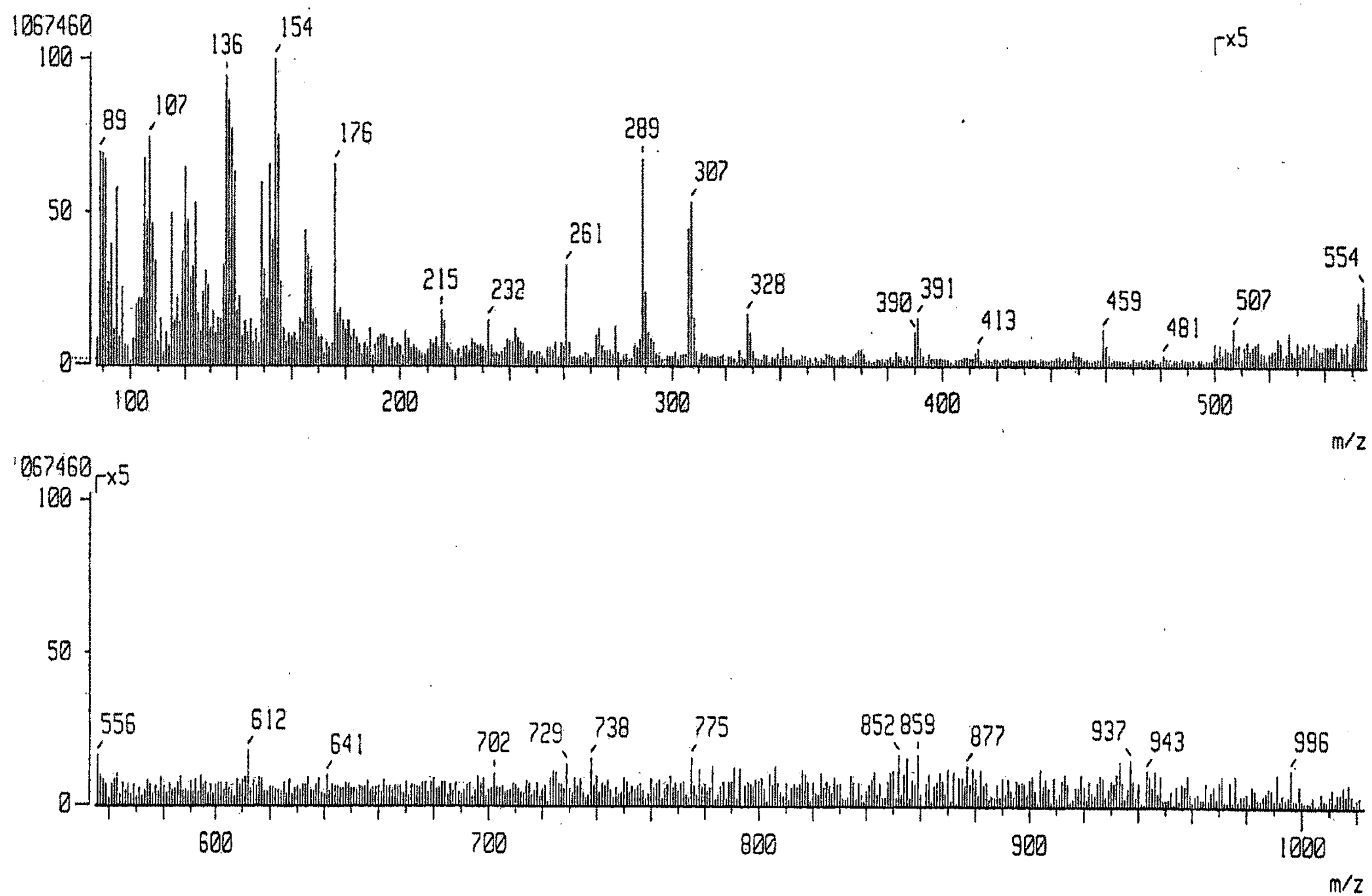
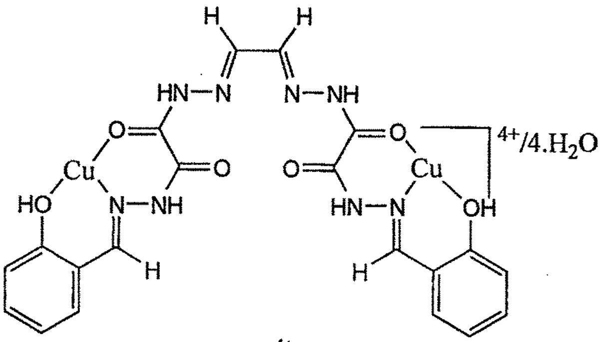
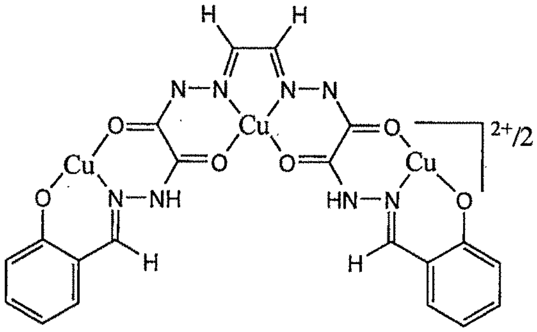


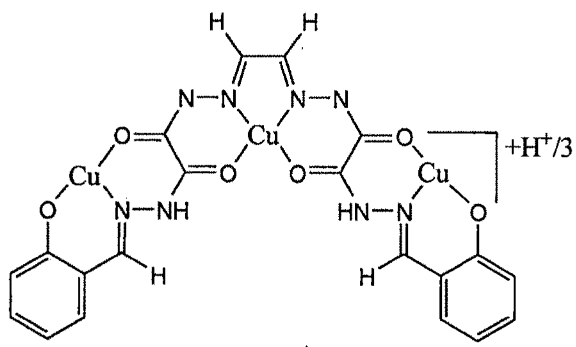
Fig.4.3 FAB-Mass spectrum of complex **[Cu_3oxdsalglx](Ac)$_2$.**



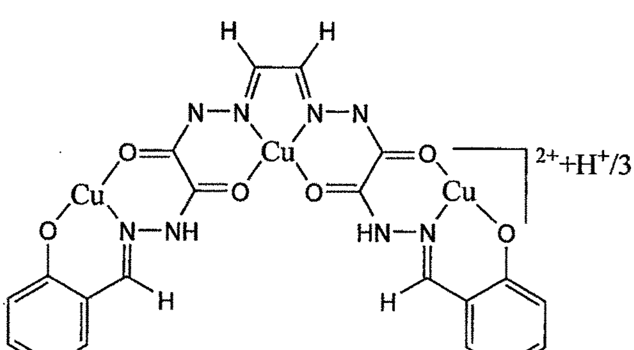
[Cu_2H_2oxdsalglx].H_2O^{4+}/4 observed at m/Z at 307.



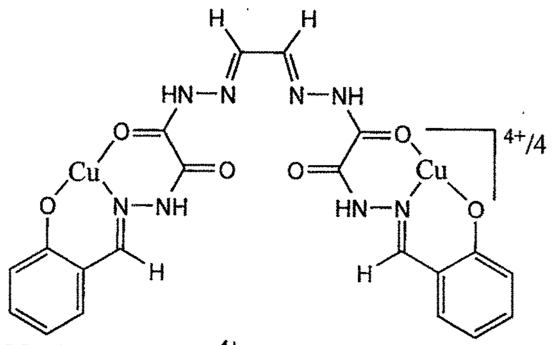
Parent ion peak corresponding to **[Cu_3oxdsalglx]$^{2+}$/2** at m/Z = 328.



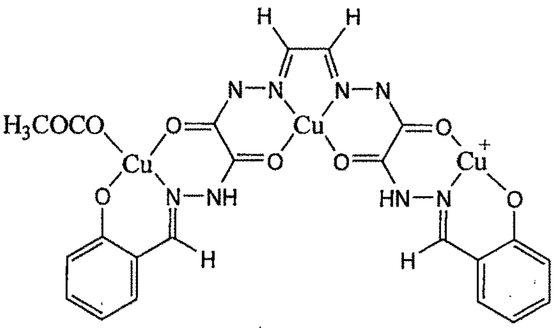
[Cu_3oxdsalglx]+H^+/3 at m/Z = 217.



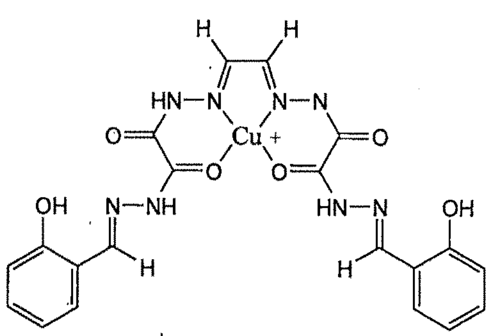
[Cu_3oxdsalglx]$^{2+}$+H^+/3 observed m/Z at 217.



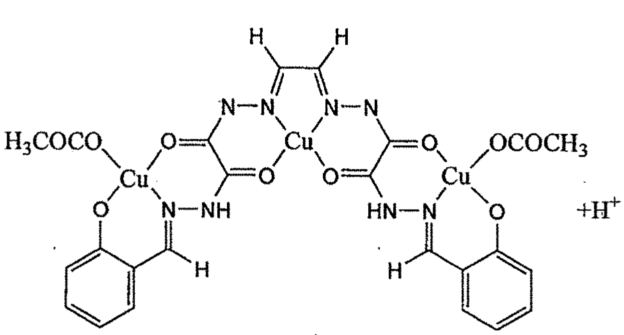
$[Cu_2H_2oxdsalglx]^{4+}/4$ observed at m/Z at 289.



$[Cu_3oxdsalglx](Ac)^+$ observed at m/Z 710.

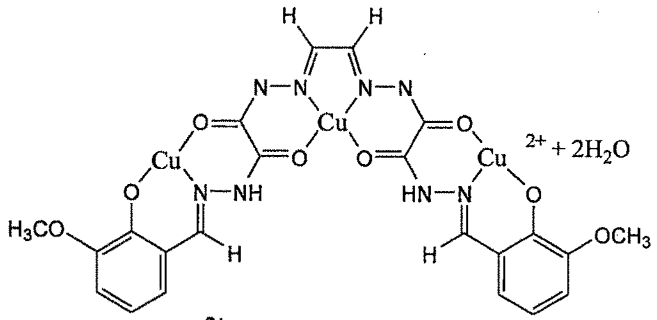


$[Cooxdglx]^+$ is observed at m/Z = 527.

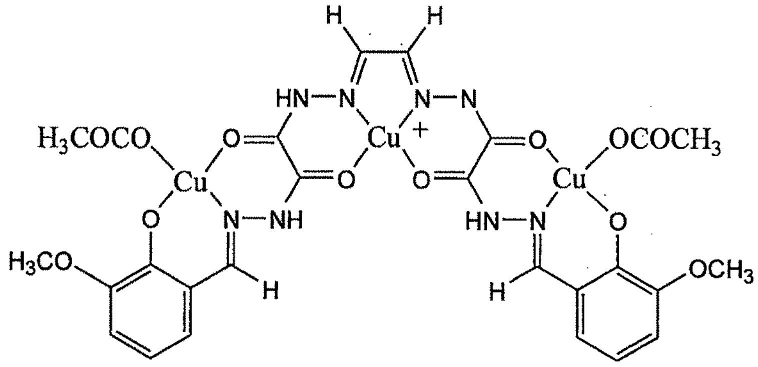


$[Cu_3oxdsalglx](Ac^-)_2$+H$^+$ observed at m/Z at 769.

In the FAB mass spectrum of the complex **[Cu_3oxdvanglx]$(Ac)_2$, (Fig.4.4)**, the parent ion peak corresponding to the whole molecule with two acetates, was observed at m/Z 832 (calcd.831) which confirms the formation of the trinuclear complex [Cu_3oxdvanglx]$(Ac)_2$. Further this complex with one acetate ion shows the peak at m/Z 773 (calcd.772) and the cationic complex [Cu_3oxdvanglx]$^{2+}$/2 with $2H_2O$ shows a peak at m/Z at 391 (calcd.392). These fragments support the complex formation. Copper clusters were observed to found at the higher molecular weights like [Cu_3oxdvanglx]$(Ac)_2$+Cu at m/Z 896 (calcd.896) for one extra copper like [Cu_3oxdvanglx]$(Ac)_2$+Cu+2H, at m/Z 961 (calcd.958), corresponding to [Cu_3oxdvanglx]2Ac$^-$+2Cu+2H, at m/Z 1019 the fragment corresponding to [Cu_3oxdvanglx]$(Ac)_2$+3Cu (cluster), calculated m/Z was 1021. All these fragments confirm the formation of complex.



[Cu_3oxdvanglx]$^{2+}$/2+$2H_2O$ is observed at m/Z at 391.



[Cu_3oxdvanglx]$(Ac)_2$ fragment is observed at m/Z 832.

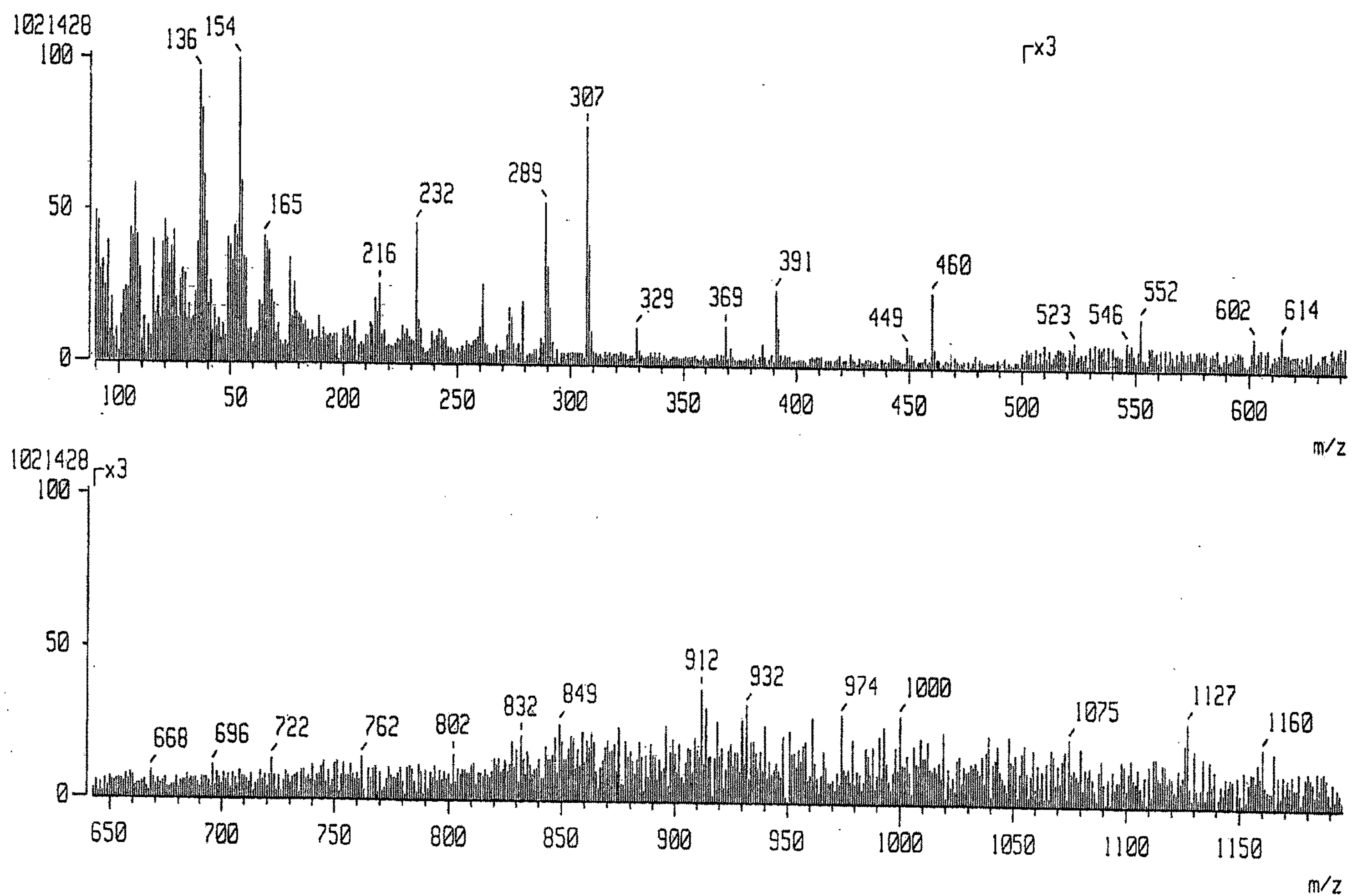
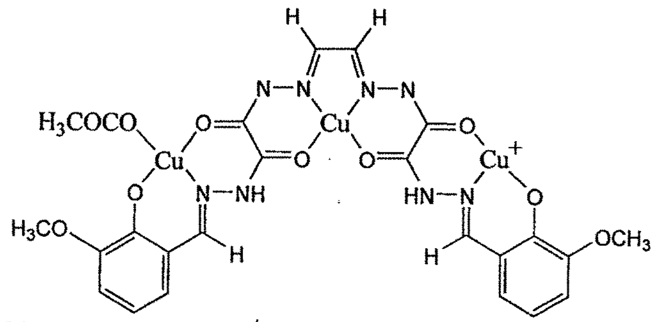
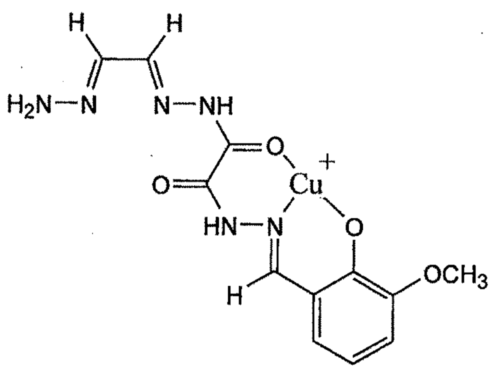


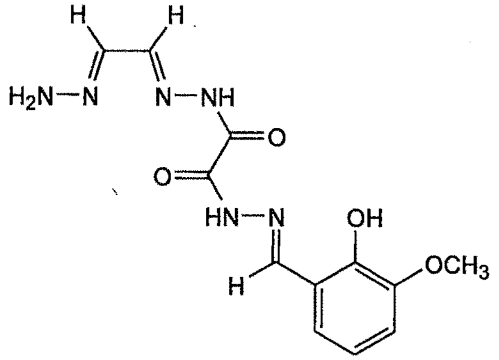
Fig.4.4 FAB-Mass spectrum of complex **[Cu_3oxdvanglx](Ac)$_2$**.



$[Cu_3oxdvanglx](Ac)^+$ fragment is observed at m/Z 773.



$[C_{12}H_{13}O_4N_6Cu]$ at m/Z = 369 (369).



$[C_{12}H_{13}O_4N_6]$ at m/Z at 307 (306).

Further the smaller fragments like m/Z at 369 and 307 confirms the formation of complex as per the proposed structures.

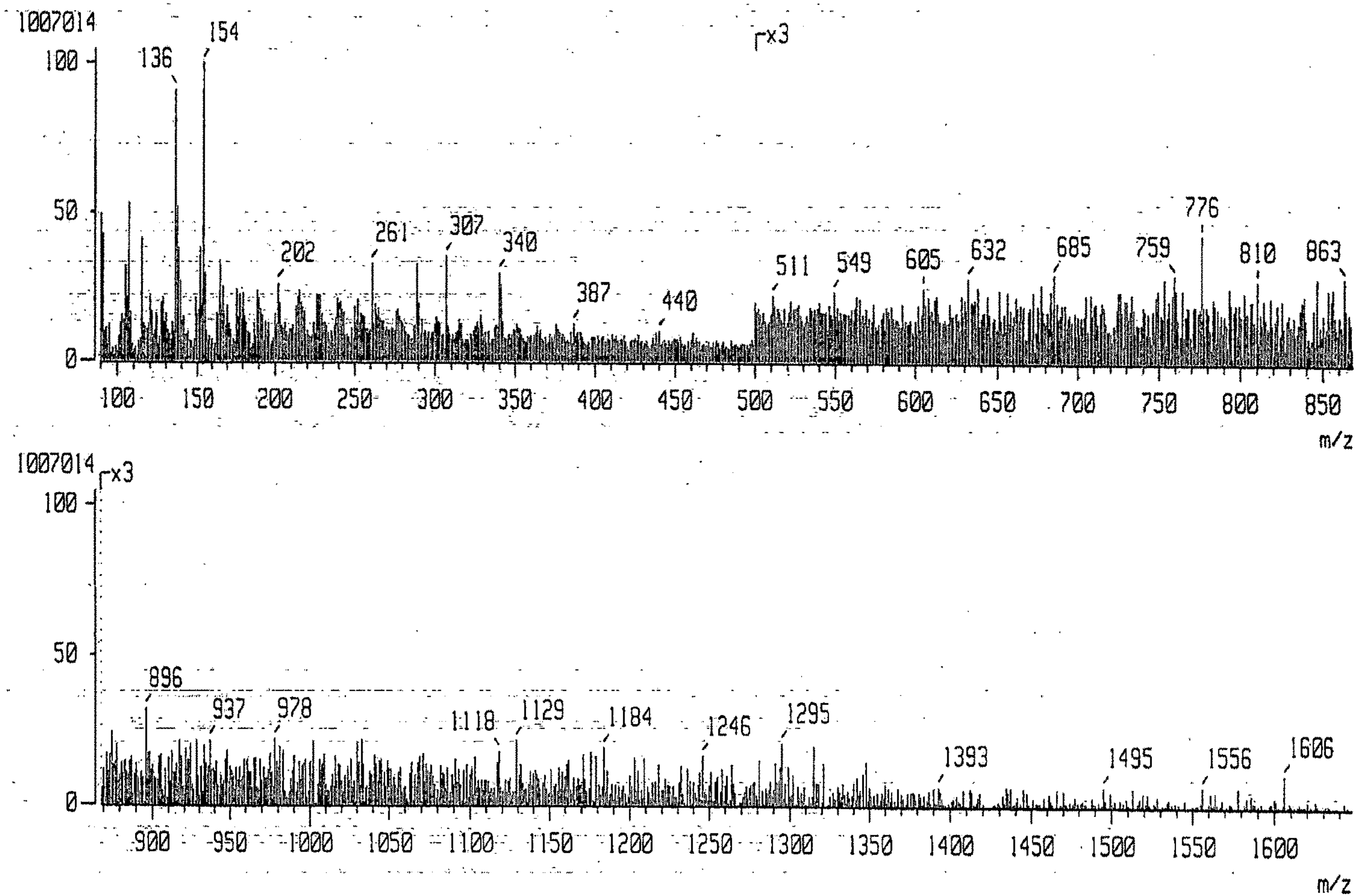
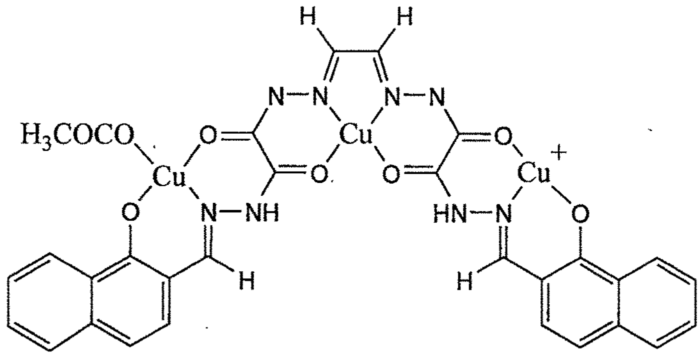
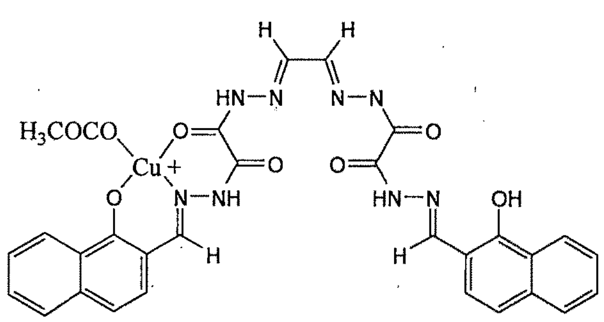


Fig.4.5 FAB-Mass spectrum of complex **[Cu_3oxdnapglx]$(Ac)_2$.**

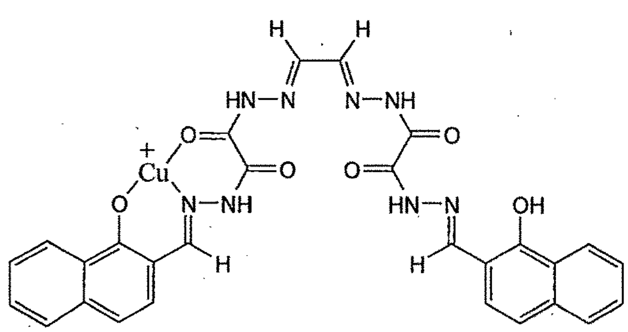
The parent ion peak, in the FAB mass spectrum of the complex [Cu_3oxdnapglx]$(Ac)_2$ **(Fig.4.5)**, was observed at m/Z 870 for the calculated value of m/Z 869.12. With one acetate, the fragment [Cu_3oxdnapglx](Ac) was observed at m/Z 810 for the calculated m/Z 810.12. The cationic complex [Cu_3oxdnapglx]$^{2+}$+$2H^+$/4+ was observed at m/Z 188 for the calculated m/Z 188.12. [Cu_3oxdnapglx]$^{2+}$/2 was calculated to be 376.5 and found to be at m/Z 377.



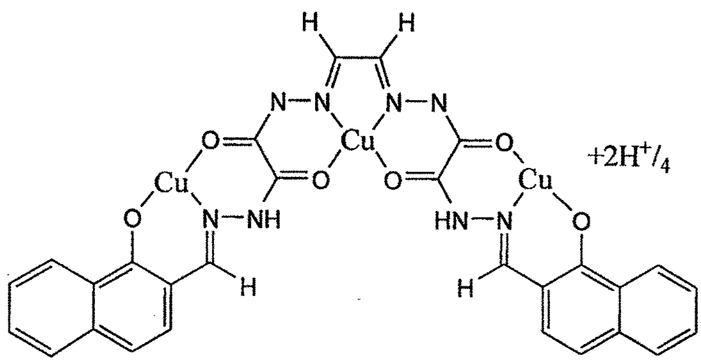
[Cu_3oxdnapglx](Ac)$^+$ at m/Z at 810.



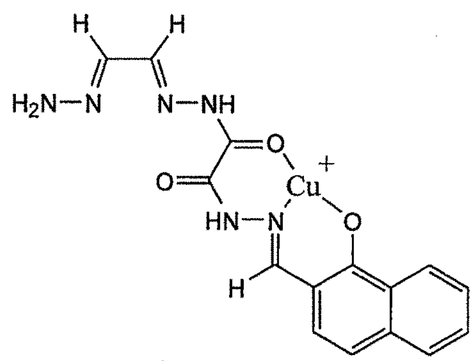
[CuHoxdnapglx]$^+$ at m/Z at 685.



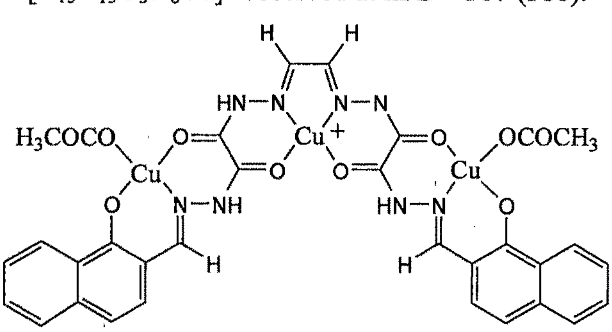
[$C_{28}H_{20}O_6N_8Cu$]$^+$ at m/Z = 628.



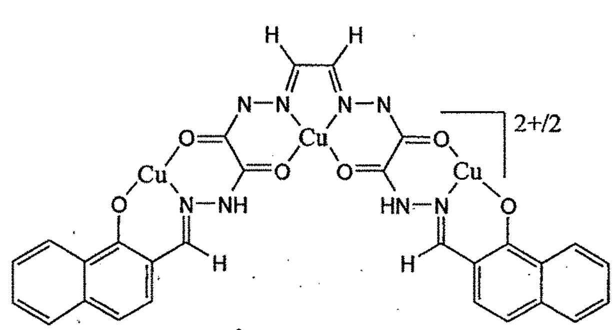
[Cu_3oxdnapglx]+2H$^+$/4 at m/Z at 188.



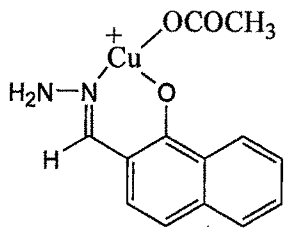
[$C_{15}H_{13}O_3N_6Cu]^+$ observed at m/Z = 387 (388).



[Cu_3oxdnapglx](Ac)$_2^+$ at m/Z at 870.



[Cu_3oxdnapglx]$^{2+}$/2 is observed at m/Z = 377.



$[C_{13}H_{12}O_3N_2Cu]^+$ at m/Z = 307.

The fragments represented above confirm the complex formation as per the suggested formulae.

Electronic and FTIR Spectral analysis of the complexes

The complexes exhibit all important features of the ligands in the UV region. The intraligand transitions have been observed between 193 to 383nm, while a low energy charge transfer transition is observed in all the complexes between 400-480nm region. The methanolic solutions being very dilute, the ligand field transitions could not be observed.

Table 4.3 UV-vis Spectral analysis of complexes

Complex	Intra Ligand Transitions (nm)	Charge Transfer Transitions (nm)
$[Cu_3oxdsalglx](Ac)_2$	195,197,204,255,370	-------
$[Cu_3oxdvanglx](Ac)_2$	217,248,270,355	427
$[Cu_3oxdnapglx](Ac)_2$	193,197,328	477
$[Cu_3oxdbrsalglx](Ac)_2$	194,196,203,253	408
$[Cu_3oxdacphglx](Ac)_2$	195,209	406
$[Cu_3oxd3m2hacphglx](Ac)_2$	197,202,209,253,374,383	469

In the IR spectra of the complexes, absorption at lower frequencies, corresponding to >C=O and >C=N stretching in complexes as compared to the respective ligands confirms the coordination of the metal ions through these functional groups. There is a decrease of 11 to 25cm^{-1} in the carbonyl stretching frequencies and a decrease of 30-40cm^{-1} in the imine stretching frequencies and 4 to 10cm^{-1} in –C-C- multiple bond stretching which supports the coordination of the metal ions to the ligands. Appearance of the carboxylate anion stretching in complexes at 1308 to 1389cm^{-1} confirms the presence and coordination of the carboxylate anions in monodentate fashion.

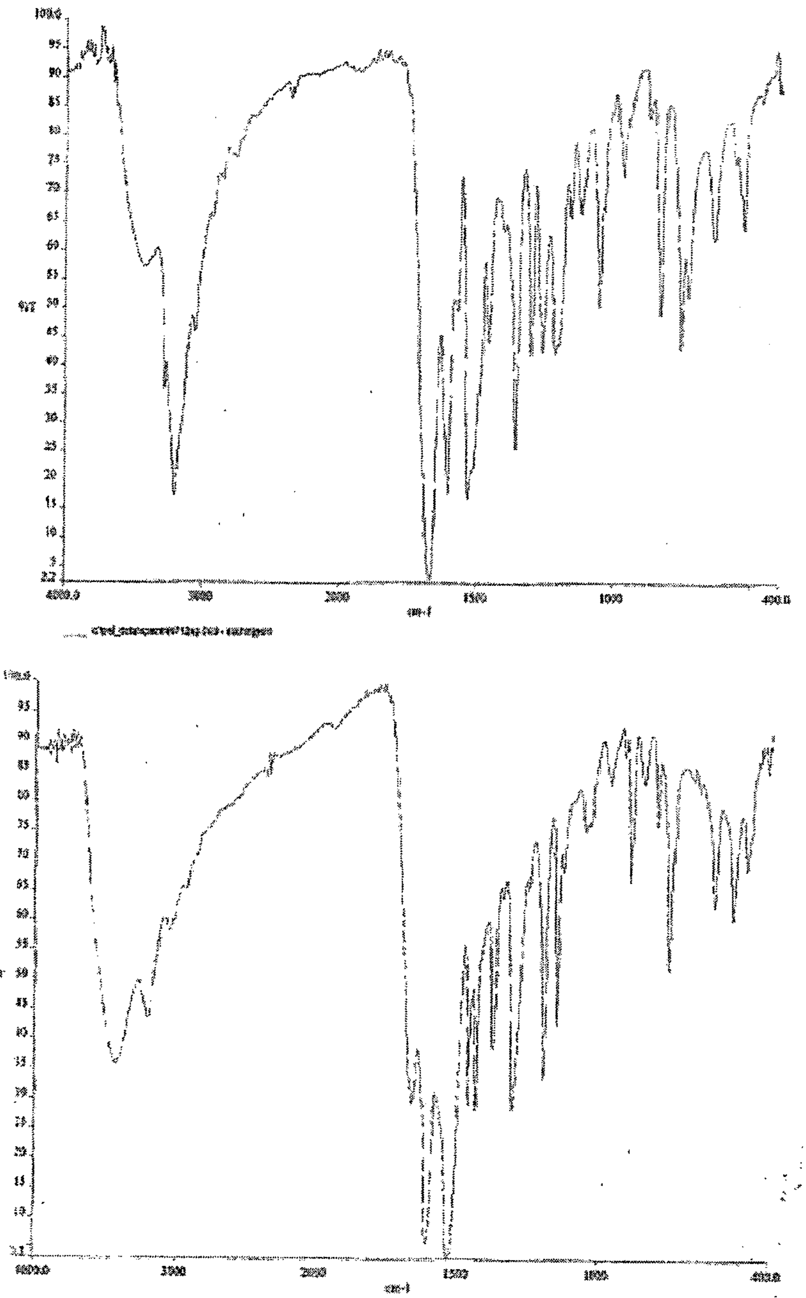


Fig.4.6 FTIR spectra of **oxdsalglx** and **[Cu$_3$oxdsalglx](Ac)$_2$.**

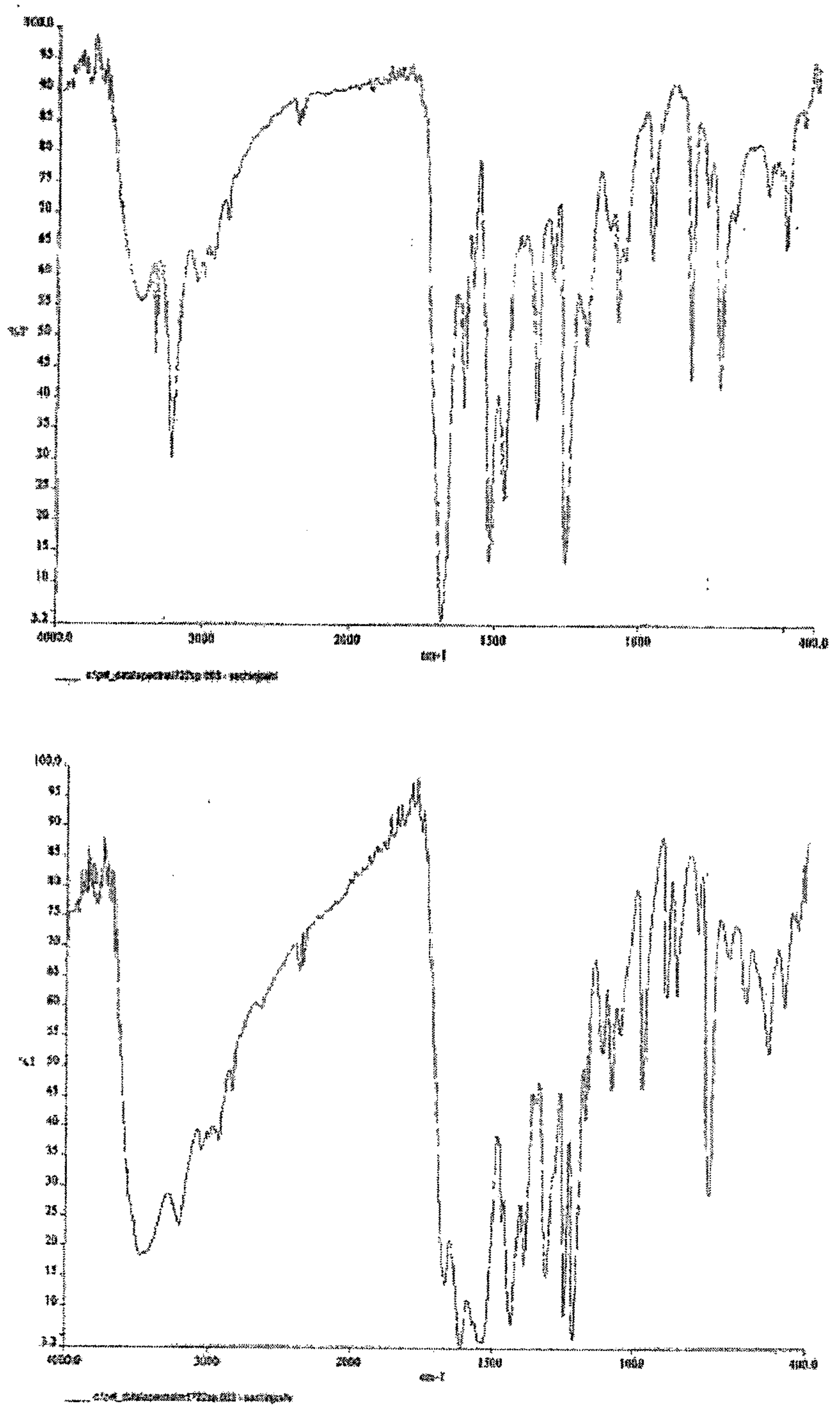


Fig.4.7 FTIR spectra of **oxdvanglx** and **[oxdvanglx](Ac)$_2$**.

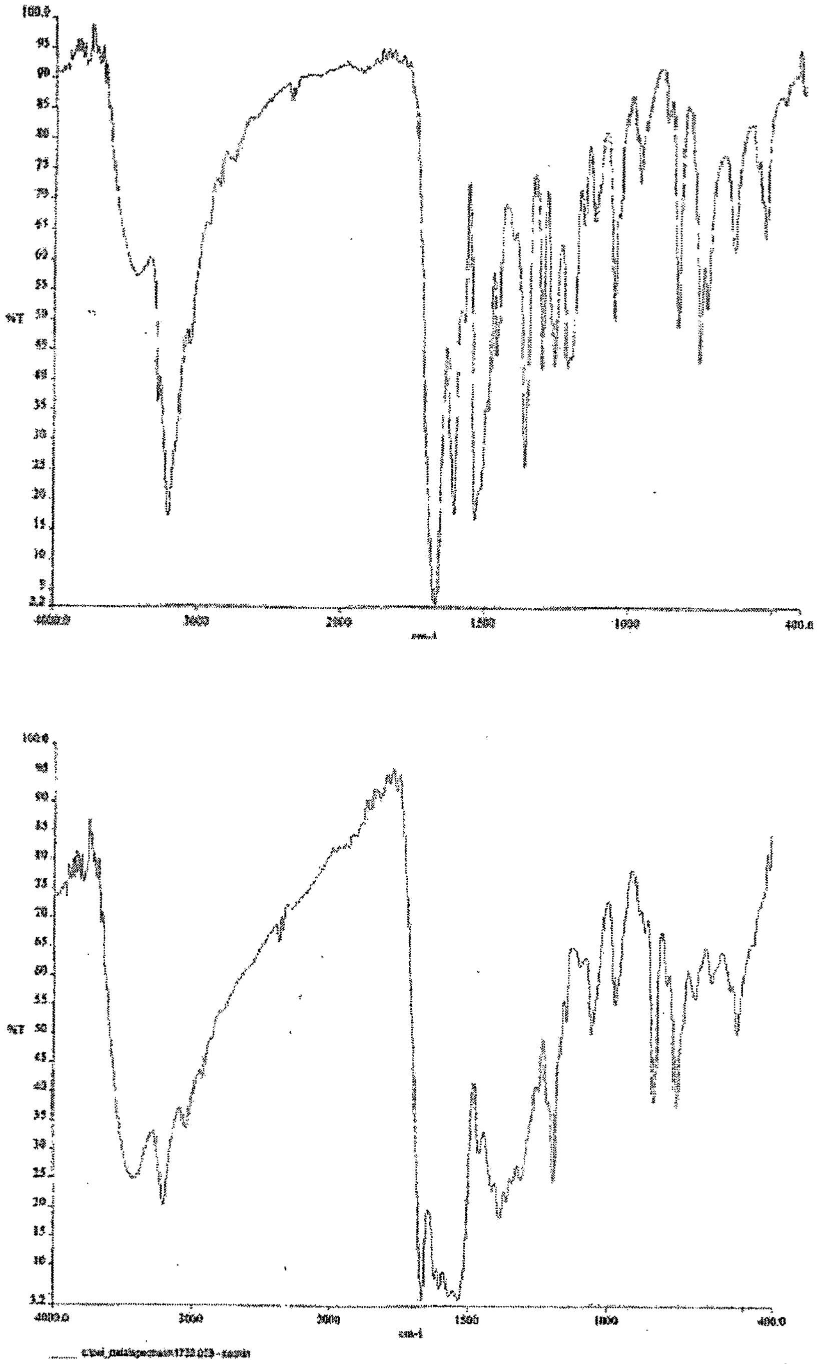


Fig.4.8 FTIR spectra of **oxdnapglx** and **[Cu$_3$oxdnapglx](Ac)$_2$**.

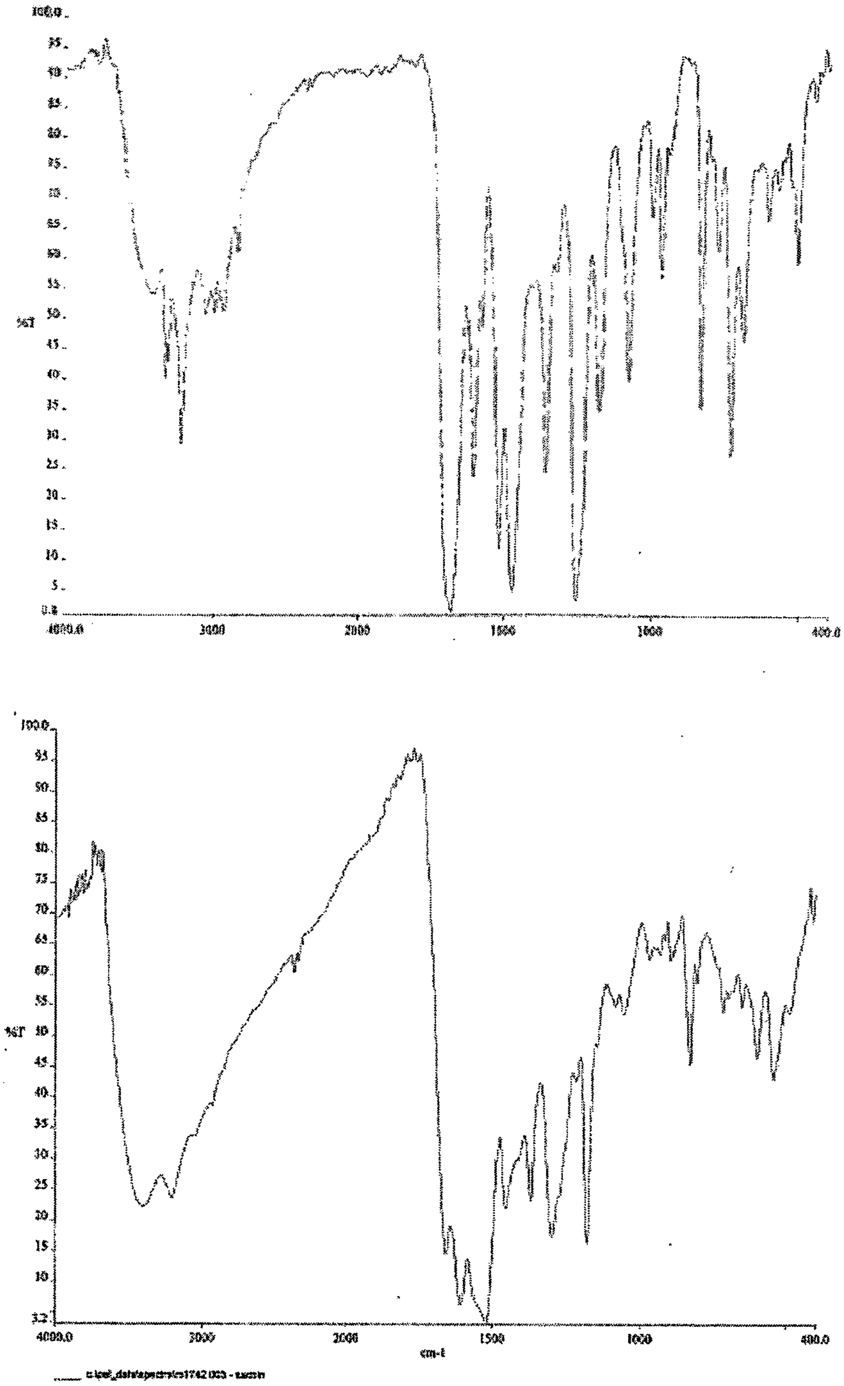


Fig.4.9 FTIR spectra of **oxdbrsalglx** and **[oxdbrsalglx](Ac)$_2$**.

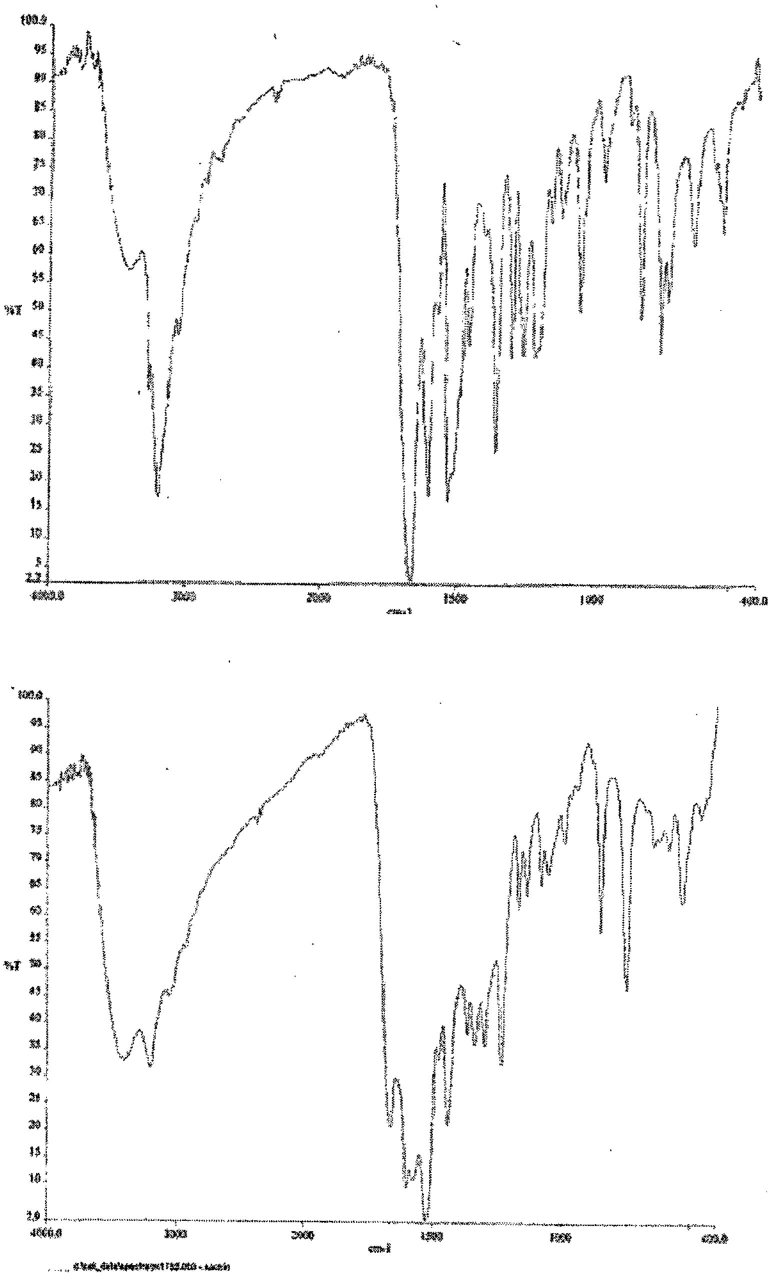


Fig.4.10 FTIR spectra of **oxdacphglx** and **[Cu_3oxdacphglx]$(Ac)_2$**

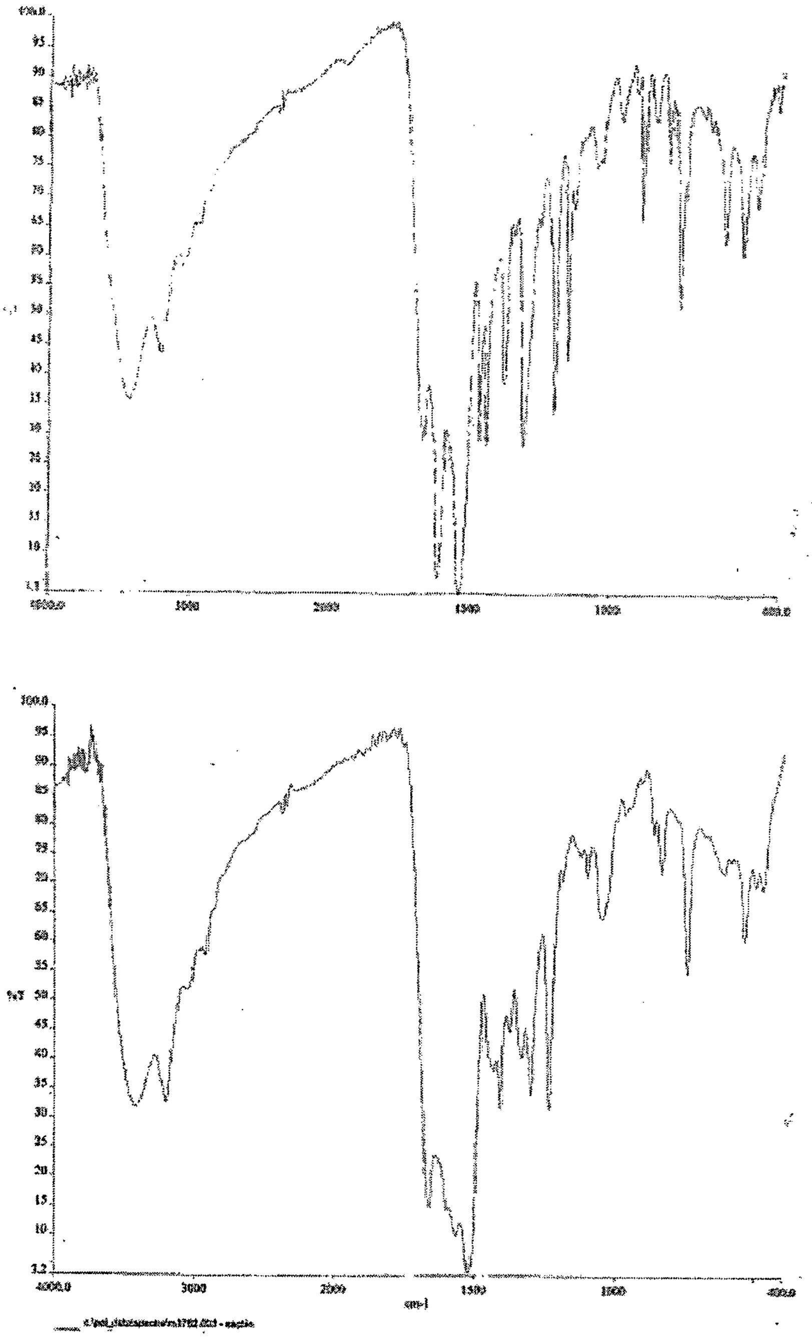


Fig.4.11 IR spectra of **oxd3m2hacphglx** and **[Cu_3oxd3m2hacphglx]$(Ac)_2$**

Table 4.4 Important frequencies in FTIR Spectra of oxdglx complexes

Complex	>C=O (strech)	>C=N- (strech)	-C-C- multiple Bond (strech) (Aromatic)	-C-N- vibration	-N-H strech In (sec) bonded amide	Carboxylate anion streching
[oxdsalglx]	1667	1604	1533, 1459	1055,1122,1161,1217	3204,3278	---------------
[Cu_3oxdsalglx]$(Ac)_2$	1643	1573	1532, 1460	1053,1133,1152,1196	3206	1308,1378
[oxdvanglx]	1678	1606	1538, 1516	1057,1080,1187	3218	---------------
[Cu_3oxdvanglx]$(Ac)_2$	1664	1577	1432,1467	1053,1171	3206	1311,1389
[oxdnapglx]	1625	1610	1561,1459	1086,1148,1210	3203,3216	---------------
[Cu_3oxdnapglx]$(Ac)_2$	1605	1562	1536,1457	1052,1144,1191	3208,3256	1359
[oxdbrsalglx]	1674	1609	1540,1569	1055,1109	3208,3271	---------------
[Cu_3oxdbrsalglx]$(Ac)_2$	1658	1578	1521,1453	1050,1080,1177,1213	3222.	1368
[oxdacphglx]	1679	1603	1563, 1440	1058,1118	3209,3289	---------------
[Cu_3oxdacphglx]$(Ac)_2$	1662	1573	1523, 1440	1052,1080,1135,1165	3207,3273	1324,1369
[oxd3m2hacphglx]	1672	1611	1546,1471.	1056,1128,1106	3214,3394	---------------
[Cu_3oxd3m2hacphglx]$(Ac)_2$	1661.	1572	1521,1440.	1044,1097,1121	3207.3289	1330,1373.

4.4 Molecular modelling

The geometry of four of the trinucleating ligands **oxdsalglx**, **oxdnapglx**, **oxdbrsalglx** and **oxd3m2hyacphglx** has been optimized by *ab intio* quantum mechanical calculations with 6-31G basis set.

The details of calculated values of bond distances are given in Table 4.5.

Table 4.5 Important bond distances in the ligands calculated on the basis of ab initio calculations using 6-31G basis set.

Ligand	oxdsalglx (Fig. 4.12) Å	oxdnapglx (Fig. 4.13) Å	oxdbrsalglx (Fig. 4.14) Å	oxd3m2hacphglx (Fig. 4.15) Å
Ar-O-H···N=C-	1.896 & 1.873	1.955 & 1.906	1.917 & 2.014	2.034 & 2.035
glx C···C	1.471	1.462	1.464	1.468
C=N	1.263 & 1.268	1.264	1.267 & 1.264	1.270 & 1.270
N···NH	1.358 & 1.378	1.376 &1.355	1.352 & 1.356	1.370 & 1.370
oxamide C···C	1.513 & 1.521	1.515 & 1.514	1.514 & 1.518	1.523 & 1.523
NH···C	1.349 & 1.366	1.359 & 1.352	1.357 & 1.412	1.342 & 1.342
four C=O	1.228,1.229, 1.218,1.214	1.216,1.216, 1.223,1.226	1.223,1.213, 1.225,1.221	1.228,1.224, 1.224,1.228
O=C···NH	1.343 & 1.355	1.355 & 1.348	1.344 & 1.355	1.344 & 1.344
NH···N	1.415 & 1.385	1.364 & 1.416	1.369 & 1.363	1.376
C=N···C	1.272 & 1.280	1.268 & 1.279	1.268 & 1.268	1.275 & 1.275
Ar···C=N	1.451 & 1.465	1.453 & 1.462	1.460 & 1.457	1.479 & 1.479
Ar···O	1.354 & 1.368	1.365 & 1.361	1.354 & 1.358	1.357 & 1.356
Ar···Br	-------	-------	1.928 & 1.929	-------
H_3C···C=N	-------	-------	-------	1.510 & 1.510
H_3C···Ar	-------	-------	-------	1.506 & 1.505

The tabulated bond distances are shown by ··· line.

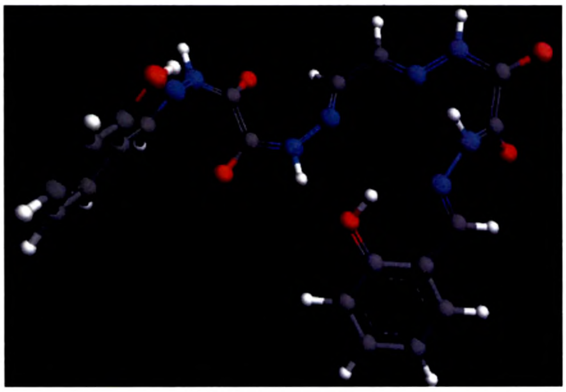


Fig.4.12 Optimized structure of ligand **oxdsalglx** by using 6-31G basis set.

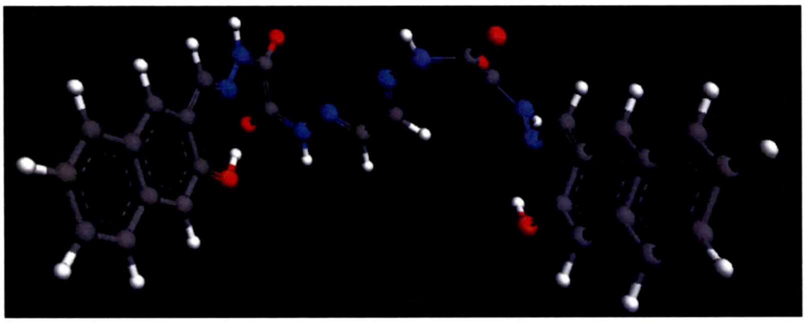


Fig.4.13 Optimized structure of ligand **oxdnapglx** by using 6-31G basis set.

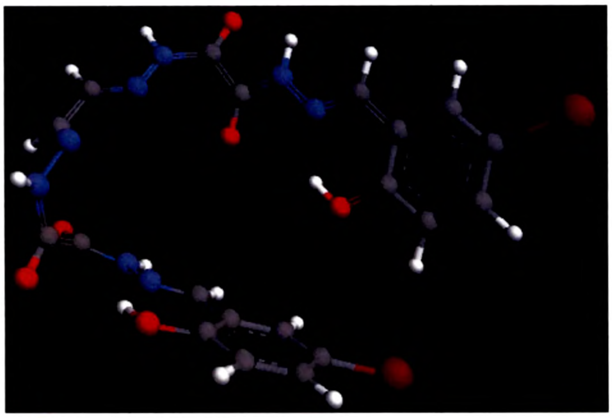


Fig.4.14 Optimized structure of ligand **oxdbrsalglx** by using 6-31G basis set.

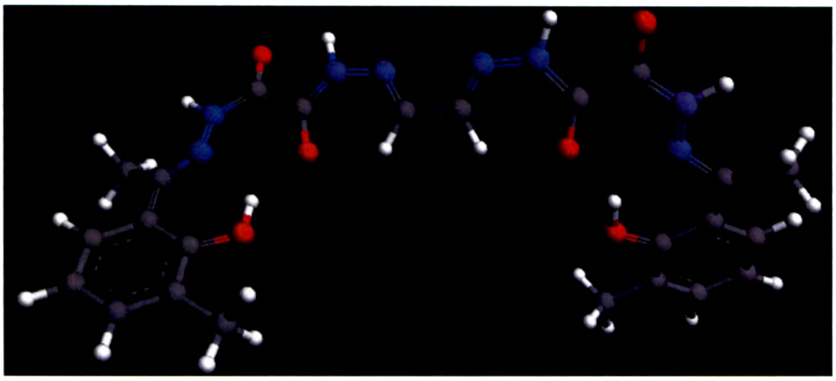


Fig.4.15 Optimized structure of ligand **oxd3m2hacphglx** by using 6-31G basis set.

4.5 Magnetic exchange

The magnetic properties of the complexes **[Cu$_3$oxdsalglx](Ac)$_2$**, **[Cu$_3$oxdvanglx](Ac)$_2$** and **[Cu$_3$oxdnapglx](Ac)$_2$** have been studied by Faraday method between Liquid Nitrogen Temperature (LNT) and RT. The plots of χ_M and μ, (calculated and observed) verses absolute temperature (K) are presented in Fig 4.16-4.18.

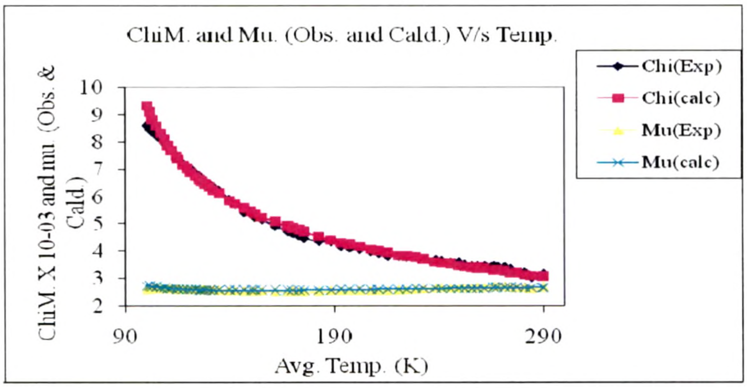


Fig.4.16 χ_M and μ calculated and observed vs. T for **[Cu$_3$oxdsalglx](Ac)$_2$**

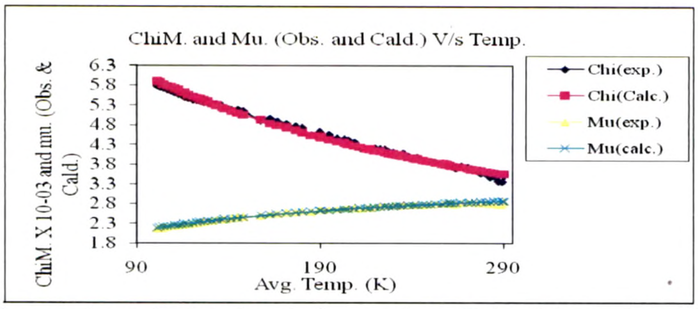


Fig.4.17 χ_M and μ calculated and observed vs. T for **[Cu$_3$oxdvanglx](Ac)$_2$**

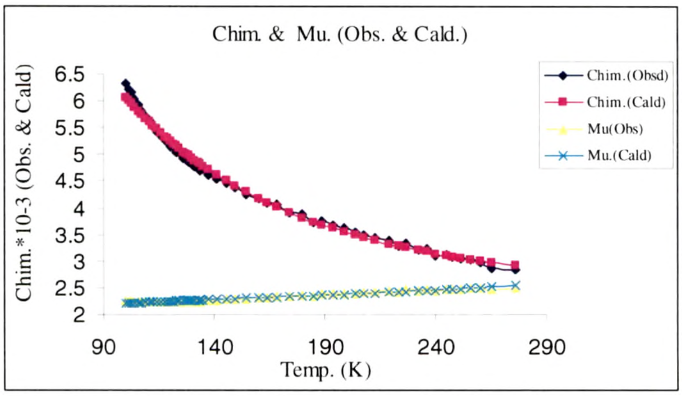


Fig.4.18 χ_M and μ calculated and observed vs. T for **[Cu$_3$oxdnapglx](Ac)$_2$**

The susceptibility data was least squares fit to the modified Van Vleck equation for a Cu_3 system using the program Magmum. The calculated values of Weiss constant θ and the coupling constants J_1 and J_2 are tabulated in **Table 4.9.** Comparative study of J and dihedral angles of complexes.

Table 4.6 Calculated values of coupling constant J and Weiss' constant θ.

Complexes	Theta	J (cm^{-1})	Dihedral Angle (°)
[Cu$_3$oxdsalglx](Ac)$_2$	-20	J_1= -160 J_2 = -200	96.7
[Cu$_3$oxdvanglx](Ac)$_2$	-150	J_1= -4.65 J_2 = -150	111.31
[Cu$_3$oxdnapglx](Ac)$_2$	-66.66	J_1 = -520 J_2 = -300	120.92

All three complexes studied here have been found to be strongly antiferromagnetic with negative values of both, θ and the exchange coupling constants J_1 and J_2. It can be seen from the structures of the complexes (**Fig.4.19, Fig.4.20 and Fig.4.21**) optimized using universal force fields[71-79] that they are highly planar except small parts of the molecules. This planarity can allow the formation of stacked super structures through the axial coordination of phenolate oxygen with copper in the neighbouring (stacked) molecule. This type of intermolecular oxygen coordination is known. This O bridging can allow intermolecular antiferromagnetic exchange as can be seen in the negative θ values in these complexes. The ligand geometries, optimized by *ab intio* quantum mechanical calculations show that there is complete π-delocalisation over the trinucleating ligands, from phenolate oxygen through the glyoximine part and the terminal aromatic O-hydroxy imines. Thus the ligands can be very efficient mediators of magnetic exchange through the π- symmetry orbitals. Also the complexes have Cu-Cu-Cu angle between 150-180°, i.e. close to linear arrangement. All these parameters ensure a strong antiferromagnetic exchange in these complexes. The effect of dihedral angle between metal coordination planes, hence, appears to be insignificant here. The values of J_1 and J_2 follow the order of π-bonding ability of the aldimine part of the ligands which follows the order naph>sal>van.

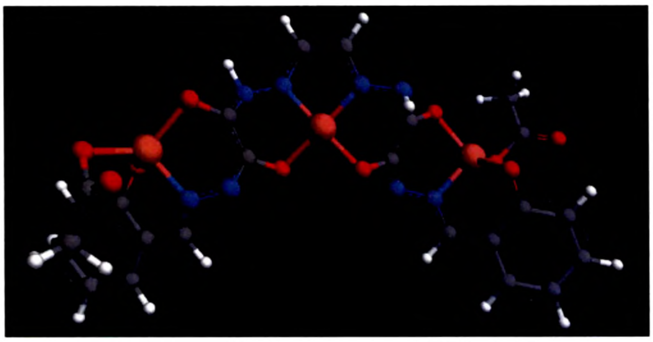


Fig. 4.19 Optimized geometry of complex **[Cu_3oxdsalglx]$(Ac)_2$** using UFF.

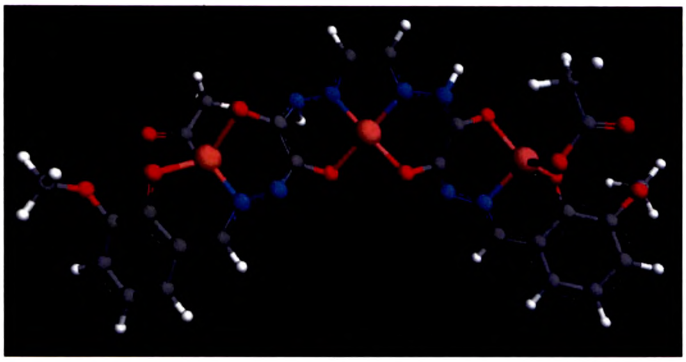


Fig.4.20 Optimized geometry of **[Cu$_3$oxdvanglx](Ac)$_2$** complex using UFF.

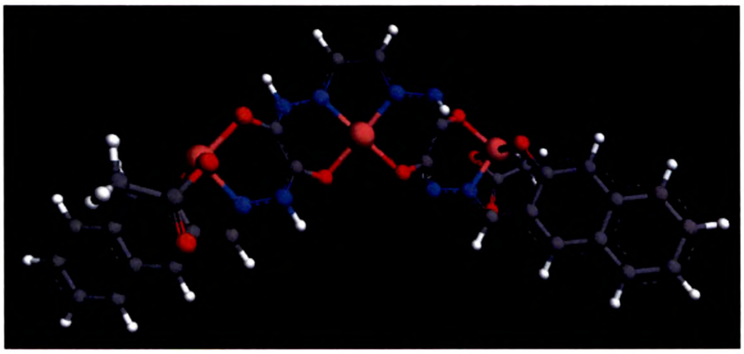


Fig.4.21 Optimized geometry of **[Cu$_3$oxdnapglx]**(Ac)$_2$ complex using UFF.

4.6 Electrochemical studies

The electrochemical behaviour of the six trinuclear complexes prepared in this series have been examined by cyclic voltammetry at platinum electrode in DMSO solutions.

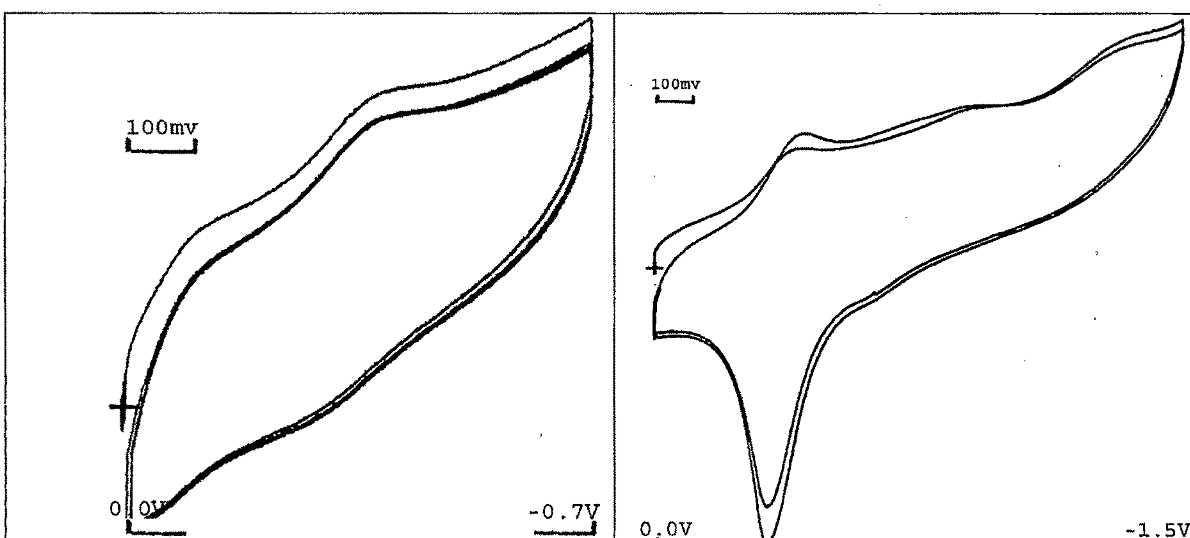
The typical cyclic voltammograms of two of the complexes, **[Cu$_3$oxdbrsalglx](Ac)$_2$** and **[Cu$_3$oxdnapbenz]**(Ac)$_2$ are represented in **Fig.4.22.**

In the complexes of trinucleating bis-oxalodihydrazones, the most prominent redox process appears between -0.31 to -0.4V. The process is almost reversible (quasireversible) when the lower limiting potential was restricted to -0.7V. The ΔE_P values for this redox couple range between 54 to 130 mV, when the lower limiting potential was restricted to -1.5V.

Table 4.7 Redox potentials of complexes.

Complexes	**Reduction Potentials**			**Oxidation Potentials**		
	$Ep_c(1)$	**$Ep_c(2)$**	**$Ep_c(3)$**	**$Ep_a(1)$**	**$Ep_a(2)$**	**$Ep_a(3)$**
$[Cu_3oxdsalglx](Ac)_2$	-0.373	-0.758	-1.284	-0.225	----	----
$[Cu_3oxdvanglx](Ac)_2$	-0.372	-0.810	-------	-0.261	----	----
$[Cu_3oxdnapglx](Ac)_2$	-0.303	-0.814	-1.229	-0.200	----	----
$[Cu_3oxdbrsalglx](Ac)_2$	-0.348	-0.733	-1.163	-0.252	----	----
$[Cu_3oxdacphglx](Ac)_2$	-0.318	-0.888	-----	-0.274	-----	-----
$[Cu_3oxd3m2hacphglx](Ac)_2$	-0.311	-0.577	-----	-0.244	-----	-----

*The potentials are referred to Cp_2Fe/Cp_2Fe^+ couple.



$[Cu_3oxdbrsalglx](Ac)_2$ (a)

$[Cu_3oxdnapbenz](Ac)_2$ (b)

Pt disk working electrode, Pt wire counter electrodes and Ag/AgNO$_3$ (0.1M in CH$_3$CN) as reference electrodes were used.

Fig.4.22 Typical cyclic voltammograms of complexes **$[Cu_3oxdbrsalglx](Ac)_2$ (a)** and **$[Cu_3oxdnapbenz](Ac)_2$ (b).**

These ΔE_P values correspond to two equivalent 1e$^-$ processes. Two more reduction processes are seen, one between -0.75 to -0.87V and a third reduction is observed around -1.2V, in the complexes of **sal**, **nap** and **brsal** complexes. In the remaining complexes this reduction takes place at more negative potentials. With the extended potential region, all processes become irreversible. It can be anticipated from the molecular formula that, the two terminal copper ions have flexible coordination geometry and therefore can accommodate Cu^{II} and Cu^{I} ions with ease. Thus the redox processes corresponding to terminal copper centres can be expected to be reversible and the first redox couple (i.e. -0.3 to – 0.4V) can be assigned to the reduction of terminal copper ions from Cu^{II} to Cu^{I}. The central copper ion is coupled with the terminal copper ions through an oxalate bridge with extended π-delocalization and has a strong ligand field. This set is also expected to have near square planar geometry to facilitate π-delocalization in the ligand. Thus the reduction of this copper centre has to occur at more negative potentials. Also Cu^{I} centre which prefers tetrahedral geometry may not be properly accommodated in the restricted square planar environment available at this site making the reduction irreversible. The third reduction about -1.2V can be unequivocally assigned to the reduction to Cu^{0} state.

Ep_c values for the first redox increase in the order $[Cu_3oxdnapglx](Ac)_2$ < $[Cu_3oxd3m2hacphglx](Ac)_2$ < $[Cu_3oxdacphglx](Ac)_2$ < $[Cu_3oxdbrsalglx](Ac)_2$ < $[Cu_3oxdsalglx](Ac)_2$ < $[Cu_3oxdvanglx](Ac)_2$. This is approximately the strength as a σ-donor or the reverse order of the π-bonding ability. As compared to the $[Cu_3oxdsalglx](Ac)_2$ complex $[Cu_3oxdvanglx](Ac)_2$ complex has electron releasing methoxy group which makes the coordinating site electron rich and hence reduction is more difficult. Whereas the $[Cu_3oxdbrsalglx](Ac)_2$ has inductive electron withdrawing effect which is making the coordinating site less σ-bonding or slightly more π-bonding as compared to $[Cu_3oxdsalglx](Ac)_2$ complex, thus making the reduction easier. Similarly the naphthyl part of the ligand is highly electron withdrawing and helps metal to ligand π-interaction, thus leading to easier reduction as compared to the other complexes in the series.

Thus it can be seen that the trinucleating ligand with π-delocalizations assists in delocalizing the electron density added to the metal ion helping the process to be stepwise and partly reversible, while the nature of the non-bridging part of the ligand affects the reduction potentials indicating that they can be tuned by small variations in the functional groups.

References

(1) Ponka, P.; Borova, J.; Neuwirt, J.; Fuchs, O.; Necas. E. A study of Intracellular Iron Metabolism using Pyridoxal Isonicotinoyl Hydrazone and Other Synthetic Chelating Agents. *Biochim Biophys Acta,* 1979, **586,** 278.

(2) Hershco, C.; Avramovici-Grisaru, S.; Link, G.; Gelfand, L.; Sarel, S. Mechanism of In Vivo Iron Chelation by Pyridoxal Isonicotinoyl Hydrazone and other Imino derivatives of Pyridoxal. *J. Lab. Clin. Med.,* 1981, **98(1),** 99.

(3) Johnson, D. K.; Murphy, T. B.; Rose, N. J.; Goodwin, W. H.; Pickart. L. Cytotoxic Chelators and Chelates 1. Inhibition of DNA Synthesis in Cultured Rodent and Human cells by aroylhydrazones and by a copper(II) complex of salicylaldehyde benzoyl hydrazone. *Inorg. Chim. Acta,* 1982, **67,** 159.

(4) Johnson, D. K.; Pippard, M. J.; Murphy, T. B.; Rose, N. J. An In Vivo Evaluation of Iron-Chelating Drugs Derived from Pyridoxal and its analogs. *J. Pharmacol. Exp. Ther.,* 1982, **221(2),** 399.

(5) Pickart, L.; Goodwin, W. H.; Burgua, W.; Murphy, T. B.; Johnson. D. K.; Inhibition of the Growth of Cultured Cells and an Implanted Fibrosarcoma by Aroylhydrazone Analogs of the Gly-Hys-Lys-Cu(II) complex. *Biochem. Pharmacol.,* 1983, **32(24),** 3868.

(6) Blatt, Julie and Stitely, Suzette, *Cancer Research,* 1987, **47,** 1749.

(7) Blatt, Julie and Stitely, Suzette, *Cancer Research,* 1998, **48,** 7189.

(8) Richadson, D. R.; Tran, F. H.; Ponka, P. *blood,* 1995, **86,** 4295.

(9) Lanzschulz, W.; Thesleff, I. and Ekblom, P. *The Journal of Cell Biology,* 1984, **98,** 596.

(10) Buss, J. L.; Arduini, E.; Ponka, P. *Biochemical Pharmacology,* 2002, **64,** 1689.

(11) Richadson, D. R. *Antimicrobial agents and Chemotherapy,* September 1997, 2061.

(12) Koh, L. L.; Kon, O. L.; Loh, K. W.; Long, Y. C.; Ranford, J. D.; Tan, A. L. C. and Tjan, Y. Y. *Journal of Inorganic Biochemistry,* 1998, **72,** 155.

(13) Off, H. A.; Siefken, W. and Domagk, G. *Z. Naturforsch., Teil B,*1952, **7,** 446.

(14) Johnson, D. K.; Murphy, T. B.; Rose, N. J.; Goodwin, W. H. and Pickart, L. *Inorg. Chim. Acta*, 1982, **67**, 159; Pickart, L.; Goodwin, W. H.; Burgua, W.; Murphy, T. B. and Johnson, D. K. *Biochem. Pharmacol.*, 1983, **32**, 3868.

(15) Arapov, O. V.; Alferva, O. F.; Levocheskaya, E. I. and Krasil'nikov, I. *Radiobiol.*, 1987, **27**, 843.

(16) Henderson, William.; Koh, Lip L.; Ranford, John D.; Robinson, Ward T.; Svensson, Jan O.; Vittal, Jagadese J.; Wang, Yu M. and Xu, Yan, *J. Chem. Soc., Dalton Trans.*, 1999, 3341.

(17) Horackova, Magda.; Ponka, Prem.; Byczko, Zenobia.; *Cardiovascular Research,* 2000, **47,** 529.

(18) Wiles, D. M. and Suprunchuk, T. *Canadian Journal of Chemistry,* 1968, **46,** 701.

(19) Bacchi, Alessia.; Carcelli, Mauro.; Pelizzi, Giancarlo.; Solinas. Costantino, and Sorace, Lorenzo.;*Inorg. Chim. Acta.* 2006, **359,** 2275.

(20) Thompson, Laurence K.; Xu, Zhiqiang.; Goeta, Andre's E.; Howard, Judith A. K.; Clase, Howard J.; and Miller, David O.; Thomson, L. K. *Inorg. Chem.* 1998, **37,** 3217.

(21) (a) Zhao, Liang.; Thomson, L. K.; Xu, Z.; Miller, D. O.; and Stirling, D. R. *J. Chem. Soc. Dalton Trans.,* 2001, 1706.

(22) Zhao, L.; Matthews, C. J.; Thomson, L. K.; and Heath, S. L., *Chem. Commun.,* 2000, 265.

(23) Mathews, C. J.; Avery, K.; Xu, Z. Thomson, L. K.; Zhao, L.; Miller, D. O.; Biradha, K.; Poirier, K.; Zaworotko, M. J.; Wilson, C.; Goeta, A. E. and Howard, J. A. K., *Inorg. Chem.,* 1999, **38,** 5276.

(24) Zhao, L.; Xu, Z.; Thomson, L. K.; Heath, S. L.; Miller, D. O. and Ohba, M. *Angew. Chem., Int. Ed.,* 2000, **39,** 3114.

(25) Waldmann, O.; Koch, R.; Schromm, S.; Muller, P.; Zhao, L. and Thomson, L. K. *Chem. Phys. Lett.,* 2000, **332,** 73.

(26) Waldmann, O.; Zhao, L. and Thomson, L. K.; *Phys. Rev. Lett.,* 2002, **88,** 66401.

(27) Thomson, L. K.; Zhao, L.; Xu, Z.; Miller, D. O. and Reiff, W. M. *Inorg. Chem.,* 2003, **42,** 128.

(28) Zhao, L.; Niel, V.; Thomson, L. K.; Xu, Z.; Milway, V. A.; Harvey, R. G.; Miller, D. O.; Wilson, C.; Leech, M.; Howard, J. A. K. and Heath, S. L. *Dalton Trans,* 2004, 1446.

(29) Elhabiri, M.; Scopelliti, R.; Bunzli, J.-C. G. and Piguet, C. *Chem. Commun.,* 1998, 2347.

(30) Rapenne, G.; Patterson, B. T.; Sauvage, J.-P. and Keene, F. R. *Chem, Commun.,* 1999, 1853.

(31) Hannon, M. J.; Panting, C. L. and Alcock, N. W. *Chem. Commun.,* 1999, 2023.

(32) Duan, C.-Y.; Liu, Z-H.; You, X.-Z.; Xue, F. and Mak, T. C. W. *Chem.*

Commun., 1997, 381.

(33) van Koningsbruggen, P. J.; Muller, E.; Haasnoot, J. G. and Reedijk, J. *Inorg. Chim. Acta,* 1993, **298,** 37.

(34) Bonardi, A.; Ianelli, S.; Pelizzi, C. and Pellizi, G. *Inorg. Chim. Acta,* 1991, **187,** 167.

(35) Baxter, P. N. W.; Lehn, J.-M.; Fisher, J. and Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* 1994, **33,** 2284.

(36) Hannan, G. S.; Volkmer, D.; Schubert, U. S.; Lehn, J.-M.; Baum, G. and Fenske, D. *Angew. Chem., Int. Ed., Engl,* 1997, **36,** 1842.

(37) Bassani, D. M.; Lehn, J.-M.; Fromm, K. and Fenske, D. *Angew. Chem., Int. Ed.,* 1998, **37,** 2364.

(38) Campos-Fernandez, C. S.; Clerac, R. and Dunbar, K. R. *Angew. Chem., Int. Ed.,* 1999, **38,** 3477.

(39) Bu, X.-H.; Morishita, H.; Tanaka, K.; Biradha, K.; Furusho, S. and Shionoya, M. *Chem. Commun.,* 2000, 971.

(40) Garcia, A. M.; Romero-Salguero, F. J.; Bassani, D. M.; Lehn, J.-M.; Baum, G. and Fense, D. *Chem. Eur. J.,* 1999, **5,** 1803.

(41) O'Connor, C. J.; Romananch, R. J.; Robertson, D. M.; Eduok, E. E. and Fronczek, F. R. *Inorg. Chem.,* 1983, **22,** 449.

(42) Woon, T. C.; Thomson, L. K. and Robichaud, P. *Inorg. Chim. Acta,* 1984, **90,** 201.

(43) Souza, P.; Matesanz, A. I. and Fernande, V. *J. Chem. Soc., Dalton Trans.,* 1996, 3011.

(44) Garcea-Jojal, J.; Garcia, J.; Cortes, R.; Rojo, T.; Urtiaga, M. K. and Arriortua, M. I. *Inorg. Chim. Acta,* 1996, **249,** 25.

(45) Mangia, A.; Pelizzi, C. and Pelizzi, G. *Acta Crystallogr., Sect. B.* 1974, *30,* 2146.

(46) Bacchi, A.; Bonini, A.; Carcelli, M.; Ferraro, F.; Leperati, E.; Pelizzi, C. and Pelizzi, G. *J. Chem. Soc. Dalton Trans.,* 1996, 2699.

(47) Koziol, A. E.; Palenik, R. C.; and Palenik, G. J. *J. Chem. Soc., Chem. Commun.,* 1986, 650.

(48) Lagrenee, M.; Sueur, S.; and Wignacourt, J. P. *Acta Crystallogr., Sect. C,* 1991, **47,** 1158.

(49) Bachchi, A.; Battaglia, L. P.; Carcelli, M.; Pelizzi, C.; Pelizzi, G.; Solinas C. and M. Zoroddu, A. *J. Chem. Soc., Dalton Trans.,* 1993, 775.

(50) Ainscough, E. W.; Brodie, A. M.; Ranford, J. D. and Waters, J. M. *Inorg. Chim.*

Acta, 1995, **236,** 83.

(51) Chen, X.; Zhan, S.; Hu, C.; Meng, Q. and Y. Liu, *J. Chem. Soc., Dalton Trans.* 1997, 245.

(52) van Koningsbruggen, P. J.; Muller, E.; Haasnoot, J. G. and Reedijk, J. *Inorg. Chim. Acta,* 1993, **208,** 37.

(53) Xu, Z.; Matthews, C. J.; Thomson, L. K. and Heath, S. L. unpublished work.

(54) Tondon, S.; Dawe, L. N.; Milway, V. A.; Collins, J. L. and Thomson, L. K. *J. Chem. Soc., Dalton Trans.* 2007, 1948.

(55) (a) Xu, Z.; Thomson, L. K. and Miller, D. O. *Inorg. Chem.,* 1997, **36,** 3985.

(56) Thomson, L. K.; Xu, Z., Goeta, A. E., Howard, J. K. A.; Clase, H. J. and Miller, D. O. *Inorg. Chem.,* 1998, **37,** 3217.

(57) Xu, Z.; Thomson, L. K.; Mathews, C. J.; Miller, D. O.; Goeta, A. E.; Wilson, C. J.; Howard, A. K.; Ohba, M. and Okawa, H. *J. Chem. Soc., Daltion Trans.,* 2000, 69.

(58) Lindstrom, Anders, and Pettersson, Gosta, *European Journal of Biochemistry,* 48, 1974, 229.

(59) Johnson, D. K.; Murphy, T. B.; Rose, N. J.; Goodwin, H.and Pickart, L. *Inorg. Chim. Acta.* 1982, **67,** 159.

(60) Chan, S. C.; Koh, L. L.; Leung, P. H.; Ranford, J. D.; Sim, K. Y. *Inorg. Chim. Acta.* 1995, **236,** 101.

(61) References mentioned in Ref. 32 and 42.

(62) (a) Iskander, M. F.; Khalil, T. E.; Werner, R.; Haase, W.; Svoboda, I. and Fuess, H.; *Polyhedron,* 2000, **19,** 949. (b) Sangeetha, M. R.; Boradi, K.; Gupta, R.; Pal, C.; Manivannan, V. and Pal, S. *Polyhedron,* 1999, **18,** 1425. (c) Ainscough, E. W.; Brodie, A. M.; Dobbs, A. J.; Ranford, J. D. and Waters, J. M. *Inorg. Chim. Acta,* 1998, 267, 27.

(63) Wu, L.; Qiu, G.; Teng, H.; Zhu, Q.; Liang, S. and Hu, X. *Inorg. Chim. Acta,* 2007, **360,** 3069.

(64) Schmidt, M.W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J.Comput.Chem.* 1993, **14,** 1347.

(65) Ditchfield, R.; Hehre, W. J.; Pople, J. A.; *J. Chem. Phys.* 1971, **54,** 724.