Synthesis and Characterization of some Macro Cyclic Polynuclear μ-Azide and Oxalate Spacer Bridged Copper Complexes

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ABSTRACT

An attempt is made to synthesize and study the coordination compounds with enhanced spacial gap between the bulky bridging moieties such as biphenyl bridges. This is possible by insertion of multi dentate spacer type bridging ions or groups. The idea is to tailor coordination compounds possessing enough room for the free entry and exit of molecules such as oxygen, carbon dioxide, nitrogen etc., for any specific model activity. In one category, the azide and oxalate bridged groups used as spacer groups separately in the complexes of $[Cu_4(dadpm\ male)_2(N_3)_4(H_2O)_4$, $[Cu_4(o.toli\ male)_2(N_3)_4(H_2O)_4$, $[Cu_4(dadpm\ male)_2(Ox)_2\ (H_2O)_4$ $[Cu_4(o.toli\ male)_2(Ox)_2\ (H_2O)_4$ and in another category, both azide and oxalates groups used together as groups such as$[Cu_4(dadpm\ male)_2\ (Ox)_2(N_3)_4$, $[Cu_4(o.toli\ male)_2(Ox)_2\ (N_3)_4$ etc., were synthesized and characterized using different techniques like Elemental analysis, DSC, ESR, IR and Electronic spectra are recorded.

Keywords: biphenyl bridging moiety, Azide and Oxalate spacer groups, model activity.

INTRODUCTION

Synthesis, characterization and investigations of biological models is the hall mark of the present research work as most of the natural biological systems owe their specific functions to the presence of active sites that contain two or more coordinated–metal centers, the major studies of biological models are carried out in the area of coordination chemistry

involving the synthesis of and investigations of Polynuclear coordination compounds where in there are more than one metal centers per molecule.

The objectives of these investigations include simulation of some of the bio-technically important biological activities such as oxygen transport[1], oxygen activation[2], nitrogen fixation[3], photosynthetic water reduction[4] and others. By keeping the above points in view, a variety of bi and polynucleating ligands and their corresponding complexes were synthesized with commonly available first row transition metals ions especially copper. This includes designing and controlling the intermetallic free space in the coordination compounds for any specific biological model activity through a suitable choice of biphenyl bridged binucleating ligands and to generate macro cyclic Polynuclear coordination compounds utilizing smaller bridging moieties as spacers such as azide and oxalate groups between the parallel biphenyl pillar bridges and to tailor together heterochemical molecular species to produce new materials for specific engineering applications such as water softening, ionic exchange and anisotropic electrical and magnetic conduction and to humbly contribute services to growth of knowledge in basic chemistry.

METHODOLOGY

The carboxy amide ligands were prepared and characterized [5] and used for the synthesis of azide and oxalate bridged complexes. [Biphenyl bridged tetradentate carboxy amide ligands were prepared by mixing hot benzene solutions of any biphenyl bridge primary diamines like 4, 4' – diamino diphenyl methane (dadpm), Benzidene (benzi.), 0-tolidene (o-toli.) and o-dianisidene (o.dianisi.) with that of any cyclic anhydrides like maleic (male), phthalic (phthal.) and succinic (succi) anhydrides. The ligands precipitated, were filtered through suction and washed repeatedly with hot benzene followed by acetone and dried in vacuum at 90°C overnight.] . The synthesis and characterization of the (i) Azide bridged, (ii) Oxalate bridged and (iii) Azide -oxalate bridged complexes is given in three parts viz (Part-A), (Part-B) and Part- C respectively.

Azide spacer Bridged complex: (Part- A) Azide spacer bridged complexes shown in Structure 1 were synthesized following general procedure. To aqueous suspension of 0.408 gm of 0.toli male ligand (1 m mole) were added as drop wise 20 ml 0f 0.1N NaOH to dissolve the carboxy amide followed by the addition of 0.0130 gm (2 m mole) sodium azide and stirred well. To this, was added an aqueous solution containing 0.214 gm (2 m moles) of cupric nitrate and the contents were slightly warmed on a water bath. Brown colored complex was obtained on stirring. This was filtered through a Buchner funnel and washed with water-methanol and air dried.

Oxalate spacer Bridged complex: (Part- B): Oxalate spacer bridged complexes shown in Structure 2 were synthesized following general procedure adapted for the azide spacer bridged complexes described above using lithium oxalate in place of sodium azide. A typical synthetic procedure is, however briefed here: 0.1974 gm (0.5 m mole) of dadpm male ligand was
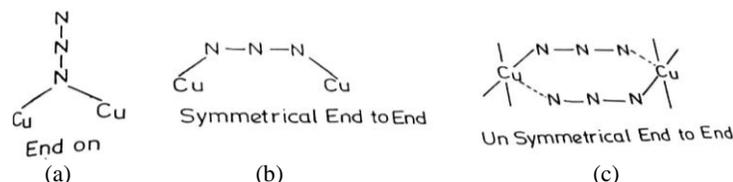
dissolved in a calculated volume of sodium carbonate solution (containing 1 m mole of Na_2CO_3). To this clear solution, was added 0.0501 gm (0.5 m mole) of lithium oxalate in an aqueous solution on a water bath at 70°C. Then an aqueous solution 0.241 gm (1 m mole) of cupric nitrate was added while stirring. The bright green colored complex precipitated was filtered, washed with water, followed by methanol and then air dried. (yield: 80%). The schematic diagram for complexes showing bridging of ligands with spacer groups is given below in Figure 1

Figure 1

RESULTS AND DISCUSSION

The C,H and N analyses for the complexes were obtained using Perkin Elmer CHN analyzer whereas the metal contents were determined following well known[6] methods after digesting complexes with conc. HNO_3. The infrared spectra of the complexes were recorded in KBr on a Perkin Elmer Model 283 spectrophotometer. Room temperature magnetic susceptibility data were collected on Gouy balance using Hg $[Co(CNS)_4]$ as the calibrant. The diamagnetic corrections were applied using Pascal's constants. The ESR spectra were recorded on a JEOL JES FE 3X ESR spectrometer. The differential scanning Calorigrams were recorded on PerkinElmer DSC-4 instrument whereas the thermogravimetric data were obtained using a fabricated TGA apparatus. The solid state electronic spectra of these complexes were obtained using a PARC Photoacoustic spectrometer or a Cary 17D spectrophotometer by reflectance or Nujol mull method.

Characterization of Azide spacer Bridged complexes

Excellent discussion on the trends of azide's bridging characteristics is reported[7-11]. The azide group can bridge two Copper (II) ions either in a symmetrical end to end (EE) fashion as shown in **Figure.2 (a)** or in a end on (E.O) fashion **2(b).** N_3^- can also bridge in an unsymmetrical end to end fashion with a short $Cu-N_\alpha$ bond and a long $Cu-N_\beta$ bond[12-13]. Such a situation occurs when each metal ion is fivefold coordinated with three coordination sites belonging to terminal ligands, the other positions being occupied by the N_α atom of an azide group and the N_β atom of another azide group as shown in **2(c).**

(a)　　　　　　　(b)　　　　　　　(c)

Figure-2 Different Modes of Azide group 1(a) End on (b) symmetrical End to End (c) Unsymmetrical End to End

The physical and analytical data of the complexes are given in the **Table 1**. The elemental including metal analysis data are in agreement with the **Structure 1b**. The copper complexes are insoluble in routine solvents. The infra red (in KBR) and electronic spectral (in Nujol mull), thermal and magnetic data are collected in **Table: 2**. A strong and slightly split IR band was observed near 2095 cm^{-1} due to asymmetric azide stretching. The symmetric stretch of the azide expected at 1300 cm^{-1} is absent in the parent complexes. It is reported that μ- 1,3 azide bridge is symmetrically bonded and that the ν_{sym} is IR inactive or at best very weak. If the azide bridging in EO (μ-1,1) fashion, the $\nu_{sym.}$ will appear at 1300 cm^{-1} with a moderate intensity. The fact that $\nu_{sym.}$ is absent in the present complexes supports the EE type azide bridged (μ-1,3 type) structural assignment as shown in **Figure 2** The split in the azide group may be due to fact where there are two pairs of azides with minor stereochemical in equivalence (vide structure 6). Very broad and strong IR band is observed for all these complexes near 3300 cm-1 which is relatively broader and stronger than the CH and NH stretches of the ligands. This supports the presence of water as a terminal ligand for penta coordination in the bis (μ-1,3azide) bridged structure. The >C=O group of the free carboxy amide ligand absorbs at 1650cm^{-1}. But in the complex, the same band is observed at 1670cm^{-1} indicating the coordination of >C=O group to the metal.

The electronic spectral data of the complexes collected in **Table 2** also supports the structure assigned to them. The d-d transitions for the present complexes observed at ~695 nm (14,300 cm-1) is very close to that reported for equatorial bis (μ-1,3 azide) apical aqua square pyramidal Copper (II) complexes (14,500cm^{-1}) .

Table: 1 Physical and Analytical data^a of Azide bridged complexes.

Compound	Mol. Formula/ Mol.wt.	Elemental analysis					M.P (°C)
		Cu	C	H	N	S	
[Cu$_4$(dadpm male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	C$_{42}$H$_{40}$N$_{16}$O$_{16}$Cu$_4$ (1279)	19.90 (19.87)	40.01 (39.43)	3.20 (3.15)	17.60 (17.52)	-	196 (d)
[Cu$_4$(o.toli male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	C$_{44}$H$_{44}$N$_{16}$O$_{16}$Cu$_4$ (1307)	17.15 (17,14)	40.42 (40.43)	3.40 (3.30)	17.15 (17.14)	-	192 (d)
[Cu$_4$(o.dianisi-male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	C$_{44}$H$_{40}$N$_{16}$O$_{16}$Cu$_4$ (1371)	16.38 (16.34)	38.56 (38.54)	3.30 (3.23)	16.38 (16.34)	-	201 (d)
[Cu$_4$(benz. male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	C$_{42}$H$_{48}$N$_{16}$O$_{16}$Cu$_4$ (1251)	17.92 (17.91)	38.51 (38.40)	2.91 (2.90)	17.92 (17.91)	-	203 (d)
[Cu$_4$(dadpm succi)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	C$_{58}$H$_{44}$N$_{16}$O$_{16}$Cu$_4$ (1287)	19.80 (19.74)	39.21 (39.19)	3.80 (3.75)	17.50 (17.41)	-	198 (d)
[Cu$_4$(dadpm phthal.)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	C$_{44}$H$_{44}$N$_{16}$O$_{16}$Cu$_4$ (1407)	18.14 (18.11	44.54 (44.51)	3.20 (3.16)	15.99 (15.97)	-	199 (d)

^{a} values in parenthesis are theoretical once　　　^{d}, decomposes

Table 2 Infrared. Electronic, Thermal and Magnetic Data of Azide Bridged Complexes

Compound	IR frequencies [a] (cm^{-1})		Electronic data [b] λ [c] ν [d]	ΔH^e deh	f
	υ_{sym} (N^{3-})	$\nu_{C=O}$ of amide grp			μ_{eff} (BM)
[Cu$_4$(dadpm male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	2065	1670	695 (14300)	188.86	1.53
[Cu$_4$(o.toli male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	2115	1675	695 (14492)	190.95	1.68
[Cu$_4$(o.dianisi-male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	2095	1672	695 (14450)	179.53	1.70
[Cu$_4$(benz. male)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	2090	1680	695 (14306)	187.77	1.71
[Cu$_4$(dadpm succi)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	2095	1675	695 (14409)	181.45	1.68
[Cu$_4$(dadpm phthal.)$_2$(N$_3$)$_4$ (H$_2$O)$_4$	2080	1672	695 (14388)	189.38	1.72

[a] recorded in KBr, [b] recorded in Nujol mull, [c] in nm, [d] in cm^{-1}

[e] in K Cal/mole of H$_2$O (dehydration), [f] per metal centre

The room temperature magnetic moment values are also presented in **Table 2** and are evidently slightly subnormal, indicating the presence of measurable anti-Ferro magnetic interaction. The two dimensional metal line up and the possible magnetic interactions are shown in **Structure 1.** As the spacial distance between 1-4, 2-3, 1-3 and 2-4 pairs of copper (II) canters is more than 12 A^o and does not possess any propagation mechanism, the observable anti ferromagnetic interaction must be between the two copper (II) centers in each of the degenerate pairs, 1-2 and 3-4. If azides are bridging in μ -1,1(i.e.EO) fashion, the Cu (II) complexes are stated to be, by and large diamagnetic. As the present complexes exhibit near normal paramagnetism, the possibility of EO type bridging may be ruled out. Variable temperature cryomagentic susceptibility measurements would have provided a great deal of information on the extent and mechanism of the anti ferromagnetic interaction. Unfortunately, such measurements could not be undertaken for want of facilities.

(1-a)   (1-b)
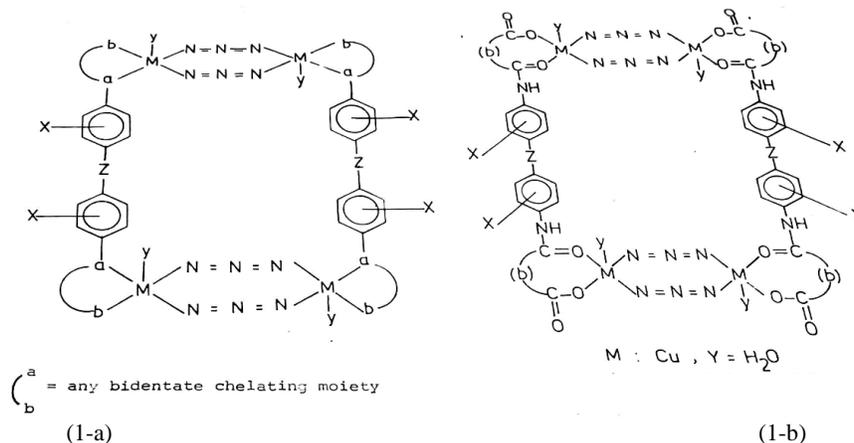
Structure 1 Azide bridged complexes

(Where X=H_2O or any terminal ligand or does not exist; X=H, 3-CH_3, 3-OCH_3 when Z= Nil; X=H, when Z=-CH_2)

Further support for these square pyramidal geometry around Cu(II) centers **Structure 1-b** arrives from ESR spectral studies of the complexes at room temperature and liquid nitrogen temperatures. As these complexes are insoluble, only poly crystalline powder spectrum could be recorded. The ESR spectra of two representative complexes are presented in Figures 4(a) and 4(b) respectively. The g $\parallel$, g⊥, go , A$\parallel$, A⊥ and A_o values for all the complexes are collected in **Table 3.** The Δ M_s = ±2 transition could not be detected as it be considerably dipolar – broadened through inter molecular interactions.

Table 3 ESR spectral data of Azide Bridged complexes

Compound	g $\parallel$	g⊥	go [a]	A$\parallel$ (cm-1) 10^4	A⊥	A_o [a] $(cm^{-1})10^4$
[Cu_4(dadpm.male)$_2$(N_3)$_4$ (H_2O)$_4$	2.34	2.00	2.11	193.8	100.0	131.3
[Cu_4(o.toli male)$_2$(N_3)$_4$ (H_2O)$_4$	2.25	2.03	2.10	108.5	85.2	93.0
[Cu_4(o.dianisi-male)$_2$(N_3)$_4$ (H_2O)$_4$	2.32	1.97	2.08	201.5	108.5	139.5
[Cu_4(benz. male)$_2$(N_3)$_4$ (H_2O)$_4$	2.25	1.98	2.07	194.0	102.0	132.6
[Cu_4(dadpm succi)$_2$(N_3)$_4$ (H_2O)$_4$	2.31	2.01	2.11	182.0	111.5	135.0
[Cu_4(dadpm phthal.)$_2$(N_3)$_4$ (H_2O)$_4$	2.25	2.10	2.15	194.0	102.5	133.0

a, calculated from equations go = ⅓[g $\mid$ +2 g⊥] , $A_{o=}$ ⅓ [A$\mid$ +2 A⊥]

To evaluate the M-OH_2 bond energy and tom prove the presence of water molecules, the complexes were investigated by Differential Scanning Calorimetry in the ambient to 350°C temperature range. The complexes exhibit strong exothermic activity in the temperature range 180- 200°C. The peaks are associated with closure shoulders. It may more plausibly be stated that compounds undergo decomposition in the range (vide Table 1). The heat of decomposition of these complexes is also collected in **Table 2**. The endothermic dehydration activity may be enveloped in the observed exothermic DSC peak, and thus, marring the calculation of the M-OH_2 bond energy. The Differential Scanning Calorigrams for two representative compounds are given in **Figure 3.**
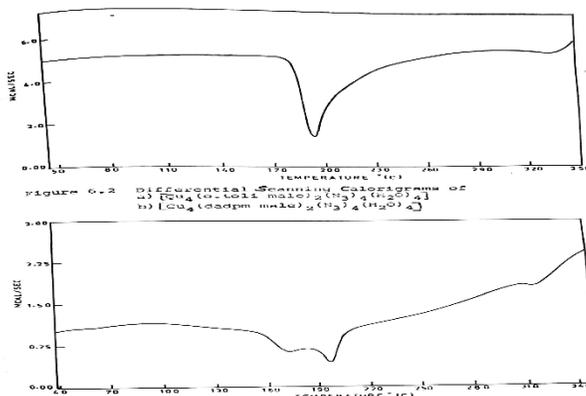
Figure 3 DSC of (a)[Cu_4(o.toli male)$_2$ (N_3)$_4$ (H_2O)$_4$ (b)[Cu_4(dadpm male)$_2$ (N_3)$_4$ (H_2O)$_4$

(4a)   **(4b)**
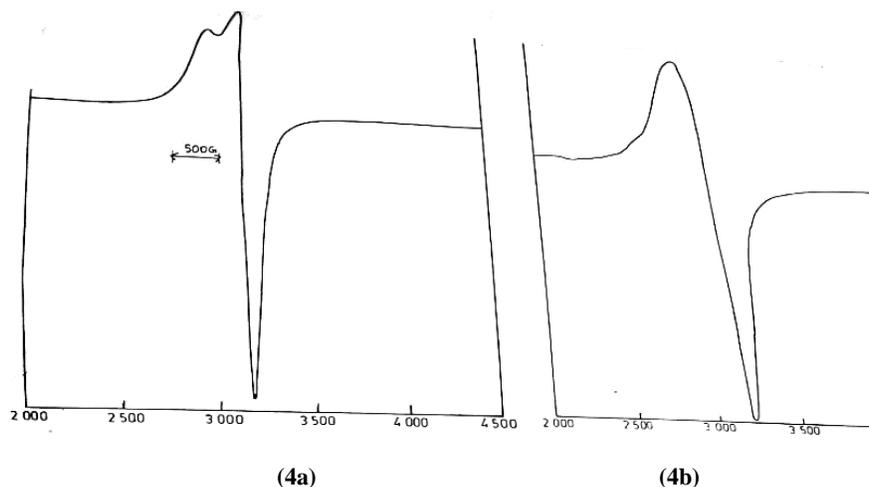
Figure 4 X-band polycrystalline ESR spectra of (a) [Cu4(o.toli male)2 (N3)4 (H2O)4 (b) [Cu4(dadpm male)2 (N3)4 (H2O)4

Based on the elemental, spectral, magnetic and thermal studies, **Structure 1b** may be assigned for these complexes.

Characterization of Oxalate spacer Bridged complexes

The structure of macromolecular tetranuclear coordination compounds where in oxalate was used as the spacer bridge is presented in **Structure 2** with biphenyl bridged carboxy amide as the pillar bridge**.** The physical and analytical data are presented in **Table -4** The C, H, N, S and Cu elemental data are in conformity with this structure. These complexes are also insoluble in routine solvents, thus limiting the investigations, to solid state samples.

Table 4 Physical and Analytical data [a] of Oxalate bridged complexes

Compound	Mol. Formula/ Mol.wt.[b]	Elemental analysis				
		Cu	C	H	N	S
[Cu4(dadpm male)2(Ox)2 (H2O)4	C44H40N4O20Cu4 (1287)	19.80 (19.74)	42.94 (42.92)	3.15 (3.13)	4.40 (4.40)	-
[Cu4(dadpm phthal.)2(Ox)2 (H2O)4	C62H48N16O16Cu4 (1487)	17.20 (17,08)	50.21 (50.07)	3.30 (3.28)	3.80 (3.76)	-
[Cu4(o.toli male)2(Ox)2 (H2O)4	C48H52N4O20Cu4 (1255)	19.22 (19.21)	43.60 (43.57)	3.92 (3.96)	4.30 (4.23)	-
Cu4(o.dianisi-male)2(Ox)2 (H2O)4	C48H44N4O28Cu4 (1267)	19.20 (17.32)	44.01 (43.83)	3.80 (3.73)	4.50 (4.26)	-
[Cu4(benz. phthal)2(Ox)2 (H2O)4	C44H48N4O20Cu4 (1295)	20.10 (20.06)	42.68 (42.66)	3.52 (3.50)	4.45 (4.42)	-
[Cu4(dadpm succi)2(Ox)2 (H2O)4	C64H48N4O20Cu4 (1295)	19.65 (19.62)	44.54 (44.51)	3.75 (3.73)	4.38 (4.32)	-

[a] values in parenthesis are theoretical once
[b], not determined due to insolubility.

The infra red spectral data of the complexes in Nujol- mull for a few important bands are collected in **Table- 5**. Oxalate ion can coordinate to metal ion in five different formats as shown in **Structure 2 b**, out of which modes (ii) and (iii) are more frequent. Since oxalate ion, as shown in **Figure 5**, exists in the canonical forms, the coordination modes (i), (iv) and (v) are less stable and hence are scarce. Complexes wherein oxalate ion coordinates in a bidentate mode i.e fashion (i) exhibits characteristic IR bands which are slightly more energetic than those wherein oxalate does in bis-bidentate mode i.e fashion (iii) The bands are attributed to asymmetric stretch of the carbonyl group. The symmetric $>C=O$ stretches ν_s (COO⁻) and δ (-COO⁻) bands of the bis bidentate, however, are more energetic than those of bidentate kind [14].
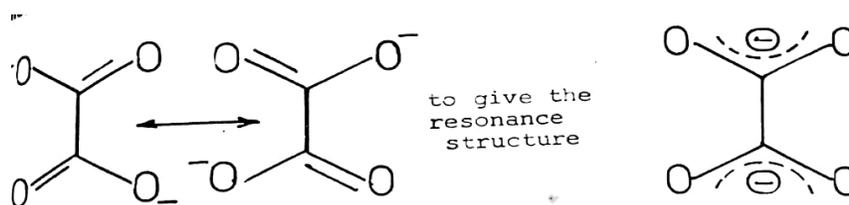
Figure 5 Canonical forms of Oxalate ion

Table 5 Infrared, Electronic, Thermal and Magnetic Data of Oxalate Bridged Complexes

Compound	IR frequencies [a] (cm⁻¹)			Electronic data [b]	d
	υ_{as} (CO)	ν_s (CO)	Δ (OCO)	λ [b] ν [c]	μ_{eff} (BM)
[Cu₄(dadpm male)₂(Ox)₂ (H₂O)₄	1645	1360 1315	800	690 (14492)	1.73
[Cu₄(dadpm succi)₂(Ox)₂ (H₂O)₄	1650	1358 1320	820	692 (14450)	1.72
[Cu₄(dadpm phthal.)₂(Ox)₂ (H₂O)₄	1648	1361 1320	815	694 (14409)	1.69
[Cu₄(o.toli male)₂(Ox)₂ (H₂O)₄	1644	1360 1320	820	699 (14306)	1.67
[Cu₄(benz. male)₂(Ox)₂ (H₂O)₄	1648	1358 1318	812	690 (14306)	1.74
Cu₄(o.dianisi-male)₂(Ox)₂ (H₂O)₄	1651	1348 1316	810	695 (14388)	1.65

[a] recorded in KBr pellet,   [b] in nm;   [c] in cm⁻¹,   [d] per metal centre at room temperature.

The electronic spectral data of these complexes in Nujol-mull are collected in **Table 5** and are very close to those of the complexes reported in Part-A . Hence the **Structure 2**, where copper is bonded in a square pyramidal geometry may be considered valid. The magnetic moment values measured for some of the complexes collected in **Table 5** are only slightly subnormal at room temperature, indicating the presence of anti Ferro magnetic interactions. The strength of which should not be concluded to be weak just because the magnetic moment is only slightly subnormal. It is well known [15] that some of the complexes show magnetic moment in range 1.9-1.95 B.M. at 270 K but drops down to ~0.1 BM at 4.2 K with estimated 2J value of ~ 62.0 cm⁻¹.

Cryo-magnetic susceptibility measurements could not be undertaken for the present complexes.

The ESR spectra of these complexes exhibit profiles characteristic of square pyramidal geometry. As the complexes are insoluble, only poly crystalline powder ESR spectra could be recorded. The powder ESR spectrum of a representative complex at room temperature is shown in **Figure 6** and the relevant. ESR data of all the compounds are collected in **Table 6.** Based on the above investigations, the **Structure 2a** is assigned to these complexes.

(a)   **(b)**

Structure:2 Oxalate bridged complexes
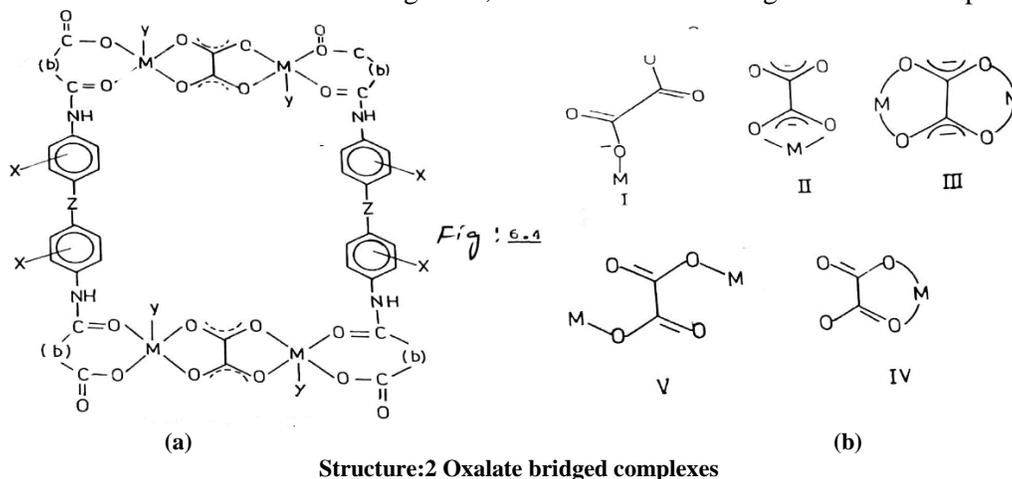
Figure 6 X-band polycrystalline ESR spectrum of [Cu$_4$(dadpm male) (OX)$_4$ (H$_2$O)$_4$ at room temperature (υ =9.234)

Table 6 ESR spectral data of Oxalate Bridged complexes

Compound	g ‖	g⊥	go [a]	A‖ (cm-1) 10^4	A⊥	A$_o$ [a] (cm^{-1})10^4
[Cu$_4$(dadpm male)$_2$(Ox)$_2$ (H$_2$O)$_4$	2.28	2.16	2.20	121.7	80.6	94.3
[Cu$_4$(o.dianisi-male)$_2$(Ox)$_2$ (H$_2$O)$_4$	2.23	2.002	2.078	204.0	85.3	124..3
[Cu$_4$(o.toli male)$_2$(Ox)$_2$ (H$_2$O)$_4$	2.35	2.040	2.14	186.0	77.5	113.6
[Cu$_4$(benz. male)$_2$(Ox)$_2$ (H$_2$O)$_4$	2.21	2.10	2.13	157.0	84.5	108.6
[Cu$_4$(dadpm succi)$_2$(Ox)$_2$ (H$_2$O)$_4$	2.23	2.05	2.11	132.0	82.5	99.0

a, calculated from equations go = ⅓[g ‖ +2 g⊥] , A$_o$= ⅓ [A‖ +2 A⊥]

Part 3: **Oxalate- Azide bridged complexes**: To assess the relative stability of macromolecular tetranuclear Cu (II) complexes, mentioned above, where azide is the spacer bridge and those

in this part where oxalate is the spacer bridge and to ascertain whether a hetero bridged tetranuclear complex would result in, a synthesis was carried out involving the collective components cupric nitrate, lithium oxalate, sodium azide and biphenyl bridged carboxy amide in a 2:1:2:1 molar ratio. The components isolated were found to be different from both the diazido bridged and oxalate bridged complexes.

The physical and analytical data of the compounds are collected in **Table 7** The elemental including metal analysis data are in consistent with an empirical formula $Li_4(Cu_4L_2(Ox)_2(N_3)_4]$. With this empirical formula, the **Structure 3** is plausible for these compounds. Thus these compounds may be viewed to have developed by substitution of the four water molecules of Structure 6 by four terminal (non-bridging) azides. The association of the tetravalent anionic complex in Structure 3. with four Li^+ ions against four Na^+ ions is justified by the lower solubility product of Li_4 [complex].

Table: 7. Physical and Analytical data[a] of some oxalate- azide bridged complexes with Azides.

Compound (Li₄ salt of)	Mol. Formula/ Mol.wt.	Elemental analysis					
		Cu	Li	C	H	N	S
$[Cu_4(dadpm\ male\ )_2\ (Ox)_2(N_3)_4$	$C_{46}H_{32}N_{16}O_{20}\ Li_4Cu_4$ (1411)	18.20 (18.01)	1.99 (1.96)	39.5 (39.20)	2.28 (2.38)	15.90 (15.88)	-
$[Cu_4(dadpm\ phthal.)_2(Ox)_2(N_3)_4$	$C_{62}H_{40}N_{16}O_{20}\ Li_4Cu_4$ (1611)	13.70 (13.67)	1.50 (1.49)	53.40 (53.38)	2.18 (2.16)	12.10 (12.07)	-
$[Cu_4(dadpm\ succi\ )_2(Ox)_2(N_3)_4$	$C_{46}H_{40}N_{16}O_{20}Li_4Cu_4$ (1418)	17.98 (17.91)	1.98 (1.95)	39.10 (38.93)	2.90 (2.84)	15.80 (15.79)	-
$[Cu_4(o.toli\ male)_2(Ox)_2(N_3)_4$	$C_{42}H_{48}N_{16}O_{16}\ Li_4Cu_4$ (1439)	17.74 (17.66)	1.95 (1.93)	40.90 (40.06)	2.60 (2.52)	15.68 (15.57)	-
$[Cu_4(o.toli\ succi)_2(Ox)_2(N_3)_4$	$C_{58}H_{44}N_{16}O_{16}\ Li_4Cu_4$ (1447)	17.60 (17.56)	1.98 (1.92)	40.21 (39.84)	3.15 (3.06)	15.58 (15.48)	-

[a] values in parenthesis are calculated ones,
[b] not determined due to insolubility and ionic character

Table 8 Infrared, Electronic, Thermal and Magnetic Data of Oxalate and Azide Bridged Complexes

| Compound (Li₄ salt of)	IR frequencies [a] (cm⁻¹)					Electronic data [b] λ [b] ν [c]	ΔH^e deh	d μ_{eff} (BM)
	υ_{as} N_3^-	$\nu_s^{(CO)}$ of amide grp	υ_{as} (CO)	$\nu_s^{(CO)}$	δ ((OCO)			
$[Cu_4(dadpm\ male\ )_2\ (OX)_2(N_3)_4$	2065	1675	1725 1640	1420	790	698 (14326)	83.01	1.68
$[Cu_4(dadpm\ phthal.)_2(OX)_2(N_3)_4$	2060	1670	1720 1650	1415	780	700 (14285)	104.2	1.70
$[Cu_4(dadpm\ succi\ )_2(OX)_2(N_3)_4$	2068	1665	1715 1645	1420	800	710 (14084)	100.05	1.67
$[Cu_4(o.toli\ male)_2(OX)_2(N_3)_4$	2064	1672	1718 1640	1422	805	695 (14388)	95.04	1.65
$[Cu_4(o.dianisi.male)_2(OX)_2(N_3)_4$	2030	1670	1720 1645	1418	790	690 (14492)	98.10	1.70
$[Cu_4(benz.\ male\ )_2\ (OX)_2(N_3)_4$	2045	1680	1722 1650	1415	795	695 (14388)	100.10	1.68

[a] recorded in KBr pellet, [b] in nm; [c] in cm⁻¹, [d] per metal centre at room temperature.

The IR spectra of these compounds exhibit strong new $\upsilon_{asym.}$ (N=N=N) and moderately intensed $\upsilon_{sym.}$ Stretching bands, characteristic of (un-bridged) terminal azide coordination. Bands characteristic of Oxalate Bridge also observed. Some of important the band assignments are collected in **Table 7**. The broad IR band due to H_2O at ~3,200 cm-1, observed in the case of compounds of Structures (1b) and (2b) is absent i
n the present complexes, indicating the case of substitution.

The room temperature magnetic moment values measured for these compounds are slightly subnormal and are very close to those observed for bis(bidentate) oxalate bridged Cu(II) complexes in the same are collected in **Table 7.** However the ESR spectra show marked difference in profile due to the change over H_2O to N_3^- at the apical position of the square pyramidal copper geometry. Important ESR data are presented in **Table 8**

The differential scanning Calorimetry performed on these compounds provide interesting results. When the carboxy amide ligand moieties are linked by a 4,4' biphenyl pillar bridged, the compounds exhibit a sharp endothermic peak at ~150°C with an apparent ΔH=83.01K.Cal. /mole. But those complexes, where the biphenyl is the counterpart seem to undergo an exothermic thermal incidence at ~190°C. However, all the compounds, irresespective of the nature of the pillar bridge undergo exothermic process at ~320°C . The differential Scanning Calorigrams of two representative compounds are shown in **Figure 6.** Considering that the endothermic peak of the dadpm based compounds at ~150°C is due to single step M-N bond (azide's) breakage, the M-N bond energy is calculated. The exothermic peak observed for the other compounds at ~ 190°C might be due to the decomposition of azide moiety alone. The exothermic process at ~320°C (in one step dadpm based compound and two successive steps for the others) might be due to the decomposition of the oxalate part. Thus it can be considered as though the compounds have MO_4 (near square planar) geometry around their metal centers in the temperature range between the thermal incidences.

Based on all the above studies, it can be concluded that the oxalate is a stronger bridging moiety than the azide and that the later can only coordinate as the terminal ligand in the presence of an oxalate bridge as highlighted in **Structure 3.**
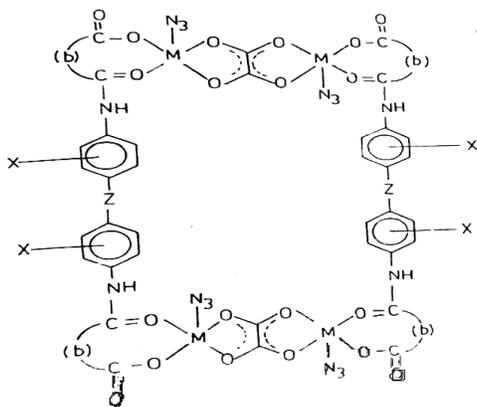
Structure 3 Oxalate-Azide bridged complexes

Table 8. ESR spectral data of Oxalate Bridged complexes with Terminal azides

Compound	$g \parallel$	$g\perp$	g_o [a]	$A\parallel$ (cm-1) 10^4	$A\perp$	A_o [a] (cm^{-1})10^4
$[Cu_4(dadpm\ male\ )_2(Ox)_2\ (N_3)_4$	2.28	2.03	2.12	155.0	69.8	98.2
$[Cu_4(dadpm.phthal.)_2(Ox)_2(N_3)_4]$	2.22	2.10	2.14	158.2	70.2	99.5
$[Cu_4(dadpm\ succi\ )_2(Ox)_2\ (N_3)_4$	2.28	2.12	2.17	178.5	82.5	114.5
$[Cu_4(o.toli\ male\ )_2(Ox)_2\ (N_3)_4$	2.34	2.03	2.13	193.8	69.7	111.1
$[Cu_4(o.dianisi\text{-}male)_2(Ox)_2\ (N_3)_4$	2.33	2.02	2.12	201.5	69.8	113.7
$Cu_4(benz.\ male\ )_2(Ox)_2\ (N_3)_4$	2.30	2.11	2.17	182.5	80.1	114.2

a, calculated from equations $g_o = \frac{1}{3}[\ g_| +2\ g_\perp]$, $A_{o=} \frac{1}{3} [A_| +2\ A_\perp]$

CONCLUSION

Biphenyl bridged Polynuclear complexes with azide and oxalate spacer groups were prepared with enhanced spacial gap and characterized using different spectroscopic techniques. Use of instrumental facilities at the University of Hyderabad, Hyderabad is gratefully acknowledged.

REFERENCES

1. Lontie. R, Vanquickenborne. L. "*Metal ions in biological systems*", 183 (3): (1974)
2. Vauneste. W.H., Zuberbunler. A., "Molecular Mechanisms of Oxygen Activation" Ed.D.Hayaishi, Academic press, New York, , p 371. (1974)
3. Newton. W.E and. Johnson. W.H.O ed's, "Dinitrogen fixation" University Park Press, Balimore, (1980).
4. Chemiae. G.M., *Annual Rev. Plant Physiology*, 467(21) : (1970),
5. Sarojini. T., Ramachandraiah. A, *Indian Journal of Chemistry* Vol. 29(A), December (6)1174-1177 (1990).
6. Vogel A.I, A laboratory text book of quantitative inorganic chemistry, (ELBS) London, (1961).
7. Charlot. M.F,.Khan. O, Chaillet. M. and.Larrieu .C, *J.Am. Chem. Soc*., (108) 2574 (1986).
8. Baily. N.A, Fenton. D.E. and. McLean. C.H *Inorg. Chim.Acta* 179 (1):(1991).
9. Casellato. V. and. Vigato. P.A, *Coord. Chem Reviews* 23(31):(1977).
10. Nelson. S.M., *Inorg. Chim. Acta*, 62 (39) (1982).
11. Goher. M.A.S and. Mak. T.C.W, *Inorg. Chim. Acta*, 117.(89) :(1984).
12. Kahn. O., Boilot. M.L, Kahn. O.," In Biological and Inorganic Aspects of Copper coordination Chemistry"; K.D. Karlin,J.Zubieta, Eds. Ademine Press. Guilder land, N.Y. (2) (1985).
13. Felthouse. T., Hendrickson. R. *Inorg. Chem*., 444 (17) :(1978),
14. Castro. J. Faus. J.,.Julve. M,.Munoj. M.C. *Inorg. Chim. Acta* 179,(59) : (1991).