

Synthesis and characterisation of some biphenyl bridged complexes of a new class of binucleating ligands containing amide groups

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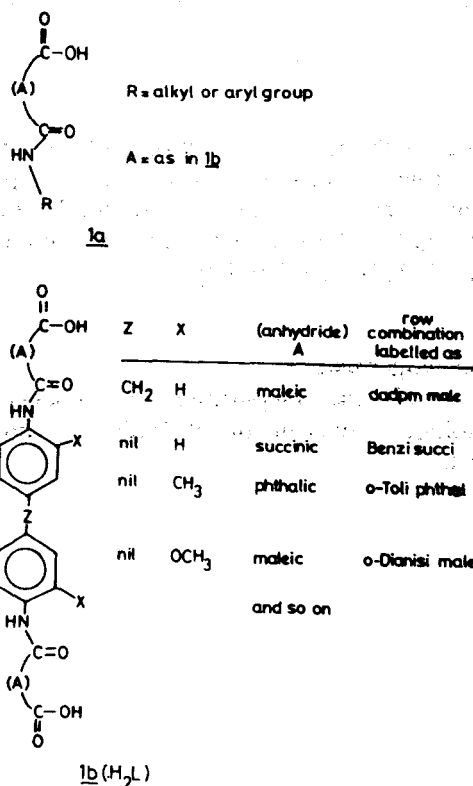
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A series of biphenyl bridged polynuclear complexes, $(M_2L_2 \cdot xH_2O)_n$, has been synthesized from a new class of binucleating ligands (H_2L), containing amide group, where $M = Fe(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$, and H_2L are ligands obtained by reacting succinic (succi), phthalic (phthal) or maleic (male) anhydride with biphenyl bridged primary diamines such as 4,4'-diaminodiphenylmethane (dadpm), benzidine (benzi), *o*-tolidine (*o*-toli) and *o*-dianisidine (*o*-dianisi). The complexes $(M_2L_2 \cdot xH_2O)_n$ have been characterized by elemental, spectral, magnetic and thermal studies. For $M = Co^{2+}$, Ni^{2+} and Zn^{2+} , $x = 4$ with two water molecules coordinated at each metal centre giving MO_6 weak field octahedral chromophores. For $M = Cu^{2+}$ and Fe^{2+} , $x = 0$ giving only MO_4 chromophores. Only normal magnetic moment values are observed at room and liquid nitrogen temperatures suggesting the absence of any strong antiferromagnetic interaction. Based on the elemental analysis, solubility and spectral data, a polymeric structure is tentatively suggested for the complexes.

Ligands containing 3-carboxyamide chain (**1**) and their metal chelates have been stated to have noteworthy pharmacological activities¹⁻⁴. Only mononucleating carboxyamide ligands (**1a**) and their chelates had been reported so far⁵⁻⁷. Recently⁸, the corresponding binucleating ligands (**1b**) have been prepared by direct mixing of hot benzene solutions of aromatic biphenyl bridged primary diamines and a cyclic anhydride in 1:2 molar ratio. Here we present the synthesis and characterisation of a few chelates of M_2L_2 type using this (**1b**) new ligand series.

Materials and Methods

The ligands, H_2L (**1b**), were prepared as reported⁸ and purified by dissolving in sodium carbonate solution and regenerating by acidification followed by repeated washings. Bivalent metal salts were commercial samples of AR grade and were used without further purification. In a typical preparation 2 mmol of the ligand was suspended in 50 ml of water to which was added a calculated volume of standard sodium carbonate solution (~ 2 mmol), while stirring. To the clear Na_2L solution thus obtained was added 2 mmol of the metal salt in 40 ml of water when a coloured metal complex immediately precipitated. The complex was filtered by suction, washed with warm dilute sodium carbonate solution followed by warm water and air-dried (yield 96-99%).



The C, H and N analyses for the complexes were obtained using Perkin Elmer CHN analyser whereas the metal contents were determined following well known⁹ methods after digesting the

Table 1 – Analytical, magnetic and spectral data of the complexes

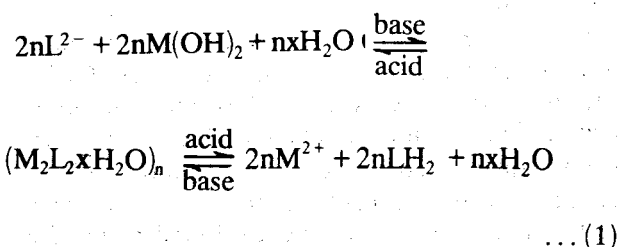
Complex	Molec. wt.	Found (Calc.) %				$\mu_{\text{eff.}}$ (B.M.) ^a	ν_{max} ^b
		M	C	H	N		
[Cu ₂ (dadpm male) ₂] _n	911.61	12.85 (12.92)	54.31 (54.29)	3.84 (3.95)	6.54 (6.58)	1.83 (1.81)	10,620
Cu ₂ O(<i>o</i> -Dianisi male) ₂] _n	1003.87	12.71 (12.66)	52.71 (52.65)	3.58 (3.60)	5.60 (5.58)	1.83 (1.82)	10,620
[Co ₂ (dadpm male) ₂ 4H ₂ O] _n	974.46	12.10 (12.09)	54.89 (54.87)	3.89 (3.86)	6.59 (6.51)	4.01 (4.02)	8,450 17,650 21,585
Ni(dadpm male) ₂ 4H ₂ O] _n	974.01	12.08 (12.06)	51.80 (51.79)	4.18 (4.14)	5.79 (5.75)	2.79 (2.80)	9,025 15,250 22,475
Zn ₂ (dadpm male) ₂ 4H ₂ O] _n	987.33	13.29 (13.24)	51.10 (51.09)	4.06 (4.08)	5.68 (5.67)	—	
[Fe ₂ (dadpm male) ₂] _n	901.23	12.98 (12.94)	55.95 (55.97)	3.54 (3.58)	6.28 (6.23)	4.87 (4.86)	

^aper metal centre at room temp.; values shown in parentheses are at liquid nitrogen temp.^brecorded in nujol mull; values are in cm⁻¹

complexes with conc. HNO₃. 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 a 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 either a PARC photoacoustic spectrometer or a Cary 17D spectrophotometer by reflectance or nujol mull method.

Results and Discussion

All the complexes were found to be high melting (m.p. not less than 300°C) and insoluble in most of the organic solvents and water. However, in strong acidic and basic media they disproportionated reversibly as shown in Eq. (1),



The disproportionation products were identified by comparison with the authentic samples of compounds.

A comparison of the infrared spectra of the ligands H₂L and their complexes revealed that the ligand coordinated through the deprotonated carboxylic oxygen and the carbonyl oxygen of the amide group. The IR band due to νNH mode observed in the H₂L ligands at 3200 cm⁻¹ remained unshifted in the spectra of the complexes whereas the strong νC=O band of the amide group observed in the ligands at 1650 cm⁻¹ was lowered by 10-15 cm⁻¹ in the spectra of the complexes. Similar observations were reported for the mononuclear analogues, obtained from the ligand series (1a) also¹⁰. Normally, δCH₂ and δH₂O modes interfere in the assignment of νC=O mode, making this assignment somewhat ambiguous. However, in the present case this problem has been overcome by comparing the spectra with those of complexes where CH₂ and H₂O groups do not exist, e.g., [Cu₂(benz. male)₂]_n. The free ligand exhibits ν_{as}(COO⁻) and ν_s(COO⁻) at ~1540 and ~1420 cm⁻¹ respectively. The corresponding frequencies in the complexes occur at ~1555 and 1398 cm⁻¹ indicating an enhancement in Δν value upon complexation where Δν is the difference between ν_{as}(COO⁻) and ν_s(COO⁻). This fact suggests that the carboxylate moiety of the present ligand system coordinates to the metal centre in a monodentate fashion^{11,12}. The stabilization of such seven-membered chelate rings, even though un-

Table 2 – ESR spectral data of $(\text{Cu}_2\text{L}_2)_n$ complexes

Complex	$g_{\parallel}$	$g_{\perp}$	g_0^a	$A_{\parallel}$ (cm^{-1}) $\times 10^4$	$A_{\perp}$ (cm^{-1}) $\times 10^4$	A_0^a (cm^{-1}) $\times 10^4$
$[\text{Cu}_2(\text{dadpm male})_2]_n$	2.25	2.06	2.12	145.74	31.00	69.25
$[\text{Cu}_2(\text{dadpm phthal})_2]_n$	2.28	2.06	2.13	151.94	40.30	79.53
$[\text{Cu}_2(o\text{-Dianisi male})_2]_n$	2.30	2.08	2.15	142.64	49.61	80.62
$[\text{Cu}_2(\text{Benzi male})_2]_n$	2.30	2.09	2.16	133.34	43.40	73.38
$[\text{Cu}_2(\text{dadpm succi})_2]_n$	2.27	2.06	2.13	142.64	37.21	72.35
$[\text{Cu}_2(o\text{-Toli male})_2]_n$	2.29	2.07	2.13	139.28	49.61	79.5

^aCalculated from the equations $g_0 = 1/3[g_{\parallel} + 2g_{\perp}]$ and $A_0 = 1/3[A_{\parallel} + 2A_{\perp}]$

usual, is not unknown. In the case of mononuclear analogues also the formation of seven-membered chelate rings was concluded^{10,13}.

The C, H, N and metal analysis data obtained for some representative compounds of $(\text{M}_2\text{L}_2 \times \text{H}_2\text{O})_n$ are collected in Table 1. These data are in agreement with the formulae of the complexes.

Electronic spectral data

Due to insolubility of the complexes in aqueous and most of the organic solvents, only solid state electronic spectra in nujol mull, reflectance and photoacoustic modes could be recorded. The copper complexes absorbed in the range 10,580–10,640 cm^{-1} , in the near infrared region. The reported mononuclear analogues were found to absorb in the range 14,500–15,100 cm^{-1} and a square-planar geometry was assigned to them¹³. When square-planar Cu(II) complex is tetrahedrally distorted, it is well known that a red shift is observed in its $d-d$ transitions¹⁴. The fact that the present binuclear complexes absorb at lower energies than the corresponding mononuclear analogues is suggestive of a distorted square-planar geometry around the Cu(II) centres in the present complexes. The Co(II) complexes exhibited three transitions at $\sim 8,500$, $\sim 17,700$ and $\sim 21,500$ cm^{-1} . These transitions, which may be assigned to ${}^4T_{2g} \leftarrow {}^4T_{1g}(F)(\nu_1)$, ${}^4E_{2g} \leftarrow {}^4T_{1g}(F)(\nu_2)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$ respectively are indicative of octahedral geometry around the Co(II) centres. This assignment is further supported by the observed value of 2.08 for the ratio ν_2/ν_1 as expected for octahedral Co(II). These observations are also in agreement with those for the mononuclear analogues¹³. The Ni(II) complexes too exhibited three bands at $\sim 9,000$, $\sim 15,200$ and $\sim 22,400$ cm^{-1} , generally expected for octahedral Ni(II) complexes due to ${}^3T_{2g} \leftarrow {}^3A_{2g}(F)(\nu_1)$, ${}^3T_{1g} \leftarrow {}^3A_{2g}(F)(\nu_2)$ and ${}^3T_{1g} \leftarrow {}^3A_{2g}(F)(\nu_3)$, transitions respectively.

These are closely related to the absorptions observed for the corresponding mononuclear analogues.

Magnetic data

The room and liquid nitrogen temperature magnetic moment data obtained for the complexes are also given in Table 1. The μ_{eff} values per metal centre were found to be normal both at room and liquid nitrogen temperatures indicating the absence of any strong intra- and inter-molecular anti-ferromagnetic interactions. This is not surprising because of the large length of the bridging biphenyl moiety (~ 11 Å). Even the super exchange mechanism due to the π -electron delocalization suffers from the discontinuity at the 1,1'-positions of the bridging biphenyl rings as the two phenyl rings are non-coplanar with the dihedral angle of more than 30° . The magnetic moment values for Co^{2+} and Ni^{2+} complexes are suggestive of weak field octahedral geometry around the metal centres and that for the Fe^{2+} is suggestive of weak field tetrahedral geometry. The fact that Fe^{2+} is in a tetrahedral geometry is supported by the Mössbauer spectral parameters (for $[\text{Fe}_2(\text{dadpm.male})_2]_n$ $\delta = 0.4390$ mm s^{-1} and $\Delta_{\text{eq}} = 0.5866$ mm s^{-1}).

ESR data

The ESR spectra of Cu(II) complexes showed well resolved parallel and perpendicular parts. The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ values for Cu(II) complexes are given in Table 2. The forbidden $\Delta M_s = \pm 2$ transition is not observed at room as well as at liquid nitrogen temperatures further suggesting the absence of antiferromagnetic interaction. The g_0 and A_0 values indicate a distorted CuO_4 square-planar site. The resolution of the parallel and perpendicular parts of ESR spectrum of Cu(II) complexes may be attributed to the fact

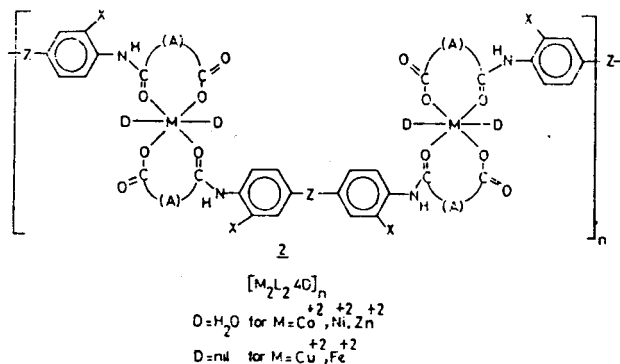
that there is considerable magnetic dilution owing to the large size of the ligand frame work. This is expected to keep the metal centres considerably separated in the solid state lattice structure thus avoiding any dipolar broadening.

Thermal data

A concrete support for the presence of MO_6 moiety in the Co^{2+} , Ni^{2+} and Zn^{2+} complexes due to involvement of two water molecules at each metal centre emerges from the thermal studies on the complexes. The differential scanning calorigrams of Co^{2+} , Ni^{2+} and Zn^{2+} complexes indicated endothermic peaks at 128, 115 and 131°C respectively. The thermogravimetric analysis on these complexes also indicated weight loss equivalent to that of two water molecules per metal centre. Peak area calculations of the differential scanning calorigrams assuming two water molecules per metal centre resulted in the values of the bond energies of $\text{Co}^{2+} - \text{OH}_2$, $\text{Ni}^{2+} - \text{OH}_2$ and $\text{Zn}^{2+} - \text{OH}_2$ as 14.02, 13.76 and 15.45 kcal per mol respectively. These values are very close to the usual metal-water bond enthalpies for corresponding metal-aquo complexes. Similar thermal studies on the Cu^{2+} and Fe^{2+} complexes did not indicate any such water loss even upto 250°C . The thermal studies, the insolubility of the complexes and the steric factors suggest the polymeric chain structure for all the complexes as represented in structure 2.

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References

- 1 Raymond K N & Carrano C J, *Acc chem Res*, 12 (1979) 183.
- 2 Sigel H & Martin R B, *Chem Rev*, 82 (1976) 1.
- 3 Williams D R, *Chem Rev*, 72 (1972) 203.
- 4 Ravinder V & Lingaiah P, *Curr Sci*, 53 (1984) 1032 and references cited therein.
- 5 Chapman E & Stephen H, *J chem Soc*, 127 (1925) 1791.
- 6 Subba Rao N V & Rathnam C V, *J scient ind Res*, 218 (1962) 45.
- 7 Ravinder V, Lingaiah P & Veera Reddy K, *Inorg chim Acta*, 87 (1984) 35.
- 8 Sarojini T & Ramachandraiah A, (Communicated to *Curr Sci*).
- 9 Vogel A I, *A laboratory text book of quantitative inorganic chemistry*, 3rd Edn (ELBS, London) 1961.
- 10 Ravinder V, Swamy S J, Sri Hari S & Lingaiah P, *Trans Met Chem*, 9 (1984) 103.
- 11 Nakamoto K, *Infrared and Raman spectra of inorganic and coordination compounds*, 3rd Edn (John Wiley & Sons, New York) 1978.
- 12 Robinson S D & Uttley M F, *J chem Soc*, (1973) 1912.
- 13 Ravinder V, *Studies on some transition metal complexes with ligands containing amide group*, Ph.D. thesis submitted to the Kakatiya University, Warangal, 1983.
- 14 Ramachandraiah A, Sarojini T, Laxma Reddy K & Zacharias P S, *Polyhedron*, (in press).