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Synthesis & characterisation of copper(II), nickel(II), cobalt(II) & dioxouranium(VI) complexes of a new series of tetradentate binucleating schiff base ligands

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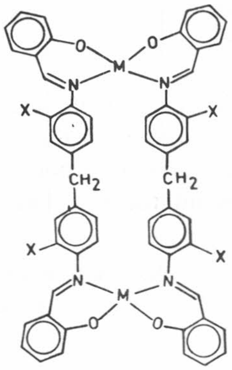
A new series of binucleating tetradentate ligands, Sal-dadpmX, and complexes of the type M_2(Sal-dadpmX)$_2$ have been synthesised and characterised by elemental analysis, spectral, magnetic and thermal studies, where Sal-dadpmX refers to 3,3′-di(X)-substituted-4,4′-bis(salicylideneimino)diphenylmethane (X = H, CH_3, OCH_3, Cl) and M = Cu(II), Ni(II), Co(II) and dioxouranium(VI). The results indicate a binuclear structure for Cu(II) complexes with pseudo-tetrahedral geometry and polynuclear structures for Ni(II), Co(II) and dioxouranium(VI) complexes with near octahedral geometry. The two Cu(II) centres of Cu_2(Sal-dadpmX)$_2$ exhibit one step two-electron cyclic voltammetric responses due to Cu(II)/Cu(I) at ~ −0.35V and Cu(II)/Cu(III) at ~ +0.45V (vs SCE).

Recent reports on binuclear Cu(II) complexes with biphenyl moieties as bridging units have shown that a considerable amount of antiferromagnetic interaction exists between the two copper(II) centres through the σ-overlap-super exchange mechanism[1,2]. The normally expected exchange mechanism involving conjugated π-delocalisation has been shown to be energetically unfavoured, eventhough a partial contribution by this mechanism is not ruled out. A discontinuity in the π-delocalisation of the biphenyl moiety can be brought about by introducing an sp_3 carbon between the two 1,1′sp_2 carbons which may lead to a different magnetic interaction mechanism. Here we present a report on the synthesis and characterisation of a new set of binuclear and polynuclear Cu(II), Ni(II), Co(II) and dioxouranium(VI) complexes of 4,4′-bis(salicylideneimino)-3,3′-disubstituted diphenylmethane, M_2 (Sal-dadpmX) (I).



(I)

M_2(Sal-dadpm X)$_2$

X = H, CH_3, OCH_3, Cl

M = Cu (II)

Materials and Methods

The molecular weight measurements were carried out on a Knauer Osmometer either in chloroform or dichloromethane for some selected complexes. Electronic spectra were recorded either on a Beckman DK-2A ratio recording spectrophotometer, or on a Cary 17D spectrophotometer. Magnetic susceptibility measurements were carried out by the Gouy method at room temperature on a Bruker BM-6 magnet employing Hg[Co(SCN)$_4$] as the calibrant. A JEOL JES PE 3X model spectrometer was used for running the ESR spectra. The cyclic voltammetric studies on Cu(II) complexes were carried out using the PARC Model-370 Electrochemistry system, in dry acetonitrile medium with tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. The thermogravimetric measurements were carried out using an apparatus fabricated by us.

4,4′-Diaminodiphenylmethane was purchased from M/s Fluka Chemicals. Its subsequent methoxylation, methylation and halogenation yielded the other diamines used in the preparation of ligands (I). The ligands were synthesised by mixing hot methanolic solution of the diamine with that of salicylaldehyde and the yellow precipitates so obtained were recrystallised from acetone-dichloromethane mixture (40:60 by volume).

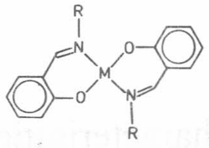
The complexes were prepared by adding 10 mmol of metal acetate in hot methanol to 10 mmol of the ligand in boiling acetone. The dark brown crystalline copper(II) complexes were recrystallised from dichloromethane, whereas the insoluble, yellow cobalt(II) and nickel(II) complexes were repeatedly washed with hot methanol and acetone and subsequently dried *in vacuo* over P_2O_5. The method of preparation and treatment of orange coloured dioxouranium(VI) complexes was similar to that of nickel(II) and cobalt(II) complexes except that aqueous uranyl nitrate was used as the source of the metal ion.

Results and Discussion

Analytical, magnetic and electronic spectral data of all the complexes are presented in Table 1. The absence of the IR band at 3200-3000 cm^{-1} due to νOH mode in the complexes, which is present in the spectra of ligands, indicates deprotonation of phenolic OH and complexation of the ligands through oxygen. The C,H,N analyses and the molecular weight measurements for some selected compounds support the binuclear formulation given in structure (I).

Copper(II) complexes: Magnetic data

The magnetic moment values are normal at room temperature indicating negligible or non-observable magnetic interaction. The possible superexchange interaction via a π-delocalised electron cloud is broken by the presence of tetrahedral carbon atom between the bridging phenyl moieties. The μ_{eff} data are close to those observed for a comparable series of compounds reported earlier[3] and also to those of the mononuclear analogues, M(Sal-N-aryl X)$_2$ shown in structure (II)[4].



(II)

R=Substituted(X) phenyl ring for M(Sal-N-aryl X)$_2$

R=H for M(Sal N-H)$_2$

Electronic spectral data

The Cu(II) complexes show two electronic absorption bands, a low energy, less intense one at ~ 10,500 cm^{-1} and a relatively more energetic and intense one at ~ 14,000 cm^{-1}. Planar Cu(Sal-N-aryl X)$_2$ complexes (structure II) exhibit only one *d-d* transition around 15,000 cm^{-1} while the tetrahedral ones are known[4] to have the transition around 12,000 cm^{-1}. An extra low intensity band assigned to $d_{x_2-y^2} \rightarrow d_{yz}$ transition was reported for certain Cu(II) schiff base complexes, with a pseudo-tetrahedral geometry[5]. The fact that the 14,000

Table 1—Analytical, magnetic and electronic spectral data of the complexes, M$_2$(Sal-dadpm X)$_2$

Complex	Mol. Wt. Found (Calc.)	Found (Calc.), %				μ_{eff} (B.M.)[a]	ν(ε)[b]
		M	C	H	N		
Cu$_2$(Sal-dadpm H)$_2$	957	13.95	69.18	4.47	6.03	1.83	10,500 (85)
	(936)	(13.58)	(69.29)	(4.31)	(5.99)		14,100 (210)
Cu$_2$(Sal-dadpm CH$_3$)$_2$	1014	12.89	70.44	4.53	5.81	1.84	10,220 (70)
	(992)	(12.81)	(70.22)	(4.88)	(5.56)		14,020 (225)
Cu$_2$(Sal-dadpm OCH$_3$)$_2$	1073	12.35	65.42	4.54	5.74	1.79	10,140 (65)
	(1056)	(12.03)	(65.97)	(4.58)	(5.31)		13,955 (235)
Cu$_2$(Sal-dadpm Cl)$_2$	1095	11.93	60.25	3.27	5.43	1.84	10,460 (80)
	(1073)	(11.84)	(60.40)	(3.38)	(5.22)		14,050 (215)
[Ni$_2$(Sal-dadpm OCH$_3$)$_2$4H$_2$O]$_n$	c	10.52	62.03	4.98	5.25	3.32	10,250
	(1118)	(10.49)	(62.29)	(5.04)	(5.02)		8,000
[Ni$_2$(Sal-dadpm Cl)$_2$ 4H$_2$O]$_m$	c	10.47	56.94	3.72	5.04	3.45	10,215
	(1136)	(10.33)	(57.08)	(3.90)	(4.93)		8,010
[Co$_2$(Sal-dadpm OCH$_3$)$_2$ 4H$_2$O]$_n$	c	10.68	62.03	4.97	5.18	4.84	15,050
	(1119)	(10.54)	(62.26)	(5.04)	(5.02)		8,255
[Co$_2$(Sal-dadpm Cl)$_2$4H$_2$O]$_n$	c	10.67	56.91	3.78	5.02	4.90	14,985
	(1137)	(10.36)	(57.03)	(3.90)	(4.94)		8,145
[(UO$_2$)$_2$(Sal-dadpm H)$_2$]$_n$	c	34.98	48.24	3.02	4.22	—	—
	(1349)	(35.29)	(48.08)	(2.98)	(4.15)		

[a]per metal centre; [b]ν in cm^{-1} and ε in lit mol^{-1} cm^{-1} in chloroform medium; [c]measurements not made.

Table 2—ESR spectral data of Cu_2(Sal-dadpm X)$_2$ complexes

Complex	$g_\parallel$	$g_\perp$	g_o	g^a_{iso}	$A_\parallel$ (cm^{-1})×10^4	$A_\perp$ (cm^{-1})×10^4	A_0 (cm^{-1})×10^4	A^a_{iso} (cm^{-1})×10^4
Cu_2(Sal-dadpm H)$_2$	2.21	2.06	2.11	2.07	46.51	29.46	35.15	38.76
Cu_2(Sal-dadpm CH_3)$_2$	2.19	2.05	2.10	2.05	45.06	29.27	34.53	36.43
Cu_2(Sal-dadpm OCH_3)$_2$	2.17	2.03	2.08	2.03	44.25	28.43	33.70	35.70
Cu_2(Sal-dadpm Cl)$_2$	2.20	2.04	2.09	2.06	46.32	29.34	35.00	37.35
Cu(Sal NH)$_2$	2.25	2.03	2.11	2.10	110.47	59.31	86.36	97.06

[a]from room temperature chloroform solution spectra.

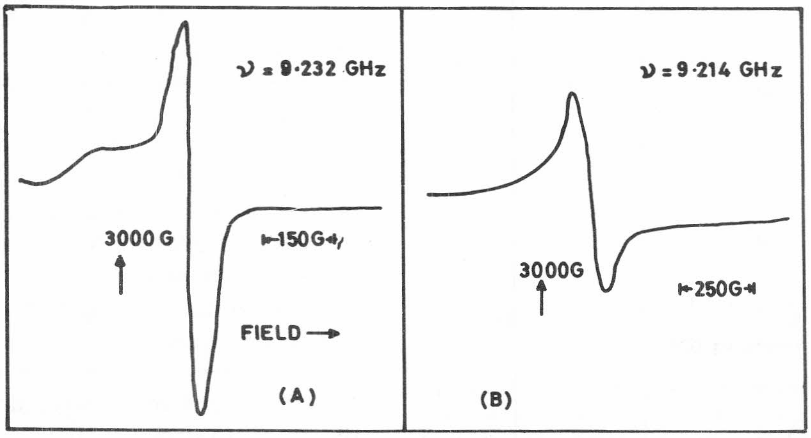


Fig. 1—The X-band room temperature ESR spectrum of Cu_2(Sal-dadpm H)$_2$ [(A), in polycrystalline form; (B), in chloroform solution]

cm^{-1} band of the present Cu(II) complexes is of lower energy than that expected for square-planar Cu(II) centres and that a low energy (~10,500 cm^{-1}) band is present indicate a pseudo-tetrahedral geometry around the Cu(II) centres. The distortion of geometry is not surprising in view of the bulkiness of the two *cis*-wise bridging 4,4′-ended 3,3′-disubstituted diphenylmethyl groups. There is greater decrease in the absorption energy when the bridging phenyl groups have OCH_3 substituents at 3,3′-positions compared with the unsubstituted compounds (Table 1).

ESR spectral studies

The X-band room temperature poly-crystalline and chloroform solution ESR spectra of Cu_2(Sal-dadpmH)$_2$ are shown in Fig. 1 as a representative case. The ESR spectral data are collected in Table 2. The room temperature powder spectra of all the Cu(II) complexes show well resolved parallel and perpendicular parts. No $\Delta M_s = \pm 2$ transition at half field is observed indicating the absence of intramolecular and intermolecular antiferromagnetic interactions. However, the chloroform solution even after considerable dilution or in the form of frozen glass did not give any hyperfine splitting. There are a few examples of pseudo-tetrahedral complexes of Cu(II) which do not show any hyperfine ESR spectra in solution[3,6-9]. This absence of hyperfine splitting is attributed to dipolar line broadening and to the much reduced nuclear hyperfine coupling constant for pseudo-tetrahedral copper(II) complexes. In the case of severe distortion from square planar geometry towards tetrahedral one, the A_0 values are lowered by nearly three times[10]. In accordance with this expectation, the observed A_0 values for the present complexes are of the order of 35×10^{-4} cm^{-1} compared with the values of ~86×10^{-4} cm^{-1} for the monomeric analogues having square planar geometry (Table 2). These ESR data further support the prediction made from the optical data that the geometry around Cu(II) centre is pseudo-tetrahedral.

Cyclic voltammetric studies

All the copper(II) complexes show a two-electron irreversible CV wave on a hanging mercury drop electrode due to Cu(II)/Cu(I) redox couple at ~ −0.35V (E_1) and another quasi-reversible one on platinum disc electrode due to Cu(III)/Cu(II) couple at ~ +0.43V (E_2) (vs SCE) in acetonitrile

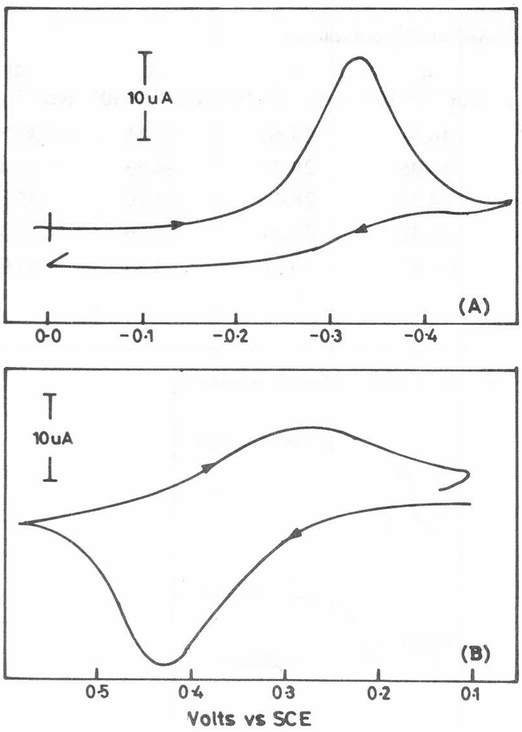


Fig. 2—Cyclic voltammetric response of Cu_2(Sal-dadpm $H)_2$ (vs SCE) in acetonitrile at 1×10^{-3} *M* [(A), on hanging mercury drop electrode (HMDE); (B), on platinum disc electrode (PDE)]

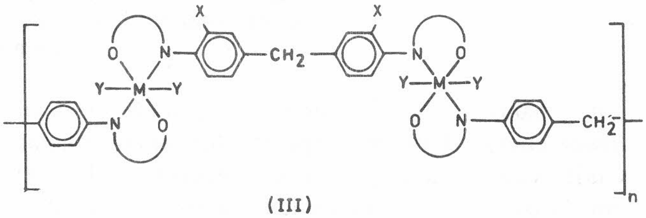
solution. Cyclic voltammograms for a representative compound, Cu_2(Sal-dadpm $H)_2$ ($E_1=-0.348$V, $E_2=+0.449$V) are given in Fig. 2. For the other complexes the E_1 and E_2 are: Cu_2(Sal-dadpm $CH_3)_2$ (-0.345 and 0.440V); Cu_2(Sal-dadpm $OCH_3)_2$ (-0.356 and $+0.460$V); and Cu_2(Sal-dadpm $Cl)_2$ (-0.340 and $+0.455$V). It is reported in literature that in non-interacting binuclear metal complexes; the electron transfer for a given redox couple at the two metal centres occurs at nearly identical potentials[11-17].

Ni(II), Co(II) and dioxouranium(VI) complexes

Nickel(II), Co(II) and dioxouranium(VI) complexes are insoluble in many organic solvents and are unstable in pyridine. Only the solid state electronic spectra by either PAS or in nujol mull could be studied. Nickel(II) complexes exhibit an absorption at ~10,200 cm^{-1}, with a weak shoulder at 8,000 cm^{-1} which may be assigned to the transitions $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{2g}$ respectively. Cobalt(II) complexes show two peaks, one at ~ 15,000 cm^{-1} and another broad one at 8,200 cm^{-1} that can be assigned to the transitions $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ and $^4T_{1g}\rightarrow{}^4T_{2g}(F)$ respectively. These electronic spectral transitions and the magnetic susceptibility data are indicative of octahedral geometry around Co(II) and Ni(II) centres. The transitions $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ for Ni(II) and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ for Co(II), expected beyond 20,000 cm^{-1} for octahedral geometries, might have been obscured by highly intense ligand transitions.

Thermal studies

The thermogravimetric analysis (TGA) indicates loss of two water molecules per metal atom in the range 165-170°C for Co(II) complexes and 183-190°C for Ni(II) complexes, respectively, whereas no mass loss is observed for Cu(II) and dioxouranium(VI) complexes. Loss of water at such high temperatures indicates that the H_2O molecules are coordinated and not lattice-held. This is in agreement with the C, H, N analysis presented in Table 1. The insolubility of Ni(II), Co(II) and dioxouranium(VI) complexes suggests a polymeric structure for these complexes. Ni(II) and Co(II) complexes involve coordination of two water molecules in *trans*-configuration along with *trans* N−O chelate rings of the ligand as shown in structure (III). The two *cis*-oxygens of dioxouranium(VI) centre may also force a polymeric structure for UO_2^{2+} complexes similar to structure (III).



(III)

M=Ni(II) & Co(II)

Y=H_2O

Reaction with ammonia

The Cu_2(Sal-dadpm $X)_2$ and [Ni_2(Sal-dadpm $X)_2\cdot H_2O]_n$ complexes, when stirred with excess ammonium hydroxide in chloroform medium, gave the monomeric planar M(Sal-NH$)_2$ complexes (structure II, Table 2). This exchange is similar to that observed for analogous series of complexes reported earlier[3].

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