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COMPLEXES OF HEXADENTATE NSO DONOR LIGANDS—II.* COPPER(II) COMPLEXES OF 1,3-DI(*o*-SALICYLALDIMINOPHENYLTHIO)PROPANE AND 1,2-DI(*o*-SALICYLALDIMINOPHENYLTHIO)XYLENE

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Abstract—The hexadentate dibasic Schiff base ligands 1,3-di(*o*-salicylaldiminophenylthio)propane (H_2DSALPTP) and 1,2-di(*o*-salicylaldiminophenylthio)xylene (H_2DSALPTX), with $N_2S_2O_2$ donor atoms, reacted with copper(II) salts, $CuX'_2 \cdot nH_2O$ ($X' = Cl$, NO_3, ClO_4 and $n = 2$, 3 and 6, respectively), to give complexes in which the flexidentate nature of the ligands is manifested in their action as monobasic tridentate chelating agents, leaving one-half of the ligands free. In all these complexes the copper(II) acceptor centre is present in a square-planar environment, the fourth coordination site being occupied either by a chloride ion or a water molecule. The EPR parameters (lowest $g < 2.03$) indicate their rhombic symmetry. All the complexes are found to exhibit quasi-reversible Cu^{III}/Cu^{II} couples in their cyclic voltammograms at room temperature in dichloromethane solution.

As part of our long-standing interest in the coordination chemistry of NS and NSO donor ligands, we have recently reported[1] the results of our studies on the iron(III) complexes of the title ligands. Copper(II) complexes of the above ligands are reported in this paper. Hexadentate ligands with N—O donor points usually encapsulate the metal ions in a 1 : 1 fashion, but incorporation of sulphur atoms in the ligand structures places some limitation on their ability to coordinate fully to a single metal ion.[2] Copper(II) is found to prefer four coordination, predominantly in a square-planar geometry. Therefore, we thought it worthwhile to study the reactions of copper(II) salts with hexadentate NSO donor ligands, to see if the ligands behave in flexidentate fashion using a portion of its donor skeleton or break down through hydrolysis to produce quadridentate or pentadentate donor systems that act as the actual coordinating agent. Such hydrolysis of Schiff base ligands in the presence of copper(II) is well known.[3,4] Moreover, interest in the coordination chemistry of sulphur–nitrogen ligands has been addressed to the design and synthesis of low molecular weight copper(II) complexes that could mimic the type I copper centre in blue copper proteins.[5] The evolution of low molecular weight synthetic models of the copper binding sites of these proteins is confronted basically with the problem of conferring a steric environment for copper(II) that would be intermediate between planar and

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* For Part I, see Ref. 1.

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tetrahedral. The limitation of our ligand system to fully encapsulate copper(II) may provide an environment around the copper(II) acceptor centre suitable for mimicking type I copper proteins. Cyclic voltammetric studies of these complexes were also carried out to find out whether these complexes exhibit the rather high Cu^{II}/Cu^{I} redox potentials characteristic of blue copper proteins.[6] The structures of the ligands have already been discussed.[1]

EXPERIMENTAL

Preparation of the ligands

This was as described in our earlier paper.[1]

Preparation of the complexes

$CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) was dissolved in methanol (20 cm^3) and added to a stirred solution of 1,3-di(*o*-salicylaldiminophenylthio)propane (H_2DSALPTP) or 1,2-di(*o*-salicylaldiminophenythio)xylene (H_2D SALPTX) (1 mmol) in chloroform (20 cm^3). The mixtures were stirred for 10–12 h, when the solutions turned green. The complexes separated out on concentrating the solutions. The products were filtered, washed with ether and then recrystallized from methanol. For complex **5**, however, 15–17 h refluxing was necessary and the green product separated out only on adding petroleum ether (60–80°C) to the solution; green crystals were obtained in each case (yield 65–80%).

Physical measurements

Elemental analyses, magnetic moments, conductivity measurements, IR and electronic spectra were performed as described earlier.[1] Chlorides were estimated argentometrically in the usual way and copper was determined gravimetrically using α-benzoinoxime. EPR measurements were made with a Varian model 109C E-line X-band spectrometer, fitted with a quartz Dewar for measurements at 77 K. All spectra were calibrated with the help of diphenyl picrylhyrazyl (dpph; $g = 2.0037$). Voltammetric measurements were performed on a PAR model 370-4 electrochemistry system. The three-electrode measurements were carried out with the use of a planar Beckman model 39273 platinum-inlay working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (S.C.E.).

RESULTS AND DISCUSSION

Both the ligands (H_2DSALPTP and H_2DSALPTX) are dibasic and potentially hexadentate with an $N_2S_2O_2$ set of donor atoms. The formulae of their copper(II) complexes [Cu(HDSALPTP)/(HDSALPTX)(H_2O)]X′ (where $X' = NO_3$ or ClO_4) and [Cu(HDSALPTP)/(HDSALPTX)Cl] (Table 1) denote that the ligands act as monobasic donors. This monobasic behaviour is further substantiated by the conductance data of these complexes in solution (Table 3) and points to deprotonation of one of the two phenolic OH groups of the ligands. The ^1H NMR and IR data of the ligands have already been discussed in our earlier communication.[1] The presence of an O—H stretching mode in the IR spectra of all the complexes denotes that the second phenolic OH group remains uncoordinated. The ν(C—O) modes of the complexes are split into two components, one of which is found to be shifted by 20–30 cm^{-1} in the higher region (Table 2), suggesting the presence of a Cu—O linkage, with the other corresponding to a free C—O moiety. The ν(C=N) frequencies in the complexes are also found to be broadened and split into two bands, one of which corresponds to that of the ligand while the other one, located at a 5–15 cm^{-1} lower frequency, indicates the participation of only one of the two azomethine nitrogens in coordination,[7] the other one remaining uncoordinated. The broad nature of the band may be due to overlap of free and coordinated ν(C=N). The presence of ν(Cu—S) bands between 360 and 280 cm^{-1} points to the coordination of thioether sulphur[7–9] to the copper(II) acceptor centre. Bands centred at 1090 or 1100, 950 and 625 cm^{-1} for complexes **3** and **6** are attributed to the presence of ionic perchlorates in these complexes.[9–12] In complexes **2** and **5**, ν_3 of uncoordinated nitrate ion occurs at 1340 and 1370 cm^{-1}, respectively.[13,14] Some important IR bands of the complexes are listed in Table 2.

The room temperature magnetic moments and molar conductance data are set out in Table 3. In all the complexes, one phenolic OH group of the ligands is deprotonated and the other remains free. The non-conducting character of the solutions of **1** and **4** suggests that the chloride ions in both cases are coordinated to the metal. However, ν(Cu—Cl) is not so prominent. For the other complexes the fourth coordination sites of Cu^{II} ions are occupied by a water molecule, the NO_3^- and ClO_4^- ions of which are present in the outer sphere of the complexes. This is deduced from the conductance values of the complexes, which are 1 : 1 electrolytes in solution, as well as by the characteristic IR bands for ionic ClO_4^- and NO_3^-.

Table 1. Analytical data for the complexes[a]

Complex	C	H	N	Cu	Cl
[Cu(HDSALPTP)Cl] (**1**)	58.2	4.3	4.7	10.6	5.1
	(58.4)	(4.2)	(4.7)	(10.7)	(5.9)
[Cu(HDSALPTP)(H_2O)]NO_3 (**2**)	54.6	4.1	4.2	9.6	—
	(54.3)	(4.2)	(4.4)	(9.9)	—
[Cu(HDSALPTP)(H_2O)]ClO_4 (**3**)	51.4	4.0	4.6	9.1	—
	(51.3)	(3.9)	(4.1)	(9.4)	
[Cu(HDSALPTX)Cl] (**4**)	62.7	4.3	4.3	10.0	6.2
	(62.0)	(4.1)	(4.2)	(9.7)	(5.4)
[Cu(HDSALPTX)(H_2O)]NO_3 (**5**)	58.3	4.1	5.8	9.5	—
	(58.1)	(4.1)	(6.0)	(9.1)	—
[Cu(HDSALPTX)(H_2O)]ClO_4 (**6**)	55.1	3.8	3.8	8.7	—
	(55.1)	(3.9)	(3.8)	(8.6)	

[a] Calculated values in parentheses.

Table 2. Some important IR bands of the complexes (cm^{-1})

Complex	ν(OH)	ν(C=N)	ν(C—O)	$\nu_3(ClO_4)$	$\nu_3(NO_3)$	ν(M—S)
[Cu(HDSALPTP)Cl] (**1**)	3400 (br)	1585,1605	1355,1380	—	—	310–280
[Cu(HDSALPTP)(H_2O)]NO_3 (**2**)	3400 (br)	1610 (br)	1350,1375	—	1340	290,280
[Cu(HDSALPTP)(H_2O)]ClO_4 (**3**)	3440 (br)	1585,1605	1350,1380	1090 (br)	—	350–320
[Cu(HDSALPTX)Cl] (**4**)	3400 (br)	1600,1610	1360,1385	—	—	Not clear
[Cu(HDSALPTX)(H_2O)]NO_3 (**5**)	3400 (br)	1600,1610	1365,1385	—	1370	360
[Cu(HDSALPTX)(H_2O)]ClO_4 (**6**)	3400 (br)	1595 (br)	1367,1385	1100 (br)	—	Not clear

Table 3. Electrical conductivity, magnetic moments and electronic spectral data of the complexes

Complex	Λ_M (ohm^{-1} cm^2 mol^{-1})[a]	Room temperature magnetic moment (B.M.)	Electronic spectral bands[b] λ_{max}, cm^{-1} (ε, dm^3 mol^{-1} cm^{-1})
[Cu(HDSALPTP)Cl] (**1**)	6.8	1.76	16,233 (708); 23,148 (sh); 35,087 (27,666)
[Cu(HDSALPTP)(H_2O)]NO_3 (**2**)	75.8	1.88	15,384 (241); 25,641 (12,250); 35,087 (27,666)
[Cu(HDSALPTP)(H_2O)]ClO_4 (**3**)	70.1	1.82	16,666 (916); 28,571 (sh); 35,087 (19,741)
[Cu(HDSALPTX)Cl] (**4**)	6.2	1.79	16,286 (404); 23,529 (15,256); 33,333 (65,206); 37,037 (79,970); 42,553 (24,330)
[Cu(HDSALPTX)(H_2O)]NO_3 (**5**)	76.1	1.80	15,625 (sh); 23,316 (10,687); 32,573 (12,225); 42,918 (23,026)
[Cu(HDSALPTX)(H_2O)]ClO_4 (**6**)	72.1	1.82	16,393 (sh); 26,666 (12,848); 33,333 (20,111); 42,918 (38,547)

[a] Measured in nitromethane.

[b] Measured in dichloromethane.

Electronic spectral data are given in Table 3. The square-planar complexes are known to exhibit two or more bands in the region 20,000–13,000 cm^{-1}.[15–19] In general, tetrahedral Cu^{II} complexes, if approximately regular, are expected to give a single broad band in the near-IR region and to exhibit none in the 20,000–10,000 cm^{-1} region. As the distortion towards square planar continues, it is predicted that both bands will move to the higher energy side. In all the complexes bands are observed in the 16,666–15,384 cm^{-1} region, suggesting square-planar geometry. Other higher energy bands (above 23,000 cm^{-1}) are of charge-transfer origin.

EPR spectra in frozen solution at liquid nitrogen temperature were recorded for two complexes of the two ligands. A four-line EPR spectrum was observed in each case (Fig. 1), which precludes any possibility of interaction between copper(II) centres. The parameters evaluated from these spectra are presented in Table 4. The lowest "g" value observed in both cases is less than 2.03; such a spectrum is observed in rhombic symmetry.[20]

The results of our voltammetric studies of the copper(II) complexes of the ligands H_2DSALPTP and H_2DSALPTX in dichloromethane are given in Table 5 and a representative cyclic voltammogram is shown in Fig. 2. The identified oxidation–reduction peaks are indicated by capital letters. On the initial positive scan, the copper(II) to copper(III) oxidation peak (denoted as D in Fig. 2a) was observed at +0.72 V and the subsequent reduction peak (denoted as E) at +0.58 V. The separation (ΔE) between these two peaks (140 mV) and the i_p(D)/i_p(E) ratio of nearly unity within the scan rate employed indicate quasi-reversible character of the redox process involved. On the initial negative scan, the peak A (at −0.72 V; Fig. 2b) corresponds to the reduction of copper(II) to copper(I). However, its oxidation counterpart could not be recorded. It has been shown that the copper(II)/copper(I) redox processes are influenced by coordination number, stereochemistry and the hard/soft character of the ligand's donor atoms. The high negative potential of the copper(II)/copper(I) couple indicates the "hard-acid" character of the ligands.[21] Continuing the scan in the positive direction, the redox potential of the copper(III)/copper(II) couple is shifted somewhat and is denoted by B and C in the figure. When scanned in the negative direction beyond −1 V, a broad peak around 0.1 V appears, which probably corresponds to oxidation of copper deposited at the electrode.[22]

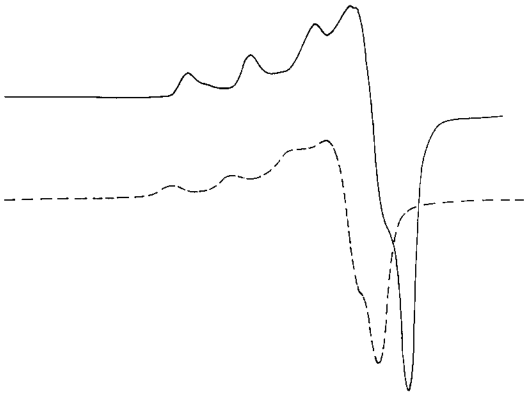


Fig. 1. X-band EPR spectra at 77 K in CH_2Cl_2: [Cu(HDSALPTP)(H_2O)]NO_3 (**2**) (- - -) and [Cu(HDSALPTX)(H_2O)]ClO_4 (**6**) (—).

Table 4. EPR g values in frozen glass (77 K)

Complex	g_1	g_2	g_3
[Cu(HDSALPTP)(H_2O)]NO_3 (**2**)	2.0067	2.0533	2.2218
[Cu(HDSALPTX)(H_2O)]ClO_4 (**6**)	1.994	2.051	2.255

From the above discussion it appears that in the complexes all the six donor points of these potentially hexadentate ligands are not coordinated to the copper(II) acceptor centre. One azomethine nitrogen and one phenolic OH group remain uncoordinated. All attempts to incorporate another copper(II) ion in the free part of the ligands, by reacting the complexes with copper acetate, resulted in the cleavage of one azomethine group of the ligands, the salicylaldehyde group being removed by copper(II) ion-catalysed hydrolysis of the C=N bond. TG–DTA results for complex **5** exhibited a weight loss compatible with the loss of a coordinated water molecule at 148°C. The IR spectra of complex **5** after heating at 148°C displayed a combination band ($\nu_1+\nu_4$) at 1680 cm^{-1} (expected near 1750 cm^{-1})[14] in the original complex, split into two weaker bands at 1690 and 1660 cm^{-1}; this is indicative of the coordination of the nitrate ion to the copper(II) centre.[14] So, after the loss of the water molecule, the ionic nitrate takes its place in the coordination zone. The presence of a coordinated water molecule in the original complex **5**, its absence after heating at 148°C and the appearance of the bands due to coordinated nitrate in this dehydrated complex support our proposed structure.

Therefore, the four-coordinated character of all the complexes is established by the analysis of IR

Table 5. Cyclic voltammetry data[a] for the complexes in CH_2Cl_2 solutions containing NBu_4ClO_4 (0.2 mol cm^{-3}) as supporting electrolyte on a platinum electrode

Complex	E_p(A)	Cu^{III}/Cu^{II} couples E_p(B)	E_p(C)	E_p(D)	E_p(E)
[Cu(HDSALPTP)Cl] (**1**)	−0.62	+0.60	+0.48	+0.58	+0.46
[Cu(HDSALPTP)(H_2O)]NO_3 (**2**)	−0.56	+0.65	+0.52	+0.50	+0.38
[Cu(HDSALPTP)(H_2O)]ClO_4 (**3**)	−0.46	+0.62	+0.52	+0.50	+0.36
[Cu(HDSALPTX)Cl] (**4**)	−0.72	+0.74	+0.52	+0.72	+0.58
[Cu(HDSALPTX)(H_2O)]NO_3 (**5**)	−0.67	+0.73	+0.53	+0.72	+0.56
[Cu(HDSALPTX)(H_2O)]ClO_4 (**6**)	−0.58	+0.86	+0.66	+0.80	+0.61

[a] In V vs. S.C.E.

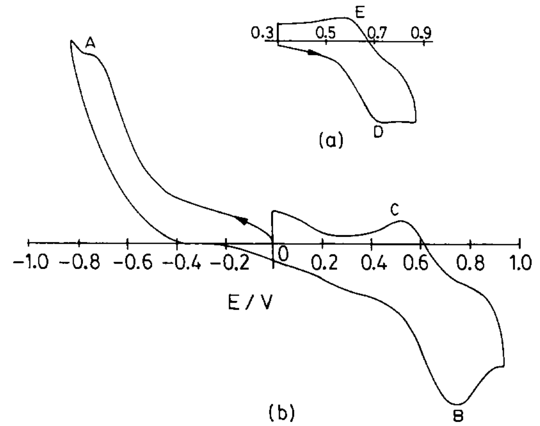
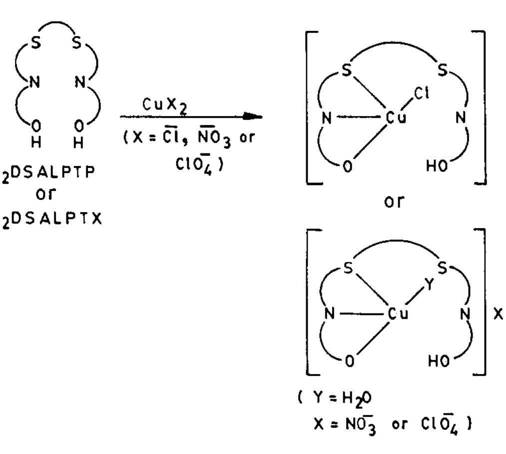


Fig. 2. Cyclic voltammograms at the platinum electrode (scan rate 50 mV s^{-1}) of [Cu(HDSALPTX)Cl] (**4**) in CH_2Cl_2 (0.2 M NBu_4ClO_4). (a) On initial positive scan. (b) On initial negative scan.

and electronic spectra, magnetic moment, solution conductance data and the presence of Cl^-/H_2O in the first coordination sphere. The flexidentate character of the two ligands is thus clearly manifested in this study and they are found to act in a tridentate monobasic fashion. The preference of the copper(II) ion for tetrahedral or square-planar geometries and the presence of the comparatively larger sulphur atom in the ligands places limitations on the ability of these ligands to fully coordinate to a single metal ion.[2,23]



Scheme.

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