

MOLECULAR ASSOCIATION, CHELATE CONFORMATION AND REACTIVITY CORRELATIONS IN SUBSTITUTED *o*-PHENYLENEBIS(SALICYLIDENAMINATO)COPPER(II) COMPLEXES: UV-VISIBLE, EPR AND X-RAY STRUCTURAL INVESTIGATIONS

E. SURESH, M. M. BHADBHADE and D. SRINIVAS*

Sophisticated Instrumentation Laboratory, Central Salt and Marine Chemicals Research Institute, Gijubhai Bhadheka Marg, Bhavnagar 364 002, India

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Abstract—Substituted *o*-phenylenebis(salicylidenaminato) complexes of copper(II), Cu(5-X-saloph), where X = H (**1**), CH₃O (**2**) and Cl (**3**) have been synthesized and characterized. Complex **1**, C₂₀H₁₄N₂O₂Cu, crystallizes in the orthorhombic space group *P*2₁2₁2₁ with two molecules (A and B) in the asymmetric unit related by a non-crystallographic centre of inversion and the nitrogen atom of A coming closer to the metal ion of B and *vice versa*. The geometry around copper is essentially square planar in both A and B with average Cu—N and Cu—O bond distances being 1.89(2) and 1.95(2) Å, respectively. The overall chelate conformation is also planar with a moderate “twist” at the “sal” groups. EPR spectra of the complexes are characterized by axial or rhombic *g* and *A*_{Cu} tensors and indicate the occupancy of an unpaired electron in a “formal” *d*_{xy} orbital. Solutions at 298 K showed superhyperfine features due to interaction of transferred unpaired spin with the nuclear spin of two magnetically equivalent ¹⁴N nuclei and the protons attached to adjacent methylene carbon atoms. The complexes exhibit solvatochromism. Substitution and σ -donor solvents show marked effects on the UV-visible and EPR spectra. MO calculations reveal that the in-plane σ and π bondings are covalent in nature. The correlation between conformational flexibility and reactivity is discussed. Copyright © 1996 Elsevier Science Ltd

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Transition metal complexes containing quadridentate Schiff base ligands have been the subject of several investigations.^{1–4} Chelates of salen and saloph [salen²⁻ = *N,N'*-ethylenebis(salicylidenaminato) and saloph²⁻ = *N,N'*-*o*-phenylenebis(salicylidenaminato)] containing cobalt(II) are known for their dioxygen uptake capabilities,^{5,6} while those of chromium, manganese, iron and nickel act as versatile catalysts for oxidation and hydroformylation reactions.^{7–9} In the course of understanding the structure–reactivity correlations,

we have reported earlier the effects on molecular association, chelate conformation and reactivity in substituted salen complexes of copper(II), Cu(5-X-salen), X = CH₃O, H and Cl.¹⁰ The ethylenediamine collar in these complexes is flexible and adopts either “stepped”, planar or “umbrella-shaped” overall molecular geometry. The conformational flexibility in the salen framework, as for metalloproteins, plays a key role for its biomimetic activity.¹¹

However, the saloph complexes of cobalt(II) and ruthenium(III), in spite of having steric phenylenic substitution in place of the ethylenic group, were found to be equally reactive towards molecular oxy-

* Author to whom correspondence should be addressed.

gen as their salen complexes.¹² With a view to understanding this, we report here spectroscopic and X-ray structural investigations on substituted Cu(5-X-saloph) complexes. It was reported earlier that Co^{II}, Pd^{II}, Ni^{II} and Cu^{II} complexes of saloph are isomorphous.^{13–16} However, the unit cell parameters reported here for Cu(saloph) are different from those of the earlier report¹³ suggesting an alternative crystal modification. It is interesting to note that Co(saloph) also crystallizes in two polymorphic forms.¹⁶ The crystalline form of Cu(saloph) under investigation contains two molecules in the asymmetric unit exhibiting an unusual molecular association which was not known before in saloph complexes. The geometry of the saloph moiety is compared with that found in other metal complexes and the reactivity is discussed in terms of conformational flexibility and electronic factors. The effects of substitution and solvent on molecular geometry are examined using UV-vis and EPR techniques.

EXPERIMENTAL

Materials

Salicylaldehyde, 5-chlorosalicylaldehyde and 5-methoxysalicylaldehyde (Aldrich) were used as received. All solvents were of AR grade and purified further using standard methods.¹⁷

Synthesis

The Schiff base ligands 5-X-saloph, where X = CH₃O, H and Cl, were prepared according to the literature procedure¹² and the purity of the ligand after recrystallization from ethanol was checked by elemental analysis, IR, UV-vis and NMR techniques.

The copper complexes Cu(5-X-saloph), (1)–(3), were synthesized by mixing equimolar absolute alcoholic solutions of Cu(CH₃COO)₂·4H₂O and the corresponding Schiff base ligand. The solutions were gently heated for 1 h while stirring and the complexes precipitated were recrystallized from ethanol. Analytical data, complex 1: Found: C, 63.0; H, 3.8; N, 7.2. Calc. for C₂₀H₁₄N₂O₂Cu: C, 63.6; H, 3.7; N, 7.4%. Complex 2: Found: C, 56.4; H, 4.6; N, 6.4. Calc. for C₂₂H₁₈N₂O₂Cu: C, 56.2; H, 4.6; N, 6.4%. Complex 3: Found: C, 53.9; H, 2.7; N, 6.2. Calc. for C₂₀H₁₂N₂O₂Cu: C, 53.7; H, 2.7; N, 6.3%.

Physical measurements

Microanalysis of the complexes was done using a C,H,N, Carlo-Erba 1106 elemental analyser. IR spectra, as KBr pellets (1% w/w), were recorded on a Carl Zeiss Specord M-80 spectrophotometer. Electronic spectra were measured using a Shimadzu UV-vis spectrometer (model UV-160). ¹H NMR spectra for chloroform solutions of ligands were taken on a JEOL FX-100 FT-NMR spectrometer with TMS as standard. EPR investigations were carried out on a Bruker ESP 300 X-band spectrometer using a 100-kHz field modulation. DPPH was used as a field marker (*g* = 2.0036). Studies on solutions at 298 and 77 K were performed by using an aqueous cell and a quartz inserting Dewar, respectively.

X-ray crystallography

Single crystals of 1 suitable for X-ray studies were obtained from acetonitrile solutions by slow evaporation. Although the volume of 1 after the least-squares refinement indicated eight molecules in the unit cell, an examination of systematic absences clearly showed the presence of 2₁ screws only and not of any glide planes, suggesting the space group to be *P*2₁2₁2₁ with two molecules in the asymmetric unit. The structure was solved by the heavy-atom method and the positions of the atoms were determined by using a direct method programme, MULTAN 82.¹⁸ The crystallographic data are summarized in Table I.

The initial cycles of refinement were carried out by a block-diagonal least-squares method. As the ratio of the number of variables to number of observed reflections was rather low, due to weak diffractions from the crystal, only one molecule of the asymmetric unit was refined at each time. The esds in the positional parameters would thus be underestimated. The difference Fourier map contained some H-atoms, the remaining were fixed at reasonable positions. The final cycles of the least-squares refinement included only the structure factor contributions from the H atoms.

All the computations were performed on a PDP 11/73 computer employing the structure determination package available from Enraf-Nonius.²⁰

Attempts to grow suitable single crystals of 2 and 3 proved unsuccessful. However, diffraction from a very thin crystal of 3 indicated a monoclinic space group *P*2₁/*c* with cell parameters *a* = 11.96(2), *b* = 8.03(1), *c* = 18.28(1) Å, β = 105.70(2)°, *V* = 1689.61(3) Å³ and one molecule in the asymmetric unit.

Table 1. Summary of crystallographic data

Experimental values	
Molecular formula	C ₂₀ H ₁₄ N ₂ O ₂ Cu
Molecular weight	377.55
Space group	orthorhombic, P2 ₁ 2 ₁ 2 ₁
Cell parameters	
<i>a</i> (Å)	9.140(6)
<i>b</i> (Å)	18.984(8)
<i>c</i> (Å)	18.004(4)
<i>V</i> (Å ³)	3123.95(26)
<i>Z</i>	8
No. of reflections used and θ range (°) used for unit cell parameters	25, 7–12
Radiation used, λ (Å)	Mo- <i>K</i> _α , 0.7107
<i>D</i> _{calc} (g cm ⁻³)	1.607
Absorption coeff, μ (cm ⁻¹)	14.156
Temperature (K)	295
Crystal colour and description	brown plates
Crystal dimensions (mm)	0.15 × 0.15 × 0.06
Data collection	
Diffractometer	Enraf–Nonius CAD-4 diffractometer
Scan mode	$\omega/2\theta$
Absorption correction ¹⁹	empirical
Transmission min, max	81.483, 99.781
Measured reflections	2176
Observed reflections <i>I</i> > 3 σ (<i>I</i>)	1383
θ_{\max} (°)	22
<i>h</i> _{min} , <i>h</i> _{max}	0, 9
<i>k</i> _{min} , <i>k</i> _{max}	0, 20
<i>l</i> _{min} , <i>l</i> _{max}	0, 19
No. of intensity control reflections, frequency and variation	3, 1 <i>h</i> , nil
No. of orientation control reflections, frequency and variation	3, every 200 refln, nil
Refinement	
Refinement on	<i>F</i>
Final <i>R</i>	0.055
Weighted <i>R</i>	0.077
Reflections used	1383
No. of parameters in the least-squares refinement	226
Hydrogen atom positions	not refined
(Δ/σ) _{max}	0.84
Weighting scheme,	1/ $\sigma(F)^2$
$\Delta\rho_{\max}$ (e Å ⁻³)	+0.526
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.571
Extinction correction	not supplied
Source of atomic scattering factors	International Tables for X-ray crystallography, Vol. IV, Kynoc Press, Birmingham (1974)

RESULTS AND DISCUSSION

IR and UV–visible spectra

IR spectra of the complexes showed broad bands in the range 1600–1630 cm⁻¹ attributable to $\nu(\text{C}=\text{N})$. For free ligands this band occurs at fre-

quencies higher by 10–20 cm⁻¹. Intense bands corresponding to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{O})$ appeared in the range 1545–1585 and 1210–1255 cm⁻¹, respectively. A broad band around 3440 cm⁻¹ due to $\nu(\text{O}-\text{H})$ for free ligands, is absent in the case of the complexes indicating the dianionic coordination of the saloph ligand.

UV-vis spectra for compounds **1–3** are shown in Fig. 1. The bands in the spectral range 256–305 nm, of ligand origin, have become blue shifted upon complexation. The moderately intense bands (400–460 nm) are charge transfer in nature, while the weak ones (579–694 nm) are due to *d–d* transitions. The electronic spectral data are given in Table 2.

Molecular structure and association

An ORTEP²¹ view of the asymmetric unit containing two molecules (A and B) for **1** is shown in Fig. 2 along with atom numbering scheme. Important bond lengths and angles are given in Table 3. The molecular geometry and conformations of A and B are essentially the same.

The geometry around the copper is almost square planar with two nitrogens and two oxygens from saloph providing the tetradentate coordination. The mean bond distances of Cu–N and Cu–O are 1.89(2) and 1.95(2) Å, respectively, and the bite angle N(1)–Cu–N(2) is 84°, which compares well with the structures of substituted Cu(salen) and other saloph complexes.^{10,14–16,22,23}

Molecules A and B are related by a non-crystallographic centre of symmetry at (0.8693, 0.1897, 0.2507) with N(2) of molecule A coming closer to the apical position of the Cu atom of molecule B and *vice versa*. Although the association between

the two molecules across the point of pseudo-inversion might be referred to as “dimerization”, the intermolecular interactions are very weak [Cu(1A)–N(2B) = 3.223 Å, Cu(1B)–N(2A) = 3.285 Å, Cu(1A)–Cu(1B) = 3.484 Å, N(2A)–Cu(1A)–N(2B) = 100.2°, Cu(1A)–N(2B)–Cu(1B) = 80°] as observed in Cu(5-X-saloph) complexes.¹⁰ The planar conformation of Cu(saloph) cannot achieve closer intermolecular approaches for steric reasons, as was observed in planar Cu(5-CH₃O-saloph). However, it is interesting to note the effect of substitution on molecular association. While Cu(salen) and Cu(5-CH₃O-saloph) form dimeric units bridged through the oxygen atom of the salen ligand, in the case of Cu(saloph) with *o*-phenylene substitution the molecules are sheared so that N(2) comes closer to Cu than oxygen. The Cu–Cu separation and O(N)–Cu–O(N) angle increases in the order Cu(saloph) > Cu(5-CH₃O-saloph) > Cu(salen) whereas Cu–O(N)–Cu increases in the reverse order. The considerable shearing in the present case does not result in dimeric bridging between molecules A and B observed in the case of Cu^{II}, Co^{II} and Fe^{III} salen complexes.^{10,24,25} As far as we are aware this forms the first report where a molecular association in which nitrogen coming closer to metal is observed in saloph complexes.

The conformations of molecules A and B are essentially planar as seen from the dihedral angles and angles between the mean planes through the N₂O₂, “sal1” and “sal2” moieties. However, there is a slight twist of the “sal” groups about the copper coordination plane (Fig. 3a and b), the best plane through atoms C(1)–C(6) makes *ca* 60° in both A and B with the CuN₂O₂ mean plane, whereas the plane through atoms C(15)–C(20) makes only *ca* 3° with the Cu coordination plane.

The molecules are packed almost parallel to diagonal directions in the *a–b* plane and are held together by van der Waals forces only. The considerable overlap between molecules A and B provides a close stacking interaction between the phenyl groups (Fig. 4). At this juncture it is interesting to note the similar packing arrangement observed for the *meso* form of the *N,N'*-cyclohexylenebis(salicylidenamino) cobalt(II) complex.²⁶

Magnetism and EPR studies

Complexes **1–3** are paramagnetic with μ_{eff} being in the range 1.97–2.02 μ_{B} , corresponding to a single unpaired electron. EPR spectra for polycrystalline samples of **1** and **3** are characterized by rhombic and axial *g* tensors, respectively. Copper hyperfine features could not be resolved at both 298 and 77

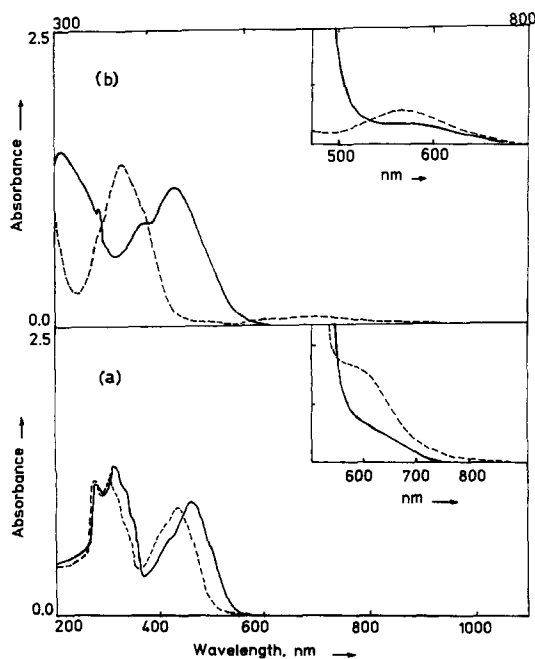


Fig. 1. UV-visible spectra showing the effect of substitution (a) Cu(5-CH₃O-saloph) (—) and Cu(5-Cl-saloph) (---) in DMF and (b) Cu(saloph) (—) and Cu(salen) (---) in CHCl₃.

Table 2. UV-visible and EPR spectral data for solutions of **1–3** at 298 K

Complex	Solvent	DN	Colour	λ (ϵ), nm (1 mol ⁻¹ cm ⁻¹)	g_{iso}	$-A_{iso}^{Cu}$ ^a	A^{Na}
Cu(saloph) (1)	C ₆ H ₆ CHCl ₃		brown		2.089	88.8	13.6
			brown	252(41,115), 309(41,346), 393(22,654) (sh) 429(28,423), 544(871)	2.099	88.5	
	CH ₂ Cl ₂	0	yellowish brown		2.099	87.3	
	CH ₃ CN	14.1	greenish yellow	245(36,914), 305(36,114), 385(18,542), 413(25,371), 561(648)	2.087	89.6	
	(CH ₃) ₂ CO	17.0	greenish yellow	304(30,962), 333(35,007), 391(29,308), 411(37,308), 561(1094)	2.092	87.3	
	THF	20.0	brown	259(13,765), 301(18,818), 410(12,720), 488(19,992), 563(394)	2.094	85.5	
	CH ₃ OH	25.7	yellow	241(35,765), 306(34,118), 411(22,098), 424(18,902), 561(601)	2.094	84.5	
	DMF	26.6	brown	278(10,842), 301(15,623), 410(10,497), 449(9956), 562(333)	2.093	87.1	14.6
	Py	33.1	green	310(35,430), 410(21,519), 455(21,696), 609(532)	2.102	77.6	
Cu(5-CH ₃ O-saloph) (2)	DMF	26.6	brown	276(24,760), 309(28,174), 441(14,196), 460(21,500), 625(419)			
	Py	33.1	green	312(50,348), 465(44,391), 636(674), 726(283)			
Cu(5-Cl-saloph) (3)	CHCl ₃		brown	256(34,334), 306(26,840), 400(13,725), 443(19,187), 576(1316), 694(932)			
	THF	20.0	brown	253(16,780), 306(25,314), 411(15,534), 463(16,422), 583(691), 670(270)	2.108	83.4	13.2
	DMF	26.6	brown	275(22,481), 306(22,865), 396(12,462), 436(17,827), 584(532), 700(135)	2.107	84.8	13.1
	Py	33.1	green	312(24,400), 410(15,153), 462(16,514), 608(495), 714(225)	2.115	77.3	12.2

^a A values are given in units of 10⁻⁴ cm⁻¹.

K, probably due to intermolecular interactions. The g values ($g_z > g_x$ or g_y) listed in Table 4 are consistent with an almost square planar geometry as revealed by the crystallographic data and indicate the occupation of an unpaired electron in the $3d_{xy}$ orbital of copper.

Solutions of **1** and **2** at 298 K gave four equally spaced resonances corresponding to interaction of the unpaired electron with the nuclear spin of copper ($I = \frac{3}{2}$). The resonances show m_I dependent line widths²⁷ with the high field line being narrower and

more intense than low field lines. Representative spectra for **1** are depicted in Fig. 5a–d, and the isotropic g and A_{Cu} values calculated by spectral fitting are listed in Table 2. The high field hyperfine feature in certain solvents shows further splitting into eleven equally spaced lines with their intensities in the ratio 1:2:3:4:5:6:5:4:3:2:1 (Fig. 5e). Similar spectral behaviour was observed for some related Cu(II) bidentate Schiff base complexes and Cu(5-X-salen).^{10,28} The superhyperfine features could be attributed to interaction of delocalized

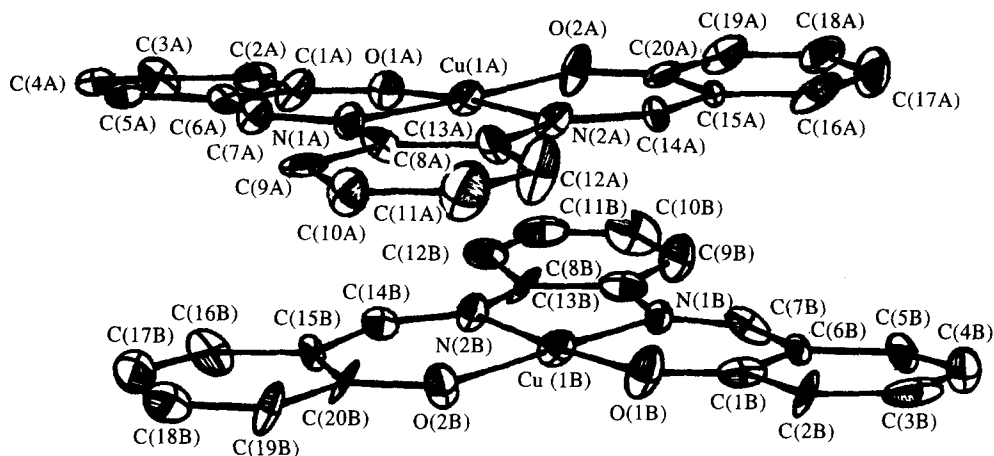


Fig. 2. ORTEP view of Cu(saloph) in the asymmetric unit.

unpaired spin with the nuclear spin of two equivalent ^{14}N nuclei and the ^1H belonging to carbons next to ^{14}N nuclei. The coupling parameters were calculated to be $A_{\text{N}}(\text{iso}) \approx 13 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\text{H}}(\text{iso}) \approx 6.5 \times 10^{-4} \text{ cm}^{-1}$.

The frozen solution of **1** at 77 K is characterized by rhombic g and A_{Cu} tensors (Fig. 5f). The hyperfine features are partially resolved in the perpendicular region. The additional line indicated by an asterisk (*) is an angular anomaly due to powder averaging. The superhyperfine features observed at 298 K could not be seen for frozen solutions. The spin Hamiltonian parameters are listed in Table 4. However, the accuracy in A_{\perp} (A_2 and A_3) values is rather low due to partial resolution.

Effect of substitution

Although the electronic spectra for **1** and **3** are similar, the band positions shift to the lower energy side with increasing electron donating capacity of the substituents (X) in the order $\text{CH}_3\text{O} > \text{H} > \text{Cl}$ (Fig. 1a and Table 2). Further, a comparison of spectra for Cu(saloph) and Cu(salen) indicate that the additional π delocalization brought about by the *o*-phenylene group also shifts both the charge transfer and $d-d$ bands from 338 to 428 nm and 608 to 614 nm, respectively (Fig. 1b). The red shift in these bands with increasing electron donating capacity of substituents, as well as with extended π delocalization, suggests lowering of ligand field stabilization energy and stabilization of the π^* orbital.

The g_{iso} , A_{iso} and g_{\parallel} values of solid complexes varies in the order $\text{Cu}(\text{salen}) > \text{Cu}(\text{5-Cl-saloph}) > \text{Cu}(\text{saloph})$ (Tables 2 and 4). Cu(salen) exists as discrete dimeric units with the geometry around copper being square pyramidal. The 5-chloro sub-

stitution, with only one molecule per asymmetric unit, results in a tetrahedrally distorted square-planar geometry. However, Cu(saloph) exhibits molecular association across a non-crystallographic centre of symmetry with the coordination geometry around copper being essentially square planar (*vide supra*). The variation of g_{\parallel} values is consistent with the variation in molecular structure.

Effect of solvents

Solvents show significant effects on colour, electronic and EPR spectra of the complexes. With increasing donor capacity of the solvents, the colour of the solution changes from brown through yellowish brown, yellow, greenish yellow to green. The charge transfer and $d-d$ bands shift to longer wavelengths. Figure 5 shows the solvent effect on EPR spectra. A correlation of g_{iso} with Gutmann donor number (DN)²⁹ of the solvents and A_{iso} values is shown in Fig. 6; g_{iso} varies linearly with A_{iso} but its variation with Gutmann donor number (DN) is non-linear, solvents having higher DN (DMSO and py) deviate from linearity. The solvatochromism and spectral changes can be attributed to coordination of solvent to metal ion or interaction of solvent molecule with the saloph moiety changing its molecular conformation. A comparison of structural data of various M(saloph) complexes does exhibit the conformational flexibility of the saloph framework (*vide supra*). Waters and Hall³⁰ have attributed the violet and brown colour in Cu^{II} Schiff bases to tetra-coordination and the green colour to strong penta-coordination for copper. The green colour observed in the case of strong donor solvents can therefore be accounted for by coordination of solvent molecules.

Table 3. Bond distances (Å) and angles (°) for Cu(saloph), with e.s.d.s. in parentheses

Cu(1B)—O(1B)	1.88(1)	C(16B)—C(17B)	1.38(3)
Cu(1B)—O(2B)	1.90(2)	C(17B)—C(18B)	1.46(4)
Cu(1B)—N(1B)	1.95(1)	C(18B)—C(19B)	1.35(3)
Cu(1B)—N(2B)	1.94(1)	C(19B)—C(20B)	1.42(3)
O(1B)—C(1B)	1.29(2)	Cu(1A)—O(1A)	1.91(2)
O(2B)—C(20B)	1.31(3)	Cu(1A)—O(2A)	1.90(2)
N(1B)—C(7B)	1.28(2)	Cu(1A)—N(1A)	1.95(2)
N(1B)—C(8B)	1.37(2)	Cu(1A)—N(2A)	1.96(4)
N(2B)—C(13B)	1.40(3)	O(1A)—C(1A)	1.26(3)
N(2B)—C(14B)	1.30(3)	O(2A)—C(20A)	1.24(2)
C(1B)—C(2B)	1.48(2)	N(1A)—C(7A)	1.26(2)
C(1B)—C(6B)	1.41(2)	N(1A)—C(8A)	1.44(3)
C(2B)—C(3B)	1.30(2)	N(2A)—C(13A)	1.41(2)
C(3B)—C(4B)	1.43(4)	N(2A)—C(14A)	1.33(3)
C(4B)—C(5B)	1.40(3)	C(8A)—C(13A)	1.38(3)
C(5B)—C(6B)	1.36(2)	C(9A)—C(10A)	1.44(3)
C(6B)—C(7B)	1.45(2)	C(10A)—C(11A)	1.34(2)
C(8B)—C(9B)	1.45(3)	C(11A)—C(12A)	1.41(2)
C(8B)—C(13B)	1.45(2)	C(12A)—C(13A)	1.36(2)
C(9B)—C(10B)	1.37(3)	C(14A)—C(15A)	1.43(4)
C(10B)—C(11B)	1.41(3)	C(15A)—C(16A)	1.34(3)
C(11B)—C(12B)	1.37(3)	C(15A)—C(20A)	1.48(2)
C(12B)—C(13B)	1.39(3)	C(16A)—C(17A)	1.39(2)
C(14B)—C(15B)	1.47(2)	C(17A)—C(18A)	1.39(3)
C(15B)—C(16B)	1.43(2)	C(18A)—C(19A)	1.36(2)
C(15B)—C(20B)	1.37(2)	C(19A)—C(20A)	1.42(3)
O(1B)—Cu(1B)—O(2B)	88.5(5)	C(11A)—C(12A)—C(13A)	120(2)
O(1B)—Cu(1B)—N(1B)	95.1(5)	N(2A)—C(13A)—C(8A)	115(2)
O(1B)—Cu(1B)—N(2B)	175.0(6)	N(2A)—C(13A)—C(12A)	125(2)
O(2B)—Cu(1B)—N(2B)	92.7(5)	C(8A)—C(13A)—C(12A)	119(2)
N(1B)—Cu(1B)—N(2B)	84.1(5)	N(1B)—C(8B)—C(9B)	125(2)
Cu(1B)—O(1B)—C(1B)	126(2)	N(1B)—C(8B)—C(13B)	116(1)
Cu(1B)—N(1B)—C(7B)	123(1)	C(9B)—C(8B)—C(13B)	119(2)
Cu(1B)—N(1B)—C(8B)	113(2)	C(8B)—C(9B)—C(10B)	117(2)
C(7B)—N(1B)—C(8B)	124(1)	C(9B)—C(10B)—C(11B)	123(2)
Cu(1B)—N(2B)—C(13B)	114(2)	C(10B)—C(11B)—C(12B)	121(2)
Cu(1B)—N(2B)—C(14B)	126(2)	C(11B)—C(12B)—C(13B)	120(2)
C(13B)—N(2B)—C(14B)	120(1)	N(2B)—C(13B)—C(8B)	113(1)
O(1B)—C(1B)—C(2B)	116(1)	N(2B)—C(13B)—C(12B)	126(2)
O(1B)—C(1B)—C(6B)	128(1)	C(8B)—C(13B)—C(12B)	120(2)
C(2B)—C(1B)—C(6B)	116(1)	N(2B)—C(14B)—C(15B)	124(1)
C(1B)—C(2B)—C(3B)	120(2)	C(14B)—C(15B)—C(16B)	115(1)
C(2B)—C(3B)—C(4B)	122(2)	C(14B)—C(15B)—C(20B)	124(1)
C(3B)—C(4B)—C(5B)	119(2)	C(16B)—C(15B)—C(20B)	122(2)
C(4B)—C(5B)—C(6B)	120(2)	C(15B)—C(16B)—C(17B)	121(2)
C(1B)—C(6B)—C(5B)	123(1)	C(16B)—C(17B)—C(18B)	114(2)
C(1B)—C(6B)—C(7B)	121(1)	C(17B)—C(18B)—C(19B)	127(2)
O(2B)—Cu(1B)—N(1B)	175.3(5)	Cu(1B)—O(2B)—C(20B)	129(2)
C(5B)—C(6B)—C(7B)	116(1)	C(18B)—C(19B)—C(20B)	116(2)
N(1B)—C(7B)—C(6B)	127(2)	O(2B)—C(20B)—C(15B)	124(2)
C(9A)—C(10A)—C(11A)	121(2)	O(2B)—C(20B)—C(19B)	116(2)
C(10A)—C(11A)—C(12A)	119(2)	C(15B)—C(20B)—C(19B)	121(2)
C(13A)—N(2A)—C(14A)	123(2)	C(1A)—C(1A)—C(2A)	119(1)
O(1A)—C(1A)—C(6A)	123(1)	C(2A)—C(1A)—C(6A)	116(1)
C(1A)—C(2A)—C(3A)	124(2)	C(2A)—C(3A)—C(4A)	118(2)
O(1A)—Cu(1A)—O(2A)	88(1)	C(3A)—C(4A)—C(5A)	118(2)
O(1A)—Cu(1A)—N(1A)	94(1)	C(4A)—C(5A)—C(6A)	124(2)

Table 3.—*continued.*

O(1A)—Cu(1A)—N(2A)	174(1)	C(1A)—C(6A)—C(5A)	116(2)
O(2A)—Cu(1A)—N(1A)	175(2)	C(1A)—C(6A)—C(7A)	123(2)
N(2A)—C(14A)—C(15A)	127(2)	C(5A)—C(6A)—C(7A)	119(2)
C(14A)—C(15A)—C(16A)	118(2)	N(1A)—C(7A)—C(6A)	125(2)
C(14A)—C(15A)—C(20A)	119(2)	N(1A)—C(8A)—C(9A)	121(1)
C(16A)—C(15A)—C(20A)	122(2)	N(1A)—C(8A)—C(13A)	116(1)
C(15A)—C(16A)—C(17A)	120(2)	C(9A)—C(8A)—C(13A)	122(1)
C(16A)—C(17A)—C(18A)	119(2)	C(8A)—C(9A)—C(10A)	116(2)
O(2A)—Cu(1A)—N(2A)	93(2)	C(17A)—C(18A)—C(19A)	120(2)
N(1A)—Cu(1A)—N(2A)	84(1)	C(18A)—C(19A)—C(20A)	123(2)
Cu(1A)—O(1A)—C(1A)	127(2)	O(2A)—C(20A)—C(15A)	126(2)
Cu(1A)—O(2A)—C(20A)	129(2)	O(2A)—C(20A)—C(19A)	120(2)
Cu(1A)—N(1A)—C(7A)	125(2)	C(15A)—C(20A)—C(19A)	112(2)
Cu(1A)—N(1A)—C(8A)	111(2)	C(7A)—N(1A)—C(8A)	123(2)
Cu(1A)—N(2A)—C(13A)	112(1)	Cu(1A)—N(2A)—C(14A)	124(2)

Ground state wavefunction and bonding parameters

Spin Hamiltonian parameters (Table 4) indicate that the unpaired electron occupies a “formal” d_{xy} orbital. The MO coefficients were calculated using the ligand field approach adopted by Maki and McGarvey²⁸ and by Kivelson and Neiman³¹ for D_{2h}

symmetry. α and β are metal d orbital coefficients for the MOs B_{1g} and A_g , representing the in-plane σ and π bonding, respectively. α' is the coefficient of the ligand orbitals forming the B_{1g} . The MO coefficients for frozen solutions are listed in Table 4. The spin-orbital coupling constant, λ and the dipolar interaction term for free Cu(II) ion, P , were

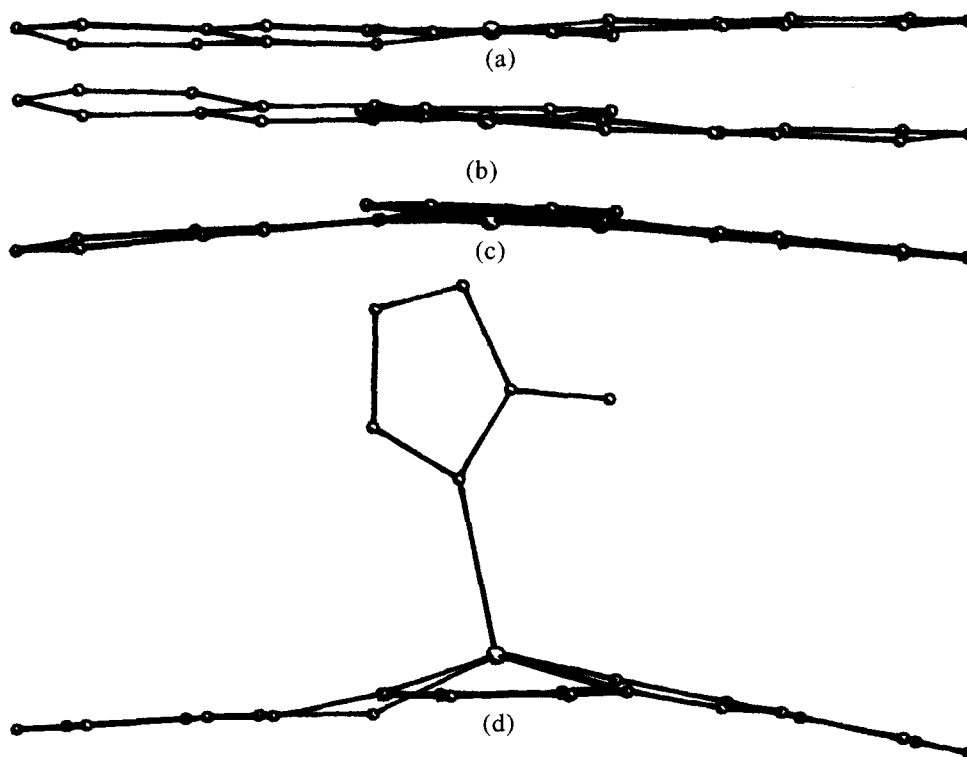
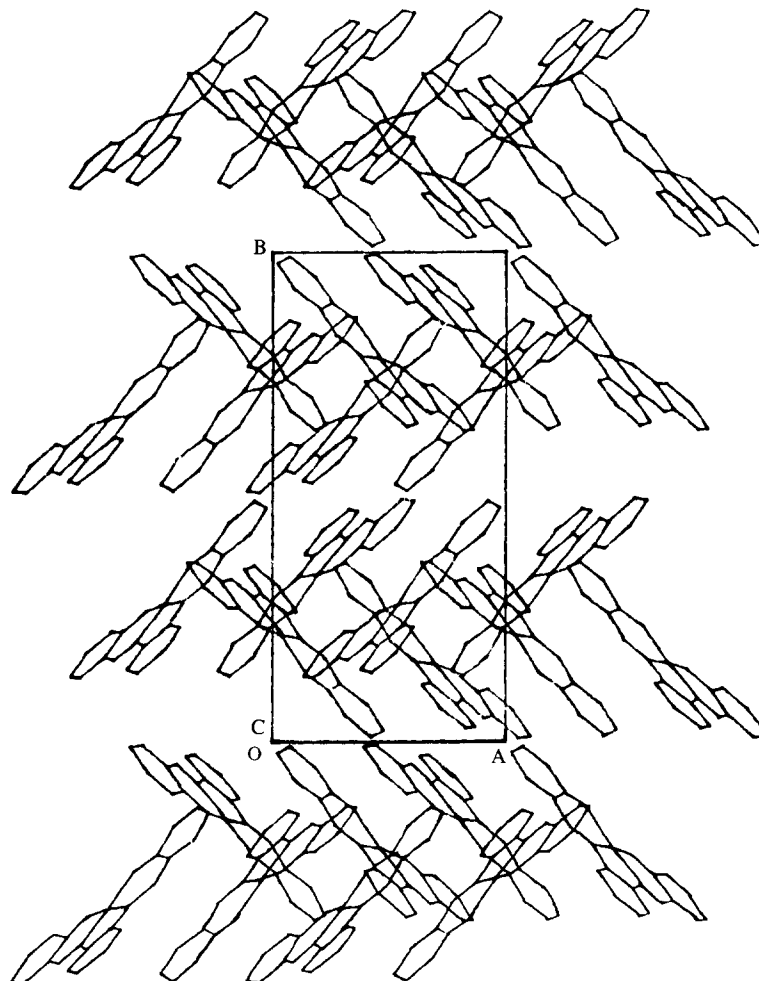


Fig. 3. PLUTO diagram showing the conformational flexibility of saloph moiety. (a) and (b) Molecules A and B of Cu(saloph); (c) Co(saloph), orthorhombic $P2_12_1$ crystal form¹⁶ and (d) Co(saloph)(2-MeIm)³⁰.

Fig. 4. Packing diagram of Cu(saloph) in *a*-*b* plane.Table 4. Spin Hamiltonian parameters at 77 K^a and MO coefficients

Complex	State ^b	g_1	g_2	g_3	$-A_1$	$-A_2$	$-A_3$	α^2	α'^2	β^2
Cu(saloph)	PC	2.129	2.094	2.065						
	DMA	2.206	2.060	2.050	205.8	28.7	28.7	0.841	0.243	0.639
	DMF	2.211	2.066	2.050	204.9	28.9	28.7	0.845	0.238	0.811
	Py	2.298	2.055	2.055	162.1	33.7	33.7	0.812	0.276	0.928
Cu(5-Cl-saloph)	PC	2.146	2.004	2.004						
Cu(salen)	PC	2.191	2.084	2.084						
	DMF	2.212	2.054	2.054	203.7	30.7	30.7	0.841	0.243	0.731
	Py	2.227	2.053	2.053	191.3	24.0	24.0	0.821	0.266	0.773
Cu(5-Cl-salen)	PC	2.181	2.060	2.060						
	DMF	2.214	2.055	2.055	198.4	23.0	23.0	0.834	0.257	0.762
	Py	2.231	2.057	2.057	188.5	17.9	17.9	0.819	0.268	0.789

^aPC = polycrystalline; DMA = *N,N'*-dimethylacetamide; DMF = *N,N'*-dimethylformamide; Py = pyridine.

^bErrors in g values are ± 0.003 and in A values are ± 0.5 . The A values are given in units of 10^{-4} cm^{-1} .

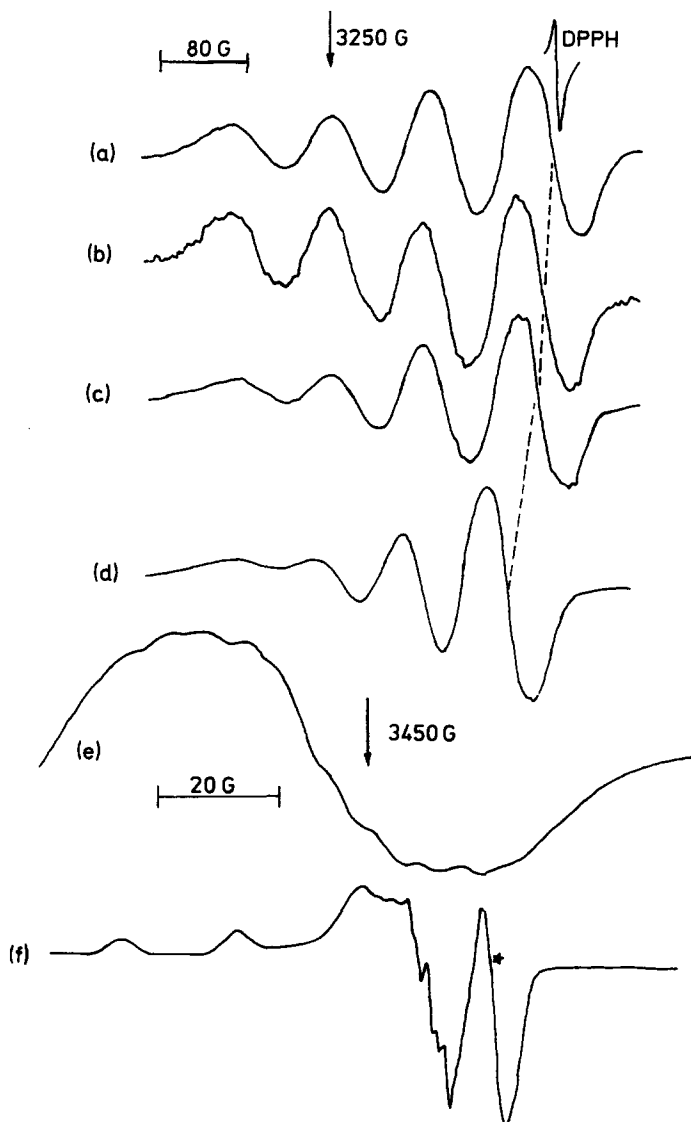


Fig. 5. X-band EPR spectra of Cu(saloph) in various solvents at 298 K: (a) CHCl_3 , (b) $(\text{CH}_3)_2\text{CO}$, (c) DMF and (d) py. Expanded view of the superhyperfine splitting of the high field signal for DMF at 298 K (e) and spectrum for frozen DMA at 77 K (f). Asterisk (*) indicates "angular anomaly" due to power averaging.

taken as -0.828 and 0.036 cm^{-1} , respectively. The overlap integral (S) and the constant $T(n)$ were assumed as 0.093 and 0.333 , respectively. As the $d-d$ band corresponding to $B_{1g} \leftrightarrow E_g$ could not be resolved, the coefficients for the out of plane π bonding, δ , could not be calculated. The MO coefficients for **1** (Table 4) suggest the in-plane σ and π bonds are covalent in nature. The in-plane π bonding is significantly affected by substitution and solvent as observed by Kivelson and Neiman for several Cu^{II} complexes.³¹ While the α^2 values decrease from Cu(salen) to Cu(saloph) the β^2 values increase. Similar variation in α^2 and β^2 values is observed with increasing σ basicity of the solvent.

Conformational flexibility and structure–reactivity correlations

The average M—O bond [$1.95(2) \text{ \AA}$] is longer than M—N [$1.89(2) \text{ \AA}$] in Cu(saloph) and Cu(5-X-salen) complexes. These bond differences are found to vary with metal complexes in the order $\text{Cu} > \text{Co} > \text{Pd} > \text{Ni}$.^{10,14–16} Moreover, upon coordination to copper the C—O [C(1)—O(1) and C(20)—O(2)] and C—C [C(1)—C(2) and C(19)—C(20)] bond lengths have significantly changed compared with those of free saloph ligand; the former is shortened while the latter is elongated. Variation of the bond lengths indicates a predominant ketonic form of

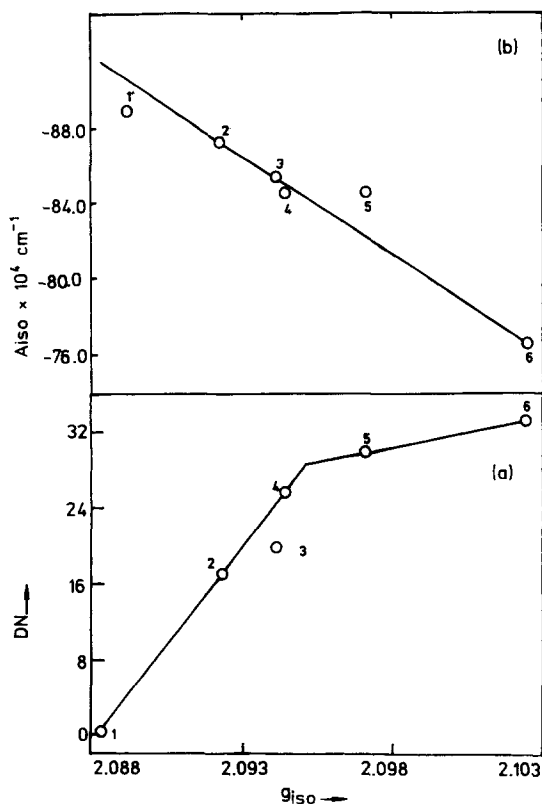


Fig. 6. Correlation of g_{iso} with (a) isotropic copper hyperfine coupling constant $A_{iso}(\text{Cu})$ and (b) Gutmann donor number (DN).

saloph in copper complexes. Although, the molecular conformation for **1** is planar, its other polymorphic form, which is isomorphous to Co, Pd and Ni complexes, possesses an "umbrella-shaped" geometry (Fig. 3C).¹⁴⁻¹⁶ In spite of having a rigid *o*-phenylene group, the flexibility of the molecular framework of saloph ("planar" ↔ "umbrella-shaped") analogous to that of salen having an ethylene collar is noteworthy. As is evident from the structures of Co(saloph)(2-MeIm),³² [Fe(saloph)]₂O,³³ [Fe(salen)]₂O³⁴ and Co(salbn(m))(py),³⁵ the conformational geometry of saloph or salen changes from planar (Fig. 3a and b) to an "umbrella-shape" (Fig. 3c and d) in the presence of a coordinating ligand like oxo, molecular oxygen, imidazole or pyridine, to accomplish the bonding between the metal centre and the incoming molecule. It is gratifying to note the similarity in flexibility between the saloph/salen framework and that of metalloproteins involved in oxygen and electron transfer reactions. In addition to the conformational flexibility, the extended π delocalization brought about by the *o*-phenylene group is also responsible for the reactivity of M (saloph) complexes.

CONCLUSIONS

The effect of substitution on molecular association, chelate conformation and reactivity in Cu(5-X-saloph) complexes is discussed. In spite of having a phenylene substitution the saloph complexes exhibit "planar" and "umbrella-shaped" molecular geometries. The flexible chelate conformation of saloph similar to that of analogous salen and some metalloproteins (e.g. oxy/deoxy-hemoglobin and myoglobin, dioxygen carriers) and the extended π delocalization are responsible for its reactivity.

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Supplementary material available—Listings of atom positions and anisotropic thermal parameters for non-H-atoms have been deposited at the Cambridge Crystallographic Data Centre.

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