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Mohan M. Bhadbhade and D. Srinivas*: Effects on Molecular Association, Chelate Conformation, and Reactivity toward Substitution in Cu(5-X-salen) Complexes, $\text{salen}^{2-} = N,N'$ -Ethylenebis(salicylideneaminato), X = H, CH_3O , and Cl: Synthesis, X-ray Structures, and EPR Investigations.

Pages 5458–5466. Page 5459 was inadvertently omitted and replaced by an incorrect page. The entire article is reprinted below.

Effects on Molecular Association, Chelate Conformation, and Reactivity toward Substitution in Cu(5-X-salen) Complexes, $\text{salen}^{2-} = N,N'$ -Ethylenebis(salicylideneaminato), X = H, CH_3O , and Cl: Synthesis, X-ray Structures, and EPR Investigations

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Three copper(II) complexes, Cu(5-X-salen), where $\text{salen}^{2-} = N,N'$ -ethylenebis(salicylideneaminato) and X = H (**1**), CH_3O (**2**), or Cl (**3**), have been synthesized and characterized by various physicochemical techniques. Single crystal X-ray data of the complexes are as follows: **1**, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{Cu}$, monoclinic $C2/c$, $a = 26.658(7)$ Å, $b = 6.983(1)$ Å, $c = 14.719(2)$ Å, $\beta = 97.42(2)^\circ$, $V = 2717(6)$ Å³, $Z = 8$, $R = 0.038$ ($R_w = 0.058$); **2**, $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{Cu}\cdot\text{CH}_3\text{OH}$, monoclinic $P2_1/n$, $a = 11.061(3)$ Å, $b = 7.537(6)$ Å, $c = 21.765(5)$ Å, $\beta = 92.86(2)^\circ$, $V = 1812(2)$ Å³, $Z = 4$, $R = 0.066$ ($R_w = 0.067$); **3**, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2\text{Cu}$, triclinic $P\bar{1}$, $a = 8.318(1)$ Å, $b = 9.502(4)$ Å, $c = 11.016(4)$ Å, $\alpha = 63.78(4)^\circ$, $\beta = 75.62(3)^\circ$, $\gamma = 78.83(4)^\circ$, $V = 753(15)$ Å³, $Z = 2$, $R = 0.039$ ($R_w = 0.059$). In solid state, **1** exists as strong dimers ($\text{Cu}\cdots\text{O}1' = 2.414(2)$ Å) whereas **2** forms weak dimers ($\text{Cu}\cdots\text{O}1' = 2.801(7)$ Å) intermolecularly bridged through phenolate oxygen and **3** is essentially a monomer. Copper is tetragonally distorted square pyramidal in **1** and **2** and tetrahedrally distorted square planar in **3**. Complexes exhibit color isomerism and solvatochromism in both solid and solution. EPR spectra are characterized by axial g and A_{Cu} tensors with $g_{\parallel} > g_{\perp}$ indicating that the unpaired electron occupies a "formal" d_{xy} orbital. A good correlation is obtained between the σ -basicity of the solvent and the spin Hamiltonian parameters. The mechanism for solvatochromism is discussed in terms of conformational changes and solvent coordination. EPR studies and extended Hückel molecular orbital calculations suggest that **3** forms more stable pyridine complexes than **1** and **2**. The effect of substitution on molecular electronic structure and reactivity toward solvent coordination is discussed.

Introduction

Environment around the metal center and conformational flexibility are the key factors for a metalloprotein to carry out a specific physiological function, e.g. dioxygen binding by hemoglobin and myoglobin, oxygen utilization by cytochrome P450 and cytochrome *c* oxidase, etc. Several model metal complexes containing porphyrin and Schiff base ligands have been synthesized and studied for their dioxygen uptake¹ and oxidative catalysis.^{2–4} Flexibility of the ethylenediamine backbone in salen, as observed in a number of transition-metal complexes with bidentate oxygen ligands,⁵ is responsible for its complexes to mimic the biological activity of proteins. Fine tuning of the

electronic structure by introducing electron donating and withdrawing substituents in ligands is known to enhance the reactivity

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of the complexes.⁶ However, reports dealing with the effect of substitution on molecular structure, spin state, electronic ground state, and reactivity of the complexes are very few.⁶⁻¹⁰ With a view to understand the correlations between the molecular electronic structure and reactivity of the complexes better, we report here systematic spectroscopic and single-crystal X-ray structural investigations on three substituted salen complexes of Cu(II), Cu(5-X-salen), where X = H, CH₃O, and Cl, 1-3.

The Schiff base ligand 5-X-salen coordinates through N₂O₂ donor atoms. The crystal structure of 1 is redetermined, as the earlier structure determinations^{11,12} were based on two-dimensional X-ray data; 2 and 3 have not been reported so far. Complexes 1-3 exhibit color isomerism/solvatochromism in solid/solution state. Although NMR,¹³ Mössbauer,¹⁴ and electronic spectral¹⁵ studies have been used to understand "solvatochromism", we report here for the first time EPR investigations on this phenomenon. Correlation between the spin Hamiltonian parameters and σ basicity of the solvent and reactivities of the complexes toward substitution for pyridine are discussed.

Experimental Section

Materials. The solvents were of AR grade and purified further by using standard methods¹⁶ and stored in dark under nitrogen. Substituted salicylaldehydes and ethylenediamine (Aldrich) were used as such.

Synthesis. The Schiff base ligands, 5-X-salenH₂, where X = H, CH₃O, or Cl, were prepared according to the literature procedures¹⁷ and their purities were checked by elemental analysis, IR, UV-visible, and NMR techniques before synthesizing the complexes. Copper complexes, Cu(5-X-salen), 1-3, were prepared 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 with stirring and allowed to cool. Good quality single crystals suitable for X-ray studies were obtained in a few days by slow evaporation of chloroform solution of 1 and methanolic solutions of 2 and 3.

Analytical data for the ligands and complexes are deposited as supplementary material.

Synthesis of Cu(5-X-salen)(py). Complexes, Cu(5-X-salen)(py), were prepared by gently heating the pyridine solutions of 1-3 with stirring for ~1 h. Upon cooling the solution, green crystals were obtained in a week's time, which decompose rapidly in air.

Physical Measurements. Microanalysis of compounds was done using a CHN Carlo Erba 1106 elemental analyzer. The IR spectra for KBr pellets (1% (w/w)) were measured at 298 K on a Carl-Zeiss Specord M-80 spectrophotometer. Electronic spectra were recorded in chloroform, methanol, DMF, and py on a Shimadzu UV-visible spectrometer (Model UV-160). ¹H NMR spectra were taken in chloroform solutions of ligands using a JEOL FX-100 spectrometer with (CH₃)₄Si as a standard. Cyclic voltammograms (CVs) were recorded by a Princeton Applied Research electrochemical system (Model 174) equipped with a precision X-Y

recorder and a three-electrode system (Pt inlay-working, Pt wire-auxiliary, and Ag/AgCl (saturated KCl) reference); Bu₄NBF₄ was used as a supporting electrolyte.

EPR investigations were carried out with a Bruker ESP-300 X-band spectrometer using a 100-kHz field modulation. DPPH was used as a field marker ($g = 2.0036$). EPR spectra were measured for polycrystalline samples and solutions. Studies on deaerated solutions at 298 K were performed using an aqueous cell and at 77 K were performed using a quartz inserting Dewar. Studies on single crystals could not be carried out as their size was too small for EPR measurements. Analysis of EPR data and EHMO calculations were performed using a HCL PC/AT 386 personal computer.

X-ray Crystallography. Crystallographic data for complexes 1-3 are summarized in Table I. All the structures were solved by the heavy-atom method and refined by the full-matrix least-squares procedures as described in Table I. The hydrogen atom positions were mostly obtained from the difference Fourier synthesis; a few were fixed stereochemically at appropriate geometries. The H atoms were included only for the structure factor calculation and were not refined in the least-squares procedures. Difference Fouriers for complex 2 showed several peaks with ~4 e Å⁻³ being the highest. Among several models of accounting them, methanol disordered over two equally populated sites has been the most satisfactory one. The first four peaks were serially assigned to O101, O102, C101, and C102 with each having half occupancy; their positions were kept fixed in the LS refinement but temperature factors (isotropic) were allowed to refine (Table II). The O101 and O102 make H-bonding contacts with the ligand oxygen O2, which gives an additional criterion for the correctness of the model for disorder. Crystals of 2 remain stable outside the mother liquor, but their quality as reflected in the data (Table I) is inferior compared to 1 and 3.

All computations were performed on a PDP-11/73 computer using the Structure Determination Package available from Enraf-Nonius.¹⁹ Final positional parameters of non-hydrogen atoms with their isotropic equivalent thermal parameters are given in Table II for complexes 1-3.

Results and Discussion

IR and Electronic Spectra. IR spectra of the complexes show a band in the range 1630-1650 cm⁻¹ attributable to azomethine group. This band for free ligands occurs at frequencies higher by ~10 cm⁻¹. A sharp band in the range 1330-1355 cm⁻¹ is assigned to ν (C-O). A broad band around 3460 cm⁻¹ due to ν (O-H) for free ligands was absent for complexes, suggesting the coordination of Schiff base as a dianionic ligand. Methanolic solutions of complexes 1-3 show intense $n-\pi^*$ and $\pi-\pi^*$ ligand charge transfer bands in the range 244-422 nm. A weak asymmetric broad band in the visible range 564-573 nm, observed only for the complexes, is assigned to d-d transitions.

Electrochemistry. The CVs of 1-3 could be attributed to three quasi-reversible redox couples. The assignments and peak positions are given in supplementary material. Couple I has an anodic wave in the range 1.24-1.27 V and a corresponding reduction wave around 1.18 V, assigned to the oxidation of Schiff base ligand. The anodic and cathodic waves are sharper for complex 1 than for 2 and 3. ΔE_p of the couple increases in the order 1 > 3 > 2. Repeated scans show increased currents in the case of 1 due to electrochemical oxidative polymerization through the para position to the phenolic group.²⁰ This is not seen for 2 and 3 as the para position is blocked by the substituents. Couple II with its cathodic and anodic waves around -1.15 and -1.0 V, respectively, is assigned to Cu(II)/Cu(I). A peak at -0.3 V related to this couple is thought to arise from the disproportionation reaction in the oxidation of Cu(I). When the scans were restricted between +0.8 and -0.6 V, broad waves with low current heights (couple III) were observed. Although the origin of these is not clear, they could be related to the oxidation of metal from +2 to +3.

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Table I. Summary of Crystallographic Data

	1	2	3
	Experimental Values		
molecular formula	C ₁₆ H ₁₄ N ₂ O ₂ Cu	(C ₁₈ H ₁₈ N ₂ O ₄ Cu)·(CH ₄ O)	C ₁₆ H ₁₂ N ₂ O ₂ Cl ₂ Cu
molecular weight	329.8	421.9	398.7
space group	monoclinic, C2/c	monoclinic, P2 ₁ /n	triclinic, P $\bar{1}$
cell parameters			
<i>a</i> (Å)	26.658(7)	11.061(3)	8.318(1)
<i>b</i> (Å)	6.983(1)	7.537(6)	9.502(4)
<i>c</i> (Å)	14.719(2)	21.765(5)	11.016(4)
α (deg)	90	90	63.78(4)
β (deg)	97.42(2)	92.86(2)	75.62(3)
γ (deg)	90	90	78.83(4)
<i>V</i> (Å ³)	2717(6)	1812(2)	753(15)
<i>Z</i>	8	4	2
no. of reflections and θ range (deg) used for unit cell parameters	25, 15–25	23, 8–12	21, 15–30
radiation used, λ (Å)	Cu Kα, 1.5418	Mo Kα, 0.7107	Cu Kα, 1.5418
<i>D</i> _{calc} (g cm ⁻³)	1.613	1.540	1.758
absorption coeff, μ (cm ⁻¹)	22.71	12.34	54.62
temperature (K)	295	295	295
crystal color & descrptn	dark green plates	wine red needles	brown needles
crystal dimensions (mm)	0.18 × 0.18 × 0.05	0.30 × 0.08 × 0.04	0.40 × 0.10 × 0.06
	Data Collection		
diffractometer used	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
scan mode	ω-2θ	ω-2θ	ω-2θ
absorption correction ¹⁸	empirical	empirical	empirical
transmission min, max	74.0, 99.8	89.7, 93.6	87.4, 99.8
measured reflections	2301	2891	2826
observed reflections <i>I</i> > 3σ(<i>I</i>)	1993	1525	2613
θ _{max} (deg)	65	24	70
<i>h</i> _{min} , <i>h</i> _{max}	0, 31	0, 12	0, 10
<i>k</i> _{min} , <i>k</i> _{max}	0, 8	0, 8	-11, 11
<i>l</i> _{min} , <i>l</i> _{max}	-17, 17	-24, 24	-13, 13
no. of intensity control reflections, frequency, and variation	3, every 1 h, nil	3, every 1 h, nil	3, every 1 h, nil
no. of orientation control reflections, frequency, and variation	3, every 200 reflns, nil	3, every 200 reflns, nil	3, every 200 reflns, nil
	Refinement		
refinement on	<i>F</i>	<i>F</i>	<i>F</i>
final <i>R</i>	0.038	0.066	0.039
weighted <i>R</i>	0.058	0.067	0.059
reflections used	1993	1525	2613
no. of parameters in the least-squares refinement	190	230	208
hydrogen atom positions	not refined	not refined	not refined
(Δ/σ) _{max}	0.01	0.02	0.04
weighting scheme, <i>w</i>	1/σ(<i>F</i>) ²	1/σ(<i>F</i>) ²	1/σ(<i>F</i>) ²
Δρ _{max} (e Å ⁻³)	+0.53	+1.00	+0.35
Δρ _{min} (e Å ⁻³)	-0.45	-0.64	-1.00
extinction correction	not applied	not applied	not applied
source of atomic scattering factors			

International Tables for X-ray Crystallography (1974, Vol. IV)

Effect of Substitution on Molecular Association and Conformation: X-ray Structures. ORTEP²¹ views of 1–3 are shown in Figure 1 along with the atom numbering. Selected bond distances and angles are given in Table III. Complex 1 forms dimers bridged through O1 across the crystallographic center of symmetry (Cu...O1' = 2.414(2) Å, Cu...Cu' = 3.196(2) Å, ∠Cu–O1...Cu' = 93.7(1)°, and ∠O1'...Cu–O1 = 86.3(1)°). Copper has a tetragonally elongated square-pyramidal configuration with donor atoms N₂O₂ forming a perfect basal plane and the apical bond Cu...O1' being almost perpendicular to this plane. The copper atom is displaced by 0.14 Å toward the bridging oxygen O1' from the best plane of the donor atoms. The complex has a "stepped" conformation as observed in the dimers of Fe(salen)Cl^{22,23} (Figure 2). The "sal1" and "sal2" planes are bent asymmetrically making angles 24.9(1)° and 3.1(6)°, respectively, with respect to the N₂O₂ plane. More buckling of "sal1" containing O1 than "sal2" provides a closer approach for O1 toward centrosymmetrically related Cu' and simultaneously

reduces the steric interaction between the benzene rings (Figure 2). The ethylenediamine carbons C8 and C9 are also buckled asymmetrically from the CuN1N2 plane, with the displacement for C8 being 0.48 Å toward the bridging molecule and for C9 being only 0.09 Å in the opposite direction. While Cu–N distances are equal, the Cu–O shows significant differences (Cu–O1 = 1.945(2) Å, Cu–O2 = 1.911(2) Å). The lengthening of Cu–O1 should be attributed to the involvement of O1 in a dimer bridge formation; similar elongations of M–O bonds have also been observed in dimers of Fe(salen)Cl^{22,23} and Co(salen).²⁴

Complex 2 with methoxy substitution also forms centrosymmetric dimers as in 1, but with a weaker dimeric bond. However, Cu...Cu' distance shows only a marginal increase from 1 (Cu...O1' = 2.801(7) Å, Cu...Cu' = 3.266(7) Å, ∠Cu–O1...Cu' = 85.7(7)° and ∠O1'...Cu–O1 = 94.3(7)°). Coordination geometry around copper is highly distorted square-pyramidal with almost coplanar N₂O₂ atoms forming a basal plane and with a long Cu...O1' apical bond. The displacement of Cu atom from this plane is negligibly small (0.06 Å). It is noteworthy that although the ethylenediamine conformation is identical to 1 with C8 out by 0.47 Å and C9 by 0.09 Å from the CuN1N2 plane, the molecule is essentially

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Table II. Positional Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B (Å ²)	atom	x	y	z	B (Å ²)
Complex 1									
Cu	0.23284(1)	0.20565(5)	0.09795(2)	2.087(8)	C7	0.3304(1)	0.0217(4)	0.1442(2)	2.95(6)
O1	0.28454(7)	0.3765(3)	0.0624(1)	2.32(4)	C8	0.2588(1)	-0.1824(4)	0.1405(2)	3.39(7)
O2	0.18423(7)	0.4082(3)	0.0889(1)	2.71(4)	C9	0.2134(1)	-0.1438(4)	0.1920(2)	3.06(6)
N1	0.28275(9)	0.0020(3)	0.1274(2)	2.56(5)	C10	0.1421(1)	0.0615(4)	0.1644(2)	2.82(6)
N2	0.18799(9)	0.0311(3)	0.1536(2)	2.53(4)	C11	0.1143(1)	0.2327(4)	0.1377(2)	2.76(6)
C1	0.3334(1)	0.3637(4)	0.0904(2)	2.44(5)	C12	0.0627(1)	0.2375(5)	0.1504(3)	4.03(7)
C2	0.3643(1)	0.5215(5)	0.0781(2)	3.19(6)	C13	0.0332(1)	0.3968(6)	0.1269(3)	4.60(8)
C3	0.4160(1)	0.5188(6)	0.1048(3)	4.26(8)	C14	0.0544(1)	0.5541(6)	0.0908(3)	4.05(7)
C4	0.4389(1)	0.3563(7)	0.1465(3)	4.67(8)	C15	0.1051(1)	0.5561(5)	0.0786(2)	3.38(6)
C5	0.4105(1)	0.2003(5)	0.1590(3)	3.90(7)	C16	0.1370(1)	0.3971(4)	0.1015(2)	2.46(5)
C6	0.3575(1)	0.1972(4)	0.1319(2)	2.77(6)					
Complex 2									
Cu	0.52494(9)	0.7995(1)	0.52613(4)	2.64(1)	C7	0.4165(7)	0.709(1)	0.4062(4)	3.4(1)
O1	0.6230(6)	0.9005(8)	0.4659(3)	3.5(1)	C8	0.2922(7)	0.673(2)	0.4907(5)	4.6(2)
O2	0.6429(4)	0.8573(8)	0.5892(3)	3.2(1)	C9	0.3200(8)	0.591(1)	0.5523(5)	3.7(1)
O3	0.6277(6)	0.796(1)	0.2156(3)	4.3(1)	C10	0.4333(7)	0.696(1)	0.6423(3)	3.1(1)
O4	0.6140(7)	0.879(1)	0.8397(3)	4.2(1)	C11	0.5307(6)	0.780(1)	0.6774(3)	2.8(1)
O101	0.109	0.082	0.443	5.3(3)*	C12	0.5274(6)	0.785(1)	0.7407(3)	3.2(1)
O102	0.141	0.043	0.445	7.3(5)*	C13	0.6125(8)	0.866(1)	0.7779(4)	3.5(1)
N1	0.4086(6)	0.714(1)	0.4627(3)	3.6(1)	C14	0.7095(7)	0.941(1)	0.7506(4)	3.3(1)
N2	0.4208(5)	0.6866(9)	0.5833(3)	3.1(1)	C15	0.7170(7)	0.936(1)	0.6863(4)	3.1(1)
C1	0.6198(7)	0.867(1)	0.4077(3)	2.8(1)	C16	0.6316(7)	0.8550(9)	0.6478(4)	2.9(1)
C2	0.7110(8)	0.925(1)	0.3707(4)	3.6(1)	C17	0.5305(9)	0.721(1)	0.1804(4)	4.1(2)
C3	0.7138(9)	0.904(1)	0.3094(4)	3.9(2)	C18	0.509(1)	0.827(2)	0.8686(4)	4.5(2)
C4	0.6164(7)	0.811(1)	0.2775(4)	3.5(1)	C101	0.082	0.209	0.471	6.9(6)*
C5	0.5241(7)	0.7493(9)	0.3117(3)	2.8(1)	C102	0.082	0.209	0.484	5.0(3)*
C6	0.5227(6)	0.7713(8)	0.3762(4)	2.6(1)					
Complex 3									
Cu	0.51180(4)	0.13313(3)	0.06709(3)	2.874(7)	C6	0.6513(3)	-0.2285(2)	0.2566(2)	2.92(4)
C11	0.94359(9)	-0.62272(7)	0.43377(7)	4.50(2)	C7	0.4775(3)	-0.1795(3)	0.2866(2)	3.16(5)
C12	0.2598(1)	0.94092(8)	-0.36906(8)	5.02(2)	C8	0.2260(3)	-0.0074(3)	0.2579(3)	3.59(6)
O1	0.7179(2)	0.0082(2)	0.0514(2)	4.08(4)	C9	0.1981(3)	0.1626(3)	0.2383(2)	3.63(6)
O2	0.5905(2)	0.3073(2)	-0.0984(2)	3.32(4)	C10	0.2583(3)	0.3976(3)	0.0349(2)	3.30(5)
N1	0.4066(2)	-0.0427(2)	0.2222(2)	3.14(4)	C11	0.3520(3)	0.4978(3)	-0.0935(2)	3.15(5)
N2	0.3050(2)	0.2539(2)	0.1077(2)	3.08(4)	C12	0.2785(3)	0.6506(3)	-0.1598(2)	3.58(5)
C1	0.7621(3)	-0.1326(3)	0.1404(2)	3.13(5)	C13	0.3550(3)	0.7514(3)	-0.2867(2)	3.69(5)
C2	0.9308(3)	-0.1971(3)	0.1208(2)	3.65(6)	C14	0.5078(3)	0.7021(3)	-0.3513(2)	3.68(5)
C3	0.9867(3)	-0.3427(3)	0.2088(3)	3.56(5)	C15	0.5823(3)	0.5552(3)	-0.2870(2)	3.52(5)
C4	0.8738(3)	-0.4350(3)	0.3214(2)	3.27(5)	C16	0.5100(3)	0.4451(3)	-0.1537(2)	3.00(5)
C5	0.7107(3)	-0.3789(3)	0.3445(2)	3.17(5)					

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. Starred values were refined isotropically.

planar. "sal1" and "sal2" planes bend symmetrically making angles of 14.5(5)° and 9.9(7)°, respectively, with the N₂O₂ plane. The planar conformation could be because of the weaker Cu...O1' bond (2.801(7) Å) in **2** which reduces the steric interaction between benzene rings as opposed to **1**. Interestingly, chloroform adduct of Cu(salen) with a dimer bond a little shorter than in **2** (Cu...O1' = 2.79 Å) has a "stepped" conformation. This brings out the fact that the ethylenediamine conformation and the overall molecular geometry are not necessarily interrelated as thought previously,²⁵ further demonstrating the flexibility of the "salen" framework. The packing of molecules in **2** creates channels because of the protruding methoxy groups, in which a methanol is included. As discussed in the Experimental Section, the solvent molecule is disordered and the disordered oxygen O101 and O102 make H-bonding contacts with O2 of the ligand not involved in dimer formation (O101...O2 = 2.90 Å and O102...O2 = 2.65 Å). The H-bonding interaction of the solvent molecule in the lattice with the ligand is observed to be one of the factors influencing dimeric association. This is best exemplified by the X-ray structures of Cu(salen) (strong dimer) and its adducts with chloroform (weak dimer)²⁶ and nitrophenol (monomer).²⁵

Chloro-substituted Cu(salen) **3** also has a molecular association across the center of symmetry as in **1** and **2** but Cu...O1' = 3.307(2) Å; Cu...Cu' = 3.502(2) Å is too long to be considered as a dimer. Moreover, the angles ∠Cu-O1...Cu'(79.5(1)°) and ∠O1'...Cu-O1 (68.2(1)°) show considerable shearing of molecules.

The donor atoms N₂O₂ do not form a perfect plane but deviate by ~±0.11 Å from their best plane to form a tetrahedrally distorted square planar geometry around Cu. Atoms C8 and C9 are displaced by 0.39 and 0.22 Å, respectively, in opposite directions from the CuN1N2 plane. The "sal" units are twisted with respect to each other (twist angle = 9.4(4)°) and make angles 11.5(2)° and 8.2(3)° with the best plane of the donor atoms. The two Cu-O bonds are similar and compare well with the literature values.^{25,26} But, Cu-N distances in **3** are somewhat shorter than in **1** (Table III), perhaps due to decrease in the coordination number of Cu from 5 to 4. The weaker dimer association in **2** was rationalized in terms of the solvent H-bonding interaction with the ligand, but no dimeric interaction in the absence of any solvent molecule in **3** could only be attributed to the chlorine substitution.

EPR Studies. The EPR spectra for polycrystalline samples of **1-3**, at 298 and 77 K are very similar (Figure 3) and characterized by an axial g tensor with g_{||} > g_⊥. The principal g values calculated using the method of Kneubühl²⁷ (Table IV) are in agreement with those reported for bidentate Cu(II) Schiff base complexes²⁸⁻³⁰ suggesting that the unpaired electron occupies a "formal" d_{xy}

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(28) Maki, A. H.; McGarvey, B. R. *J. Chem. Phys.* 1958, 29, 31 and 35. McGarvey, B. R. *J. Phys. Chem.* 1956, 60, 71.

(29) Gresmann, H. R.; Swalen, J. D. *J. Chem. Phys.* 1962, 36, 3221. Kivelson, D.; Neiman, R. *J. Chem. Phys.* 1961, 35, 149.

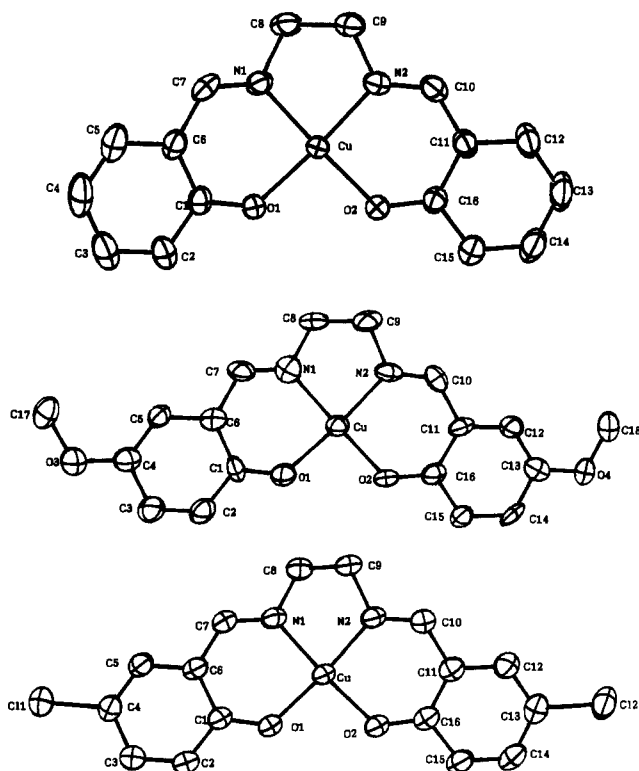


Figure 1. ORTEP views of (a, top) Cu(salen), (b, middle) Cu(5-CH₃O-salen), and (c, bottom) Cu(5-Cl-salen).

orbital. Hyperfine coupling due to the metal ion (A_{Cu})³¹ could not be resolved even at 77 K due to exchange narrowing of EPR lines.

The substituents (X) and molecular geometry have significant effect on both g_{\parallel} and g_{\perp} values. As seen from Table IV, **1** and **2** have almost the same g_{\perp} value whereas **3** has a much lower value. Further, the line width for the g_{\perp} feature is relatively smaller for **3** (~50 G) than for **1** and **2** (~85 G). But the g_{\parallel} values vary in the order **1** > **2** > **3**. The variations in g_{\parallel} could be interpreted due to the changes in the coordination number and intermolecular Cu...O1' distances. The increase in g_{\perp} value can be correlated with the distortions from the square planarity of N₂O₂.

The increase in the principal g components with lowering of temperature to 77 K indicates small changes in the molecular conformation. The absence of characteristic signals due to dimers in **1** and **2** is due to weak magnetic interactions between two copper units intermolecularly bridged by phenolate oxygen.

Color Isomerism and Solvatochromism. Complexes **1**–**3** show color isomerism in solid state. Complex **1** gave green solid from alcohol while green and deep red solids were obtained from chloroform. The green compound is analyzed in the present study as dimeric Cu(salen) whereas the deep red product was characterized by Waters and Hall²⁶ as a chloroform adduct of dimeric Cu(salen). Methanolic solutions of **2** and **3** yielded wine red and brown crystals while their ethanolic solutions yielded green crystals. Single crystals of **2** and **3** exhibit dichroism by showing different colors in reflected and transmitted lights. However, these color isomers did not show any marked spectral changes.

Complexes exhibit solvatochromism; the color of the solution changes from violet through blue to green as the σ donation capability of the solvent³² increases (Table IV). Waters and

Hall³³ have reported color changes for Cu(II) Schiff bases in a few solvents attributing violet and brown colors to tetracoordination and green color to strong pentacoordination of copper.³⁴ However, this color rule does not hold good for all the copper complexes^{26,35} as various other factors (*vide infra*) influence the chromic properties.

The electronic spectra of the complexes are similar in various solvents, but the charge transfer (~380 nm) and d-d (~565 nm) bands shift to higher wavelengths as the basicity of the solvent increases. Cyclic voltammetry of **1**–**3** indicate the solvent effect on the redox couples of I and II. The anodic and cathodic waves of couple II (Cu(II)/Cu(I)) shift to negative potentials with the increase in the donicity of the solvent. In a highly σ -donor solvent, py, couple I shifts to more positive potentials.

The EPR spectra of **1**–**3** at 298 K in solution show four equally spaced resonances attributable to the interaction of electron spin with the nuclear spin of Cu(II). But ⁶³Cu and ⁶⁵Cu hyperfine features could not be resolved. The resonances show m_1 dependent line widths,³⁶ with the high field line being narrower and more intense than the low field line. Representative spectra for **2** are shown in Figure 4. The isotropic g and A_{Cu} calculated by spectral fitting are listed in Table IV.

Figure 5 shows good correlations between g_{iso} and A_{iso} , and g_{iso} and the Gutmann donor number (DN).³² With increasing donor capacity of the solvent, the g_{iso} value increases with a concomitant decrease in the magnitude of the A_{iso} . These agree with the changes in electronic spectral data and $E_{1/2}$ values for couple II implying the decrease in ligand field splitting with increase in σ basicity of the solvent. The deviation observed for py should be due to its strong coordination to copper.

The superhyperfine splitting with about 15 lines on the high field isotropic copper hyperfine feature (Figure 4) cannot be attributed to the interaction with two equivalent ¹⁴N nuclei alone, but the splittings and the line intensities could be very well accounted for the interaction of two equivalent proton spins along with the two ¹⁴N nuclei. The superhyperfine coupling parameters were calculated to be $A_{\text{N}}(\text{iso}) = 13.9 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\text{H}}(\text{iso}) = 7.5 \times 10^{-4} \text{ cm}^{-1}$. The protons here belong to the carbon atoms adjacent to ¹⁴N nuclei. Similar observations were reported for some bidentate salicylidinimine Schiff base Cu(II) complexes.²⁸

EPR spectra of frozen solutions of **1**–**3** at 77 K are characterized by axial g and A tensors (Figure 3). Three of the four parallel hyperfine features are well resolved while the fourth one is overlapped by g_{\perp} features which are partially resolved. Apart from this an extra line indicated by an asterisk (*) for frozen glasses is an "angular anomaly" due to powder averaging.²⁹ The superhyperfine features at 298 K were not seen in the frozen solution spectra except for pyridine. The g_{\parallel} , g_{\perp} , and A_{\parallel} values could be readily calculated from the spectra. However, the accuracy of A_{\perp} values is lower because of the partially resolved perpendicular features. As the σ basicity or DN of the solvent increases, the g_{\parallel} values increase whereas A_{\parallel} values decrease (Table IV).

Ground-State Wave Function and Bonding Parameters. The spin Hamiltonian parameters (Table IV) indicate that the unpaired electron occupies a "formal" d_{xy} orbital. The MO coefficients have been calculated using the ligand field approach adopted by Maki and McGarvey²⁸ and later by Kivelson and Neiman²⁹ for a 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; δ is the coefficient for the MO E_g

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(31) Copper has two magnetic nuclei ⁶³Cu and ⁶⁵Cu with nuclear gyromagnetic ratios (g_N) being 1.484 and 1.588 and abundances being 69.2% and 30.8%, respectively; both the nuclei have a spin of $I = 3/2$.

(32) Gutmann donor number (DN) was chosen as a measure of the Lewis basicity of solvent molecules. Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978. Gutmann, V. *Coordination Chemistry in Non-aqueous Solutions*; Springer: Vienna, 1968.

(33) Waters, T. N.; Hall, D. J. *J. Chem. Soc.* **1959**, 1200.

(34) Llewellyn, F. J.; Waters, T. N. *J. Chem. Soc.* **1960**, 2639.

(35) Hall, D.; Sheat, S. V.; Waters, T. N. *J. Chem. Soc.* **1968**, 460.

(36) Lewis, W. B.; Morgan, L. O. *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1968, Vol. 4, p 33.

Table III. Bond Distances in Angstroms and Bond Angles in Degrees^a

Complex 1											
atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Cu	O1	1.945(2)	N2	C10	1.273(4)	C10	C11	1.434(4)			
Cu	O2	1.911(2)	C1	C2	1.401(4)	C11	C12	1.413(4)			
Cu	N1	1.958(2)	C1	C6	1.426(4)	C11	C16	1.431(4)			
Cu	N2	1.959(2)	C2	C3	1.382(4)	C12	C13	1.380(5)			
O1	C1	1.319(4)	C3	C4	1.393(6)	C13	C14	1.374(6)			
O2	C16	1.299(3)	C4	C5	1.354(6)	C14	C15	1.385(5)			
N1	C7	1.271(4)	C5	C6	1.419(4)	C15	C16	1.412(4)			
N1	C8	1.460(4)	C6	C7	1.444(4)						
N2	C9	1.474(4)	C8	C9	1.533(5)						
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Cu	O2	91.43(9)	C9	N2	C10	119.5(3)	N2	C9	C8	108.0(3)
O1	Cu	N1	91.16(9)	O1	C1	C2	118.7(3)	N2	C10	C11	125.1(3)
O1	Cu	N2	170.40(8)	O1	C1	C6	124.1(3)	C10	C11	C12	117.4(3)
O2	Cu	N1	171.3(1)	C2	C1	C6	117.2(2)	C10	C11	C16	122.9(3)
O2	Cu	N2	92.56(9)	C1	C2	C3	122.2(4)	C12	C11	C16	119.8(3)
N1	Cu	N2	83.7(1)	C2	C3	C4	120.1(3)	C11	C12	C13	121.3(3)
Cu	O1	C1	125.5(2)	C3	C4	C5	119.6(4)	C12	C13	C14	119.4(3)
Cu	O2	C16	127.4(2)	C4	C5	C6	122.0(3)	C13	C14	C15	121.0(3)
Cu	N1	C7	126.8(3)	C1	C6	C5	118.9(3)	C14	C15	C16	121.9(3)
Cu	N1	C8	112.0(2)	C1	C6	C7	122.9(2)	O2	C16	C11	124.4(3)
C7	N1	C8	120.8(2)	C5	C6	C7	118.2(3)	O2	C16	C15	118.9(3)
Cu	N2	C9	113.6(2)	N1	C7	C6	124.8(3)	C11	C16	C15	116.7(3)
Cu	N2	C10	126.7(3)	N1	C8	C9	107.2(2)				
Complex 2											
atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Cu	O1	1.908(6)	N1	C7	1.24(2)	C6	C7	1.46(2)			
Cu	O2	1.895(5)	N1	C8	1.49(1)	C8	C9	1.49(1)			
Cu	N1	1.948(7)	N2	C9	1.47(2)	C10	C11	1.43(1)			
Cu	N2	1.942(7)	N2	C10	1.286(9)	C11	C12	1.38(2)			
O1	C1	1.290(9)	C1	C2	1.40(1)	C11	C16	1.45(2)			
O2	C16	1.29(2)	C1	C6	1.44(2)	C12	C13	1.36(1)			
O3	C4	1.36(2)	C2	C3	1.35(1)	C13	C14	1.38(1)			
O3	C17	1.41(1)	C3	C4	1.43(1)	C14	C15	1.41(1)			
O4	C13	1.35(2)	C4	C5	1.38(1)	C15	C16	1.38(2)			
O4	C18	1.41(1)	C5	C6	1.41(2)						
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Cu	O2	90.4(3)	C9	N2	C10	121.7(7)	N2	C9	C8	109.0(8)
O1	Cu	N1	91.6(3)	O1	C1	C2	121.6(7)	N2	C10	C11	126.4(7)
O1	Cu	N2	176.4(3)	O1	C1	C6	123.0(8)	C10	C11	C12	118.8(6)
O2	Cu	N1	173.9(3)	C2	C1	C6	115.4(7)	C10	C11	C16	121.1(7)
O2	Cu	N2	92.9(3)	C1	C2	C3	126.2(8)	C12	C11	C16	120.1(7)
N1	Cu	N2	85.0(3)	C2	C3	C4	118.6(9)	C11	C12	C13	123.4(7)
Cu	O1	C1	127.6(5)	O3	C4	C3	114.1(8)	O4	C13	C12	126.6(8)
Cu	O2	C16	127.7(5)	O3	C4	C5	128.0(8)	O4	C13	C14	115.8(8)
C4	O3	C17	117.4(8)	C3	C4	C5	117.8(7)	C12	C13	C14	117.6(8)
C13	O4	C18	117.5(7)	C4	C5	C6	123.0(7)	C13	C14	C15	120.6(7)
Cu	N1	C7	129.2(6)	C1	C6	C5	118.8(6)	C14	C15	C16	122.8(7)
Cu	N1	C8	109.6(5)	C1	C6	C7	123.5(7)	O2	C16	C11	124.7(7)
C7	N1	C8	120.7(7)	C5	C6	C7	117.4(6)	O2	C16	C15	119.7(7)
Cu	N2	C9	112.9(6)	N1	C7	C6	122.6(7)	C11	C16	C15	115.5(7)
Cu	N2	C10	125.4(5)	N1	C8	C9	108.1(7)				
Complex 3											
atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Cu	O1	1.904(2)	N1	C8	1.467(3)	C6	C7	1.433(3)			
Cu	O2	1.911(1)	N2	C9	1.474(3)	C8	C9	1.511(4)			
Cu	N1	1.943(2)	N2	C10	1.281(3)	C10	C11	1.437(3)			
Cu	N2	1.945(2)	C1	C2	1.423(3)	C11	C12	1.398(3)			
C11	C4	1.748(2)	C1	C6	1.424(3)	C11	C16	1.422(3)			
C12	C13	1.748(2)	C2	C3	1.363(3)	C12	C13	1.374(3)			
O1	C1	1.310(2)	C3	C4	1.403(3)	C13	C14	1.398(3)			
O2	C16	1.300(2)	C4	C5	1.363(3)	C14	C15	1.358(4)			
N1	C7	1.280(3)	C5	C6	1.402(3)	C15	C16	1.435(3)			
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Cu	O2	91.63(6)	O1	C1	C2	118.9(2)	N2	C9	C8	107.5(3)
O1	Cu	N1	92.63(7)	O1	C1	C6	124.3(2)	N2	C10	C11	125.0(3)
O1	Cu	N2	172.41(9)	C2	C1	C6	116.8(2)	C10	C11	C12	116.7(2)
O2	Cu	N1	171.8(1)	C1	C2	C3	122.5(2)	C10	C11	C16	122.4(2)
O2	Cu	N2	92.98(6)	C2	C3	C4	119.2(3)	C12	C11	C16	120.8(2)
N1	Cu	N2	83.56(8)	C11	C4	C3	119.7(2)	C11	C12	C13	120.7(2)
Cu	O1	C1	127.3(1)	C11	C4	C5	119.8(1)	C12	C13	C12	120.0(2)
Cu	O2	C16	127.0(1)	C3	C4	C5	120.6(2)	C12	C13	C14	119.7(2)
Cu	N1	C7	126.8(1)	C4	C5	C6	121.1(2)	C12	C13	C14	120.3(2)
Cu	N1	C8	112.6(1)	C1	C6	C5	119.9(2)	C13	C14	C15	119.8(2)
C7	N1	C8	120.5(2)	C1	C6	C7	122.6(2)	C14	C15	C16	122.7(3)
Cu	N2	C9	112.8(1)	C5	C6	C7	117.7(2)	O2	C16	C11	125.4(2)
Cu	N2	C10	127.0(1)	N1	C7	C6	125.2(2)	O2	C16	C15	118.8(2)
C9	N2	C10	120.2(2)	N1	C8	C9	106.4(3)	C11	C16	C15	115.8(2)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

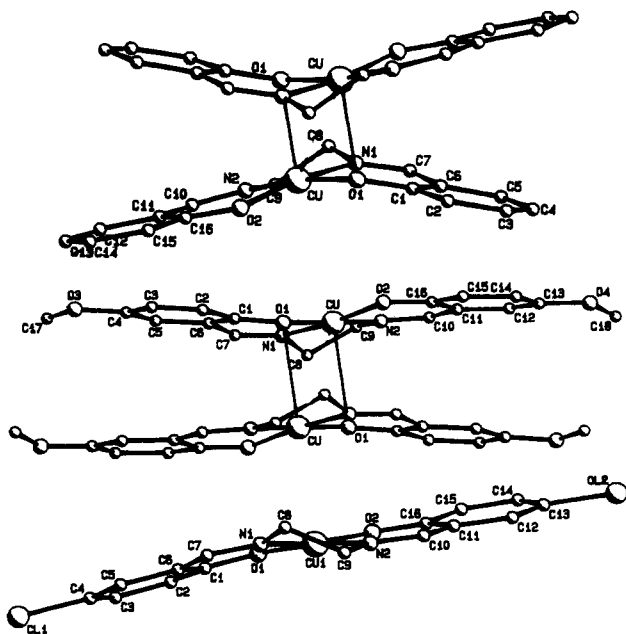


Figure 2. Diagrams illustrating the effect of substitutions on molecular association and chelate conformation: (a, top) dimers of Cu(salen) in "stepped" conformation ($\text{Cu}\cdots\text{O}1' = 2.414(2)$ Å and $\text{Cu}\cdots\text{Cu}' = 3.1962(2)$ Å); (b, middle) weak dimers of Cu(5-CH₃O-salen) with an overall planar geometry for salen ($\text{Cu}\cdots\text{O}1' = 2.801(7)$ and $\text{Cu}\cdots\text{Cu}' = 3.266(7)$ Å); (c, bottom) monomers of Cu(5-Cl-salen).

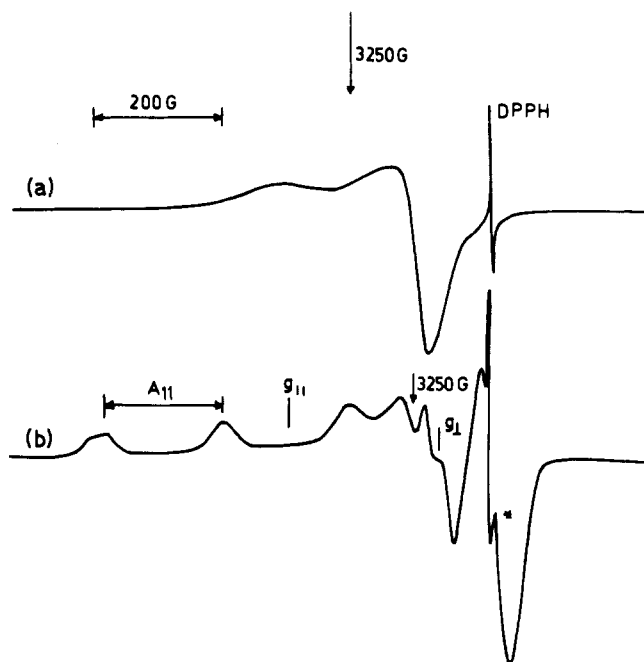


Figure 3. X-band EPR spectra of (a) polycrystalline Cu(5-Cl-salen) at 298 K and (b) Cu(salen) in DMF at 77 K. Asterisk (*) indicates "angular anomaly" due to power averaging.

representing the out-of-plane π bonding and α' is the coefficient for ligand orbitals forming the B_{1g} orbital. The MO coefficients listed in Table V were obtained by using the value of -828 cm^{-1} for λ , the spin-orbit coupling constant, and 0.036 cm^{-1} for P , the dipolar interaction term for free Cu(II) ion. The overlap integral S and the constant $T(n)$ were assumed as 0.093 and 0.333 , respectively. A clear excitation band for $B_{1g} \leftrightarrow A_g$ was observed for all the complexes in the range 16750 – 17699 cm^{-1} . However, the d–d band for $B_{1g} \leftrightarrow E_g$ was not observed in all the cases, as it overlapped by a charge transfer band. Therefore, the coefficient δ was calculated only in those cases where this band was observed. The MO coefficients (Table V) suggest that the in-plane σ and π bondings are covalent while the out-of-plane π bonding is ionic in nature. The present study shows marked changes in the in-

plane π bonding with substitution and solvent as observed by Kivelson and Neiman for several Cu(II) complexes.²⁹ The α^2 values decrease in the order $1 > 2 > 3$ while the β^2 values increase in the same order. Similar variations in α^2 and β^2 values are observed with increasing σ -basicity of the solvent. Although the in-plane σ and π bonding parameters are equally important, the latter is probably a better indicator of covalent bonding. The extra superhyperfine coupling due to ^{14}N nuclei in solvents ($A_N(\text{iso}) = 13.9 \times 10^{-4}$ cm^{-1}) has yielded an indirect estimate of 0.771 and 0.322 for α^2 and α'^2 , respectively. These are in agreement within experimental errors with those listed in Table V.

EHMO calculations were carried out on 1–3 by the method described by Hoffmann³⁷ using the positional parameters from X-ray studies. However, as the basis set was very large to handle, calculations were performed on acacen type model systems; we believe such a simplification should not alter the results significantly. The off-diagonal elements were calculated using a weighted Wolfberg–Helmholz formula³⁸ with the Hückel constant of 1.75 . The input parameters, such as Coulomb integrals and orbital exponents for Cu, O, N, C, and H, were taken from ref 39. The HOMOs for complexes 1–3 are as follows.

$$\psi(1) = -0.898d_{xy} - 0.177d_{z^2} - 0.150d_{x^2-y^2} - 0.240d_{yz}$$

$$\psi(2) = -0.949d_{xy} - 0.120d_{xz}$$

$$\psi(3) = -0.785d_{xy} - 0.375d_{z^2} + 0.130d_{xz} + 0.140d_{yz}$$

In the calculations using the EPR spin Hamiltonian parameters, we have assumed that the ground state is a linear combination of proper ligand orbitals and copper d_{xy} orbital. But the EHMO calculations reveal that the ground-state d_{xy} is admixed with copper d_{z^2} orbital. However, the MO coefficients obtained by both the methods are in excellent agreement. It is interesting to note that as the electron donating power of the substituent decreases changing the geometry of CuN_2O_2 from perfect to tetrahedrally distorted square planar, the HOMO having a predominant d_{xy} character gets increasingly admixed with the d_{z^2} orbital and the electron density at the metal decreases in the order $2 > 1 > 3$.

Mechanisms for Color Isomerism or Solvatochromism. Color isomerism in copper complexes has been the subject of several structural investigations.^{25,26,33} Waters and Hall³³ have correlated green color to pentacoordination and brown or violet color to tetracoordination for copper. Complex 1 forms green plates obeying this color rule. However, complex 2 with the same coordination geometry around copper exhibits wine red color. There are a few more exceptions to the color rule like 2^{26,35} suggesting that other parameters like H-bonding interactions between the solvent (guest) and the copper complex (host) also play a vital role. The crystal structures and solution studies further reveal that conformational flexibility of the ligand should also be responsible for changes in the ligand field strength thereby influencing the color, even though there may not be any change in the metal coordination number. Thus color isomerism/solvatochromism exhibited by complexes 1–3 can now be understood in terms of not only the fifth coordination of the solvent molecule but involving more subtle molecular features like changes in the ethylenediamine conformation from the equally displaced one (in 3) to the envelope conformation (in 1 and 2) as well as weak interactions of the ligand with the solvent molecules (2).

Reactivity. The variations of isotropic g and A_{Cu} in several donor solvents (Table IV) reveal that complex 3 is more reactive toward forming pentacoordinated complexes than 1 and 2. In

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Table IV. EPR Spin Hamiltonian Parameters for Cu(5-X-salen) Complexes

complex	solvent	DN ^b	color	g_{iso}^c	g_{\parallel}^c	g_{\perp}^c	$A_{Cu(iso)}^d \times 10^{-4} \text{ cm}^{-1}$	$A_{\parallel}^d \times 10^{-4} \text{ cm}^{-1}$	$A_{\perp}^d \times 10^{-4} \text{ cm}^{-1}$
Cu(salen), 1	solid ^a		green		2.198 (2.191)	2.090 (2.084)			
	CHCl ₃		deep violet	2.0964	2.180	2.054	-88.3	-211.6	-33.5
	CH ₂ Cl ₂	0	bluish violet	2.0986	2.192	2.052	-88.8	-204.7	-33.5
	CH ₃ CN	14.1	peacock blue	2.0993	2.193	2.052	-87.5	-207.8	-33.5
	DMF	26.6	blue	2.0999	2.212	2.054	-86.0	-203.7	-30.7
	CH ₃ OH	25.7	green	2.1002	2.214	2.057	-85.0	-201.5	-30.7
	THF	20.0	brownish green	2.1002	2.216	2.056	-84.3	-198.6	-26.9
	pyridine	33.1	green	2.1094	2.227	2.053	-78.5	-191.3	-24.0
Cu(5-CH ₃ O-salen), 2	solid ^a		wine red		2.189 (2.188)	2.078 (2.082)			
	CHCl ₃		brownish green	2.0958	2.204	2.047	-88.0	-203.0	-30.6
	CH ₂ Cl ₂	0	green	2.0967	2.209	2.047	-87.7	-203.5	-28.0
	CH ₃ CN	14.1	green	2.0980	2.211	2.050	-87.7	-203.3	-27.5
	DMF	26.6	green	2.0999	2.213	2.050	-87.2	-201.1	-25.5
	CH ₃ OH	25.7	brownish green	2.1008	2.216	2.055	-85.7	-198.6	-23.0
	THF	20.0	green	2.1012	2.216	2.057	-85.3	-198.6	-20.5
	pyridine	33.1	green	2.1069	2.226	2.057	-78.3	-193.3	-18.0
Cu(5-Cl-salen), 3	solid ^a		brown red		2.189 (2.187)	2.064 (2.060)			
	CHCl ₃		reddish brown	2.0964	2.208	2.057	-88.7	-202.7	-25.6
	CH ₂ Cl ₂	0	green	2.0974	2.212	2.054	-87.8	-201.0	-23.0
	CH ₃ CN	14.1	blue	2.0990	2.221	2.057	-86.2	-196.2	-18.0
	DMF	26.6	blue	2.1028	2.214	2.055	-85.5	-198.4	-23.0
	CH ₃ OH	25.7	green	2.1030	2.214	2.055	-84.4	-198.4	-17.9
	THF	20.0	green	2.1037	2.215	2.054	-84.4	-198.5	-23.0
	pyridine	33.1	green	2.1130	2.231	2.057	-77.8	-188.5	-17.9

^a Polycrystalline sample; g values in parentheses are those at 77 K. ^b Gutmann donor number. ^c Errors in g_{iso} , g_{\parallel} , and g_{\perp} are ± 0.0005 , ± 0.001 and ± 0.001 , respectively. ^d Errors in $A_{Cu(iso)}$, A_{\parallel} , and A_{\perp} are ± 0.5 , ± 1.0 and ± 1.0 , respectively.

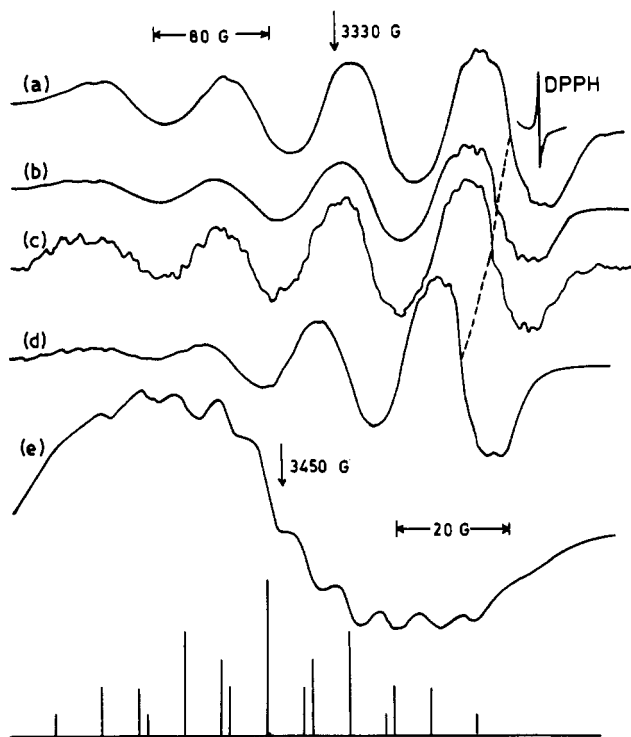


Figure 4. Effect of solvents on the X-band EPR spectra of Cu(5-CH₃O-salen) at 298 K: (a) CH₃CN, (b) DMF, (c) CH₃OH, (d) py, and (e) superhyperfine structure due to two ¹⁴N and ¹H nuclei each on the high field side of the copper hyperfine features in (b) and its simulated stick plot.

fact, strong σ donor py forms axial ligand complexes, but the complex with 3 seems to be more stable than with 1 and 2. EPR spectrum for the py complex of 3 in polycrystalline form recorded immediately after taking out from the mother liquor is characterized by $g_{\parallel} = 2.223$ and $g_{\perp} = 2.087$ at 298 K. The higher g_{\parallel} value than for the parent complex 3 (Table IV) is consistent with the square pyramidal geometry implying axial py coordination. Complexes 1–3 clearly demonstrate the conformational flexibility affecting the metal environment achieved by the varying nature

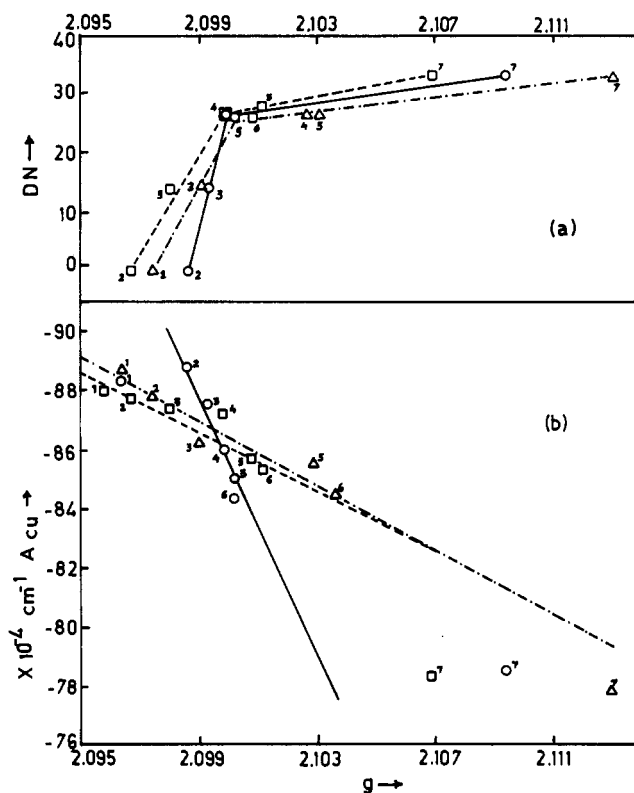


Figure 5. Variations of (a) Gutmann donor number (DN) of the solvents and (b) isotropic copper hyperfine coupling constant (A_{Cu}) with g_{iso} : CH₃CN (1), CH₂Cl₂ (2), CHCl₃ (3), DMF (4), CH₃OH (5), THF (6), and py (7); Cu(salen) (—), Cu(5-CH₃O-salen) (---), and Cu(5-Cl-salen) (- · -).

of substituents. The higher reactivity of 3 with electron-withdrawing Cl group can be explained in terms of molecular and electronic features as follows: (i) tetrahedrally distorted square planar geometry for copper, (ii) distorted half-chair form for the ethylenediamine ring, and (iii) admixture of electronic ground state d_{xy} with more d_{z^2} orbital and a lower electron density on the metal ion.

Table V. Electronic d-d Transitions (cm⁻¹) and Molecular Orbital Coefficients Calculated in D_{2h} Symmetry

complex	solvent	α^2	α'^2	β^2	δ^2	$\Delta E_{x^2-y^2}$	$\Delta E_{xz,yz}$
Cu(salen)	CH ₂ Cl ₂	0.823	0.263	0.698		17 731	
	DMF	0.841	0.243	0.731		17 361	
	CH ₃ OH	0.838	0.247	0.751		17 699	
	py	0.821	0.266	0.773		16 750	
Cu(5-CH ₃ O-salen)	CH ₂ Cl ₂	0.835	0.250	0.740		17 699	
	DMF	0.833	0.252	0.747		17 513	
	CH ₃ OH	0.831	0.254	0.765		17 699	
	py	0.828	0.258	0.764		16 779	
Cu(5-Cl-salen)	CH ₂ Cl ₂	0.834	0.252	0.752	0.972	17 731	24 390
	DMF	0.834	0.257	0.762	0.984	17 361	23 810
	CH ₃ OH	0.829	0.257	0.769	0.975	17 731	23 529
	py	0.819	0.268	0.789		16 779	

It may be mentioned that Cl substitution in salen was reported to form stable py complexes with Ni(III).⁴⁰ Also, the Mn(5-Cl-salen) interacted with molecular oxygen forms stable bis(μ -oxo)manganese(IV) complex.⁴¹ In order to probe further into the molecular geometry of the py-bound Cu complexes, attempts to grow X-ray quality crystals are underway. Although, more complex and dynamic situations are encountered in metalloproteins, it is tempting to mention the resemblance of copper environment in **3**, to a certain degree, with that of blue copper proteins⁴² and superoxide dismutase.⁴³

Concluding Remarks. Flexibility of the salen ligand and fine tuning of the electronic structure by introducing varying electron-donating and electron-withdrawing substituents in Schiff base and axial ligands are the crucial factors governing the reactivity of the metal center. The present study shows the effect of substituents H, CH₃O, and Cl on molecular association, chelate conformation, and electronic structure. In solid state, complex **1** forms strong dimers with a "stepped" conformation for salen,

whereas **2** having an electron-donating CH₃O substituent forms weak dimers with a solvent molecule in the lattice. The overall planarity of **2** with asymmetric ethylenediamine backbone is the first example so far known for the dimeric copper complex. Perhaps, complex **2** demonstrates a delicate balance between a dimeric and a monomeric association. The molecular association described in the crystalline state need not necessarily relate to the thermodynamic stability of complexes in solution. Electron-withdrawing chloro-substituted **3** is essentially a monomer in solid state and distorts the square planar geometry of CuN₂O₂ admixing the ground state d_{xy} orbital with d_{z²} and thereby enhances the stability of electron-rich axial ligand complexes. It is also seen that color isomerism is related not only to the coordination number of the metal ion but also to the ligand conformational changes vis-a-vis the H-bonding interactions with the solvent molecules. Work on similar lines to examine the effect of substitution on spin-state transition and reactivity toward molecular oxygen by manganese, iron, and cobalt complexes will be reported in the future.

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See page 5466 of the original paper for supplementary material available.

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