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IN SITU SYNTHESIS AND SPECTROSCOPIC STUDIES OF COPPER(II) AND NICKEL(II) COMPLEXES OF 1-HYDROXY-2-NAPHTHYLSTYRYLKETONEIMINES

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Bis-chelates of *N-R*-1-hydroxy-2-naphthylstyrylketoneimines of copper(II) and nickel(II) [$R = \text{H, Me, Et}$] were synthesised *in situ* from the ring opening reaction of 7,8-benzoflavanone with the respective metal(II) chlorides and aliphatic monoamines. Likewise, 1,2-ethanediamine (en) and 1,3-propanediamine (pn) afforded *N,N'*-ethylene-bis(1-hydroxy-2-naphthylstyrylketoneimine) and *N,N'*-propylene-bis(1-hydroxy-2-naphthylstyrylketoneimine) copper and nickel complexes, respectively. However, 1-hydroxy-2-naphthylstyrylketone reacts with MeNH_2 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to give bis(*N*-methyl-1-hydroxy-2-acetonaphthoneimine)copper(II). The complexes were characterised by analytical, IR, electronic and EPR methods and magnetic susceptibility measurements. The copper complexes of *N-R*-1-hydroxy-2-naphthylstyrylketoneimines have a distorted *trans* square planar structure. In nickel complexes, when the substituent *R* changes from H to Et through Me, the geometry changes from *trans* square planar to tetrahedral through a *quasi*-octahedral structure. The copper complexes of the tetradentate Schiff bases are square planar. The nickel complex of the en tetradentate Schiff base is *cis* square planar whereas that of pn is octahedral. EPR study reveals that copper(II) has a distorted square planar geometry, with a *trans* configuration in the bidentate Schiff base complexes and *cis* in the tetradentate Schiff base complexes. MO coefficients derived from EPR parameters indicate a high degree of covalency in these complexes.

Keywords: Copper, nickel, naphthylstyrylketoneimines, synthesis, esr.

INTRODUCTION

In situ synthesis of metal complexes is a well established procedure where isolation of ligands is difficult owing to their instability.^{1,2} In most of these syntheses the reactants are open chain compounds. 1-Hydroxy-2-naphthylstyrylketone undergoes cleavage at the double bond in the presence of amines to give 1-hydroxyacetonaphthoneimine.³ Also, heterocyclic ring cleavage is found to occur with 7,8-benzoflavanone in the presence of a base to give 1-hydroxy-2-naphthylstyrylketone.⁴ This observation prompted us to use this ring-opening reaction as a route for the *in situ* preparation of metal complexes of 3-(1-hydroxy-2-naphthyl)-5-(4-*X*-phenyl)pyrazolines.⁵ In this paper we report the *in situ* synthesis of copper(II) and nickel(II) Schiff base complexes from 7,8-benzoflavanone and their characterisation.

EXPERIMENTAL

Metal(II) chlorides used were of AR grade. MeNH_2 (S. Merck, 40% aqueous solution) and EtNH_2 (SD's, 70% aqueous solution) were used without further purification.

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$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (S. Merck) and $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (Riedel, W. Germany) were distilled and dried over NaOH pellets before use. Elemental analyses were performed at VHNSN College, Virudhunagar, India. Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. EPR spectra were recorded on a Varian E-112 spectrometer (X-band) with a 100 KHz field modulation and phase sensitive detection. EPR spectra of the complexes in toluene were recorded at 300K. The same solution was cooled to 77K in an immersion type quartz dewar which fitted into the EPR cavity. DPPH was used as internal field marker. Metal contents and other measurements were performed as reported elsewhere.⁶

CuL₂, NiL₂ (L = N-R-1-hydroxy-2-naphthylstyrylketoneimines), (NRHNSKI)

A mixture of 7,8-benzoflavanone⁷ (10 mmol) in EtOH (50 cm³) and the appropriate amine (NH_3 , MeNH_2 , EtNH_2) solution (5 cm³) was heated at reflux for an hour. To the cooled solution was added metal(II) salt (5 mmol) ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) in EtOH (25 cm³). The precipitated complex was suction-filtered, washed with aqueous EtOH and dried *in vacuo* over anhydrous CaCl_2 (Yield: 42–73%).

CuL, NiL (L = N,N'-ethylene-bis(1-hydroxy-2-naphthylstyrylketoneimine), (NNEBNSKI), and N,N'-propylene-bis(1-hydroxy-2-naphthylstyrylketoneimine), (NNPBNSKI)

An ethanolic solution (50 cm³) of 7,8-benzoflavanone (10 mmol) and $\text{NH}_2\text{CH}_2/\text{CH}_2\text{NH}_2$ or $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (5 cm³) was refluxed for an hour. To the clear solution was added metal(II) salt (5 mmol) ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) in EtOH (20 cm³) and the mixture was refluxed for a further hour. The complex, which separated slowly, was collected on a filter, washed with portions of aqueous EtOH (1:1 v/v) and dried *in vacuo*.

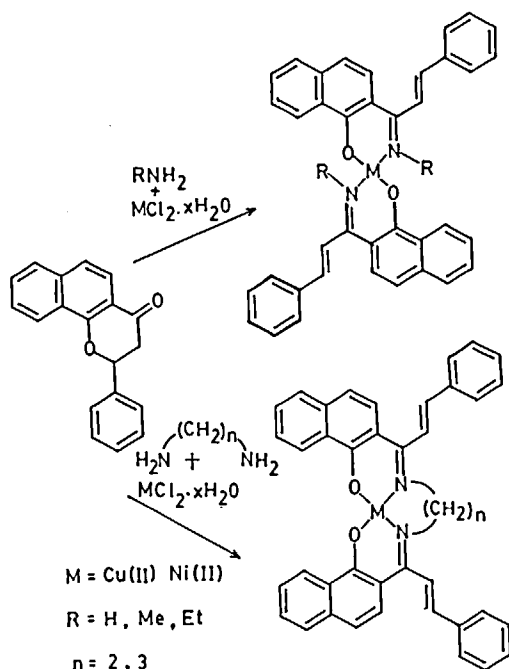
RESULTS AND DISCUSSION

In situ reaction of en and pn with 7,8-benzoflavanone and metal salts gave tetradentate Schiff base complexes whereas RNH_2 ($R = \text{H, Me, Et}$) gave bis-chelates (Scheme I).

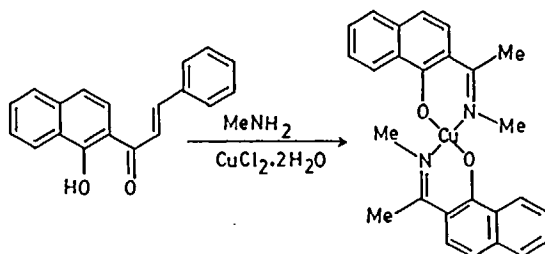
Attempt to prepare the copper(II) complex from 1-hydroxy-2-naphthylstyrylketone, methylamine and copper(II) chloride directly gave bis(1-hydroxy-2-acetonaphthone-imine)copper(II) (Scheme II). This was confirmed by preparing an authentic sample of bis(1-hydroxy-2-acetonaphthoneimine)copper(II)⁸ from 1-hydroxy-2-acetonaphthone, methylamine and copper(II) chloride and comparing its IR spectrum with that of the product obtained in Scheme II; they were found to be identical.

It is interesting to note that the Schiff base complexes of 1-hydroxy-2-naphthylstyrylketoneimine were obtained in a facile manner by reaction *in situ* from 7,8-benzoflavanone.

All the complexes are amorphous powders, with colours varying from green to brown. The metal chelates are insoluble in water while the copper(II) imines ($R = \text{Me, Et}$) and the nickel(II) imine ($R = \text{Et}$) complex are freely soluble in most organic solvents. Molar conductance measurements in CH_3CN indicate that the complexes are non-ionic. Analytical data (Table I) are consistent with the assigned molecular formulae. Purity was checked by TLC experiments. All complexes show only a single spot.



Scheme I



Scheme II

Magnetic Properties

The magnetic moments of all the copper(II) complexes lie between 1.84–2.08 BM, showing the presence of one unpaired electron in a distorted planar geometry. The complex bis(*N*-H-1-hydroxy-2-naphthylstyrylketoneimine)nickel(II) Ni(NHNSKI)₂ is diamagnetic with a *trans* square planar structure. The magnetic moment for the *N*-methyl-1-hydroxy-2-naphthylstyrylketoneimine, Ni(NMeNSKI)₂, complex is 2.69 BM, a value which suggests association between planar monomers in solid state leading to *quasi*-octahedral coordination⁹ to nickel(II). The magnetic moment of

TABLE I
Elemental analyses and colours of copper(II) and nickel(II) complexes of *N-R-1-hydroxy-2-naphthylstyrylketoneimines*.

Complex	Colour	Analysis ^a			
		M	C	H	N
Cu(NHNSKI)	Yellow	10.57	75.53	4.72	4.67
Cu(C ₁₉ H ₁₄ ON) ₂		(10.46)	(75.06)	(4.61)	(4.61)
Cu(NMeNSKI) ₂	Orange red	9.35	75.25	5.25	4.81
Cu(C ₂₀ H ₁₆ ON) ₂		(10.00)	(75.53)	(5.04)	(4.41)
Cu(NEtNSKI) ₂	Green brown	9.76	75.20	5.21	4.74
Cu(C ₂₁ H ₁₈ ON) ₂		(9.58)	(75.96)	(5.43)	(4.22)
Cu(NNEBNSKI)	Brown	10.22	76.25	5.12	4.13
Cu(C ₄₀ H ₂₈ O ₂ N ₂)		(10.03)	(75.76)	(4.74)	(4.42)
Cu(NNPBNSKI)	Brown	9.98	76.11	5.51	4.47
Cu(C ₄₁ H ₃₀ O ₂ N ₂)		(9.81)	(75.98)	(4.94)	(4.32)
Ni(NHNSKI)	Yellow	9.12	75.14	4.77	4.42
Ni(C ₁₉ H ₁₄ ON) ₂		(9.74)	(75.66)	(4.65)	(4.65)
Ni(NMeNSKI)	Orange red	10.11	76.77	5.43	4.32
Ni(C ₂₀ H ₁₆ ON) ₂		(9.31)	(76.10)	(5.07)	(4.44)
Ni(NEtNSKI) ₂	Dark brown	8.92	76.12	5.44	4.12
Ni(C ₂₁ H ₁₈ ON) ₂		(8.91)	(76.51)	(5.47)	(4.25)
Ni(NNEBNSKI)	Green brown	9.44	76.11	4.92	4.47
Ni(C ₄₀ H ₂₈ O ₂ N ₂)		(9.34)	(76.35)	(4.77)	(4.45)
Ni(NNPBNSKI)	Yellow brown	9.75	76.94	5.23	4.51
Ni(C ₄₁ H ₃₀ O ₂ N ₂)		(9.13)	(76.55)	(4.98)	(4.36)

^a Calculated values are given in parentheses.

3.89 BM for the nickel(II) complex of *N-ethyl-1-hydroxy-2-naphthylstyrylketoneimine*, Ni(NEtNSKI)₂, is indicative of tetrahedral geometry and this is supported by electronic spectroscopic data (*vide infra*). *N,N'*-ethylene-bis(1-hydroxy-2-naphthylstyrylketoneimine) gives a diamagnetic nickel(II) complex consistent with a *cis* square planar structure. On the contrary, *N,N'*-propane-bis(1-hydroxy-2-naphthylstyrylketoneimine(II)), Ni(NNPBNSKI), has a moment of 2.43 BM. This complex may possess six-coordinate geometry as proposed for other tetradenate Schiff base complexes.¹⁰

Ligand field spectra

The poor solubilities of most of the complexes in common, non-coordinating solvents prevent the determination of intensity and ligand field parameters. All the copper(II) chelates in CHCl₃ exhibit ligand field bands in the 15380–16130 cm⁻¹ range. In Cu(NNEBNSKI) an additional feature appears at 18 650 cm⁻¹. All the low energy bands arising from a combination of ²B_{1g} → ²A_{1g} and ²B_{1g} → ²B_{2g} transitions and the higher energy band, ²B_{1g} → ²E_g, are characteristic of D_{4h} symmetry. In pyridine solution, all complexes but Cu(NHNSKI)₂ and Cu(NEtNSKI)₂ show a negative shift (500–800 cm⁻¹), indicative of adduct formation. Since the shifts are not large, no efforts were made to quantify these data.

TABLE II

Electronic spectral data (cm^{-1}) and magnetic moments for copper(II) and nickel(II) complexes of *N-R-1-hydroxy-2-naphthylstyrylketoneimine*.

Complex	Solvent		μ_{eff} [BM]
	CHCl_3	Py	
$\text{Cu}(\text{NHNSKI})_2$	16 130	16 130	1.87
$\text{Cu}(\text{NMeNSKI})_2$	15 870	15 380	2.00
$\text{Cu}(\text{NEtNSKI})_2$	15 380	15 380	1.87
$\text{Cu}(\text{NNEBNSKI})$	15 380, 18 650	17 860	2.08
$\text{Cu}(\text{NNPBNSKI})$	15 380	15 380	1.84
$\text{Ni}(\text{NHNSKI})_2$	18 250	17 090	dia
$\text{Ni}(\text{NMeNSKI})_2$	13 420	13 330	2.69
$\text{Ni}(\text{NEtNSKI})_2$	13 420, 14 810, 16 130	12 500	3.89
$\text{Ni}(\text{NNEBNSKI})$	17 700	19 230	dia
$\text{Ni}(\text{NNPBNSKI})$	15 780	16 390, 19 610	2.43

$\text{Ni}(\text{NHNSKI})_2$ in CHCl_3 displays a band at $18\,520\text{ cm}^{-1}$ which may be assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}(\nu_2)$ transition, consistent with a *trans* square planar environment,¹¹ while $\text{Ni}(\text{NEtNSKI})_2$ exhibits strong multicomponent absorptions as a triplet at $13\,420$, $14\,820$ and $16\,130\text{ cm}^{-1}$. These may be assigned to a ${}^3T_1 \rightarrow {}^3T_1(P)(\nu_3)$ transition, consistent with tetrahedral coordination.¹¹ The tetradentate en Schiff base complex shows a band at $17\,700\text{ cm}^{-1}$ due to the ${}^1A_{1g} \rightarrow {}^1A_{2g}(\nu_2)$ transition, as is consistent with square planar geometry.

In pyridine, $\text{Ni}(\text{NHNSKI})_2$ shows an appreciable shift of the main feature, thus indicating adduct formation. In $\text{Ni}(\text{NEtNSKI})_2$, a new band at $12\,500\text{ cm}^{-1}$ suggests a change from tetrahedral to octahedral geometry; the band may be assigned to a ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition. In the square planar $\text{Ni}(\text{NNEBNSKI})$ complex, ν_2 is shifted to higher frequency ($19\,230\text{ cm}^{-1}$) in pyridine, indicating adduct formation. $\text{Ni}(\text{NNPBNSKI})$ shows not only a positive shift for ν_2 to $16\,390\text{ cm}^{-1}$, but the high energy ν_3 band occurs at $19\,610\text{ cm}^{-1}$, indicating a change from *pseudo*-octahedral to nearly octahedral structure due to bispyridine adduct formation. For the nickel complexes the low energy band could not be recorded in our spectrophotometer.

Infrared spectra

All the Schiff base complexes show a medium intensity band between 1600 and 1625 cm^{-1} (Table III), which has been assigned⁹ to $\nu(\text{C}=\text{N})$. In 1-hydroxy-2-acetonaphthoneimine complexes¹² $\nu(\text{C}=\text{N})$ occurs in the same region, a fact which implies that $\text{C}=\text{N}$ is not conjugated with $\text{C}=\text{C}$. The $\nu(\text{C}=\text{C})$ mode appears as a band of low intensity around 1620 cm^{-1} . The intense band in the $1375\text{--}1410\text{ cm}^{-1}$ range is assigned to a phenolic $\nu(\text{C}-\text{O})$ stretch, by reference to the parent chalcone complexes. The intense $\nu(\text{Ph}-\text{C}=\text{C})$ band observed in the $1540\text{--}1575\text{ cm}^{-1}$ region in 1-hydroxy-2-naphthylstyrylketone⁶ is shifted to higher frequency in Schiff base complexes, indicating mesomeric interaction of the phenyl group with the metal is decreased and hence the basic nature of nitrogen is not much altered. This suggests

TABLE III
I.r. data (cm^{-1}) for copper(II) and nickel(II) complexes of *N-R-1-hydroxy-2-naphthylstyrylketoneimines*.

Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{Ph}-\text{C}=\text{C})$	$\nu(\text{C}-\text{O})$
Cu(NHNSKI) ₂	1600	1567	1388
Ni(NHNSKI) ₂	1602	1570	1395
Cu(NMeNSKI) ₂	1600	1570	1398
Ni(NMeNSKI) ₂	1605	1575	1380
Cu(NEtNSKI) ₂	1604	1560	1410
Ni(NEtNSKI) ₂	1608	1564	1394
Cu(NNEBNSKI)	1610	1575	1404
Ni(NNEBNSKI)	1625	1583	1398
Cu(NNPBNSKI)	1607	1570	1397
Ni(NNPBNSKI)	1620	1580	1375

that the ligand field strength of *N-R-1-hydroxy-2-naphthylstyrylketoneimine* is comparable to that of *N-R-1-hydroxy-2-acetonaphthoneimines*.

Compared with nickel complexes, the copper complexes register lower $\nu(\text{C}=\text{N})$ ($2-15 \text{ cm}^{-1}$) and $\nu(\text{Ph}-\text{C}=\text{C})$ ($3-10 \text{ cm}^{-1}$) modes. This shows increased interaction of copper ion with the Schiff base. The higher stability of copper complexes is simply due to the electron-rich d^9 configuration of the copper(II) ion.¹³

EPR spectra

The solution spectra of all Cu complexes show four well-resolved hyperfine features due to copper. The high-field line of this quartet is further split into a five line multiplet with intensity ratio 1:2:3:2:1, arising from super-hyperfine interaction of the two nitrogens of the N_2O_2 chromophore. Typical spectra are shown in Figures 1 and 2. Frozen solution spectra at 77K consist of four well-resolved parallel features. Perpendicular features were resolved only in the case of Cu(NMeNSKI)₂. Hence, g_{\perp} and A_{\perp} values were calculated from the following equations.¹⁴

$$g_{\text{iso}} = 1/3g_{\parallel} + 2/3g_{\perp}$$

$$A_{\text{iso}} = 1/3A_{\parallel} + 2/3A_{\perp}$$

EPR parameters are collected in Table IV. For tetragonally elongated copper(II) complexes, the unpaired electron is present in $d_{x^2-y^2}$ orbitals¹⁵ and hence $g_{\parallel} > g_{\perp}$. For a tetragonally compressed system d_{z^2} will be the ground state with $g_{\perp} > g_{\parallel} \approx 2.0023$. All complexes show axially symmetric spectra with $g_{\parallel} > g_{\perp}$ indicating the presence of the unpaired electron in the $d_{xy}/d_{x^2-y^2}$ orbital. Further, the A_{\parallel} values observed for the complexes are characteristic of square planar geometry. For Cu(NNEBNSKI) there is a large reduction in the A_{\parallel} value, indicating a lower site symmetry for the copper ion, since the ground state is admixture of d_{xy} and d_{z^2} orbital.¹⁶ This can be rationalized by the fact that in Cu(NNEBNSKI) the two nitrogens can be only *cis* (Scheme I), whereas in the other complexes the two nitrogens can be *trans* (D_{2h}). EPR data can be used to investigate the covalency of metal-ligand bonding.¹⁴⁻¹⁸ In the complexes studied an effective D_{2h} symmetry is assumed, as suggested by Gersmann and Swalen¹⁹ for copper(II) acetylacetonate. The molecular orbitals involved and

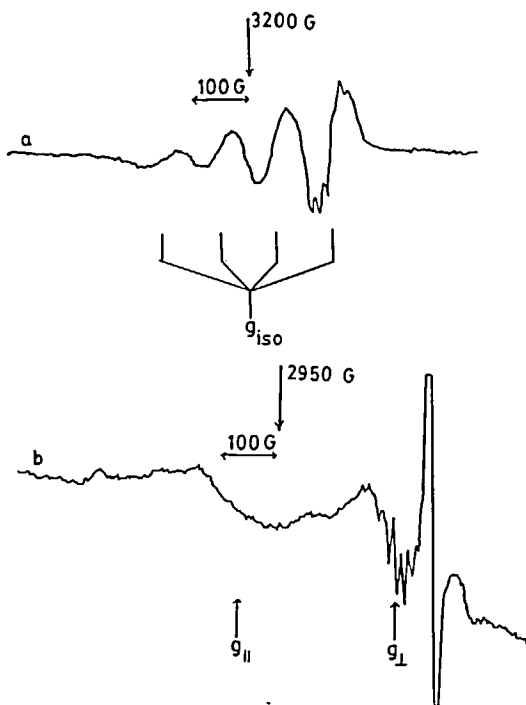


FIGURE 1 X-band EPR spectrum of Cu(NMeNSKI)₂ in toluene, (a) at 300K; (b) at 77K.

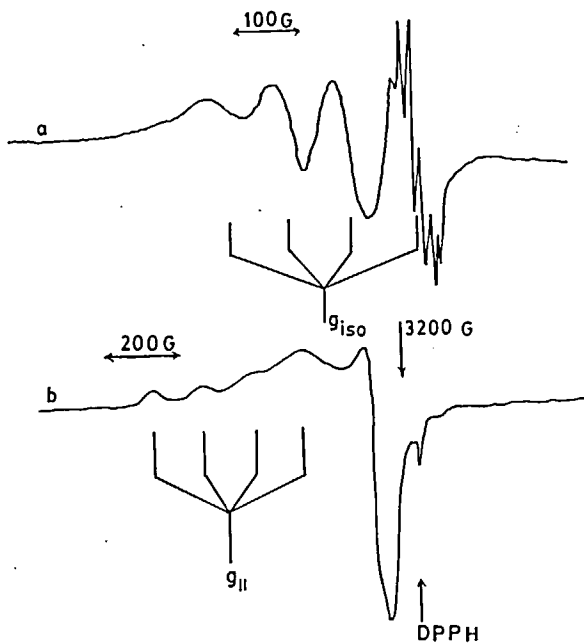


FIGURE 2 X-band EPR spectrum of Cu(NNEBNSKI) in CHCl₃, (a) at 300K; (b) at 77K.

TABLE IV
 EPR parameters for the copper complexes.

Compound	Solvent	g_{iso}	g_{\parallel}	g_{\perp}	$(63_{Cu}A\text{-tensor}) \times 10^4 \text{cm}^{-1}$			^{14}N	$E_{x^2-y^2}$
					A_{iso}	A_{\parallel}	A_{\perp}		
Cu(NHNSKI) ₂	Benzene	2.1280	2.3030	2.0406	79.5	198.6	27.52	12.52	16 130
Cu(NMeNSKI) ₂	Toluene	2.1112	2.2449	2.044	76.9	200.6	15.07	12.57	15 870
Cu(NEtNSKI) ₂	Toluene	2.1126	2.2209	2.0177	72.7	179.1	22.66	12.33	15 385
Cu(NNEBNSKI)	Chloroform	2.0844	2.3617	2.0580	89.2	147.0	19.22	13.24	15 870, 18 650
Cu(NHSALI) ₂ ^a	Crystal		2.2004	2.0450		185.0			16 300
Cu(NMeSALI) ₂ ^b	Chloroform/ toluene	2.1110	2.222			1820			16 700
Cu(NNBESALI) ^b	Dopped powder	2.110	2.190			208.0			18 000

^a Reference 20. ^b Reference 8.

 TABLE V
 MO coefficients for the copper complexes.

Complex	From anisotropic data		From isotropic data		From ligand hyperfine coupling	
	α	β	α	β	α	α'
Cu(NHNSKI) ₂	0.969	0.921	0.899	0.993	0.839	0.543
Cu(NMeNSKI) ₂	0.932	0.818	0.866	0.880	0.838	0.544
Cu(NEtNSKI) ₂	0.876	0.813	0.852	0.836	0.842	0.539
Cu(NNEBNSKI)	0.875		0.834		0.829	0.559
Cu(NHSALI) ₂ ^a	0.999		0.999			
Cu(NMeSALI) ₂ ^b	0.890	0.86				
Cu(NNEBSALI) ^b	0.910	0.80				

^a Reference 20. ^b Reference 8.

the expressions connecting EPR parameters with MO coefficients are taken from the literature.^{14,19} In this calculation, average values of 0.0845 and 0.275 are used for S and T(n). Molecular orbital coefficients were computed using both the anisotropic and isotropic data starting with the following equations.^{8,14,19}

$$\alpha_{\text{aniso}}^2 = 7/4[A_{\parallel}/P - A_{\text{iso}}/P + (2/5)g_{\parallel} - (5/21)g_{\perp} - 6/7]$$

$$\alpha_{\text{iso}}^2 = A_{\text{iso}}/PK - (g_{\text{iso}} - 2.0023)/K$$

Here, the free ion dipole term $P = 0.036 \text{ cm}^{-1}$ and the Fermi contact term $K = 0.43$; λ is the spin-orbit coupling constant for the free Cu^{2+} ion and is equal to -828 cm^{-1} . The computed MO coefficients are collected in Table V along with those of related compounds. Values of α (a measure of in-plane σ -bonding) and β (a measure of in-plane π -bonding) reveal that both in-plane σ -bonding and π -bonding increase in the order $\text{Et} > \text{Me} > \text{H}$. A similar trend is also noticed for in-plane σ -bonding of

salicylalimine complexes. Further, it is also seen that these complexes are more covalent than the salicylalimine complexes. Swett *et al.*⁸ have also noticed that Schiff bases of naphthaldehyde derivatives are more covalent than the corresponding benzaldehyde compounds. The α values derived from isotropic data show more covalency than those obtained from anisotropic data. In order to verify this we have also computed α' directly from the nitrogen hyperfine coupling using the following expression.²⁰

$$W = -(4\pi/9\gamma\beta_o\beta_N(\alpha')^2\delta(\gamma))$$

Values of α and α' (Table V) indicate more covalent metal-ligand bonding than the data obtained from copper hyperfine features. MO coefficients of Cu(NNEBNSKI) indicate that the *cis* tetradentate Schiff base is more covalent than the *trans* bidentate Schiff base. However, more weight can not be given to this observation since the coefficients are also derived with the assumption of a d_{xy} ground state and D_{2h} symmetry for the tetradentate Schiff base complex.

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