

SPEED programs (HP-5985 system). Results from both spectrometers were consistent. Mass spectral abundances for duplicate samples are based on an average of at least six independent measurements. Control experiments showed no scrambling of deuterium occurred before or after ionization of the insertion products.

All solvents were dried over sodium benzophenone ketyl. Absolute ethanol was used without further purification. Ethyl alcohol-*d* was obtained from Merck Isotopes. *tert*-Butyl alcohol-*d* was prepared by the reaction of D₂O with lithium *tert*-butoxide. *n*-Butyldimethylsilane-*d*₁ was prepared by the reduction of *n*-butyldimethylchlorosilane with lithium aluminum deuteride. The isotopic composition of the reagent alcohols and silane were determined by the weights of nondeuterated and isotopically pure (as determined by IR and mass spectroscopy) deuterated reagents added.

Competition Experiments. Photolysis of Dodecamethylcyclohexasilane with Ethyl Alcohol and Ethyl Alcohol-*d* in Ethyl Ether. A typical procedure is as follows. Dodecamethylcyclohexasilane⁷ (59 mg, 0.17 mmol), ethanol (142 mg, 3.09 mmol), and ethyl alcohol-*d* (160 mg, 3.33 mmol) were dissolved in 2.2 mL of dry ethyl ether and photolyzed for 90 min. Products were ethoxydimethylsilane and ethoxydimethylsilane-*d*₃. No tetramethylsiloxane, from the insertion of dimethylsilylene into water, could be detected.³

Photolysis of Dodecamethylcyclohexasilane with *tert*-Butyl Alcohol and *tert*-Butyl Alcohol-*d* in Ethyl Ether. Dodecamethylcyclohexasilane (34 mg, 0.10 mmol), *tert*-butyl alcohol (61 mg, 0.82 mmol), and *tert*-butyl alcohol-*d* (65 mg, 0.86 mmol) were dissolved in 2.3 mL of dry ethyl ether and photolyzed for 90 min. Products were *tert*-butoxydimethylsilane and *tert*-butoxydimethylsilane-*d*₃.

Photolysis of Octamethyl-2,3-diphenyltetrasilane with *tert*-Butyl Alcohol and *tert*-Butyl Alcohol-*d* in Ethyl Ether. Octamethyl-2,3-diphenyltetrasilane⁸ (90 mg, 0.23 mmol), *tert*-butyl alcohol (153 mg, 2.07 mmol), and *tert*-butyl alcohol-*d* (82 mg, 1.10 mmol) were dissolved in 2.2 mL of dry ethyl ether and photolyzed for 90 min. Products were *tert*-butoxymethylphenylsilane, *tert*-butoxymethylphenylsilane-*d*₃, and hexamethyldisilane.

Photolysis of Dodecamethylcyclohexasilane with *n*-Butyldimethylsilane and *n*-Butyldimethylsilane-*d* in Ethyl Ether. Dodecamethylcyclohexasilane (51 mg, 0.15 mmol), *n*-butyldimethylsilane (110 mg, 0.94 mmol), and *n*-butyldimethylsilane-*d* (37 mg, 0.32 mmol) were dissolved in 2.2 mL of dry ethyl ether. Products were *n*-butyltetramethyldisilane and *n*-butyltetramethyldisilane-*d*₃.

Control Experiments. Control experiments were run the same as competition experiments except only a deuterated trap was used.

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Registry No. Dodecamethylcyclohexasilane, 4098-30-0; octamethyl-2,3-diphenyltetrasilane, 40907-20-8; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; *n*-butyldimethylsilane, 1001-52-1; D₂, 7782-39-0.

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Single-Crystal EPR and Optical Spectra of and INDO-MO Calculations on Planar Cu(NCS)₄²⁻

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The halocuprates¹ have often been used to test the application of bonding models of transition-metal complexes since they are found to exhibit a wide variety of stereochemistries. Such studies on chlorocuprates have been already reported in the literature.¹⁻¹³ Several molecular orbital (MO) calculations

Table I. Experimental and Calculated Spin Hamiltonian Parameters^a for the Cu(NCS)₄²⁻ Ion

	exptl values				INDO-MO based calcd values	
	powder		single crystal		planar	tetragonal
	RT	LNT	RT	LNT		
<i>g</i>	2.275	2.279	2.272	2.274	2.190	2.255
<i>g</i> _⊥	2.053	2.053	2.056	2.056	2.036	2.048
<i>A</i>	173 ± 2	174 ± 2	171 ± 2	171 ± 2	-169.5	-175.2
<i>A</i> _⊥			54 ± 3	54 ± 3	-63.9	-60.0

^a Hyperfine values in 10⁻⁴ cm⁻¹.

have also been carried out on this ion.¹⁴⁻¹⁶ Several pseudohalo complexes of transition ions, particularly those of nickel and copper, follow in general the properties of the chlorocuprates such as changes in stereochemistry, and they have been studied in detail by Forster and Goodgame.^{17,18} While larger cations seem to favor independent dissociated tetrahedral anion entities, smaller ones seem to allow the association of neighboring anions, resulting in a tetragonal symmetry around each metal atom. Of these, in CuHg(SCN)₄, the Cu²⁺ is in a tetragonal ligand field and is surrounded by four nitrogens and two sulfur atoms. Similar environment has also been reported¹⁷ to be present for Cu²⁺ in [(C₂H₅)₄N]₂Cu(NCS)₄. The present study confirms the above predictions and suggests a fairly square-planar ligand field around the cupric ion. We report here the single-crystal EPR and optical spectral properties of this complex which contains planar Cu(NCS)₄²⁻ groups possibly linked by axial bonds to sulfurs of the nearby molecule to produce a centrosymmetric distorted octahedral coordination geometry.

Experimental Section

The complex tetraethylammonium tetrakis(isothiocyanato)cuprate(II) was prepared by the method of Forster and Goodgame.¹⁷ It belongs to the orthorhombic space group *Pbca* and crystallizes as pale green plates with well-developed (100) planes when grown from a solution of nitromethane-ether maintained at a temperature of 0-5 °C. The optical spectra at room temperature (RT) and liquid-nitrogen temperature (LNT) were measured in a Carl-Zeiss DMR-21 instrument using a single-crystal mount on a cold finger. Our attempts to measure the direction of polarization failed since the unique axis of all the molecules in the unit cell was found to be along the *a*-axis direction which happens to grow too thin to permit the use of the polarized radiation. However, the EPR measurements were done in three orthogonal planes including the well-developed (100) planes by using a Varian E-4 spectrometer with a 100-kHz modulation. DPPH (*g* = 2.0036) was used to calibrate the *g* value.

Results and Discussion

When the magnetic field was in the (100) plane, the EPR

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Table II. Spectral Transition Energies^a in $[(C_2H_5)_4N]_2Cu(NCS)_4$ ^b and Planar Tetrahalocuprate(II)^c

transition	$Cu(NCS)_4^{2-}$					
	CuCl ₄ ²⁻ , exptl, single crystal	exptl, powder in Nujol mull	exptl, single crystal		INDO-MO calcd	
			RT	LNT	planar	tetragonal
$d_{xz} \rightarrow d_{x^2-y^2}$	14.15		16.26	16.67	16.67	20.78
$d_{yz} \rightarrow d_{x^2-y^2}$	14.40	16.4				
$d_{xy} \rightarrow d_{x^2-y^2}$	12.50			12.66	12.43	11.61
$d_{z^2} \rightarrow d_{x^2-y^2}$	8.30	16.4	16.26	16.67		
charge-transfer bands		23.81	25.00	23.53		
				26.45		

^a All energies in 10^3 cm^{-1} . ^b This work. ^c References 12 and 13.

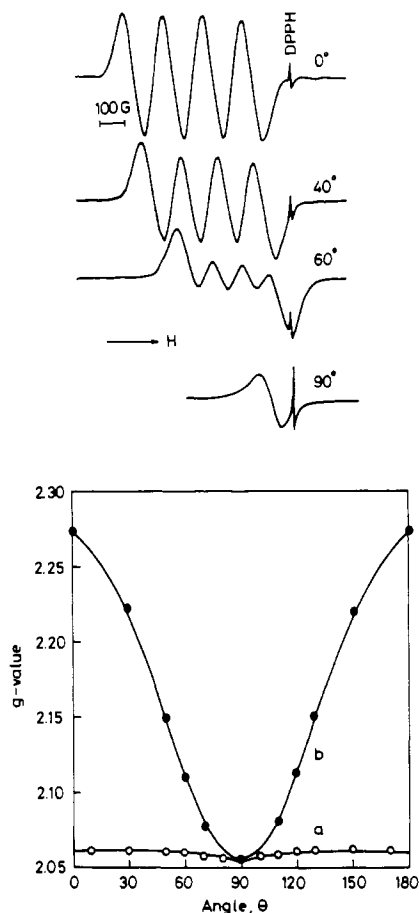


Figure 1. Top: Typical X-band EPR spectra of $[(C_2H_5)_4N]_2Cu(NCS)_4$ crystals in the (010) and (001) planes. The top four-line spectrum corresponds to $H \parallel a$ axis (tetragonal axis of the molecule) and the bottom one-line spectrum to $H \parallel b$ axis or c axis (in the equatorial plane of the molecule). Bottom: Angular-variation plot for the g values in the (100) plane (a) and in the (001) and (010) planes (b).

spectrum gave a single absorption at $g = 2.056$ irrespective of the orientation. However, in both the magnetic planes (010) and (001), we observed an EPR spectrum composed of four well-separated lines (when H was parallel to the a axis) that slowly merged into a single line at $g = 2.056$ (when H was parallel to the b or c axis). The typical experimental EPR spectrum and the g -value variations are shown in Figure 1 (a, b). This definitely indicates that all $Cu(NCS)_4^{2-}$ groups are stacked along the a axis and the $Cu(NCS)_4^{2-}$ chromophore is essentially planar. In the absence of the crystal structure, one can also propose the possibility of weak axial coordination of these complex ions with the sulfur atoms of the nearest two other complex ions. In fact, on the basis of infrared spectroscopic evidence, Forster and Goodgame¹⁷ have already proposed such a tetragonal ligand field for Cu^{2+} in this salt because of association of the complex ions. Moreover, in

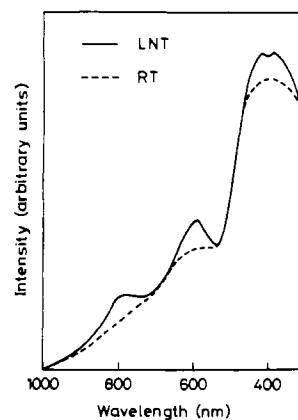


Figure 2. Electronic spectra of a single crystal of $[(C_2H_5)_4N]_2Cu(NCS)_4$ with light incident on the (100) plane at two different temperatures.

solutions such an association is lost without a change in coordinating atoms of the $Cu(NCS)_4^{2-}$ ion which becomes tetrahedral. Here the coordination is via the nitrogen atom as proved by the solution EPR spectrum revealing the presence of nitrogen hyperfine lines, though poorly resolved. All EPR results are given in Table I. Though the hyperfine value $A_{\perp}(^{63,65}Cu)$ was not directly measurable, it was easily obtained by correlating the $A_{\parallel}(^{63,65}Cu)$ and $A_{\perp}(^{63,65}Cu)$ at other orientations by using the equation $g_{\parallel}^2 A_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 A_{\perp}^2 \sin^2 \theta = A^2 g^2$. The high magnitude of A_{\parallel} is again a direct indication of the complex ion being essentially planar or being the most weakly coordinated at the axial positions since for distorted tetrahedral complexes the A_{\parallel} values are much lower. Also in crystals containing planar Cu_4^{2-} groups comparable g values had been observed.¹²

The presence of planar $Cu(NCS)_4^{2-}$ groups stacked along the a axis makes it easier to study the optical spectra with light incident on the (100) plane. But no useful band-polarization experiments could be performed since such an experiment could be of use only if the light is incident on the (010) or (001) plane. Unfortunately the crystals grow as thin flakes along the a axis. The optical spectra measured at RT and LNT indicate that the crystals are thermochromic. The RT spectrum indicates a broad shoulder at 16260 cm^{-1} and a highly broadened band in the region of 25000 cm^{-1} . But the LNT spectrum clearly reveals two peaks at 12660 and 16670 cm^{-1} , the latter being a slightly hyperchromic-shifted shoulder found at room temperature. Moreover, the high-energy band splits into two bands at 23530 and 26450 cm^{-1} . The spectra are shown in Figure 2 and the spectral values given in Table II.

It is of interest to compare the low-temperature optical spectra of $Cu(NCS)_4^{2-}$ ion with those of the other planar halide $CuCl_4^{2-}$. In analogy with the results of Hitchman and Cassidy,^{12,13} it is possible to immediately assign the transition at 12660 cm^{-1} to the ${}^2B_{1g} \rightarrow {}^2B_{2g} (xy \rightarrow x^2 - y^2)$ transition while this transition occurs at 12500 cm^{-1} for $CuCl_4^{2-}$ ion. Similarly

the band at $16\,670\text{ cm}^{-1}$ can be assigned either to both the transitions ${}^2B_{1g} \rightarrow {}^2E_g$ ($xz, yz \rightarrow x^2 - y^2$) and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ($z^2 \rightarrow x^2 - y^2$) or only to ${}^2B_{1g} \rightarrow {}^2E_g$ ($xz, yz \rightarrow x^2 - y^2$). The first suggestion is very possible since in CuCl_4^{2-} the bands do occur respectively at $\sim 14\,300$ and 8300 cm^{-1} . Higher energies for all these transitions are an indication of stronger ligand field provided by the isothiocyanate ligand. The other higher energy bands must be of charge-transfer origin.

We have further proof of this possibility through our INDO-MO calculation on this complex. The unrestricted Hartree-Fock scheme of the Roothan LCAO type at the INDO level of approximation has been used along with the parameterization scheme of Clack et al.¹⁹ Other details on this nature of calculation are found elsewhere.²⁰ The two molecular species—planar $[\text{Cu}(\text{NCS})_4]^{2-}$ and tetragonally elongated $[\text{Cu}(\text{NCS})_4(\text{SCN})_2]^{4-}$ —were both studied to find out the effect of distant and bridging SCN groups on both the optical and EPR properties. Though no crystal structure is available on $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$, the bond distances²¹ of $\text{CuHg}(\text{SCN})_4$ were used in view of the high similarity of the optical absorption spectra of both complexes at least at room temperature. The calculations reveal the ground-state ${}^2B_{1g}$ for the complex ion with the one-electron molecular orbital ordering as $z^2 < xz, yz < xy < x^2 - y^2$ for both the species. The calculations were also performed for the excited states ${}^2B_{2g}$, 2E_g , and ${}^2A_{1g}$. The calculated values found in Table II agree very well with the experimental ones. However, the calculated energy for ${}^2A_{1g}$ was found to be unreasonably large and hence not reported here. At least the first two transitions ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ which are needed for the interpretation of EPR results have been found to be in excellent agreement, especially for the planar species.

So that the observed spin Hamiltonian parameters could be compared with the calculated ones, equations for g_{\parallel} , g_{\perp} , A_{\parallel} , and A_{\perp} were derived by employing the complete set of MO coefficients including those of ligands as obtained from the INDO-MO results. Calculated transition energies, a spin-orbit coupling constant (λ_{Cu}) of 817 cm^{-1} , a value of 0.34 for the Fermi contact term, β , a value of $402 \times 10^{-4}\text{ cm}^{-1}$ for P_{Cu} ($=g_{\parallel}\beta_{\text{N}}g_{\text{e}}\beta_{\text{e}}(r^{-3})$), and all overlap values were also employed. Appropriate spin-orbit coupling constants for the ligand atoms²² were also introduced. The calculated values given in Table I are in very good agreement with the experimental parameters of the planar complex except for g_{\parallel} . The agreement is even better in the case of the assumed tetragonal complex. The metal coefficients associated with the molecular orbitals b_{1g} , e_g , and b_{2g} are respectively 0.734, 0.969, and 0.953 for the planar complex and 0.756, 0.936, and 0.931 for the tetragonal symmetry as obtained from the INDO-MO calculations. All this tends to prove that the $\text{Cu}(\text{NCS})_4^{2-}$ group is essentially planar with the possibility of weak coordination of the neighboring groups. Particular mention may be made of the observation from both theory and experiment that the four pseudohalide ligands are located in a square-planar fashion in this solid rather than its tetrahedral form. It is hoped that this may be borne out by the crystal structural investigation under progress. Yet another interesting observation pertains to the tetraethylammonium tetrakis(isothiocyanato)cuprate(II), which exhibits magnetic parameters similar to that of the isothiocyanates.

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Coordination Modes of Histidine. Circular Dichroism Study of Copper(II) Complexes of the Schiff Bases Derived from (1R)-3-(Hydroxymethylene)camphor and Histidine Derivatives

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The presence of histidine has been established in a large number of enzyme active centers,¹ and the histidyl residue is probably the most important metal-binding site in biological systems.^{2,3} In addition, histidine appears to be involved in copper(II) transport in blood.⁴ The investigation of the coordination mode of histidine and histidyl residues in metal complexes is thus very important for the elucidation of structures and functions of histidine-containing biological systems. The results of X-ray crystal and spectral studies of several metal complexes containing histidine^{2,5} or histidyl residues⁶ have shown that each of the three potential coordination sites of the amino acid can be used for bonding to metal ions, depending upon the pH, the presence of other ligands, and the coordination geometry of the metal ion. However, correlations between spectral and structural data are complicated by the apparent tendency of the histidine residues to form complexes with mixed chelation modes in solution. We report here the chiroptical properties of copper(II) complexes of the Schiff bases formed between (1R)-3-(hydroxymethylene)camphor and histidine derivatives (I).^{7,8} In these complexes the contribution to the optical activity of glycine-like the histamine-like coordination modes of the histidine residues can be unambiguously established.

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 (7) Abbreviations: (1R)-3-(hydroxymethylene)camphor anion = hmc; L- or D-histidinate anion = L- or D-his; L- or D-histidine methyl ester = L- or D-hisOCH₃; phenylalaninate anion = phe; glycinate anion = gly; amino acid anion = aa; histamine = him; N⁷-methylhistamine = himNCH₃; pyridine = py; acetate ion = OAc.
 (8) The free ligands I and II undergo a tautomeric equilibrium in solution between the enamine and Schiff base forms. In the copper(II) complexes, however, the ligands are bound in the Schiff base form.¹⁰