Copper(I) and Copper(II) Complexes of Tripod Ligands, Tris(2-alkylthioethyl)amine

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A series of five-coordinate copper(II) complexes with tripod ligands, tris(2-alkylthioethyl)amines (NS_3–R, R=CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, and t-C_4H_9), [Cu(NS_3-R)L](ClO_4)$_n$, where L represents Cl^-, Br^-, I^-, NCS^-, im(imidazole), py(pyridine) and H_2O, $n=1$ or 2 were prepared and characterized. The electronic, infrared and ESR spectral data suggest that [Cu(NS_3-Me)im](ClO_4)$_2$ and [Cu(NS_3-Me)OH_2](ClO_4)$_2$ have a five-coordinate square pyramidal geometry, the other complexes having distorted trigonal bipyramidal or trigonal bipyramidal geometry. The copper(I) complexes with NS_3–Me, [Cu(NS_3-Me)]ClO_4 and [Cu(NS_3-Me)NCS] were also prepared and characterized.

The stereochemistry of various cobalt(II) and nickel-(II) complexes with tripod ligands, tris(2-alkylthioethyl)-amine (NS_3–R), has been extensively studied, the bulkiness of the terminal donor groups being found to exhibit a marked influence on the geometry of the complexes.[1,2] In general, tripod ligands (L) such as tris(2-aminoethyl)amine and tris(2-dimethylamino-ethyl)amine form penta-coordinated copper(II) com-plexes, [CuLX]$^+$ with additional monodentate anionic ligands (X) and the ligands (L) carrying bulky substit-uents bound to terminal donor atoms tend to form trigonal bipyramidal complexes.[3,4] For similar type ligands (NS_3–R) containing sulfur, however, only a little information is available on the stereochemistry of their copper(II) complexes, only the Cu(II) complex of tris(2-methylthioethyl)amine, [Cu(NS_3-Me)Br]Br being known to take a trigonal bipyramidal geometry.[1]

In the present work, copper(II and I) complexes with tripod ligands, NS_3–R (I) have been studied by varying the terminal alkyl groups R with additional monodentate ligands. The stereochemistry of the com-plexes is discussed in terms of IR, ESR, and electronic spectra. A study of this kind of copper complex containing sulfur would give useful information on the chemistry of so-called copper proteins which some-times exhibit unusual behavior as copper complex-es.[5–8]

$$\begin{array}{c} \diagup CH_2CH_2S\text{–}R \\ N\text{—}CH_2CH_2S\text{–}R \\ \diagdown CH_2CH_2S\text{–}R \end{array}$$

(I)
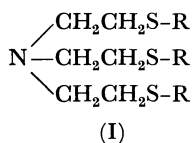
R=Me, Et, n-Pr, i-Pr, or t-Bu

Experimental

Ligands.   Tris(2-alkylthioethyl)amine (NS_3–R), where R refers to methyl, ethyl, n-propyl, isopropyl, and t-butyl, were prepared according to the procedure of Ciampolini et al.[1]

Complexes.   [Cu(NS_3-R)X]ClO_4 (R=Me, Et, n-Pr, i-Pr, and t-Bu; X=Cl^- and Br^-)   A methanol solution of copper-(II) halide (1 mmol) was mixed with NS_3–R (1 mmol) in methanol. To this mixture (20 cm^3) was added a methanol solution (20 cm^3) of sodium perchlorate (2 mmol). Green crystals were immediately precipitated. In the case of the bromo complexes of NS_3-i-Pr and NS_3-t-Bu, ether was added to the reaction mixture to promote crystallization.

[Cu(NS_3-R)NCS]ClO_4 (R=Me or Et). NH_4NCS (1 m-mol) in methanol (10 cm^3) was added to a methanol solution (20 cm^3) of Cu(ClO_4)$_2$·6H_2O (1 mmol) and NS_3–R (1 mmol). The complex soon precipitated as dark green crystals.

[Cu(NS_3-R)OH_2](ClO_4)$_2$ (R=Me or Et).   A metha-nol solution (20 cm^3) of NS_3–R (1 mmol) was mixed with Cu(ClO_4)$_2$·6H_2O (1 mmol) in methanol (20 cm^3). Addi-tion of ether gave green crystals.

[Cu(NS_3-Me)I]ClO_4.   A cold methanol solution (20 cm^3) of NaI (1 mmol) was added to an ice-cold solution of Cu(ClO_4)$_2$·6H_2O (1 mmol) and NS_3-Me (1 mmol) in metha-nol (20 cm^3) and the mixture was left to stand in a refrigerator overnight. The complex was obtained as a dark green powder.

[Cu(NS_3-R)Y](ClO_4)$_2$ [R=Me or Et; Y=Pyridine (py) or Imidazole (im)].   A methanol solution (20 cm^3) of NS_3–R (1 mmol) was mixed with Cu(ClO_4)$_2$·6H_2O (1 mmol) in methanol (20 cm^3). To the mixture was added 1 mmol of pyridine or imidazole in methanol (10 cm^3). Green (Y=py) or dark blue (Y=im) crystals were obtained upon cooling.

[Cu(NS_3-Me)]ClO_4.   [Cu(CH_3CN)$_4$]ClO_4 (1 mmol)[9] was added to a methanol solution (20 cm^3) of NS_3-Me (1 mmol) and the mixture was heated on a water bath for few minutes. A small amount of insoluble material was filtered off and the filtrate was cooled in a refrigerator. The com-plex was obtained as colorless crystals.

[Cu(NS_3-Me)NCS].   [Cu(NS_3-Me)]ClO_4 (1 mmol) was dissolved in warm methanol (30 cm^3). NH_4NCS (1 mmol) in methanol (10 cm^3) was added to the solution. Colorless crystals were immediately precipitated.

All complexes were air-dried at room temperature. The results of elemental analyses are given in Table 1.

Measurements.   Electronic spectra in solid state and in solution were obtained with a Hitachi EPS-3T recording spectrophotometer, and infrared spectra with a Hitachi 295 infrared spectrophotometer by means of a KBr disk. Elec-trolytic conductivities were measured with a Yokogawa·Hewlett-Packard 4261A LCR meter in approximately 10^{-3} mol/dm^3 N,N-dimethylformamide (DMF) solution at 25 °C. Molecular weights were determined in DMF at 53 °C with a Hitachi Osmometer Type-115, calibrated with benzil. The concentration of each sample was approximately 10^{-2} mol/dm^3, the results being reproducible in ±3%.

Results and Discussion

Pyridine or imidazole reacted with equimolar [Cu-(NS_3-R)OH_2]$^{2+}$ to form [Cu(NS_3-R)py]$^{2+}$ or [Cu-(NS_3-R)im]$^{2+}$. However, addition of pyridine or im-idazole in great excess resulted in displacement of

Table 1. Elemental analyses

Complex	Found(Calcd), %		
	C	H	N
[Cu(NS₃-Me)Cl]ClO₄	24.64 (24.69)	4.78 (4.83)	3.36 (3.20)
[Cu(NS₃-Me)Br]ClO₄	22.31 (22.41)	4.25 (4.39)	2.95 (2.90)
[Cu(NS₃-Me)I]ClO₄	20.31 (20.42)	3.98 (4.00)	2.67 (2.65)
[Cu(NS₃-Me)NCS]ClO₄	25.48 (26.08)	4.46 (4.60)	6.24 (6.08)
[Cu(NS₃-Me)OH₂](ClO₄)₂	20.63 (20.79)	4.46 (4.46)	2.67 (2.67)
[Cu(NS₃-Me)im](ClO₄)₂	25.03 (25.29)	4.37 (4.42)	7.00 (7.37)
[Cu(NS₃-Me)py](ClO₄)₂	28.76 (28.94)	4.35 (4.51)	4.77 (4.82)
[Cu(NS₃-Et)Cl]ClO₄·H₂O	28.96 (28.94)	5.49 (5.86)	2.80 (2.81)
[Cu(NS₃-Et)Br]ClO₄	27.34 (27.48)	5.11 (5.19)	2.66 (2.61)
[Cu(NS₃-Et)NCS]ClO₄	31.00 (31.07)	5.38 (5.41)	5.54 (5.57)
[Cu[NS₃-Et)OH₂](ClO₄)₂	25.49 (25.65)	5.15 (5.20)	2.43 (2.49)
[Cu(NS₃-Et)py](ClO₄)₂·H₂O	31.83 (31.85)	5.10 (5.35)	4.41 (4.37)
[Cu(NS₃-n-Pr)Cl]ClO₄	34.04 (34.51)	6.32 (6.37)	2.64 (2.68)
[Cu(NS₃-n-Pr)Br]ClO₄	31.57 (31.80)	5.90 (5.87)	2.51 (2.47)
[Cu(NS₃-i-Pr)Cl]ClO₄	34.46 (34.51)	6.47 (6.37)	2.71 (2.68)
[Cu(NS₃-i-Pr)Br]ClO₄	31.77 (31.80)	5.88 (5.87)	2.48 (2.47)
[Cu(NS₃-t-Bu)Cl]ClO₄	37.87 (38.32)	6.83 (6.97)	2.51 (2.48)
[Cu(NS₃-t-Bu)Br]ClO₄	35.26 (35.52)	6.55 (6.46)	2.38 (2.30)
[Cu(NS₃-Me)]ClO₄	26.88 (26.86)	5.25 (5.26)	3.58 (3.48)
[Cu(NS₃-Me)NCS]	33.03 (33.26)	5.77 (5.86)	7.77 (7.76)
[Cu(NS₃-Me)]I₃	15.74 (15.81)	3.06 (3.10)	2.08 (2.05)
H(NS₃-Me)[CuCl₃]	26.27 (26.34)	5.32 (5.40)	3.47 (3.41)
H(NS₃-Me)[CuBr₃]	19.84 (19.88)	4.07 (4.08)	2.54 (2.58)

Table 2. Powder ESR and reflectance spectral data of complexes

Group	Complex	g_1	$g_{\parallel}$	g_2	g_3	$g_{\perp}$	$\nu/10^3\ cm^{-1}$		
c	[Cu(NS₃-Me)Cl]ClO₄	2.037		2.096	2.129		11.56	15.04	27.55
d	[Cu(NS₃-Me)Br]ClO₄						11.43	15.15	24ˢ a)
d	[Cu(NS₃-Me)I]ClO₄						11.05	15.08	20ˢ a)
c	[Cu(NS₃-Me)NCS]ClO₄	2.015		2·109	2.162		12.99	16.15ˢ 22ˢ a)	
a	[Cu(NS₃-Me)OH₂](ClO₄)₂		2.130			2.086	12.69	24ˢ a)	
a	[Cu(NS₃-Me)im](ClO₄)₂		2.142			2.064	14.08	17.24ˢ	27.10
c	[Cu(NS₃-Me)py](ClO₄)₂	2.006		2.090	2.136		12.58	16.67ˢ	26.74
b	[Cu(NS₃-Et)Cl]ClO₄·H₂O		2.005			2.128	11.63	15.06	27.03
b	[Cu(NS₃-Et)Br]ClO₄		2.006			2.094	11.24	15.02	23ˢ a)
b	[Cu(NS₃-Et)OH₂](ClO₄)₂		2.034			2.133	11.72		26.95
b	[Cu(NS₃-Et)py](ClO₄)₂·H₂O		2.012			2.117	12.82	16.66ˢ	26.32
d	[Cu(NS₃-Et)NCS]ClO₄						12.42	15.15ˢ 22ˢ a)	
c	[Cu(NS₃-n-Pr)Cl]ClO₄	2.026		2.107	2.138		11.70	15.11	26.5—28.0
d	[Cu(NS₃-n-Pr)Br]ClO₄						11.11	14.95	23ˢ a)
b	[Cu(NS₃-i-Pr)Cl]ClO₄		2.012			2.117	11.63	15.08	26.5—28.0
c	[Cu(NS₃-i-Pr)Br]ClO₄	2.031		2.065	2.124		11.49	15.06	23ˢ
b	[Cu(NS₃-t-Bu)Cl]ClO₄		2.043			2.116	11.11	14.71	26.5—28.0
b	[Cu(NS₃-t-Bu)Br]ClO₄		2.036			2.092	10.70	14.43	23ˢ a)

s: Shoulder. a) No peak observed up to 29,000 cm⁻¹.

the ligand NS₃-R to form [Cu(py)₄]²⁺ or [Cu(im)₄]²⁺. A similar displacement was observed with various bidentate ligands such as ethylenediamine, 2,2′-bipyridine, and glycine. This tendency suggests that the thioether group in the NS₃-R ligands has poor affinity to a copper(II) ion.

The chloro, bromo, and aquo complexes were considerably stable in acidic solution. For example, [Cu(NS₃-Me)Cl]ClO₄ could be recrystallized from hot 6 mol dm⁻³ hydrochloric acid, though NS₃-Me was replaced by chloride anions to give [CuCl₃] [H(NS₃-Me)] in hot concd hydrochloric acid.

The coloration of NS₃-R complexes in solution gradually fades on standing, this being attributable to the reduction of Cu(II) to Cu(I). When a basic aqueous solution of [Cu(NS₃-Me)OH₂](ClO₄)₂ was heated for a few minutes, a small amount of a monovalent copper complex [Cu(NS₃-Me)]ClO₄ was ob-
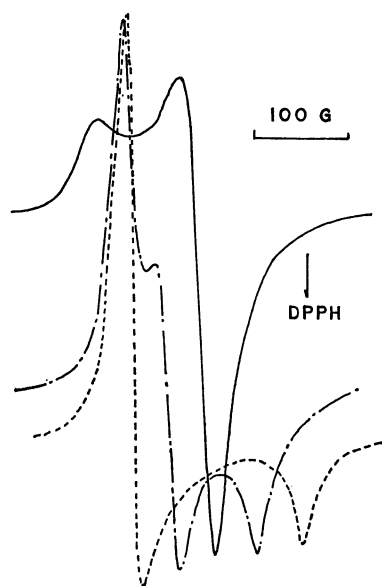
Fig. 1.   The powder ESR spectra of [Cu(NS₃-Me)im]-(ClO₄)₂   (——),   [Cu(NS₃-Me)Cl]ClO₄   (—·—),   and [Cu(NS₃-Et)Cl]ClO₄ (----).
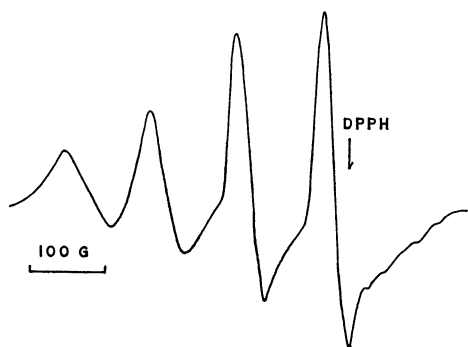
Fig. 2.   ESR spectrum of [Cu(NS₃-Et)Cl]ClO₄ in DMF at liquid nitrogen temperature.

tained as colorless crystals.

[Cu(NS₃-R)I]ClO₄ is extremely unstable, reddish brown [Cu(NS₃-Me)]I₃ being isolated from the aqueous solution. This is due to the reduction of the Cu(II) ion by the coordinated iodide ion.

The powder ESR data are summarized in Table 2. The powder technique provides only crystal g-values rather than molecular g-values, the results sometimes causing misinterpretation.[10-12] However, the technique was useful for a rough estimation of the electronic ground state of the copper(II) complexes we studied. The results are supported by the electronic spectra as well as by the frozen solution ESR spectra.

The complexes are classified into four groups (a—d) from their ESR patterns (Table 2). The representative spectra of each group are given in Fig. 1 except for that of (d). The group (a) complex, [Cu(NS₃-Me)im](ClO₄)₂ shows an axial spectrum with $g_\parallel >$ $g_\perp$, suggesting a $d_{x^2-y^2}$ electronic ground state.[12] Thus, a penta-coordinated square pyramid or a hexa-coordinated octahedron can be considered as a possible geometry. For the octahedron, coordination of one perchlorate anion is essential. However, the coordinated perchlorate anion was absent since no split-
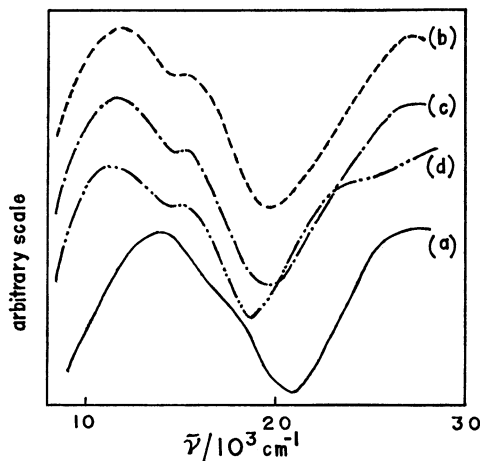

Fig. 3.   Reflectance spectra of [Cu(NS₃-Me)im](ClO₄)₂ (——), [Cu(NS₃-Me)Cl]ClO₄ (—·—), [Cu(NS₃-Me)-Br]ClO₄ (—··—), and [Cu(NS₃-Et)Cl]ClO₄ (----).

ting of the ν(Cl-O) was observed in the infrared spectrum.[13] It can be assumed that group (a) complexes should have the penta-coordinated square pyramidal geometry. Group (b) complexes show axial spectra with $g_\parallel < g_\perp$ and group (c) complexes rhombic ones in which one of the g-values is less than 2.04. It is reasonable to suppose that group (b) and (c) complexes have a d_{z^2} or $ad_{z^2}+bd_{x^2-y^2}$ (a≫b) ground state in trigonal bipyramidal or distorted trigonal bipyramidal geometry.[12] Group (d) complexes showed broad ESR spectra and could not be characterized.

The ESR spectra were also measured in DMF and nitromethane at room temperature and at liquid nitrogen temperature. Only three complexes, [Cu(NS₃-Me)Cl]ClO₄, [Cu(NS₃-Et)Cl]ClO₄, and [Cu(NS₃-t-Bu)Cl]ClO₄ exhibited relatively simple spectra at liquid nitrogen temperature.[14] The spectrum of [Cu(NS₃-Et)Cl]ClO₄ (Fig. 2) is a typical one for trigonal bipyramidal copper(II) complexes.[15-17]

Since the frozen solution spectra of these complexes were unresolved in high field region, $g_\parallel$-values were calculated using $<g>$ values $[<g>=(g_\parallel+2g_\perp)/3]$ from the room temperature spectra with $g_\perp$-values from the frozen solution spectra with the following results: $g_\parallel =2.015$, $g_\perp=2.122$ for [Cu(NS₃-Me)Cl]-ClO₄; $g_\parallel=2.023$, $g_\perp=2.120$ for [Cu(NS₃-Et)Cl]-ClO₄; $g_\parallel=2.023$, $g_\perp=2.128$ for [Cu(NS₃-t-Bu)Cl]-ClO₄. The $g_\parallel$-values suggest that the complexes have a geometry of trigonal bipyramid or distorted trigonal bipyramid in DMF as well as in solid state.

The reflectance spectral data are also given in Table 2. The complexes [Cu(NS₃-R)X]ClO₄ (X=Cl⁻, Br⁻, I⁻, and NCS⁻) belonging to group (b), (c), or (d) show an intense band at lower energy side and a less intense band at higher energy side (Fig. 3). These spectra are closely similar to those of trigonal bipyramidal complexes, [Cu(NS₃-Me)Br]Br[1] and [Cu-(Me₆-tren)Br]Br[18] where Me₆-tren represents tris(2-dimethylaminoethyl)amine. The energy shift of the d-d bands can be correlated with the position of the coordinated anion X in the spectrochemical series. The spectral similarity suggests that [Cu(NS₃-R)X]-

ClO_4 in groups (b), (c), and (d) have similar geometry, i.e., trigonal bipyramidal or distorted trigonal bipyramidal. Ciampolini et al.[1] assigned two bands at 11400 and 15200 cm^{-1} observed for [Cu(NS$_3$-Me)-Br]Br to the electronic transitions of $d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$, and d_{xz}, $d_{yz} \rightarrow d_{z^2}$, respectively. Their assignment seems to be valid for the present [Cu(NS$_3$-R)X]ClO$_4$ type complexes. It should be noted that these complexes have extremely high intensities ($\varepsilon = 700$—1000) of the d-d bands at the lower energy side as compared with that of [Cu(Me$_6$-tren)Br]Br ($\varepsilon = 450$).[18] It is probably due to the lower symmetry of the complexes. The molar extinction coefficients were reported to be 390 at 11400 cm^{-1} in nitromethane for [Cu(NS$_3$-Me)-Br]Br,[1] but ca. 900 for freshly prepared solution for [Cu(NS$_3$-Me)Br]ClO$_4$. This discrepancy is attributed to the instability of these complexes in solution. They exhibit some bands in the near ultraviolet and ultraviolet region (Table 2), and probably contain electronic transitions of X (σ and π) and S (σ and/or π) to Cu(II), since the free ligands showed no absorption in this region.

It should be noted that [Cu(NS$_3$-Me)im](ClO$_4$)$_2$ of group (a) has a d-d band maximum at 14080 cm^{-1} whereas [Cu(NS$_3$-Me)py](ClO$_4$)$_2$ of group (c) has one at 12580 cm^{-1}. Since imidazole and pyridine have similar ligand field strength, the large difference in the d-d transition energy should be attributed to the difference in their geometry. This is in line with the grouping by powder ESR spectra. The grouping of [Cu(NS$_3$-Me)OH$_2$](ClO$_4$)$_2$ to (a) and [Cu(NS$_3$-Et)OH$_2$](ClO$_4$)$_2$ to (b) is also supported by the electronic spectral data.

Although no principle controlling the stereochemistry of the tripod ligand copper(II) complexes could be found in the present investigation, the combination of the bulkiness of the terminal alkyl groups and the ligand field strength of the fifth monodentate ligands may have some influence on the geometry of the complexes.

Copper(I) Complexes. The copper(II) complexes undergo self reduction to the copper(I) complexes in solution. In fact, the copper(I) complexes isolated are very stable towards molecular oxygen even in solution. Although direct evidence for structure determination is lacking, it could be assumed from the steric requirement of the tripod ligands that [Cu(NS$_3$-Me)]ClO$_4$ is trigonal pyramidal and [Cu(NS$_3$-Me)-NCS] trigonal bipyramidal or square pyramidal.

The infrared spectrum of [Cu(NS$_3$-Me)NCS] showed the CN stretching vibration of NCS$^-$ at 2080 cm^{-1} which indicates the coordination of NCS$^-$ in the solid state.[19] On the other hand, the conductivity measurement in DMF reveals that the complex is an 1:1 electrolyte which could be formulated as [Cu(NS$_3$-Me)]NCS or [Cu$_2$(NS$_3$-Me)$_2$NCS]NCS. The molar conductance based on the former was 43 Ω^{-1} cm^2 mol^{-1}, being typical for an uni-univalent electrolyte.[20] Molecular weight determination[18] revealed that the van't Hoff factor i values are 1.3 for the former

and 2.6 for the latter. These values suggest that the complex is monomeric in DMF. The low conductance value based on the monomeric form seems to be attributable to the following equilibrium in DMF:

$$[Cu(NS_3\text{-}Me)NCS] \rightleftharpoons [Cu(NS_3\text{-}Me)]^+ + NCS^-$$
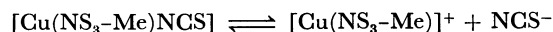
The conductivity of [Cu(NS$_3$-Me)]ClO$_4$ in DMF suggests that the complex can be formulated as [Cu$_n$(NS$_3$-Me)$_n$](ClO$_4$)$_n$ ($\Lambda = 79$ Ω^{-1} cm^2 mol^{-1} for $n=1$, $\Lambda = 158$ Ω^{-1} cm^2 mol^{-1} for $n=2$ etc.). The van't Hoff factor i values were $1.7 \times n$. It is probable that the complex is monomeric with the formula, [Cu(NS$_3$-Me)]ClO$_4$ in DMF.

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