mer di-μ-chloro-tetrakis(diethylamine)dicopper(I). In Table I are presented the X-ray diffraction powder lines of medium and strong intensity (estimated visually) of these three solids. It can be concluded from these data that the sample of composition $(C_2H_5)_2NH_2Cl \cdot CuCl \cdot 2(C_2H_5)_2NH$ is not a mixture of the other two solids; this supports its formulation as an anionic complex.

TABLE I

X-RAY DIFFRACTION POWDER PATTERN DATA[a]

$(C_2H_5)_2NH_2Cl \cdot CuCl \cdot 2(C_2H_5)_2NH$	$(C_2H_5)_2NH_2Cl$	$[CuCl \cdot 2(C_2H_5)_2NH]_2$
10.18 m		
8.80 m		
7.92 s		
		7.49 m
7.27 s	7.37 m	
	6.57 s	6.58 s
4.51 m		
4.14 w	4.07 m	
3.91 s		
		3.79 m, 3.75 m
3.64 m	3.68 s	
3.48 m		3.56 w
3.28 m	3.34 m	3.23 s
3.08 m	3.17 m	
2.98 w		2.98 m
2.80 w		2.70 m
2.58 w	2.62 w	2.48 s
2.31 w	2.26 w	2.33 m

[a] *d* spacings of strong (s) and medium (m) intensity lines of the three solids are shown; values with ±0.10 are placed on the same line for comparison, and any weak (w) lines within this range are included.

The nonvolatile liquid material of composition $(C_2H_5)_2NH_2Cl \cdot CuCl \cdot (C_2H_5)_2NH$ has the same composition as a mixture of 1 mole of diethylammonium chloride plus 0.25 mole of the tetrameric complex $[CuCl \cdot (C_2H_5)_2NH]_4$ and can be alternately prepared by mixing these solid components. Its saltlike formulation as $(C_2H_5)_2NH_2[CuCl_2 \cdot (C_2H_5)_2NH]$ with three-coordinate copper seems unusual and implies two types of diethylamine present, one protonated and the other coordinated to copper(I). The proton nmr spectrum of this viscous neat liquid shows very broad absorptions, without resolution of multiplets, at (ppm, relative to external tetramethylsilane): 1.53 (CH_3), 3.18 (CH_2), and 6.64 (NH), with integrated intensities of 12.2:8.1:3.0. These intensities are the unresolved sum of $(C_2H_5)_2NH_2^+$ and $(C_2H_5)_2NH \rightarrow Cu$. This spectrum may be compared with those of diethylamine (neat): 1.04 (3, CH_3), 2.57 (4, CH_2), 0.74 (NH); and of diethylammonium chloride (20% in ethanol): 1.20 (3, CH_3, overlap with solvent), 3.11 (4, CH_2), 5.69 (very broad, NH_2^+, overlap with solvent). The inability to demonstrate two structurally different diethylamine units might be attributed to rapid exchange and/or viscosity broadening.

These results with diethylamine contrast with those in the analogous triethylamine systems previously reported.[2] Copper(I) chloride forms only a 1:1 complex with triethylamine. Triethylammonium dichlorocuprate(I) is itself a liquid at room temperature and reacts with only 1 mole of triethylamine. As has been noted in previous studies of amine complexes,[2,4,9] the major practical effect of greater steric hindrance is in the limitation of the maximum coordination number shown by a metal ion to the amine ligand.

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[9] H. M. Hilliard and J. T. Yoke, *Inorg. Chem.*, **5**, 57 (1966).

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The Synthesis of a Molecular Metal Complex Containing Both M–N and M–S Bonded Thiocyanate Ions

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Although linkage isomerism of the type thiocyanato (M–SCN)–isothiocyanato (M–NCS) in metal complexes is now well known,[1-5] to the best of our knowledge no compound[5a] containing two or more coordinated thiocyanate ions shows mixed M–NCS and M–SCN bonding *in the same molecule*, with the exception of bridge compounds.[6] The complex [Cu(tren)(NCS)(SCN)][7] is perhaps such a compound.

Farago and James[8] have recently shown that the infrared spectra of Cu(II) and Ni(II) complexes in the C–N and C–S stretching regions can be used to differentiate between M–NCS and M–SCN bonding. The structure of $[Ni(en)_2(NCS)_2]$ shows the complex is almost octahedral and Ni–NCS bonded.[9] The corresponding copper(II) complex is unique in that it is sulfur bonded, whereas first-row transition metals are usually nitrogen bonded.[10] Yet in the tetragonal complex $[Cu(py)_2(NCS)_2]_n$ the thiocyanate coordinates

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(1) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).
(2) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).
(3) A. Sabatini and I. Bertini, *ibid.*, **4**, 1665 (1965).
(4) H. H. Schmidtke, *J. Am. Chem. Soc.*, **87**, 2522 (1965).
(5) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).
(5a) NOTE ADDED IN PROOF.—While this paper was in press, we learned of two other examples of this type. Bertini and Sabatini [*Inorg. Chem.*, **5**, 1025 (1966)] report the compound [Pd(4,4′-dimethylbipy)(NCS)(SCN)] and Nicpon and Meek have prepared the compound Pd[diphenyl(*o*-diphenylarsinophenyl)phosphine](NCS)(SCN) [*ibid.*, submitted for pubication.
(6) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1416 (1961).
(7) tren = $N(CH_2CH_2NH_2)_3$.
(8) M. E. Farago and J. M. James, *Inorg. Chem.*, **4**, 1706 (1965).
(9) B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **16**, 753 (1963).
(10) B. W. Brown and E. C. Lingafelter, *ibid.*, **17**, 254 (1964).

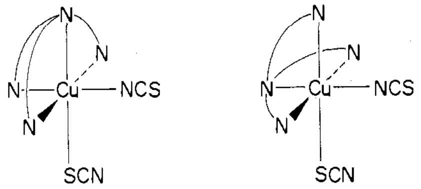

Figure 1.—The possible structures for [Cu(tren)(NCS)(SCN)].

through nitrogen in the plane, with axial coordination *via* a Cu---SCN–Cu bridge.[11] The axial Cu–S bond strengths must be very weak, because the bond distances found approach the estimated sum of the van der Waals radii.[10]

It thus appears that, for Cu(II) complexes, in the strongly coordinating equatorial position thiocyanate ion bonds through nitrogen, but in the elongated axial position it coordinates through sulfur. Therefore, such complexes which contain axial and equatorial thiocyanate ions as ligands may exhibit sulfur and nitrogen bonding, respectively. It was this postulate that prompted the synthesis and investigation of the compound described here.

In octahedral or tetragonal complexes the quadridentate ligand tren forces the remaining two ligands to occupy *cis* positions (Figure 1). If, in a tetragonal complex, three of the tren nitrogens coordinate in the equatorial plane, the remaining two coordination positions must be axial and equatorial. The infrared spectrum of [Cu(tren)(NCS)(SCN)] in a Nujol mull has two strong C–N stretching frequencies at 2094 and 2060 cm^{-1} and two medium-intensity spikes at 818 and 745 cm^{-1}. The 2094- and 818-cm^{-1} bands fall within the range for Cu–NCS bonding and 2060- and 745-cm^{-1} bands are within the Cu–SCN and SCN$^-$ range.[8] The infrared absorption spectra of this and some similar complexes are compared in Table I.

TABLE I

A COMPARISON OF THE INFRARED SPECTRUM IN THE C–N AND C–S STRETCHING REGIONS OF [Cu(tren)(NCS)(SCN)] WITH SOME OTHER THIOCYANATE COMPLEXES

Complex	ν_{C-N}	ν_{C-S}
[Cu(tren)(NCS)(SCN)]	2094 s	818 m
	2060 s	745 m
$[Cu(py)_2(NCS)_2]_n$[a]	2119 s	800 w
	2080 s	811 w
$[Cu(en)_2(SCN)_2]$[a]	2020 s	730 m
$[Ni(tren)(NCS)_2]$	2080	775 m
	2095	785 m

[a] From ref 8.

In dilute methanol solution [Cu(tren)(NCS)(SCN)] is a 1:1 electrolyte (10^{-3} *M*, $\Lambda = 95$) and $[Cu(en)_2(SCN)_2]$ is a 2:1 electrolyte (10^{-4} *M*, $\Lambda = 224$). These complexes were compared with $(n\text{-}C_4H_9)_4NBr$ (10^{-3} *M*, $\Lambda = 89$).[12] However, it seems unlikely that an ionic species such as [Cu(tren)(NCS)]SCN exists in the solid state, since [Cu(tren)(NCS)(SCN)] has the same space group and similar lattice parameters as $[Ni(tren)(NCS)_2]$, which has a distorted octahedral structure.[13] X-Ray precession photographs of [Cu(tren)(NCS)(SCN)] show orthorhombic symmetry and the extinctions: *h*00, *h* odd; 0*k*0, *k* odd; and 00*l*, *l* odd. This implies the space group $P2_12_12_1$. The theoretical density of 1.50 for four molecules in the unit cell compares well with the value of 1.51 ± 0.02 found by flotation. The unit-cell parameters are: $a = 11.16$, $b = 14.16$, $c = 9.11$ A. Those of $[Ni(tren)(NCS)_2]$ are: $a = 10.82$, $b = 14.72$, $c = 8.62$ A.[13]

The compound [Cu(tren)(NCS)(SCN)] was readily prepared[14] by dissolving 0.60 g (2.4 mmoles) of tren·3HCl and 0.34 g (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 10 ml of water. The solution was made neutral by the addition of *ca.* 0.7 ml of 10 *M* NaOH. A hot solution of 1.2 g (8 mmoles) of KSCN in 10 ml of water was added to the deep blue copper solution. This was then passed through a suction filter; the filtrate was evaporated to 10 ml on a steam bath and cooled very slowly to 5°. After 24 hr, large, deep blue crystals were collected on a suction filter, washed with ethanol, and air dried at room temperature; yield 0.5 g, mp 187° dec. *Anal.* Calcd for $CuC_8H_{18}N_6S_2$: C, 29.48; H, 5.56; N, 25.78; Cu, 19.49. Found: C, 29.90; H, 5.60; N, 26.19; Cu, 19.54.

The complex $[Cu(en)_2(SCN)_2]$ was prepared by the method of Brown and Lingafelter,[10] mp 141°. *Anal.* Calcd for $CuC_6H_{16}N_6S_2$: Cu, 21.19. Found: Cu, 21.35.

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(11) M. A. Porai-Koshits and G. N. Tischenco, *Soviet Phys. Cryst.*, **4**, 216 (1959).

(12) All conductivities were measured at 25°.

(13) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(14) P. Paoletti, private communication, had also previously prepared this compound in connection with some of his investigations on the heats of reaction of transition metal ions with polyamines.