adduct formed between hydrogen chloride and dimethylfluoramine is not known, but it is likely that ionization, at least in solution, to $[(CH_3)_2N(H)F]^+$ and Cl^- occurs.

Experimental Section

The Preparation of Dimethylfluoramine.—A solution of 1.24 g (10.0 mmoles) of dimethylsulfamide in 50 ml of water was placed into a cylindrical reactor tube (25-mm i.d.) equipped with a magnetic stirrer and a gas dispersion tube which was immersed as deeply as possible. The reactor was held at 30° by a water bath while fluorine diluted with 90 vol. % helium was introduced at a rate of 20 mmoles of fluorine/hr. The off-gas was passed through a series of traps which were maintained at −78, −126, and −196°. The contents of the −78 and −126° cold traps were removed after approximately 30 mmoles of fluorine had been passed through the reactor. The fluorination was then continued until an additional 30 mmoles of fluorine had been passed through the reactor. The contents of the −78 and −126° traps were combined with those from the first half of the fluorination, and the crude product was refractionated twice through traps held at −78, −126, and −196°. A product of 90–98% purity (0.21 g) was obtained in the −126° trap. Further purification could be achieved by reaction of the adduct formed with hydrogen chloride and trimethylamine N-oxide.

Anal. Calcd for C_2H_6NF: C, 38.1; H, 9.6; N, 22.2. Found: C, 37.9; H, 9.5; N, 21.9.

Preparation of $(CH_3)_2NF \cdot HCl$.—A 0.931-g (14.8 mmoles) sample of $(CH_3)_2NF$ was placed in a U tube on the vacuum line and cooled to −78°. Hydrogen chloride gas, 40.4 mmoles, contained in a 1-l. bulb was bled into the U tube at a rate such that the pressure did not exceed 50 mm, until no further takeup occurred. The mixture was warmed to −23° and the excess HCl was removed. A 24.9-mmole sample of HCl was recovered. Sublimation of the crude product at 25° yielded 1.43 g of white crystals which melted at 64–65° in a sealed tube.

Anal. Calcd for C_2H_7ClFN: C, 24.1; H, 7.1; N, 14.1. Found: C, 23.8; H, 7.1; N, 13.4.

Reaction of $(CH_3)_2NF \cdot HCl$ with Bases.—A 4.67-mmole sample of $(CH_3)_2NF \cdot HCl$ was sublimed into a reactor containing 1.0 g of $(CH_3)_3N \rightarrow O$ in 10 ml of sulfolane. As the mixture was warmed, slow gas evolution occurred above the melting point. After standing at 30° for 2 hr, the mixture was fractionated through −78 and −126° cold baths. A 2.59-mmole sample of pure $(CH_3)_2NF$ was obtained from the −126° cold trap.

Spectral Properties.—The F^{19} nmr spectra of $(CH_3)_2NF$ and $(CH_3)_2NF \cdot HCl$ were obtained in CCl_3F and C_2H_5OH solutions, respectively, at approximately 0° using a Varian Model 4310 A spectrometer operating at 40 Mc. The mass spectrum of $(CH_3)_2NF$ was obtained with a Consolidated Engineering Corp. Model 21-260 spectrometer operating with an ionization voltage of 100 v. The data below summarize the mass number, molecular ion assignment, and the relative abundance for $(CH_3)_2NF$: 63, $(CH_3)_2NF^+$, 26.0%; 62, $CH_3NFCH_2^+$, 40.3%; 43, $CH_3NCH_2^+$, 52.6%; 42, $(CH_2)_2N^+$, 100%; 41, $C_2H_3N^+$, 18.9%; 40, $C_2H_2N^+$, 14.3%; 39, C_2HN^+, 4.8%; 38, C_2N^+, 3.8%; 31, CF^+, 18.5%; 28, CH_2N^+, 33.4%; 27, CHN^+, 5.0%; 20, HF^+, 31.6%; 15, CH_3^+, NH^+, 79.8%; 14, CH_2^+, N^+, 11.8%; 13, CH^+, 4.6%.

Vapor Pressure of $(CH_3)_2NF$.—The vapor pressure of $(CH_3)_2NF$ was determined in an all-glass apparatus equipped with a Bourdon spoon gauge which was used as a null indicator. The values obtained (T(°K), P_{mm}) are: 249.1, 63.0; 253.0, 77; 255.9, 88.8; 257.3, 100.0; 260.2, 116.0; 262.3, 142.1; 268.0, 165.2; 273.2, 221.0. This gives a value of 22.8 for the Trouton constant and 6.9 kcal/mole for the heat of vaporization.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Neutral and Anionic Complexes of Copper(I) Chloride with Diethylamine[1]

BY JAMES R. CLIFTON AND JOHN T. YOKE III

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Reactions of copper(I) and copper(II) chlorides with triethylamine have been reported previously.[2] Reactions of copper(I) chloride with diethylamine and diethylammonium chloride have now been studied. The only examples of coordination of a copper(I) halide by a secondary aliphatic amine have been given by Peters,[3] who reported a series of dimethylamine complexes.

Experimental Section

Materials.—Copper(I) chloride and diethylamine were purified as described previously.[2,4] The amine hydrochloride, after recrystallization from 1-propanol and drying *in vacuo*, had mp 228° (lit. 228–229°).

Procedure.—All materials were handled in a dry nitrogen filled box or in a high vacuum line. Spectrovac stopcock grease was found to be preferable to other vacuum greases for work with diethylamine. Infrared spectra were obtained with a Beckman IR-8 spectrophotometer, and nmr spectra were obtained with a Varian A-60 spectrometer. X-Ray diffraction powder patterns were obtained using rotated thin-wall sealed glass capillary tubes and a Model A4969A General Electric Co. 14.32-cm diameter powder camera with copper Kα radiation.

The System Diethylamine–Copper(I) Chloride.—An excess of diethylamine was distilled onto a weighed sample of copper(I) chloride in a tube attached to the vacuum line, and diethylamine was then removed at 0° in the course of pressure–composition measurements on the system. The isotherm is shown in Figure 1. When amine had been removed until constant weight was achieved, the reaction tube was transferred to the drybox and opened, and the product was taken for analysis. *Anal.* Calcd for $CuCl \cdot (C_2H_5)_2NH$: mole ratio, 1.00; Cu, 36.9; Cl, 20.6; $(C_2H_5)_2NH$, 42.5. Found: mole ratio, 1.00; Cu, 36.7; Cl, 20.6; $(C_2H_5)_2NH$, 42.2.

Solution of Copper(I) Chloride in Diethylamine.—Copper(I) chloride dissolved slowly but appreciably in diethylamine. The solution showed no measurable conductance. When a piece of sodium was added, the rate of hydrogen evolution resembled that of the pure solvent and was much slower than that of a suspension of diethylammonium chloride in diethylamine. The molecular weight of the solute species was determined at 28.0° by solvent vapor pressure lowering measurements, using Raoult's law. A value of 390 ± 20 was obtained; the formula weight of copper(I) chloride is 99.0. The infrared spectrum of a 4.5 wt % solution of copper(I) chloride in diethylamine was identical with that of the solvent. The solution showed a large thermal coefficient of solubility in the region of room temperature, giving a white crystalline product on cooling. This was separated by filtration under nitrogen in the drybox, washed with petroleum ether, dried briefly in a nitrogen stream, and analyzed. *Anal.* Calcd for $CuCl \cdot 2(C_2H_5)_2NH$: Cu, 26.0; Cl, 14.5; $(C_2H_5)_2NH$, 59.7. Found: Cu, 25.8; Cl, 14.9; $(C_2H_5)_2NH$, 60.3. The

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[1] Presented at the 21st Northwest Regional Meeting of the American Chemical Society, Vancouver, Canada, June 1966. Based on part of the work submitted by J. R. C. to the Graduate School, Oregon State University, in partial fulfillment of the requirements for the Ph.D. degree.

[2] J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963); J. F. Weiss, G. Tollin, and J. T. Yoke, *ibid.*, **3**, 1344 (1964).

[3] W. Peters, *Z. Anorg. Allgem. Chem.*, **89**, 191 (1914).

[4] W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

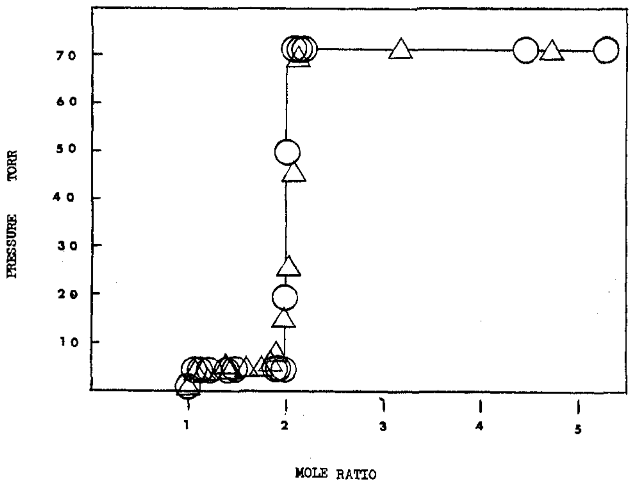


Figure 1.—0° isotherm: ○, mole ratio $(C_2H_5)_2NH/CuCl$; △, mole ratio $(C_2H_5)_2NH/(C_2H_5)_2NH_2[CuCl_2]$.

molecular weight of $CuCl \cdot 2(C_2H_5)_2NH$ (formula weight 245) was determined cryoscopically in nitrobenzene; a value of 481 was obtained.

The System Diethylammonium Chloride–Diethylamine.—The 0° pressure–composition isotherm of this system showed no interaction of the components. Diethylammonium chloride showed only slight solubility in diethylamine, and the mixture showed negligible conductance, in agreement with the previous report of Elsey.[5]

Reaction of Diethylammonium Chloride with Copper(I) Chloride.—A yellow solution of 1.00 g of diethylammonium chloride and 0.90 g of copper(I) chloride in 10 ml of ethanol, plus 1 ml of concentrated hydrochloric acid, was cooled in an ice–salt bath and gave white crystals. These were washed three times with absolute ethanol and then with petroleum ether and dried at room temperature *in vacuo*. *Anal.* Calcd for $(C_2H_5)_2NH_2CuCl_2$: Cu, 30.5; Cl, 34.0. Found: Cu, 30.2; Cl, 33.9.

The System Diethylammonium Dichlorocuprate(I)–Diethylamine.—The 0° isothermal pressure–composition phase diagram for this system is shown in Figure 1. A sharp pressure drop at mole ratio 2.0 indicates reaction of 2 moles of diethylamine with 1 mole of diethylammonium dichlorocuprate(I) to give a white crystalline product; this material loses 1 mole of diethylamine at an equilibrium pressure of 5 mm to give a nonvolatile light brown liquid product containing 1 mole of diethylamine per mole of diethylammonium dichlorocuprate(I).

Reaction of the $CuCl \cdot (C_2H_5)_2NH$ Complex with Diethylammonium Chloride.—When equivalent amounts of these two white solids were ground together in a mortar in a nitrogen-filled drybox, the mixture quickly formed a light brown liquid identical in appearance with that described above.

Results and Discussion

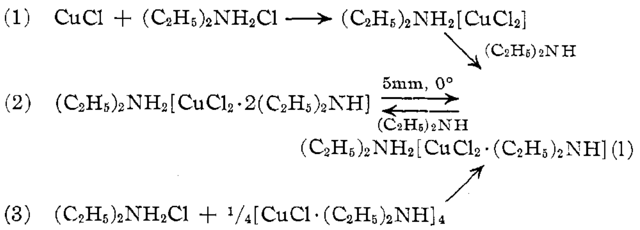
Studies of solutions of copper(I) chloride in diethylamine show a fourfold molecular weight for the solute and indicate the absence of aminolysis. The 0° phase diagram for the system indicates the existence of two complexes, $CuCl \cdot 2(C_2H_5)_2NH$ and $CuCl \cdot (C_2H_5)_2NH$. This behavior resembles that of copper(I) chloride–long chain primary amine systems previously studied by Wilkins and Burkin.[6] The complex $CuCl \cdot 2(C_2H_5)_2NH$ shows a twofold molecular weight in nitrobenzene and is to be formulated as the bridged dimer, di-μ-chloro-tetrakis(diethylamine)dicopper(I). It is converted to the more stable $CuCl \cdot (C_2H_5)_2NH$ complex either by loss of amine ligand at an equilibrium pressure of 4 mm at 0° or upon dissolution in liquid diethylamine. Since the molecular weight of the solute in such a solution corresponds to four times the value for copper(I) chloride, the solute species is presumed to be the tetrameric form of the 1:1 complex. Tetrameric 1:1 complexes were observed for primary amines with copper(I) halides by Wilkins and Burkin[6] and are well known for copper(I) halides with phosphines and arsines.[7]

The equilibrium dissociation pressure of the system in the region of existence of both complexes was measured at several temperatures, and the following results were obtained: 0°, 4 mm; 21.2°, 35.9 mm; 25.0°, 50.8 mm; 29.7°, 64.9 mm. From these results, using the Clausius–Clapeyron relation, the thermodynamic functions for the process

$$2[CuCl \cdot 2(C_2H_5)_2NH]_2(c) \longrightarrow 4(C_2H_5)_2NH(l) + [CuCl \cdot (C_2H_5)_2NH]_4(c)$$

at 25.0° were calculated to be: $\Delta F^\circ = +3.82$ kcal, $\Delta H^\circ = +31.4$ kcal, and $\Delta S^\circ = 92.4$ eu. In this calculation ΔH_{vap} of diethylamine was taken as 7.90 kcal/mole on the basis of its vapor pressure–temperature relation, our values being in good agreement with the literature.[8]

A variety of products is obtained in the copper(I) chloride–diethylammonium chloride–diethylamine system. The following reaction scheme accounts for the stoichiometry observed and for the properties of the compounds.



$$(1)\quad CuCl + (C_2H_5)_2NH_2Cl \longrightarrow (C_2H_5)_2NH_2[CuCl_2] \searrow^{(C_2H_5)_2NH}$$

$$(2)\quad (C_2H_5)_2NH_2[CuCl_2 \cdot 2(C_2H_5)_2NH] \underset{(C_2H_5)_2NH}{\overset{5mm,\ 0^\circ}{\rightleftharpoons}} (C_2H_5)_2NH_2[CuCl_2 \cdot (C_2H_5)_2NH](l)$$

$$(3)\quad (C_2H_5)_2NH_2Cl + {}^1/_4[CuCl \cdot (C_2H_5)_2NH]_4 \nearrow$$

The phase diagram in Figure 1 indicates the reaction of 2 moles of diethylamine with 1 mole of diethylammonium dichlorocuprate(I) to give a solid complex; this loses 1 mole of diethylamine at 5 mm to give a nonvolatile liquid. These products are formulated as diethylammonium dichlorocuprate(I) complexes containing additional diethylamine coordinated in the anion. A single line in Figure 1 suffices for both the diethylamine–copper(I) chloride system and the diethylamine–diethylammonium dichlorocuprate(I) system. It might be supposed that the two systems are the same, an extra mole of diethylammonium chloride playing a passive role in the latter case. The solid postulated to be $(C_2H_5)_2NH_2[CuCl_2 \cdot 2(C_2H_5)_2NH]$ could alternately be a mixture of 1 mole of diethylammonium chloride plus 0.5 mole of the bridged di-

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(5) H. M. Elsey, *J. Am. Chem. Soc.*, **42**, 2454 (1920).

(6) R. G. Wilkins and A. R. Burkin, *J. Chem. Soc.*, 127 (1950).

(7) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 864; F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).

(8) E. Pohland and W. Mehl, *Z. Physik. Chem.*, **164A**, 48 (1933); J. L. Copp and D. H. Everett, *Discussions Faraday Soc.*, **15**, 174 (1953).

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

BY KENNETH N. RAYMOND AND FRED BASOLO

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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).