

Coordination and Oxidation of Ethylamine and Diethylamine by Copper(II) Chloride¹

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Received August 7, 1967

Anhydrous copper(II) chloride binds 6, 5, 4, and 2 moles of ethylamine and 2 moles of diethylamine at 0°. Both the bis(amine) complexes have negligible dissociation pressures at room temperature. On heating, they dissociate at a temperature dependent on the volume of vapor space to give transient 1:1 complexes. These decompose by oxidation-reduction; ethyl groups are dehydrogenated and polymeric alkylammonium dichlorocuprate(I)-amine complexes are formed. These resemble the previously described simple dichlorocuprate(I) complexes.^{3,4} The course of these internal oxidation-reduction reactions differs from that of the analogous triethylamine complex.⁵ The dichlorobis(amine)copper(II) complexes have normal magnetic behavior; their epr spectra are presented. Their "d-d" transition shifts to higher energy in the sequence ammonia < ethylamine < diethylamine, but the triethylamine complex is not in order, its transition being at a lower energy than that of the ammonia complex.

Introduction

Triethylamine, in its dichlorobis(amine)copper(II) complex, is surprisingly easily oxidized. The first part of the internal oxidation-reduction reaction takes place at 0°, and the reaction is complete at room temperature.⁵ Oxidation-reduction reactions in copper-amine complex systems are of importance in polymerization catalysis and in biochemistry. It was of interest to study the analogous coordination and oxidation-reduction reactions of ethylamine and diethylamine with copper(II) chloride. No copper(II) chloride complexes of diethylamine have been reported; a number of poorly characterized ethylamine complexes have been claimed.⁶

Experimental Section

Materials and Procedure.—These have been described previously.³⁻⁵

Spectra.—A Beckman DK-2 spectrophotometer was used both for solution and for reflectance spectra in the range 4–50 kK. A pair of 1-cm near-infrared silica cells was used for solutions. For powders, magnesium oxide was the reflectance standard. Scotch Brand Magic Mending Tape was placed over both the magnesium oxide and the powdered sample. These were contained in circular depressions on aluminum plates, which were mounted vertically in the reflectance housing. The wavelength scale of the instrument was calibrated with a holmium oxide filter. Infrared spectra in the sodium chloride region were obtained by the Nujol mull technique for complexes, or with smears of oxidation-reduction residues, using a Beckman IR-8 spectrophotometer. A Beckman IR-11 spectrophotometer was used, with Nujol mulls placed between polyethylene disks, to obtain spectra in the 460–146-cm⁻¹ region. Electron paramagnetic resonance spectra were obtained by Professor Gordon Tollin at the University of Arizona, using a 100-kc modulation Varian V4501 spectrometer. The klystron frequency was determined to be 9.056×10^9 sec⁻¹ by observation of the Fieldial setting

(3229 gauss) for the center of the resonance of DPPH ($g = 2.0037$). The g values for the epr signals of powdered samples of the complexes were then determined from the equation $g = hv/\beta H$ by observation of the field strengths at which resonance occurred. As a test of the method, the epr signal of powdered copper(II) chloride dihydrate was redetermined. The line shape was in perfect agreement with that reported by Kneubühl,⁷ and the three anisotropic components of g agreed numerically to within 4 ppt with those observed in oriented single-crystal work.

Magnetic Susceptibilities.—The Gouy method was used. Measurements were normally made at a field strength of about 5 kgauss, using an Alpha AL7500 water-cooled magnet with 4-in. pole faces and a 1.5-in. air gap. The Gouy tube was calibrated at each temperature of study; the gram susceptibility of the calibrant, mercury(II) tetrathiocyanatocobaltate(II), was calculated using the data cited by Cotton, *et al.*⁸ Diamagnetic corrections were made using Pascal's constants⁹ for copper, chloride, and carbon and hydrogen of ethylamine. The value for nitrogen in primary amines and the susceptibility of diethylamine itself have been given by Francois and Hoarau.¹⁰ A temperature-independent paramagnetism for copper of 60×10^{-6} cgs emu was assumed.⁹

Vapor Phase Chromatography.—A Perkin-Elmer 154B Fractometer was used, with helium as the carrier gas. A mixture of authentic primary, secondary, and tertiary ethylamines was well separated using a 6 ft column of silicone oil SF-96 on Chromosorb W at 33°.

Analyses.—Copper was determined iodometrically and chloride gravimetrically. The amine content of the copper(II) complexes was determined by back titration with sodium hydroxide of a solution of the complex in an excess of standard hydrochloric acid.

Dichlorobis(triethylamine)copper(II).—This was prepared as described previously.⁵ Its reflectance spectrum, as measured with a Beckman DU spectrophotometer, was given in the previous report. The visible to near-infrared portion of the spectrum was redetermined using the DK-2 spectrophotometer, which has a much greater capability in this region, to permit direct comparison to the spectra of the other amine complexes. For this purpose, it was necessary to maintain the sample below the 0° decomposition temperature. It was mounted on a chilled aluminum plate in a nitrogen-filled drybox. Flasks of boiling nitrogen were placed inside the door of the spectrophotometer re-

(1) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. Abstracted from the Ph.D. Dissertation of J. R. C., Oregon State University, 1967.

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flectance housing, which was surrounded with a plastic glove bag and purged with dry nitrogen.

The System Copper(II) Chloride-Diethylamine.—When a sample of anhydrous copper(II) chloride was exposed to diethylamine vapor at room temperature, an exothermic reaction took place to give a red tar. A similar result was obtained when liquid diethylamine and copper(II) chloride powder were mixed at room temperature. When an excess of diethylamine was condensed on a known amount of copper(II) chloride in a vacuum line reaction tube immersed in a -22.9° cold bath, the components readily interacted to form a bulky purple material. The system was allowed to equilibrate at room temperature for 1 day. Then, at 0° , the diethylamine was removed in portions by distillation in the vacuum system in the course of isothermal pressure-composition measurements. The resulting phase diagram is shown in Figure 1. It indicates the formation of a single complex, with a negligible dissociation pressure, at 0° in this system. The reaction tube was opened to the vacuum line pumping system and brought to constant weight. It was then opened in a nitrogen-filled drybox, and a sample of the purple product was taken for analysis. *Anal.* Calcd for $\text{CuCl}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$: Cu, 22.6; Cl, 25.3; $(\text{C}_2\text{H}_5)_2\text{NH}$, 52.1. Found: Cu, 22.1; Cl, 25.3; $(\text{C}_2\text{H}_5)_2\text{NH}$, 51.7.

The System Copper(II) Chloride-Ethylamine.—Similarly, ethylamine was condensed at 0° on copper(II) chloride to give a bulky blue solid. Pressure-composition isotherms were obtained at 0, 25, and 50° and are shown in Figure 2. The formation of compounds containing 6, 5, 4, and 2 moles of ethylamine per mole of copper(II) chloride is indicated. No evidence was found for the existence in this temperature range of complexes containing 3 and 3.33 mmoles of amine per mole of copper(II) chloride, which were reported by Simon, *et al.*⁶ The reaction tube was brought to constant weight by pumping, and the aqua blue product was removed in a drybox. *Anal.* Calcd for $\text{CuCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$: Cu, 28.4; Cl, 31.5; $\text{C}_2\text{H}_5\text{NH}_2$, 40.1. Found: Cu, 28.8; Cl, 31.2; $\text{C}_2\text{H}_5\text{NH}_2$, 40.1. Samples of the darker blue 4:1 complex could also be obtained, by removing the excess of ethylamine from the reaction mixture until the point corresponding to mole ratio 4.00 in Figure 2 was just reached.

Solubilities of the Complexes.—Dichlorobis(diethylamine)copper(II) was decomposed by water, though it was stable in dry air at room temperature. Dissolution was accompanied by color changes in several solvents, as follows: slightly soluble in nitromethane (green); soluble in glyme (blue) and in dimethyl sulfoxide (yellow). Purple solutions were formed in dioxane, in tetrahydrofuran, and in the parent amine. The solubilities were not sufficient to permit molecular weight determination. However, solution spectra were obtained.

Dichlorotetrakis(ethylamine)copper(II) lost ethylamine on standing in air. Dichlorobis(ethylamine)copper(II) was stable in air, but decomposed by water. It was insoluble in benzene, ethanol, and the parent amine, very slightly soluble in dioxane (aqua), acetone (green), and nitrobenzene (light blue), and slightly soluble in dimethylformamide (green) and tetrahydrofuran (light blue). The solubilities were not adequate to permit molecular weight determination.

Conductivities.—These were determined with an Industrial Instruments RC16B2 bridge. A cell with dipping platinum electrodes and a cell constant of 0.100 cm^{-1} was used. Approximately $10^{-3} M$ solutions were used. In nitrobenzene, the molar conductances of the complexes were as follows: $\text{CuCl}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$, 3.50; $\text{CuCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$, 0.50; $\text{CuCl}_2 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$, 0.58; $(\text{C}_2\text{H}_5)_4\text{NI}$ (for comparison), $17.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$. In tetrahydrofuran, the molar conductances were as follows: $\text{CuCl}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$, 1.9×10^{-2} ; $\text{CuCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$, 3.5×10^{-2} ; $\text{CuCl}_2 \cdot 4\text{C}_2\text{H}_5\text{NH}_2$, 7.8×10^{-2} ; $(n\text{-C}_4\text{H}_9)_4\text{NI}$ (for comparison), $1.78 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$.

X-Ray Diffraction.—Powder patterns and d spacings were obtained as described previously.³ Intensities were estimated visually. The results are given in Table I.

Dichlorodiaminecopper(II).—It has been reported that two forms of this compound exist.¹¹ A so-called blue α form is said

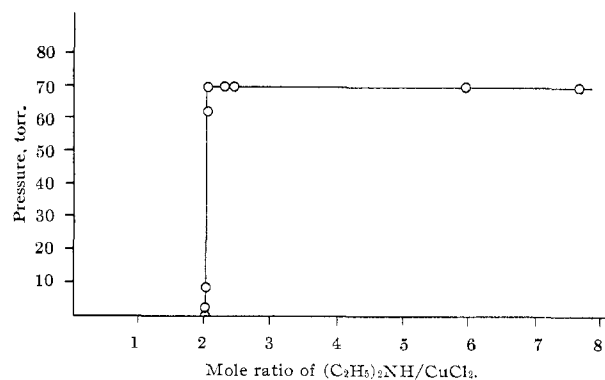


Figure 1.—System $(\text{C}_2\text{H}_5)_2\text{NH}-\text{CuCl}_2$; 0° isotherm.

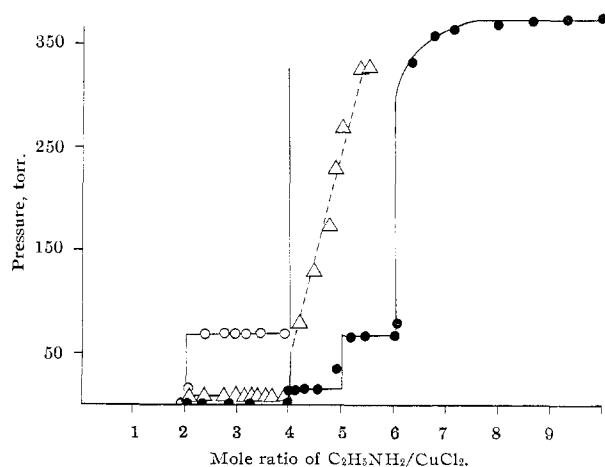
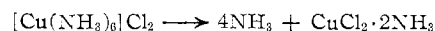


Figure 2.—System $\text{C}_2\text{H}_5\text{NH}_2-\text{CuCl}_2$: ●, 0° isotherm; △, 25° isotherm; ○, 50° isotherm.

to be formed by nucleophilic displacement of two chloride ions by two ammonia molecules from the tetrachlorocuprate(II) ion in acetone. A green β form is said to be formed by nucleophilic displacement of ammonia molecules by two chloride ions from the hexaamminecopper(II) ion in the course of the solid-vapor reaction



An X-ray structural study of two different forms of the bromide has been reported by Hanic,¹² and a discussion of these results in relation to the common structural coordination chemistry of copper(II) and the Jahn-Teller distortion has been given by Wells.¹³ Reported powder diffraction patterns¹¹ and electronic reflectance and infrared spectra¹⁴ of the supposed two forms of the chloride, in contrast to the bromide, showed very little difference. No analytical data from samples of the chloride prepared in the two different ways have been reported.

Attempts to prepare the α form by following the directions of Gazo, *et al.*,¹¹ failed to give a pure material. A 0.100-mole quantity of liquid ammonia was allowed to vaporize and pass through a capillary under the surface of a stirred solution of 0.050 mole of copper(II) nitrate trihydrate and 0.30 mole of lithium chloride in 250 ml of acetone. The dark red color of the tetrachlorocuprate(II) ion was discharged and a green precipitate was formed. This turned light blue shortly before all of the ammonia had been added; the ammonia was totally absorbed. The product was filtered on a fritted-glass filtering tube attached to the reaction flask under dry nitrogen, washed with acetone, and

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(12) F. Hanic and I. A. Cakajdova, *Acta Chym.*, **11**, 610 (1958); F. Hanic, *ibid.*, **12**, 739 (1959).

(13) A. F. Wells, "Structural Inorganic Chemistry," 3rd. ed, Oxford University Press, London, 1962, pp 873, 874.

(14) R. J. H. Clark and C. S. Williams, *J. Chem. Soc., Sect. A*, 1425 (1966).

TABLE I

X-RAY DIFFRACTION POWDER DATA

$CuCl_2 \cdot 4C_2H_5NH_2$		$CuCl_2 \cdot 2C_2H_5NH_2$		$CuCl_2 \cdot 2(C_2H_5)_2NH$	
<i>d</i>	Intens ^a	<i>d</i>	Intens ^a	<i>d</i>	Intens ^a
8.31	s	5.92	w	7.30	m
5.68	w	5.28	s	6.51	b, s
3.86	s	4.16	s	4.81	m
3.37	w	3.82	vw	4.57	m
3.05	m	3.62	m	4.19	w
2.91	m	3.43	m	3.90	w
2.78	s	3.27	m	3.76	w
2.54	w	3.09	s	3.56	m
2.34	s	2.79	s	3.23	s
2.11	m	2.59	vw	2.92	m
1.91	m	2.27	m	2.70	w
1.80	w	2.25	w	2.55	w
1.75	w	2.17	vw	2.44	m
1.45	vw	2.07	m	2.36	vw
1.41	vw	1.98	vw	2.26	m
		1.89	w	2.15	w
		1.79	w	2.05	w
		1.68	vw	1.93	w
		1.59	vw	1.85	w
		1.52	w	1.79	w
				1.70	vw
				1.62	w
				1.56	vw

^a s, strong; m, medium; w, weak; vw, very weak; b, broad.

dried *in vacuo* at 57° over phosphorus(V) oxide. The analysis did not correspond to any pure material. Similar results were obtained when the chloride:copper ratio, the volume of solvent, and the drying temperature were varied in a number of runs.

The green so-called β form was prepared in pure form by pumping on hexaamminecopper(II) chloride in the high-vacuum system at room temperature until constant weight was achieved. Anal. Calcd for $CuCl_2 \cdot 2NH_3$: Cu, 37.7; Cl, 37.7; Cl, 42.1; NH_3 , 20.1. Found: Cu, 37.7; Cl, 41.6; NH_3 , 20.1.

Viscosity Measurements.—Viscosities of sets of dimethyl sulfoxide solutions of known concentrations of the oxidation-reduction products were measured at 30.0° by the flow rate method using Ostwald viscometers. Three different viscometers were used with each set of solutions. The flow times of pure solvent and of each solution were used to calculate the specific viscosity by the relation $\eta_{sp} = (t/t_0) - 1$.

Results

Spectra and Magnetism of the Copper(II) Complexes.

—The electronic reflectance spectra of the complexes are shown in Figure 3. The spectra of solutions in which there was no color change were similar. The data are summarized in Table II. Because of the breadth of the visible-near-infrared absorption, λ_{max} was difficult to specify and fairly large differences in λ_{max} between reflectance and solution spectra do not really correspond to a large shift in the center of gravity or change in shape of the absorption peak. The ultraviolet absorptions were shifted to higher energies in solution. Solution spectra in the visible region were obtained with $1-5 \times 10^{-3} M$ solutions, while ultraviolet spectra were obtained with $5-25 \times 10^{-5} M$ solutions. The infrared spectra of the complexes indicated the absence of aminolysis and resembled the spectra of the free amines, except for a shift of the N-H stretching absorptions to lower energies as follows: $C_2H_5NH_2$, 3367, 3289; $CuCl_2 \cdot 2C_2H_5NH_2$, 3226, 3154; $CuCl_2 \cdot 4C_2H_5NH_2$, 3367 and 3258, 3155; $(C_2H_5)_2NH$,

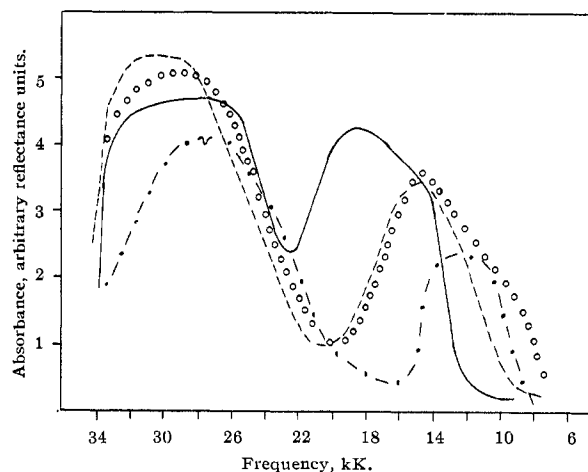


Figure 3.—Reflectance spectra: ———, $CuCl_2 \cdot 2(C_2H_5)_2NH$; - - - - , $CuCl_2 \cdot 2C_2H_5NH_2$; oooooo, $CuCl_2 \cdot 2NH_3$.

TABLE II

ELECTRONIC SPECTRA OF
DICHLOROBIS(AMINE)COPPER(II) COMPLEXES

Complex	λ_{max} , $m\mu$	Log ϵ	λ_{max} , $m\mu$	Log ϵ	Solvent
$CuCl_2 \cdot 2NH_3$	689 ^a	...	346	...	Reflectance
$CuCl_2 \cdot 2C_2H_5NH_2$	660	...	336	...	Reflectance
$CuCl_2 \cdot 2C_2H_5NH_2$	680	2.12	291	3.72	Tetrahydrofuran
$CuCl_2 \cdot 2C_2H_5NH_2$	720	2.17	290	3.72	Dimethylformamide
$CuCl_2 \cdot 4C_2H_5NH_2$	640	...	315	...	Reflectance
$CuCl_2 \cdot 4C_2H_5NH_2$	660	2.15	290	3.78	Tetrahydrofuran
$CuCl_2 \cdot 4C_2H_5NH_2$	720	2.24	284	3.67	Dimethylformamide
$CuCl_2 \cdot 2(C_2H_5)_2NH$	530	...	335	...	Reflectance
$CuCl_2 \cdot 2(C_2H_5)_2NH$	540	1.99	291	3.21	Tetrahydrofuran
$CuCl_2 \cdot 2(C_2H_5)_2NH$	570	2.06	290	3.82	Diethylamine
$CuCl_2 \cdot 2(C_2H_5)_2N$	771	...	360, 370 ^b	...	Reflectance

^a Reference 14 gives 680 $m\mu$. ^b Reference 5.

3280; $CuCl_2 \cdot 2(C_2H_5)_2NH$, 3226 cm^{-1} . The observed instability of the 4:1 complex of ethylamine with copper(II) chloride, the similarity of its electronic spectrum to that of the bis(amine) complex, and the observation of two peaks for the N-H asymmetric stretching frequency in its infrared spectrum all suggest that half of its amine content is bound less tightly than the other half and may occupy lattice positions rather than being specifically coordinated. Far-infrared spectral absorptions for the dichlorobis(amine)-copper(II) complexes were observed at 260 and 185 cm^{-1} with ammonia; 313, 263, 250 (sh), and 186 cm^{-1} with ethylamine; and 323, 295, and 200 cm^{-1} with diethylamine. Tentative assignments for complexes of this type have been suggested by Clark and Williams¹⁴ and by Goldstein, *et al.*¹⁵

The electronic paramagnetic resonance spectra of the bis complexes of ethylamine and diethylamine are given in Figure 4; that for the corresponding triethylamine complex has been reported previously.⁵ The anisotropic nature of the resonance signal is apparent. The powder spectra are interpreted by the method of Kneubühl.⁷ The components of g are given in Table III. The average value of g , $\langle g \rangle$, is given by $\langle g \rangle^2 = \frac{1}{3}(g_1^2 + g_2^2 + g_3^2)$ or $\frac{1}{3}(g_{||}^2 + 2g_{\perp}^2)$. It is used to

(15) M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *J. Inorg. Nucl. Chem.*, **21**, 105 (1965).

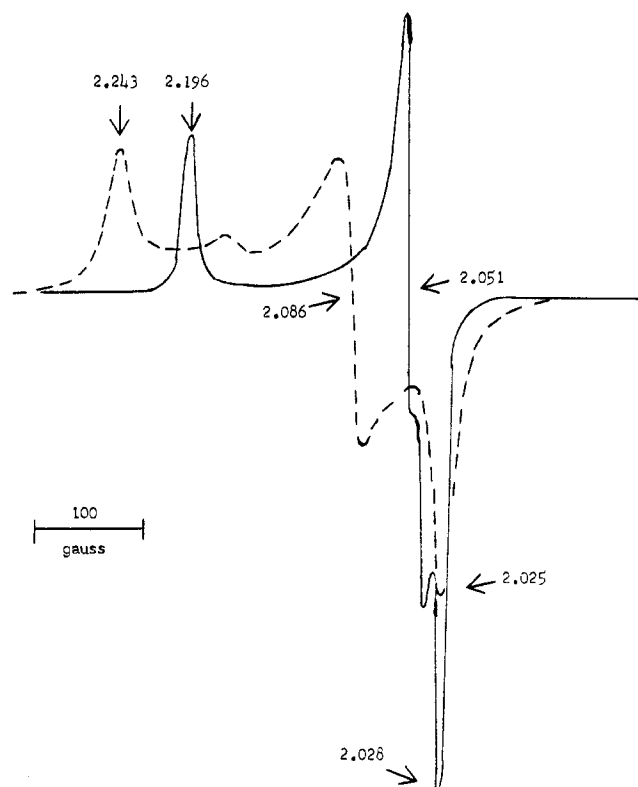


Figure 4.—Electron paramagnetic resonance spectra: ———, $\text{CuCl}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$; - - - -, $\text{CuCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$.

TABLE III
MAGNETIC PROPERTIES OF
DICHLOROBIS(AMINE)COPPER(II) COMPLEXES

Complex	g_1	g_2	g_3	$\langle g \rangle$	μ_{eff} , epr	Gouy	θ , °K
$\text{CuCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$	2.025	2.086	2.243	2.120	1.84	1.76	-6
$\text{CuCl}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$	2.028	2.051	2.196	2.093	1.81	1.83	-4
	g_{\perp}		g_{\parallel}				
$\text{CuCl}_2 \cdot 2(\text{C}_2\text{H}_5)_3\text{N}^a$	2.27		2.04	2.20	1.90

^a Data from ref 5, interpreted by the method of ref 7.

calculate the effective magnetic moment μ_{eff} (Bohr magnetons) by the equation $\mu_{\text{eff}} = \langle g \rangle [S(S + 1)]^{1/2}$, where $S = 1/2$ for d^9 copper(II). The values of μ_{eff} calculated from the epr data are in reasonable agreement with those calculated from bulk susceptibility measurements. The latter, determined at room, Dry Ice, and liquid nitrogen temperatures, are not of high precision but indicate approximate Curie-Weiss law behavior. The Weiss temperatures, θ , given in Table III are obtained from plots of $1/\chi_M^{\text{cor}}$ vs. absolute temperature and may not differ significantly from zero.

Thermal Behavior of the Dichlorobis(amine)copper(II) Complexes.—Dichlorobis(diethylamine)copper(II) decomposed sharply in a sealed melting point capillary tube at 134° to a red-brown tar. There was no change in appearance or paramagnetism of a sample in a small sealed Gouy tube over a 3-hr period in the temperature range 100 – 125° . Ultraviolet irradiation had no effect. However, after 9 min at 135° the sample became diamagnetic and appeared completely decomposed. Discoloration with tar formation and loss of paramagnetism were always found to occur simultaneously.

A sample was heated in an evacuated tube on the vacuum line, open only to a manometer. The total volume of this system was about 50 ml. A dissociation pressure of 4 torr developed at 100° . In the temperature range 100 – 120° , the dissociation pressures did not follow the Clausius-Clapeyron relation and at 120° changed rapidly with time. This was accompanied by discoloration and decomposition. Such decomposition was very rapid at 133° . The material in the vapor phase was found to be pure diethylamine by chromatography. When the reaction tube was cooled to 0° , the pressure dropped to 70 torr, the vapor pressure of diethylamine at this temperature. The pressure became negligible after 1 day, indicating complete reabsorption of the gas phase.

In a variation of the above experiment, the same system but also including a liquid nitrogen cooled trap was used. The reaction tube was heated at 140° to give rapid decomposition of the sample, with all evolved volatile material being condensed in the cold trap. The weight loss of the reaction tube corresponded, in duplicate runs, to loss of $52 \pm 1\%$ of the original amine content. In this case, the volatile material was found to be nearly all diethylamine, but to include also a trace of ethyl chloride. These reacted on being warmed to room temperature to give a deposit of triethylammonium chloride.

These results clearly indicated the dependence of the decomposition temperature on the volume of vapor space in the system and suggested that evolution of half of the coordinated amine occurred prior to oxidation-reduction. Attempts were therefore made to isolate the 1:1 complex, which would be the intermediate in the decomposition reaction, by pumping on the bis(amine) complex at a temperature lower than that required for oxidation-reduction. When this was done at 100° , discoloration and decomposition accompanied the removal of diethylamine. At 77° , in duplicate runs, $50.7 \pm 0.2\%$ of the original content of amine could be pumped off without appreciable change in the appearance of the sample. As soon as additional amine was removed, rapid discoloration and tar formation ensued.

When a sample of dichlorobis(diethylamine)copper(II) was stored in a vacuum desiccator for 6 months over sulfuric acid, it lost approximately half of its content of amine and became slightly decomposed as indicated by infrared spectral evidence of formation of alkylammonium species.

The thermal behavior of the primary amine complex, dichlorobis(ethylamine)copper(II), was in all ways analogous, except that somewhat higher decomposition temperatures were involved. In a sealed melting point capillary, or in a small Gouy tube, decomposition to a red-brown liquid accompanied by a complete loss of paramagnetism took place in the range 150 – 155° . There was no change in appearance or in paramagnetism on prolonged heating at 120° in a small sealed tube. When a sample was heated at 100° while open to the vacuum line pumping system, partial loss of

paramagnetism and discoloration were observed. When ethylamine was removed by pumping at 120° , little decomposition was observed until the amine:copper(II) chloride mole ratio dropped to 1:1, and then rapid decomposition ensued. A sample of dichlorobis(ethylamine)copper(II) was heated at 150° in an evacuated tube connected to a manometer. Decomposition with buildup of pressure was very rapid. The reaction tube was then cooled to 0° . The pressure became negligible within 1 day, indicating reabsorption of all of the volatile material. Another sample was heated at 150° in an evacuated tube connected to a liquid nitrogen cooled trap. The loss in weight of the reaction tube accompanying decomposition corresponded, in duplicate runs, to loss of $54.8 \pm 0.9\%$ of the original amine content. The condensed volatile materials consisted of ethylamine and a small trace of ammonia. Again apparent in these experiments were the dependence of the decomposition temperature on the vapor space available and the intermediate formation of a 1:1 complex.

Stoichiometry of the Oxidation-Reduction Reaction.

—During the thermal decomposition of both dichlorobis(ethylamine)copper(II) and dichlorobis(diethylamine)copper(II) in a closed system, amine was evolved which was later completely reabsorbed when the residues were cooled. The total volatile amine content of these resulting final reaction products was determined (a) in the case of diethylamine by distillation of the amine from a mixture of the sample with concentrated sodium hydroxide into an excess of standard hydrochloric acid and back titration and (b) in the case of ethylamine by heating the residue with ignited quicklime in a vacuum line trap followed by purification of the evolved ethylamine by trap to trap fractionation. The purified amine was then weighed. Of the original 2 moles of amine per mole of copper in the complexes, the part which could not be recovered in this way was taken as representing material oxidized to nonvolatile products. It was found that 0.39 ± 0.02 mole of diethylamine or 0.47 ± 0.02 mole of ethylamine was oxidized per mole of copper(II) reduced to copper(I).

Nature of the Reaction Products.—The infrared spectra of the red-brown tarry products corresponded to those of the protonated forms of the original amines. There was no evidence of free or protonated enamines. The product from dichlorobis(diethylamine)copper(II) showed absorptions at 2762–3030, 2457, and 1583–1600 cm^{-1} characteristic of an $R_2NH_2^+$ ion. The product from dichlorobis(ethylamine)copper(II) showed absorptions at 2470–3150 and 1583 cm^{-1} characteristic of the RNH_3^+ species.

Both tarry products were soluble in dimethyl sulfoxide and in hydrochloric acid and insoluble in water and in aqueous sodium hydroxide. Both neutral and alkaline hydrolysis liberated the starting amines. No other volatile component was obtained from the ethylamine product; slight traces of ethylamine and of acetaldehyde were detected by vapor phase chromatography in the diethylamine obtained on hydrolysis.

Some slight separation of a white precipitate of copper(I) chloride was observed on trituration of the residues with water. However, repeated steps of dissolving the materials in dimethyl sulfoxide, or in hydrochloric acid, and then causing separation from solution by addition of water, or of sodium hydroxide, failed to separate the organic and inorganic fractions effectively. Tan precipitates were obtained by this process. These were used in preparing dimethyl sulfoxide solutions for viscosity measurements. Extrapolation of plots of the specific viscosity/concentration quotient *vs.* concentration to infinite dilution gave the intrinsic viscosities. The intrinsic viscosity found with the diethylamine oxidation product was 0.106, while that of the ethylamine oxidation product was 0.081. The intrinsic viscosity of the triethylamine oxidation product from the decomposition of dichlorobis(triethylamine)copper(II), determined similarly by Weiss,¹⁶ was 0.122. Such values are characteristic of polymer systems.¹⁷

Reaction of the Oxidation-Reduction Products with the Parent Amines.—Both of the dichlorobis(amine)copper(II) complexes evolved close to half of their amine content on decomposition, and this amine was subsequently reabsorbed on standing for 1 day at 0° . The abilities of the final products so obtained to interact with additional amounts of the corresponding amines were studied. Excess amounts of the amines were added through the vacuum system to the reaction products, the systems were allowed to equilibrate, and amine was then removed in the course of pressure-composition measurements of the systems. The resulting isotherms are shown in Figure 5. In this figure, the mole ratio axis is given on an original amine:copper(II) basis. Thus, the bis(amine) complexes prior to decomposition would correspond to mole ratio 2.00, the immediate decomposition products after half the amine had been evolved would correspond to mole ratio 1.0, the reabsorption of this amine would correspond to a return to the point at mole ratio 2.0, and the interaction with the additional amine subsequently added would correspond to mole ratios greater than 2.0. The isotherms of Figure 5 show some curvature due to solubility phenomena involving the tarry products and deviate somewhat from integral stoichiometric ratios. They do indicate the general nature of the interactions; the decomposition product from dichlorobis(ethylamine)copper(II) reacts with 1 and 2 additional moles of ethylamine, and the decomposition product from dichlorobis(diethylamine)copper(II) reacts with 1 additional mole of diethylamine.

Discussion

The observations relating to the oxidation-reduction reactions may be most simply accounted for in

(16) J. F. Weiss, Ph.D. Dissertation, University of Arizona, 1964.

(17) For use in the relation $\eta_{intrinsic} = k(\text{mol wt})^a$, a value of 3.18×10^{-4} for k and a value of 0.85 for a were suggested as being appropriate approximations by Professor C. S. Marvel (private communication). The amine oxidation products would then have approximate molecular weights as follows: from triethylamine, 1×10^4 ; from diethylamine, 8×10^3 ; from ethylamine, 5×10^3 .

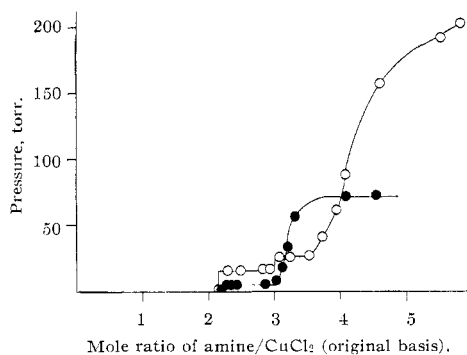
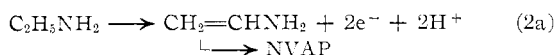
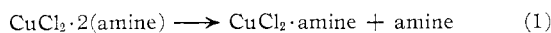
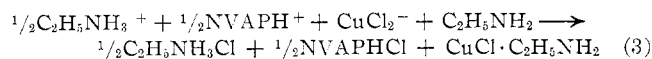
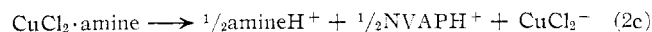
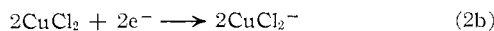
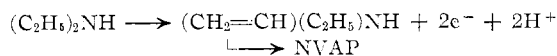


Figure 5.—System amine-CuCl₂·2(amine) oxidation-reduction product; 0° isotherms: ● (C₂H₅)₂NH; ○, C₂H₅NH₂.

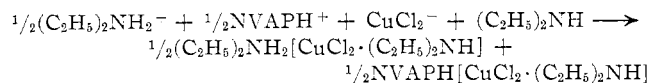
terms of the following postulates for the over-all course of the reactions



or

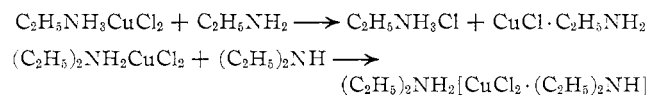


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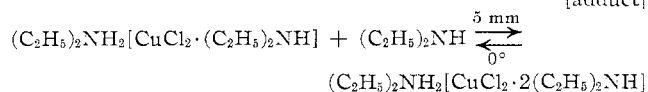
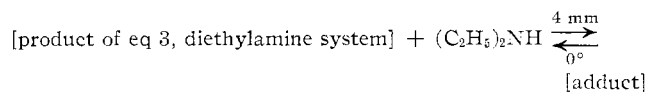
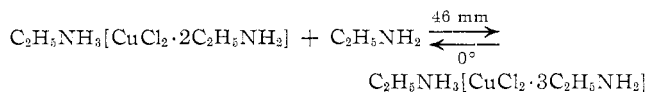
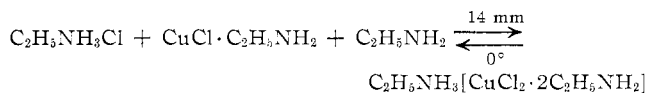
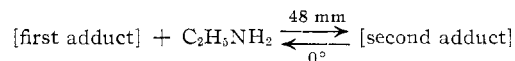
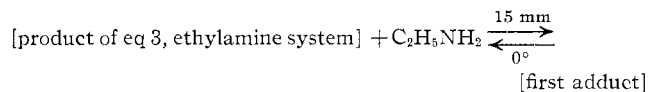


Equation 1, common to both the primary and secondary amine systems, indicates dissociation of the original bis(amine) complexes to intermediate 1:1 complexes prior to decomposition. Equation 2, also common to the primary and secondary amine systems, is an indication of stoichiometry rather than mechanism (*vide infra*). Equation 2a indicates the suggested half-reaction for a two-electron oxidation of an ethyl group to a vinyl group, with two protons being released. The enamines then polymerize to saturated nonvolatile amine polymers (NVAP), ethylamine giving polyvinylamine and diethylamine giving N-ethylpolyvinylamine. Equation 2b, the half-reaction for reduction, indicates conversion of copper(II) chloride to the dichlorocuprate(I) ion by a one-electron process. Equation 2c sums up these steps, indicating conversion of the 1:1 intermediate copper(II) complex to a mixture of alkylammonium dichlorocuprate(I) species, in which half the cation charge is due to the protonated form of the starting amine, and half is due to protonated nonvolatile polymeric amine. Equation 3 indicates the reabsorption of the amine evolved in step 1 by alkylammonium dichlorocuprate(I) products of step 2, to give final nonvolatile reaction products containing all of the material originally present in the starting bis(amine)copper(II) complexes. Equation 3 is written to show a different type of product in the ethylamine system than in the diethylamine system.

This is based on our prior observations that pure ethylammonium dichlorocuprate(I) reacts with 1 mole of ethylamine to give as the nonvolatile reaction product an equimolar mixture of ethylammonium chloride and the neutral 1:1 copper(I) complex,⁴ while pure diethylammonium dichlorocuprate(I) reacts with 1 mole of diethylamine to give as the nonvolatile reaction product an anionic complex.³ The reactions in the simple amine-pure dichlorocuprate(I) systems are



The above postulates are given strong support by a comparison of the reactions of the oxidation-reduction products with still additional amounts of the parent amines (as shown in Figure 5) with the previously described^{3,4} reactions in the simple pure alkylammonium dichlorocuprate(I)-amine systems. The final oxidation-reduction products shown in eq 3, corresponding to the mole ratio value 2.0 of Figure 5, resulted from the take-up by the alkylammonium dichlorocuprate(I) species of 1 mole of the corresponding amine. It is known that in the simple pure amine-dichlorocuprate(I) systems, a second mole of diethylamine or second and third moles of ethylamine are taken up to give anionic complexes. This is just the behavior shown in Figure 5 for the oxidation-reduction reaction products. The close correspondence of the equilibrium pressures in the systems also supports the postulates made for the course of the reaction. Thus, the following reactions may be written for the pressure-composition breaks of Figure 5 and compared to the analogous reactions in the simple amine-pure copper(I) systems^{3,4}



The reactions proposed above are idealizations, based on an oxidation-reduction stoichiometry of 0.5 mole of amine oxidized per mole of copper(II) reduced. The actual relation is 0.5 mole of ethyl groups oxidized per mole of copper(II) reduced. For ethylamine, which has one ethyl group, the experimental value is very close to this, *viz.*, 0.47 ± 0.02 mole of amine per mole of copper. With diethylamine, the second ethyl group

might also be oxidized in some cases, and a more serious deviation from the idealized stoichiometry occurs, the experimental value being 0.39 ± 0.02 mole of amine per mole of copper. Note that the pressure-composition breaks of Figure 5 also deviate from exact integral molar relationships. In part, this may be attributed to side reactions, since traces of by-products (ethyl chloride, and on hydrolysis ethylamine and acetaldehyde in the diethylamine oxidation, and ammonia in the ethylamine oxidation) were observed.

These reactions differ from those proposed⁶ for the internal oxidation-reduction of the analogous triethylamine complex. In that case, the oxidation occurred in discrete steps, first one ethyl group being oxidized to give a diamagnetic product containing diethylvinylamine, and then disproportionations occurring to give transient paramagnetic species and an eventual six-electron oxidation product. The latter corresponded to dehydrogenation of all three ethyl groups. The stoichiometry then approximated $1/6$ mole of amine oxidized per mole of copper(II) reduced. When more than one ethyl group per amine is converted to a vinyl group, more cross-linking in the resulting polymeric amine is to be expected. The observed sequence in the intrinsic viscosities and in the molecular weights derived from them¹⁷ is in accord with this reasoning.

The difficulty in separating the organic and inorganic portions of the oxidation-reduction product may be attributed to the strong coordinating tendencies of the polymeric amines. A copper complex of authentic polyvinylamine, stable in aqueous solution, has been described.¹⁸

The outstanding difference between the ethylamine and diethylamine complexes, on the one hand, and the triethylamine complex, on the other, is in the thermal stability with respect to decomposition by oxidation-reduction. Dichlorobis(triethylamine)copper(II) was stable with respect to dissociation into its components and did not undergo a predissociation at 0° to an intermediate 1:1 copper(II) complex prior to irreversible decomposition. Such decomposition, however, commenced at 0° and the several steps in the reaction were complete at room temperature.⁵ The dichlorobis(ethyl- or diethylamine)copper(II) complexes are stable at elevated temperatures nearly up to their melting points, unless amine is removed from them. Predissociation to intermediate 1:1 copper(II) complexes is involved as the first step in their oxidative decomposition, and the decomposition temperature depends on the size of the apparatus and the operation of the LeChatelier principle (pumping off or quenching dissociated amine in a cold trap).

Possible reasons for this difference in kind in behavior may be sought in a consideration of the structures of the complexes. That is, an attempt may be made to relate chemical differences to differences in the details of the coordination of the dichlorobis(amine)-copper(II) complexes. The electronic spectra (Figure 3) and epr spectra (Figure 4, and also Figure 2 of

ref 5) are pertinent to this consideration. The bulk susceptibility data and μ_{eff} values are not useful criteria of details of structure in normal copper(II) complexes.

Qualitative consideration of the electronic spectra does show one immediate difference of the triethylamine complex from the others. For the dichlorobis(amine)-copper(II) complexes, there is a progression to higher energy for the "d-d" band in the series ammonia < ethylamine < diethylamine. Triethylamine is completely out of order, the transition in its complex coming at a lower energy than that of the ammonia complex. It would be incorrect, simply to ascribe the observed order to any inductive effect of alkyl substitution on the position of the amines in the spectrochemical series. The degree of distortion and donor atom-metal distance undoubtedly change in this series of highly distorted complexes, ruling out any simple ligand field relation of transition energies to factors affecting the Lewis base strengths of the amines. The unsymmetrical shape of the band envelope of the visible transition of the diethylamine complex is especially noteworthy.

Qualitative consideration of the epr spectra also shows a difference in kind between the ethylamine and diethylamine complexes, on the one hand, and the triethylamine complex, on the other. The spectra of Figure 4 show a threefold anisotropy in the g tensor, while the anisotropic spectrum of the triethylamine complex (Figure 2 of ref 5) shows only g_{\perp} and g_{\parallel} components.

No single-crystal X-ray or other direct structural data are available for these complexes. Complexes of the formula $CuX_2 \cdot 2(\text{ligand})$ do have a general type of structure, involving infinite chains with two halide bridges between each copper and with two neutral polar ligands in axial positions above and below each copper.¹³ This structure is based on a local distorted octahedron about each copper. In the ordinary case ($CuCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2py$, $\alpha-CuBr_2 \cdot 2NH_3$) there are two sets of copper-halogen bridging distances, and the symmetry of the local coordination group is D_{2h} . One extreme variation of the general structure would occur when the longer copper-halogen pair becomes so distant (perhaps due to steric hindrance of bulky neutral polar ligands) that their interaction becomes negligible. The crystal would then be a molecular lattice of *trans*-square-planar complex molecules. This has been suggested for $CuX_2 \cdot 2L$ complexes of substituted pyridines.¹⁵ The other extreme variation of the general structure would occur when the two sets of copper-halogen distances become equal; the local coordination group would then have the higher symmetry D_{4h} . This structure has been reported for $\beta-CuBr_2 \cdot 2NH_3$, which is crystallographically disordered.¹² For $CuBr_2 \cdot 2NH_3$, the α form has two NH_3 groups at 1.93 Å, two Br atoms at 2.54 Å, and two Br at 3.08 Å from each Cu, while the β form has two NH_3 groups at 2.03 Å and four Br atoms at 2.88 Å from each Cu. A reasonable explanation for the lower energy "d-d" transition of the triethylamine complex and for its simpler epr spectrum would be that it has this second type of structure, possibly due to

steric hindrance or to the absence of hydrogen bonding (which could occur in crystals of the ammonia and primary and secondary amine complexes). The latter group of complexes would then have the more common, less symmetrical type of structure.

Carrying over this structural speculation to a discussion of the internal oxidation-reduction reactions leads to a consideration of the mechanism of amine oxidation. Such a mechanism involves an over-all two-electron oxidation coupled with a one-electron reduction. One-electron oxidation to an amine radical ion, which then undergoes disproportionation, has been postulated.^{5,19} For such a disproportionation, the proximity of two one-electron oxidation products in the metal complex structure would be important and would depend on the coordination symmetry. An alternative possibility would be transfer of two electrons from an amine into the molecular orbitals of the polynuclear copper(II) system. The failure of irradiation in the charge-transfer bands of the complexes to promote decomposition and the lack of antiferro-

magnetic interactions in the complexes would seem to make this alternative less probable.

Predissociation of the bis(ethyl- and diethylamine) complexes to 1:1 complex intermediates would presumably result in five-coordinate structures, one axial amine ligand position being vacated. Predissociation of dichlorodiamminecopper(II) to a 1:1 complex prior to its irreversible decomposition by oxidation-reduction has also been reported.²⁰ Complexes having such coordinatively unsaturated structures apparently are then more reactive with respect to internal oxidation-reduction.

Acknowledgments.—We wish to thank Professor Gordon Tollin for obtaining the epr spectra. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The research was also supported in part by the National Institutes of Health, Public Health Service, through Grant GM 12642-01. The X-ray and far-infrared equipment were obtained with Institutional Grants from the National Science Foundation, for which we express our thanks.

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The Reaction of Dimethylaminodifluorophosphine with Copper Chlorides¹

BY KIM COHN AND R. W. PARRY

Received July 27, 1967

$(\text{CH}_3)_2\text{NPF}_2$ will form complexes with CuCl . The formation constants of the complexes $\text{CuCl}[(\text{CH}_3)_2\text{NPF}_2]$ and $\text{CuCl}[(\text{CH}_3)_2\text{NPF}_2]_2$ have been determined by isothermal pressure-composition phase studies. On the basis of infrared and nmr spectroscopy, it is suggested that the bonding occurs through the phosphorus atom rather than the nitrogen atom. Enhancement of the basicity of the phosphorus atom in the ligand by donation of the nitrogen electron pair to the empty phosphorus d orbitals is postulated. CuCl_2 will oxidize $(\text{CH}_3)_2\text{NPF}_2$ to the phosphorane, $(\text{CH}_3)_2\text{NPF}_2\text{Cl}_2$. This new phosphorane has been completely characterized by chemical analysis, molecular weight, and infrared and nmr spectroscopy.

Introduction

Recent investigations have demonstrated the coordinating ability of the ligand dimethylaminodifluorophosphine, $(\text{CH}_3)_2\text{NPF}_2$, with various electron acceptors. Ter Haar and Sr. Fleming² working in this laboratory noted that the ligand will displace carbon monoxide from $\text{B}_4\text{H}_8\text{CO}$ to give $\text{B}_4\text{H}_8[(\text{CH}_3)_2\text{NPF}_2]$. A similar displacement of carbon monoxide from metal carbonyls led Schmutzler³ to the compounds $\text{Ni}[(\text{CH}_3)_2\text{NPF}_2]_4$ and $\text{Mo}(\text{CO})_3[(\text{CH}_3)_2\text{NPF}_2]_3$. Sr. Fleming⁴ reported that either borane or boron trifluoride

will add to the ligand in a 1:1 ratio. Cavell⁵ also reported the addition of BF_3 to $(\text{CH}_3)_2\text{NPF}_2$. A single-crystal X-ray diffraction study of the B_4H_8 adduct by Nordman and Douglas⁶ has established that bonding occurs through phosphorus rather than nitrogen. Less certain, but still rather strongly suggestive data indicate that boron trifluoride coordinates to the nitrogen and not the phosphorus in this same ligand.⁴

A preliminary investigation by Gilje⁷ has shown that nickel(II) bromide forms a weak complex with the ligand. In this study, the reactions of $(\text{CH}_3)_2\text{NPF}_2$ with anhydrous copper(I) chloride and copper(II) chloride have been investigated.

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