"Fused Salts" at Room Temperature. Vibrational Spectroscopic and Other Studies of Liquid Chlorocuprates(I)[1]

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Abstract: When equimolar amounts of copper(I) chloride and of trialkyl- (ethyl or larger) phosphonium or ammonium chlorides are brought into contact as dry powders at room temperature, immediate reaction occurs to give conducting oils, $BH^+[CuCl_2^-]$. A steric effect of the cation on the lattice energy of dichlorocuprate(I) salts is suggested. Some nmr data are presented. The $[CuCl_2^-]$ frequencies have been identified in the far-infrared and Raman spectra of those "fused salts," and perturbation of the anion by hydrogen bonding is considered. Equilibria involving other complex anions, such as $[Cu_2Cl_3^-]$, are inferred from changes in the vibrational spectra on addition of chloride ion or of copper(I) chloride to the liquid salts. The liquid state is stabilized by the melting point depression of mixed species. Nucleophiles react with the $[CuCl_2^-]$ ion both by displacement and by addition.

In view of current interest in the use of fused salts as reaction media at as low a temperature as possible[4] and the known activity of copper(I) in reactions of carbon monoxide, olefins, etc., the existence of chlorocuprate(I) salts as liquids at and below room temperature may be of practical importance. When equimolar amounts of triethylammonium chloride and copper(I) chloride are brought together under nitrogen at room temperature, the two white powders combine[5] to give a light green oil of composition $(C_2H_5)_3NH^+[CuCl_2^-]$. Triethylchlorophosphonium chloride reacts similarly[6] with 1 or 2 molar equiv of copper(I) chloride, giving room temperature liquids of formal compositions $(C_2H_5)_3PCl^+[CuCl_2^-]$ (light green) and $(C_2H_5)_3PCl^+[Cu_2Cl_3^-]$ (green-black).

Because it seemed odd that materials formulated as ionic salts would be liquids at room temperature, we undertook the synthesis of additional examples and some physical studies, especially of their far-infrared and Raman spectra. Some reactions with nucleophiles were also observed.

Solid chlorocuprate(I) salts are known with a variety of cations.[7] Apparent anion formulas $CuCl_2^-$, $CuCl_3^{2-}$, and $Cu_2Cl_3^-$ are common. X-Ray diffraction studies have shown four structural types in solids: (a) discrete linear $CuCl_2^-$ ions, as in $[(C_6H_5)_2P(O)CH_2CH_2NH(C_2H_5)_2][CuCl_2]$,[8] (b) infinite chains of $CuCl_4$ tetrahedra sharing edges, as in $[Cu(NH_3)_4][CuCl_2]_2$,[9] (c) infinite chains of $CuCl_4$ tetrahedra sharing corners, as in $K_2[CuCl_3]$,[10] and (d) infinite double chains of $CuCl_4$ tetrahedra sharing corners, as in $Cs[Cu_2Cl_3]$.[11] It is significant that the cation in case (a) is a substituted triethylammonium ion.

In previous vibrational studies, assignments for a discrete linear $CuCl_2^-$ ion were made as follows. Rodley, Goodgame, and Cotton[12] obtained the far-infrared spectrum of solid $[((C_6H_5)_2CH_3AsO)_4Cu][CuCl_2]_2$ and assigned a band at 410 cm^{-1} to the asymmetric stretch, ν_3. Creighton and Lippincott[13] found a single partially polarized Raman line at 296 cm^{-1} for an ether extract of an aqueous hydrochloric acid–copper(I) chloride solution and assigned it to the symmetric stretch, ν_1. Waters and Basak[14] studied a tri-*n*-butyl phosphate solution of lithium and copper(I) chlorides and placed the above frequencies at 405 and 300 cm^{-1}, respectively. They also observed the bending frequency, ν_2, at 109 cm^{-1}.[14a]

Experimental Section

Air- and moisture-sensitive materials were handled[15] under purified nitrogen in Schlenk apparatus, in a Forma welded steel drybox with a moisture and BTS catalytic oxygen removal recirculation system, and in a glass high-vacuum line. Solvents were purified by standard methods and deoxygenated with nitrogen. Infrared spectra were obtained with Beckman IR 8 and IR 11 and Perkin-Elmer 137B, 180, and 621 spectrophotometers; polyethylene cells were used in the region below 600 cm^{-1}. Raman spectra were obtained using a Coherent Radiation Laboratories argon ion laser; the Oregon State work was done at 514.5 nm using a Cary Model 82 instrument, while the Hampden-Sydney work was done at 488.0 nm using the Jarrell-Ash instrument of the University of North Carolina at Chapel Hill. Raman samples were in sealed glass capillaries. Nmr spectra were obtained with Varian HA-60 and HA-100 instruments; ^{31}P nmr were obtained with the latter at 40.5 MHz. Phosphorus chemical shifts, reported in ppm *vs.* H_3PO_4, were referenced to H_3PO_4 by tube interchange or to an internal capillary of P_4O_6. Conductivities were measured with an Industrial Instruments RC-16B2 bridge using a specially designed

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[14a] NOTE ADDED IN PROOF: For additional examples, see G. A. Bowmaker, L. D. Brockliss, and R. Whiting, *Aust. J. Chem.*, **26**, 29 (1973).

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freshly replatinized and calibrated cell (constant 0.1). X-Ray powder patterns were obtained using sealed Lindemann capillaries and a 114.6 mm diameter powder camera with nickel-filtered Cu K$\bar{\alpha}$ radiation. Chloride was determined gravimetrically, and copper was determined by oxidation and EDTA back-titration using PAN indicator. Carbon, hydrogen, and phosphorus microanalyses were done by Galbraith Laboratories, Knoxville, Tenn. Whenever data are given for an unanalyzed multicomponent system, the composition specified is based on weighing of the analyzed components and is exact to three significant figures.

Triethylphosphonium Chloride. This was prepared in benzene from triethylphosphine and hydrogen chloride,[16] dried *in vacuo*, and sublimed at 130° *in vacuo*, mp (sealed tube) 217–221° (lit.[17] 205–210°). Ir (P–H, Nujol, cm^{-1}) 2275, 888, 855 (sh) (lit.[17] 2300, 895, 860); ^1H nmr ($CHCl_3$) δ 1.40 (m), 2.63 (m), 6.97 (d, J_{PH} = 489 Hz); ^{31}P nmr −20.5 (d, J_{PH} = 489 Hz). *Anal.* Calcd for $C_6H_{16}PCl$: C, 46.61; H, 10.43; Cl, 22.93. Found: C, 46.70; H, 10.37; Cl, 22.42. The X-ray powder data are reported elsewhere.[1]

System Triethylphosphonium Chloride–Copper(I) Chloride. When triethylphosphonium chloride was added to an exactly equimolar amount of copper(I) chloride under nitrogen, the two white powders reacted on contact, even without stirring, to give a pale yellow-green liquid, $(C_2H_5)_3PH^+[CuCl_2^-]$. ^1H nmr ($CHCl_3$) δ 1.39 (m), 2.46 (m), 6.60 (d, J_{PH} = 482 Hz); ^{31}P nmr −21.0 (d, J_{PH} = 477 Hz); ir (neat, cm^{-1}) 2980 (s), 2950 (s), 2920 (s), 2370 (w), 1453 (s), 1408 (s), 1260 (m), 1240 (m), 1044 (s), 860 (s), 773 (s). Similarly, 2.58 mmol of triethylphosphonium chloride and 5.16 mmol of copper(I) chloride gave a yellow-green oil of composition $(C_2H_5)_3PH^+[Cu_2Cl_3^-]$. ^1H nmr (neat) 2.04 (m), 3.11 (m), 7.31 (d, J_{PH} = 482 Hz); ^{31}P nmr −20.5 (d, J_{PH} = 485 Hz); ir (neat, cm^{-1}) 2996 (s), 2960 (s), 2928 (s), 2898 (s), 2429 (w), 1462 (s), 1453 (s), 1406 (s), 1266 (m), 1244 (m), 1046 (s), 868 (s), 775 (s), 763 (sh), 735 (w). Similarly, 2.60 mmol of triethylphosphonium chloride and 1.30 mmol of copper(I) chloride gave a yellow-green oil of composition $((C_2H_5)_3PH^+)_2[CuCl_3^{2-}]$. ^1H nmr (CH_2Cl_2) δ 0.97 (m), 2.16 (m), 6.51 (d, J_{PH} = 489 Hz); ^{31}P nmr −20.9 (d, J_{PH} = 477 Hz); ir (neat, cm^{-1}) 3050–2850 (s), 2400 (m), 2300 (w), 1465 (s), 1417 (m), 1392 (w), 1283 (s), 1250 (s), 1053 (s), 1004 (m), 968 (m), 882 (s), 767 (s), 740 (sh), 708 (sh).

System Triethylphosphonium Dichlorocuprate(I)–Triethylphosphine. Exactly equimolar quantities of triethylphosphine and triethylphosphonium dichlorocuprate(I) formed a white solid. ^1H nmr (CH_2Cl_2) δ 1.30 (m), 2.55 (m), 7.13 (d, J_{PH} = 498 Hz); ^{31}P nmr +10.9 (s), −19.6 (d, J_{PH} = 488 Hz). The ir (Nujol and Fluorolube) closely resembled those of triethylphosphine and triethylphosphonium chloride, except in the 2000–2500-cm^{-1} (P–H) region (see Results and Discussion). The X-ray powder data are given elsewhere.[1] A sample of the same composition was prepared by removal of solvent *in vacuo* from an equimolar solution of triethylphosphonium chloride and chloro(triethylphosphine)copper(I)[6] in acetonitrile. ^1H nmr (CH_2Cl_2) δ 1.33 (m), 2.55 (m), 7.14 (d, J_{PH} = 497 Hz); ^{31}P nmr +10.8 (s), −20.1 (d, J_{PH} = 491 Hz). When a large excess of triethylphosphine was used, 3.0 mol were taken up per mol of triethylphosphonium dichlorocuprate(I). The ir (Nujol) of the white solid product corresponded to that of triethylphosphonium chloride plus triethylphosphine slightly modified by coordination.

Liquid Alkylammonium Chlorocuprates(I). Triethylammonium dichlorocuprate(I) was prepared as described previously,[5] as were the solids chloro(triethylamine)copper(I) and the product of reaction of equimolar amounts of triethylamine and triethylammonium dichlorocuprate(I). The X-ray powder data for the solids are given elsewhere.[1] The visible spectrum of triethylammonium dichlorocuprate(I) (neat, 1-mm silica cell) consisted of a tail rising very sharply from 450 to 400 nm into an intense uv absorption. An oil of composition $(C_2H_5)_3NH^+[Cu_2Cl_3^-]$ was prepared by briefly warming a mixture of 11.26 mmol of triethylammonium chloride and 22.51 mmol of copper(I) chloride to 75° and cooling to room temperature. An attempt was made to prepare a sample of composition $((C_2H_5)_3NH^+)_2[CuCl_3^{2-}]$ by dissolution of an equimolar amount of triethylammonium chloride in the oil triethylammonium dichlorocuprate(I). However, only about one-half of the solid dissolved at room temperature.

Similarly, room temperature liquids were obtained by direct combination of solid copper(I) chloride with equimolar amounts of *N*-ethylpiperidinium chloride, tri-*n*-butylammonium chloride, and tri-*n*-octylammonium chloride, giving compositions $AmH^+[CuCl_2^-]$. Liquids of composition $(C_4H_9)_3NH^+[Cu_2Cl_3^-]$ and $(C_2H_5)(CH_2)_5NH^+[Cu_2Cl_3^-]$ were obtained by combining copper(I) chloride with tri-*n*-butylammonium or *N*-ethylpiperidinium chlorides in 2:1 molar proportions. A liquid was prepared by adding extra *N*-ethylpiperidinium chloride to *N*-ethylpiperidinium dichlorocuprate(I) up to the solubility limit; greater solubility in the tri-*n*-butylammonium system permitted the similar preparation of the formal composition $((C_4H_9)_3NH^+)_2[CuCl_3^{2-}]$ as a liquid at 60°, but the liquid crystallized on cooling.

Solid Alkylammonium Chlorocuprates(I). An acetonitrile solution containing *equimolar* amounts of copper(I) chloride and of the alkylammonium chloride was reduced in volume, *in vacuo*, to give a white solid, which was recrystallized from absolute ethanol. Tetraethylammonium dichlorocuprate(I), mp (sealed tube) 105–108° dec. *Anal.* Calcd for $(C_2H_5)_4N[CuCl_2]$: Cu, 24.0, Cl, 26.8. Found: Cu, 24.7; Cl, 26.9. Quinuclidinium trichlorodicuprate(I), mp (sealed tube) 158–159°. *Anal.* Calcd for $C_7H_{13}NH[Cu_2Cl_3]$: Cu, 36.8; Cl, 30.8. Found: Cu, 35.4; Cl, 30.6. Trimethylammonium trichlorodicuprate(I), mp 100–105° dec (lit.[18] 100° dec). *Anal.* Calcd for $(CH_3)_3NH[Cu_2Cl_3]$: Cu, 43.3; Cl, 36.4. Found: Cu, 43.0; Cl, 34.5.

Tetraphenylborates. Triethylammonium, tri-*n*-butylammonium, and *N*-ethylpiperidinium tetraphenylborates were precipitated by mixing aqueous solutions of the ammonium chloride and sodium tetraphenylborate. They were washed with water and dried *in vacuo*.

Results and Discussion

$[CuCl_2^-]$ Salts. For alkylammonium or -phosphonium dichlorocuprate(I) salts to be liquid at room temperature, it appears that trialkyl (ethyl or larger) substitution is important. Salts with the cations triethylphosphonium, triethylchlorophosphonium,[6] and triethyl-, tri-*n*-butyl-, and tri-*n*-octylammonium are liquids. If two of the alkyl groups are pinned back in a ring, in the *N*-ethylpiperidinium cation, a liquid is also obtained, but when all three are pinned back, in the quinuclidinium cation, the solid $C_7H_{13}NH[Cu_2Cl_3]$ results. (In some cases, solid salts of the composition $AmH[Cu_2Cl_3]$ are obtained from solution despite the use of equimolar amounts of the amine hydrochloride and copper(I) chloride.) The mono-, di-, tri-, and tetramethylammonium[18] and the mono-,[19] di-,[20] and tetraethylammonium salts are solids. Such melting points as have been reported are in excess of 100°. These results suggest an important steric effect on the lattice energy.

These room temperature "fused salts" are oils which become viscous and form glasses on cooling. The specific conductances, as neat oils at 25°, are (ohm^{-1} cm^{-1}) 1.35×10^{-2} for triethylphosphonium dichlorocuprate(I) and 3.84×10^{-3} for triethylammonium dichlorocuprate(I); these may be compared to 3.27 for molten copper(I) chloride[21] at 430° and 2.77×10^{-3} for 0.02 *M* aqueous potassium chloride at 25°. Their yellow-green color is not due to contamination with copper(II) species but results from the visible tail of an ultraviolet charge transfer band, which shifts to higher wavelengths in the more highly condensed species.[22] However, the liquid salts are extraordinarily oxygen sensitive and darken rapidly if protection is inadequate.

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[16] The white precipitate was converted reversibly to an immiscible oil on continued passage of hydrogen chloride, presumably due to the formation of $(C_2H_5)_3PH[HCl_2]$.

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Table I. Vibrational Spectra of Liquid Chlorocuprate(I) Salts[a] (cm^{-1})

Cation		$[CuCl_2^-]$ composition	$[CuCl_2^-] + Cl^-$ composition[b]	$[CuCl_2^-] + CuCl$ composition[c]	
		Absorptions Assigned to Complex Anions			
$(C_2H_5)_3PH^+$	Ir	400–415 s, 438 vw, sh	402–412 s, 435 w	380–420 s, vb[d]	
	R	301 s, 411 w, 438 w	300–310 s, 440 vw	270–310 m, vb, 442 w	
$(C_2H_5)_3NH^+$	Ir	412 s		412 s, b, 450 w, sh	
	R	302 s, 413 s	300 vs, 415 s	260–290 m, vb, 413 m, 455 w,sh	
$(C_4H_9)_3NH^+$	R	300 s	300 s	250–300 s, vb[d]	
EtPipH+ [e]	R	295 m	305 s, 438 m, sh	265–295 s, vb, 435 w	
		Absorptions Assigned to Organic Cations			Chlorides[f]
$(C_2H_5)_3PH^+$	Ir	380 b, sh	250–300 m, vb, 347 w	250–300 m, vb, 355–380 s, vb	260–280 m, b, 365 s, 413 w
	R	331 m, 630 s	332–342 m,[g] 350–360 m, b,[g] 624 s	338 m, 625 s	325 m, 369 m, 636 s
$(C_2H_5)_3NH^+$	Ir	465 w		462 m, b	462 s, 471 m
	R	250 w, vb, 457 m	325 w, sh, 470 m, b	465 w	283 w, 339 w, 465 vs
$(C_4H_9)_3NH^+$	R	222 w, sh, 264 s, 350 vw, 400 vw, b	223 s, 270 m, 350 m, 378 w, 408 w, b	221 s, 323 w, sh, 349 m, 376 w	224 s, 256 s, 268 m, 333 vw, 353 m, 380 w, 407 vw
EtPipH+ [e]	R	269 m, 350 s, 373 s, 456 s	268 w, 352 s, 378 s, 462 vs	255 m, sh, 353 w, 374 s, 464 s	270 w, 350 m, 379 s, 454 sh, 467 s

[a] Abbreviations: b, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak. [b] Limiting composition $[CuCl_3^{2-}]$. [c] Composition $[Cu_2Cl_3^-]$. [d] Not resolved from cation absorption. [e] *N*-Ethylpiperidinium. [f] Solid samples (Nujol mull in ir). [g] Band intensity greater than cation contribution only.

$[Cu_2Cl_3^-]$ and $[CuCl_3^{2-}]$ Compositions. Solution equilibrium data for $[Cu_mCl_n^{-(n-m)}]$ species, $m = 1$-5 and $n = 1$-9, have been reported.[23] Similar species may be postulated to exist in the liquid chlorocuprate(I) salts. Equilibria such as

$$CuCl_2^- + Cl^- \rightleftharpoons CuCl_3^{2-} \quad (1)$$

$$CuCl_2^- + CuCl \rightleftharpoons Cu_2Cl_3^- \quad (2)$$

$$Cu_2Cl_3^- + Cl^- \rightleftharpoons 2CuCl_2^- \quad (3)$$

would be shifted by addition of chloride ion donors or of copper(I) chloride as a chloride ion acceptor. With several of the liquid salts of composition $BX^+[CuCl_2^-]$, an additional mole of copper(I) chloride can be dissolved at room temperature to give liquids of formal composition $BX^+[Cu_2Cl_3^-]$. With the liquid phosphonium dichlorocuprate(I) salts, an additional mole of the phosphonium chloride can be dissolved at room temperature to give liquids of formal composition $(BX^+)_2[CuCl_3^{2-}]$; the trialkylammonium dichlorocuprates(I) could be enriched in chloride ion at room temperature, but a full mole of the trialkylammonium chloride would not dissolve without warming, and the resulting liquids crystallized on cooling to room temperature.

Vibrational Spectra. The low-frequency spectra of solid triethylphosphonium chloride and of the various trialkylammonium chlorides were obtained to locate the cation absorptions. These absorptions were also observed in approximately the same positions for the liquid salts; additional absorptions not thus accounted for were assigned to the anions. The results are given in Table I. In agreement with previous workers,[12-14] we observe for the liquids formally containing the $[CuCl_2^-]$ anion, a strong sharp Raman absorption at 295 (*N*-ethylpiperidinium), 300 (tri-*n*-butylammonium), 301 (triethylphosphonium), or 302 cm^{-1} (triethylammonium), corresponding to the symmetric stretch ν_1, as well as the infrared absorption for the asymmetric stretch ν_3 at 410 (triethylphosphonium) or 412 cm^{-1} (triethylammonium). The Raman activity of the latter, especially in the triethylammonium system, indicates perturbation from the $D_{\infty h}$ symmetry of $[CuCl_2^-]$ postulated by the earlier workers. The low-frequency infrared and Raman spectra of the triethylchlorophosphonium salts[6] showed strong cation absorptions coincident with both the ν_1 and ν_3 dichlorocuprate(I) frequencies. This precluded their use in the present study.

The effects of added copper(I) chloride (giving the formal composition $[Cu_2Cl_3^-]$) and of added chloride (giving in the limit the formal composition $[CuCl_3^{2-}]$) on these frequencies of the dichlorocuprate(I) ion are of special interest. The results are given in Table I.

By far the biggest change is seen in the Raman spectra of all four systems enriched in copper(I) chloride. The strong, sharp ν_1 band for $[CuCl_2^-]$ at about 300 cm^{-1} is very greatly broadened and shifted to lower energy in the spectra of $[Cu_2Cl_3^-]$ compositions. This is illustrated in Figure 1 for the triethylammonium system as a representative example. Apparently, several transitions are unresolved in the broad band envelope in the 250–310-cm^{-1} region. The principal effect of added copper(I) chloride on the ν_3 infrared absorption of $[CuCl_2^-]$ at about 410 cm^{-1} is to broaden it in the spectra of $[Cu_2Cl_3^-]$ compositions, without any large shift in frequency.

Addition of chloride ion does not cause such a marked change in the $[CuCl_2^-]$ spectra. The major effect of added chloride is to sharpen and intensify the ν_1 absorption at about 300 cm^{-1}. There is no change in the ν_3 region at about 410 cm^{-1}. When the Raman spectra of the various triethylphosphonium compositions were normalized to constant intensity of the strong cation absorption at about 630 cm^{-1} and the spectrum of triethylphosphonium chloride then subtracted to leave the spectra of the complex anions, the chloride-enriched system of formal composition $[CuCl_3^{2-}]$ showed significantly greater residual intensity in the 340–350-cm^{-1} region than did the other systems.

The observed shifts indicate that several anionic complexes are present at equilibrium in these fused salts. That the salts are liquids at and below room tempera-

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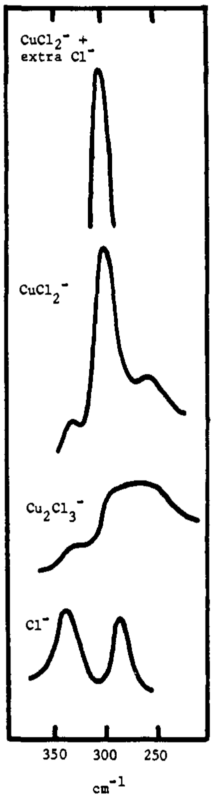

Figure 1. Raman spectra of triethylammonium chlorocuprates(I) (neat liquids) and of triethylammonium chloride (powder).

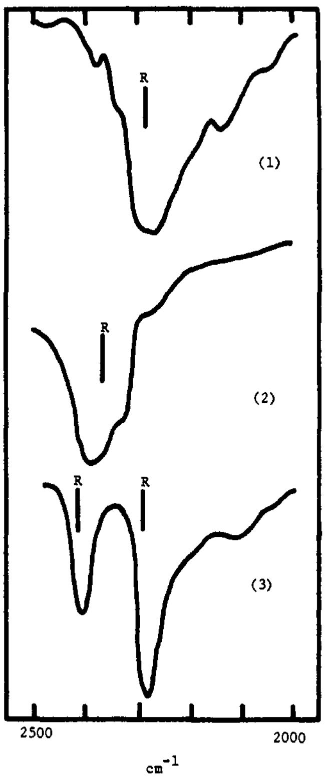

Figure 2. Infrared spectra in the P–H region: (1) triethylphosphonium chloride; (2) triethylphosphonium dichlorocuprate(I); (3) the product of reaction of triethylphosphine with triethylphosphonium dichlorocuprate(I) in equimolar amounts, showing two kinds of triethylphosphonium cations. The R markers correspond to the centers of very strong Raman bands.

ture may be attributed in part to the melting point depression of mixed species. While the spectra do not permit unambiguous specification of the complex anions present, other than [$CuCl_2^-$], the shifts can be discussed qualitatively in terms of the simple possible species of eq 1–3.

The largest shift is in the ν_1 region of [$CuCl_2^-$] on addition of copper(I) chloride to give the [$Cu_2Cl_3^-$] composition. A [$Cu_2Cl_3^-$] ion is the first member of a possible series of polynuclear complex anions. A simple postulate for the structure of [$Cu_2Cl_3^-$] would lead to C_{2v} symmetry, with linear Cl–Cu–Cl bonds at two-coordinate copper and a bent Cu–Cl–Cu bridge due to the lone pairs on the bridging chloride. Nine vibrational modes, all Raman active and eight infrared active, four of which correspond to bond stretches, are predicted in this symmetry. It is reasonable that two of the stretching modes, primarily involving motions of the terminal chlorides, should fall near the same region as the ν_3 vibration of [$CuCl_2^-$], that several of the modes should be included among the several unresolved peaks in the 250–310-cm^{-1} region, and that others, including stretches primarily involving motions of the bridging chloride, would be at still lower frequencies. Part of the added copper(I) chloride might be present as such, in polymeric molecular form, in equilibrium with polynuclear anions. The strongest infrared absorption for matrix-isolated copper(I) chloride is reported[24] at 393 cm^{-1}, a frequency region encompassed by the broadened absorption centered at about 410 cm^{-1}.

The sharpening and intensification of the ν_1 frequency of [$CuCl_2^-$] on addition of chloride ion may be explained by eq 3 as due to the consumption of some [$Cu_2Cl_3^-$] present at equilibrium in the oils of formal composition [$CuCl_2^-$]. It is possible that some [$CuCl_3^{2-}$] is formed in oils enriched in chloride ion, according to eq 1. The limiting [$CuCl_3^{2-}$] composition was attained in room temperature oils only with the phosphonium cations. The real existence of the trichlorocuprate(I) anion in the triethylphosphonium oil cannot be demonstrated from the spectral data; the evidence is limited to some greater intensity in the 340–350-cm^{-1} region than would be attributed to cation absorption. For a [$CuCl_3^{2-}$] ion, D_{3h} symmetry would be expected, as there have been several recent reports of trigonal-planar three-coordinate copper(I).[25]

Hydrogen Bonding. Cation–anion hydrogen bonding is not an essential feature in the liquid chlorocuprate(I) salts; the triethylchlorophosphonium salts are examples where it is impossible. Nevertheless, in the trialkylammonium and -phosphonium salts it may play a role in the perturbation of the complex anions. In Figure 2, a large shift of ν_{P-H} is observed for triethylphosphonium dichlorocuprate(I) (2370 cm^{-1}) compared to the chloride (2275 cm^{-1}). The P–H frequency is found at 2400 cm^{-1} for the oil of composition (($C_2H_5)_3PH^+)_2$[$CuCl_3^{2-}$] and at 2429 cm^{-1} for the oil of composition $(C_2H_5)_3PH^+$[$Cu_2Cl_3^-$]. This indicates that there is much less hydrogen bonding to the complex

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anion than to chloride and resembles the results of the $(C_6H_5)_3PH^+[HCl_2^-]$ *vs.* $(C_6H_5)_3PHCl$ comparison made by van den Akker and Jellinek.[17] Similarly, the position of the N–H stretch of the triethylammonium cation increases from the chloride (2550 cm^{-1}) to the dichlorocuprate(I) (2775 cm^{-1}) to the tetraphenylborate (3200 cm^{-1}) where there should be no hydrogen bonding.

The nmr data of Table II provide additional evidence that hydrogen bonding in these liquid chlorocuprate(I) salts is intermediate between that in chlorides and in tetraphenylborates. It is assumed that increasing hydrogen bonding corresponds to less shielding of the acidic proton.[26]

Table II. Chemical Shift (δ) of the Acidic Proton

	Cl^-	$CuCl_2^-$	$B(C_6H_5)_4^-$	Solvent
$(C_2H_5)(CH_2)_5NH^+$	11.56	8.10	3.34	CH_3CN
$(C_4H_9)_3NH^+$	11.34	6.98	4.73	CH_3CN
$(C_2H_5)_3NH^+$	10.42	8.30	5.67	CH_3CN
$(C_2H_5)_3PH^+$	6.99	6.60		$CHCl_3$

Reactions with Nucleophiles. Besides the study of added chloride ion discussed above, reactions were investigated of the liquid salts $BH^+[CuCl_2^-]$ with the parent amine or phosphine B. Two possibilities are (a) nucleophilic displacement of chloride ion from the complex anion

$$BH^+[CuCl_2^-] + B \longrightarrow BHCl + CuCl\cdot B \qquad (4)$$

and (b) addition of B to the coordination sphere of the complex anion

$$BH^+[CuCl_2^-] + B \longrightarrow BH^+[CuCl_2\cdot B^-] \qquad (5)$$

The postulate[5] that triethylammonium dichlorocuprate(I) and triethylamine react according to eq 4 is confirmed by the X-ray powder data.[1] The d spacings of the reaction product consist of the sum of the d spacings of triethylammonium chloride and of the presumably tetrameric complex $CuCl\cdot N(C_2H_5)_3$. Similar reaction behavior has been observed in the analogous ethylamine–ethylammonium[19] and triethylphosphine–triethylchlorophosphonium[6] systems. In contrast, diethylamine and solid diethylammonium dichlorocuprate(I) gave[20] a liquid adduct, according to eq 5.

Liquid triethylphosphonium dichlorocuprate(I) reacts with 3 molar equiv of triethylphosphine to give a solid product, whose infrared spectrum is the sum of the spectra of triethylphosphonium chloride and of chlorotris(triethylphosphine)copper(I).[6]

$$(C_2H_5)_3PH^+[CuCl_2^-](l) + 3(C_2H_5)_3P(l) \longrightarrow (C_2H_5)_3PHCl(c) + CuCl\cdot 3P(C_2H_5)_3(c) \qquad (6)$$

However, *equimolar* amounts of triethylphosphonium dichlorocuprate(I) and triethylphosphine react to give a more complicated mixture of products, apparently by pathways corresponding to both 4 and 5.

$$(C_2H_5)_3PH^+[CuCl_2^-](l) + (C_2H_5)_3P(l) \begin{array}{l} \nearrow (C_2H_5)_3PHCl(c) + CuCl\cdot P(C_2H_5)_3(c) \\ \searrow (C_2H_5)_3PH^+[CuCl_2\cdot P(C_2H_5)_3^-](c) \end{array} \qquad (7)$$

Only lines of chloro(triethylphosphine)copper(I)[6] can be identified in the poorly defined powder pattern[1] of the reaction product. The infrared spectrum (Figure 2) clearly shows *two* types of triethylphosphonium cations in the product, one strongly hydrogen bonded to chloride ion and one with the P–H stretch shifted to higher frequency as in a complex anion salt. The ^{31}P nmr spectrum shows a singlet at +10.8 typical of coordinated triethylphosphine, in addition to the doublet at −20.1 characteristic of the triethylphosphonium cation.

Conclusions

Chlorocuprate(I) salts are solids, most commonly[9–11] with four-coordinate copper, except when trialkyl-substituted (ethyl or larger) ammonium or phosphonium cations are present. The importance of a steric effect on the lattice energy is indicated by comparison of those cations which give room temperature liquids with those which give solids.

The room temperature liquids are conducting oils containing an equilibrium mixture of mononuclear complex anions, $[CuCl_2^-]$ and possibly $[CuCl_3^{2-}]$, with the dinuclear species $[Cu_2Cl_3^-]$ and possibly polynuclear species. The liquid state is stabilized by the melting point depression of mixed species. The complex anion equilibria are readily shifted by addition of chloride ion or of copper(I) chloride to the oils. In the latter case, a very marked effect on the ν_1 frequency in the Raman spectrum is observed as the dichlorocuprate(I) ion is converted to more condensed species. Hydrogen bonding is not required in the formation of room temperature liquids but does exist (to a lesser extent than in the chlorides) in trialkylammonium and -phosphonium dichlorocuprates(I) and may play a role in the reduction of the symmetry of the anion.

With nucleophiles (amines or phosphines), the dichlorocuprate(I) ion can react either by addition or by nucleophilic displacement of chloride ion.

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