

action in solution and probably in the presence of lithium, the loss being 18.1% and the gain 8.2%. These results appear to be in accord with an earlier study in which thiosulfate was heated alone.²³ Sulfite, sulfate, polysulfide, and sulfur were all detected, although no simple stoichiometry was suggested to explain these products.

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Registry No. K₂SO₇, 7790-62-7; SO₄²⁻, 14808-79-8; SO₃, 7446-11-9; NaCl, 7647-14-5; Cl₂, 7782-50-5; S, 7704-34-9; SO₂, 7446-09-5; Na₂SO₃, 7757-83-7; Na₂S, 1313-82-2; Na₂CO₃, 497-19-8; Na₂S₂O₅, 7772-98-7; K₂S₂O₈, 16731-55-8; Na₂S₂O₃, 7772-98-7; V₂O₅, 1314-62-1; CO₂, 124-38-9; nickel(II) sulfate, 7786-81-4; silica, 7631-86-9; polysulfide, 9080-49-3.

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Copper(I) and Copper(II) Chloro Complexes in the Basic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Ionic Liquid

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Potentiometry and absorption spectroscopy were used to study copper(I) and copper(II) chloro complex formation in the aluminum chloride-1-methyl-3-ethylimidazolium chloride (AlCl₃-MEIC) room-temperature ionic liquid. Analysis of data resulting from potentiometric titration experiments with the cell Al|AlCl₃-MEIC (66.7:33.3 mol %)|fritted disk|AlCl₃-MEIC, CuCl(dil)|Cu at 40, 60, and 100 °C indicated that copper(I) formed very stable, mononuclear chloro complexes of the type CuCl_p^{1-p} in basic (chloride ion rich) compositions of this ionic liquid. At 40 °C, CuCl₂⁻ and CuCl₄³⁻ were the principal species. However, the relative fractions of these two complexes appeared to decrease in favor of CuCl₃²⁻ as the temperature of the solvent was raised to 100 °C. Estimates of the stoichiometric formation constants for copper(I) chloro complexes in AlCl₃-MEIC are as follows. CuCl₂⁻: 2.5 × 10²³, 40.0 °C; 2.6 × 10²², 60.0 °C; 2.0 × 10¹⁹, 100 °C. CuCl₃²⁻: 1.0 × 10²⁴, 60.0 °C; 1.9 × 10²¹, 100 °C. CuCl₄³⁻: 9.2 × 10²⁵, 40.0 °C; 8.4 × 10²⁴, 60.0 °C; 1.2 × 10²², 100 °C. Absorption spectra for copper(II) in basic AlCl₃-MEIC exhibited maxima at 293 and 407 nm. These spectra were very similar to those obtained for the unsolvated CuCl₄²⁻ ion in *N,N*-dimethylformamide containing lithium chloride.

Introduction

Mixtures of aluminum chloride and either 1-*n*-butylpyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC) are ionic liquids at room temperature.^{1,2} Both systems have been found to be good solvents for electrochemistry and spectroscopy. They are compatible with a wide variety of inorganic, organometallic, and organic solutes, and they are miscible with several molecular solvents like benzene, toluene, and acetonitrile. The Lewis acid-base properties of these ionic liquids can be varied by adjusting the ratio of AlCl₃ to organic salt. Melts in which the apparent mole fraction of AlCl₃ exceeds 0.5 are acidic, while those with an AlCl₃ mole fraction less than 0.5 are basic, since they contain uncomplexed chloride ion.

The comprehensive solvation properties of these melts with regard to transition-metal solutes have not been characterized to any extent. However, the results obtained during several studies suggest that some transition-metal cations exhibit a propensity to form stable, well-defined chloro complex anions in both basic AlCl₃-BPC and AlCl₃-MEIC. Cobalt(II), iron(II), iron(III), molybdenum(III), molybdenum(IV), nickel(II), and silver(I) chloro complexes have been identified in these melts.³⁻⁸ Tetrahedral MCl₄ⁿ⁻⁴ chloro complexes were dominant for cobalt(II), nickel(II), iron(III), and iron(II).³⁻⁶

Unsolvated MoCl₆ⁿ⁻⁶ chloro complexes were found for molybdenum(III) and molybdenum(IV) in basic AlCl₃-MEIC.⁷ Silver(I) formed several different mononuclear complexes, e.g., AgCl_p^{1-p} (2 ≤ p ≤ 4), in basic AlCl₃-BPC and AlCl₃-MEIC melts. At 40 °C, AgCl₂⁻ and AgCl₄³⁻ were the predominant complex species, but AgCl₃²⁻ became important as the temperature of the solvent was increased.⁸

No previous study of the solvation or complexation of copper(I) and copper(II) in room-temperature chloroaluminate ionic liquids appears in the literature. However, potentiometric studies indicate that copper(I) is complexed as CuCl₂⁻ in molten AlCl₃-NaCl at 175 °C with a stability constant of 6.5 × 10⁴.⁹ Spectroscopic studies of copper(II) in molten LiCl-KCl were interpreted in terms of tetrahedral and tetragonally distorted tetrahedral CuCl₄²⁻ species.¹⁰⁻¹² Copper(II) absorption spectra in molten AlCl₃ indicated octahedral coordination by two Al₂Cl₇⁻ groups.¹³ Copper(I) and copper(II) chloro complex formation has been studied extensively in nonaqueous organic solvents containing extrinsic chloride ion. CuCl and CuCl₂⁻ are the principal copper(I) species usually found in these solvents, while CuCl⁺, CuCl₂, CuCl₃⁻, and CuCl₄²⁻ are examples of copper(II) complexes that have been identified.¹⁴⁻¹⁶ In the present study we have examined chloro

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complex formation for copper(I) and copper(II) in basic AlCl_3 -MEIC. Our interest in copper(I) stems from the similarity of its chloro complex chemistry to that reported for silver(I). Investigation of copper(II) chloro complexation provides additional information concerning the coordination of divalent 3d ions in basic room-temperature chloroalumininate ionic liquids.

Experimental Section

Instrumentation. The drybox system and electrochemical instrumentation used for this study were identical with those described previously.^{4,5,8} Absorption spectra were recorded in quartz cells on a Perkin-Elmer Hitachi 200 UV-vis spectrophotometer.

Cells and Electrodes. The titration vessel, furnace, and glassy carbon electrode were the same as those used in previous studies.^{5,8} Copper indicator electrodes were fashioned from 1.0-mm-diameter copper wire (Alfa Products, m3N5 purity). These electrodes were polished with fine emery cloth, rinsed with acetone, and dried in vacuo before use.

Chemicals. The procedures used for sublimation of AlCl_3 , synthesis and purification of MEIC, and preparation of the AlCl_3 -MEIC melt are described in previous publications.^{8,17} Spectrophotometric grade *N,N*-dimethylformamide (DMF) (Burdick and Jackson, distilled in glass) was used without pretreatment. Copper(I) was introduced into the AlCl_3 -MEIC melt by coulometric oxidation of the copper indicator electrodes described above. Likewise, copper(II) solutions were prepared by coulometric oxidation of these copper(I) solutions in a cell constructed from a glassy carbon crucible. Solutions of copper(I) and copper(II) identical with those prepared by coulometric oxidation could be obtained by dissolving the anhydrous chloride salts. However, the coulometric oxidation procedure permitted more precise control of the solute concentration. Solutions of copper(II) in DMF were prepared by dissolution of anhydrous copper(II) chloride (Alfa Products). Lithium chloride (Fisher, Certified) was dried at 100 °C for 24 h before use. The chloroalumininate melt compositions specified in this paper are given in terms of the apparent mole percent (mol %) or mole fraction, X_{AlCl_3} , of AlCl_3 in the melt.

Results and Discussion

Copper(I) Potentiometric Titration Experiments. Copper(I) chloro complex formation was examined by using a potentiometric titration procedure. This approach was found useful during several previous studies.^{3-6,8} Potentiometric measurements involving the Cu(I)/Cu couple were carried as a function of melt composition by use of the cell formally depicted by



The left-hand compartment of the cell was filled with 66.7 mol % melt; the melt composition in this compartment remained constant during the course of a titration experiment. The experimental technique for performing these titrations was the same as that described previously.^{5,8}

Potentiometric titration curves for the Cu(I)/Cu couple in AlCl_3 -MEIC melt at 40, 60, and 100 °C are shown in Figure 1. The overall shape of these curves is approximately the same as that found for the Ag(I)/Ag system.⁸ The large negative change in cell potential, ΔE , observed during titration experiments when the melt composition is made less than 50 mol % in AlCl_3 , is associated with chloro complex formation.^{3-5,8} The magnitude of this change reflects the stability of the complex species formed. Quantitatively, this change is slightly larger for the Cu(I)/Cu system compared to that for the Ag(I)/Ag system.⁸ Solutions of copper(I) were colorless in both the acidic and basic compositions of the melt. Copper(I) precipitated as CuCl during titration experiments when the

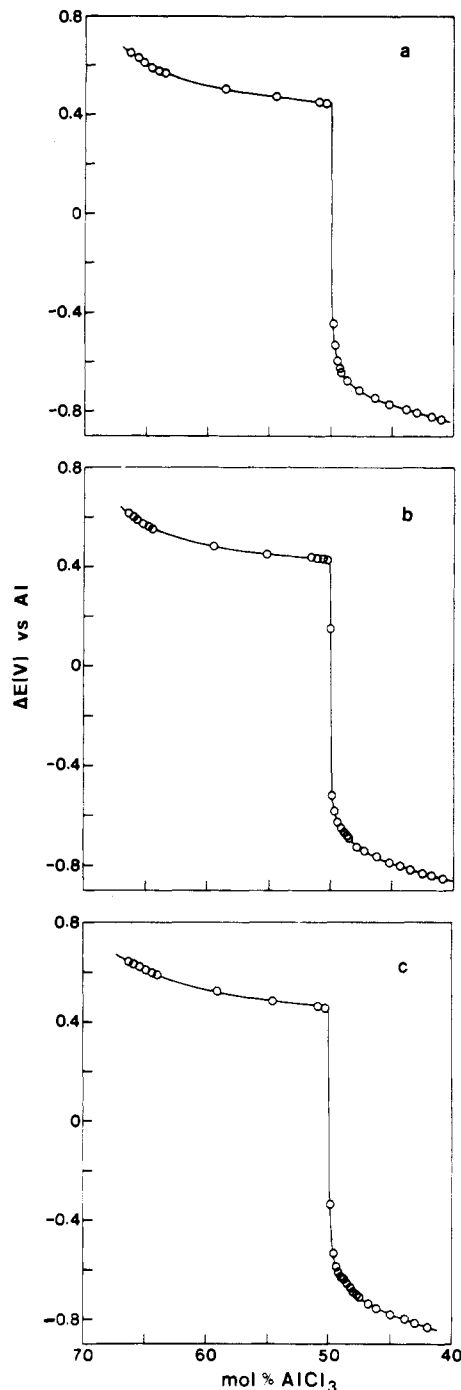


Figure 1. Potentiometric titration curves for copper(I) in AlCl_3 -MEIC melt: a, 40.0 °C; b, 60.0 °C; c, 100 °C.

AlCl_3 content of the melt was 50.0 mol %. CuCl redissolved when the AlCl_3 content of the melt was adjusted above or below this value.

A small decrease in ΔE also was noted in acidic melts as the AlCl_3 content of the melt was decreased (Figure 1). This decrease was larger than expected, based on copper(I) dilution. The mechanism responsible for this increase in stability is not understood at the present time; however, it may reflect changes in the copper(I) activity coefficient as a function of changes in the anionic constitution of the melt. In very acidic melt, e.g., 66.7 mol %, the anions consist principally of Al_2Cl_7^- , while in acidic melt close to the 50 mol % composition the melt anions are mostly AlCl_4^- .

Copper(I) Chloro Complex Models. The formation of *m* types of mononuclear copper(I) chloro complex ions of the type CuCl_p^{1-p} was considered in basic melt. Cationic, polynuclear

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Table I. Apparent Standard Potentials for the Cu(I)/Cu Electrode Reaction in 66.7 mol % AlCl₃-MEIC

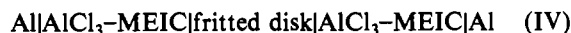
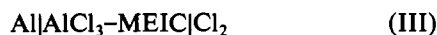
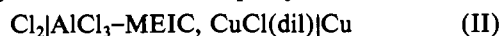
$E^{\circ'}_{\text{Cu(I)/Cu}}, \text{V}$	$dE/d \log X_{\text{Cu(I)}}, \text{V}$		$t, ^{\circ}\text{C}$
	exptl	theor	
0.843 ± 0.005	0.061	0.062	40.0
0.850 ± 0.001	0.066	0.066	60.0
0.862 ± 0.004	0.070	0.070	80.0
0.871 ± 0.005	0.075	0.074	100.0

complex ions were not considered; the formation of these species is unlikely in solutions that contain a large excess of chloride ion relative to copper(I), which is the case in basic melts. The identity and stability of copper(I) chloro complexes in basic melt can be deduced by curve fitting titration data to the equation

$$\Delta E = E^{\circ'}_{\text{Cu(I)/Cu}} + 2.3 \frac{RT}{F} \log X_{\text{Cu(I)}} - 2.3 \frac{RT}{F} \log \sum_{p=1}^m [\beta_p' (X_{\text{Cl}})^p] + E_j \quad (1)$$

In this expression $E^{\circ'}_{\text{Cu(I)/Cu}}$ is the apparent standard potential of the Cu(I)/Cu couple in melt with negligible chloride ion activity on the mole fraction scale, E_j is the cell liquid-junction potential, $X_{\text{Cu(I)}}$ is the total mole fraction of copper(I) in the melt, and X_{Cl} is the chloride ion mole fraction. The mole fraction based formation constant for the p th copper(I) complex ion, measured relative to copper(I) in the 66.7 mol % melt, is given by β_p' . It should be noted that $E^{\circ'}_{\text{Cu(I)/Cu}}$ varies with the melt composition in acidic melt. The magnitude of each β_p' is therefore dependent on the choice of the reference melt. The 66.7 mol % melt composition was chosen as the reference point for calculations of β_p' , since the chloride activity for melt of this composition is negligible. Estimates of $E^{\circ'}_{\text{Cu(I)/Cu}}$ for the Cu(I)/Cu couple in 66.7 mol % melt were obtained from the intercepts of Nernst plots and are given in Table I. These plots were constructed from data obtained by coulometric generation of copper(I) at a copper indicator electrode. The variation in $E^{\circ'}_{\text{Cu(I)/Cu}}$ with temperature in 66.7 mol % melt, $dE^{\circ'}_{\text{Cu(I)/Cu}}/dt$, was found to be $(4.8 \pm 0.3) \times 10^{-4} \text{ V}/^{\circ}\text{C}$.

Cell I can be considered as a series combination of cells II-IV. Only cell IV exhibits a liquid junction. Thus, the



liquid-junction potential for cell I is identical with that for a chloroaluminate concentration cell with transference. Studies have shown experimentally that the liquid-junction potentials of these cells are small under most conditions.^{18,19} Therefore, E_j in eq 1 was considered negligible and ignored in subsequent calculations.

The curve-fitting technique used to fit eq 1 to ΔE vs. $\log X_{\text{Cl}}$ data is identical with that used for silver(I).⁸ The results obtained from fitting different copper(I) chloro complex models to experimental data at 40, 60, and 100 °C are collected in Table II. The best model for copper(I) in basic melt at 40 °C cannot be determined with certainty. The inclusion of an additional term into the 2-4 model representing CuCl_3^{2-} to obtain the 2-3-4 model does not result in significant improvement in the variance of the fit. Therefore, it is doubtful that CuCl_3^{2-} is important at 40 °C. Similar results were obtained with the silver(I) system at 40 °C.⁸ At 60 °C the 1-2-3 and 2-3-4 models exhibit the lowest variances. However, the 1-2-3 model probably can be eliminated by virtue

Table II. Results for Least-Squares Fit to Eq 1

$t, ^{\circ}\text{C}$	model	$\log \beta_1'$	$\log \beta_2'$	$\log \beta_3'$	$\log \beta_4'$	variance ^a	
40.0	1-2			b			
	1-3	21.1	...	25.2	...	7.73×10^{-6}	
	1-4	21.7	26.2	7.48×10^{-5}	
	2-3	...	23.1	25.1	...	1.34×10^{-5}	
	2-4	...	23.5	...	26.1	3.61×10^{-6}	
	3-4			b			
	1-2-3			b			
	1-2-4			b			
	1-3-4			b			
	2-3-4	...	23.4	24.5	26.0	3.13×10^{-6}	
	1-2-3-4			b			
	60.0	1-3	19.9	...	24.4	...	3.33×10^{-5}
		1-4	20.7	25.4	6.71×10^{-4}
		2-3	...	22.3	24.3	...	3.98×10^{-5}
2-4		...	22.6	...	25.2	3.64×10^{-5}	
3-4				b			
1-2-3		19.6	22.0	24.3	...	2.71×10^{-5}	
1-2-4				b			
1-3-4				b			
2-3-4		...	22.4	24.0	24.9	1.87×10^{-5}	
1-2-3-4				b			
100.0	3	21.5	...	1.06×10^{-5}	
	1-2			b			
	1-3	16.8	...	21.5	...	6.03×10^{-6}	
	1-4	17.8	22.6	2.13×10^{-4}	
	2-3	...	18.9	21.5	...	6.55×10^{-6}	
	2-4	...	19.7	...	22.5	1.41×10^{-5}	
	3-4			b			
	1-2-3			b			
	1-2-4			b			
	1-3-4			b			
	2-3-4	...	19.3	21.3	22.1	2.33×10^{-6}	
	1-2-3-4			b			

^a Variance of the fit based on the relative error and number of model parameters. ^b Program would not converge or the attempted fit resulted in negative β' values.

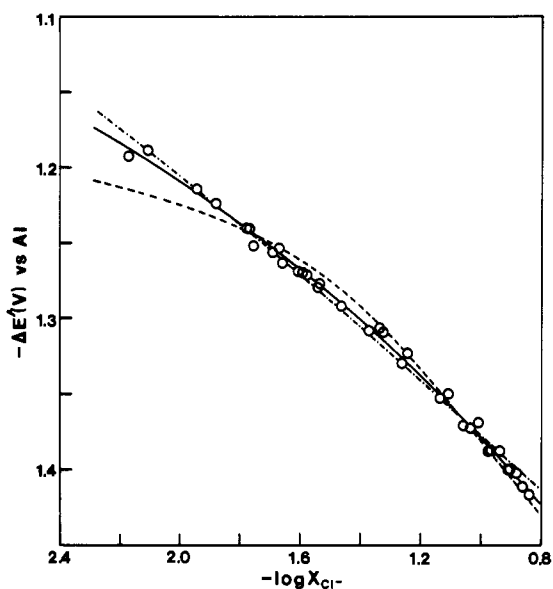


Figure 2. Variation of the corrected cell potential, $\Delta E'$, with the calculated chloride ion mole fraction in basic $\text{AlCl}_3\text{-MEIC}$ melt at 40.0 °C: —, 2-4 model; ---, 1-4 model; - · - ·, 2-3 model.

of the insolubility of CuCl (vide supra). The 2-3-4 model is clearly superior to the other models tested at 100 °C. Figures 2-4 show plots of the cell potential corrected for dilution of copper(I), $\Delta E'$, as a function of $\log X_{\text{Cl}}$ in basic melt. $\Delta E'$ is related to the experimental cell potential as shown in eq 2.

$$\Delta E' = \Delta E - E^{\circ'}_{\text{Cu(I)/Cu}} - 2.3 \frac{RT}{F} \log X_{\text{Cu(I)}} \quad (2)$$

The solid lines that appear in Figures 2-4 were calculated from

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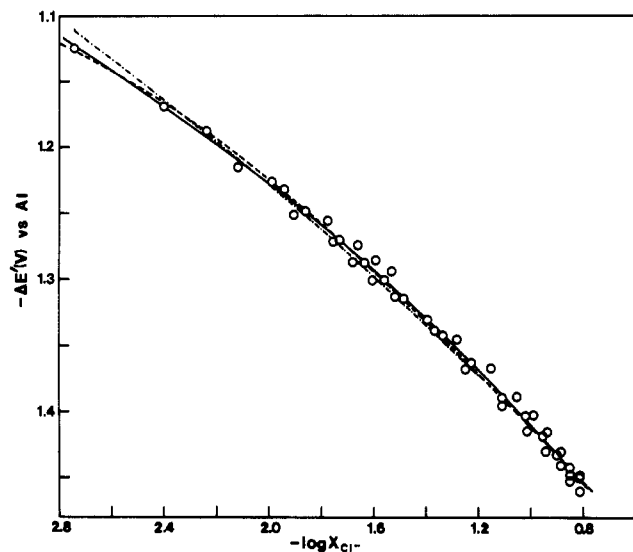


Figure 3. Variation of the corrected cell potential, $\Delta E'$, with the calculated chloride ion mole fraction in basic AlCl_3 -MEIC at 60.0 °C: —, 2-3-4 model; ---, 1-2-3 1-4 model; ···, 2-3 model.

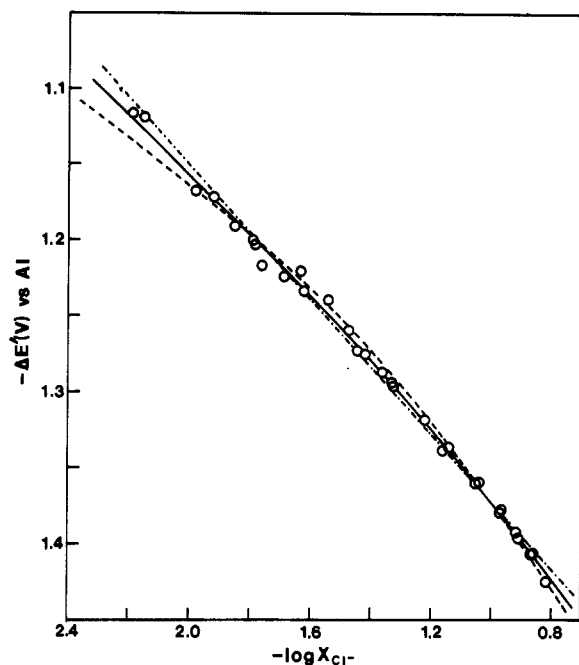
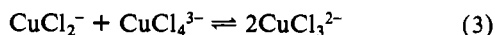


Figure 4. Variation of the corrected cell potential, $\Delta E'$, with the calculated chloride ion mole fraction in basic AlCl_3 -MEIC melt at 100 °C: —, 2-3-4 model; ---, 2-4 model; ···, 3 model.

β' values for the 2-3-4 model. Additional lines, calculated by using alternate models, are shown in these figures for comparison.

Copper(I) Chloro Complex Formation Curves. Formation curves for copper(I) chloro complexes in basic AlCl_3 -MEIC melt at 60 and 100 °C were calculated from the stability constants for the 2-3-4 models listed in Table II. These curves suggest that as the temperature of the melt is raised, the fraction of copper(I) complexed as CuCl_3^{2-} appears to become important. The increase in CuCl_3^{2-} with increased temperature apparently occurs at the expense of CuCl_2^- and CuCl_4^{3-} as a result of a shift in the equilibrium



in favor of CuCl_3^{2-} . Equilibrium constants for this reaction, estimated from the data that appear in Table II, are ca. 5.0 and 16 at 60 and 100 °C, respectively. The calculated shift in chloro complex speciation in favor of CuCl_3^{2-} that can be

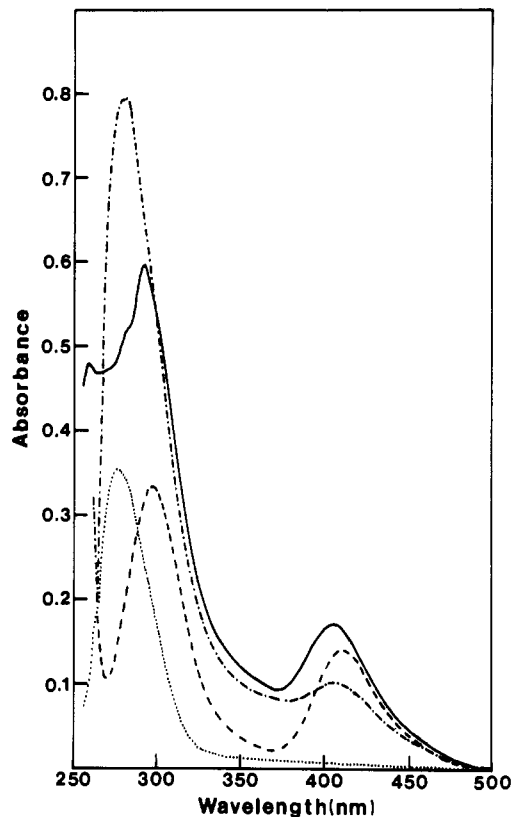


Figure 5. Copper(II) absorption spectra in solvents containing chloride ion: —, 47.3 mol % AlCl_3 -MEIC melt, 6.8×10^{-5} M in copper(II); ---, DMF + 2.7 M LiCl, 5.4×10^{-5} M in copper(II); ···, DMF + 3.0 M MEIC, 5.0×10^{-5} M in copper(II); - · - ·, DMF + 0.4 M MEIC, no copper(II).

noted as the temperature of the melt solution is raised is very similar to the result obtained for silver(I) in basic room-temperature ionic liquids.⁸

Copper(II) Absorption Spectroscopy. Copper(II) chloro complex formation was examined in basic melt by using absorption spectroscopy. Potentiometric titration experiments involving the Cu(II)/Cu(I) couple were attempted, but the resulting titration data were irreproducible and could not be analyzed in a meaningful way. The exact cause of this behavior could not be determined.

Figure 5 shows absorption spectra for copper(II) dissolved in 47.3 mol % AlCl_3 -MEIC melt and DMF containing either LiCl or MEIC as the chloride source. The spectrum for copper(II) in DMF, containing high concentrations of LiCl, exhibits maxima at 295 and 411 nm. These absorption maxima have been reported for copper(II) in propylene carbonate and dimethyl sulfoxide, also. They are characteristic of the unsolvated CuCl_4^{2-} ion.^{14,15} A spectrum of copper(II) in 47.3 mol % AlCl_3 -MEIC exhibits maxima at 293 and 407 nm. The molar absorptivity for the 407-nm peak compares favorably with that for the 410-411-nm peaks found in DMF and other solvents (Table III). However, the peak at 293 nm, observed for copper(II) in basic melt, seems distorted and exhibits a significantly higher absorptivity than that observed for the 294-295-nm peaks in organic solvents containing LiCl. An absorption spectrum for copper(II) in DMF with MEIC as the source of chloride ion exhibits maxima at 282 and 408 nm and an ill-defined shoulder near 292 nm (Figure 5). The molar absorptivity for the 292-nm shoulder cannot be estimated with certainty, but it appears to be larger than that for the peak observed at ca. 295 nm in organic solvents (Table III). However, the absorptivity for the 408-nm peak compares favorably with those calculated for the 407- and 411-nm maxima obtained for copper(II) in 47.3 mol % AlCl_3 -MEIC

Table III. Spectroscopic Data for Copper(II) in Solvents Containing Chloride Ion

solvent system	<i>t</i> , °C	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)	ref
47.3 mol % AlCl ₃ -MEIC	25	293 (8652), 407 (2596)	this work
DMF ^a + 2.7 M LiCl	25	295 (5974), 411 (2594)	this work
DMF + 3.0 M MEIC	25	282 (16 503), 292 ^b (13 000), 408 (2547)	this work
DMF + 3 M LiCl	25	296 (5060), 411 (2220)	15
Me ₂ SO ^c + 1 M LiCl	25	294 (5720), 410 (2720)	16
PC ^d + 0.1 M Et ₄ NCl ^e	25	294 (5840), 410 (2650)	16
LiCl-KCl	367	260 (1520), 370 (680)	12

^a *N,N*-Dimethylformamide. ^b Shoulder. ^c Dimethyl sulfoxide.
^d Propylene carbonate. ^e Tetraethylammonium chloride.

melt and organic solutions containing lithium chloride, respectively. An absorption spectrum of MEIC dissolved in DMF, without added copper(II), is shown in Figure 5 also. It can be seen that this solution absorbs strongly around 282 nm.

Considered together, the evidence presented above indicates that copper(II) is probably complexed as CuCl₄²⁻ in the 47.3 mol % AlCl₃-MEIC melt and in DMF containing MEIC.

However, the spectra observed for these solutions are distorted at wavelengths proximate to 295 nm by strong absorption due to the 1-methyl-3-ethylimidazolium cation. In fact, the UV cutoff for the basic AlCl₃-MEIC melt is located at about 290 nm. The most compelling evidence for CuCl₄²⁻ is the 407-nm absorption peak. It should be noted that no other mononuclear copper(II) chloro complexes, e.g., CuCl⁺, CuCl₂, or CuCl₃⁻, are reported to exhibit significant absorption close to this wavelength.^{15,16} One possible exception may be CuCl₅³⁻.²⁰ However, virtually no solution spectroscopy has been reported for this species to allow comparison. It should be noted that copper(II), octahedrally coordinated in molten AlCl₃, exhibits an absorption maximum around 862 nm.¹³

Absorptivities for the 407-nm peak in the spectrum of copper(II) in basic AlCl₃-MEIC melt were measured as a function of melt composition. The average value obtained was 2474 ± 250 M⁻¹ cm⁻¹ over the composition range extending from 48.2 to 45.3 mol %. This suggests that CuCl₄²⁻ may be the dominant copper(II) chloro complex in basic AlCl₃-MEIC melt over this composition range.

Acknowledgment. Financial support for this work was provided by the National Science Foundation, Grant No. CHE-8025235.

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Structure and Spectroscopic Properties of Ternary Complexes of Copper(II) *N*-Tosylglycinates. Crystal and Molecular Structure of *catena*-(μ -Aqua)bis(*N*-tosylglycinato)bis(4-methylpyridine)copper(II). A Case of a Linear-Chain Water-Bridged Copper(II) Polymer

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Two compounds of the type [Cu(TsglyH)₂X₂·H₂O] (TsglyH = *N*-tosylglycinate monoanion and X = pyridine (py) and 4-methylpyridine (4-Mepy)) were prepared and characterized by means of magnetic, EPR, electronic, and IR spectra. For one of them, *catena*-(μ -aqua)bis(*N*-tosylglycinato)bis(4-methylpyridine)copper(II), the crystal structure was also determined. The crystals are monoclinic, space group C2/c, with four molecules in a unit cell of dimensions *a* = 19.089 (10) Å, *b* = 15.891 (5) Å, *c* = 10.883 (3) Å, and β = 100.45 (1)°. The structure was solved by the heavy-atom technique and refined by the full-matrix least-squares method to a final *R* index of 0.047 for 1965 unique reflections. The copper environment consists of two centrosymmetrically related carboxylic oxygens and two 4-methylpyridine nitrogens in a square-planar arrangement. Two centrosymmetric water molecules, lying on the twofold axis, complete the coordination polyhedron to tetragonal bipyramid and bridge the copper atoms, forming chains running along the [001] axis. The dependence of the d-d band maximum on the Cu-O(axial) contact (2.755 (1) Å) and bipyramid distortion angle (5.0°) is discussed. The EPR parameters are also consistent with a CuN₂O₄ chromophore. The infrared spectra are discussed in comparison with those of other structurally known copper(II)-*N*-tosylglycinate complexes.

Introduction

The coordination behavior of *N*-tosylglycine toward copper(II) ion in the solid state and in aqueous solution, as a function of pH, has been investigated in our previous papers.^{2,3}

These studies have unequivocally demonstrated the importance of the tosyl group (4-toluenesulfonyl)² on the nitrogen atom in activating the coordination sites on the amino acid. In fact, at pH < 5 only the carboxyl group binds the metal ion, the peptide nitrogen being undeprotonated,^{2,3} while at pH ≥ 5 the presence of the tosyl group enables the deprotonation of the

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