

## Coordination structures of transition-metal ions in ionic liquids.

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### Introduction

Our subject of interest is the selective-site interactions of transition-metal ions in ionic liquids having polyamine chelate. We have been studying the preparations of alkylpolyaminium protic ionic liquids (= PILs) and of silver(I) ionic liquids (= AgILs) [1, 2] and the interactions of transition metal ions in the PILs. In this study, we have prepared a series of the PILs, where 4-5 kinds of copper(II) salts were dissolved. The coordination structures around the copper(II) ions were determined using EXAFS analysis.

### Experimental

The PILs were obtained by neutralizations of hexylethylenediamine (= Hexen) with HTf<sub>2</sub>N (= bis(trifluoromethanesulfonyl)amide acid) or with HTFA (= trifluoroacetic acid) and of hexylamine (= Hexam) with HTf<sub>2</sub>N. [2, 3] We studied the interactions of copper(II) ions in the PILs with an addition of the copper(II) salts such as chloride, bromide, tetraammine, bis-Tf<sub>2</sub>N, and bis-TFA complexes.

EXAFS measurements were performed at room temperature in a transmission mode at BL-7C or 9C. The solid samples were mixed with boron nitride to make a tablet specimen. The PILs were sealed into polyethylene bags for measurements; the metal concentration was adjusted to 0.10 mol kg<sup>-1</sup>. In order to extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compounds (an aqueous solution of [Cu(en)<sub>2</sub>]SO<sub>4</sub> and an ethylenediamine solution of [Cu(en)<sub>3</sub>]SO<sub>4</sub>) were used in this experiment. The structural parameters for the respective copper(II) samples were determined referred to those for the corresponding copper(II) reference compounds.

### Results and Discussion

The Fourier transformed  $|F(r)|$  of the  $k^3 \chi(k)$  curves were obtained for various kinds of bis(ethylenediamine) and tris(ethylenediamine) copper(II) complexes in solution or in solid state whose structures have been well established, and for copper(II) ions in the PILs; their spectra were compared each other.

Copper(II) ions in the en PILs show characteristic peaks due to a second shell contribution of carbon as well as single monatomic first shells of nitrogen and oxygen.

**Table 1** Least-Squares Refinements of Structure Parameters for Copper(II) Ethylenediamine Complexes in Solution

System	interaction	10r	10σ(D-W)	CN	
		/nm	/nm	(fixed)	
STDS	[Cu(en)] <sup>2+</sup>	Cu-Neq	2.05	0.1	4
		Cu-Nax	2.39	0.18	2
		Cu---C	2.89	0.1	4
	[Cu(en) <sub>2</sub> (H <sub>2</sub> O)] <sup>2+</sup>	Cu-Neq	2.03	0.07	4
		Cu-Oax	2.34	0.14	2
		Cu---C	2.91	0.07	4
Free-Ligand	Cu <sup>2+</sup> in Hexen	Cu-Neq	2.06	0.1	4
		Cu-Nax	2.49	0.15	2
		Cu---C	2.86	0.09	4
Hexen-PILs	Cu <sup>2+</sup> in HHexen(Tf <sub>2</sub> N)	Cu-Neq	2.04	0.08	4
		Cu-Oax	2.41	0.15	2
		Cu---C	2.86	0.08	4
	Cu <sup>2+</sup> in HHexen(TFA)	Cu-Neq	2.05	0.1	4
		Cu-Oax	2.22- 2.28	0.14	2
		Cu---C	2.85- 2.91	0.1	4

The spectra showed that the copper(II) ions strongly coordinate to the en-chelate ring in the HHexen cation rather than the Tf<sub>2</sub>N anion despite the electrostatic disadvantage; the coordination mode around the copper(II) ion indicates the formation of bis-en complex in the HHexen-PILs. The selective interaction was almost independent on the kinds of copper(II) salts. These interactions of the metal ions with the PILs and analogous liquids are consistent with the results obtained by the paramagnetic <sup>13</sup>C and <sup>15</sup>N NMR line broadenings and the UV-vis absorption spectra.

Curve-fittings for the FT curves were performed by fixing the coordination numbers which were determined by the UV-vis absorption spectra; the results are listed in Table 1. The obtained  $r$  and  $\sigma$  values indicate that the en-headgroups of the PILs coordinate to the copper(II) ion in the equatorial position and the counter anions are located in the axial position. (Jahn-Teller effect)

### References

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