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Coordination structures of transition-metal ions in ionic liquids.

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Introduction

A series of protic ionic liquids (= PILs) comprising chelate amines have been prepared by our research group and the characteristic interactions of some transition metal ions in such unique type PILs have been studied. [1] In order to see the effect of the number of amines in the head group on the interactions, we herein newly prepared the PILs with diethylenetriamine chelate. After dissolving some kinds of copper(II) salts, we determined the coordination structures around the copper(II) ion in the PILs using EXAFS spectroscopy.

Experimental

The PILs were obtained by a neutralization of prepared *N*-hexyldiethylenetriamine (= Hexdien) or 2-ethylhexyldiethylenetriamine (= EtHexdien) with HTf_2N (= bis(trifluoromethanesulfonyl)amide acid) or with HTFA(= trifluoroacetic acid). The PILs thus obtained are abbreviated as HHexdien(Tf_2N), HHexdien(TFA), HEthexdien(Tf_2N), and HEthexdien(TFA) hereafter. Copper salts of $CuCl_2$, $Cu(Tf_2N)_2$, and $Cu(TFA)_2$ were added to the PILs or to the neat Hexdien (or EtHexdien), liquid and the interactions of Cu^{2+} with the PILs were compared with those of the neat Hexdien (or EtHexdien) liquid. The analogous Hexdien and EtHexdien copper(II) complexes were also synthesized, and then their structures in solid state and in molecular solvents were studied using EXAFS for comparison.

EXAFS measurements were performed at room temperature in a transmission mode at BL-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 in solution was adjusted to 0.10 mol kg^{-1}. To extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compound ($Cu(dien)_2Br_2$ in solid) was used in this experiment. The structural parameters for the respective copper(II) samples were determined referred to those for the copper(II) reference compounds and to the results of VIS absorption spectra.

Results and Discussion

The Fourier transformed $|F(r)|$ of the $k^3\chi(k)$ curve was obtained for $Cu(dien)_2Br_2$ in solid state as a standard, whose crystalline structure has been determined. The copper(II) ion in the dien PILs as well as those in the isolated dien complexes shows a characteristic peak owing to a weak second shell contribution of carbon, together with a single monatomic first shell of nitrogen or oxygen. Differently from the en complexes, a series of the hexdien complexes were not simply classified into the two groups based on the intensities of FT spectra. Therefore, we at first determined the Debye-Waller (σ, as below) parameters from the analysis of the FT spectrum for the reference $Cu(dien)_2Br_2$ complex and then the curve-fittings for the copper(II) ion in the PILs and in the free ligands were performed so as to the D-W parameters have the similar values as that for the reference complex. On the basis of the VIS absorption spectra, the *CN* values could be roughly estimated.[2] However, as the nitrogen and oxygen atoms are not discriminated on the EXAFS analysis, we herein analyzed the FT spectra by taking the initial *CN* values in the solutions same as those for the reference dien complex. Some of the results are listed in Table1. There is a trend that in the PILs the *CN* values for the Cu-N bonds are larger and the σ values are slightly smaller compared to those in the neat ligands. The parameters for the Cu-C bond may have larger errors due to the smaller and overlapped peak

Table 1. EXAFS parameters determined from the curve-fittings of the copper(II) FT spectra.
($[Cu^{2+}]$ = 0.1 mol kg^{-1} for solutions)

Medium	System	Bond	10 *r* / nm	*CN*	10 σ / nm	*R*(%)
Solid	$[Cu(dien)_2]Br_2$ Solid (STD)	Cu-N(eq)	2.04	4.0(fix)	0.09	1.0
		Cu-N(ax)	2.42	2.0(fix)	0.12	
		Cu-C	2.92	8.0(fix)	0.11	
Neat Ligand	$Cu(Tf_2N)_2$ in Hexdien	Cu-N(eq)	2.04	3.8	0.10	1.9
		Cu-N(ax)	2.40	1.7	0.15	
		Cu-C	2.91	8.8	0.11	
	$Cu(Tf_2N)_2$ in Ethexdien	Cu-N(eq)	2.04	3.6	0.10	2.2
		Cu-N(ax)	2.43	1.7	0.14	
		Cu-C	2.91	8.0	0.11	
Hexdien (Tf_2N)-PIL	$Cu(Tf_2N)_2$ in HHexen (Tf_2N)	Cu-N(eq)	2.08	4.5	0.09	0.9
		Cu-N(ax)	2.43	2.3	0.12	
		Cu-C	2.94	7.4	0.11	
EtHexdien (Tf_2N)-PIL	$Cu(Tf_2N)_2$ in HEthexdien (Tf_2N)	Cu-N(eq)	2.03	4.3	0.09	2.9
		Cu-N(ax)	2.33	1.7	0.12	
		Cu-C	2.95	7.1	0.10	

References

[1] S. Takemura, S. Kawakami, M. Harada, M. Iida, *Inorg. Chem*., **53**, 9667-9678 (2014).
[2] C. Nakayama and M. Iida, "the 5th Symposium on Ionic Liquids of Japan", 1P21, Yokohama (2014).
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