

Efficient Synthesis of Metal Contained Ionic-liquids

by

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Abstract

An 1-Ethyl-3-methylimidazolium-based room-temperature (RT) ionic liquid containing cobalt (II) ions $[\text{emim}]_2[\text{Co}^{\text{II}}\text{Cl}_4]$ was investigated. (emim = 1-Ethyl-3-methylimidazolium Cation) The novel synthesis has been prepared for study in ambient-temperature ionic liquid. The salts have been characterized both thermodynamic property and crystallographical property. The crystals are isomorphous, and contain two distinct anions with differing interaction within the hydrogen-bonded structures.

Key word ; X-ray, ionic liquid

Introduction

The choice of solvent is the very important in organic synthesis, and various organic solvents have been used so far. However, the problem still remains that due to their nature, organic solvents tend to be volatile and flammable. Therefore recently several new environmental-friendly solvents have been developed. The importance of green chemistry or a green sustainable chemistry is becoming more and more clear. Ionic liquids are ionic solvents that combine the advantages of both traditional molecular solvents and melt salts, are considered as promising new reaction media, and have found wide use in catalytic and non-catalytic reactions.¹ Not only can these useful materials dissolve many organic or inorganic substances, but they are also readily recycled. The

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interest in Ionic liquids is also a direct result of the diverse properties of these liquids and the way in which they may be systematically varied, e.g., the density, viscosity, and water miscibility. Since they also have effectively zero vapour pressure, this makes them ideal engineering solvents for reactive chemistry, allowing direct distillation of solutes from the solvent and simple solvent recycling without the production of volatile organic compounds.²

The ionic liquid is very interesting in the field of an inorganic chemistry. The role and nature of cation-anion interactions in ambient-temperature ionic liquids are the subjects of much current interest. Herein this report was the novel synthesis of has been prepared for study in ambient-temperature ionic liquid [emim]₂[Co^{II}Cl₄] (1). We also reported on structural properties were investigated.

Experimental

Materials.

Anhydrous cobalt (II) chloride CoCl₂ (99.99%) and cobalt cobalt (II) hexahydrate CoCl₂ · 6H₂O (99.99%) was obtained from Aldrich and used without purification. [emim]Cl was purchased from Tokyo Kasei (>97%) and purified according to the literature procedure.³ Organic solvents were distilled prior to use.

Methods.

Melting (T_m, onset of the endothermic peak), and decomposition (T_d) temperatures were determined by differential scanning calorimetry (DSC) thermograms (10°C min⁻¹ cooling/heating rate) on a Shimadzu DSC-60 and the temperature was calibrated by water and indium. A suitable crystal of 1 was mounted in a glass capillary under argon atmosphere and then onto a goniometer head. Data for complex 1 were collected by a Rigaku AFC-7R diffractometer with a graphite-monochromated Mo^oK radiation and a 12 kW rotating anode generator. The incident beam collimator was 1.0 mm, and the crystal-to-detector distance was 235 mm. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections, corresponded to the cells with dimensions listed in Table 2, where details of the data collection are summarized. The weak reflections (I < 10(I)) were rescanned (maximum of three rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Three standard reflections were chosen and monitored every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. The

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data were corrected for Lorentz and polarization effects. Each decay of intensities of three representative reflections was -0.56% , and thus linear correction factors were applied to observed data. Determination and Refinement. The systematic absence ($h\ 0\ 1$) with $h+1 = \text{odd}$ and ($0\ k\ 0$) with $k = \text{odd}$ indicated the space group $P21/n$ (no. 14). The structure of the complex was solved by Peterson methods (DIRDIF92 PATTY)⁴ and refined by the full-matrix least-squares method. Measured nonequivalent reflections with $I > 3.0\ \sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2) / (4F_o^2)$. The positions of all non-hydrogen atoms and the hydrogen atom, H(8), were found from a difference Fourier electron density map. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms, except for H(8), were placed in calculated positions ($C-H = 0.95\ \text{\AA}$) and kept fixed. All calculations were performed using the TEXSAN crystallographic software package, and an illustration was drawn with ORTEP.

Syntheses of $[\text{emim}][\text{Co}^{\text{II}}\text{Cl}_4]$ (1)

Equimolar $[\text{emim}][\text{EtSO}_4]$ (1.60 g, 1.0 mmol) and CoCl_2 or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.70 g, 1.89 g, 1.0 mmol, respectively) were mixed at RT without any solvent and the dark blue liquid (1) that formed was stirred for 30 minutes at RT. Crystallization of (1) was left this ionic liquid at RT in Draft Box.

Thermal Properties.

Thermal property of (1) are shown in Figure 1. The salts 1 is liquids at RT with the melting points within 98°C . Decomposition temperature of 1 is as high as 230°C , leading to the wide liquid range. On cooling, a transformation from crystalline form to glass form passing through the supercooling liquid state was absent down to 100°C .

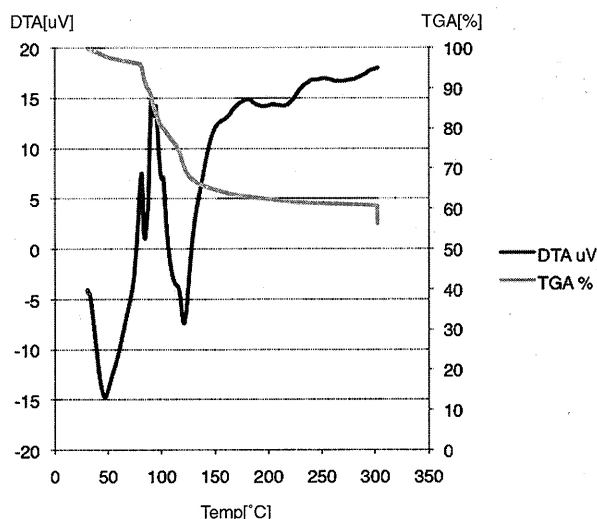


Figure 1. TGA-DTG of $[\text{emim}]_2[\text{Co}^{\text{II}}\text{Cl}_4]$

Crystal Structure of 1⁴.

The crystal of (1) was prepared by recrystallization from solution of ethyl acetate. We could not make the crystal using anhydrous CoCl_2 . The crystals was isolated and dried under vacuum. Our synthesis method was newly, easy and efficient compared with former report.⁴ The peak positions and intensities of Bragg reflections were similar to those of the reported $[\text{emim}]_2[\text{Fe}^{\text{III}}\text{Cl}_4]$ and $[\text{emim}]_2[\text{Ni}^{\text{II}}\text{Cl}_4]$ salts,⁵ and thus the structure parameters of the $\text{Co}^{\text{II}}\text{Cl}_4$ salt were used as the starting model for the refinement. The salt 1 belongs to the tetragonal system: These data were shown by Table 1, Table 2 and Figure 2.

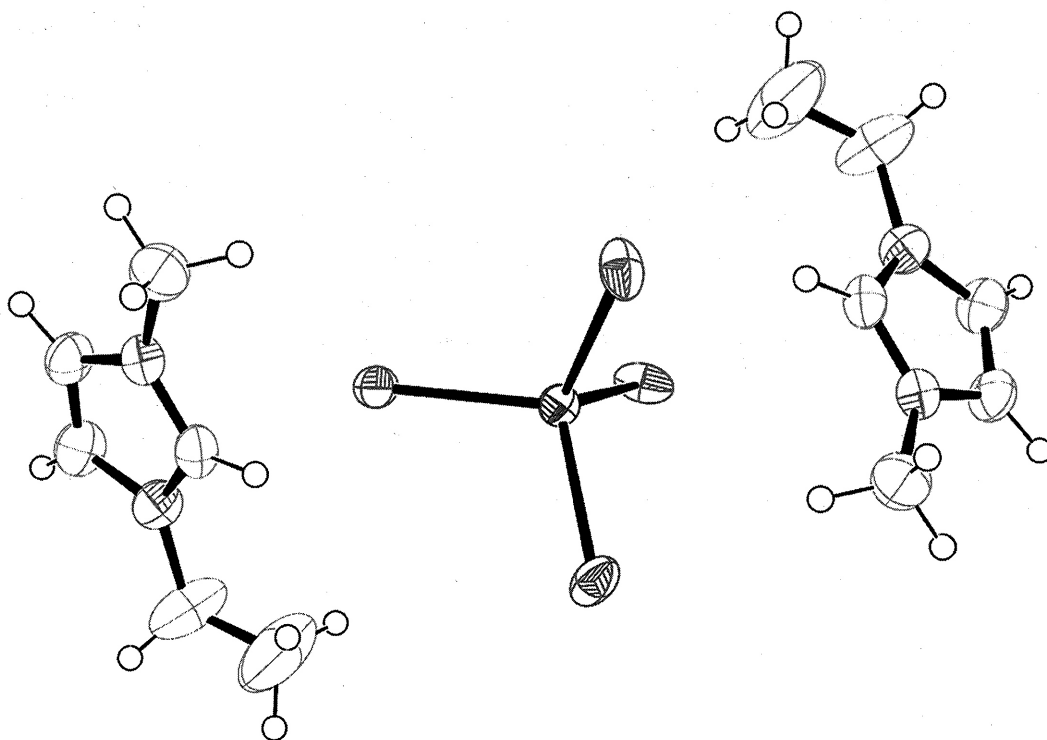
Table 1. Crystal data and structure refinement for $[\text{emim}]_2[\text{CoCl}_4]$ (1)

Identification code	$[\text{emim}]_2[\text{CoCl}_4]$ (1)	
Empirical formula	$\text{C}_{12}\text{H}_{22}\text{Cl}_4\text{CoN}_4$	
Formula weight	423.07	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$I4(1) / a$	
Unit cell dimensions	$a = 14.0553(9)$	Å $\alpha = 90^\circ$.
	$b = 14.0553(9)$	Å $\beta = 90^\circ$.
	$c = 19.139(2)$	Å $\gamma = 90^\circ$.
Volume	3781.0(6) Å ³	
Z	8	
Density (calculated)	1.486 Mg/m ³	
Absorption coefficient	1.471 mm ⁻¹	
F(000)	1736	
Crystal size	0.40 x 0.30 x 0.30 mm ³	
Theta range for data collection	1.80 to 27.14°.	
Index ranges	$-17 \leq h \leq 14$, $-17 \leq k \leq 13$, $-24 \leq l \leq 23$	
Reflections collected	9126	
Independent reflections	1980 [R(int) = 0.0181]	
Completeness to theta = 25.00°	100.0%	
Absorption correction	Empirical	
Max. and min. transmission	0.6666 and 0.5907	
Refinement method	Full-matrix least-squares on F ₂	
Data / restraints / parameters	1980 / 0 / 97	
Goodness-of-fit on F ₂	1.233	
Final R indices [I > 2sigma(I)]	R1 = 0.0341, wR2 = 0.1363	
R indices (all data)	R1 = 0.0375, wR2 = 0.1427	
Largest diff. peak and hole	0.511 and -0.554 e. Å ⁻³	

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Table 2. Hydrogencordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [emim] [Co^{II}Cl₄] (1).

	x	y	z	U (eq)
H(3)	8544	4778	9794	51
H(1)	5751	4608	9421	44
H(2)	8101	6101	9013	55
H(6A)	6677	3767	10637	84
H(6B)	7662	3365	10340	84
H(6C)	6682	3081	9970	84
H(4A)	6163	6859	8912	94
H(4B)	6520	6365	8210	94
H(5A)	5251	5612	8074	192
H(5B)	4902	6610	8384	192
H(5C)	4959	5695	8880	192

Figure 2. The local structure around a single cation in [emim]₂[Co^{II}Cl₄]

Conclusion

The novel synthesis of has been prepared for study in ambient-temperature ionic liquid. The salts have been characterized both thermodynamic property and crystallographical property. The crystals are isomorphous, and contain two distinct anions with differing interaction within the hydrogen-bonded structures. It appears that its lower melting point than those of isomorphous $\text{Co}^{\text{II}}\text{Cl}_4$ salts is related to its expanded lattice. We now are interested in making magnetic RT ionic liquids.

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Reference

- [1] (1) (a) Wasserscheid, P., Welton, T., Eds. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany 2002. (b) Reviews on ionic liquid, see: Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773; J. Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. ReV.* **2002**, *102*, 3667; Welton, T. *Chem. ReV.* **1999**, *99*, 3667; Gordon, C. M. *Appl. Catal., A* **2001**, *222*, 101; Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 419.
- [2] Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.*, **1982**, *21*, 1263.
- [3] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
- [4] P. B. Hitchcock, K. R. Seddon, and T. Welton, *J. Chem. Soc., Dalton Trans.*, **1993**, 2639.
- [5] Yoshida, Y.; Otsuka, A.; Saito, G. Natsume, S.; Nishibori, E.; Takata, M.; Sakata, M.; Takahashi, M. Yoko, T. *Bull. Chem. Soc. Jpn.*, **2005**, *78*, 1921.