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Two Cyano-Functionalized, Cadmium-Containing Ionic Liquids

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Dedicated to Wu Xin-Tao on the occasion of his 70th birthday

Keywords: Ionic liquids / Cadmium / Crystal structure / Hydrogen bonds / Thermal behavior

The new ionic liquids 3-cyanomethyl-1-methylimidazolium tetrachlorocadmate (**1**) and 3-(4-cyanobutyl)-1-methylimidazolium tetrachlorocadmate (**2**) were obtained from the reaction of the respective alkylimidazolium chlorides with cadmium chloride in 2:1 molar ratios. Structural characterization of **1** by single-crystal X-ray diffraction reveals the existence of $[CdCl_4]^{2-}$ tetrahedra and substantial C–H···Cl hydrogen bonding. Although compound **1** melts congruently at 105 °C, once molten it can be retained as a liquid at room temperature. Compound **2** just forms a glass upon solidification at approximately –42 °C.

Introduction

Since ionic liquids have quite unique physical properties and a widely tunable character and can be used as solvents in organic synthesis, electrolytes in electrochemistry, and catalysts in catalysis chemistry, they recently gained a lot of attention from both chemists and physicists.[1–2] Up to date, the most widely studied ionic liquids are dialkylimidazolium-, quaternary ammonium-, and *N*-alkylpyridinium-based salts. By melting metal chlorides with dialkylimidazolium chlorides, many dialkylimidazolium chlorometalate ionic liquids have been obtained in the past few years.[3–15] Attention was focused on tuning the properties of these ionic liquids by varying the complex anions by using different metal cations. Recently, ionic liquids that contain a carboxylic group in the aliphatic side chain of the imidazolium ring with bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$ as the counter anion were found to be capable to solvate many metal oxides.[16–17] In order to investigate the effect of other functional groups that potentially can coordinate to metal cations on the structure and physical properties of ionic liquids, we synthesized two cyano-containing compounds, reacted them with cadmium chloride and obtained two new cadmium-containing ionic liquids.

Results and Discussion

Compound **1** crystallizes in the orthorhombic space group *Pbca* (no. 61) with eight formula units per unit cell. The asymmetric unit contains one $[CdCl_4]^{2-}$ anion and two 3-cyanomethyl-1-methylimidazolium ($[CMMIM]^+$) cations. The Cd–Cl distances in the $CdCl_4$ tetrahedron range from 2.428(2) to 2.483(2) Å, and the Cl–Cd–Cl angles range from 103.13(6) to 114.29(6)° (see Table 1), which are all comparable to those found in other $CdCl_4$-containing compounds.[18–19] No interaction of the cyano group with the cadmium cation is found, as the chloride anion is the stronger Lewis base.

Table 1. Selected bond lengths [Å] and angles [°] in **1**.

Cd(1)–Cl(2)	2.428(2)	Cd(1)–Cl(4)	2.468(2)
Cd(1)–Cl(1)	2.435(2)	Cd(1)–Cl(3)	2.483(2)
Cl(2)–Cd(1)–Cl(1)	107.68(6)	Cl(2)–Cd(1)–Cl(3)	109.79(6)
Cl(2)–Cd(1)–Cl(4)	113.58(6)	Cl(1)–Cd(1)–Cl(3)	114.29(6)
Cl(1)–Cd(1)–Cl(4)	108.48(7)	Cl(4)–Cd(1)–Cl(3)	103.13(6)

Both intra- and intermolecular C–H···Cl hydrogen bonds are found in the structure (only those with H···Cl distances less than 3.0 Å and C–H···Cl angles greater than 140° are considered).[20–21] These hydrogen bonds play an important role in the assembly of cations and anions.

The linkage of intramolecular hydrogen bonds [C(3)–H(3A)···Cl(1) 3.654(7) Å, C(4)–H(4A)···Cl(3) 3.756(6) Å, C(9)–H(9A)···Cl(2) 3.558(7) Å, and C(10)–H(10A)···Cl(4) 3.805(7) Å] between two $[CMMIM]^+$ cations and one $[CdCl_4]^{2-}$ anion leads to the formation of ion pairs that correspond to one formula unit of $[CMMIM]_2[CdCl_4]$ in **1**

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(see Figure 1, Table 2). As a result, the C–C edges of the imidazolium rings are directed to the $[CdCl_4]^{2-}$ anion. It is evident that the C(3)–C(4) edge of one imidazolium ring is almost parallel to the Cl(1)–Cl(3) edge of the $[CdCl_4]^{2-}$ tetrahedron, and the C(9)–C(10) edge is parallel to the Cl(2)–Cl(4) edge. These ion pairs are further linked into a 3D supramolecular structure by intermolecular C–H···Cl hydrogen bonds [C(1)–H(1B)···Cl(3) 3.738(7) Å, symmetry code: $x - 1/2, -y + 3/2, -z$; C(11)–H(11B)···Cl(3) 3.735(7) Å, symmetry code: $x - 1/2, y, -z + 1/2$; C(5)–H(5B)···Cl(4) 3.815(8) Å, symmetry code: $-x, -y + 1, -z$; C(2)–H(2A)···Cl(4) 3.564(6) Å, symmetry code: $-x, -y + 1$] with opposite orientation of the imidazolium cations alternating along the *c* axis [see Figure 2(a)].

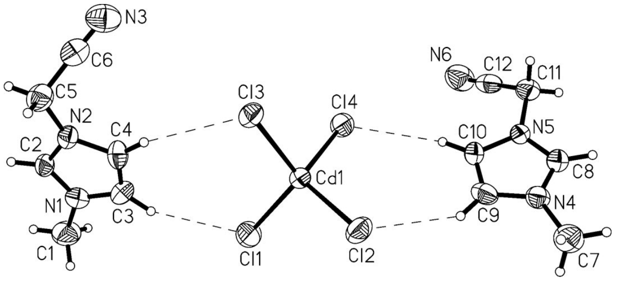

Figure 1. ORTEP representation of the asymmetric unit of **1** (50% probability ellipsoids).

Table 2. Hydrogen-bonding interactions in **1**, distances [Å] and angles [°].[a]

D–H···A	Distance (D–H)	Distance (H···A)	Distance (D···A)	Angle (D–H···A)
C(3)–H(3A)···Cl(1)	0.93	2.76	3.654(7)	160.4
C(4)–H(4A)···Cl(3)	0.93	2.89	3.756(6)	155.7
C(9)–H(9A)···Cl(2)	0.93	2.74	3.558(7)	147.4
C(10)–H(10A)···Cl(4)	0.93	2.89	3.805(7)	169.2
C(1)–H(1B)···Cl(3)#1	0.96	2.92	3.738(7)	143.4
C(11)–H(11B)···Cl(3)#2	0.97	2.83	3.735(7)	155.2
C(5)–H(5B)···Cl(4)#3	0.97	2.93	3.815(8)	152.1
C(2)–H(2A)···Cl(4)#3	0.93	2.73	3.564(6)	149.8

[a] Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2, -y + 3/2, -z$; #2 $x - 1/2, y, -z + 1/2$; #3 $-x, -y + 1, -z$.

Alternatively, the whole structure can also be seen as being built from 1D chains. $[CMMIM]^+$ cations and $[CdCl_4]^{2-}$ anions are linked by intermolecular hydrogen bonds into 1D chains [see Figure 2(b)], and these chains further assemble into a 3D supramolecular structure by the linkage of intramolecular hydrogen bonds [see Figure 2(c)]. It is also found that two cations between neighboring chains are related by an inversion center. Compared with the intramolecular hydrogen bonds, the intermolecular ones are strong (Table 2).

Figure 3 shows the thermal behavior of **1**. When crystalline **1** is heated, it melts at 105.3 °C. Prior to the melting peak, one endothermic peak (centered at 98.8 °C) is observed. It overlaps with the melting peak and has a weak intensity. Potentially, this can be attributed to a solid–solid phase transition. Upon cooling compound **1**, a glass transition is observed at about –20 °C (onset). For compound **2**, only glass transitions can be observed in both the heating and cooling processes (see Figure 4). This observation is typical for many ionic liquids, as homogeneous crystallization is often strongly inhibited.

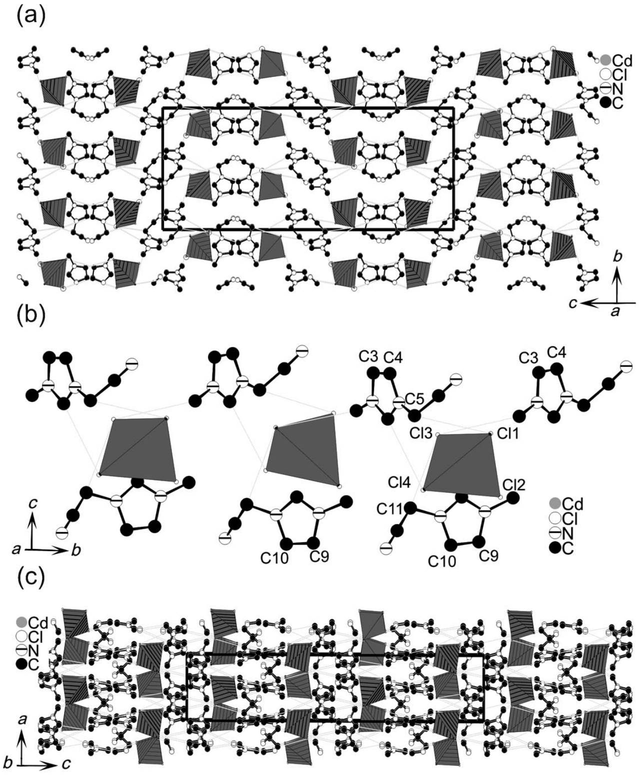

Figure 2. (a) View of the structure of **1** down the *a* axis. (b) View of the 1D chain along the *a* direction. (c) View of the structure of **1** down the *b* axis. $[CdCl_4]^{2-}$ tetrahedra are shaded in medium gray with hatching. Cd, C, N, and Cl atoms are drawn as light gray, black, medium gray with hatching, and open circles, respectively. One 1D chain is highlighted without hatching and the hydrogen bonds are presented by dotted lines.

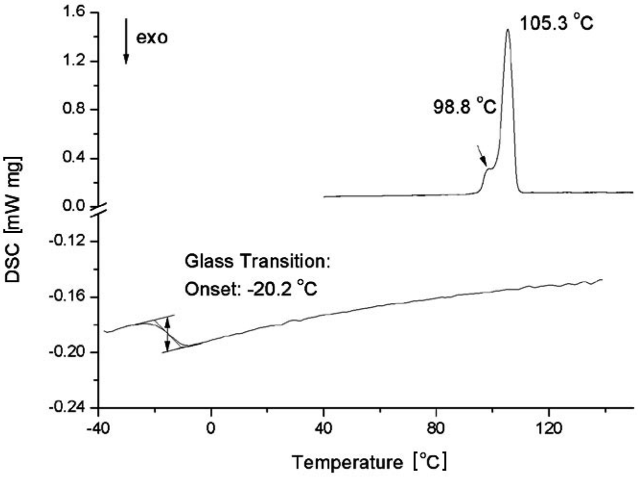

Figure 3. DSC thermogram of compound **1**.

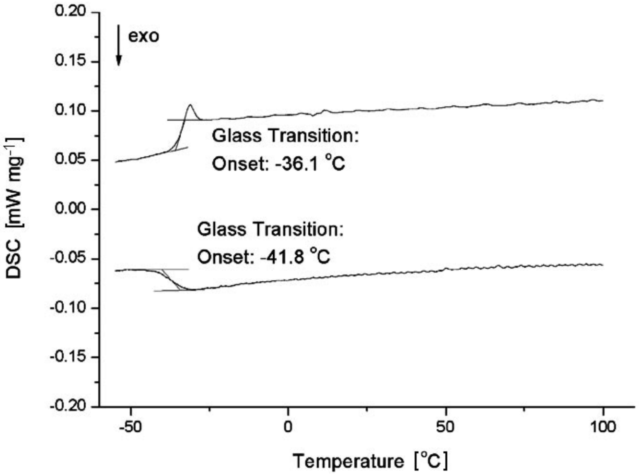

Figure 4. DSC thermogram of compound **2**.

Conclusions

In conclusion, two cyano-functionalized, cadmium-containing ionic liquids, 3-cyanomethyl-1-methylimidazolium tetrachlorocadmate (**1**) and 3-(4-cyanobutyl)-1-methylimidazolium tetrachlorocadmate (**2**), have been synthesized. The identity and purity of the synthesized compounds were confirmed by elemental analysis (EA), infrared spectroscopy (IR), and powder X-ray diffraction (PXRD). Their thermal behavior was investigated by DSC. The melting point of compound **1** is slightly above 100 °C, whereas compound **2** only has a glass transition temperature around –36 °C. Once molten, both compounds can be retained as liquids at room temperature. In the case of **1**, we were able to obtain full single-crystal X-ray structural information. As expected, Cd^{2+} is surrounded tetrahedrally by Cl^-. The complex anion is hydrogen-bonded to the 3-cyanomethyl-1-methylimidazolium cations. From the structural characterization, it becomes evident that the cyano group, although an electron-donor functionality, does not coordinate to the cadmium center. This work helps us gain a valuable insight into the effect of the decoration of the side chain, and further modification of the cation will be the aim of our further studies.

Experimental Section

General Remarks: All materials were handled and stored under inert gas. Reactions were carried out by using standard Schlenk inert gas techniques in an argon glovebox.

Materials: 1-Methylimidazole (ACROS), 2-chloroacetonitrile (ACROS), 5-chloropentanenitrile (ACROS), and anhydrous cadmium chloride (Aldrich) were used as purchased.

3-Cyanomethyl-1-methylimidazolium chloride ([CMMIM]Cl) and 3-(4-cyanobutyl)-1-methylimidazolium chloride ([CBMIM]Cl): These compounds were synthesized according to the literature.[22] For [CMMIM]Cl: $C_6H_8ClN_3$ (157.60): calcd. C 45.73, H 5.12, N 26.66; found C 45.72, H 5.04, N 26.76. IR: $\tilde{\nu}$ = 3177 (w), 3032 (m), 2979 (s), 2909 (s), 2838 (m), 2420 (w), 2258 (w), 1824 (w), 1805 (w), 1769 (w), 1684 (w), 1655 (w), 1576 (s), 1566 (s), 1442 (m), 1338 (m), 1303 (w), 1255 (m), 1244 (m), 1169 (vs), 1106 (m), 1095 (m), 1027 (m), 947 (w), 917 (s), 885 (m), 772 (vs), 761 (s), 633 (m), 612 (vs), 477 (m), 402 (m) cm^{-1}. For [CBMIM]Cl: $C_9H_{14}ClN_3$ (199.68): calcd. C 53.43, H 6.98, N 21.04; found C 54.13, H 7.07, N 21.04. IR: $\tilde{\nu}$ = 3374 (b, w), 3139 (w), 3047 (m), 2948 (m), 2870 (m), 2242 (m), 1570 (s), 1456 (m), 1427 (m), 1385 (w), 1335 (w), 1297 (w), 1163 (vs), 1090 (w), 1019 (w), 871 (m), 840 (m), 754 (s), 698 (w), 652 (m), 622 (vs), 417 (w), 409 (w) cm^{-1}.

3-Cyanomethyl-1-methylimidazolium Tetrachlorocadmate (1): 3-Cyanomethyl-1-methylimidazolium chloride and $CdCl_2$ were mixed in a Schlenk tube in a 2:1 molar ratio. The mixture was stirred for 2 h at 120 °C until a homogeneous reaction mixture was visible. Upon cooling to room temperature, colorless, brick-shaped crystals formed. $C_{12}H_{16}CdCl_4N_6$ (498.51): calcd. C 28.91, H 3.24, N 16.86; found C 29.02, H 3.21, N 16.99. IR: $\tilde{\nu}$ = 3152 (m), 3109 (m), 3083 (m), 2973 (m), 2939 (w), 1625 (w), 1584 (s), 1557 (s), 1425 (s), 1173 (vs), 1112 (m), 1090 (m), 934 (m), 851 (m), 834 (s), 754 (vs), 674 (w), 622 (s), 610 (s), 473 (m) cm^{-1}. The powder XRD pattern also confirms the identity and purity of **1** (see Supporting Information). The melting point (maximum of melting peak of crystalline material) of **1** was determined to be 105.3 °C.

3-(4-Cyanobutyl)-1-methylimidazolium Tetrachlorocadmate (2): Compound **2** was synthesized by using the same method as that for compound **1**, except for the replacement of [CMMIM]Cl by [CBMIM]Cl. So far, we were unable to crystallize this compound. DSC measurements show only a glass transition around –36 °C. $C_{18}H_{28}CdCl_4N_6$ (582.67): calcd. C 37.10, H 4.84, N 14.42; found C 36.77, H 4.85, N 14.68. IR: 3145 (w), 3102 (m), 2946 (w), 2876 (vw), 2245 (w), 1562 (s), 1456 (m), 1424 (m), 1387 (w), 1363(w), 1337 (w), 1160 (vs), 1089 (w), 837 (m), 747 (s), 697 (w), 650 (m), 621 (vs), 412 (vw) cm^{-1}.

Crystal Structure Determination of 1: A suitable single crystal of **1** was selected under dry argon, mounted in a glass capillary and measured at room temperature. Data collection was performed at room temperature with a Stoe IPDS diffractometer (Mo-K_α radiation, λ = 71.073 pm). Data reduction was carried out with the program package X-red,[23] and numerical absorption corrections were carried out with the program X-Shape.[24] Crystal structure solution by direct methods with SIR92[25] yielded the heavy atom positions. Subsequent difference Fourier analyses and least-squares refinement with SHELXL-97[26] allowed for the location of the remaining atomic positions. In the final step of the crystal structure refinement, hydrogen atoms of idealized $–CH_2$ and $–CH_3$ groups were added and treated with the riding atom mode; their isotropic displacement factor was chosen as 1.2 times that of the preceding carbon atom.

Crystal Data for 1: $C_{12}H_{16}CdCl_4N_6$, M_r = 498.51 $g mol^{-1}$, orthorhombic, *Pbca*, a = 7.750(2) Å, b = 14.500(3) Å, c = 34.670(7) Å, V = 3896(1) $Å^3$, Z = 8, $2\theta_{max}$ = 56.18°, λ = 0.71073 Å, T = 293(2) K, ρ = 1.700 $g cm^{-3}$, μ = 1.675 mm^{-1}, $F(000)$ = 1968. 23930 reflections were collected, of which 4296 were unique (R_{int} = 0.1091). GOF = 0.631. R_1/R_2 = 0.0404/0.0940 [$I > 2\sigma(I)$].

CCDC-715694 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Powder X-ray diffraction pattern for compound **1** and IR spectra for compounds **1** and **2**.

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[1] N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123.
[2] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, **1998**.
[3] T. B. Scheffler, M. S. Thomson, *Seventh International Conference on Molten Salts*, Montreal, Canada, **1990**, p. 281.
[4] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.* **2001**, 2010.
[5] A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, *Inorg. Chem.* **2004**, *43*, 3447.
[6] R. J. C. Brown, P. J. Dyson, D. J. Ellis, T. Welton, *Chem. Commun.* **2001**, 1862.
[7] P. B. Hitchcock, R. J. Lewis, T. Welton, *Polyhedron* **1993**, *12*, 2039.
[8] P. B. Hitchcock, K. R. Seddon, T. Welton, *J. Chem. Soc., Dalton Trans.* **1993**, 2639.
[9] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, N. Winterton, *Inorg. Chem.* **1999**, *38*, 5637.
[10] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, C. Femoni, A. Steiner, N. Winterton, *Inorg. Chem.* **2001**, *40*, 795.
[11] A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, J. A. Zora, *J. Chem. Soc., Dalton Trans.* **1995**, 3467.
[12] Y. Katayama, I. Konishiike, T. Miura, T. Kishi, *J. Power Sources* **2002**, *109*, 327.
[13] W. Xu, E. I. Copper, C. A. Angell, *J. Phys. Chem. B* **2003**, *107*, 6170.
[14] P. Kölle, R. Dronskowski, *Inorg. Chem.* **2004**, *43*, 2803.
[15] C.-M. Zhong, T. Sasaki, A. Jimbo-Kobayashi, E. Fujiwara, A. Kobayashi, M. Tada, Y. Iwasawa, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2365–2374.
[16] P. Nockemann, B. Thijs, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Cryst. Growth Des.* **2008**, *8*, 1353–1363.
[17] P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen, K. Binnemans, *Inorg. Chem.* **2008**, *47*, 9987–9999.
[18] F. Neve, O. Francescangeli, A. Crispini, *Inorg. Chim. Acta* **2002**, *338*, 51–58.
[19] I. Casals, P. GonzBlez-Duarte, J. Sola, *J. Chem. Soc., Dalton Trans.* **1987**, 2391–2395.
[20] T. Steiner, *Acta Crystallogr., Sect. B* **1998**, *54*, 456–463.
[21] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.
[22] D.-B. Zhao, Z.-F. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197–2205.
[23] *X-red*, Stoe & Cie, Darmstadt, Germany, **2002**.
[24] *X-Shape*, Stoe & Cie, Darmstadt, Germany, **2002**.
[25] A. Altomare, G. Cascarano, C. Giacovazzo, *J. Appl. Crystallogr.* **1993**, *26*, 343.
[26] W. S. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.

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