

Crystal Structures of Piperazinium Tetrahalogenometallates (II) [C₄H₁₂N₂]MX₄ (M = Zn, Hg; X = Br, I)

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The crystal structures of piperazinium tetrahalogenometallates (II) [C₄H₁₂N₂]MX₄ (M = Zn, Hg; X = Br, I), orthorhombic with space group $P2_12_12_1$ and $Z = 4$ are isostructural with [C₄H₁₂N₂]CdI₄. The structure consists of piperazinium cations and isolated tetrahedral MX₄ anions. [C₄H₁₂N₂]ZnBr₄ (**1**): $a = 850.4(2)$, $b = 1146.5(3)$, and $c = 1228.4(4)$ pm at 300(2) K, [C₄H₁₂N₂]ZnI₄ (**2**): $a = 886.89(6)$, $b = 1209.11(9)$, and $c = 1293.79(9)$ pm at 223(2) K, [C₄H₁₂N₂]HgBr₄ (**3**): $a = 865.48(14)$, $b = 1158.7(3)$, and $c = 1233.3(2)$ pm at 293(2) K, [C₄H₁₂N₂]HgI₄ (**4**): $a = 899.6(2)$, $b = 1230.0(2)$, and $c = 1299.5(3)$ pm at 293(2) K. All crystals show a structural phase transition at about 560 K and decomposition temperatures above 600 K. The lattice stability of the crystals is well explained by N-H...X hydrogen bond networks.

Key words: Crystal Structure, Hydrogen Bond, Piperazinium Tetrahalogenometallates (II), DSC, Phase Transition

Introduction

We have been studying crystal and molecular structures of cadmium(II) halide [1–13] and zinc(II) halide complexes [7, 12, 14, 15] and their phase transitions for the last decade by X-ray structure analysis and nuclear quadrupole resonance (NQR). A variety of polymeric structures of anions in the Cd compounds were detected, whereas only isolated tetrahedral ZnX₄²⁻ anions exist in the Zn compounds. In contrast to the above mentioned general trend, piperazinium tetraiodocadmiate (II) was found to adopt an isolated anion structure in our previous work [13]. Furthermore, we found that a series of salts [C₄H₁₂N₂]MX₄ (II) (M = Zn, Cd, Hg; X = Br, I) show a single first-order structural phase transition around 560 K [16]. Crystals of all these complexes seem stable, with decomposition temperatures above 600 K without any phase transitions between *ca.* 130 K and *ca.* 560 K. In order to elucidate this rather unusual lattice stability and the mechanism of the transitions at high temperatures, we determined the structures of [C₄H₁₂N₂]MX₄ (M = Zn, Hg; X = Br, I).

Results and Discussion

Crystal structure

The crystal structures of [C₄H₁₂N₂]MX₄ (M = Zn, Hg; X = Br, I) were found to be isostructural with [C₄H₁₂N₂]CdI₄ [13]. They are orthorhombic with space group $P2_12_12_1$ and $Z = 4$. The positional coordinates and equivalent isotropic thermal parameters U_{eq} are given in Table 1. Intramolecular bond distances and angles are given elsewhere [17]. The anions form an isolated tetrahedral structure with four crystallographically nonequivalent halogen atoms in the unit cell, which agree with the four resonance signals observed in our NQR measurements [16].

Fig. 1 shows a projection of the unit cell of **1** along [100] onto the *bc* plane. The crystal consists of isolated ZnBr₄ tetrahedra and piperazinium cations. The cations and anions are combined alternatively with hydrogen bonds of N-H...Br type, forming one-dimensional chains along the *c*-direction. There is a short interionic contact C(1)-H(12)...Br(4) between these chains. The hydrogen network scheme of the present crystals with six N-H...X hydrogen bonds and

Table 1. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} . U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The temperature factor has the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. Anisotropic displacement parameters U_{ij} , and atomic coordinates for hydrogen atoms are given elsewhere [17].

Atom	x	y	z	U_{eq} [[10 ⁻¹ pm ²]]
[C₄H₁₂N₂][ZnBr₄ (1)]				
Zn	0.7299(2)	0.53549(15)	-0.09348(15)	40.5(4)
Br(1)	0.7524(2)	0.65474(15)	0.06494(13)	48.5(4)
Br(2)	0.9414(2)	0.09549(14)	-0.09574(14)	43.6(4)
Br(3)	0.4840(2)	0.42616(14)	-0.09813(14)	44.4(4)
Br(4)	0.7376(2)	0.64478(13)	-0.25913(13)	41.9(4)
N(1)	0.4236(13)	0.4776(12)	0.1653(10)	40(3)
N(2)	0.0899(15)	0.4746(12)	0.1448(11)	46(3)
C(1)	0.3362(18)	0.5884(14)	0.1527(13)	43(3)
C(2)	0.1859(17)	0.5693(15)	0.0912(14)	45(3)
C(3)	0.1793(19)	0.3660(14)	0.1599(17)	52(4)
C(4)	0.3275(19)	0.3880(16)	0.2215(14)	49(4)
[C₄H₁₂N₂][ZnI₄ (2)]				
Zn	-0.23339(10)	-0.96363(7)	-0.90740(7)	26.22(17)
I(1)	-0.23889(6)	-0.85226(4)	-0.73514(4)	26.88(12)
I(2)	-0.45036(5)	-1.11096(4)	-0.90559(4)	27.55(12)
I(3)	-0.25884(7)	-0.83680(4)	-1.06860(4)	33.37(14)
I(4)	0.01880(6)	-1.08053(4)	-0.90323(13)	29.31(13)
N(1)	0.4026(7)	-1.0228(6)	-1.1476(5)	28.5(13)
N(2)	0.0814(7)	-1.0171(6)	-1.1666(5)	26.2(17)
C(1)	0.3123(8)	-0.9399(7)	-1.0951(7)	30.4(15)
C(2)	0.1672(17)	-0.9133(7)	-1.1530(7)	30.6(16)
C(3)	0.1734(10)	-1.1018(6)	-1.2213(6)	29.7(15)
C(4)	0.3165(10)	-1.1258(7)	-1.1634(7)	30.8(16)
[C₄H₁₂N₂][HgBr₄ (3)]				
Hg	0.76497(5)	0.04168(4)	0.90597(4)	42.9(2)
Br(1)	0.7439(2)	0.16730(11)	1.07730(10)	45.8(3)
Br(2)	0.54411(12)	-0.11266(10)	0.90295(11)	37.8(3)
Br(3)	0.76051(13)	0.14838(10)	0.72097(9)	37.0(3)
Br(4)	1.02702(12)	-0.07885(11)	0.89852(11)	39.6(3)
N(1)	1.0926(10)	0.0243(10)	0.6470(8)	38(3)
N(2)	1.0762(11)	-0.0149(9)	1.1604(8)	34(2)
C(1)	1.1856(14)	0.1314(12)	0.6616(12)	41(3)
C(2)	0.8330(14)	0.3941(11)	1.2789(11)	38(3)
C(3)	0.6681(14)	0.4091(12)	0.8534(11)	39(3)
C(4)	0.8151(13)	0.4314(10)	0.9115(11)	37(3)
[C₄H₁₂N₂][HgI₄ (4)]				
Hg	0.73797(5)	-0.04221(4)	0.90778(3)	42.81(14)
I(1)	0.96064(8)	0.11745(6)	0.90518(5)	37.5(2)
I(2)	0.75875(10)	-0.17374(6)	1.07903(5)	48.7(2)
I(3)	0.74097(8)	-0.14948(5)	0.72010(4)	37.6(2)
I(4)	0.47339(8)	0.08417(6)	0.90214(5)	40.7(2)
N(1)	0.3998(9)	-0.0197(8)	0.6473(7)	37(2)
N(2)	0.4154(10)	0.0135(8)	1.1649(6)	38(2)
C(1)	1.1859(12)	-0.0645(9)	1.0941(8)	39(2)
C(2)	0.8308(12)	-0.4087(9)	0.8527(8)	39(2)
C(3)	0.6714(13)	-0.4022(9)	1.2799(7)	39(2)
C(4)	0.3107(13)	-0.1226(10)	0.6648(8)	44(3)

Table 2. PizMX ((C₄H₁₂N₂)MX₄): Transition point T_r , transition enthalpy ΔH , transition entropy ΔS , unit cell volume V , N-H...X hydrogen bond distance, their average, and C-H...X contact.

	PizZnBr	PizCdBr ^a	PizHgBr	PizZnI	PizCdI ^b	PizHgI
T_r [K]	549	556	566	557	558	566
ΔS [JK ⁻¹ mol ⁻¹]	1.2	0.8	0.6	0.8	0.9	1.3
ΔH [kJ mol ⁻¹]	0.68	0.4	0.3	0.45	0.5	0.72
$V \cdot 10^{-6}$ [pm ³]	1197.7		1236.8	1387.4	1448.6	1437.9
$d(N-H \cdots X)$ [pm]	3.336 3.472 3.329 3.320 3.339 3.415		3.392 3.341 3.372 3.383 3.495 3.341	3.530 3.555 3.603 3.537 3.642 3.537	3.579 3.703 3.551 3.584 3.608 3.614	3.586 3.611 3.595 3.587 3.686 3.562
Av. [pm]	3.369		3.387	3.567	3.607	3.605
$d(C-H \cdots X)$ [pm]	3.431		3.526	3.619	3.716	3.713

^a Anhydrous sample formed by dehydration [14]; ^b ref. [13].

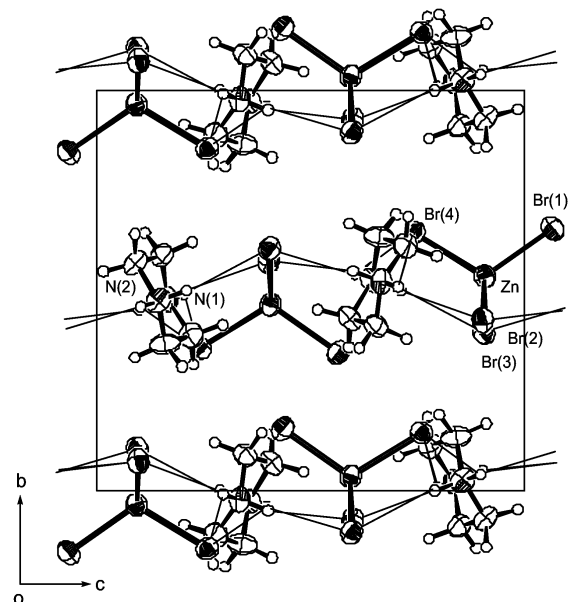


Fig. 1. The projection of the unit cell of piperazinium tetrabromozincate(II) (1) along [100] onto the bc plane. Hydrogen bonds are shown with thin lines.

one short C-H...X contact are fairly similar throughout [C₄H₁₂N₂][MX₄] (II) (M = Zn, Cd, Hg; X = Br, I). The temperature variations in the ⁸¹Br or ¹²⁷I NQR frequencies of these crystals are slight with an unusual linear dependence [16]. This observation is explainable in terms of the N-H...X hydrogen bonds.

The correlation of phase transitions with crystal structures

The [C₄H₁₂N₂][MX₄] (M = Zn, Cd, Hg; X = Br, I) crystals exhibit a single structural phase transition

Table 3. Experimental conditions for the crystal structure determinations and crystallographic data of $[\text{C}_4\text{H}_{12}\text{N}_2]\text{ZnBr}_4$ (**1**), and $[\text{C}_4\text{H}_{12}\text{N}_2]\text{ZnI}_4$ (**2**), diffractometer Nonius CAD4; wavelength 71.093 pm (Mo- K_α), monochromator: graphite (002) for (**1**) and diffractometer Oxford Diffraction Xcalibur CCD; wavelength 71.073 pm (Mo- K_α), monochromator: graphite (002) for (**2**). For $[\text{C}_4\text{H}_{12}\text{N}_2]\text{HgBr}_4$ (**3**) and $[\text{C}_4\text{H}_{12}\text{N}_2]\text{HgI}_4$ (**4**), diffractometer Stoe IPDS; wavelength 71.073 pm (Mo- K_α), monochromator: graphite (002). (**1**): $\text{C}_4\text{H}_{12}\text{Br}_4\text{ZnN}_2$ $M = 473.19$, (**2**): $\text{C}_4\text{H}_{12}\text{I}_4\text{ZnN}_2$ $M = 661.13$, (**3**): $\text{C}_4\text{H}_{12}\text{Br}_4\text{HgN}_2$ $M = 608.39$, (**4**): $\text{C}_4\text{H}_{12}\text{I}_4\text{HgN}_2$ $M = 796.35$.

Compound	1	2	3	4
Crystal size [mm ³]	0.80 × 0.38 × 0.20	0.68 × 0.48 × 0.38	0.31 × 0.28 × 0.27	0.35 × 0.29 × 0.21
Temperature [K]	300(2)	223(2)	293(2)	293(2)
Absorption coeff. [mm ⁻¹]	15.33	10.631	25.321	19.254
θ -Range for data collected	2.43° ≤ θ ≤ 34.97°	2.78° ≤ θ ≤ 30.17°	2.41° ≤ θ ≤ 26.03°	2.28° ≤ θ ≤ 26.06°
Index ranges	-13 ≤ h ≤ 1, -18 ≤ k ≤ 1, -19 ≤ l ≤ 19	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -18 ≤ l ≤ 10	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15	-11 ≤ h ≤ 10, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Lattice parameters:				
a [pm]	850.4(2)	886.89(6)	865.48(14)	899.6(2)
b [pm]	1146.5(3)	1209.11(9)	1158.7(3)	1230.0(2)
c [pm]	1228.4(4)	1293.79(9)	1233.3(2)	1299.5(3)
α [°]	90.00	90.00	90.00	90.00
β [°]	90.00	90.00	90.00	90.00
γ [°]	90.00	90.00	90.00	90.00
$V \times 10^{-6}$ [pm ³]	1197.7(6)	1387.39(17)	1236.8(4)	1437.9(5)
Formula units Z	4	4	4	4
ρ_{cal} [Mg m ⁻³]	2.624(1)	3.1653(4)	3.2671(11)	3.6786(13)
$F(000)$	880	1168	1080	1368
Reflections collected	6800	31333	21516	20283
Independent reflections	5253[$R(\text{int}) = 0.0970$]	3764[$R(\text{int}) = 0.0641$]	2431[$R(\text{int}) = 0.1544$]	2794[$R(\text{int}) = 0.2261$]
Data ($I > 2\sigma(I)$)	2510	3691	2060	2553
Restraints/parameters	0/101	0/102	0/113	0/114
Goodness of fit $S(\text{obs./all})$	1.201/1.048	1.077/1.077	1.021/0.973	0.881/0.861
Final $R(I > 2\sigma(I))$	$R = 0.0863$, $wR = 0.2461$	$R = 0.0363$, $wR = 0.0948$	$R = 0.0398$, $wR = 0.0946$	$R = 0.0345$, $wR = 0.0810$
R (all data)	$R = 0.1898$, $wR = 0.3099$	$R = 0.0371$, $wR = 0.0955$	$R = 0.0499$, $wR = 0.0982$	$R = 0.0380$, $wR = 0.0828$
Largest diff. (peak, hole) [$10^{-6}\text{e}(\text{pm}^3)$]	1.674 and -1.515	1.717 and -1.386	1.482 and -2.458	1.941 and -1.530
Max. and min. trans.	0.0482 and 0.057	0.0908 and 0.0289	not measured	not measured
Extinction coeff.	0.0151(21)	0.0036(2)	0.0054(3)	0.0054(3)
Flack parameter	0.05(6)	0.58(5)	-0.03(2)	0.420(8)
Point positions	all atoms in 4a	all atoms in 4a	all atoms in 4a	all atoms in 4a

No absorption correction has been applied for the IPDS data.

around 560 K [16]. These phase transitions are considered to be of first-order according to the shapes of DSC (differential scanning calorimetry) curves. In addition, they appear to be of the displacive type, because the observed transition entropies ΔS_{tr} are very small. The DSC results are given in Table 2. All of these complexes decompose above 600 K, and no phase transition was observed between *ca.* 130 K and *ca.* 560 K. This lattice stability seems to result from the relatively strong N-H...X hydrogen bonds in these crystals.

$[\text{N}(\text{CH}_3)_4]_2\text{MBr}_4$ ($M = \text{Zn}, \text{Cd}, \text{and Hg}$) undergo a structural phase transition below room temperature. The low-temperature phases of these compounds have the space group $P2_1/c$, which is also found the room-temperature phase of $[\text{CH}_3\text{NH}_3]_2\text{MBr}_4$ and

$[(\text{CH}_3)_2\text{NH}_2]_2\text{MBr}_4$ ($M = \text{Zn}, \text{Cd}, \text{and Hg}$) [18]. These compounds do not undergo a structural phase transition between about 130 K and room temperature and the $P2_1/c$ phase is stable up to 450–480 K in $[\text{CH}_3\text{NH}_3]_2\text{MBr}_4$ and 360–400 K in $[(\text{CH}_3)_2\text{NH}_2]_2\text{MBr}_4$ [18]. We found that the transition temperatures increase as the number of N-H...Br hydrogen bonds increases, suggesting that N-H...Br hydrogen bonds stabilize the crystal lattices.

There is no correlation between transition points and unit-cell volumes or average hydrogen bond distances as can be seen from Table 2. On the other hand, we reported that transition points of $[\text{N}(\text{CH}_3)_4]_2\text{MX}_4$ ($M = \text{Zn}, \text{Cd}, \text{Hg}, X = \text{Cl}, \text{Br}, \text{I}$) depend on their unit-cell volume; that is, transition points decrease

with increasing size of the unit cell [19]. This difference is explained by the existence or nonexistence of N-H...X hydrogen bonds as follows. Many of $[\text{N}(\text{CH}_3)_4]_2\text{MX}_4$ compounds are known to undergo successive phase transitions. These transitions are due to a delicate balance of interactions among constituent ions which is easily broken by a subtle change of temperature, pressure etc. Therefore, phase transition temperatures depend also on unit-cell volumes. There is no possibility to form the N-H...X hydrogen bonds in $[\text{N}(\text{CH}_3)_4]_2\text{MX}_4$, but such bonds exist in $[\text{C}_4\text{H}_{12}\text{N}_2]\text{MX}_4$. The hydrogen bond networks in the latter compounds stabilize the lattices and make their phase transition temperatures insensitive to the unit-cell volume changes among them.

All of the phase transitions from $P2_1/c$ to a high-temperature phase in $[\text{CH}_3\text{NH}_3]_2\text{MBr}_4$, $[(\text{CH}_3)_2\text{NH}_2]_2\text{MBr}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{MBr}_4$ (M = Zn, Cd, and Hg) are caused by an orientational disordering of cations [18]. On the other hand, the phase transitions in $[\text{C}_4\text{H}_{12}\text{N}_2]\text{MX}_4$ are of displacive type. Probably an

unfavorable molecular structure of the piperazinium ion for rotations and the hydrogen bond scheme in $[\text{C}_4\text{H}_{12}\text{N}_2]\text{MX}_4$ contribute to the absence of order-disorder type phase transitions as well as to the lattice stability.

Experimental Section

The piperazinium complexes were prepared according to [16]. The structures of $[\text{C}_4\text{H}_{12}\text{N}_2]\text{ZnBr}_4$ (**1**) and $[\text{C}_4\text{H}_{12}\text{N}_2]\text{ZnI}_4$ (**2**) were determined using a four-circle X-ray diffractometer Nonius CAD4 and Oxford Diffraction Xcalibur CCD, respectively. The structures of $[\text{C}_4\text{H}_{12}\text{N}_2]\text{HgBr}_4$ (**3**) and $[\text{C}_4\text{H}_{12}\text{N}_2]\text{HgI}_4$ (**4**) were determined using a Stoe IPDS instrument. From measured intensities corrected for Lorentz-polarization and absorption effects, the structures were solved by the direct techniques and Fourier syntheses, and refined by least-squares methods with programs given in ref [20]. The experimental conditions and crystallographic data are listed in Table 3. The X-ray crystal structure determination of $[\text{C}_4\text{H}_{12}\text{N}_2]\text{ZnI}_4$ (**2**) was done at 223 K, in order to improve the intensity collection and reduce thermal motion.

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