

Crystal Structures of Piperazinium Tetrabromocadmiate(II)-Monohydrate $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdBr}_4 \cdot \text{H}_2\text{O}$, Piperazinium Tetraiodocadmiate(II) $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdI}_4$, and Bis(trimethylsulphonium) Tetrabromocadmiate(II) $[(\text{CH}_3)_3\text{S}]_2\text{CdBr}_4$

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Crystal Structure, Halogenocadmiate(II)

Piperazinium tetrabromocadmiate(II)-monohydrate, $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdBr}_4 \cdot \text{H}_2\text{O}$ (**1**) crystallizes with isolated $[\text{CdBr}_4]^{2-}$ anions, piperazinium cations, and water molecules (monoclinic, $P2_1/c$, $Z = 4$, $a = 698.7(1)$, $b = 1348.6(3)$, and $c = 1432.4(3)$ pm, $\beta = 92.97(3)^\circ$ at 293 K). The crystal structure of **1** is almost the same as that reported in *Inorg. Chim. Acta* **187**, 141 (1991). The crystal of piperazinium tetraiodocadmiate(II), $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdI}_4$ (**2**) consists of isolated $[\text{CdI}_4]^{2-}$ anions and piperazinium cations (orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 903.2(5)$, $b = 1226.3(6)$, and $c = 1307.9(7)$ pm at 293 K). The room temperature phase of bis(trimethylsulphonium) tetrabromocadmiate(II), $[(\text{CH}_3)_3\text{S}]_2\text{CdBr}_4$ (**3**) has isolated $[\text{CdBr}_4]^{2-}$ anions and trimethylsulphonium cations (orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 911.3(1)$, $b = 1329.2(2)$, and $c = 1454.7(2)$ pm at 293 K).

Introduction

We have been studying structures of cadmium(II) halide complexes for the last decade [1 - 10]. During this work it became apparent that the structure of the cations and the number of hydrogen bonds are important factors to determine the shape of the cadmium(II) halide complex anions. The shapes of the complex anions are quite variable: Isolated tetrahedra [7, 8], complex chain structures [4, 9, 10], and two-dimensional layered structures [6]. Especially when forming a two-dimensional layered structure, the size of the cations must be limited [6]. Recently, bis(4-nitroanilinium) tetrachlorocadmiate(II) has been reported to be a layered structure with the 4-nitroanilinium cations accommodated between the layered complex anions [11]. The size of a piperazine ring is almost the same as that of a benzene ring. Therefore, we tried the formation of a layered anion structure with piperazinium cations. Trimethylsulphonium cations have no hydrogen atoms that can participate in hydrogen bonding. We also tried to obtain a layered anion structure with these counterions.

Experimental Section

The piperazinium complexes were formed by mixing piperazine and cadmium(II) carbonate in the molar ratio of 1:1 in concentrated hydrobromic or hydroiodic acid. Crystals of $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdBr}_4 \cdot \text{H}_2\text{O}$ (**1**) form colorless prisms. $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdBr}_4 \cdot \text{H}_2\text{O}$: calcd. C 8.92, H 2.62, N 5.20; found C 8.98, H 2.63, N 5.24. Crystals of $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdI}_4$ (**2**) form pale yellow rods. $[\text{C}_4\text{H}_{12}\text{N}_2]\text{CdI}_4$: calcd. C 6.78, H 1.70, N 3.95; found C 6.83, H 1.67, N 3.99. Crystalline powder of $[(\text{CH}_3)_3\text{S}]_2\text{CdBr}_4$ (**3**) was prepared according to the literature method [8] and was used for the powder X-ray diffraction studies, because it was very difficult to get small single crystals for X-ray work at room temperature.

The structures were determined using a four-circle X-ray diffractometer Stoe IPDS. From measured intensities corrected for Lorentz-polarization and absorption effects, the structures were solved by the direct method and Fourier synthesis, and refined by least-squares methods with programs given in [12]. The powder X-ray diffractometer was a Stoe-Stadi P, and the analysis was done by the Riet-

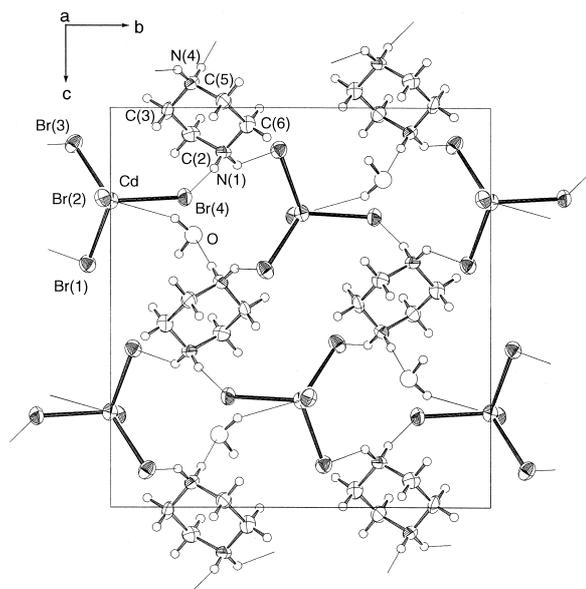


Fig. 1. The projection of the unit cell of piperazinium tetrabromocadmate(II)-monohydrate (**1**) along [100] onto the *bc* plane. Hydrogen bonds are shown with thin lines.

veld method using the RIETAN-97 program [13]. Atomic positions were estimated by the energy minimization method [14].

Results and Discussion

Piperazinium tetrabromocadmate(II)-monohydrate, $[C_4H_{12}N_2]CdBr_4 \cdot H_2O$ (**1**)

The structure of **1** was reported by Battaglia *et al.* [15] and our results are almost the same as theirs; **1** is monoclinic with space group $P2_1/c$ at 293 K. The experimental conditions and crystallographic data are given elsewhere [16]. Fig. 1 shows a projection of the unit cell along [100] onto the *bc* plane. The crystal consists of isolated $CdBr_4$ tetrahedra, piperazinium cations, and water molecules. The Br(1), Br(3), and Br(4) atoms form hydrogen bonds with $=NH_2$ groups of the cations, and Br(2) with a water molecule.

Piperazinium tetraiodocadmate(II), $[C_4H_{12}N_2]CdI_4$ (**2**)

The structure of **2** is orthorhombic with space group $P2_12_12_1$ at 293 K; the lattice constants *etc.* are listed in Table 1. Table 2 lists the positional coordinates and equivalent isotropic thermal parameters U_{eq} [16]. Intramolecular bond distances

Table 1. Experimental conditions for the crystals structure determinations and crystallographic data of piperazinium tetraiodocadmate(II) $[C_4H_{12}N_2]CdI_4$ (**2**), diffractometer Stoe IPDS; wavelength 71.073 pm (Mo- K_α), monochromator: graphite (002). **2**: $C_4H_{12}CdI_4N_2$, $M = 708.18$.

Crystal size [mm ³]	0.1 × 0.1 × 0.15
Temperature [K]	293(2)
Absorption coeff. [mm ⁻¹]	10.003
θ -Range for data collected	$2.28^\circ \leq \theta \leq 29.99^\circ$
Index ranges	$-12 \leq h \leq 12$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Space group	$P2_12_12_1$
Lattice parameters: <i>a</i> [pm]	903.2(5)
<i>b</i> [pm]	1226.3(6)
<i>c</i> [pm]	1307.9(7)
$V \times 10^{-6}$ [pm ³]	1448.6(13)
Formula units <i>Z</i>	4
ρ_{cal} [Mg m ⁻³]	3.247(3)
$F(000)$	1240
Reflections collected	17630
Independent reflections	4231 [$R(int) = 0.0277$]
Data ($I > 2\sigma(I)$)	4029
Restraints / parameters	0 / 113
Goodness of fit <i>S</i> (obs./all)	0.969 / 0.982
Final $R(I > 2\sigma(I))$	$R_1 = 0.0235$, $wR_2 = 0.0624$
R (all data)	$R_1 = 0.0258$, $wR_2 = 0.0649$
Largest diff. (peak, hole) [$10^{-6}e(pm^3)$]	1.212 and -1.001
Max. and min. trans.	0.001 and 0.000
Extinction coeff.	0.0050(1)
Flack parameter	$-0.01(5)$
Point positions	all atoms in 4a

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq} [$10^{-1}pm^2$] for **2**, $[C_4H_{12}N_2]CdI_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The temperature factor has the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. The data for **2**, anisotropic displacement parameters U_{ij} , and atomic coordinates for hydrogen atoms are given in [16].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cd	2647.7(4)	391.5(3)	908.8(3)	41.1(1)
I(1)	2586.0(4)	1481.9(3)	2768.7(3)	40.9(1)
I(2)	2414.1(6)	1743.4(3)	$-772.7(3)$	53.9(1)
I(3)	5284.0(4)	$-825.6(3)$	961.4(3)	44.0(1)
I(4)	383.0(4)	$-1152.4(3)$	934.5(3)	41.0(1)
N(1)	5833(5)	$-144(4)$	$-1650(4)$	41(1)
N(4)	9002(5)	$-211(5)$	$-1499(4)$	45(1)
C(2)	6705(7)	$-987(5)$	$-2204(4)$	42(1)
C(3)	8103(7)	$-1231(5)$	$-1636(5)$	49(1)
C(5)	8150(6)	646(5)	$-954(5)$	42(1)
C(6)	6710(7)	876(5)	$-1515(5)$	45(1)

and angles are given in Table 3. Fig. 2 shows a projection of the unit cell along [100] onto the *bc*

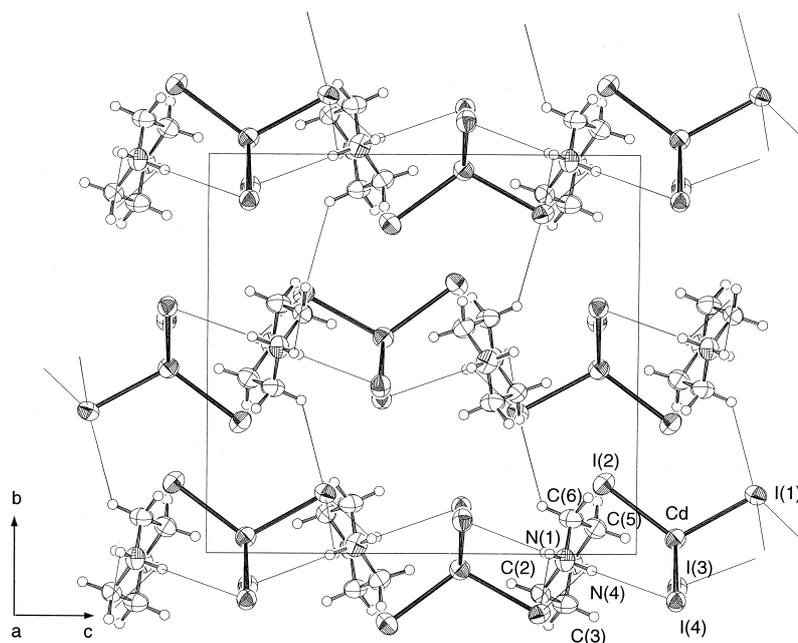


Fig. 2. The projection of the unit cell of piperazinium tetraiodocadmate(II) (**2**) along [100] onto the *bc* plane. Hydrogen bonds are shown with thin lines.

Table 3. Bond lengths [pm], bond angles [°], and hydrogen bond scheme for **2**, $C_4H_{12}CdI_4N_2$. The hydrogen atoms have been determined in the least-squares refinements of the structures by fixing the bond lengths of X-H and bond angles with the atoms involved.

Connection	<i>d</i>	Connection	Angle
Cd-I(1)	277.7(1)	I(1)-Cd-I(2)	114.02(4)
Cd-I(2)	276.2(1)	I(1)-Cd-I(3)	104.55(2)
Cd-I(3)	281.1(1)	I(1)-Cd-I(4)	107.57(2)
Cd-I(4)	278.7(1)	I(2)-Cd-I(3)	113.76(2)
N(1)-C(6)	149.2(8)	I(2)-Cd-I(4)	111.18(3)
N(1)-C(2)	148.8(7)	I(3)-Cd-I(4)	105.11(4)
N(4)-C(3)	148.8(8)	C(2)-N(1)-C(6)	111.0(5)
N(4)-C(5)	148.5(7)	C(3)-N(4)-C(5)	112.2(4)
C(2)-C(3)	151.6(8)	N(1)-C(2)-C(3)	110.3(5)
C(5)-C(6)	152.0(8)	N(4)-C(3)-C(2)	110.1(5)
		N(4)-C(5)-C(6)	110.0(5)
		N(1)-C(6)-C(5)	110.8(5)

Connection	<i>d</i> (H...I)	<i>d</i> (N/C...I)	Angle
N(1)-H(11)...I(3)	267.1(5)	355.1(6)	165.8(5)
N(1)-H(12)...I(1) ^{#1}	298.0(5)	357.9(5)	125.6(5)
N(4)-H(41)...I(4) ^{#2}	292.8(6)	360.8(6)	133.7(5)
N(4)-H(41)...I(1) ^{#3}	305.9(5)	358.4(3)	119.1(5)
N(4)-H(42)...I(3) ^{#3}	272.1(6)	361.4(6)	172.4(5)
C(6)-H(62)...I(1) ^{#4}	301.7(6)	371.6(7)	130.0(6)

^{#1} $-x + 1/2, -y, z - 1/2$; ^{#2} $x + 1, y, z$; ^{#3} $-x + 3/2, -y, z - 1/2$; ^{#4} $x + 1/2, -y + 1/2, -z$.

plane. The crystal consists of isolated CdI_4 tetrahedra and piperazinium cations. In comparison with

the structure of **1**, the alternate sheet structure which consists of cations and anions combined with hydrogen bonds of N-H...I type is much more dominant. There is a short interionic contact C(6)-H(62)...I(1) between these layers. The result of ^{127}I NQR measurement shows the hydrogen bonds of N-H...I to be considerably strong. This observation is also supported by considering the positive charges on the hydrogen atoms of =NH₂ groups which were estimated by MO calculation [17].

The results of MO calculations show that the optimized structure of the $[C_4H_{12}N_2]^{2+}$ cation (D_{3d} symmetry with $d(C-C) = 152.2$ pm, $d(C-N) = 152.7$ pm, $\angle(C-N-C) = 109.3^\circ$, and $\angle(N-C-C) = 112.3^\circ$) is more stable by 483.99 and 352.47 kJ/mol than the structures of cations in **1** and in **2**, respectively [18]. On the other hand, the optimized structures of the $[CdBr_4]^{2-}$ and $[CdI_4]^{2-}$ anions have almost the same formation energy as the structures of the anions in **1** and **2**, respectively. These results show that the $[C_4H_{12}N_2]^{2+}$ cations must be affected by the crystal field.

Bis(trimethylsulphonium)tetrabromocadmate(II), $[(CH_3)_3S]_2CdBr_4$ (**3**)

The powder diffraction pattern was analyzed by the Rietveld method using the program RIETAN-

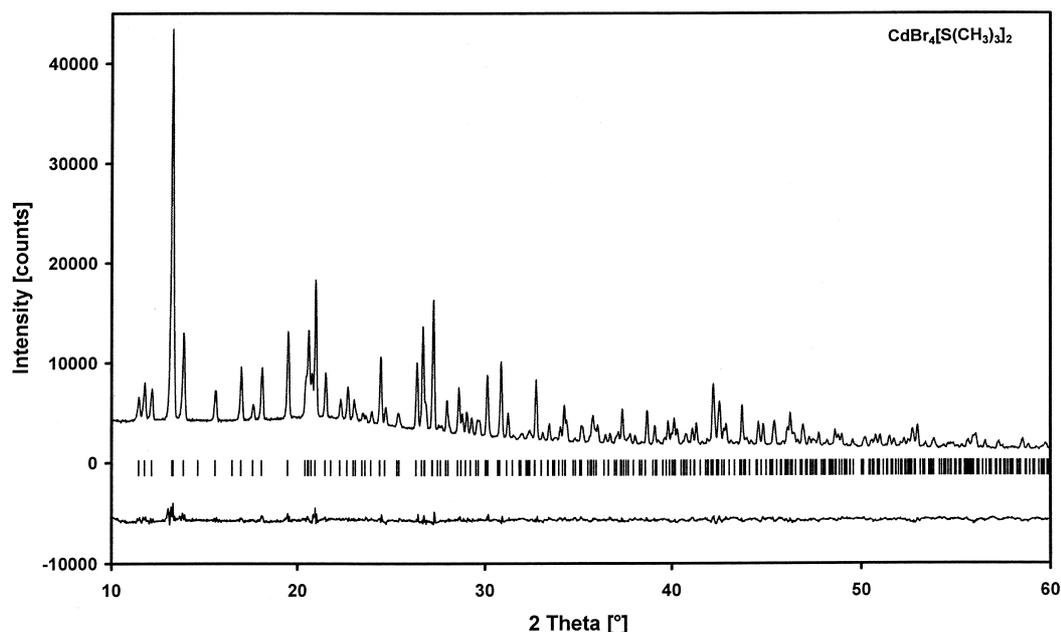


Fig. 3. Final difference plot of the Rietveld analysis of *bis*-trimethylsulphonium tetrabromocadmate(II) (**3**). In the upper portion the observed data are shown by dots; the calculated patterns are given by the solid lines. The lower parts are plots of the difference.

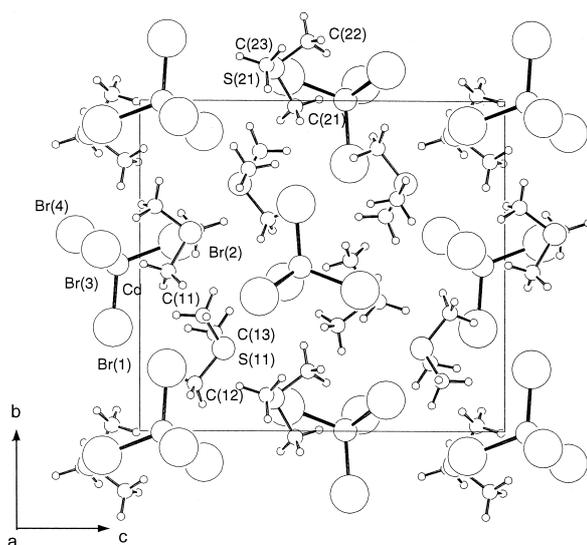


Fig. 4. The projection of the unit cell of **3** along [100] onto the *bc* plane.

97 [13]. Atomic positions of the $[(\text{CH}_3)_3\text{S}]^+$ cation were estimated by energy minimization. Two cations have been placed in the cavities of the $[\text{CdBr}_4]^{2-}$ framework. Trial packings were generated systematically by varying the orientation of the cations. 20 unique low energy structures

remained after energy minimization, which were further ranked by their similarity with the X-ray data [14]. Fig. 3 shows the final best-fit profile together with the difference between the raw data and the best-fit. Fig. 4 shows the crystal structure of **3**. The crystallographic data and experimental details are listed in Table 4, the positional and thermal parameters B_{iso} in Table 5, and the structural parameters (some bond distances and angles) in Table 6 [16]. The structure of **3** is orthorhombic with space group $P2_12_12_1$ at 293 K. The crystal consists of isolated CdBr_4 tetrahedra and trimethylsulphonium cations. The Br(2) and Br(3) atoms have interionic contacts with the hydrogen atoms of the $-\text{C}(11)\text{H}_3$ and $-\text{C}(12)\text{H}_3$ groups and with the S(11) atom. Although a first-order phase transition takes place at $T = 304$ K [8], there are no distinct features in the crystal structure at 293 K. The results of MO calculation show that the optimized structure of the $[(\text{CH}_3)_3\text{S}]^+$ cation (C_{3v} symmetry with $d(\text{C}-\text{S}) = 180.3$ pm and $\angle(\text{C}-\text{S}-\text{C}) = 103.5^\circ$) is more stable by 44.72 and 42.80 kJ/mol than the structures of the $[(\text{CH}_3)_3\text{S}(11)]^+$ and $[(\text{CH}_3)_3\text{S}(21)]^+$ cations in the crystal of (**3**), respectively [19]. On the other hand, the optimized structure of the $[\text{CdBr}_4]^{2-}$ anion has almost the same energy as the structure of

Table 4. Experimental conditions for the crystal structure determination and crystallographic data of *bis*-trimethylsulphonium tetrabromocadmate(II) [(CH₃)₃S]₂CdBr₄ (**3**). Refinement method: RIETAN-97 + energy minimization, Diffractometer: Stoe-Stadi P, Measurement method: transmission Debye-Scherrer Mode, Detector: Stoe linear PSD, Wavelength: 154.0598 pm (Cu-K_α), Radiation-polarization ratio: 0.788993, Monochromator: Ge(111), C₆H₁₈Br₄CdS₂: MW = 586.35.

Temperature [K]	293(2)
Absorption coeff. [mm ⁻¹]	11.756
2θ-Range for data collection	10.00° ≤ 2θ ≤ 89.98°
Increment of data collection	0.02°
Space group	P2 ₁ 2 ₁ 2 ₁
Lattice parameters: <i>a</i> [pm]	911.3(1)
<i>b</i> [pm]	1329.2(2)
<i>c</i> [pm]	1454.7(2)
V × 10 ⁻⁶ [pm ³]	1762.1(5)
Formula units Z	4
ρ _{cal} [Mg m ⁻³]	2.210(1)
Reflections collected	4000
Refinement points	2501
R Values	R _{wp} = 0.0380, R _p = 0.0288, R _R = 0.0955, R _c = 0.0163, R _I = 0.0111, R _F = 0.0054
Parameters	93
Restraints	66
Goodness of fit on F ²	S = 2.34
Durbin-Watson statistic	d = 0.4411
Point positions	all atoms in 4a

the anion in the crystal of **3**. These results show that the [(CH₃)₃S]⁺ cations must be affected by the crystal field, although there remains an uncertainty of the atomic positions associated with the powder method.

1, **2**, and **3** have isolated [CdX₄]²⁻ anions, but not a layered complex anion structure. The number of hydrogen bonds must be an important factor to form layered complex anions. In compounds with layered complex anions, [H₃N(CH₂)₃NH₃]CdBr₄ and [C₃H₇NH₃]₂CdBr₄, hydrogen atoms of -NH₃ groups make three contacts with the layered anions [6]. In **1** and **2**, two hydrogen atoms attached to each nitrogen atom of a piperazinium cation can participate in two strong hydrogen bonds at most,

Table 5. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters B_{iso} [10⁻²nm²] for **3**. Atomic coordinates for hydrogen atoms are given in [16].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B _{iso}
Cd(1)	692(9)	4966(6)	4382(6)	0.600
Br(1)	420(15)	6888(8)	4266(9)	0.900
Br(2)	170(12)	4264(9)	6025(8)	0.900
Br(3)	3326(13)	4510(9)	3946(7)	0.900
Br(4)	8906(13)	4062(10)	3262(8)	0.900
S(11)	1231(39)	7509(24)	7277(20)	1.300
C(11)	2083(78)	6524(50)	6725(57)	1.300
C(12)	1236(97)	8577(50)	6500(56)	1.300
C(13)	9393(89)	7057(68)	7037(57)	1.300
S(21)	3865(32)	8999(25)	8634(18)	1.300
C(21)	3484(80)	176(56)	9243(54)	1.300
C(22)	3647(89)	8190(55)	9595(53)	1.300
C(23)	5753(73)	8917(73)	8456(51)	1.300

Table 6. Bond lengths (in pm) and bond angles (°) for **3**.

Connection	<i>d</i>	Connection	Angle
Cd-Br(1)	257.2(13)	Br(1)-Cd-Br(2)	113.4(5)
Cd-Br(2)	260.9(15)	Br(1)-Cd-Br(3)	108.0(5)
Cd-Br(3)	255.6(14)	Br(1)-Cd-Br(4) ^{#1}	111.0(5)
Cd-Br(4) ^{#1}	259.8(15)	Br(2)-Cd-Br(3)	108.3(5)
S(11)-C(11)	173(8)	Br(2)-Cd-Br(4) ^{#1}	107.1(5)
S(11)-C(12)	182(8)	Br(3)-Cd-Br(4) ^{#1}	108.9(5)
S(11)-C(13) ^{#1}	181(9)	C(11)-S(11)-C(12)	107(4)
S(21)-C(21) ^{#2}	183(9)	C(11)-S(11)-C(13)	94(4)
S(21)-C(22)	177(8)	C(12)-S(11)-C(13) ^{#1}	98(4)
S(21)-C(23)	174(7)	C(21) ^{#2} -S(21)-C(22)	97(3)
		C(21) ^{#2} -S(21)-C(23)	108(4)
		C(22)-S(21)-C(23)	101(4)

^{#1} *x* - 1, *y*, *z*; ^{#2} *x*, 1 + *y*, *z*.

and there is no hydrogen atom in **3** to form hydrogen bonds.

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- [19] The formation energies were calculated by using MOPAC ver. 2 with PM3; the formation energy of [(CH₃)₃S(11)]⁺ with the atomic coordinates in **1** is 671.58 kJ/mol, 669.66 kJ/mol for [(CH₃)₃S(21)]⁺, and 626.86 kJ/mol for its optimized structure, respectively; -706.49 kJ/mol for [CdBr₄]²⁻ with the atomic coordinates in **1** and -708.40 kJ/mol for its optimized structure.