Isolated versus Condensed Anion Structure V: X-ray Structure Analysis and ^{81}Br NQR of *t*-butylammonium tribromocadmate(II)-1/2 water, *i*-propylammonium tribromocadmate(II), and *tris*-trimethylammonium heptabromodicadmate(II)

Hideta Ishihara, Keizo Horiuchi[a], Shi-qi Dou[b], Thorsten M. Gesing[b], J.-Christian Buhl[b]
Helmut Paulus[c], Ingrid Svoboda[c], and Hartmut Fuess[c]

Faculty of Culture and Education, Saga University, Saga 840-8502, Japan
[a] Faculty of Science, University of the Ryukyus, Okinawa 903-0213, Japan
[b] Institut für Mineralogie, Universität Hannover, Welfengarten 1, 30167 Hannover
[c] Materials Science, University of Technology, Petersenstraße 23, 64287 Darmstadt

Reprint requests to Prof. H. I.; E-mail: isiharah@cc.saga-u.ac.jp

Z. Naturforsch. **54a,** 628 – 636 (1999); received September 6, 1999

The crystal structures of the condensed bromocadmate anions with chains built of $[CdBr_3]_\infty$ were determined by X-ray structure analysis at 300 K. In addition, the temperature dependence of the ^{81}Br NQR frequencies was observed. $[(t\text{-}C_4H_9NH_3)CdBr_3]_2\text{-}H_2O$ (**1**) crystallizes with a double Br bridged chain (monoclinic, P2/c, $Z = 4$, $a = 1963.4(8)$, $b = 887.7(4)$, $c = 1432.1(6)$ pm, and $\beta = 110.66(2)°$). Six ^{81}Br NQR lines are observed at temperatures between 77 and 330 K. $(i\text{-}C_3H_7NH_3)CdBr_3$ (**2**) crystallizes with a triple Br bridged chain (orthrhombic, Pbca, $Z = 8$, $a = 1975.4(6)$, $b = 1415.8(4)$, $c = 690.1(2)$ pm). (**2**) shows three ^{81}Br NQR lines at temperatures between 77 and 193 K. A phase transition occurs at 224 K. The structure of $[(CH_3)_3NH]_3Cd_2Br_7]$ (**3**) was redetermined. (**3**) consists of a triple Br bridged chain and a discrete $[CdBr_4]$ tetrahedron (hexagonal, $P6_3mc$, $Z = 8$, $a = 1483.5(2)$, $c = 685.7(5)$ pm). The structure of (**3**) is identical to the one reported by Daoud, Perret, and Dusausoy, Acta Crystallogr., **B35,** 2718 (1979). Three ^{81}Br NQR lines are observed at temperatures between 77 and 243 K.

Introduction

In recent studies of complex salts with bromocadmate anions by X-ray diffraction and ^{79,81}Br NQR, a variety of polymer anionic structures [1–6] and an isolated $[CdBr_4]^{2-}$ tetrahedron [7, 8] were found. Isolated complex anions are reported to be $[CdX_4]^{2-}$, $[CdX_6]^{4-}$ [1, 5], or $[CdX_5]^{3-}$ [9, 10]. On the other hand, complex anions with other compositions show a tendency to form condensed structures, especially $[CdX_3]^-$ is found in chain structures [3, 4]. In addition, the size and shape of the cation affect the shape of the anions, for example, the layered $[CdBr_4]$ unit exists in $[H_3N(CH_2)_3NH_3]CdBr_4$ and in $[n\text{-}C_3H_7NH_3]_2CdBr_4$ [7], and double chains of octahedra $[CdBr_6]$ exist in $[H_2NNH_3]CdBr_3$ and $[NH_4]CdBr_3$ complexes [3]. We determined the crystal structures and observed Br NQR of the compounds with the one-dimensional anion chains.

Experimental

$[(t\text{-}C_4H_9NH_3)CdBr_3]_2\text{–}H_2O$ (**1**) was prepared by the following two methods: (a) 0.2 mol of *t*-butylammonium bromide was added to an H_2O solution with 0.1 mol of $CdBr_2\text{-}4H_2O$. The water solvent was evaporated by P_2O_5 in a dessicator at room temperature. Colorless needles crystallized from the solution. (b) 0.1 mol of *t*-butylammonium bromide was added to an H_2O solution with 0.1 mol of $CdBr_2\text{-}4H_2O$. The water solvent was evaporated by heating the solution at about 70 °C. Colorless needles crystallized when the hot concentrated solution was cooled down to room temperature. $(i\text{-}C_3H_7NH_3)CdBr_3$ (**2**) was prepared by the following method: 0.1 mol of *i*-propylammonium bromide was added to an H_2O solution with 0.1 mol of $CdBr_2\text{-}4H_2O$. The water solvent was evaporated by P_2O_5 in a dessicator or by heating. Colorless needles were obtained from the solution. $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**) was prepared by the following method: 0.3 mol of trimethylammonium bromide was added to a hydrobromic acid solution of 0.2 mol of $CdBr_2$. Excess of HBr is necessary to obtain (**3**). The solvent was removed by P_2O_5 in a dessicator and colorless prisms were obtained.

The structures were determined using four circle X-ray diffractometers, Stoe-Stadi-4 for (**1**) and (**2**), and Enraf Nonius CAD4 for (**3**). From the measured intensities corrected for Lorentz-polarization and absorption ef-

0932-0784 / 99 / 1000-0628 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

Table 1. Experimental conditions for the crystal structure determinations and crystallographic data of *t*-butylammonium tribromocadmate(II)-1/2 water $[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**), *i*-propylammonium tribromocadmate(II) $(i\text{-}C_3H_7NH_3)\,CdBr_3$ (**2**), and *tris*-trimethylammonium heptabromodicadmate(II) $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**). Diffractometer: Stoe-Stadi 4 for (**1**) and (**2**), Enraf Nonius CAD4 for (**3**). Wavelength: 71.069 pm (MoKα), Monochromator: Graphite(002); scan 2ω/θ. (**1**): $C_8H_{26}Br_6Cd_2N_2O$, MW = 870.62, (**2**): $C_3H_{10}Br_3CdN$, MW = 412.24 (**3**): $C_9H_{30}Br_7Cd_2N_3$, MW = 964.59.

Compound	(**1**)	(**2**)	(**3**)
Crystal size/(mm^2)	1.0×0.45×0.3	1.5×0.4×0.2	0.55×0.075×0.062
Temperature/K	300(2)	300(2)	299(2)
Absorption coeff./mm^{-1}	11.756	14.219	12.34
θ range (/°) for data collection	$2.22 \le \theta \le 22.46$	$2.06 \le \theta \le 22.46$	$1.59 \le \theta \le 29.94$
Index ranges	$-20 \le h \le 21$, $0 \le k \le 9$, $-15 \le l \le 1$	$0 \le h \le 21$, $-15 \le k \le 3$, $0 \le l \le 7$	$-18 \le h \le 20$, $-20 \le k \le 0$, $-9 \le l \le 1$
Lattice constants			
a/pm	1963.4(8)	1975.4(6)	1483.5(2)
b/pm	887.7(4)	1415.8(4)	1483.5(2)
c/pm	1432.1(6)	690.1(2)	685.7(2)
α/°	90.0	90.0	90.0
β/°	110.66(2)	90.0	90.0
γ/°	90.0	90.0	120.0
$V \times 10^{-6}$/pm^3	2336(2)	1930.1(10)	1306.9(5)
Space group	P2/c	Pbca	P6$_3$mc
Formular units Z	4	8	2
ρ_{cal}(Mg · m^{-3})	2.476	2.838	2.451
F(000)	1608	1504	892
Reflections collected	3204	1560	4125
Symmetry independent	3047	1252	762
[R_{int}]	0.0230	0.0722	0.0915
Data	3045	1251	762
Restraints	1	0	2
Parameters	178	74	46
Goodness of fit on F^2	1.052	1.122	1.070
Final $R(I>2\sigma(I))$	R_1=0.0387, wR_2=0.0990,	R_1=0.0825, wR_2=0.2138,	R_1=0.0401 wR_2=0.0926
R(all data)	R_1=0.0530, wR_2=0.1113,	R_1=0.0937, wR_2=0.2435,	R_1=0.0707 wR_2=0.1134
Large diff(peak, hole) $\times 10^{-6}$/(e · pm^{-3})	1.040 and −0.737	3.008 and −2.965	1.056 and −2.364
Max. and Min. Trans.	0.0570 and 0.0174	0.0564 and 0.0055	0.5356 and 0.4524
Extinction Coeff.	0.0038(2)	0.030(3)	0.0029(7)
Point positions	O(1) in 2e, O(2) in 2f, others in 4g	All atoms in 8c	All atoms in 12d

fects, the structures were solved by direct methods and Fourier syntheses, and refined by least-squares methods with the programs given in [11]. The ^{79,81}Br NQR spectra were recorded by an NQR spectrometer working with the superregenerative mode. The sample temperature was measured with a copper-constantan thermocouple and the frequencies were determined by counting techniques. DTA was measured by a home-made apparatus.

Results and Discussion

Crystal Structures

A) $[(t\text{-}C_4H_9NH_3)CdBr_3]_2\text{-}H_2O$ (**1**)

t-Butylammonium tibromocadmate(II)-1/2 water (**1**) is monoclinic with C^4_{2h}-P2/c at 300 K; the lattice constants and the experimental conditions are presented in Table 1 [12]. Table 2 gives the positional coordinates and equivalent isotropic displacement parameters. Intramolecular bond distances and angles in the anions are given in Table 3. In Fig. 1, a formula unit is drawn with numbering of atoms and thermal ellipsoids. Two Cd atoms, six Br atoms, two *t*-butylammonium ions, and two water molecules with half an occupancy exist as crystallographically inequivalent units in the unit cell. Figure 2 shows the projection of the unit cell along [010] onto the *ac* plane. The crystal structure consists of edge sharing $[CdBr_5]$ trigonal bipyramids which form chains running parallel to [001]. A similar chain was found in $[4\text{-}(CH_3)C_5H_4NH]CdBr_3$ [4]. Br(2) and Br(5) are terminal atoms. *t*-Butylammonium cations are located between $[CdBr_3]_\infty$ chains. Two oxygen atoms of water molecules

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**), $(i\text{-}C_3H_7NH_3)CdBr_3$ (**2**), and $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**). U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij}. 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 in which atoms are involved. The atomic coordinate of hydrogen atoms are given in [12].

Atom	x	y	z	$U_{eq} \times 10^{-1}$/ pm^2
		$[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**)		
Cd(1)	0.02010(4)	0.12396(7)	0.62265(6)	54(0)
Cd(2)	0.47740(4)	0.37987(7)	0.10346(5)	53(0)
Br(1)	0.07146(6)	–0.1312(1)	0.59239(7)	59(0)
Br(2)	0.06591(6)	0.3904(1)	0.61774(8)	60(0)
Br(3)	–0.09965(5)	0.1065(1)	0.66251(7)	55(0)
Br(4)	0.40110(5)	0.4004(1)	0.24337(7)	53(0)
Br(5)	0.43414(6)	0.1129(1)	0.05314(8)	62(0)
Br(6)	0.42734(6)	0.6340(1)	0.02252(7)	56(0)
O(1)	0.0000	–0.3054(11)	0.7500	66(3)
O(2)	0.5000	0.8106(12)	0.2500	69(3)
N(1)	0.3949(4)	0.0031(9)	0.2971(7)	63(2)
N(2)	0.1056(4)	0.4988(9)	0.3971(6)	62(2)
C(11)	0.3139(5)	–0.0334(12)	0.2545(8)	58(3)
C(12)	0.2865(6)	0.0089(14)	0.1460(9)	80(3)
C(13)	0.3059(8)	–0.1991(14)	0.2703(11)	102(5)
C(14)	0.2796(6)	0.0603(15)	0.3141(10)	86(4)
C(21)	0.1852(5)	0.4545(12)	0.4330(8)	58(3)
C(22)	0.1905(7)	0.2913(14)	0.4630(10)	95(4)
C(23)	0.2110(6)	0.4756(16)	0.3479(10)	91(4)
C(24)	0.2239(7)	0.5555(17)	0.5189(11)	108(5)
		$[i\text{-}C_3H_7NH_3]\ CdBr_3$ (**2**)		
Cd(1)	0.41856(5)	0.24998(6)	0.4471(2)	38(1)
Br(1)	0.42254(8)	0.4073(1)	0.6960(2)	44(1)
Br(2)	0.51355(8)	0.1710(1)	0.6902(2)	42(1)
Br(3)	0.32477(8)	0.3238(1)	0.2006(2)	40(1)
N(1)	0.5896(6)	0.039(1)	0.312(2)	59(4)
C(1)	0.639(1)	0.115(1)	0.292(2)	73(6)
C(2)	0.694(1)	0.097(2)	0.433(3)	92(7)
C(3)	0.660(1)	0.123(2)	0.091(3)	102(7)
		$[(CH_3)_3NH]_3Cd_2Br_7$ (**3**)		
Cd(1)	0.0000	0.0000	1.2773(2)	35(1)
Cd(2)	0.3333	0.6667	0.6125(3)	46(1)
Br(1)	–0.0847(1)	0.0847(1)	1.0266(2)	39(1)
Br(2)	0.3333	0.6667	0.2265(4)	44(1)
Br(3)	0.4288(1)	0.5712(1)	0.7245(3)	65(1)
N(1)	0.2080(5)	0.416(1)	1.079(2)	54(3)
C(1)	0.1748(6)	0.350(1)	0.905(3)	67(5)
C(2)	0.282(1)	0.398(1)	1.198(3)	80(4)

Table 3. Bond distances (pm) and angles (°) in anions of $[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**), $[i\text{-}C_3H_7NH_3]\ CdBr_3$ (**2**), and $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**).

$[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**)

Connection	d(Cd-Br)/ pm	Connection	∠(Br-Cd-Br)/°
Cd(1)-Br(1)	257.7(1)	Br(1)-Cd(1)-Br(2)	130.56(5)
Cd(1)-Br(2)	254.0(2)	Br(1)-Cd(1)-Br(3)	114.85(4)
Cd(1)-Br(3)	261.2(2)	Br(2)-Cd(1)-Br(3)	114.58(4)
Cd(2)-Br(4)$^{\#1}$	261.6(2)	Br(4)$^{\#1}$-Cd(2)-Br(5)	114.73(4)
Cd(2)-Br(5)	253.5(2)	Br(4)$^{\#1}$-Cd(2)-Br(6)	114.08(4)
Cd(2)-Br(6)	256.7(1)	Br(5)-Cd(2)-Br(6)	131.03(5)

Symmetry coordinate #1: $-x+1$, y, $-z+1/2$.

$[i\text{-}C_3H_7NH_3]\ CdBr_3$ (**2**)

Connection	d(Cd-Br)/ pm	Connection	∠(Br-Cd-Br)/°
Cd(1)-Br(1)	281.4(2)	Br(1)-Cd(1)-Br(2)	86.02(5)
Cd(1)-Br(1)$^{\#2}$	282.2(2)	Br(1)-Cd(1)-Br(3)	95.56(5)
Cd(1)-Br(2)	275.5(2)	Br(1)-Cd(1)-Br(1)$^{\#2}$	176.79(7)
Cd(1)-Br(2)$^{\#2}$	281.4(2)	Br(1)-Cd(1)-Br(2)$^{\#2}$	92.93(5)
Cd(1)-Br(3)	272.4(2)	Br(1)-Cd(1)-Br(3)$^{\#1}$	86.04(5)
Cd(1)-Br(3)$^{\#1}$	275.3(2)	Br(2)-Cd(1)-Br(3)	178.42(5)
		Br(2)-Cd(1)-Br(1)$^{\#2}$	91.98(5)
		Br(2)-Cd(1)-Br(2)$^{\#2}$	95.22(6)
		Br(2)-Cd(1)-Br(3)$^{\#1}$	85.27(6)
		Br(3)-Cd(1)-Br(1)$^{\#2}$	86.44(5)
		Br(3)-Cd(1)-Br(2)$^{\#2}$	84.70(5)
		Br(3)-Cd(1)-Br(3)$^{\#1}$	94.84(6)
		Cd(1)-Br(1)-Cd(1)$^{\#1}$	75.51(4)
		Cd(1)-Br(2)-Cd(1)$^{\#1}$	76.57(6)
		Cd(1)-Br(3)-Cd(1)$^{\#2}$	78.10(5)

Symmetry code #1: x, $-y+1/2$, $z+1/2$; #2: x, $-y+1/2$, $z-1/2$.

$[(CH_3)_3NH]_3Cd_2Br_7$ (**3**)

Connection	d(Cd-Br)/ pm	Connection	∠(Br-Cd-Br)/°
Cd(1)-Br(1)$^{\#1}$×3	276.7(2)	Br(1)-Cd(1)-Br(1)$^{\#1}$	94.28(3)
Cd(1)-Br(1)$^{\#5}$×3	277.2(2)	Br(1)-Cd(1)-Br(1)$^{\#3}$	179.86(6)
Cd(2)-Br(3) ×3	257.0(2)	Br(1)-Cd(1)-Br(1)$^{\#4}$	94.28(3)
Cd(1)-Br(2)	264.6(4)	Br(1)-Cd(1)-Br(1)$^{\#5}$	85.63(5)
		Br(1)-Cd(1)-Br(1)$^{\#6}$	85.63(5)
		Br(2)-Cd(2)-Br(3) ×3	107.40(7)
		Br(3)-Cd(2)-Br(3)$^{\#8}$×3	111.46(7)

Symmetry code #1: y, $-x+y$, $z+1/2$; #3: $-x$, $-y$, $z+1/2$; #4: $x-y$, x, $z+1/2$; #5: $-y$, $x-y$, z; #6: $-x+y$, $-x$, z; #8: $-y+1$, $x-y+1$, z.

are located at 2f and 2e positions with half an occupancy, and they are in the hollows of anion chains, which consist of two $[CdBr_5]$ units. Two water molecules form hydrogen bonds with both anions and cations; O(1)···Br(1), O(2)···Br(6)$^{\#1}$, N(1)···O(2)$^{\#2}$, and N(2)···O(1)$^{\#4}$, as shown in Table 4. All Br atoms are connected to cations or water molecules through hydrogen bonds as shown in Figure 2.

B) $(i\text{-}C_3H_7NH_3)CdBr_3$ (2)

i-Propylammonium tribromocadmate(II) is orthorhombic D_{2h}^{15}-Pbca at 300 K; the lattice constants etc. are shown in Table 1 [12]. Table 2 gives the positional coordinates and equivalent isotropic displacement parameters. Intramolecular bond distances and angles in anions are given in Table 3. In Fig. 3, a formula unit is drawn

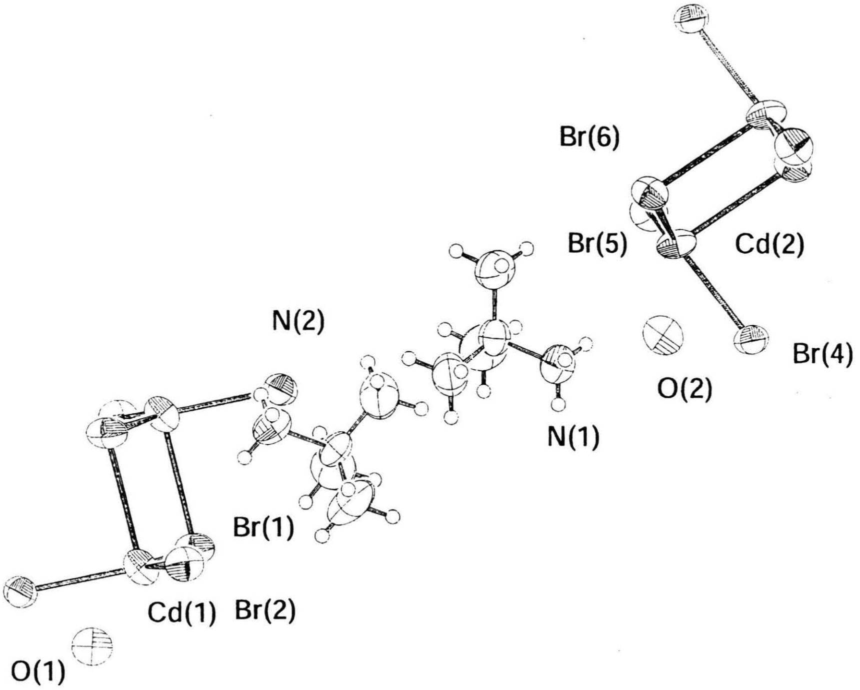

Fig. 1. The formula unit of *t*-butylammonium tribromocadmate(II)-1/2 water (**1**) with the numbering of atoms. Anions are shown as a part of bridged structures. The thermal ellipsoids (50% electrons as counter) are shown, too.

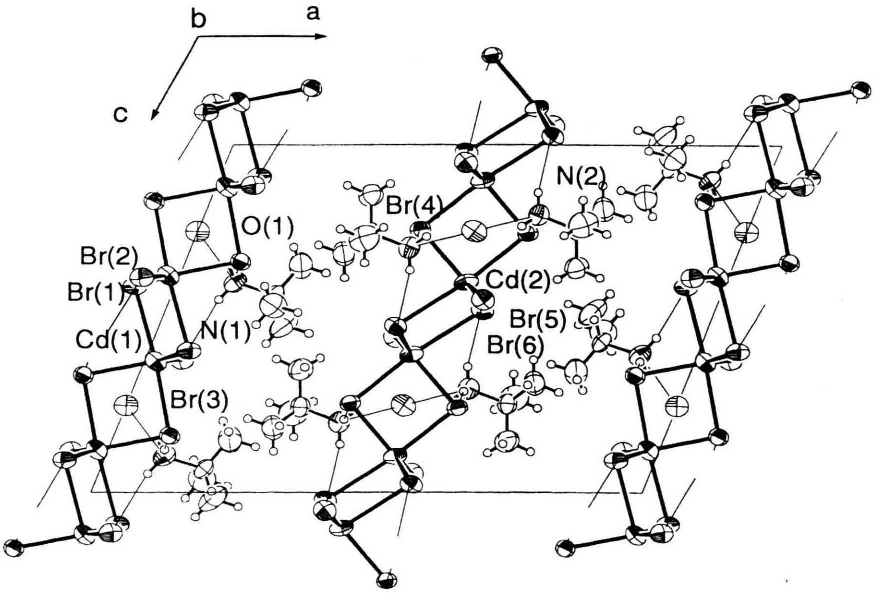

Fig. 2. The projection of the unit cell of (**1**) along [010] onto the *ac* plane. Hydrogen bonds are shown by thin lines.

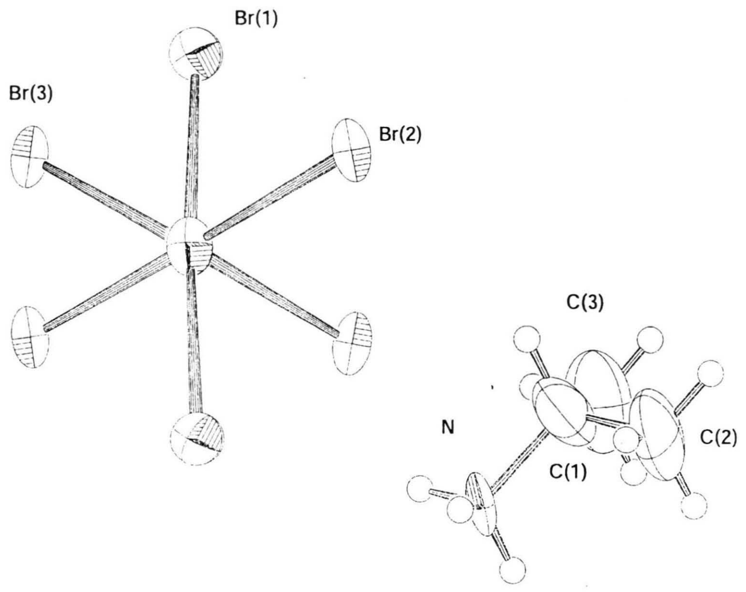

Fig. 3. The formula unit of *i*-propylammonium tribromocadmate(II) (**2**) with the numbering of atoms. The thermal ellipsoids (50% electrons as counter) are shown, too.

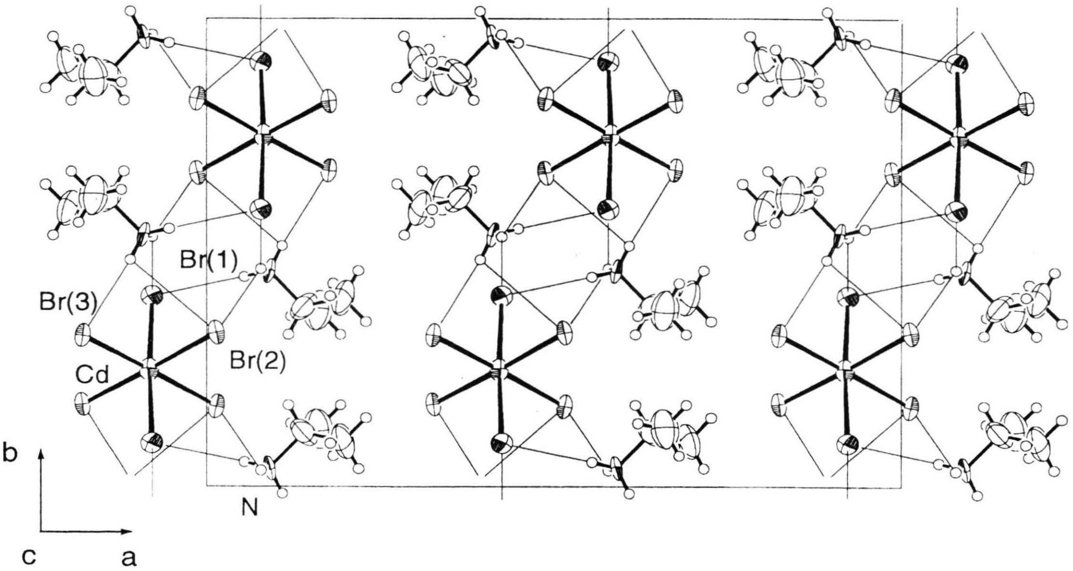

Fig. 4. The projection of the unit cell of (**2**) along [001] onto the *ab* plane. Hydrogen bonds are shown by thin lines.

with numbering of atoms and thermal ellipsoids. One Cd atom, three Br atoms, and one *i*-propylammonium ion as crystallographically inequivalent unit are in the unit cell. Figure 4 shows the projection of the unit cell along [001] onto the *ab* plane. The $[CdBr_3]_\infty$ chain with triple Br bridges which consist of face-connected $[CdBr_6]$ octahedra is running along the *c* axis. The cations are located between these chains and are connected to anions through hydrogen bonds as shown in Fig. 4 and Table 4, which lead to layered packing parallel to the *bc* plane.

C) $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**)

The crystal structure of *tris*-trimethylammonium heptabromodicadmate(II) has been reported by Daoud et al. [13]. Our results are similar to the former ones. (**3**) is hex-

Table 4. Bond distances (pm) and bond angles (°) in cations and hydrogen bonds in $[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**), $[i\text{-}C_3H_7NH_3]CdBr_3$ (**2**), and $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**).

$[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**)

Connection	*d*/pm	Connection	Angle/°
N(1)-C(11)	152(1)	C(12)-C(11)-C(13)	112(1)
N(2)-C(21)	152(1)	C(12)-C(11)-C(14)	112(1)
C(11)-C(12)	150(2)	C(13)-C(11)-C(14)	111(1)
C(11)-C(13)	150(2)	C(12)-C(11)-N(1)	107.7(8)
C(11)-C(14)	151(2)	C(13)-C(11)-N(1)	107.3(9)
C(21)-C(22)	150(2)	C(14)-C(11)-N(1)	105.6(8)
C(21)-C(23)	149(2)	C(23)-C(21)-C(24)	112(1)
C(21)-C(24)	150(2)	C(23)-C(21)-C(22)	110(1)
		C(24)-C(21)-C(22)	112(1)
		C(23)-C(21)-N(2)	107.4(8)
		C(24)-C(21)-N(2)	106.7(9)
		C(22)-C(21)-N(2)	107.8(9)

Hydrogen bond

Connection	*d*(O···Br, N···Br, N···O) /pm	*d*(H···Br, H···O) /pm	∠(O-H···Br, N-H···Br, N-H···O)/°
O(1)···Br(1)	341.9(5)		
O(2)-H(O21)···Br(6)$^{\#1}$	343.9(5)	246(6)	165(18)
N(1)-H(N11)···Br(5)$^{\#6}$	362.9(9)	274.8(9)	166.7(2)
N(1)-H(N12)···Br(4)	362.1(8)	273.9(8)	171.0(2)
N(1)-H(N13)···O(2)$^{\#2}$	294(1)	210(1)	156.0(2)
N(2)-H(N21)···Br(2)	364.0(9)	277.7(9)	163.8(2)
N(2)-H(N23)···Br(3)$^{\#5}$	359.9(8)	271.3(8)	173.5(1)
N(2)-H(N22)···O(1)$^{\#4}$	293(1)	207(1)	162.5(3)

Symmetry code #1: $-x+1, y, -z+1/2$; #2: $x, y-1, z$; #4: $-x, -y, -z+1$; #5: $-x, -y+1, -z+1$, #6: $x, -y, z+1/2$.

$[i\text{-}C_3H_7NH_3]CdBr_3$ (**2**)

Connection	*d*(C-C, N-C)/pm	Connection	∠(C-C-C, N-C-C)/°
N(1)-C(1)	146(2)	C(3)-C(1)-C(2)	116(2)
C(1)-C(2)	149(3)	N(1)-C(1)-C(2)	107(1)
C(1)-C(3)	145(3)	N(1)-C(1)-C(3)	110(2)

Hydrogen bond

Connection	*d*(N···Br) /pm	*d*(H···Br) /pm	∠(N-H···Br)/°
N(1)-H(N1)···Br(2)	354	290	130.5
N(1)-H(N2)···Br(3)$^{\#2}$	349	265	158.3
N(1)-H(N3)···Br(1)$^{\#1}$	348	267	152.2

Symmetry code #1: $x, -y+1/2, z-1/2$; #2: $-x+1, y-1/2, -z+1/2$.

$[(CH_3)_3NH]_3Cd_2Br_7$ (**3**)

Connection	*d*(C-C, N-C)/pm	Connection	∠(C-C-C, N-C-C)/°
N(1)-C(1)	147(2)	C(1)-N(1)-C(2) ×2	110.7(9)
N(1)-C(2) ×2	149(2)	C(2)-N(1)-C(2)$^{\#7}$	111(2)

Symmetry code #7: $-x+y, y, z$.

Table 4. (continued)

Hydrogen bond

Connection	*d*(N···Br) /pm	*d*(H···Br) /pm	∠(N-H···Br)/°,
N(1)-H(N1)···Br(2)$^{\#8}$	338	263	124.6
N(1)-H(N2)···Br(3)	380	308	122.8

Symmetry code #8: $-y+1, x-y+1, z+1$.

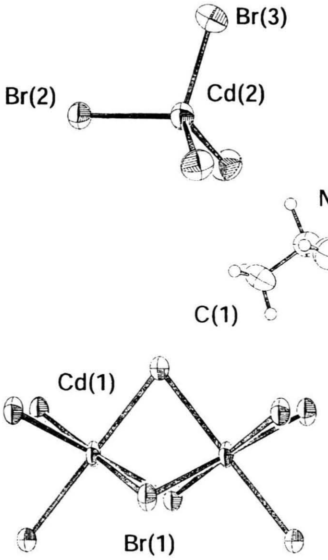

Fig. 5. The formula unit of *tris*-trimethylammonium heptabromodicadmate(II) (**3**) with the numbering of atoms. The thermal ellipsoids (50% electrons as counter) are shown, too.

agonal C_{6v}^4-$P6_3mc$ at 299 K; the lattice constants etc. are listed in Table 1. The atomic coordinates and the isotropic displacement parameters are listed in Table 2. The intramolecular bond distances and angles of anions are given in Table 3. In Fig. 5, the formula unit is drawn with the numbering of atoms and the thermal ellipsoids. The bond distances of Cd-Br bonds in the tetrahedral ion, *d*(Cd(2)-Br(3)) = 257.0 and *d*(Cd(2)-Br(2)) = 264.6 pm, disagree with the corresponding distances, 267.1 and 255.6 pm, reported in [13]. Figure 6 shows the projection of the unit cell along [001] onto the *ab* plane. The anions consist of a $[Cd(1)Br_3]_\infty$ chain running along the *c* axis, and a $[Cd(2)Br_4]$ tetrahedron. The hydrogen bonds are formed between cations and the $[Cd(2)Br_4]$ tetrahedron is shown in Figure 6.

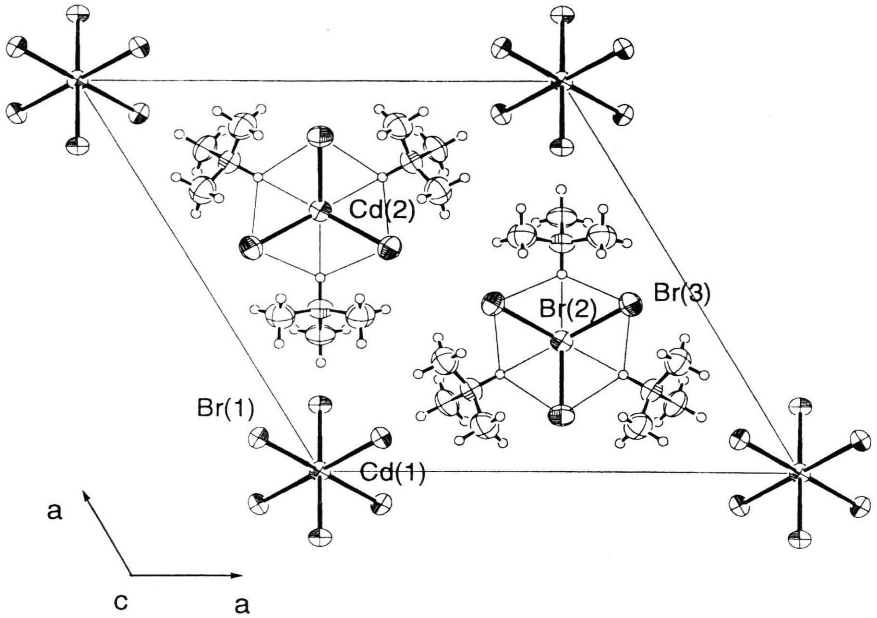

Fig. 6. The projection of the unit cell of (**3**) along [0001] onto the *ab* plane. Hydrogen bonds are shown by thin lines.

Nuclear Quadrupole Resonance (NQR) and Phase Transitions

The NQR frequencies of the title compounds at several temperatures are listed in Table 5. The temperature dependence of the ^{81}Br NQR frequencies of $[(t\text{-}C_4H_9NH_3)CdBr_3]_2\text{-}H_2O$ (**1**) is shown in Figure 7. Six NQR lines were observed at 77 K. Two high-frequency NQR lines are assigned to two terminal Br atoms and the other four lines to the bridged atoms. Two high-frequency lines disappear at about 286 K with increasing temperature. The disappearance of these two lines is probably due to the fluctuation of the electric field gradient at the Br atoms by cationic motion. The other four lines disappear with increasing temperature at about 333 K. There is a large heat anomaly at 335 K in the DTA curve on heating, which suggests probable dehydration. The disappearance of these four lines around 333 K can be ascribed to dehydration.

The temperature dependence of ^{81}Br NQR frequencies of $(i\text{-}C_3H_7NH_3)CdBr_3$ (**2**) is shown in Figure 8. Three NQR lines are observed at 77 K and disappear at 193 K with increasing temperature. In the DTA curve there is an anomaly at 224 K on heating. The disappearance of NQR lines far below the transition point is due to cationic motion. This motion probably affects the electric field gradients at Br sites through the hydrogen bonds.

Table 5. The ^{81}Br NQR frequencies of the title compounds at several temperatures.

Compound	ν/MHz (*T*/K)	ν/MHz (*T*/K)
$[(t\text{-}C_4H_9NH_3)CdBr_3]_2 \cdot H_2O$ (**1**)	77.32(77)	74.73(273)
	76.16(77)	73.92(273)
	58.50(77)	58.73(273)
	56.45(77)	57.27(273)
	47.41(77)	47.57(273)
	45.74(77)	46.25(273)
$[i\text{-}C_3H_7NH_3]$ $CdBr_3$ (**2**)	44.60(77)	44.13(192)
	40.37(77)	40.55(191)
	39.06(77)	39.48(192)
$[(CH_3)_3NH]_3Cd_2Br_7$ (**3**)	66.92(77)	65.56(230)
	55.48(77)	55.42(231)
	45.88(77)	45.28(230)

The temperature dependence of ^{81}Br NQR frequencies of $[(CH_3)_3NH]_3Cd_2Br_7$ (**3**) is shown in Figure 9. Three NQR lines are observed at 77 K with intensity ratio of 3 : 1 : 3 in decreasing frequency order. This intensity ratio is in agreement with the results of our structure determination. From the relation between the bond distances and NQR frequencies, the highest-frequency line can be assigned to three Br atoms with a shorter

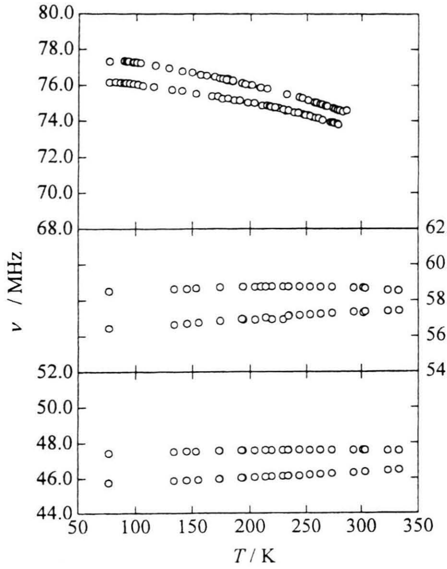

Fig. 7. The temperature dependence of ^{81}Br NQR frequencies of *t*-butylammonium tribromocadmate(II)-1/2 water (**1**).

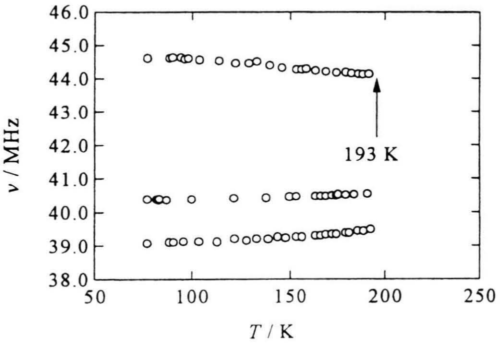

Fig. 8. The temperature dependence of ^{81}Br NQR frequencies of *i*-propylammonium tribromocadmate(II) (**2**).

Cd-Br bond in the tetrahedral $[Cd(2)Br_4]^{2-}$ ion and the middle-frequency line is due to one Br atom with a longer Cd-Br bond located on the three-fold axis of $[Cd(2)Br_4]^{2-}$ ion. The findings of Daoud et al. are different from our results on these two bond distances, as mentioned earlier. Three NQR lines disappear at about 243 K, which is probably due to cationic motion, although there is a heat anomaly due to a phase transition at 436 K in a DTA curve. The middle-frequency line could not be observed at temperatures between 120 and 200 K.

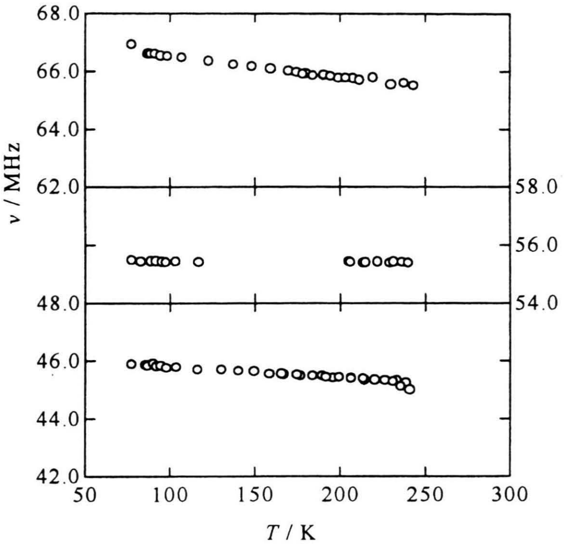

Fig. 9. The temperature dependence of ^{81}Br NQR frequencies of *tris*-trimethylammonium heptabromodicadmate(II) (**3**).

Conclusion

The bromocadmate(II) complex with the composition of $[CdBr_3]$ has a pronounced tendency to form chain structures. $[(CH_3)_3NH]CdBr_3$ at room temperature was reported to have triple Br bridged chain [14]. This tendency is not observed for Zn halide complexes. The reason of this property shown by halogenocadmate complexes is partly due to the atomic radius and the possible deformation of outer shell orbitals.

[1] V. G. Krishnan and Al. Weiss, J. Mol. Struct. **176,** 323 (1988).
[2] V. G. Krishnan, Shi-qi Dou, H. Paulus, and Al. Weiss, Ber. Bunsenges. Phys. Chem. **95,** 1256 (1991).
[3] V. G. Krishnan, Shi-qi Dou, and Al. Weiss, Z. Naturforsch. **46a,** 1063 (1991).
[4] H. Ishihara, V. G. Krishnan, Shi-qi Dou, and Al. Weiss, Z. Naturforsch. **49a,** 213 (1994).
[5] V. G. Krishnan, Shi-qi Dou, and Al. Weiss, Z. Naturforsch. **49a,** 223 (1994).
[6] H. Ishihara, Shi-qi Dou, K. Horiuchi, V. G. Krishnan, H. Paulus, H. Fuess, and Al. Weiss, Z. Naturforsch. **51a,** 1027 (1996).
[7] H. Ishihara, Shi-qi Dou, K. Horiuchi, V. G. Krishnan, H. Paulus, H. Fuess, and Al. Weiss, Z. Naturforsch. **51a,** 1216 (1996).

[8] H. Ishihara, K. Horiuchi, Shi-qi Dou, T. M. Gesing, J. C. Buhl, H. Paulus, and H. Fuess, Z. Naturforsch. **53a,** 717 (1998).

[9] T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernel, Inorg. Chem, **9,** 459 (1970).

[10] W. E. Estea, D. Y. Jeter, J. C. Hempel, and W. E. Hatfield, Inorg. Chem. **10,** 2074 (1971).

[11] G. M. Sheldrick, SHELX 86, Program for the solution of crystal structures, University of Göttingen, Germany 1986. SHELX 93, Program for crystal structure determination, University of Göttingen, Germany 1993.

[12] Tables of the atomic coordinates including hydrogen atoms, thermal parameters, bond distances and angles have been deposited as CCDC 127660 for (**1**), CCDC 133338 for (**2**), and CCDC 133339 for (**3**) at the Cambridge Crystallographic Data Center.

[13] P. A. Daoud, R. Perret, and Y. Dusausoy, Acta Crystallogr. **B35,** 2718 (1979).

[14] S. Kashida and S. Sato, J. Phys. Soc. Japan, **55,** 1163 (1986).