Isolated versus Condensed Anion Structure II; the Influence of the Cations (1,3-propanediammonium, 1,4-phenylendiammonium, and *n*-propylammonium) on Structures and Phase Transitions of $CdBr_4^{2-}$ Salts. A ^{79,81}Br NQR and X-ray Structure Analysis

Hideta Ishihara[a], Shi-qi Dou, Keizo Horiuchi[b], V. G. Krishnan[c], Helmut Paulus, Hartmut Fuess, and Alarich Weiss †

Fachbereich Materialwissenschaft, Fachgebiet Strukturforschung,
Technische Hochschule Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany
[a] Faculty of Education, Saga University, Honjo-machi 1, Saga 840, Japan
[b] Faculty of Science, University of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-01, Japan
[c] Department of Physics, Osmania University, Hyderabad 500 007, India

Z. Naturforsch. **51 a,** 1216–1228 (1996); received August 12, 1996

The influence of the cations on the condensation of anions $CdBr_4{}^{2-}$ in salts (A')$CdBr_4$(II) and $(A)_2CdBr_4$(II) is studied by ^{79,81}Br NQR and X-ray crystal structure determinations. (A')$CdBr_4$: A' = $[H_3N(CH_2)_3NH_3]^{2+}$ (**1**) crystallizes with a layer-type anion structure at 298 K and A' = $[1,4\text{-}(H_3N)_2C_6H_4]^{2+}$(**2**) crystallizes with a chain-type anion structure at 298 K. $(A)_2CdBr_4$: A = $[n\text{-}H_3C(CH_2)_2NH_3]^+$ (**3**) crystallizes with a layer-type anion structure at 293 K. (**1**) shows successive phase transitions at 328, 363, and 495 K according to the NQR and DSC measurements. Phase IV of (**1**): at 298 K orthorhombic, Pnma, $Z = 4$, $a = 772.1(4)$, $b = 1905.4(9)$, $c = 789.8(4)$ pm. ^{81}Br NQR spectrum showed a doublet at 77 K (phase IV) with $\nu_1 = 61.177$ and $\nu_2 = 45.934$ MHz and also a doublet at 350 K (phase III) with $\nu_1 = 57.581$ and $\nu_2 = 48.747$ MHz. (**2**): at 295 K orthorhombic, Pnma, $Z = 4$, $a = 802.5(3)$, $b = 1775.1(6)$, $c = 881.9(3)$ pm; the five-coordinated Cd atom and one-dimensional $[CdBr_4]^{2-}$ anion chain structure was observed. This coordination and chain structure are very rare for (A')CdX_4(II) or $(A)_2CdX_4$(II). Two ^{81}Br NQR lines were observed at 77 K: $\nu_1 = 70.159$ and $\nu_3 = 40.056$ MHz. One more line appeared at 85 K: $\nu_2 = 53.622$ MHz. A ^{81}Br NQR triplet was observed at 273 K: $\nu_1 = 67.919$, $\nu_2 = 56.317$, and $\nu_3 = 40.907$ MHz. (**3**) shows successive phase transitions at 121, 135, 165, and 208 K according to the NQR, DSC, and DTA measurements. Phase I of (**3**): at 293 K orthorhombic, Cmca, $Z = 4$, $a = 783.4(4)$, $b = 2480.2(10)$, $c = 806.5(4)$ pm. ^{81}Br NQR doublet was observed at 77 K (phase V) and at 300 K (Phase I) with $\nu_1 = 61.060$ and $\nu_2 = 54.098$ MHz (77 K); $\nu_1 = 55.835$ and $\nu_2 = 55.964$ MHz (373 K). No NQR line could be observed in phases II, III, and IV.

Introduction

The perovskite type layer compounds $[C_nH_{2n+1}NH_3]_2CdCl_4$ and $[NH_3(CH_2)_{1n}NH_3]CdCl_4$ have attracted a great deal of attention for many years. For alkylammonium and alkylenediammonium tetrachlorocadmates, an extensive study by ^{1}H NMR on the phase transitions was reported by Blinc *et al.* [1]. In these tetrachlorocadmates, phase transitions originate from the dynamics of the $NH_3{}^+$ groups which form hydrogen bonds with the halogen atoms of the anion layers and hindered rotational motions of the entire alkyl or alkylene groups around the long molecular axis. The crystal structure and phase transition of $[n\text{-}C_3H_7NH_3]_2CdCl_4$ have been investigated by Chapuis [2] and the crystal structure of $[NH_3(CH_2)_3NH_3]CdCl_4$ by Willett [3]. In recent time we have studied a number of complex salts with the bromocadmate anions $[CdBr_{2+n}]^{n-}$ by ^{79,81}Br NQR and X-ray diffraction, and a variety of polymer anion structures [4-7] or the isolated $[CdBr_4]^{2-}$ ion structure have been observed [8]. In the following, we report on ^{79,81}Br NQR and crystal structure studies of $[H_3N(CH_2)_3NH_3]CdBr_4$ (**1**), $[1,4\text{-}(NH_3)_2C_6H_4]CdBr_4$ (**2**), and $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ (**3**) and discuss the relation between Br NQR and structural properties.

Reprint requests to Prof. H. Ishihara.

0932-0784 / 96 / 1200-1216 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

Table 1. Experimental conditions for the crystal structure determinations and crystallographic data of 1,3-propanediammonium tetrabromocadmate(II), $[H_3N(CH_2)_3NH_3]CdBr_4$ (**1**), 1,4-phenylenediammonium tetrabromocadmate(II), $[1,4\text{-}(NH_3)_2C_6H_4]CdBr_4$ (**2**), *n*-propylammonium tetrabromocadmate(II), $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ (**3**). Diffractometer: Stoe-stadi 4; wavelength: 71.069 pm (MoKα); Monochromator: Graphite (002); scan $2\omega/\theta$. (**1**): $C_3H_{12}Br_4CdN_2$, M = 508.21; (**2**): $C_6H_{10}Br_4CdN_2$, M = 542.22; (**3**): $C_6H_{20}Br_4CdN_2$, M = 552.32.

Compound	(**1**)	(**2**)	(**3**)
Crystal size/$(mm)^3$	$0.5\times0.45\times0.45$	$2\times0.12\times0.10$	$2.4\times0.4\times0.38$
Temperature/K	298(2)	298(2)	293(2)
Absorption coeff./m^{-1}	15194	14060	11271
θ-range (/°) for data collected	$2.14\leq\theta\leq24.93$	$2.29\leq\theta\leq24.99$	$1.64\leq\theta\leq25.00$
Index ranges	$-9\leq h\leq 1$, $-22\leq k\leq 22$, $0\leq l\leq 9$	$0\leq h\leq 9$, $-21\leq k\leq 21$, $-10\leq l\leq 8$	$-9\leq h\leq 9$, $0\leq k\leq 29$, $-9\leq l\leq 9$
Lattice constants			
a /pm	772.1(4)	802.5(3)	783.4(4)
b /pm	1905.4(9)	1775.1(6)	2480.2(10)
c /pm	789.8(4)	881.9(3)	806.5(4)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
$V\cdot10^{-6}/(pm)^3$	1161.9(10)	1256.1(8)	1567.0(13)
Space group	D_{2h}^{16}–Pnma	D_{2h}^{16}–Pnma	D_{2h}^{18}–Cmca
Formula units *Z*	4	4	4
$\rho_{calc}/(Mg\cdot m^{-3})$	2.905(4)	2.867(3)	2.341(3)
F(000)	928	992	1032
Reflections collected	2270	4130	2661
Symmetry independent	1051	1144	754
$[R_{int}]$	0.0534	0.0225	0.1018
Data	1049	1144	754
Restraints	0	0	1
Parameters	50	85	41
Goodness of fit on F^2	1.909	0.890	1.034
Final *R* ($I>2\sigma(I)$)	$R_1 = 0.0767$, $wR_2 = 0.2271$	$R_1 = 0.0187$ $wR_2 = 0.0479$	$R_1 = 0.0512$, $wR_2 = 0.1206$
R (all data)	$R_1 = 0.0845$, $wR_2 = 0.2333$	$R_1 = 0.0220$, $wR_2 = 0.0512$	$R_1 = 0.0540$, $wR_2 = 0.1250$
Largest diff: (peak,hole) /$(10^{-6}e(pm)^3)$	2.537 and −1.823	0.419 and −0.544	1.296 and −0.976
Max. and Min. Trans.		0.328 and 0.220	0.0857 and 0.0245
Extinction Coeff.	0.0028(9)	0.0084(3)	0.0026(3)
Point positions:	Cd in 4b; $C^{(1)}$ in 4c; $Br^{(1)}$, $Br^{(2)}$, $C^{(2)}$, N, H atoms in 8d	Cd, $Br^{(1)}$, $Br^{(2)}$ in 4c; N, $C^{(1)}$, $C^{(2)}$, $C^{(3)}$, H atoms in 8d	Cd in 4a; $Br^{(2)}$ in 8e; $Br^{(1)}$, $N^{(1)}$, $C^{(2)}$, $C^{(3)}$, $C^{(4)}$, $H^{(N1,1)}$, $H^{(C4,1)}$ in 8f; other H atoms in 16g

Table 2. Atomic coordinates ($\times10^4$) and isotropic and anisotropic displacement parameters U_{eq} and U_{ij} (in pm^2), respectively, for $[H_3N(CH_2)_3NH_3]CdBr_4$(**1**), $[1,4\text{-}(NH_3)_2C_6H_4]CdBr_4$ (**2**), $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ (**3**). U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij}. The temperature factor has the form: $T = \exp\{-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. The 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 H atoms are involved.

$[H_3N(CH_2)_3NH_3]CdBr_4$ (**1**)

Atom	*x*	*y*	*z*	U_{eq}
Cd	0	5000	5000	247(6)
$Br^{(1)}$	2267(2)	4803(1)	2257(2)	351(6)
$Br^{(2)}$	134(2)	3605(1)	5524(2)	375(6)
N	−299(16)	3787(7)	−249(17)	433(31)
$H^{(N,1)}$	138(16)	4156(7)	296(17)	520
$H^{(N,2)}$	−1450(16)	3811(7)	−236(17)	433
$H^{(N,3)}$	74(16)	3788(7)	−1316(17)	519
$C^{(1)}$	−388(34)	2500	−232(29)	473(52)
$H^{(C1,1)}$	−40(34)	2500	−1412(29)	570
$H^{(C1,2)}$	−1644(34)	2500	−193(29)	570
$C^{(2)}$	266(21)	3138(8)	590(20)	475(40)
$H^{(C2,1)}$	−127(21)	3145(8)	1757(20)	570
$H^{(C2,2)}$	1521(21)	3123(8)	601(20)	570

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	263(9)	260(9)	219(9)	7(4)	−11(5)	16(5)
$Br^{(1)}$	329(9)	426(10)	296(90	−4(5)	114(5)	15(5)
$Br^{(2)}$	525(11)	265(9)	345(10)	−5(5)	2(5)	23(6)
N	611(77)	309(71)	378(65)	−57(58)	−24(57)	8(57)
$C^{(1)}$	713(138)	377(128)	329(105)	0(0)	−43(100)	0(0)
$C^{(2)}$	611(93)	431(105)	382(76)	42(68)	−169(66)	12(67)

Experimental

The title compounds were synthesized from commercial amines (Aldrich), $CdBr_2$, and HBr. The compound was crystallized from the solution in air at pH = 3. Compound (**2**) was kept with P_2O_5 in a desiccator to avoid the oxidation of the amine. The results of chemical analyses are as follows (in weight %, observed/calculated); (**1**): C, 5.25/5.51 ; H, 2.34/2.38; N, 7.09/7.09. (**2**): C, 13.33/13.29; H, 1.85/1.86; N, 5.17/5.17. (**3**): C, 12.93/13.05; H, 3.40/3.65; N, 4.97/5.07.

Small single crystals of the title compounds were grown from aqueous solution for the X-ray diffraction experiments. The structures were determined with a four circle X-ray diffractometer (Stoe). From the measured intensities, after appropriate correction for Lorentz-polarization factor and absorption, the structures were determined by direct methods, Fourier syntheses, and least-squares refinement with the programs given in [9].

The $^{79,81}Br$ NQR spectra were recorded with an NQR spectrometer working in the superregenerative mode. The temperature (*T*) at the sample site was created by a flow of temperature-regulated nitrogen-gas and by immersing the sample in liquid nitrogen

Table 2 (cont).

$[1,4\text{-}(NH_3)_2C_6H_4]CdBr4$ (**2**)

Atom	x	y	z	U_{eq}
Cd	1585(1)	7500	5562(1)	375(2)
$Br^{(1)}$	2880(1)	7500	8279(1)	394(2)
$Br^{(2)}$	4024(1)	7500	3378(1)	378(2)
$Br^{(3)}$	849(1)	6089(1)	4983(1)	341(1)
N	6927(5)	8829(2)	3721(5)	364(7)
$H^{(N,1)}$	6460(67)	8424(36)	3995(68)	780(188)
$H^{(N,2)}$	6894(7)	8852(29)	2771(73)	724(177)
$H^{(N,3)}$	7927(73)	8839(27)	4043(57)	573(141)
$C^{(1)}$	5926(4)	9437(2)	4377(4)	298(7)
$C^{(2)}$	5437(5)	9380(2)	5869(4)	387(9)
$H^{(C2)}$	5665(51)	8945(24)	6429(46)	383(105)
$C^{(3)}$	5510(5)	10050(2)	3503(4)	380(8)
$H^{(C3)}$	5800(55)	10074(23)	2525(53)	543(129)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	520(3)	286(2)	320(2)	0	–79(2)	0
$Br^{(1)}$	406(3)	438(3)	337(3)	0	–98(2)	0
$Br^{(2)}$	350(3)	350(3)	434(3)	0	2(2)	0
$Br^{(3)}$	387(2)	302(2)	334(2)	–12(1)	–9(2)	–12(1)
N	342(17)	358(17)	393(20)	51(14)	–25(16)	–65(14)
$C^{(1)}$	269(16)	302(17)	322(18)	14(13)	–43(13)	–84(14)
$C^{(2)}$	529(23)	284(18)	347(19)	96(16)	–22(17)	32(15)
$C^{(3)}$	509(22)	358(19)	273(17)	46(17)	28(17)	–3(15)

$[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$(**3**)

Atom	x	y	z	U_{eq}
Cd	5000	5000	0	40(1)
$Br^{(1)}$	5000	6054(1)	540(1)	63(1)
$Br^{(2)}$	2500	4859(1)	2500	53(1)
$N^{(1)}$	5000	9128(4)	–301(12)	70(3)
$H^{(N1,1)}$	5000	9402(4)	412(12)	85
$H^{(N1,2)}$	4072	9146(4)	–936(12)	85
$C^{(2)}$	5000	8626(10)	603(31)	135(9)
$H^{(C2,1)}$	4016	8658(10)	1326(31)	163
$C^{(3)}$	5000	8208(7)	264(31)	218(21)
$H^{(C3,1)}$	4017	8179(7)	–461(31)	262
$C^{(4)}$	5000	7677(6)	1163(24)	134(8)
$H^{(C4,1)}$	5000	7388(6)	371(24)	161
$H^{(C4,2)}$	3999	7652(6)	1846(24)	161

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	37 (1)	48 (1)	34 (1)	–4 (1)	0	0
$Br^{(1)}$	95 (1)	46 (1)	49 (1)	–1 (1)	0	0
$Br^{(2)}$	41 (1)	78 (1)	42 (1)	0	10 (1)	0
$N^{(1)}$	96 (8)	60 (5)	55 (5)	3 (4)	0	0
$C^{(2)}$	194 (26)	81 (16)	132 (16)	38 (14)	0	0
$C^{(3)}$	398 (63)	50 (13)	207 (28)	15 (16)	0	0
$C^{(4)}$	209 (24)	63 (9)	131 (17)	21 (10)	0	0

(77 K). T was measured via copper-constantan thermocouple and the frequencies by counting technique. The ^{79,81}Br NQR lines recorded using a lock-in amplifier with a time constant of 10 s had a signal to noise ratio (S/N) of 40 to 50 and their line widths were 30 to 40 kHz. DSC was carried out above 130 K with a differential scanning calorimeter DSC220 from Seiko Instruments Inc. under the following condition: sample weight *ca.* 10 mg, heating rate 10 K min^{-1} with flowing dry N_2 gas at 40 ml min^{-1}. DTA was measured by a homemade apparatus.

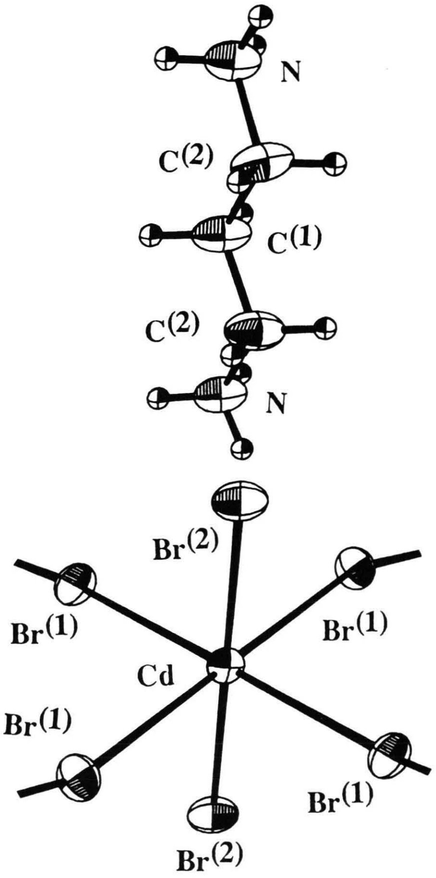


Fig. 1. Formula unit of 1,3-propanediammonium tetrabromocadmate(II) (**1**) with the numbering of the atoms. The thermal ellipsoids (50 % of electrons as contour) are shown, too.

Results

Crystal Structure $[H_3N(CH_2)_3NH_3]CdBr_4$ (**1**)

In Table 1 the experimental details and some crystallographic data are given for the title compounds. (**1**) undergoes three phase transitions at 328, 363, and 495 K with four solid phases between 77 K and the melting point of 554 K; on the other hand,

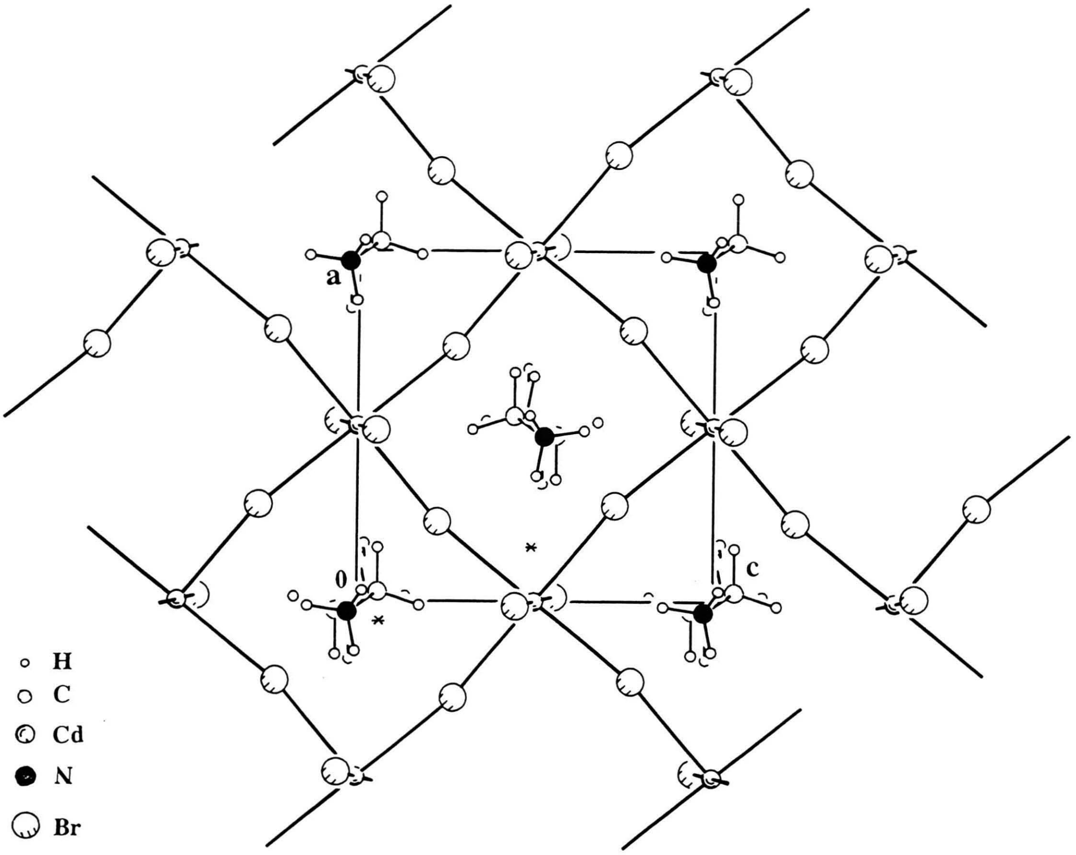


Fig. 2. Projection of a half of the unit cell of (**1**) along [010] (from $y = 0$ to $y = 0.5$) onto the *ac* plane.

the chloride analogue shows a phase transition at 376 K [1]. These phases are denoted as phases I, II, III, and IV in the order of decreasing temperatures. The room temperature phase IV of 1,3-propanediammonium tetrabromocadmate(II) (**1**) is isostructural with the room temperature phase of the chloride analogue [3], and (**1**) crystallizes orthorhombic, D_{2h}^{18} – Pnma, $Z = 4$. Crystallographic data are given in Table 1 [10]. Table 2 lists the positional coordinates and isotropic and anisotropic displacement parameters U_{eq} and U_{ij}, respectively. In Fig. 1 the formula unit is drawn with the numbering of the atoms and the thermal ellipsoids. Figure 2 shows the projection of a half ($0 \leq y \leq 1/2$) of the unit cell along [010] onto the *ac* plane, Fig. 3 the projection of the unit cell along [100] onto the *bc* plane. Cd is surrounded by six bromine atoms, and a nearly regular octahedron $CdBr_6$ is formed. Two bromines $Br^{(2)}$ are terminal atoms and four bromines $Br^{(1)}$ bridging atoms and shared with the neighboring octahedra which results in two-dimensional anion planes located at $y = 0$ and $y = 1/2$. As one expects, the distance Cd-$Br^{(2)}$ (269 pm) is somewhat shorter than the Cd-$Br^{(1)}$ distances (279 pm and 281 pm) as can be seen from Table 3. The cations $[H_3NC^{(2)}H_2C^{(1)}H_2C^{(2)}H_2NH_3]^{2+}$ are centered at the carbon atom $C^{(1)}$ and the distances N-$C^{(2)}$ and $C^{(1)}$-$C^{(2)}$ in (**1**) are equal (147 pm) within error (see Table 4) and they are within the range one expects for aliphatic C-C and N-C bond lengths; For example, for 1,3-propanediammonium dibromide and diiodide we have observed $150 \leq d(\text{C-C})/\text{pm} \leq 154$, $149 \leq d(\text{C-N})/\text{pm} \leq 151$ [11]. Six hydrogen atoms for one formula unit are able to form hydrogen bonds N-H···Br.

In Table 3 we have listed the hydrogen bond scheme for (**1**) (distances and angles). Each NH_3 group is connected to two different terminal $Br^{(2)}$ atoms and to one bridging $Br^{(1)}$ atom.

Table 3. Intramolecular (intraionic) bond distances (in pm) and bond angles (in degree) within the anion coordination for the layer structures, and hydrogen bond scheme.

$[H_3N(CH_2)_3NH_3]CdBr_4$(**1**)

Connection	*d*/pm	Connection	Angle/°
Cd-Br$^{(1')}$ (2×)	278.7(2)	Br$^{(2)}$-Cd-Br$^{(2')}$	180.0
Cd-Br$^{(1)}$ (2×)	281.0(2)	Br$^{(1)}$-Cd-Br$^{(1'')}$ (2×)	180.0
Cd-Br$^{(2)}$ (2×)	269.1(2)	Br$^{(1)}$-Cd-Br$^{(2)}$ (2×)	87.87(4)
		Br$^{(1)}$-Cd-Br$^{(1''')}$ (2×)	92.26(4)
		Br$^{(1)}$-Cd-Br$^{(2')}$ (2×)	92.13(4)
		Br$^{(1'''')}$-Cd-Br$^{(2)}$ (2×)	89.69(4)
		Br$^{(1''')}$-Cd-Br$^{(2)}$ (2×)	90.31(4)

Hydrogen bond scheme

Connection	*d*/pm	Angle (N-H···Br)/°
N···Br$^{(1)}$	340.6	155.8
H$^{(N,1)}$)···Br$^{(1)}$	257	
N···Br$^{(2'')}$	354.5	153.6
H$^{(N,2)}$···Br$^{(Br2'')}$	272.6	
N···Br$^{(2''')}$	337.2	176.1
H$^{(N,3)}$···Br$^{(2''')}$	248.4	

Br$^{(1')}$: $-x + 1/2, -y + 1, z - 1/2$; Br$^{(1'')}$: $-x, -y + 1, -z + 1$; Br$^{(1''')}$: $-x + 1/2, -y + 1, z + 1/2$; Br$^{(1'''')}$: $x - 1/2, y, -z + 1/2$; Br$^{(2')}$: $-x, -y + 1, -z + 1$; Br$^{(2'')}$: $x - 1/2, y, -z + 1/2$; Br$^{(2''')}$: $x, y, z - 1$.

$[1,4\text{-}(NH_3)_2C_6H_4]CdBr_4$ (**2**)

Connection	*d*/pm	Connection	Angle/°
Cd-Br$^{(1)}$	261.2(1)	Br$^{(1)}$-Cd-Br$^{(2)}$	111.09(3)
Cd-Br$^{(1')}$	314.4(2)	Br$^{(1)}$-Cd-Br$^{(3)}$ (2×)	105.55(1)
Cd-Br$^{(2)}$	274.6(1)	Br$^{(2)}$-Cd-Br$^{(3)}$	91.39(2)
Cd-Br$^{(3)}$ (2×)	262.3(1)	Br$^{(3)}$-Cd-Br$^{(3')}$	145.37(3)
		Cd-Br$^{(1)}$-Cd'	132.42(1)
		Br$^{(1)}$-Cd-Br$^{(1')}$	94.67(3)
		Br$^{(2)}$-Cd-Br$^{(1')}$	154.44(1)
		Br$^{(3)}$-Cd-Br$^{(1')}$	81.38(2)

Hydrogen bond scheme

Connection	*d*/pm	Angle (N-H···Br)/°
N···Br$^{(2)}$	332.9	143.8
H$^{(N,1)}$···Br$^{(2)}$	260.9	
N···Br$^{(3')}$	38.2	162.8
H$^{(N,2)}$···Br$^{(3')}$	257.1	
N···Br$^{(3'')}$	334.2	178.2
H$^{(N,3)}$···Br$^{(3'')}$	249.0	

Br$^{(1')}$: $x - 1/2, y, 3/2 - z$; Cd': $1/2 + x, y, 3/2 - z$; Br$^{(3')}$: $1/2 + x, 3/2 - y, 1/2 - z$; Br$^{(3'')}$: $1 + x, 1/2 + y, z$.

Crystal Structure $[1,4\text{-}(NH_3)_2C_6H_4]CdBr_4$ (2)

1,4-phenylenediammonium tetrabromocadmate(II) (**2**) crystallizes at 298 K orthorhombic, D_{2h}^{18}-Pnma; for the lattice constants etc. see Table 1, for the atomic coordinates and displacement parameters see Table 2.

$[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ (**3**)

Connection	*d*/pm	Connection	Angle/°
Cd-Br$^{(1)}$ (2×)	265.1(1)	Br$^{(1)}$-Cd-Br$^{(1')}$	180.0
Cd-Br$^{(2)}$ (4×)	283.3(1)	Br$^{(1)}$-Cd-Br$^{(2)}$	90.30(3)
		Br$^{(1)}$-Cd-Br$^{(2')}$	89.70(3)
		Br$^{(2)}$-Cd-Br$^{(2')}$	180.0
		Br$^{(2)}$-Cd-Br$^{(2'')}$	87.48(4)
		Br$^{(2)}$-Cd-Br$^{(2''')}$	92.52(4)
		Br$^{(2'')}$-Cd-Br$^{(2''')}$	180.0
		Cd-Br$^{(2)}$-Cd'	165.76(4)

Hydrogen bond scheme

Connection	*d*/pm	Angle (N-H···Br)/°
N$^{(1)}$···Br$^{(1'')}$	348.4(10)	110.10(6)
H$^{(N1,2)}$···Br$^{(1'')}$	297.4(10)	
N$^{(1)}$···Br$^{(2'''')}$	349.6(8)	133.54(16)
H$^{(N1,1)}$···Br$^{(2'''')}$	282.2(7)	
N$^{(1)}$···Br$^{(1'')}$	338.4(10)	110.10(6)
H$^{(N1,2')}$···Br$^{(1'')}$	297.4(10)	

Cd': $x - 1/2, -y + 1, z + 1/2$; Br(1'): $-x + 1, -y + 1, -z$; Br(1'): $x, -y + 3/2, z - 1/2$; Br(2'): $-x + 1, -y + 1, -z$; Br(2"): $-x + 1, y, z$; Br(2'''): $x, -y + 1, -z$; Br(2''''): $x + 1/2, y + 1/2, z$; H$^{(N1,2')}$: $-x + 1, y, z$.

Table 4. Intramolecular (intraionic) distances (in pm) and angles (in degree) within the cations of the title compounds.

$[H_3N(CH_2)_3NH_3]CdBr_4$(**1**)

Connection	*d*/pm	Connection	Angle/°
N-C$^{(2)}$ (2×)	147(2)	N-C$^{(2)}$-C$^{(1)}$ (2×)	113.3(14)
C$^{(2)}$-C$^{(1)}$ (2×)	147(2)	C$^{(2)}$-C$^{(1)}$-C$^{(2)}$	112(2)

The distances N-H , C$^{(1)}$-H, and C$^{(2)}$-H are fixed to 89, 97, and 97 pm, respectively.

$[1,4\text{-}(NH_3)_2C_6H_4]CdBr_4$ (**2**)

Connection	*d*/pm	Connection	Angle/°
N-C$^{(1)}$	146.4(5)	N-C$^{(1)}$-C$^{(2)}$	118.7(3)
C$^{(1)}$-C$^{(2)}$	137.6(5)	N-C$^{(1)}$-C$^{(3)}$	119.7(3)
C$^{(1)}$-C$^{(3)}$	137.5(3)	C$^{(1)}$-C$^{(2)}$-C$^{(3)}$	121.6(3)
C$^{(2')}$-C$^{(3)}$	138.2(5)	C$^{(1)}$-C$^{(2)}$-C$^{(2')}$	119.3(3)
C$^{(2)}$-H$^{(C2)}$	93(4)	C$^{(1)}$-C$^{(2)}$-C$^{(3')}$	119.1(3)
C$^{(3)}$-H$^{(C3)}$	89(5)	C$^{(1)}$-N-H$^{(N,1)}$	106(4)
N-H$^{(N,1)}$	85(7)	C$^{(1)}$-N-H$^{(N,2)}$	110(4)
N-H$^{(N,2)}$	84(6)	C$^{(1)}$-N-H$^{(N,3)}$	112(3)
N-H$^{(N,3)}$	85(6)	H$^{(N,1)}$-N-H$^{(N,2)}$	108(5)
		H$^{(N,1)}$-N-H$^{(N,3)}$	110(5)
		H$^{(N,2)}$-N-H$^{(N,3)}$	111(5)

C(2') and C(3'): $1 - x, 1 - y, 1 - z$.

The intramolecular (intraionic) distances are listed in Table 3. In Fig. 4 the formula unit is sketched with the atomic numbering and the thermal ellipsoids of the atoms. The projection of the unit cell along [001] on to the *ab* plane is shown in Figure 5. The Cd atom

Table 4 (cont).

$[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ (**3**)

Connection	d/pm	Connection	Angle/°
$N^{(1)}$-$C^{(2)}$	144(2)	$N^{(1)}$-$C^{(2)}$-$C^{(3)}$	135(3)
$C^{(2)}$-$C^{(3)}$	107(3)	$C^{(2)}$-$C^{(3)}$-$C^{(4)}$	136(3)
$C^{(3)}$-$C^{(4)}$	150.3(1)	$C^{(2)}$-$N^{(1)}$-$H^{(N1,1)}$	110.2(12)
		$C^{(2)}$-$N^{(1)}$-$H^{(N1,2)}$	109.1(6)
		$N^{(1)}$-$C^{(2)}$-$H^{(C2,1)}$	103.9(7)
		$C^{(3)}$-$C^{(2)}$-$H^{(C2,1)}$	102.9(11)
		$C^{(4)}$-$C^{(3)}$-$H^{(C3,1)}$	103.4(8)
		$C^{(2)}$-$C^{(3)}$-$H^{(C3,1)}$	102.6(11)
		$C^{(3)}$-$C^{(4)}$-$H^{(C4,1)}$	110.6(14)
		$C^{(3)}$-$C^{(4)}$-$H^{(C4,2)}$	108.9(7)

The distances $N^{(1)}$-H, $C^{(2)}$-H, $C^{(3)}$-H, and $C^{(4)}$-H are fixed to 89, 97, 97 and 96 pm, respectively. The angles H-$N^{(1)}$-H, H-$C^{(2)}$-H, H-$C^{(3)}$-H, and H-$C^{(4)}$-H are fixed to 109.5, 105.6, 105.5, and 109.5, respectively.

is coordinated by five bromine atoms, two of which, $Br^{(1)}$, connect the two adjacent $[CdBr_4]^{2-}$ anions and form chains. It is for the first time that a chain structure like (**2**) is observed in the case of $(A')CdBr_4$ or $(A)_2CdBr_4$, as far as we know. The anion polymerization is weaker than in (**1**). The position of the bridging atom $Br^{(1)}$ is quite unsymmetric between two cadmium atoms, $d(\text{Cd-Br}^{(1)}) = 261$ pm, $d(\text{Cd'-Br}^{(1)}) = 314$ pm, see Table 3. The coordination of the Cd atom is somewhere between the octahedral one in (**1**) and the isolated $CdBr_4$ tetrahedron. We have calculated the plane through the bridging atom $Br^{(1)}$ and the terminal atoms $Br^{(2)}$ and $Br^{(3)}$ (2×). The plane equation is

$$4.116(2)x + 7.570(3)z = 4.168(2), \qquad (1)$$

the deviation of the atoms from the plane being less than 5 pm. The other $Br^{(1)}$ is the top atom of the tetragonal pyramid $CdBr_5$. The cation $[1,4\text{-}(NH_3)_2C_6H_4]^{2+}$ is plane, as one expects. Including the nitrogen atoms,

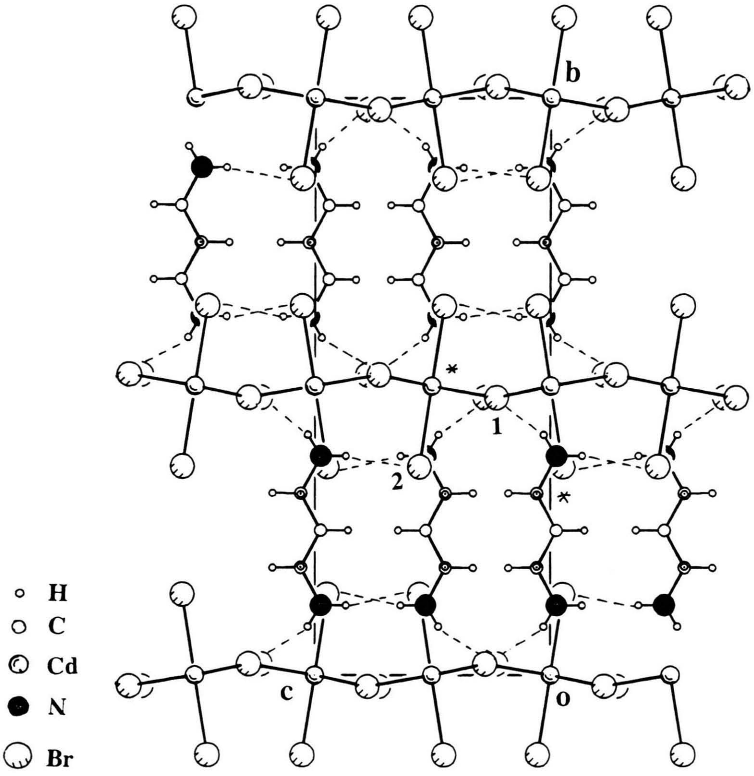


Fig. 3. Projection of the unit cell of (**1**) along [100] on the *bc* plane. Hydrogen bonds are marked by dashed lines.

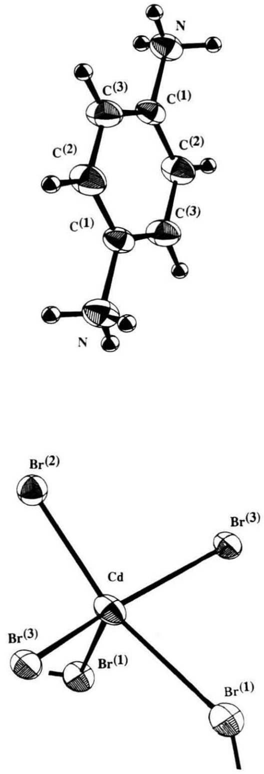


Fig. 4. Formula unit of 1,4-phenylenediammonium tetrabromocadmate(II) (**2**) with the numbering of the atoms. The thermal ellipsoids (50 % of electrons as contour) are shown, too.

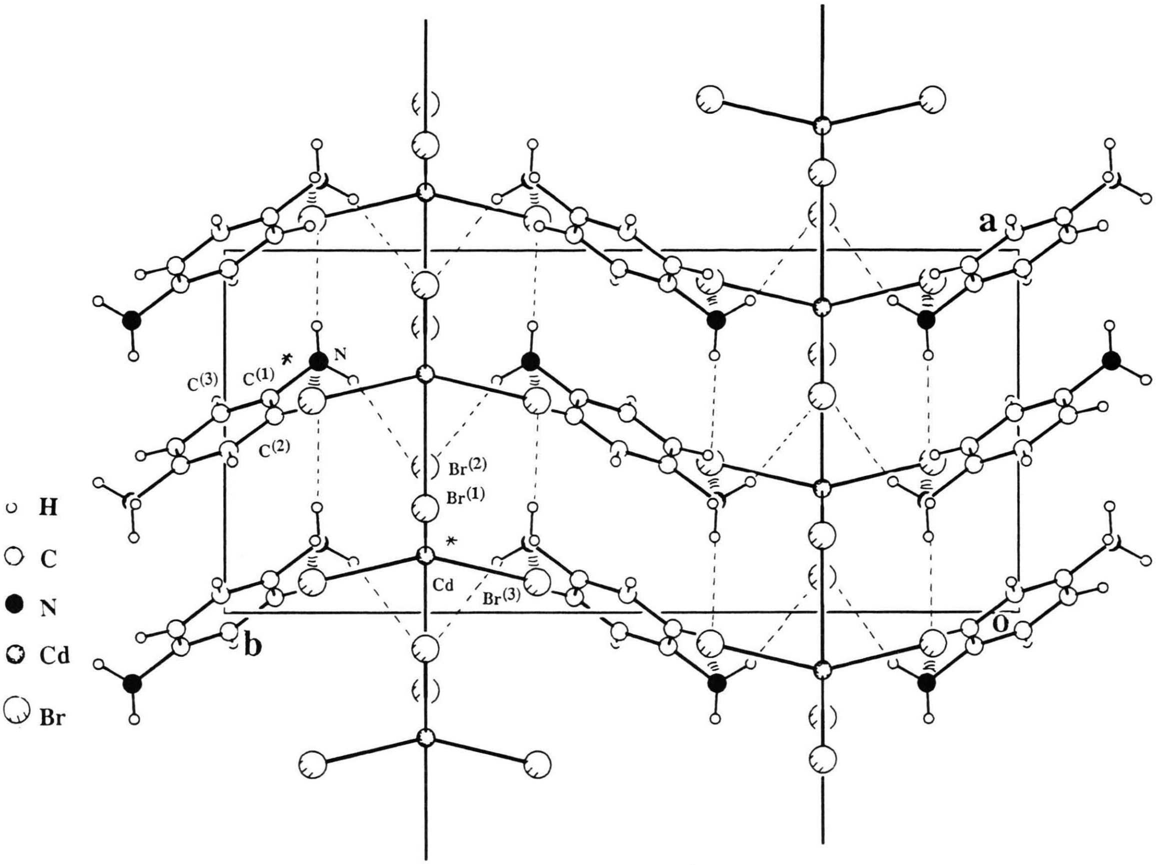


Fig. 5. Projection of the unit cell of (**2**) along [001] onto the *ab* plane. The ions marked by * are the ones for which the coordinates are given in Table 2. Hydrogen bonds are marked by dashed lines.

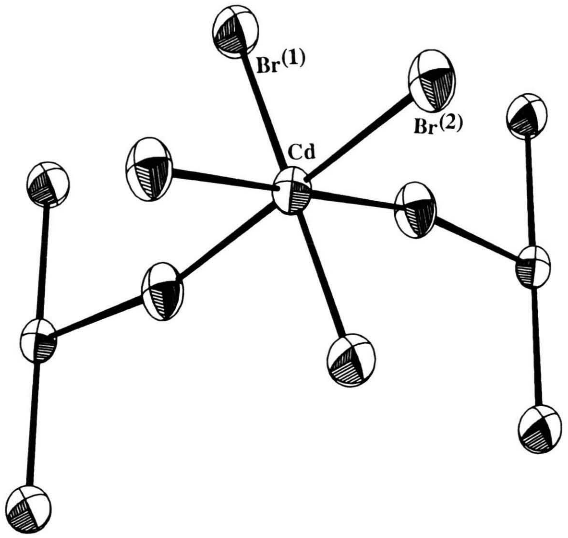
the plane N_2C_6 is given by

$$6.713(6)x + 8.264(25)y + 2.547(18)z = 12.894(19), \quad (2)$$

with deviations of the atoms from the plane of 0.2 pm. The cations are stacked along [100] and centered at $x = 0$ and 1/2, and the anions are located between cation stacks, lying on planes parallel to the *ac* plane. The hydrogen bond scheme N-H···Br is such that each of the six hydrogens is bonded to bromine atoms. Each of the three terminal bromines receives two hydrogen atoms whereas the bridging $Br^{(1)}$ has no connection to the NH_3^+ group.

*Crystal Structure $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ (**3**)*

The highest temperature phase (phase I) of *n*-propylammonium tetrabromocadmate(II) (**3**) crystallizes orthorhombic, D_{2h}^{18} – Cmca, $Z = 4$. For the lattice constants etc, see Table 1, for the atomic coordinates and displacement parameters see Table 2, and for the intramolecular (intraionic) distances see Table 3. In Fig. 6 the formula unit is shown with atomic numbering and the thermal ellipsoids of the atoms. In Fig. 7 the projection of the unit cell along [100] onto the *bc* plane is given, and in Fig. 8 the projection of the unit cell along [001] onto the *ab* plane. The Cd atom is located on an inversion center and on a mirror plane perpendicular to the *a* axis. The Cd atom is surrounded by six Br atoms and a nearly regular octahedron $CdBr_6$ is formed. Two bromines $Br^{(1)}$ are terminal atoms in this octahedron, and four bromines $Br^{(2)}$ at edges join the neighboring octahedra making two-dimensional anion planes located at $y = 0$ and $y = 1/2$. The Cd-$Br^{(1)}$ distance of 265 pm is shorter than the



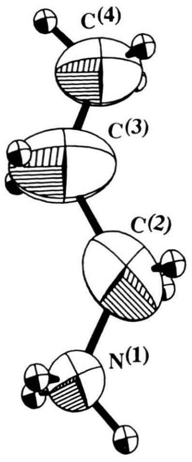


Fig. 6. Formula unit of *n*-propylammonium tetrabromocadmate(II) (**3**) with the numbering of the atoms. The thermal ellipsoids (50 % of electrons as contour) are shown, too.

Cd-Br$^{(2)}$ distance of 283 pm. The cations are located between the anion layers and lie on the mirror plane perpendicular to the *a* axis. There is a non-bonded interaction between the methyl ends of the aliphatic chains which are packed to form successive layers along the *b* axis. The N$^{(1)}$-C$^{(2)}$ and C$^{(3)}$-C$^{(4)}$ distances are 144 and 150 pm, respectively. On the other hand, the C$^{(2)}$-C$^{(3)}$ distance of 107 pm is chemically unrealistic and the thermal ellipsoid of the C$^{(2)}$ atom exhibits a large component parallel to the C$^{(2)}$-C$^{(3)}$ bond. Similar features were found in [n-C$_3$H$_9$NH$_3$]$_2$CdCl$_4$ [2] and [n-C$_4$H$_9$NH$_3$]$_2$CdCl$_4$ [12], and are explained by the dynamic disorder caused by rotational motion of the aliphatic chains or the oscillation of carbon atoms. Six hydrogen atoms for one formula unit are able to form hydrogen bonds N-H···Br. In Table 3 we have listed the hydrogen bond scheme for (**3**) (distances and angles). Each NH$_3$ group is connected to two different terminal Br$^{(1)}$ atoms and one bridging Br$^{(2)}$ atom.

^{79,81}*Br NQR and Differential Scanning Calorimetry*

To study the chemical bond M-Br in the solid phase, the molecular and crystal structures of the compounds of interest, and their phase transitions in the solid state, we have performed ^{79,81}Br NQR as a function of temperature. In Fig. 9 the temperature dependence of the bromine NQR spectrum of (**1**) is shown. The spectrum of ^{79}Br(and of ^{81}Br) is a doublet in both phases IV and III. This is expected for the phase IV for which we report the crystal structure. In Table 5 we give the NQR frequencies at selected temperatures and the a_i of the power series development of both [H$_3$N(CH$_2$)$_3$NH$_3$]CdBr$_4$ and the partially deuterated compound [D$_3$N(CH$_2$)$_3$ND$_3$]CdBr$_4$. The a_i's are defined by

$$\nu = \sum_i a_i T^i, -1 \leq i \leq 2. \quad (3)$$

The assignment of the NQR lines was done according to the frequency shifts by the deuteration of (**1**). The frequency shift of ν_2 is larger than that of ν_1, as shown in Table 5, and hence we assign the ν_2 line to the terminal bromine atom Br$^{(2)}$ and ν_1 to the bridging bromine atom Br$^{(1)}$. This is because each Br$^{(2)}$ atom in the phase IV has two hydrogen bonds with the hydrogen atoms of the NH$_3^+$ group, whereas Br$^{(1)}$ has a single N-H···Br hydrogen bond; therefore the deuteration frequency shift of the NQR line arising from Br$^{(2)}$ must be larger. The frequency-temperature curves changed continuously at 328 K, but the gradients of the curves changed discontinuously, suggesting that a second-order phase transition takes place. DSC measurement on (**1**) was done up to the melting point of 554 K to investigate the phase transitions. The results are listed in Table 6 [13]. The observed DSC curves suggest second-order character of the phase transition III↔IV at 328 K and first-order character of the other two transitions. Considering the results of ^{2}D NMR for the partially deuterated sample of (**1**), [D$_3$N(CH$_2$)$_3$ND$_3$]CdBr$_4$ [13], jumping reorientation of the whole 1,3-propanediammonium ions takes place about their long axes among 3 or 4 orientations

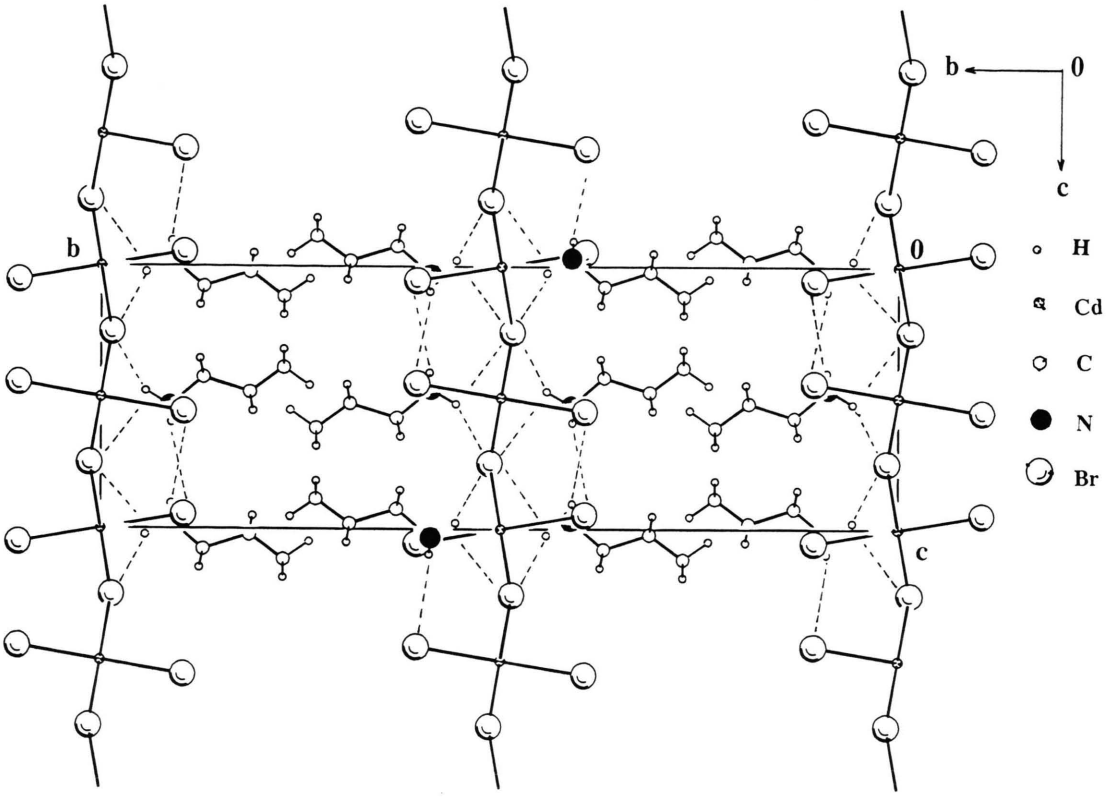


Fig. 7. Projection of the unit cell of (**3**) along [100] onto the *bc* plane. Hydrogen bonds are marked by dashed lines.

above the transition point of 328 K, because the transition entropy of the transition III↔IV, ΔS = 10.5 $\mathrm{JK^{-1}mol^{-1}}$, is nearly equal to R ln 3 = 9.13 or R ln 4 = 11.5 $\mathrm{JK^{-1}mol^{-1}}$. This motion gives rise to the dynamically-disordered cations in the crystal above 328 K, which results in the phase transition accompanied by the change of the hydrogen bond schemes, like in $\mathrm{[NH_3(CH_2)_3NH_3]MnCl_4}$ [14].

The ^{79,81}Br NQR spectrum of (**2**) is shown in its temperature dependence in Fig. 10, and frequencies at selected temperatures are given in Table 5, which includes also the coefficients of (3). According to the crystal structure determined, a triplet spectrum should be observed for both isotopes, ^{79}Br and ^{81}Br. There is no phase transition in the temperature range between 77 and 350 K, although the ν_2 line disappeared at 77 K and all NQR lines faded out above 350 K. With increasing temperature the ν_2 line appeared at 85 K and then gradually its intensity increased. The intensity ratio of the NQR lines at 273 K was 1:2:1 in order of decreasing frequency. We can assign the NQR lines to the Br atoms in the crystal of (**2**) according to this intensity ratio and the theory of the electric field gradients which results in the relation $\nu = f(1/d^3)$ [5]. In such a simple approach, the shortest Cd-Br distance would correspond to the highest ^{81}Br NQR frequency, the longest distance to the lowest frequency line. Therefore, ν_1 could be assigned to $\mathrm{Br^{(1)}}$, ν_2 to $\mathrm{Br^{(3)}}$, and ν_3 to $\mathrm{Br^{(2)}}$. As shown in Table 3, $\mathrm{Br^{(3)}}$ and $\mathrm{Br^{(2)}}$ form hydrogen bonds with $\mathrm{NH_3^+}$ groups and as shown in Fig. 10, ν_2 and ν_3 show positive temperature dependences, in contrast to the normal temperature dependence expected from the Bayer theory [15]. We consider that these positive temperature dependences are due to the hydrogen bonds, as observed in several other cases [16]. The hydrogen bond will lower the Br NQR frequency because of the opposite contribution of the electric field gradient (EFG) at the Br atom created by the H···Br hydrogen bond and created by the Cd-Br bond. Some molecular

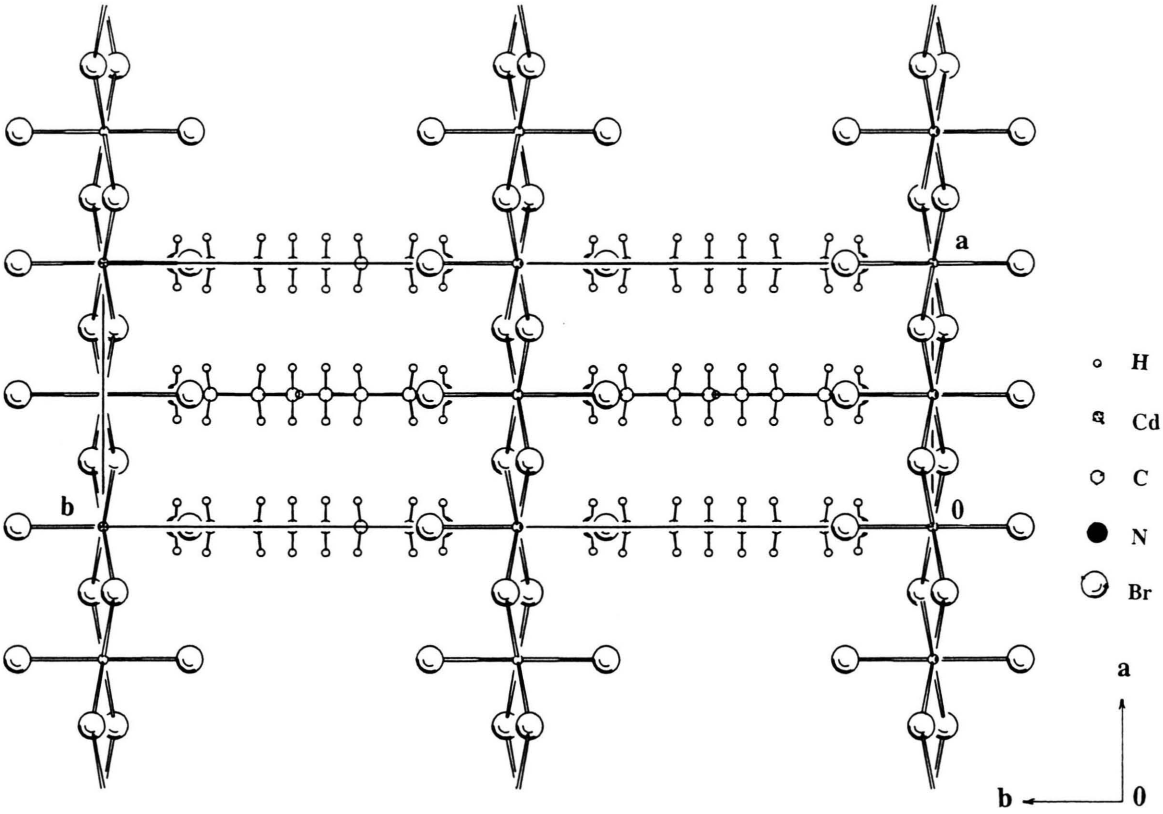


Fig. 8. Projection of the unit cell of (**3**) along [001] onto the *ac* plane.

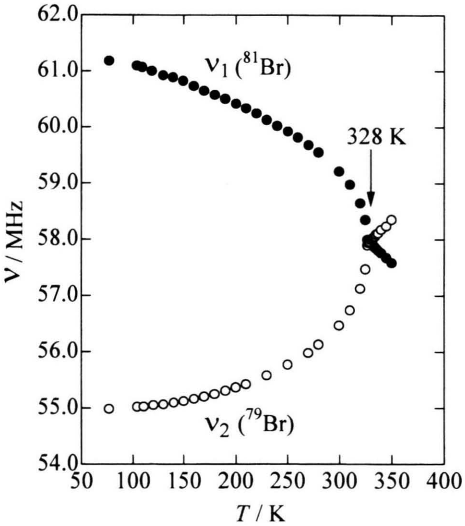


Fig. 9. Temperature dependence of ^{79,81}Br NQR frequencies of 1,3-propanediammonium tetrabromocadmate(II) (**1**).

motion will be activated with increasing temperature and then the breakage of the hydrogen bond will lead to the increase in the Br NQR frequency.

The ^{79,81}Br NQR spectra of (**3**) are also reported here; the data are given in Table 5, and $\nu = f(T)$ is shown in Figure 11. Two NQR lines were observed between 77 and 109 K and above 208 K. The assignment of NQR lines in the same way for (**1**) is difficult because the deuteration frequency shifts for two NQR lines are of the same magnitude; the NQR frequencies for the partially deuterated sample [n-$H_3C(CH_2)_2ND_3]_2CdBr_4$ were $\nu_1(^{81}Br) = 57.293$ and $\nu_2(^{81}Br) = 55.391$ MHz at 273 K, while for the protonated sample $\nu_1(^{81}Br) = 57.079$ and $\nu_2(^{81}Br) = 55.093$ MHz at 273 K. According to the results of DSC and DTA measurements listed in Table 6, there are four phase transitions between 77 K and the melting point of 456 K. The observed DSC curves suggested second-order character of the transition at 208 K and first-order character of the two transitions at 135 and

Table 5. NQR frequencies of ^{79,81}Br at selected temperature and coefficients a_i of the power series with the least squares approximation $\nu(^{79,81}\mathrm{Br}) = \Sigma_i\, a_i \cdot T^i$, $-1 \leq i \leq 2$ of $[\mathrm{H_3N(CH_2)_3NH_3}]\mathrm{CdBr_4}$ (**1a**) and $[\mathrm{D_3N(CH_2)_3ND_3}]\mathrm{CdBr_4}$ (**1b**); phase III and phase IV. Z is the number of experimental point, σ is the mean squares deviation. The ^{81}Br NQR results are listed for $[1,4\text{-}(\mathrm{NH_3})_2\mathrm{C_6H_4}]\mathrm{CdBr_4}$ (**2**) and for $[n\text{-}\mathrm{H_3C(CH_2)_2NH_3}]_2\mathrm{CdBr_4}$ (**3**).

Frequencies at selected temperatures.

$[\mathrm{H_3N(CH_2)_3NH_3}]\mathrm{CdBr_4}$ (**1a**)

ν_i	Phase IV ν/MHz(T/K)		Phase III ν/MHz(T/K)	
$\nu_1(^{81}\mathrm{Br})$	61.177(77)	59.675(270)	57.955(329)	57.581(350)
$\nu_2(^{81}\mathrm{Br})$	45.934(77)	46.765(270)	48.416(329)	48.747(350)
$\nu_1(^{79}\mathrm{Br})$	73.229(77)	71.431(270)	69.372(329)	68.924(350)
$\nu_2(^{79}\mathrm{Br})$	54.983(77)	55.978(270)	57.955(329)	58.351(350)

The frequencies $\nu_2(^{81}\mathrm{Br})$ and $\nu_1(^{79}\mathrm{Br})$ are calculated from the measured values of $\nu_1(^{81}\mathrm{Br})$ and $\nu_2(^{79}\mathrm{Br})$, respectively, using the relation of $\nu(^{79}\mathrm{Br})/\nu(^{81}\mathrm{Br}) = 1.19707$.

$[\mathrm{D_3N(CH_2)_3ND_3}]\mathrm{CdBr_4}$ (**1b**)

ν_i	Phase IV$^{a)}$ ν/MHz(T/K)		Phase III$^{a)}$ ν/MHz(T/K)	
$\nu_1(^{81}\mathrm{Br})$	61.162(77)	59.619(270)	57.959(329)	57.639(348)
$\nu_2(^{81}\mathrm{Br})$	46.102(77)	47.047(270)	48.624(329)	48.876(348)
$\nu_1(^{79}\mathrm{Br})$	73.210(77)	71.363(270)	69.377(329)	68.994(348)
$\nu_2(^{79}\mathrm{Br})$	55.184(77)	56.315(270)	58.203(329)	58.504(348)

a) Phases are named corresponding to those for the protonated sample (**1a**).

b) The frequencies $\nu_2(^{81}\mathrm{Br})$ and $\nu_1(^{79}\mathrm{Br})$ are calculated from the measured values of $\nu_1(^{81}\mathrm{Br})$ and $\nu_2(^{79}\mathrm{Br})$, respectively, using the relation of $\nu(^{79}\mathrm{Br})/\nu(^{81}\mathrm{Br}) = 1.19707$.

$[1,4\text{-}(\mathrm{NH_3})_2\mathrm{C_6H_4}]\mathrm{CdBr_4}$ (**2**)

ν_i	ν/MHz(T/K)	ν/MHz(T/K)
$\nu_1(^{81}\mathrm{Br})$	70.159(77)	67.919(273)
$\nu_2(^{81}\mathrm{Br})$	53.622(85)	56.317(273)
$\nu_3(^{81}\mathrm{Br})$	40.056(77)	40.907(273)

$[n\text{-}\mathrm{H_3C(CH_2)_2NH_3}]_2\mathrm{CdBr_4}$ (**3a**)

ν_i	Phase V ν/MHz(T/K)		Phase I ν/MHz(T/K)	
$\nu_1(^{81}\mathrm{Br})$	61.060(77)	61.002(109)	57.853(208)	55.835(373)
$\nu_2(^{81}\mathrm{Br})$	54.098(77)	54.082(109)	54.312(208)	55.964(373)

$[\mathrm{H_3N(CH_2)_3NH_3}]\mathrm{CdBr_4}$ (**1a**)

Phase T/K range	ν	Z	σ kHz	a_0 MHz	a_{-1} MHzK	$a_1 \cdot 10^3$ MHzK^{-1}	$a_2 \cdot 10^6$ MHzK^{-2}
IV							
77, 260	$\nu_1(^{81}\mathrm{Br})$	18	10	61.363	–0.031	–0.652	–0.205
	$\nu_2(^{79}\mathrm{Br})$	15	8	55.171	0.134	–4.300	0.265
270, 325	$\nu_1(^{81}\mathrm{Br})$	6	36	35.969	0.555	1.794	–3.397
	$\nu_2(^{79}\mathrm{Br})$	6	44	86.380	–4.142	–226.782	423.572
III							
327, 350	$\nu_1(^{81}\mathrm{Br})$	13	7	60.566	–0.022	1.241	–27.948
	$\nu_2(^{79}\mathrm{Br})$	13	13	55.834	–0.133	–5.164	35.307

$[\mathrm{D_3N(CH_2)_3ND_3}]\mathrm{CdBr_4}$ (**1b**)

Phase T/K range	ν	Z	σ kHz	a_0 MHz	a_{-1} MHzK	$a_1 \cdot 10^3$ MHzK^{-1}	$a_2 \cdot 10^6$ MHzK^{-2}
IV							
77, 273	$\nu_1(^{81}\mathrm{Br})$	9	10	61.286	0.108	0.099	–0.225
	$\nu_2(^{79}\mathrm{Br})$	10	29	55.358	0.224	–4.344	28.212
298, 321	$\nu_1(^{81}\mathrm{Br})$	7	11	–5.517	20.557	446.913	–771.629
	$\nu_2(^{79}\mathrm{Br})$	7	23	146.794	4.670	–6.167	1055.401
III							
323, 348	$\nu_1(^{81}\mathrm{Br})$	8	7	61.398	0.292	–3.858	–19.985
	$\nu_2(^{79}\mathrm{Br})$	15	17	56.214	0.185	–4.533	31.960

$[1,4\text{-}(\mathrm{NH_3})_2\mathrm{C_6H_4}]\mathrm{CdBr_4}$ (**2**)

ν	Z	σ kHz	a_0 MHz	a_{-1} MHzK	$a_1 \cdot 10^3$ MHzK^{-1}	$a_2 \cdot 10^6$ MHzK^{-2}
$\nu_1(^{81}\mathrm{Br})$	60	23	70.475	1.170	–2.208	–26.804
$\nu_2(^{81}\mathrm{Br})$	73	28	50.111	138.055	23.400	–10.538
$\nu_3(^{81}\mathrm{Br})$	61	33	39.767	0.154	2.402	5.885

$[n\text{-}\mathrm{H_3C\ (CH_2)_2NH_3}]_2\mathrm{CdBr_4}$ (**3**)

Phase T/K range	ν	Z	σ kHz	a_0 MHz	a_{-1} MHzK	$a_1 \cdot 10^3$ MHzK^{-1}	$a_2 \cdot 10^6$ MHzK^{-2}
V							
77, 109	$\nu_1(^{81}\mathrm{Br})$	32	44	59.233	0.387	–3.888	–13.600
	$\nu_2(^{81}\mathrm{Br})$	50	37	50.372	0.049	24.186	–24.576
I							
208, 373	$\nu_1(^{81}\mathrm{Br})$	10	22	60.959	0.142	3.057	–24.541
	$\nu_2(^{81}\mathrm{Br})$	10	20	53.393	0.626	16.195	–92.942

165 K. The NQR data of phase I are in agreement with the crystal structure of (**3**) determined at 293 K. The cause of the disappearance of NQR lines between 109 and 208 K is not clear. $[n\text{-}\mathrm{H_3C(CH_2)_2NH_3}]_2\mathrm{CdCl_4}$ shows the incommensurate phase between 158 and 180 K [17]. If the incommensurate phase appears between 121 and 208 K also in the bromine analogue, the NQR lines become undetectable due to the modulated structure with disordered $\mathrm{CdBr_6}$ octahedra in the crystal of (**3**).

Discussion

Tetrachloro complex salts of metal ions such as Mn(II), Cu(II), and Fe(II) form perovskite type layer structures with cations $[\mathrm{RNH_3}]^+$ and $[\mathrm{H_3NR'NH_3}]^{2+}$, and these compounds are often found in the literature

Table 6. The transition points T_{tr}, transition enthalpies ΔH_{tr}, and transition entropies ΔS_{tr} in $[H_3N(CH_2)_3NH_3]CdBr_4$(**1**) and $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$(**3**).

Compounds	Trans.	T_{tr}/K	ΔH_{tr}/ kJmol^{-1}	ΔS_{tr}/ JK^{-1}mol^{-1}
$[H_3N(CH_2)_3NH_3]CdBr_4$	I↔II	495	0.76	1.5
(**1**)	II↔III	363	0.71	2.0
	III↔IV	328	3.3	10.5
$[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$	I↔II	208	0.77	4.0
(**3**)	II↔III	165	0.08	0.5
	III↔IV	135	0.32	2.4
	IV↔V	121[a)]	—	—

a) The temperature was determined by DTA measurement.

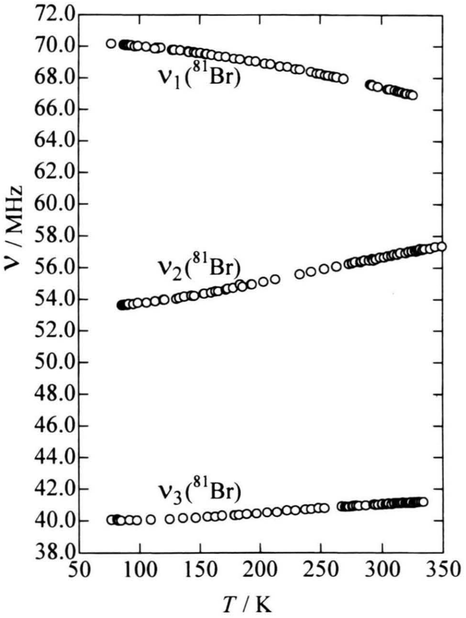


Fig. 10. Temperature dependence of ^{81}Br NQR frequencies of 1,4-phenylenediammonium tetrabromocadmate(II) (**2**).

during the last 20 years. Characteristic for these compounds are first- and/or second-order phase transitions which have their origin in the dynamics of the cations, and crystal structures built up by condensed octahedral layers $[MCl_6]_\infty$. The alkylammonium and alkylenediammonium cations are located between the layers, and the NH_3 groups form hydrogen bonds with the halogen atoms of the layers $[MCl_6]_\infty$. Many $CdCl_4{}^{2-}$(II) complexes form perovskite type layer structures like the above compounds [1]. But $CdBr_4^{2-}$(II) complexes mostly take

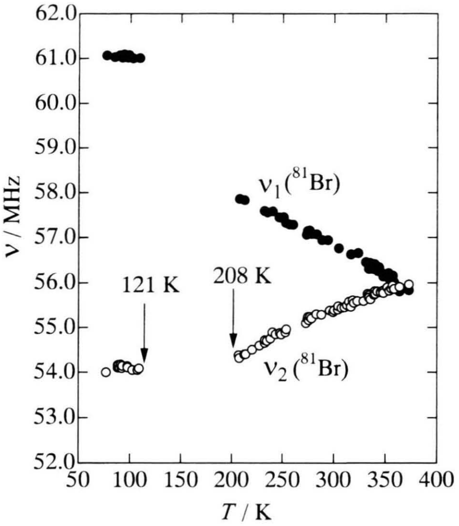


Fig. 11. Temperature dependence of ^{81}Br NQR frequencies of *n*-propylammonium tetrabromocadmate(II) (**3**).

one of two types of structures, either the perovskite type layer structure or the isolated tetrahedral anion structure. For example, $[CH_3NH_3]_2CdBr_4$ has an isolated tetrahedral anion structure [18], and the present report is concerned with layer structures of (**1**) and (**3**). All of $ZnX_4{}^{2-}$(II) (X =Cl, Br) complexes show isolated anion structures without exception [19].

What are the driving forces for the polymerization of the complex $M(Hal)_4^{2-}$(II)? One such force is the bridging power between the halogen atom and the central M(II) atom. We suppose that there is ordinarily a stronger tendency of the Cl atom to form bridging bonds than of the Br atom, and that there is little tendency between halogen and Zn(II) atoms, on the other hand, Fe(II), Cu(II), Mn(II) complexes show a strong tendency toward forming bridges. The second parameter influencing the condensation of anions seems to be the size of the cation, and the third one the formation of hydrogen bonds between NH_3^+ groups of the cation and the halogens of the anion, because $[N(CH_3)_4]MX_4$(M=Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg) has an isolated tetrahedral anion structure in general. The interplay of these parameters determining structures is not clear yet, and we need still more experimental work (structural and NQR) to elucidate it.

The $CdBr_4{}^{2-}$ salts of (**1**) and (**3**) form two-dimensional anion layers, probably because these formations are supported by the cation size and hydrogen bonds N-H···Br. In the crystal structure of 2,2-dimethyl-1,3-propanediammonium tetrabromocadmate(II) monohydrate [8], dimethylammonium tetrabromocadmate(II) [20], and N-methyl-1,3-propanediammnoium tetrabromocadmate(II) [21], isolated $CdBr_4$ tetrahedra are observed. This shows that for the rather large and "round" cations there is no space to occupy between condensed $CdBr_4$ layers, and the cations have no suitable geometries to form hydrogen bond networks like those observed for (**1**) and (**3**). Anion polymerization is not only a question of the bridging power of the respective halogen with metal atoms but also of the cation size and the support of the condensation of the anion by hydrogen bonds.

Acknowledgement

K. H., V. G. K., and H. I. are thankful to the Alexander von Humboldt-Stiftung for a fellowship. The support of the Deutsche Forschungsgemeinschaft and of the "Fonds der Chemische Industrie" is acknowledged, too.

[1] R. Blinc, M. Burger, B. Lozar, J. Seliger, J. Slak, V. Rutar, H. Arend, and R. Kind, J. Chem. Phys. **66**, 278 (1977).

[2] G. Chapuis, Acta Crystallogr. Sect B, **B34**, 1506 (1978).

[3] R. D. Willett, Acta Crystallogr. Sect B, **B33**, 1641 (1978).

[4] V. G. Krishnan and Al. Weiss , J. Mol. Struct. **176**, 323 (1988).

[5] V. G. Krishnan, S. q. Dou, and Al. Weiss, Z. Naturforsch. **46a**, 1063 (1991).

[6] H. Ishihara, V. G. Krishnan, S. q. Dou, and Al. Weiss, Z. Naturforsch. **49a**, 213 (1994).

[7] V. G. Krishnan, S. q. Dou, and Al. Weiss, Z. Naturforsch. **49a**, 223 (1994).

[8] H. Ishihara, S. q. Dou, K. Horiuchi, V. G. Krishnan, H. Paulus, H. Fuess, and Al. Weiss, Z. Naturforsch. **51a**, in press.

[9] G. M. Sheldrick, SHELX86. Program for the solution of crystal structures, University of Göttingen, Germany (1986). SHELX93. Program for crystal structure determination, University of Göttingen, Germany 1993.

[10] Further information on the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellshaft für wissenschaftlichtechnische Information mbH, D-76322 Eggenstein-Leopoldshafen, Germany. Inquires should be accompanied by the depository number CSD-58550, the names of the authors and the full literature reference.

[11] S. q. Dou, H. Paulus, and Al. Weiss, J. Mol. Struct. **345**, 1 (1995).

[12] B. Doudin and G. Chapuis, Acta Crystallogr. Sect C, **C48**, 1218 (1992).

[13] H. Ishihara, K. Horiuchi, K. Yamada, T. Okuda, V. G. Krishnan, and Al. Weiss, Chem. Lett. **1996**, 371.

[14] J. C. Crowley, H. W. Dodgen, R. D. Willett, J. Phys. Chem., **86**, 4046 (1982). R. Kind, S. Plesko, and J. Roos, Phys. Status Solidi A **47**, 233 (1978).

[15] H. Bayer, Z. Phys. **130**, 227 (1951).

[16] D. Nakamura, R. Ikeda, and M. Kubo, Coord. Chem. Rev. **17**, 281 (1975).

[17] B. Doudin and G. Chapuis, Acta Crystallogr. Sect B, **B44**, 495 (1988).

[18] D. Altermatt, H, Arend, A. Niggli, and W. Peter, Mat. Res. Bull. **14**, 1391 (1979).

[19] K. Horiuchi, H. Ishihara, S. q. Dou, H. Paulus, H. Fuess, and Al. Weiss, Z. Naturforsch. to be submitted.

[20] A. Wakowska, Z. Kristallogr., **209**, 752 (1994).

[21] H. Ishihara, S. q. Dou, K. Horiuchi, H. Fuess, and Al, Weiss, Z. Naturforsch. to be submitted.