Structure and Bonding of Tribromocadmates, $ACdBr_3$, $A = NH_4$, Rb, Cs, $[CH_3NH_3]$, $[(CH_3)_2NH_2]$, $[(CH_3)_4N]$, $[H_2NNH_3]$, and $[(H_2N)_3C]$. An X-ray Diffraction and ^{79,81}Br NQR Study

V. G. Krishnan*, Shi-qi Dou, and Alarich Weiss

Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt,
Darmstadt, Germany

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The ^{79,81}Br NQR spectra of tribromocadmates with the cations $K^{\oplus}$, $NH_4^{\oplus}$, $Rb^{\oplus}$, $Cs^{\oplus}$, $CH_3NH_3^{\oplus}$, $(CH_3)_2NH_2^{\oplus}$, $(CH_3)_4N^{\oplus}$, $H_2NNH_3^{\oplus}$, and $C(NH_2)_3^{\oplus}$ were studied as functions of temperature from 77 K on up to $T > 300$ K. $CsCdBr_3$ shows a singlet ^{81}Br NQR spectrum over the whole temperature range studied. $[CH_3NH_3]CdBr_3$, with one ^{81}Br NQR line spectrum at room temperature, experiences a phase transition at 167 K; below this temperature an 18-line spectrum is observed. In $[(CH_3)_4N]CdBr_3$ (phase II), at 290 K, a singlet ^{81}Br NQR is present as is in the high temperature phase I ($T_{II,I} = 390$ K); the low temperature phase III ($T_{II,III} = 160$ K has a triplet ^{81}Br NQR spectrum. $KCdBr_3$ shows an ^{81}Br NQR doublet spectrum, as do $RbCdBr_3$, $[H_2NNH_3]CdBr_3$, and $[C(NH_2)_3]CdBr_3$. ^{81}Br NQR triplets are observed for $[(CH_3)_2NH_2]CdBr_3$ and NH_4CdBr_3.

Several crystal structures were determined (at room temperature). $[(CH_3)_4N]CdBr_3$: $P6_3/m$, $Z = 2$, $a = 940$ pm, $c = 700$ pm, disordered cation, single chain Perovskite with face connected $[CdBr_6]$-octahedra (nearly $CsNiCl_3$-type). $[(CH_3)_2NH_2]CdBr_3$: $P2_1/c$, $Z = 4$, $a = 898$ pm, $b = 1377$ pm, $c = 698$ pm, $\beta = 97.2°$, face connected $[CdBr_6]$-octahedra single chain Perovskite. NH_4CdBr_3: Pnma, $Z = 4$, $a = 950$ pm, $b = 417$ pm, $c = 1557$ pm, with a double chain of condensed $[CdBr_6]$-octahedra, NH_4CdCl_3-type. $[N_2H_5]CdBr_3$: $P2_1/c$, $Z = 4$, $a = 395$ pm, $b = 1749$ pm, $c = 997$ pm, $\beta = 94.2°$, double chain polyanion similar to NH_4CdBr_3. $[C(NH_2)_3]CdBr_3$: $C2/c$, $Z = 4$, $a = 778$ pm, $b = 1598$ pm, $c = 746$ pm, $\beta = 110.2°$, a single chain Perovskite with a chain of condensed trigonal bipyramids $[CdBr_5]$.

Three types of anion chains of $CdBr_3^-$ have been observed: Single octahedral chains, face connected; double octahedral chains, edge connected; a trigonal-bipyramidal chain, edge connected. The relation between the crystal structure and the Br NQR is discussed.

Introduction

Many solids with the composition ABX_3 crystallize in their high temperature phase with the structure of the Perovskite, $CaTiO_3$, space group O_h^1-Pm3m, number of formula units in the unit cell $Z = 1$. The atom A is located at the corners of the cubic unit cell (0, 0, 0), B is at the center of the cell $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and X at the centers of the cube faces $(\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2})$. The main feature of the crystal structure is the three-dimensional network of corner sharing octahedra BX_6. Such an arrangement is not a very stable one and therefore the Perovskite type structures often experience phase transitions, whereby the symmetry of the lattice is lowered and the three-dimensional net of octahedra is changing to two-dimensional connections, planes of octahedra, or to one-dimensional chains of octahedra. The oxides ABO_3 have been treated in numerous investigations within the last 40 years, mainly because of their interesting dielectric properties (ferroelectric phases).

Also with X = halogen, a good number of solid phases ABX_3, belonging to the class of Perovskites, have been described in literature. As for A and B, the group is more restricted than the family of oxide Perovskites because $A = A^I$ and $B = B^{II}$. On the other hand X may be F, Cl, Br, and I, B may be Zn^{II}, Cd^{II}, Hg, Ge^{II}, Sn^{II}, Pb^{II}.

In the course of investigations of the structure and bonding of hexahalogeno complexes, we have studied by ^{79,81}Br nuclear quadrupole resonance, NQR, some

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* Permanent address: Physics Department, Osmania University, Hyderabad-500 007, India.

Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, W-6100 Darmstadt, FRG.

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compounds $A_4[CdBr_6]$, in which the bond Cd–Br is strongly ionic [1]. Continuing this work, we have not been able to prepare by variation of A new complexes with isolated ions $[CdBr_6]^{4\ominus}$. A compound with the composition $(A)_2CdBr_6$, A = ethylenediammonium (enH_2) is, according to the crystal structure determination and to the ^{79,81}Br NQR spectrum, a double salt of composition $(enH_2^{2\oplus})_2[CdBr_4]^{2\ominus} \cdot 2\,Br^{\ominus}$ [2]. During the progress of these experiments a number of solids with the general composition $A^{I}CdBr_3$ have been prepared and their crystal structures, ^{79,81}Br NQR, and phase transitions have been investigated. Here, we report about this work.

Experimental

Preparation, Chemical Analysis

The compounds were prepared from stoichiometric amounts of aqueous solutions of $CdBr_2$ and the aqueous solution of the elected base plus HBr. If the corresponding bromide ABr was available, it was used. All chemicals were of laboratory grade (Aldrich). The compounds were crystallized from solution at room temperature at a pH 4–5. In Table 1 we list the compounds investigated, the habitus and their chemical analyses, except for $KCdBr_3$ and $RbCdBr_3$. These two compounds have been prepared and studied by ^{79,81}Br NQR. The preparation, crystal structure, and some other properties of $RbCdBr_3$ are described in [3, 4].

Crystal Structure Determination

The crystal structures of the title compounds, if unknown, were determined by single crystal X-ray diffraction technique on a four-circle diffractometer. Small crystals for X-ray diffraction were grown from aqueous solution of the corresponding compound. All crystal structure studies were done at room temperature. After collection of the intensity data, they were corrected in an appropriate way for absorption and Lorentz-Polarization factor. The point positions of the atoms were determined by direct methods, using the program SHELX 86 [5], and the final positional and thermal parameters were found by least squares refinement using SHELX 76 [6]. In some cases, the hydrogen atoms could not be located due to the heavy atoms Cd and Br and/or due to strong librational motions of the cations (or parts (groups) of the cations).

^{79,81}Br Nuclear Quadrupole Resonance

The NQR spectra of the Br nuclei were taken as functions of temperature on polycrystalline samples. A superregenerative receiver was used. Frequency measurements, temperature generation and measurement at the sample site, and estimate of the experimental error have been performed as described earlier, see e.g. [2]. The signal to noise ratio, (S/N), for the NQR lines is taken from registered spectra, lock in technique, 10 s time constant.

Table 1. Melting point Mp (in K), habitus, colour, and chemical analysis (in weight%) of the studied compounds $ACdBr_3$.

Compound [A]	Mp/K	Habitus, colour	Chemical analysis (found/calculated)			
			C	H	N	Br
$[(CH_3)_4N]$		needles colourless	11.09/11.27	2.73/2.84	3.21/3.29	55.17/56.24
$[(CH_3)_2NH_2]$	539	needles colourless	6.05/6.13	2.03/2.06	3.52/3.57	60.63/61.12
$[CH_3NH_3]$	559	needles slightly yellow	3.04/3.13	1.52/1.57	3.59/3.65	61.73/62.40
[Cs]		needles colourless				49.91/49.43
$[NH_4]$	488	needles colourless				63.27/64.76
$[N_2H_5]$	514	needles colourless		1.32/1.31	7.12/7.27	60.83/62.24
$[C(NH_2)_3]$	591	needles prisms colourless	2.75/2.91	1.49/1.47	9.73/10.19	57.61/58.16

Table 2. Experimental conditions for the crystal structure determinations and crystallographic data of $ACdBr_3$, $A = [N(CH_3)_4]$, $[(CH_3)_2NH_2]$, $[NH_4]$, $[N_2H_5]$, $[C(NH_2)_3]$. Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm MoKα); monochromator: Graphite (002); scan: $\omega/2\vartheta$. For detailed information, see [30].

A	$[N(CH_3)_4]$	$[(CH_3)_2NH_2]$	$[NH_4]$	$[N_2H_5]$	$[C(NH_2)_3]$
Formula	$C_4H_{12}Br_3CdN$	$C_2H_8Br_3CdN$	Br_3CdH_4N	$Br_3CdH_5N_2$	$CH_6Br_3CdN_3$
Habitus	needles	needles	needles	needles	prisms
Size	(0.17 × 0.20 × 2.3)	(0.13 × 0.15 × 1.2)	(0.14 × 0.18 × 0.75)	(0.15 × 0.17 × 1.0)	(0.45 × 0.5 × 0.8) mm^3
Molar mass	426.27	398.22	369.2	385.2	412.2
Temperature/K	294	299	295	299	297
Absorption coefficient μ/m^{-1}	13070	16330	22660	20306	16090
$F(000)$	392	720	656	688	784
$(\sin\vartheta/\lambda)_{max}/pm^{-1}$					
No. of reflexions measured	1578	2500	1184	2501	1215
Symmetry independent reflexions	345	1509	619	1207	1000
Reflexions considered	340	1439	604	1190	921
Number of free parameters	25	71	43	71	49
$R(F)$	0.073	0.051	0.032	0.035	0.047
$R_w(F)$	0.067	0.049	0.032	0.033	0.044
Lattice constants:					
a/pm	940.0(3)	898.2(3)	949.9(2)	394.7(2)	777.8(3)
b/pm	940.0(3)	1376.5(5)	416.9(1)	1749.4(6)	1598.3(6)
c/pm	699.6(2)	697.9(2)	1556.5(4)	996.8(3)	746.0(3)
$\beta/°$		97.19(5)	90.00(0)	94.19(1)	110.18(1)
Unit cell, $V \cdot 10^{-6}/(pm^3)$	535.35(39)	856.08(83)	616.39(44)	686.44(78)	870.47(95)
Space group	C_{6h}^2-$P6_3/m$	C_{2h}^5-$P2_1/c$	D_{2h}^{16}-Pnma	C_{2h}^5-$P2_1/c$	C_{2h}^6-$C2/c$
Formula units per unit cell, Z	2	4	4	4	4
$\varrho_{calc}/(Mg \cdot m^{-3})$	2.644(3)	3.089(3)	3.977(3)	3.726(4)	3.144(3)
$\varrho_{pykn}/(Mg \cdot m^{-3})$	2.58	3.07	3.95	3.69	3.14

Point positions:

$[(CH_3)_4N]$: Cd in 2b: $(0, 0, 0)$, $(0, 0, \frac{1}{2})$; N in 2c: $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$; $C^{(1)}$, Br in 6h: $(x, y, \frac{1}{4})$, $(\bar{y}, x-y, \frac{1}{4})$, $(y-x, \bar{x}, \frac{1}{4})$, $(\bar{x}, \bar{y}, \frac{3}{4})$, $(y, y-x, \frac{3}{4})$, $(x-y, x, \frac{3}{4})$; $C^{(2)}$ in 12i: (x, y, z), $(\bar{y}, x-y, z)$, $(y-x, \bar{x}, z)$, $(\bar{x}, \bar{y}, \bar{z})$, $(y, y-x, \bar{z})$, $(x-y, x, \bar{z})$, $(\bar{x}, \bar{y}, \frac{1}{2}+z)$, $(y, y-x, \frac{1}{2}+z)$, $(x-y, x, \frac{1}{2}+z)$, $(x, y, \frac{1}{2}-z)$, $(\bar{y}, x-y, \frac{1}{2}-z)$, $(y-x, \bar{x}, \frac{1}{2}-z)$.

$[(CH_3)_2NH_2]$ and $[N_2H_5]$: All atoms in 4e: (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$, $(x, \frac{1}{2}-y, \frac{1}{2}+z)$.

$[NH_4]$: Cd, $Br^{(1,2,3)}$, N in 4c: $(\bar{x}, \frac{3}{4}. \bar{z})$, $(x, \frac{1}{4}, z)$, $(\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z)$, $(\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$.

$[C(NH_2)_3]$: Cd, $Br^{(1)}$, C, $N^{(1)}$ in 4e: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)+(0, y, \frac{1}{4})$, $(0, \bar{y}, \frac{3}{4})$; all other atoms in 8f: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)+(x, y, z)$, $(\bar{x}, \bar{y}, \bar{z})$, $(\bar{x}, y, \frac{1}{2}-z)$, $(x, \bar{y}, \frac{1}{2}+z)$.

Results

In Table 2 we have listed the experimental conditions for the crystal structure determinations and some crystallographic data of the title compounds, such as lattice constants, space group, reliability factor R etc. The ^{81}Br NQR frequencies for selected temperatures are collected in Table 3, and, as usual, we have parameterized the temperature dependence of the Br NQR frequencies on the basis of

$$\nu = \sum_{i=-1}^{3} a_i T^i. \tag{1}$$

For the title compounds the coefficients of the polynomial are listed in Table 4.

Tetramethylammonium tribromocadmate, $[(CH_3)_4N]CdBr_3$

Tetramethylammonium tribromocadmate crystallizes hexagonal, with the space group C_{6h}^2-$P6_3/m$, $Z = 2$, as reported by Daoud [7]. From the cell dimensions and the space group, the author concludes isomorphism of the compound with $[(CH_3)_4N]CdCl_3$ [8] and $[(CH_3)_4N]Mn^{II}Cl_3$ [9]. The crystal structure determination of $[(CH_3)_4N]CdBr_3$ reported here is, as

Table 3. ^{79,81}Br NQR frequencies of the title compounds $\mathrm{ACdBr_3}$ at selected temperatures. The signal to noise (S/N) was measured with lock in technique, time constant 10 s. All frequencies are given in MHz. (S/N) is given for $\nu(^{81}\mathrm{Br})$.

[A]	ν_i	77 K			273 K			360 K		
		$\nu(^{81}\mathrm{Br})$	$\nu(^{79}\mathrm{Br})$	(S/N)	$\nu(^{81}\mathrm{Br})$	$\nu(^{79}\mathrm{Br})$	(S/N)	$\nu(^{81}\mathrm{Br})$	$\nu(^{79}\mathrm{Br})$	(S/N)
$[(\mathrm{CH_3})_4\mathrm{N}]$	ν_1	50.233 *	60.109 *	(30)	46.259 **	55.368 **	(>100)	45.812 **	54.831 **	(>100)
	ν_2	47.394 *	56.723 *	(30)						
	ν_3	46.573 *	55.745 *	(30)						
$[(\mathrm{CH_3})_2\mathrm{NH_2}]$	ν_1	49.126	58.793	(20)	48.626	58.199	(10)	48.037	57.492	(3)
	ν_2	42.711	51.118	(20)	42.393	50.739	(10)	40.788	48.816	(3)
	ν_3	40.442	48.393	(20)	39.333	47.077	(10)	38.768	46.397	(3)
$[\mathrm{CH_3NH_3}]$	ν	***	***	(8)	42.638	51.044	(>100)	42.512	50.887	(>100)
[Cs]	ν	43.616	52.218	(>100)	43.194	51.719	(>100)	42.959	51.431	(>100)
$[\mathrm{NH_4}]$	ν_1	50.778	60.778	(25)	51.705	61.886	(12)	52.449	62.767	(3)
	ν_2	47.445	56.779	(23)	47.687	57.072	(12)	47.537	56.888	(3)
	ν_3	15.897	19.021	(23)	15.781	18.881	(12)	15.744	18.833	(3)
$[\mathrm{N_2H_5}]$	ν_1	49.583	59.344	(15)	50.747	60.737	(5)	51.329	61.434	(3)
	ν_2	47.487	56.833	(50)	46.307	55.422	(40)	45.784	54.794	(20)
$[\mathrm{C(NH_2)_3}]$	ν_1	75.834		(15)	74.191		(10)	73.302		(4)
	ν_2	52.895	63.310	(25)	53.579	64.128	(20)	53.651	64.213	(15)
[Rb]	ν_1	56.681	67.839	(23)	57.128	68.374	(10)	57.344	68.631	(4)
	ν_2	48.971	58.632	(25)	48.751	58.365	(10)	48.603	58.188	(4)
[K]	ν_1	59.419	71.111	(15)	59.141	70.779	(8)	58.846	70.422	(3)
	ν_2	50.655	60.621	(12)	50.502	60.438	(8)	50.419	60.338	(3)

* Phase III. ** Phase II.

*** ν_1; $\nu(^{81}\mathrm{Br})$ ($\nu(^{79}\mathrm{Br})$); ν_1: 53.853 (64.447); ν_3: 49.631 (59.396); ν_2: 47.685 (57.063); ν_7: 47.329 (56.691); ν_4: 47.131 (56.401); ν_{13}: 45.104 (53.973); $\nu_{5,8,11}$: 44.503 (53.258); $\nu_{6,14}$: 43.772 (52.402); ν_9: 42.561 (50.932); ν_{12}: 42.224 (50.528); ν_{10}: 41.819 (50.043); $\nu_{17,18}$: 39.901 (47.756); ν_{15}: 39.711 (47.524); ν_{16}: 39.042 (46.726). The numbering $\nu_{1\ldots18}$ is done at the phase transition point, see Fig. 5b.

Table 4. Power series development of $\nu_1 = f(T)$ of the title compounds $\mathrm{ACdBr_3}$ according to Eq. (1), $\nu = \sum a_1 T^i$. Z is the number of measurements taken for the least squares adjustment, σ is the mean deviation, $\Delta T = T_1 \ldots T_2$ is the temperature range for which the polynomial approximation is valid.

[A]	$\nu_1(^{79,81}\mathrm{Br})$	Z	$\frac{\sigma \cdot 10^3}{\mathrm{MHz}}$	$\frac{a_{-1}}{\mathrm{MHz \cdot K}}$	$\frac{a_0}{\mathrm{MHz}}$	$\frac{a_1 \cdot 10^3}{\mathrm{MHz \cdot K^{-1}}}$	$\frac{a_2 \cdot 10^9}{\mathrm{MHz \cdot K^{-2}}}$	$\frac{a_3 \cdot 10^9}{\mathrm{MHz \cdot K^{-3}}}$	$\frac{\Delta T}{\mathrm{K}}$
$[(\mathrm{CH_3})_4\mathrm{N}]$	$\nu_1(^{81}\mathrm{Br})$	13	14	−2440.258	144.978	−1.345	8.486	−19.934	77 … 140
	$\nu_2(^{81}\mathrm{Br})$	17	9	139.023	43.39	39.523	−142.18	–	77 … 160.6
	$\nu_3(^{81}\mathrm{Br})$	19	3	45.996	45.299	13.765	−64.626	–	77 … 160.6
	$\nu_1(^{81}\mathrm{Br})$	28	10	272.671	43.575	13.048	−24.945	–	162 … 385
$[(\mathrm{CH_3})_2\mathrm{NH_2}]$	$\nu_1(^{81}\mathrm{Br})$	21	14	−145.501	52.985	−0.0336	0.114	−0.154	77 … 380
	$\nu_2(^{81}\mathrm{Br})$	21	14	−236.267	49.428	−0.0663	0.274	−0.4185	77 … 380
	$\nu_3(^{81}\mathrm{Br})$	22	14	−114.116	43.645	−0.0276	0.072	−0.085	77 … 380
$[\mathrm{CH_3NH_3}]$	$\nu_1(^{81}\mathrm{Br})$	26	3	148.122	41.257	0.0054	−8.443	–	166 … 422
[Cs]	$\nu_1(^{79}\mathrm{Br})$	28	4	4.855	52.294	−1.729	−1.719	–	77 … 426
						3.53	7.90	–	77 … 360
$[\mathrm{NH_4}]$	$\nu_1(^{81}\mathrm{Br})$	27	11	34.157	50.023				
	$\nu_2(^{81}\mathrm{Br})$	20	4	−121.251	49.266	−4.97	3.027	–	77 … 360
	$\nu_3(^{81}\mathrm{Br})$	27	3	–	15.952	−0.606	0.032	–	77 … 360
$[\mathrm{N_2H_5}]$	$\nu_1(^{81}\mathrm{Br})$	39	10	22.002	49.266	0.909	13.51	–	77 … 388
	$\nu_2(^{81}\mathrm{Br})$	31	7	7.796	47.450	0.215	−13.6	–	77 … 388
$[\mathrm{C(NH_2)_3}]$	$\nu_1(^{81}\mathrm{Br})$	31	15	−10.317	76.599	−7.649	−4.077	–	77 … 446
	$\nu_2(^{81}\mathrm{Br})$	44	3	5.558	52.405	5.988	−7.129	–	77 … 448
[Rb]	$\nu_1(^{81}\mathrm{Br})$	21	4	5.528	56.402	2.687	−0.35	–	77 … 360
	$\nu_2(^{79}\mathrm{Br})$	23	3	−0.342	58.696	−0.614	−2.218	–	77 … 360
[K]	$\nu_1(^{81}\mathrm{Br})$	25	5	−0.332	59.387	0.962	−6.930	–	77 … 360
	$\nu_2(^{81}\mathrm{Br})$	25	2	3.360	50.642	−3.270	−0.859	–	77 … 360

much as symmetry and lattice constants are concerned, in good agreement with the determination of these properties by Daoud. In Fig. 1 we show the projection of the unit cell of the compound along [001]. In the figure, there are several positions with varying occupancy factor *K* for both crystallographically different carbon atoms of the tetramethylammonium ion, originating in a dynamical disorder of the cation. The positional coordinates are listed in Table 5 which contains the thermal parameters, too. Included in this table are also the intra- and intermolecular (ionic) distances and angles.

In Fig. 2 the ^{81}Br NQR spectrum of the title compound is plotted in its dependence on temperature. From 77 K up to about 160 K the spectrum has a triplet structure with a frequency spread of about 3.5 MHz at 77 K. This low temperature phase III transforms at 160 K to phase II; the ^{81}Br NQR spectrum is a singlet. Phase II is stable up to 390 K; the crystal structure we report is that of phase II. A definite change in the slope of $\nu(^{81}\mathrm{Br}) = f(T)$ marks the transition from phase II to phase I (see the insert in Figure 2). For the three phases of tetramethylammonium tribromocadmate ^{79,81}Br NQR frequencies at selected temperatures are found in Table 3, and the coefficients of the parameterized curves $\nu(^{81}\mathrm{Br}) = f(T)$ are listed in Table 4.

Dimethylammonium tribromocadmate, $[(CH_3)_2NH_2]CdBr_3$

Dimethylammonium tribromocadmate crystallizes with the space group C_{2h}^5-$P2_1/c$, $Z = 4$, see Table 2. In Table 6 the positions of the atoms in the unit cell are given together with the thermal parameters, and in Table 7 one finds intra- and intermolecular (ionic) distances and angles. In Fig. 3a we show the projection of the unit cell along the *a*-axis of the crystal. Chains of face connected octahedra $[CdBr_6]$ are running along the *c*-direction of the unit cell. The hydrogen bonds N–H ··· Br are marked in the figure by dotted lines. In Fig. 3b the numbering of the atoms within one formula unit is given, connected to Fig. 3a by the ions marked there by stars.

In the unit cell, the bromine atoms are located at the general point position 4e, and with $Z = 4$ there are three crystallographically independent bromines in the solid compound, see Table 2. The ^{81}Br NQR spectrum of dimethylammonium tribromocadmate is a three line spectrum, as predicted by the crystal structure. In Fig. 4 the NQR frequencies are plotted as functions of temperature. No sign of a phase transition within the temperature range covered can be recognized. For selected temperatures the frequencies are listed (Table 3) and the parameters of the polynomial description of $\nu = f(T)$ (1) are found in Table 4.

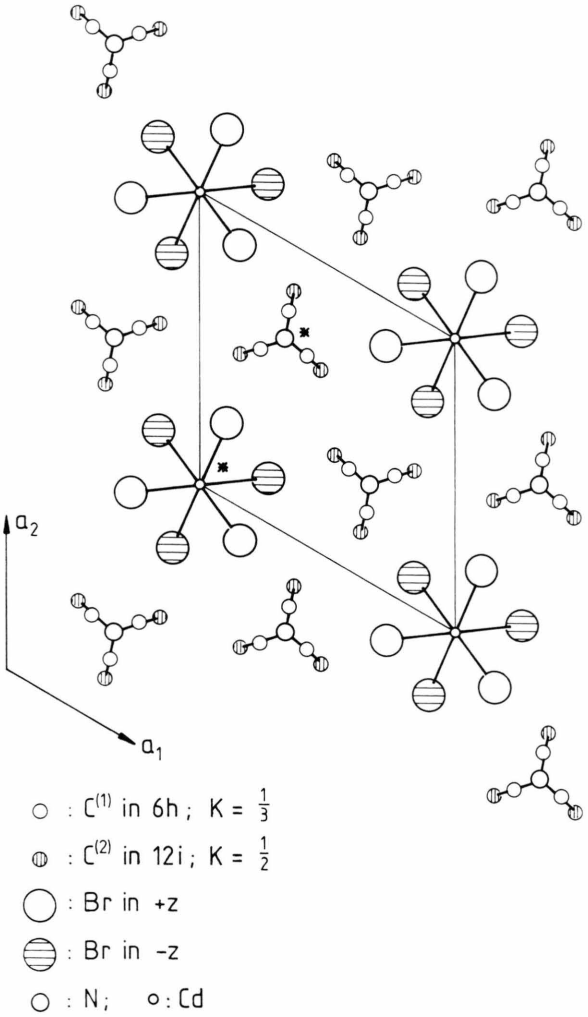


Fig. 1. Projection of the unit cell of $[(CH_3)_4N]CdBr_3$ along [001] onto the hexagonal basis plane. The cation and anion for which the coordinates are given in Table 5 are marked by *. The structure, taken at room temperature, is characterized by the disorder of the cation $[(CH_3)_4N]^{\oplus}$.

Methylammonium tribromocadmate, $[CH_3NH_3]CdBr_3$

The crystal structure of methylammonium tribromocadmate was determined by Fuess and coworkers

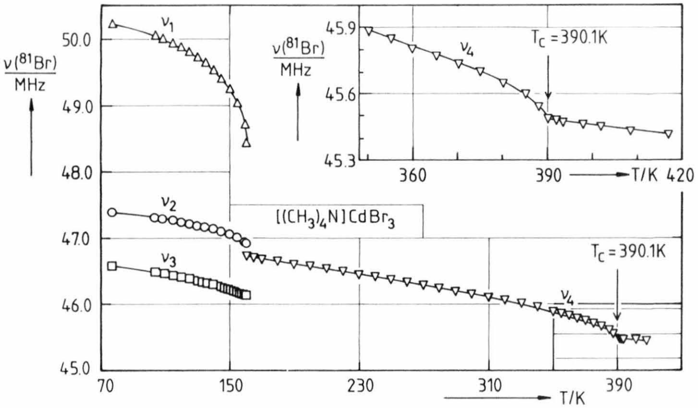


Fig. 2. $\nu(^{81}\mathrm{Br})$ as a function of temperature for $[(\mathrm{CH_3})_4\mathrm{N}]\mathrm{CdBr_3}$. The transition Phase II ↔ Phase I is shown separately in the insert of the figure.

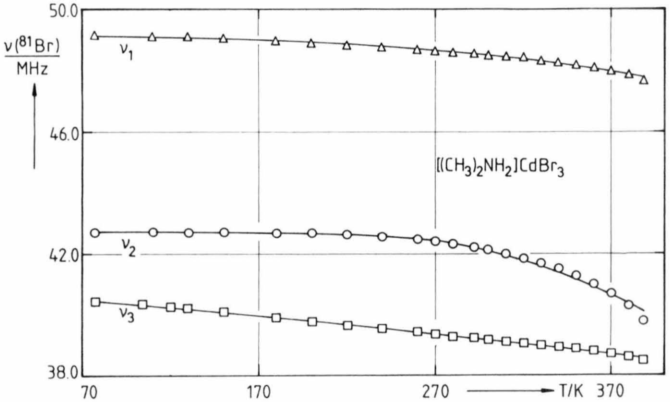


Fig. 4. Temperature dependence of the ^{81}Br NQR spectrum (triplet) of dimethylammonium tribromocadmate.

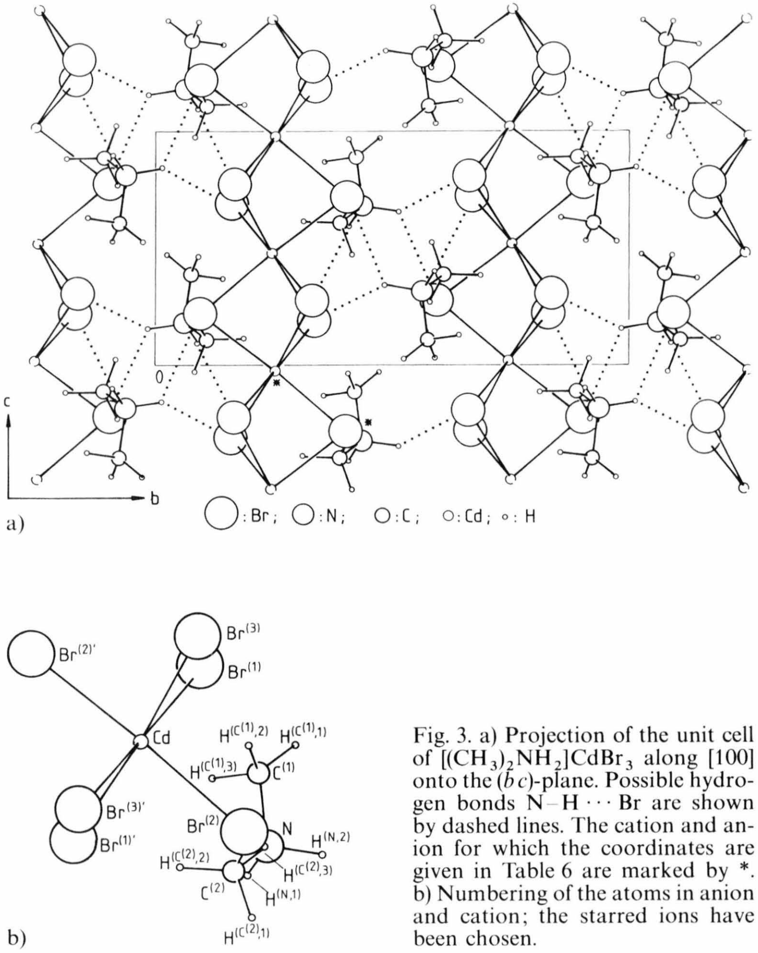


Fig. 3. a) Projection of the unit cell of $[(\mathrm{CH_3})_2\mathrm{NH_2}]\mathrm{CdBr_3}$ along [100] onto the $(b\,c)$-plane. Possible hydrogen bonds N–H ··· Br are shown by dashed lines. The cation and anion for which the coordinates are given in Table 6 are marked by *. b) Numbering of the atoms in anion and cation; the starred ions have been chosen.

Table 5. Positions and thermal parameters of tetramethylammonium tribromocadmate $[(CH_3)_4N]CdBr_3$; the temperature factor is of 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 U_{ij} are given in $(pm)^2$; U is the isotropic mean for the hydrogen atoms.

Atom	x/a	y/a	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0.0	0.0	0.5	353(8)	353(8)	353(8)	177(4)	0	0
Br	0.2652(3)	0.1579(3)	0.25	309(12)	415(14)	305(11)	133(10)	0	0
N	0.3333	0.6667	0.25	332(70)	332(70)	332(70)	166(35)	0	0
$C^{(1)}$ a)	0.1587(28)	0.5284(59)	0.25	485(180)					
$C^{(2)}$ b)	0.2346(68)	0.5825(89)	0.0751(44)	1850(311)					

a) $K = 1/3$; b) $K = 1/2$

Intra- and intermolecular distances (d/pm) and angles (°)

Connection	d/pm	Connections		Angles/°
Cd–Br	278.9(2)	Br–Cd–Br		84.8(0)
$C^{(1)}$–N	150.0(1)	Cd–Br–Cd		77.7(1)
$C^{(2)}$–N	150.0(1)	Br–Cd–Br	(6×)	180.0
Cd–Cd	349.8(0)		(6×)	95.2
Br–Br (interplanar)	411.7(2)		(6×)	84.8
Br–Br (intraplanar)	376.2(2)			

Table 6. Positions and thermal parameters of dimethylammonium tribromocadmate, $[(CH_3)_2NH_2]CdBr_3$; the temperature factor is of 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 U_{ij} are given in $(pm)^2$; U is the isotropic mean for the hydrogen atoms.

Atom	x/a	y/b	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0.7840(1)	0.2535(1)	−0.0219(2)	509(7)	444(7)	242(6)	52(6)	66(5)	19(6)
$Br^{(1)}$	0.5809(2)	0.3378(1)	0.1919(2)	367(8)	472(10)	322(9)	50(7)	33(7)	−7(8)
$Br^{(2)}$	0.7889(2)	0.4039(2)	−0.2797(2)	607(10)	344(10)	278(9)	−4(8)	32(8)	−4(8)
$Br^{(3)}$	0.9993(2)	0.1683(1)	−0.2237(2)	409(9)	585(12)	335(9)	140(8)	56(7)	−30(9)
N	0.2172(16)	0.4374(11)	−0.3189(20)	744(97)	713(114)	278(81)	151(86)	−21(73)	2(83)
$C^{(1)}$	0.2043(23)	0.4237(16)	−0.1097(26)	1096(165)	949(185)	265(105)	54(136)	199(111)	−30(115)
$C^{(2)}$	0.3501(19)	0.3911(16)	−0.3900(32)	791(135)	947(169)	665(149)	299(133)	213(120)	−243(140)
$H^{(N,1)}$	0.1175(16)	0.4091(11)	−0.4026(20)	600					
$H^{(N,2)}$	0.2243(16)	0.5148(11)	−0.3430(20)	600					
$H^{(C(1),1)}$	0.1458(23)	0.4741(16)	−0.0270(26)	600					
$H^{(C(1),2)}$	0.3141(23)	0.4089(16)	−0.0334(26)	600					
$H^{(C(1),3)}$	0.1413(23)	0.3569(16)	−0.1297(26)	600					
$H^{(C(2),1)}$	0.3804(19)	0.4161(16)	−0.5266(26)	600					
$H^{(C2),2)}$	0.3536(19)	0.3127(16)	−0.3855(26)	600					
$H^{(C(2),3)}$	0.4282(19)	0.4201(16)	−0.2738(26)	600					

[10]. At room temperature, the compounds crystallizes hexagonal with the space group D^4_{6h}-$P6_3/mmc$, $Z = 2$. The bromine atoms are located at the point position 6h. Chains of octahedra $CdBr_6$, running along the *c*-axis, determine the frame of the crystal structure.

The ^{81}Br NQR spectrum, at room temperature, agrees with the crystal structure. Only one resonance line is observed. However, the spectrum becomes very complicated below 167 K; the singlet transforms into a complicated 18-line spectrum as shown in Figures 5a, b. The phase transition was already reported and a structure model proposed for the low temperature phase II [10]. We find phase II existing from 167 K down to 77 K. There was a phase III observed [10], stable below 60 K. Again, we have listed the ^{81}Br NQR frequencies at certain temperatures (Table 3) and $\nu(^{81}Br) = f(T)$ in parameterized form (Table 4).

Table 7. Dimethylammonium tribromocadmate, $[(CH_3)_2NH_2]CdBr_3$; intra- and intermolecular distances (d/pm) and angles (°).

Connection	d/pm	Connection	Angle/°
$\mathrm{Cd{-}Br}^{(1)}$	275.3(2)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(2)}$	95.9(1)
$\mathrm{Cd{-}Br}^{(2)}$	274.7(2)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(3)}$	177.4(1)
$\mathrm{Cd{-}Br}^{(3)}$	278.9(2)	$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(3)}$	85.3(1)
$\mathrm{Cd{-}Br}^{(1)\prime}$	282.5(2)	$\mathrm{C}^{(1)}\mathrm{{-}N{-}C}^{(2)}$	115.8(16)
$\mathrm{Cd{-}Br}^{(2)\prime}$	274.5(2)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(1)\prime}$	99.4(1)
$\mathrm{Cd{-}Br}^{(3)\prime}$	286.8(2)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(2)\prime}$	87.7(1)
$\mathrm{N{-}C}^{(1)}$	149.1(21)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	82.8(1)
$\mathrm{N{-}C}^{(2)}$	149.2(19)	$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(2)\prime}$	176.3(1)
$\mathrm{Br}^{(1)*}\ldots\mathrm{N}$	363.9(16)	$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	83.8(1)
$\mathrm{Br}^{(1)*}\ldots\mathrm{H}^{(\mathrm{N},2)}$	279.8(16)	$\mathrm{Br}^{(3)}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	94.8(1)
$\mathrm{Br}^{(2)*}\ldots\mathrm{N}$	354.6(15)	$\mathrm{Br}^{(1)\prime}\mathrm{{-}Cd{-}Br}^{(2)\prime}$	86.2(1)
$\mathrm{Br}^{(2)*}\ldots\mathrm{H}^{(\mathrm{N},2)}$	285.0(14)	$\mathrm{Br}^{(1)\prime}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	175.6(1)
$\mathrm{Br}^{(3)*}\ldots\mathrm{N}$	354.2(15)	$\mathrm{Br}^{(2)\prime}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	97.4(1)
$\mathrm{Br}^{(3)*}\ldots\mathrm{H}^{(\mathrm{N},1)}$	258.6(15)	$\mathrm{Cd{-}Br}^{(1)}\mathrm{{-}Cd'}$	76.9(1)
		$\mathrm{Cd{-}Br}^{(2)}\mathrm{{-}Cd'}$	78.9(1)
		$\mathrm{Cd{-}Br}^{(3)}\mathrm{{-}Cd'}$	76.2(1)
		$\mathrm{Br}^{(3)*}\ldots\mathrm{H}^{(\mathrm{N},1)}\mathrm{{-}N}$	147.3(3)
		$\mathrm{Br}^{(1)*}\ldots\mathrm{H}^{(\mathrm{N},2)}\mathrm{{-}N}$	134.7(3)
		$\mathrm{Br}^{(2)*}\ldots\mathrm{H}^{(\mathrm{N},2)}\mathrm{{-}N}$	122.4(3)

$\mathrm{Br}^{(1)*}$: $1-x,\ 1-y,\ -z$

$\mathrm{Br}^{(2)*}$: $1-x,\ 1-y,\ -z-1$

$\mathrm{Br}^{(3)*}$: $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

$\mathrm{Br}^{(1)\prime}$: $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

$\mathrm{Br}^{(2)\prime}$: $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

$\mathrm{Br}^{(3)\prime}$: $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

$\mathrm{Cd'}$: $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

Table 9. Ammonium tribromocadmate, NH_4CdBr_3, intra- and intermolecular distances (d/pm) and angles (°).

Connection	d/pm	Connection	Angle/°
$\mathrm{Cd{-}Br}^{(1)}$	264.8(1)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(2)}$	94.1
$\mathrm{Cd{-}Br}^{(2)}$	278.9(1)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(2)\prime}$	94.1
$\mathrm{Cd{-}Br}^{(3)}$	285.3(1)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(3)}$	177.3
$\mathrm{Cd{-}Br}^{(3)\prime}$	279.6(1)	$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	92.6
		$\mathrm{Br}^{(1)}\mathrm{{-}Cd{-}Br}^{(3)\prime\prime}$	92.6
		$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(2)\prime}$	96.7
$\mathrm{Br}^{(2)*}\ldots\mathrm{N}$	357.5(13)	$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(3)}$	87.8
$\mathrm{Br}^{(2)*}\ldots\mathrm{H}^{(\mathrm{N},2)}$	259.5(27)	$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	84.3
$\mathrm{Br}^{(2)**}\ldots\mathrm{N}$	349.1(10)	$\mathrm{Br}^{(2)}\mathrm{{-}Cd{-}Br}^{(3)\prime\prime}$	173.2
$\mathrm{Br}^{(2)**}\ldots\mathrm{H}^{(\mathrm{N},2)}$	308.6(71)	$\mathrm{Br}^{(2)\prime}\mathrm{{-}Cd{-}Br}^{(3)}$	87.8
$\mathrm{Br}^{(1)*}\ldots\mathrm{N}$	341.6(10)	$\mathrm{Br}^{(2)\prime}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	84.3
$\mathrm{Br}^{(1)*}\ldots\mathrm{H}^{(\mathrm{N},1)}$	305.0(70)	$\mathrm{Br}^{(2)\prime}\mathrm{{-}Cd{-}Br}^{(3)\prime\prime}$	173.2
$\mathrm{Br}^{(1)*}\ldots\mathrm{H}^{(\mathrm{N},3)}$	289.6(53)	$\mathrm{Br}^{(3)}\mathrm{{-}Cd{-}Br}^{(3)\prime}$	85.6
$\mathrm{Br}^{(1)**}\ldots\mathrm{N}$	347.7(11)	$\mathrm{Br}^{(3)}\mathrm{{-}Cd{-}Br}^{(3)\prime\prime}$	85.6
$\mathrm{Br}^{(1)**}\ldots\mathrm{H}^{(\mathrm{N},3)}$	278.2(47)	$\mathrm{Br}^{(3)\prime}\mathrm{{-}Cd{-}Br}^{(3)\prime\prime}$	93.9
		$\mathrm{Cd{-}Br}^{(2)}\mathrm{{-}Cd'}$	96.7
		$\mathrm{Cd{-}Br}^{(3)\prime}\mathrm{{-}Cd'}$	93.9
		$\mathrm{Cd{-}Br}^{(3)\prime}\mathrm{{-}Cd''}$	94.4
		$\mathrm{Cd'{-}Br}^{(3)\prime}\mathrm{{-}Cd''}$	94.4
		$\mathrm{Br}^{(2)*}\ldots\mathrm{H}^{(\mathrm{N},2)}\ldots\mathrm{N}$	166.2(80)
		$\mathrm{Br}^{(2)**}\ldots\mathrm{H}^{(\mathrm{N},2)}\ldots\mathrm{N}$	105.6(45)
		$\mathrm{Br}^{(1)*}\ldots\mathrm{H}^{(\mathrm{N},1)}\ldots\mathrm{N}$	103.0(44)
		$\mathrm{Br}^{(1)*}\ldots\mathrm{H}^{(\mathrm{N},3)}\ldots\mathrm{N}$	113.2(36)
		$\mathrm{Br}^{(1)**}\ldots\mathrm{H}^{(\mathrm{N},3)}\ldots\mathrm{N}$	127.1(40)

$\mathrm{Br}^{(2)\prime}$: $x,\ y-1,\ -z$

$\mathrm{Br}^{(3)\prime}$: $-x,\ \frac{1}{2}+y,\ -z$

$\mathrm{Br}^{(3)\prime\prime}$: $-x,\ -y,\ -z$

$\mathrm{Cd'}$: $x,\ 1+y,\ z$

$\mathrm{Cd''}$: $-x,\ 1-y,\ -z$

$\mathrm{Br}^{(1)*}$: $x,\ y-1,\ z$

$\mathrm{Br}^{(1)**}$: $\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}-z$

$\mathrm{Br}^{(2)*}$: $1-x,\ 1-y,\ -z$

$\mathrm{Br}^{(2)**}$: $x,\ y-1,\ z$

Ammonium tribromocadmate, NH_4CdBr_3

The orthorhombic ammonium tribromocadmate crystallizes with the space group D_{2h}^{16}-Pnma, $Z=4$, see Table 2. In Table 8 the point positions and thermal parameters of the atoms are given; Table 9 presents intra- and intermolecular (-ionic) distances and angles. Looking on space group and lattice constants, one may assume that the compound is isotypic to NH_4CdCl_3. Brasseur and Pauling [11] and Mac Gillavry et al. [12] have determined the crystal structure of NH_4CdCl_3. A refinement of the structure is due to Rolies and De Ranter [13]. Transforming their setting Pmnb to the one used here, Pnma, they report for the lattice constants of ammonium trichlorocadmate $a = 902.6$ pm, $b = 399.4$ pm, $c = 1493.8$ pm. In the three determinations, the point positions found agree

Table 8. Positions and thermal parameters of ammonium tribromocadmate, NH_4CdBr_3; the temperature factor is of 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 U_{ij} are given in (pm)^2; U is the isotropic mean for the hydrogen atoms.

Atom	x/a	y/b	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0.1640(1)	0.2500	−0.0569(1)	222(7)	262(6)	234(6)	0	−44(5)	0
$\mathrm{Br}^{(1)}$	0.2818(1)	0.2500	−0.2111(1)	213(8)	295(8)	190(7)	0	−27(7)	0
$\mathrm{Br}^{(2)}$	0.3311(1)	0.7500	0.0046(1)	156(8)	224(7)	227(8)	0	−31(6)	0
$\mathrm{Br}^{(3)}$	0.0271(2)	0.2500	0.1021(1)	157(8)	256(8)	150(83)	0	−1(6)	0
N	0.4317(14)	0.2500	0.1737(8)	209(78)	537(90)	192(71)	0	39(62)	0
$\mathrm{H}^{(\mathrm{N},1)}$	0.3280(23)	0.2500	0.1625(64)	300					
$\mathrm{H}^{(\mathrm{N},2)}$	0.4830(94)	0.2500	0.1176(33)	300					
$\mathrm{H}^{(\mathrm{N},3)}$	0.4573(56)	0.0524(8)	0.2066(19)	300					

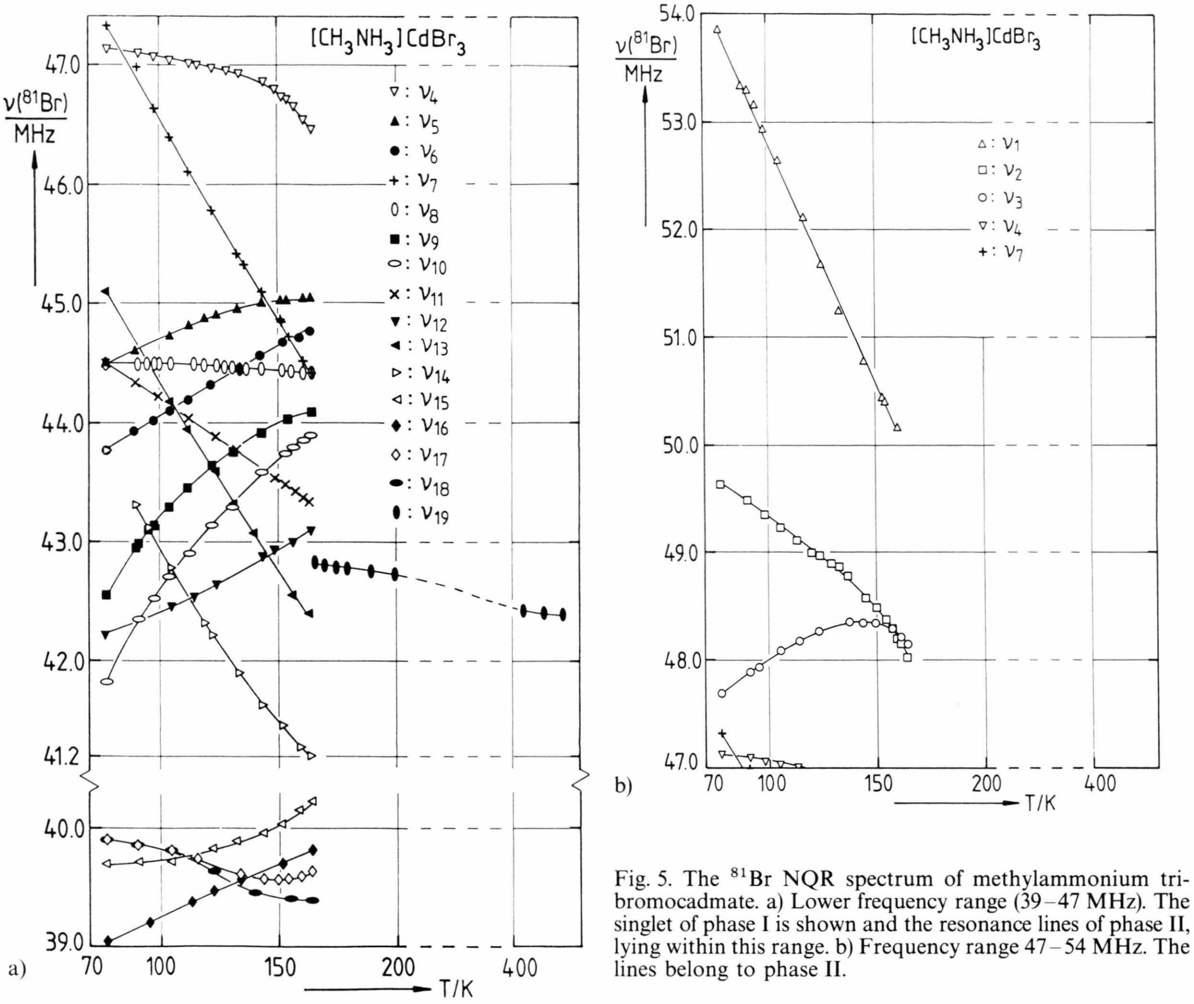


Fig. 5. The ^{81}Br NQR spectrum of methylammonium tribromocadmate. a) Lower frequency range (39–47 MHz). The singlet of phase I is shown and the resonance lines of phase II, lying within this range. b) Frequency range 47–54 MHz. The lines belong to phase II.

well, and the structure determination for NH_4CdBr_3 presented here shows the same point positions, Cl ↔ Br. The title compound is a member of the NH_4CdCl_3-type family. In Fig. 6 the projection of the unit cell of NH_4CdBr_3 along the axis [010] is shown. Chains of edge connected octahedra $CdBr_6$ are running along the *b*-direction, and two neighbouring chains are edge connected to a double string along *b*. The cations $(NH_4)^{\oplus}$ are located on the *bc*-plane at $x = 0 \pm 0.06$ and $x = \frac{1}{2} \pm 0.06$.

The Br atoms occupy three times the point position 4c. The ^{81}Br NQR spectrum is, in agreement therewith, a three line spectrum as shown in Figure 7. The three crystallographically independent bromines experience strongly differing electric field gradients, EFG's, differing in magnitude and in their temperature dependence. According to the Br NQR spectrum in its dependence on temperature, no phase transition takes place in the range $77 \leq T/\text{K} \leq 360$. There is a pronounced influence of the dynamics of the NH_4 ion on the ^{81}Br NQR spectrum, which we shall discuss later. Frequencies at selected temperatures and the coefficients of the polynomial description of $\nu(^{81}\text{Br}) = f(T)$ are given in Tables 3 and 4, respectively.

Cesium tribromocadmate, $CsCdBr_3$

The crystal structure of $CsCdBr_3$ was determined by Møller [14] and by McPherson et al. [15]. The compound crystallizes at room temperature with the $CsNiCl_3$-structure (D^4_{6h}-$P6_3/mmc$, $Z = 2$). One observes chains of octahedra $[CdBr_6]$, sharing a common

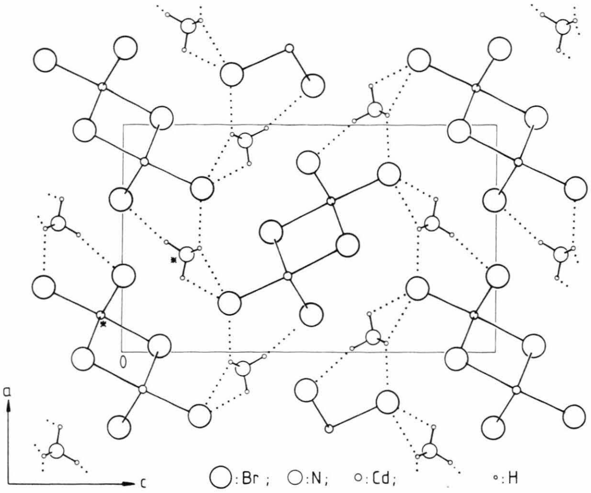


Fig. 6. Projection of the unit cell of NH_4CdBr_3 along [010] onto the (*ac*)-plane. The ions, for which the coordinates are given in Table 8, are marked by *. The possible hydrogen bonds N–H ··· Br are marked by dotted lines.

plane. Accordingly, the ^{81}Br NQR spectrum is a single line spectrum within the temperature range we have worked in, $77 \leq T/K \leq 425$, as seen in Figure 8. $\nu(^{81}Br)$ decreases nearly linearly with increasing temperature. Selected NQR frequencies are listed in Table 3 as are the coefficients of the parameterization of $\nu(^{81}Br) = f(T)$ in Table 4.

Guanidinium tribromocadmate, [C(NH$_2$)$_3$] CdBr$_3$

The monoclinic tribromocadmate of guanidinium crystallizes with the space group C_{2h}^6-C2/c, four formula units in the cell, see Table 2. In Table 10 the point positions of the atoms and their thermal parameters are given, and Table 11 contains intra- and interatomic distances and angles. In Fig. 9a the projection of the unit cell along [100] is shown. One recognizes a chain of $[CdBr_5]$ units running along the *c*-axis and being located in the *ac*-plane at $y = 0$ and $y = \frac{1}{2}$. The hydrogen bond system, the guanidinium ion forms with the anion, is marked by dotted lines. Calculating the best plane through C, N_1, and N_2 of the guanidinium ion, one finds

$$7.4146\,x + 0.0004\,y - 0.3379\,z = 7.1612\,.$$

The deviation of the atoms C, N_1, and N_2 from this plane is, within the limits of error zero. $H(N_1)$ is -78.6 pm below this plane, $H_1(N_2)$ is 46.9 pm above, $H_2(N_2)$ is 59.5 pm above. Figure 9b gives the numbering of the atoms within the anion and the cation. To Fig. 9a, Fig. 9b is related by the stars in Figure 9a.

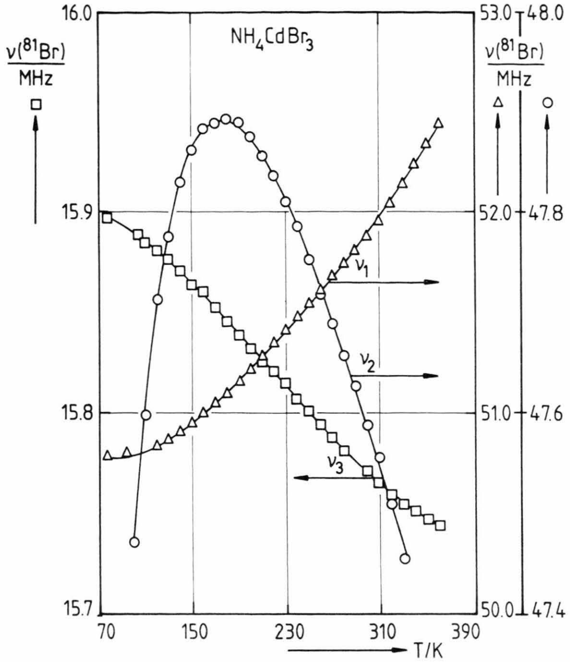


Fig. 7. Temperature dependence of the ^{81}Br NQR spectrum of ammonium tribromocadmate. The curves $\nu(T)$ are quite divergent in their slopes. There is a large total spread in the frequencies.

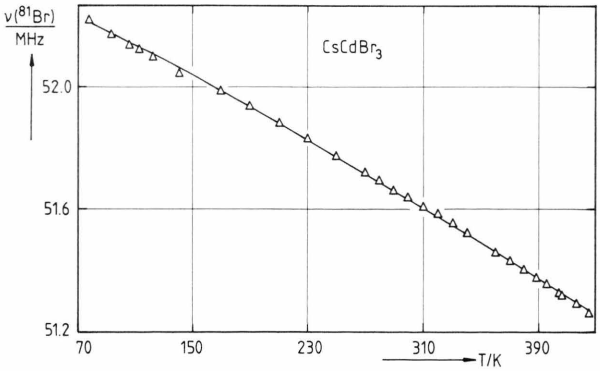


Fig. 8. $CsCdBr_3$: $\nu(^{81}Br)$ as a function of temperature.

The Br atoms are located at two point positions of the space group, in 4e and 8f (see Table 2). The inequivalence in symmetry and therefore in the acting EFG at the two different sites is reflected by the Br NQR spectrum. In Fig. 10 the frequencies of the

Table 10. Positions and thermal parameters of guanidinium tribromocadmate, $[C(NH_2)_3]CdBr_3$; the temperature factor is of the form:

$$T = \exp\{-2\pi^2(U_{11}\,h^2 a^{*2} + U_{22}\,k^2 b^{*2} + U_{33}\,l^2 c^{*2} + 2\,U_{12}\,h k a^* b^* + 2\,U_{13}\,h l a^* c^* + 2\,U_{23}\,k l b^* c^*)\}\,.$$

The U_{ij} are given in (pm)^2; U is the isotropic mean for the hydrogen atoms.

Atom	x/a	y/b	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0.5000	0.5473(1)	0.2500	427(6)	289(6)	350(6)	0	229(5)	0
Br$^{(1)}$	0.5000	0.7068(1)	0.2500	708(11)	256(8)	309(7)	0	170(7)	0
Br$^{(2)}$	0.7337(1)	0.5414(1)	0.6523(1)	285(5)	402(6)	228(5)	−65(4)	80(4)	23(4)
C	1.0000	0.3135(10)	0.7500	496(90)	237(77)	496(91)	0	108(75)	0
N$^{(1)}$	1.0000	0.2335(10)	0.7500	1374(191)	287(82)	771(127)	0	481(129)	0
N$^{(2)}$	0.9929(16)	0.3537(7)	0.5941(12)	805(76)	496(67)	300(47)	−14(58)	266(49)	92(43)
H$^{(N(1),1)}$	0.8910(107)	0.1978(63)	0.6833(157)	600					
H$^{(N(2),1)}$	1.0531(134)	0.3920(58)	0.5277(112)	600					
H$^{(N(2),2)}$	0.9083(130)	0.3151(56)	0.4981(97)	600					

Table 11. Guanidinium tribromocadmate, $[C(NH_2)_3]CdBr_3$; intra- and intermolecular distances (d/pm) and angles (°).

Connection	d/pm	Connection	Angle/°
Cd–Br$^{(1)}$	255.0(2)	Br$^{(1)}$–Cd–Br$^{(2)}$	91.9(0)
Cd–Br$^{(2)}$	292.5(1)	Br$^{(1)}$–Cd–Br$^{(2)\prime}$	123.0
Cd–Br$^{(2)\prime}$	260.0(1)	Br$^{(1)}$–Cd–Br$^{(2)\prime\prime}$	91.8
C–N$^{(1)}$	127.9(21)	Br$^{(1)}$–Cd–Br$^{(2)\prime\prime\prime}$	123.0
C–N$^{(2)}$	131.3(11)	Br$^{(2)}$–Cd–Br$^{(2)\prime}$	86.7
		Br$^{(2)}$–Cd–Br$^{(2)\prime\prime}$	176.3
Br$^{(1)*}$ … N$^{(2)}$	349.3(10)	Br$^{(2)}$–Cd–Br$^{(2)\prime\prime\prime}$	91.3
Br$^{(1)*}$ … H$^{(N(2),2)}$	280.1(93)	Br$^{(2)\prime}$–Cd–Br$^{(2)\prime\prime}$	91.3
Br$^{(2)*}$ … N$^{(2)}$	366.2(11)	Br$^{(2)\prime}$–Cd–Br$^{(2)\prime\prime\prime}$	113.9
Br$^{(2)*}$ … H$^{(N(2),1)}$	268.8(32)	Br$^{(2)\prime\prime}$–Cd–Br$^{(2)\prime\prime\prime}$	86.7
		Cd–Br$^{(2)}$–Cd′	93.3
		N$^{(1)}$–C–N$^{(2)}$	119.3(8)
		N$^{(2)}$–C–N$^{(2)\prime}$	121.4(15)
		Br$^{(1)*}$ … H$^{(N(2),2)}$–N$^{(2)}$	126.6(80)
		Br$^{(2)*}$ … H$^{(N(2),1)}$–N$^{(2)}$	165.7(98)

Br$^{(1)*}$: $\frac{1}{2}-x$, $y-\frac{1}{2}$, z Br$^{(2)\prime\prime}$: $x-\frac{1}{2}$, y, $\frac{1}{2}-z$
Br$^{(2)*}$: $1-x$, $1-y$, $1-z$ Br$^{(2)\prime\prime\prime}$: x, $1-y$, $z-\frac{1}{2}$
Br$^{(2)\prime}$: $x-\frac{1}{2}$, $1-y$, $1-z$ Cd′: x, $1-y$, $\frac{1}{2}+z$

(expected) two-line ^{81}Br NQR spectrum are plotted as functions of temperature. The frequencies show quite different temperature coefficients. In the range $77 \leq T/\mathrm{K} \leq 440$ the existence of only one stable phase can be deduced from the NQR spectrum. Selected frequencies and coefficients describing the parameterization of the ^{81}Br NQR temperature dependence are given in Table 3 and Table 4, respectively.

Hydrazinium tribromocadmate, $[H_2NNH_3]CdBr_3$

The last title compound for which we determined the crystal structure is hydrazinium tribromocadmate. The compound crystallizes monoclinic, space group C_{2h}^5-$P2_1/c$, and $Z=4$. In Table 12 the relative coordinates of the atoms within the unit cell are given together with the thermal parameters, and Table 13 lists intra- and intermolecular distances and angles.

Table 12. Positions and thermal parameters of hydrazinium tribromocadmate, $[N_2H_5]CdBr_3$; the temperature factor is of the form:

$$T = \exp\{-2\pi^2(U_{11}\,h^2 a^{*2} + U_{22}\,k^2 b^{*2} + U_{33}\,l^2 c^{*2} + 2\,U_{12}\,h k a^* b^* + 2\,U_{13}\,h l a^* c^* + 2\,U_{23}\,k l b^* c^*)\}\,.$$

The U_{ij} are given in (pm)^2; U is the isotropic mean for the hydrogen atoms.

Atom	x/a	y/b	z/c	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0.2859(2)	0.5685(1)	0.1485(1)	264(4)	433(5)	301(4)	−4(3)	4(3)	20(3)
Br$^{(1)}$	0.3054(3)	0.7103(1)	0.2480(1)	337(6)	313(5)	361(5)	−20(4)	−43(4)	55(4)
Br$^{(2)}$	0.8186(2)	0.5172(1)	0.3170(1)	266(5)	313(5)	249(5)	8(4)	9(4)	39(4)
Br$^{(3)}$	0.2531(2)	0.4059(2)	0.0425(1)	262(5)	356(6)	225(5)	−2(4)	4(4)	25(4)
N$^{(1)}$	0.5774(26)	0.6375(5)	0.5765(9)	575(64)	297(51)	329(47)	33(46)	143(45)	50(39)
N$^{(2)}$	0.8271(26)	0.6873(5)	0.5260(10)	445(59)	363(54)	469(53)	−73(47)	−105(48)	−33(46)
H$^{(N(1),1)}$	0.6440(310)	0.5992(68)	0.5441(111)	600					
H$^{(N(1),2)}$	0.5506(304)	0.6397(61)	0.6645(115)	600					
H$^{(N(2),1)}$	0.8093(286)	0.7318(63)	0.5827(110)	600					
H$^{(N(2),2)}$	0.8435(299)	0.6847(66)	0.4366(113)	600					
H$^{(N(2),3)}$	1.0717(319)	0.6656(63)	0.5392(105)	600					

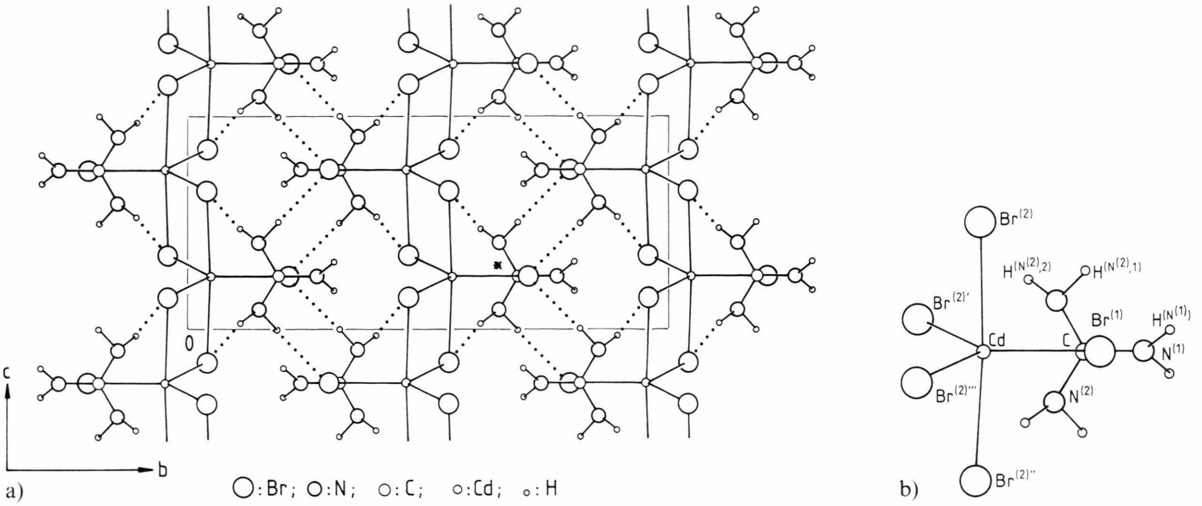


Fig. 9. Projection of the unit cell of guanidinium tribromocadmate, a) along [100] onto the (bc)-plane. The ions, for which the coordinates are listed in Table 10, are marked by a star. b) Numbering of the atoms in the formula unit; the figure connected to 9a by the star there. Dotted lines show the possible hydrogen bonds N–H ··· Br.

Table 13. Hydrazinium tribromocadmate, $[N_2H_5]CdBr_3$; intra- and intermolecular distances (d/pm) and angles (°).

Connection	d/pm	Connection	Angle/°
Cd–Br$^{(1)}$	267.1(1)	Br$^{(1)}$–Cd–Br$^{(2)}$	94.5(0)
Cd–Br$^{(2)}$	273.4(1)	Br$^{(1)}$–Cd–Br$^{(2)\prime}$	94.4(0)
Cd–Br$^{(3)}$	303.3(1)	Br$^{(1)}$–Cd–Br$^{(3)}$	178.4(0)
Cd–Br$^{(3)\prime}$	276.4(1)	Br$^{(1)}$–Cd–Br$^{(3)\prime}$	95.9(0)
N$^{(1)}$–N$^{(2)}$	143.4(13)	Br$^{(1)}$–Cd–Br$^{(3)\prime\prime}$	96.0(0)
		Br$^{(2)}$–Cd–Br$^{(2)\prime}$	92.2(0)
Br$^{(2)}$ ... N$^{(1)}$	351.8(9)	Br$^{(2)}$–Cd–Br$^{(3)}$	83.8(0)
Br$^{(2)}$ ... H$^{(N(1),1)}$	280.8(115)	Br$^{(2)}$–Cd–Br$^{(3)\prime}$	169.5(0)
Br$^{(1)*}$ ... N$^{(1)}$	338.2(9)	Br$^{(2)}$–Cd–Br$^{(3)\prime\prime}$	83.5(0)
Br$^{(1)*}$ ... H$^{(N(1),2)}$	293.7(110)	Br$^{(2)\prime}$–Cd–Br$^{(3)}$	83.8(0)
Br$^{(1)*}$ ... N$^{(2)}$	332.5(9)	Br$^{(2)\prime}$–Cd–Br$^{(3)\prime}$	87.8(0)
Br$^{(1)*}$ ... H$^{(N(2),1)}$	266.5(110)	Br$^{(2)\prime}$–Cd–Br$^{(3)\prime\prime}$	169.6(0)
Br$^{(1)}$ ... N$^{(2)}$	348.9(11)	Br$^{(3)}$–Cd–Br$^{(3)\prime}$	85.7(0)
Br$^{(1)}$ ... H$^{(N(2),2)}$	274.9(114)	Br$^{(3)}$–Cd–Br$^{(3)\prime\prime}$	84.4(0)
		Br$^{(3)\prime}$–Cd–Br$^{(3)\prime\prime}$	90.7(0)
		Cd–Br$^{(2)\prime}$–Cd′	92.2(0)
		Cd–Br$^{(3)\prime}$–Cd′	90.7(0)
		Cd–Br$^{(3)\prime}$–Cd″	94.3(0)
		Cd′–Br$^{(3)\prime}$–Cd″	95.6(0)
		Br$^{(1)*}$ ... H$^{(N(1),2)}$ ... N$^{(1)}$	111.9(80)
		Br$^{(1)*}$ ... H$^{(N(2),1)}$ ... N$^{(2)}$	126.6(84)
		Br$^{(1)**}$ ... H$^{(N(2),2)}$ ... N$^{(2)}$	140.2(97)
		Br$^{(2)}$ ... H$^{(N(2),2)}$ ... N$^{(2)}$	148.9(90)

Br$^{(2)\prime}$:	$1+x$,	y,	z	Cd″:	$1-x$,	$1-y$,	$-z$
Br$^{(3)\prime}$:	$1-x$,	$1-y$,	$-z$	Br$^{(1)*}$:	$x-1$,	$1\frac{1}{2}-y$,	$1-z$
Br$^{(3)\prime\prime}$:	$-x$,	$1-y$,	$-z$	Br$^{(1)**}$:	x,	$1\frac{1}{2}-y$,	$1-z$
Cd″:	$1+x$,	y,	z				

In Fig. 11 we show a projection of the unit cell of $[H_2NNH_3]CdBr_3$ along the a-axis onto the bc-plane. One recognizes, similar to $[NH_4]CdBr_3$, a double chain of octahedra $[CdBr_6]$, parallel to the a-axis, at $y=0$, $z=\frac{1}{2}$ and $y=\frac{1}{2}$, $z=0$. The hydrogen bonds are marked by dotted lines and the ions, for which the coordinates are listed in Table 12, are marked by stars.

Two ^{81}Br NQR frequencies are observed, with opposite temperature coefficient, and no sign of a phase transition in the range $77 \leq T/K \leq 390$ can be deduced from the curves, see Figure 12. As Table 12 shows, the 12 bromine atoms the unit cell contains, are distributed crystallographically inequivalent over the point position 4e. There is a discrepancy between the structure and the ^{81}Br NQR spectrum observed, since the two resonances found are equal in intensity. The explanation is, that we did not observe one of the expected resonances, besides the fact that the intensities of the two lines registered have been quite good (S/N: 5–50)). We assume that the frequency of the third resonance is very low. We have searched for it, without success down to 10 MHz. Tables 3 and 4 give the necessary numerical information about the ^{81}Br NQR spectrum of $[H_2NNH_3]CdBr_3$.

Potassium tribromocadmate, $KCdBr_3$, and Rubidium tribromocadmate, $RbCdBr_3$

For $KCdBr_3$ we have studied the ^{81}Br NQR spectrum in the range $77 \leq T/K \leq 360$. A doublet is ob-

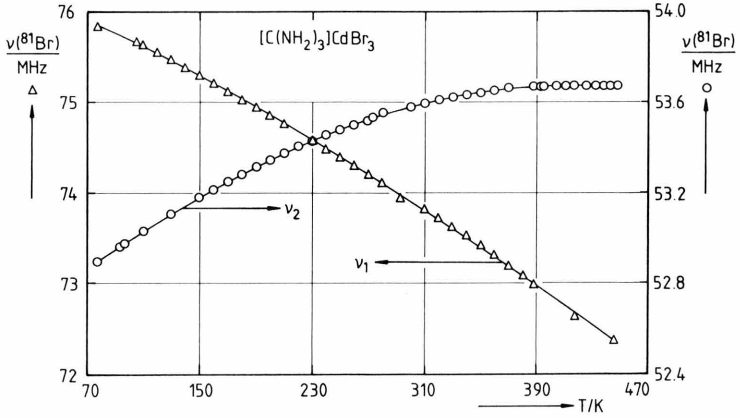


Fig. 10. Guanidinium tribromocadmate: $\nu(^{81}\mathrm{Br}) = f(T)$.

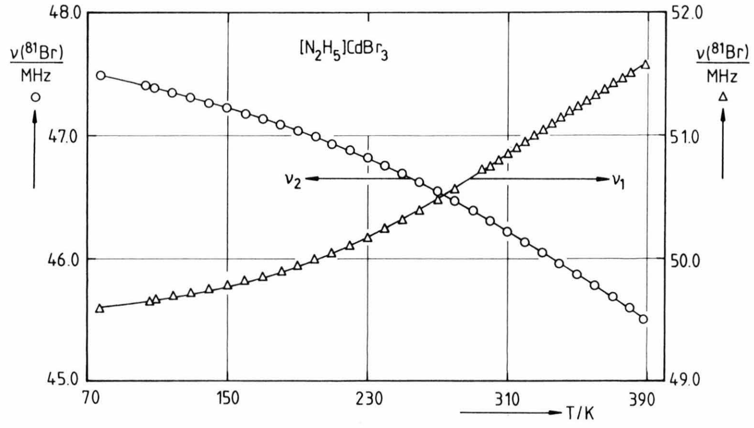


Fig. 12. ^{81}Br NQR frequencies of $[\mathrm{H_2NNH_3}]\mathrm{CdBr_3}$ as a function of temperature.

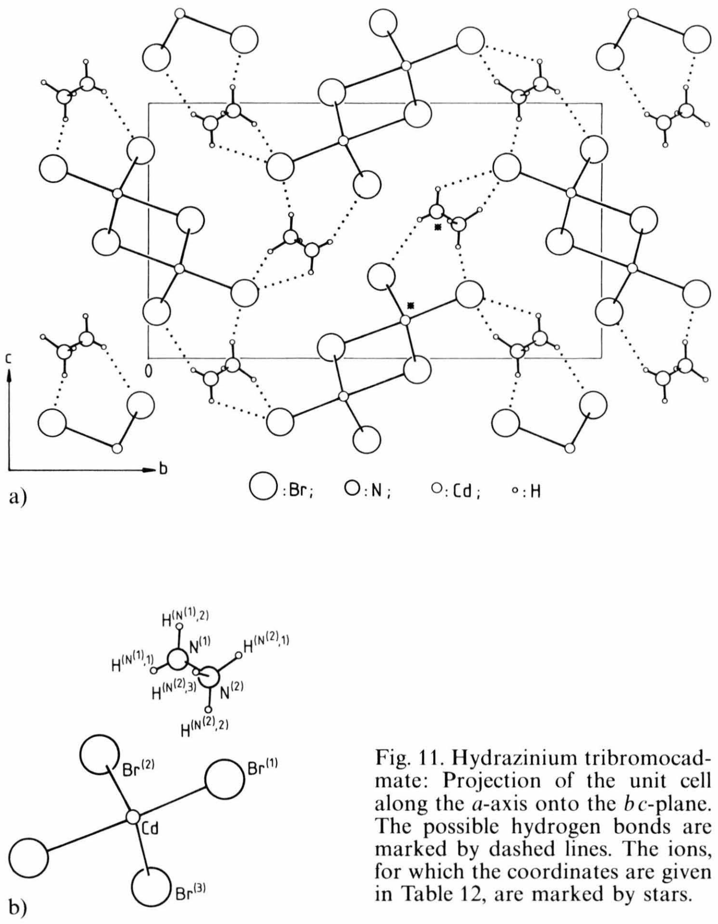


Fig. 11. Hydrazinium tribromocadmate: Projection of the unit cell along the *a*-axis onto the *bc*-plane. The possible hydrogen bonds are marked by dashed lines. The ions, for which the coordinates are given in Table 12, are marked by stars.

served within this range with no sign of a phase transition. The spectrum is plotted as a function of temperature in Figure 13. We do not know the crystal structure of the compound but like to mention that after heating the substance to 420 K, a sample was left which gave no more an NQR signal.

$RbCdBr_3$ shows also an ^{81}Br NQR doublet, with opposite temperature coefficients of the resonance lines. The spectrum as a function of temperature is shown in Fig. 14, the numerical description of the $\nu(T)$ curves is given in Tables 3 and 4. Heating up the compound to 475 K and returning to room temperature did not change the sample and an identical ^{81}Br NQR spectrum was observed after this treatment. The crystal structure of $RbCdBr_3$ is known [3, 4]. Natarajan et al. [3] found that $RbCdBr_3$ crystallizes orthorhombic in the space group D_{2h}^{16}-Pnma, $Z=4$, and belongs to the Perovskite group of the NH_4CdCl_3-type (as does NH_4CdBr_3, see above). Of the same type is $RbCdCl_3$ [4]. There is a discrepancy between the ^{81}Br NQR doublet observed and the crystal structure of $RbCdBr_3$, which asks for a triplet spectrum. Again, we blame the failure in detecting the third line to the low frequency it, most probably, will have. It may well be that the phase diagram of $RbBr-CdBr_2$ is as complicated as the system $RbCl-CdCl_2$, where several phases of $RbCdCl_3$ have been observed [16], and the phase we studied was not of NH_4CdCl_3-type. Kind and Ross have studied by ^{35}Cl NQR the phase diagramm of $RbCdCl_3$ [17]. They did not detect a phase with a triplet ^{35}Cl NQR spectrum, which should appear for the NH_4CdCl_3-type phase of $RbCdCl_3$.

Discussion

Structure and bonding in the tribromocadmates, we deal with, are governed by the polymerization of the anion $[CdBr_3]$ into octahedra with the cadmium in the center and the octahedral coordination of the bromines in such a way that octahedral faces, or edges, or corners are shared. Guanidinium tribromocadmate deviates from the rule as ethylenediammonium tribromocadmate monohydrate does. The three-, the two-, and the one-dimensional networks formed in this way are called Perovskite type structures these days, and a large number of compounds AB(Halogen)$_3$ are known.

The Hexagonal Compounds [A]CdBr$_3$, [A] = [Cs], [CH$_3$NH$_3$], and [(CH$_3$)$_4$N]: Anion Single Chain Perovskites

Let us consider first the three title compounds $ACdBr_3$ with A = cesium, methylammonium, and tetramethylammonium. The crystal structure of $CsCdBr_3$ is well known [12, 13]. In the hexagonal unit cell, space group $P6_3/mmc$, with $Z=2$, Cd is located in the point position 2a, that is at (0, 0, 0) and (0, 0, $\frac{1}{2}$), and the bromines (point position 6h) are forming regular triangles at $z=1/4$ and $z=3/4$. In this way a chain of face sharing octahedra is developed, the centers of the octahedra and the centers of the sharing faces (bromine triangles) being in line.

The space group $P6_3/mmc$, $Z=2$, is also found for $(CH_3NH_3)CdBr_3$ at room temperature, and Cd and Br occupy the same point position than they do in the cesium compound [10]. As in the Cs-compound, face sharing octahedra form a straight chain along the *c*-axis. The high symmetry one finds for methylammonium tribromocadmate, phase I, at room temperature, is due to the dynamics of the cation. Below the transition temperature the motion of the cation may stop; the crystal structure becomes more complicated, as seen from the Br NQR spectrum of phase II. We assume that hydrogen bonds $N-H\cdots Br$ play an important role in this phase transition.

As listed in Table 2, tetramethylammonium tribromocadmate, at room temperature (phase II), crystallizes with the space group $P6_3/m$. This leads to a straight chain of face-connected octahedra $[CdBr_6]$ along the *c*-axis, too. It may well be that the high temperature phase I belongs to the space group $P6_3/mmc$, as the Cs-salt and the methylammonium salt at room temperature do. The *R*-value (see Table 2) is not good because of the dynamics of the cation $[(CH_3)_4N]^{\oplus}$ which is difficult to handle in the structure determination. This was shown by Stucky [18], who studied the crystal structure of $[(CH_3)_4N]NiCl_3$, by Stucky et al. [19], who determined the structure of $[(CH_3)_4N]NiBr_3$, and by Morosin and Graeber [20], who reported the crystal structure of $[(CH_3)_4N]MnCl_3$. In all cases the space group $P6_3/m$, $Z=2$ was found, and we conclude that these compounds and $[(CH_3)_4N]CdBr_3$ are isomorphous. A disordered arrangement of the cation $[(CH_3)_4N]^{\oplus}$ must be assumed.

The phase transitions of $[(CH_3)_4N]CdBr_3$ have been investigated in recent time by Vanek et al. [21]

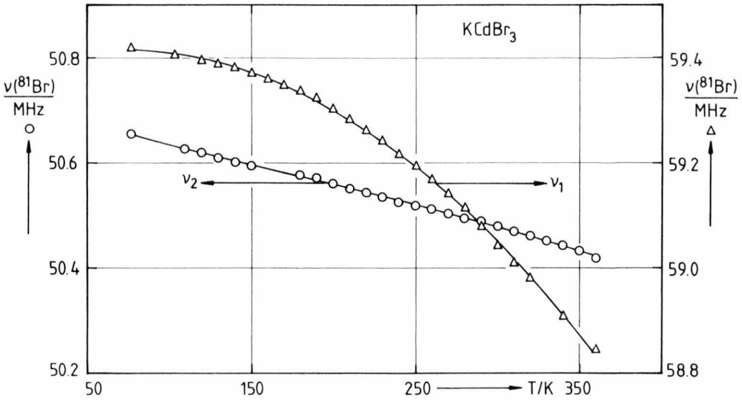


Fig. 13. KCdBr$_3$: ^{81}Br NQR spectrum (frequencies) as a function of temperature.

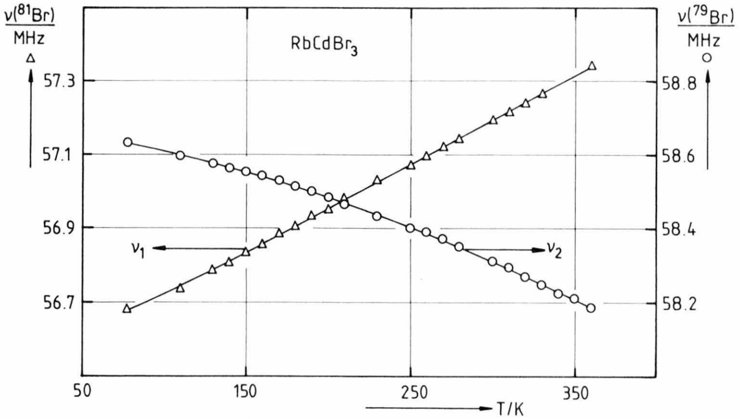


Fig. 14. Temperature dependence of the ^{81}Br NQR frequencies of RbCdBr$_3$.

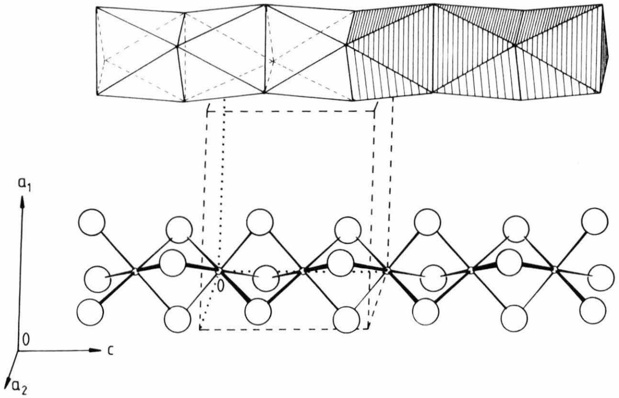


Fig. 15. The single chain "Perovskite" ACdBr$_3$ on hand of [(CH$_3$)$_4$N]CdBr$_3$. The chain along the *c*-axis is shown: a) face connected octahedra CdBr$_6$, b) the edges of the octahedra, and c) the look on a model of the chain.

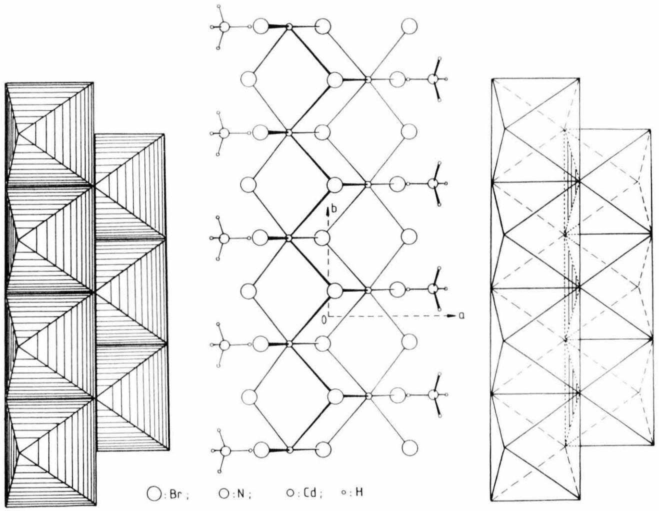


Fig. 16. The octahedral double chain in the "Perovskite" NH$_4$CdBr$_3$. Middle part: The bonds and the chain in the lattice; the cations are sketched, too. Right side: The connection of the octahedra (edges are drawn). Left side: The look on a model of the double chain.

and by Gesi [22]. The authors were particularly interested in the dielectric properties of the title compound, and the phase transition at 160 K is discussed in the light of an order-disorder mechanism of the cation within the lattice of tetramethylammonium tribromocadmate. A ^{1}H NMR study (T_1, M_2) on $[(CH_3)_4]CdBr_3$ was reported by Venu et al. [23] who conclude from their studies an isotropic tumbling of the cation at room temperature down to low temperatures and a tunneling of the CH_3 groups below 77 K. For the isomorphic $[(CH_3)_4N]CdCl_3$ an extensive study of the cation dynamics was done by Tsang and Utton [24]. In the light of this study it may be worthwhile to study the dynamics of the tetramethylammonium cation in more detail on the title compound.

In Fig. 15 we show as an example for the hexagonal single chain Perovskites $ACdBr_3$ the chain along [001] in the hexagonal cell of $[(CH_3)_4N]CdBr_3$. The chain is built up of units $[Cd_2Br_6]^{2\ominus}$, which determine the length of the *c*-axis in the unit cell in the $CsNiCl_3$-type solids. Characteristic is the single line halogen NQR spectrum.

Dimethylammonium tribromocadmate, $[(CH_3)_2NH_2]CdBr_3$, an Anion Single Chain Perovskite

Dimethylammonium tribromocadmate is an anion single chain compound, as the hexagonal title compounds discussed above are. Whereas in the hexagonal compounds, [A]=[Cs], $[CH_3NH_3]$, and $[(CH_3)_4N]$, the cations are spherical or, at room temperature, dynamically spherical; the hydrogen bonds and the symmetry of the cation prohibit rotations of the cation $[(CH_3)_2NH_2]$. The symmetry of the crystal is low. In Fig. 3a we have shown the unit cell of the compound in projection. The two hydrogens of the NH_2-group are crystallographically different (Table 6, Figure 3b). The distances N ··· Br are in the range 354 pm to 363 pm.

The single chain link $[Cd_2Br_6]^{2\ominus}$ determines the length of the *c*-axis; *c* of the hexagonal tetramethylammonium salt and of the monoclinic dimethylammonium compound are quite similar, 700 pm and 698 pm, respectively.

Ammonium tribromocadmate, NH_4CdBr_3, Hydrazinium tribromocadmate, $[H_2NNH_3]CdBr_3$, and $RbCdBr_3$, Anion Double Chain Compounds

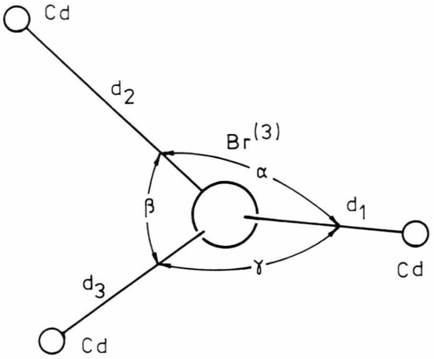
Ammonium tribromocadmate, crystallizing orthorhombic, Pnma, $Z=4$, belongs to the NH_4CdCl_3-type, the prototype of a double chain Perovskite. In Fig. 16 we show the chain structure of NH_4CdBr_3. Three crystallographically different bromine atoms form the double chain of $[CdBr_6]$ octahedra. $Br^{(1)}$ is a terminal atom (single bonded to Cd). $Br^{(2)}$ is linked to two Cd atoms and $Br^{(3)}$ is triple connected (to three different Cd atoms). In the figure the different views of the anion structure are exposed. There are weak hydrogen bonds N–H ··· Br. In the ^{81}Br NQR spectrum one line has a quite anomalous temperature behaviour. It goes through a maximum. Quite a similar behaviour we have observed also for $(NH_4)_4CdBr_6$, and we found that the maximum in the latter compound is shifted to lower temperatures by exchanging H by D [1]. Sagisawa et al. [25] and Chihara et al. [26, 27] have shown for NH_4HgCl_3 and other ammonium salts, that an anomalous curvature of $\nu=f(T)$ has to do with the dynamics of the $NH_4^{\oplus}$-ion, and, from relaxation time measurements of the Cl NQR and ^{1}H NMR, they were able to calculate the rotational jumping frequency of $NH_4^{\oplus}$. In accordance with the crystal structure there are three ^{81}Br NQR lines. The one which has a frequency maximum is the one most strongly influenced by the tumbling $NH_4^{\oplus}$-ion. Whereas $\nu_1(^{81}Br)$ and $\nu_2(^{81}Br)$ are around 50 MHz, $\nu_3(^{81}Br)$ lies very low (around 15 MHz). This suggests the assignment of ν_3 to $Br^{(3)}$, the atom which is within the double chain connected to three different Cd atoms.

The failure to detect ν_3 in $RbCdBr_3$ and $[N_2H_5]CdBr_3$ may be due to the relatively symmetric coordination of $Br^{(3)}$ in the double chain Perovskites of NH_4CdCl_3-type and in structures related to this type. In Table 14 we have listed the distances d(Cd–Br) and angles the atom $Br^{(3)}$ forms with its three Cd neighbours. The atom $Br^{(3)}$ is the common corner of three joining edges, belonging to three different octahedra, see Figure 16. The table shows that the three angles are not too far from 90°, which makes the EFG, created by the Cd atoms at the $Br^{(3)}$ position, very small. Also the distances d(Cd–Br) differ little (except d_1 of the hydrazinium compound). A very low ^{81}Br NQR frequency for $Br^{(3)}$ is understandable. Zeeman split NQR would help to clear up the problem, as would extended point charge calculations of the EFG.

Without any knowledge of the crystal structure, we assume that $KCdBr_3$ belongs to the double chain Perovskites, too, and we failed by the given reasons, to detect the third Br–NQR line.

Table 14. Angles (α, β, and γ) and distances $d(\text{Cd}-\text{Br}^{(3)})$ the $\text{Br}^{(3)}$ in double chain Perovskites ACdBr_3 forms with the three nearest Cd atoms. For the definition of $d_1 \ldots \gamma$, see the sketch.

Cation [A]	d_1/pm	d_2/pm	d_3/pm	α/°	β/°	γ/°
$[\text{NH}_4]$	279.7	285.3	285.3	94.4	93.9	94.4
[Rb]	278.2	286.6	286.6	94.6	94.3	94.6
$[\text{N}_2\text{H}_5]$	303.4	276.4	278.6	94.3	90.7	95.6



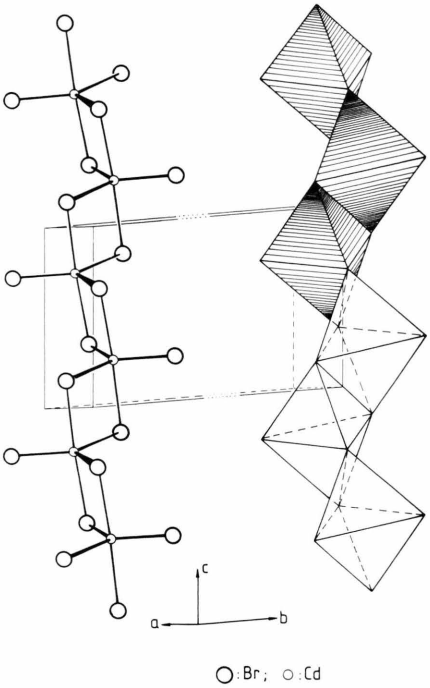


Fig. 17. Trigonal-bipyramidal single chain of guanidinium tribromocadmate. The bonds Cd–Br are shown, also the edge connections of the bipyramids, and the view on a model of the chain.

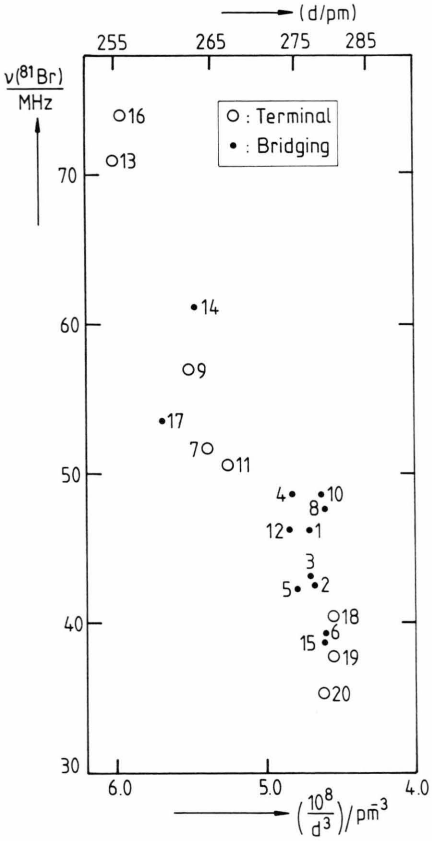
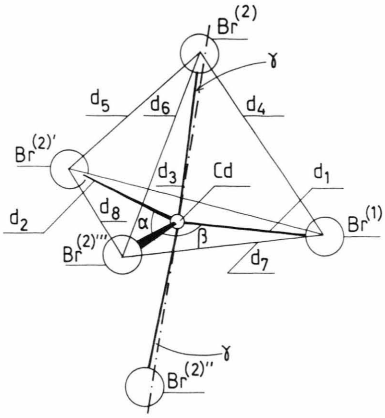


Fig. 18. ^{81}Br NQR frequencies of the title compounds ACdBr_3 as a function of the distance d(Cd–Br). $\nu(^{81}\text{Br}) = c(d(\text{Cd}-\text{Br})_3^{\ominus}$.

Table 15. The structure of the trigonal bipyramid, the chain link in guanidinium tribromocadmate, $[C(NH_2)_3]CdBr_3$. The equation of the plane through the atoms Cd, $Br^{(1)}$, $Br^{(2)\prime}$, $Br^{(2)\prime\prime\prime}$ is: $2.4416x + 0.0y + 5.8403z = 2.6809$. $a(X)$ is the distance of the atom X from this plane. The intra-bipyramidal distances $d_1 \ldots d_8$ and angles α, β, and γ are sketched below; γ is the angle between the normal on the plane with Cd as center (see above) and d_3.

Connection	d/pm	$a(X)$	d/pm
d_1	255.0	$a(Cd)$	0
d_2	260.0	$a(Br^{(1)})$	0
d_3	292.5	$a(Br^{(2)})$	+292.0
d_4	294.2	$a(Br^{(2)\prime})$	0
d_5	379.9	$a(Br^{(2)\prime\prime\prime})$	0
d_6	395.8	$a(Br^{(2)\prime\prime})$	−292.0
d_7	452.7		
d_8	435.9		
α	113.9°		
β	123.0°		
γ	3.33°		



Compound	N_0	d(Cd–Br) pm	$\nu(^{81}Br)$ MHz	V pm^3	Reference Struct.	Reference NQR
Anion: Single octahedral chain						
$[(CH_3)_4]CdBr_3$	1	278.9	46.259	267.7	*	*
$[(CH_3NH_3]CdBr_3$	2	277.5	42.638	185.3	[10]	*
$[Cs]CdBr_3$	3	277.0	43.194	171.5	[15]	*
$[(CH_3)_2NH_2]CdBr_3$	4	274.7	48.626	214.0	*	*
	5	275.3	42.393			
	6	278.9	39.333			
Anion: Double octahedral chain						
$[NH_4]CdBr_3$	7	264.8	51.705	154.1	*	*
	8	278.9	47.687			
		285.3	15.781			
$[Rb]CdBr_3$	9	262.6	57.128	154.7	[3]	*
	10	278.8	48.751			
$[N_2H_5]CdBr_3$	11	267.1	50.747	171.6	*	*
	12	274.4	46.307			
Anion: Octahedral-tetrahedral chain						
$[enH_2](CdBr_3) \cdot H_2O$	13	254.8	71.302	188.2 [a]	[2]	[2]
	14	263.3	61.214			
	15	278.9	38.741			
Anion: Chain of trigonal bipyramides						
$[C(NH_2)_3]CdBr_3$	16	255.9	74.191	217.6	*	*
	17	260.0	53.579			
Anion: Isolated octahedron						
$[Rb]_4CdBr_6$	18	280.1	40.495	153.9 [b]	[1]	[1]
$[NH_4]CdBr_6$	19	280.1	37.927			[1]
$[Mg(H_2O)_6]CdBr_6$	20	278.8	35.338	192.7	[28]	[1]

Table 16. Bond lengths d(Cd–Br) and ^{81}Br NQR frequencies (at room temperature) of compounds with polymerized anions $CdBr_3^{\ominus}$. For comparison the compounds with isolated anions $[CdBr_6]^{4\ominus}$ are included. In the 4th column the volume of one formula unit V_f is given. The 2nd column, N_0, relates the table to Figure 18.

* This paper.

[a] Normalized to one unit $CdBr_3$.

[b] Normalized to one $CdBr_3$ by subtracting the volume of 3 RbBr and 1.5 $[Mg(H_2O)_6Br_2]$, respectively.

Guanidinium tribromocadmate, $[C(NH_2)_3]CdBr_3$, a Single Chain Perovskite with the Polyanion of Condensed Trigonal Bipyramids $[CdBr_5]$

An interesting aspect of this work is the observation of the structure and ^{81}Br NQR of guanidinium tribromocadmate. The condensation of the $CdBr_3$ ions in this compound to single chain polyanions is seen in the projection of the unit cell along [100], Figure 6. Part of the unit cell we show in Figure 17. The trigonal-bipyramidal anion chain along the direction of the *c*-axis is drawn. One recognizes the condensation of the bipyramids, and in the figure the view of a model is presented, too. In Table 15 it is pointed out that the trigonal bipyramid is only little distorted. The plane through the Cd atom and its three nearest Br neighbours is almost ideal. Within the limits of error, the four atoms are on the trigonal plane. Cd is nearly in the center of the plane and the angles Br–Cd–Br in the plane deviate only little from 120° (114° and 123°). The naming of the chain link as trigonal bipyramid is adequate.

The investigations show that in compounds $ACdBr_3$ the anion polymerization can vary considerably. Single octahedral chains, octahedral double chains, octahedral-tetrahedral chains and trigonal-bipyramidal ones have been observed. We cannot offer a simple reasoning for the appearance of such a variety of condensations. The influence of the cation on the condensation of the ions $CdBr_3^\ominus$ is not clear yet. Size, symmetry, and the interaction of the cation via Coulomb forces, van der Waals forces, and hydrogen bonds with the anion, all these interactions guide the condensation.

There is a clear connection between the bond distances d(Cd–Br) and the ^{79,81}Br NQR frequencies. This was pointed out many times in the discussion of chemical bond ↔ NQR frequencies, see e.g. [29]. In Table 16 we have collected bond distances, ^{81}Br NQR frequencies and the volumes of one unit $ACdBr_3$ in the elementary cell of the structure. Clearly, there is a dependence of $\nu(^{81}Br)$ on d(Cd–Br) as expected and it follows the rule $\nu \propto 1/r^3$. We show this in the graph, Figure 18. Terminal Br atoms have short distances to the Cd atoms and the ^{81}Br NQR frequencies are "high". Bridging atoms belong to longer distances and lower frequencies. The triple connected atoms are not shortened in their bond distances d(Cd–Br) in comparison to the bridging atoms, but low NQR frequencies (low EFG's) are caused by the "symmetrized" surrounding. There is another interesting effect seen in Table 16. The volume of the formula unit, calculated from the unit cell size and Z, is decreasing with increasing condensation of the anion into chains. For an ion $[B^{II}(Hal)_3]^\ominus$, one can think about more arrangements as the four discussed here.

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[30] Further information on the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany. Inquiries should be accompanied by the depository number CSD-55640, the names of the authors, and the full literature reference.