Bromine NQR and Crystal Structures of Tetraanilinium Decabromotricadmate and 4-Methylpyridinium Tribromocadmate *

Hideta Ishihara [1], V. G. Krishnan [2], Shi-qi Dou [3], Helmut Paulus [3], and Alarich Weiss [3]

[1] Faculty of Education, Saga University, 1-Honjou, Saga 840, Japan
[2] Department of Physics, Osmania University, Hyderabad-500 007, India
[3] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-64287 Darmstadt, Germany

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The ^{79,81}Br NQR spectra of tetraanilinium decabromotricadmate (**1**) and 4-methylpyridinium tribromocadmate (**2**) were studied as function of temperature and their crystal structures were determined. $(C_6H_5NH_3)_4Cd_3Br_{10}$ (**1**): Space group D_{2h}^{15}–Pbca, $Z=4$, $a=2507.8(7)$ pm, $b=1985.4(5)$ pm, $c=763.0(2)$ pm. Characteristic for the structure are trioctahedral units $[Cd_3Br_{10}]$ condensed to planes. Within the units the octahedra are face connected and further condensed to planes via common corners. Two types of hydrogen bonds are observed. The ^{81}Br NQR lines with frequencies (MHz, 298 K) of 62.98, 52.59, 43.39, 41.82, and 40.71 are little temperature dependent with positive and negative coefficients. The wide frequency range of the NQR lines is reflected by the wide range of the intraionic distances, $263 \leq d(\mathrm{Br-Cd})/\mathrm{pm} \leq 300$.

$(4\text{-}(CH_3)C_5H_4NH)CdBr_3$ (**2**): C_{2h}^{5}–$P2_1/n$, $Z=4$, $a=1228.8(5)$ pm, $b=1168.5(5)$ pm, $c=758.3(3)$ pm, $\beta=95.30(1)°$; the $CdBr_3^{\ominus}$ ions are condensed to chains. The ^{81}Br NQR spectrum is a triplet with frequencies (MHz, 298 K) of 66.01, 55.39, and 50.75. The temperature dependence is small, with positive and negative temperature coefficients. The distances $d(\mathrm{Cd-Br})$ are 256 pm $(\mathrm{Cd-Br^{(2)}})$, 261 pm $(\mathrm{Cd-Br^{(1)}})$, and 284 pm $(\mathrm{Cd-Br^{(3)}})$ and in the chain $[CdBr_3]Br^{(1)}$ and $Br^{(3)}$ are bridging atoms.

The relations between Br-NQR and crystal structures are discussed.

Introduction

Halogeno complexes of elements M^{II}, such as Cd, Hg, Sn, Pb crystallize with a wide variety of polymer anion structures, from the three-dimensional connected Perovskite ($CaTiO_3$) lattice to isolated octahedra $[M^{II}X_6]^{4\ominus}$. In recent time we became interested in the study of such complexes, particularly with X = Cl, Br, I; M^{II} = Sn, Pb [1–3] and X = Br; M^{II} = Cd [4–6], and we have been working in the field by combining halogen NQR and crystal structure determinations. In case of the bromocadmate complex salts it turns out that the cation is quite important in the construction of the polymer anion $[Cd_nBr_m]^{(2n-m)\ominus}$ and the variety of anion condensation patterns increases much if the cation is such that hydrogen bonds can be formed between the cation and bromine atoms. Interesting cations are e.g. $RNH_3^{\oplus}$, $RR'NH_2^{\oplus}$ etc., see [5–7].

Within this approach we have studied the ^{79,81}Br NQR spectra as function of temperature T and the crystal structures of tetraanilinium decabromotricadmate $(C_6H_5NH_3^{\oplus})_4\,[Cd_3Br_{10}]^{4\ominus}$ (**1**) and of (4-methylpyridinium) tribromocadmate, $(4\text{-}(CH_3)C_5H_4NH)^{\oplus}\,CdBr_3^{\ominus}$ (**2**). The results of this study are presented. Not all frequencies for the isotopes ^{79}Br and ^{81}Br are reported here, but there is no problem to derive the frequencies of ^{79}Br NQR from ^{81}Br NQR and vice versa by the ratio of the nuclear quadrupole moments, which is $Q(^{79}\mathrm{Br})/Q(^{81}\mathrm{Br}) = 1.1971$.

Experimental

The preparation of the compounds was done using commercial chemicals 4-methylpyridine (γ-picoline), aniline, cadmium bromide, and aqueous HBr. The polycrystalline compounds for the NQR studies and the single crystals for the X-ray diffraction were prepared by slow concentration of stoichiometric aqueous (pH around 3) solutions at room temperature. In Table 1 the results of the chemical analysis and the macroscopic characterization of the substances is given.

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Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie (III), Technische Hochschule, Petersenstraße 20, D-64287 Darmstadt, Germany.

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For the crystal structure determinations small crystals were selected and diffraction intensities collected using a 4-circle X-ray goniometer. In Table 2 the experimental details are given together with crystallographic data of **1** and **2**. The structures were determined from the collected reflexion intensities, after appropriate correction for absorption and Lorentz-polarization factor, by direct methods, SHELX86 [8]. The final positions and thermal parameters of the atoms were found by least squares refinement, SHELX76 [9]. Due to the strong scattering power of the heavy atoms Br and Cd, most hydrogen positions could not be found from Fourier synthesis. They have been fixed under certain assumptions (bond lengths, bond angles).

Table 1. Chemical analysis (given in weight %) and some crystal properties of **1** and **2**.

	$(C_6H_5NH_3)_4Cd_3Br_{10}$ (**1**)	$(4\text{-}(CH_3)C_5H_4NH)CdBr_3$ (**2**)
Habitus	needles	needles
Color	colorless	colorless
Analysis (%)	found/calc	found/calc
Br	51.94/52.81	53.71/53.72
C	18.61/19.05	16.10/16.00
H	1.92/ 2.13	1.59/ 1.81
N	3.66/ 3.70	3.09/ 3.10

The ^{79,81}Br NQR spectra were studied by use of a CW-NQR spectrometer working in the superregenerative mode. The frequencies were determined by counting to ±10 kHz, the accuracy limited by the line width. The temperatures T at the sample site were produced by liquid N_2 (77 K), respectively by using a petroleum ether-liquid nitrogen or a silicone oil bath. T was measured to ±1 K via a copper-constantan thermocouple.

Results

Crystal Structures

1 crystallizes centrosymmetric with the space group D_{2h}^{15}–Pbca, $Z=4$ ($C_{24}H_{32}Br_{10}Cd_3N_4$) in the unit cell. The lattice constants are $a=2507.8(7)$ pm, $b=1985.4(5)$ pm, $c=763.0(2)$ pm (see also Table 2). In Table 3

Table 2. Experimental conditions for the crystal structure determinations and crystallographic data of $(C_6H_5NH_3)_4Cd_3Br_{10}$) (**1**) and $(4\text{-}(CH_3C_5H_4NH)CdBr_3$ (**2**). Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoKα); monochromator: Graphite (002); scan: $2\vartheta/\omega$; $M=1512.8$ and 446.2, respectively.

Formula	$C_{24}H_{32}Br_{10}Cd_3N_4$, (**1**)	$C_6H_8Br_3CdN$, (**2**)
Crystal habitus	colorless, prism	colorless, prism
Size/mm^3	$0.25\times0.5\times1.3$	$0.45\times0.25\times3.5$
Temperature/K	299	296
Absorption Coefficient (μ/m^{-1})	11993	12910
$(\sin\vartheta/\lambda)_{max}$	0.00595	0.00595
Number of reflexions:		
Measured	4514	4090
Symmetry independent	3329	1887
Considered $F>2\sigma(F)$	2829	1785
Number of free parameters	236	104
$F(000)$	2792	816
$R(F)$	0.075	0.097
$R_w(F)$	0.066	0.094
Lattice constants:		
a/pm	2507.8(7)	1228.8(5)
b/pm	1985.4(5)	1168.5(5)
c/pm	763.0(2)	758.3(3)
β/°		95.30(1)
Volume of unit cell $V\cdot10^{-6}$/(pm)^3	3799.0(9)	1084.2(34)
Space group	Pbca-D_{2h}^{15}	$P2_1/n$–C_{2h}^5
Formula units Z per unit cell	4	4
ϱ_{calc}/(Mg · m^{-3})	2.644(2)	2.733(3)
ϱ_{pyk}/(Mg · m^{-3})	2.53	2.70
Point positions	Cd$^{(1)}$ in 4a: all other atoms in 8c	all atoms in 4e

Table 3. Positional and thermal parameters of **1**. The U_{eq} are given in ($Å^2 \cdot 1000$).

Atom	x/a	y/b	z/c	U_{eq}
$\mathrm{Br}^{(1)}$	0.5436(1)	0.6231(1)	0.0275(2)	31(1)
$\mathrm{Br}^{(2)}$	0.4311(1)	0.5382(1)	0.2601(2)	30(1)
$\mathrm{Br}^{(3)}$	0.5724(1)	0.4351(1)	0.2405(2)	35(1)
$\mathrm{Br}^{(4)}$	0.4585(1)	0.7738(1)	−0.1549(2)	37(1)
$\mathrm{Br}^{(5)}$	0.3330(1)	0.6811(1)	0.0506(3)	43(1)
$\mathrm{Cd}^{(1)}$	0.5	0.5	0	34(1)
$\mathrm{Cd}^{(2)}$	0.4365(1)	0.6606(1)	0.0305(2)	31(1)
$\mathrm{C}_{\mathrm{I}}^{(1)}$	0.2114(6)	0.1095(7)	0.4974(20)	29(9)
$\mathrm{C}_{\mathrm{I}}^{(2)}$	0.2534(6)	0.1368(8)	0.5908(24)	37(9)
$\mathrm{C}_{\mathrm{I}}^{(3)}$	0.3026(7)	0.1056(9)	0.5874(27)	46(10)
$\mathrm{C}_{\mathrm{I}}^{(4)}$	0.3069(7)	0.0417(11)	0.4927(22)	49(10)
$\mathrm{C}_{\mathrm{I}}^{(5)}$	0.2639(7)	0.0159(9)	0.4098(25)	49(12)
$\mathrm{C}_{\mathrm{I}}^{(6)}$	0.2147(7)	0.0512(9)	0.4065(25)	44(10)
N_{I}	0.1600(6)	0.1457(7)	0.4903(20)	40(8)
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{C}2)}$	0.2480(6)	0.1821(8)	0.6672(24)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{C}3)}$	0.3363(7)	0.1268(9)	0.6562(27)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{C}4)}$	0.3448(7)	0.0159(11)	0.4858(22)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{C}5)}$	0.2681(7)	−0.0318(9)	0.3428(25)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{C}6)}$	0.1811(7)	0.0316(9)	0.3339(25)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{N},1)}$	0.1641(6)	0.1958(7)	0.5440(20)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{N},2)}$	0.1368(6)	0.1150(7)	0.5787(20)	60
$\mathrm{H}_{\mathrm{I}}^{(\mathrm{N},3)}$	0.1401(6)	0.1485(7)	0.3649(20)	60
$\mathrm{C}_{\mathrm{II}}^{(1)}$	0.4094(6)	0.3619(8)	0.4927(22)	32(9)
$\mathrm{C}_{\mathrm{II}}^{(2)}$	0.4075(7)	0.2998(9)	0.4158(24)	41(10)
$\mathrm{C}_{\mathrm{II}}^{(3)}$	0.3593(8)	0.2675(8)	0.4047(26)	50(12)
$\mathrm{C}_{\mathrm{II}}^{(4)}$	0.3131(7)	0.2998(11)	0.4803(25)	55(13)
$\mathrm{C}_{\mathrm{II}}^{(5)}$	0.3173(8)	0.3607(8)	0.5561(25)	45(11)
$\mathrm{C}_{\mathrm{II}}^{(6)}$	0.3645(8)	0.3919(8)	0.5644(24)	43(11)
N_{II}	0.4610(6)	0.3980(8)	0.5020(26)	65(9)
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{C}2)}$	0.4431(7)	0.2774(9)	0.3618(24)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{C}3)}$	0.3542(8)	0.2194(8)	0.3403(26)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{C}4)}$	0.2744(7)	0.2759(11)	0.4779(25)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{C}5)}$	0.2831(7)	0.3850(8)	0.6142(25)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{C}6)}$	0.3681(8)	0.4401(8)	0.6289(24)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{N},1)}$	0.4595(6)	0.4471(8)	0.5626(26)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{N},2)}$	0.4835(6)	0.4010(8)	0.3816(26)	60
$\mathrm{H}_{\mathrm{II}}^{(\mathrm{N},3)}$	0.4801(6)	0.3628(8)	0.5900(26)	60

Table 4. Selected intra- and intermolecular (ionic) distances (in pm) and angles (in degrees) of **1**, determined by X-ray diffraction. Since most of the distances C−N and N−H have been fixed to 108 pm, the angles C−C−N and C−N−H to 120° and 109°, respectively, we do not list neither C−H and C−N distances nor the corresponding angles. The hydrogen bond distances and angles are, however, given as they appear from the calculations.

Connection	Distance	Connection	Angle
$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(1)}$	268.5(1)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(1)}-\mathrm{Br}^{(2)}$	87.0(0)
$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(1)}$	273.9(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(1)}-\mathrm{Br}^{(3)}$	95.8(0)
$\mathrm{Br}^{(3)}-\mathrm{Cd}^{(1)}$	288.5(2)	$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(1)}-\mathrm{Br}^{(3)}$	93.4(1)
$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}$	278.6(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(2)}$	80.3(1)
$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(2)}$	299.9(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(3')}$	83.7(1)
$\mathrm{Br}^{(3)}-\mathrm{Cd}^{(2)}$	281.7(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4)}$	91.2(1)
$\mathrm{Br}^{(4)}-\mathrm{Cd}^{(2)}$	271.2(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4')}$	86.6(1)
$\mathrm{Br}^{(4)}-\mathrm{Cd}^{(2)}$	278.6(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(5)}$	172.8(1)
$\mathrm{Br}^{(5)}-\mathrm{Cd}^{(2)}$	263.1(2)	$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(3')}$	83.0(1)
$\mathrm{Cd}^{(1)}\cdots\mathrm{Cd}^{(2)}$	357.1(1)	$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4)}$	170.2(1)
		$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4')}$	83.4(1)
		$\mathrm{Br}^{(2)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(5)}$	92.7(1)
		$\mathrm{Br}^{(3')}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4)}$	101.1(1)
		$\mathrm{Br}^{(3')}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4')}$	164.4(1)
		$\mathrm{Br}^{(3')}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(5)}$	94.0(1)
		$\mathrm{Br}^{(4)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4')}$	91.2(1)
		$\mathrm{Br}^{(4)}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(5)}$	95.9(1)
		$\mathrm{Br}^{(4')}-\mathrm{Cd}^{(2)}-\mathrm{Br}^{(5)}$	94.2(1)
		$\mathrm{Cd}^{(1)}-\mathrm{Br}^{(1)}-\mathrm{Cd}^{(2)}$	81.5(1)
		$\mathrm{Cd}^{(1)}-\mathrm{Br}^{(2)}-\mathrm{Cd}^{(2)}$	76.9(1)
		$\mathrm{Cd}^{(1)}-\mathrm{Br}^{(3')}-\mathrm{Cd}^{(2)}$	77.6(1)
		$\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4)}-\mathrm{Cd}^{(2'')}$	142.8(1)
		$\mathrm{Cd}^{(2)}-\mathrm{Br}^{(4')}-\mathrm{Cd}^{(2'')}$	142.8(1)
$\mathrm{C}_{\mathrm{I}}^{(1)}-\mathrm{C}_{\mathrm{I}}^{(2)}$	138.2(22)	$\mathrm{C}_{\mathrm{I}}^{(1)}-\mathrm{C}_{\mathrm{I}}^{(2)}-\mathrm{C}_{\mathrm{I}}^{(3)}$	119.6(16)
$\mathrm{C}_{\mathrm{I}}^{(2)}-\mathrm{C}_{\mathrm{I}}^{(3)}$	138.2(23)	$\mathrm{C}_{\mathrm{I}}^{(2)}-\mathrm{C}_{\mathrm{I}}^{(3)}-\mathrm{C}_{\mathrm{I}}^{(4)}$	117.7(16)
$\mathrm{C}_{\mathrm{I}}^{(3)}-\mathrm{C}_{\mathrm{I}}^{(4)}$	146.4(26)	$\mathrm{C}_{\mathrm{I}}^{(3)}-\mathrm{C}_{\mathrm{I}}^{(4)}-\mathrm{C}_{\mathrm{I}}^{(5)}$	120.0(16)
$\mathrm{C}_{\mathrm{I}}^{(4)}-\mathrm{C}_{\mathrm{I}}^{(5)}$	135.2(24)	$\mathrm{C}_{\mathrm{I}}^{(4)}-\mathrm{C}_{\mathrm{I}}^{(5)}-\mathrm{C}_{\mathrm{I}}^{(6)}$	121.0(17)
$\mathrm{C}_{\mathrm{I}}^{(5)}-\mathrm{C}_{\mathrm{I}}^{(6)}$	142.0(24)	$\mathrm{C}_{\mathrm{I}}^{(5)}-\mathrm{C}_{\mathrm{I}}^{(6)}-\mathrm{C}_{\mathrm{I}}^{(1)}$	117.8(17)
$\mathrm{C}_{\mathrm{I}}^{(6)}-\mathrm{C}_{\mathrm{I}}^{(1)}$	135.2(23)	$\mathrm{C}_{\mathrm{I}}^{(6)}-\mathrm{C}_{\mathrm{I}}^{(1)}-\mathrm{C}_{\mathrm{I}}^{(2)}$	123.6(16)
$\mathrm{C}_{\mathrm{I}}^{(1)}-\mathrm{N}_{\mathrm{I}}$	147.7(20)	$\mathrm{C}_{\mathrm{I}}^{(6)}-\mathrm{C}_{\mathrm{I}}^{(1)}-\mathrm{N}_{\mathrm{I}}$	116.8(15)
		$\mathrm{C}_{\mathrm{I}}^{(2)}-\mathrm{C}_{\mathrm{I}}^{(1)}-\mathrm{N}_{\mathrm{I}}$	119.5(14)
$\mathrm{C}_{\mathrm{II}}^{(1)}-\mathrm{C}_{\mathrm{II}}^{(2)}$	136.6(24)	$\mathrm{C}_{\mathrm{II}}^{(1)}-\mathrm{C}_{\mathrm{II}}^{(2)}-\mathrm{C}_{\mathrm{II}}^{(3)}$	118.6(17)
$\mathrm{C}_{\mathrm{II}}^{(2)}-\mathrm{C}_{\mathrm{II}}^{(3)}$	137.2(24)	$\mathrm{C}_{\mathrm{II}}^{(2)}-\mathrm{C}_{\mathrm{II}}^{(3)}-\mathrm{C}_{\mathrm{II}}^{(4)}$	118.3(17)
$\mathrm{C}_{\mathrm{II}}^{(3)}-\mathrm{C}_{\mathrm{II}}^{(4)}$	144.4(26)	$\mathrm{C}_{\mathrm{II}}^{(3)}-\mathrm{C}_{\mathrm{II}}^{(4)}-\mathrm{C}_{\mathrm{II}}^{(5)}$	120.6(17)
$\mathrm{C}_{\mathrm{II}}^{(4)}-\mathrm{C}_{\mathrm{II}}^{(5)}$	134.4(28)	$\mathrm{C}_{\mathrm{II}}^{(4)}-\mathrm{C}_{\mathrm{II}}^{(5)}-\mathrm{C}_{\mathrm{II}}^{(6)}$	120.4(18)
$\mathrm{C}_{\mathrm{II}}^{(5)}-\mathrm{C}_{\mathrm{II}}^{(6)}$	133.8(25)	$\mathrm{C}_{\mathrm{II}}^{(5)}-\mathrm{C}_{\mathrm{II}}^{(6)}-\mathrm{C}_{\mathrm{II}}^{(1)}$	120.1(17)
$\mathrm{C}_{\mathrm{II}}^{(6)}-\mathrm{C}_{\mathrm{II}}^{(1)}$	138.5(24)	$\mathrm{C}_{\mathrm{II}}^{(6)}-\mathrm{C}_{\mathrm{II}}^{(1)}-\mathrm{C}_{\mathrm{II}}^{(2)}$	122.0(16)
$\mathrm{C}_{\mathrm{II}}^{(1)}-\mathrm{N}_{\mathrm{II}}$	148.2(21)	$\mathrm{C}_{\mathrm{II}}^{(6)}-\mathrm{C}_{\mathrm{II}}^{(1)}-\mathrm{N}_{\mathrm{II}}$	118.8(16)
		$\mathrm{C}_{\mathrm{II}}^{(2)}-\mathrm{C}_{\mathrm{II}}^{(1)}-\mathrm{N}_{\mathrm{II}}$	119.2(16)

the positional and the mean thermal parameters of the atoms are given. For the thermal ellipsoids and the F_0, F_c values see [10]. In Fig. 1 the unit cell is projected along *c* onto the *ab* plane. Intra- and intermolecular (ionic) distances and angles are listed in Table 4.

2 is centrosymmetric, too, space group $C_{2h}^5-P2_1/n$, $Z = 4(C_6H_8Br_3CdN)$ in the unit cell; $a = 1228.8(5)$ pm, $b = 1168.5(5)$ pm, $c = 758.3(3)$ pm, $\beta = 95.30(1)°$. In Table 5 the positional and mean thermal parameters are listed. For the parameters of the thermal ellipsoids and F_0, F_c. see [10]. Figure 2 gives a view of the structure, a projection of the unit cell along [010] onto the *ac* plane. In Fig. 3 half of the unit cell is projected along [010] onto the *ab* plane. Relevant atomic distances and bond angles one finds in Table 6.

Bromine NQR

1 shows, in agreement with the symmetry elements of the crystal structure, a quintet ^{81}Br NQR spectrum.

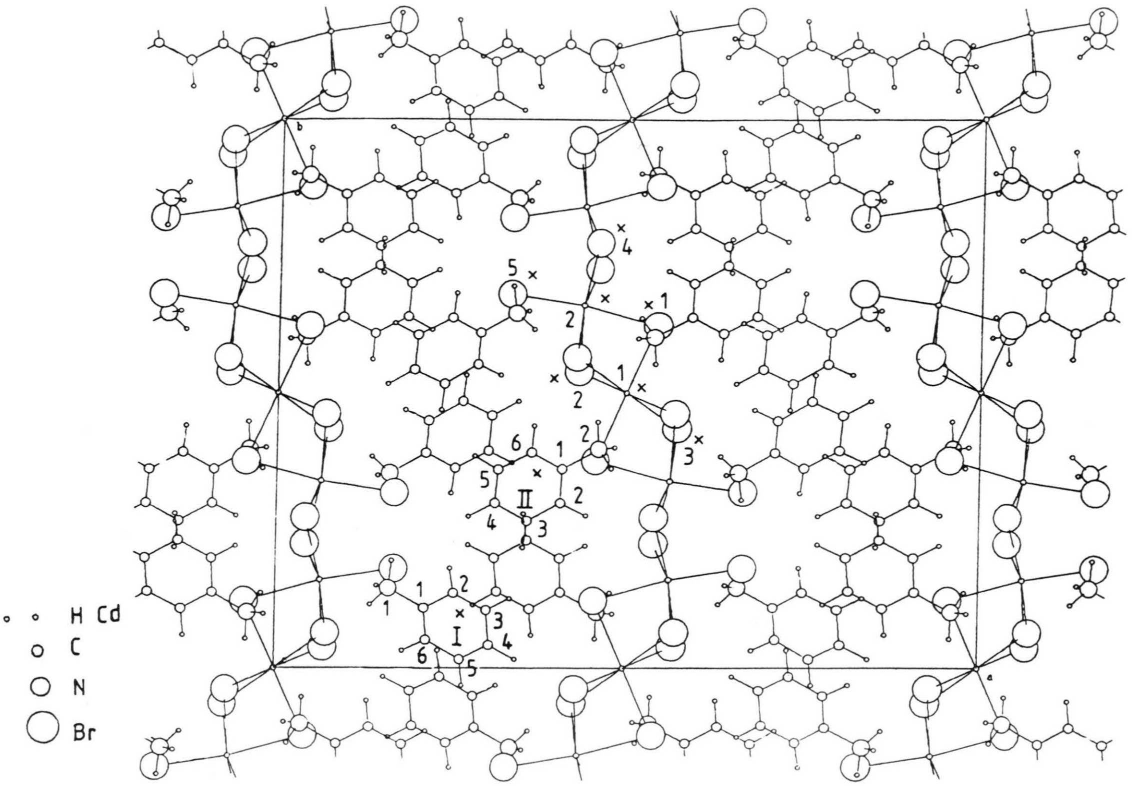


Fig. 1. Projection of the unit cell of $(C_6H_5NH_3)_4Cd_3Br_{10}$ (**1**) along [001] onto the *ab* plane. The anilinium ions, the Cd ions, and the Br ions for which the point positions are given in Table 2 are marked by an asterisk.

Table 5. Positional and thermal parameters of **2**. The hydrogen positions have not been found in the Fourier synthesis. We have fixed the distances N–H and C–H to 108 pm, the angles to 120° and 109°, respectively; the temperature factors U_{eq} are given in ($Å^2 \cdot 1000$).

Atom	x/a	y/b	z/c	U_{eq}
$Br^{(1)}$	0.0655(1)	0.1368(1)	0.4649(2)	38(1)
$Br^{(2)}$	0.1905(1)	−0.1939(1)	0.2400(3)	44(1)
$Br^{(3)}$	0.1183(1)	0.1017(1)	−0.0213(2)	33(1)
Cd	0.0438(1)	−0.0386(1)	0.2503(1)	32(1)
$C^{(2)}$	0.5463(16)	−0.1442(15)	0.3277(29)	55(11)
$C^{(3)}$	0.6333(15)	−0.0752(13)	0.3268(25)	44(9)
$C^{(4)}$	0.6221(14)	0.0385(12)	0.2669(21)	33(8)
$C^{(5)}$	0.5149(15)	0.0760(18)	0.2194(24)	47(9)
$C^{(6)}$	0.4288(15)	0.0051(21)	0.2243(27)	58(12)
$C^{(7)}$	0.7169(13)	0.1173(15)	0.2607(26)	47(9)
N	0.4441(13)	−0.1023(13)	0.2792(22)	54(10)
$H^{(C2)}$	0.5565(16)	−0.2326(15)	0.3675(29)	60
$H^{(C3)}$	0.7138(15)	−0.1036(13)	0.3774(25)	60
$H^{(C5)}$	0.5015(15)	0.1644(18)	0.1822(24)	60
$H^{(C6)}$	0.3477(15)	0.0320(21)	0.1740(27)	60
$H^{(C7,1)}$	0.8023(13)	0.0966(15)	0.2894(26)	60
$H^{(C7,2)}$	0.7071(13)	0.2091(15)	0.2548(26)	60
$H^{(C7,3)}$	0.6870(13)	0.0803(15)	0.1349(26)	60
$H^{(N)}$	0.3724(13)	−0.1546(13)	0.2889(22)	60

In Fig. 4 the temperature dependence of the spectrum is plotted for the range $77 \leq T/K \leq 340$. In Table 7 we have listed bromine NQR frequencies for two selected temperatures and also the coefficients of the power series development of $\nu(^{79,81})Br = f(T)$ for **1** and **2**. There is no sign of phase transition in the NQR spectrum of **1**.

The NQR spectrum of **2** has triplet structure, in accordance with the symmetry elements of the unit cell of the compound. In Fig. 5 the temperature dependence of the resonance frequencies is plotted and selected frequencies and coefficients of the power series development of $\nu(^{79,81}Br) = f(T)$ are given in Table 7. Also the $^{79,81}Br$ NQR spectrum of **2** as $f(T)$ gives no reason to assume a phase transition. The numbering of the frequencies of a multiplet in this paper is $\nu_1 > \nu_2 > \nu_3 \ldots$, adapted at $T = 298$ K. The power series used for the description of $\nu = f(T)$ is $\nu = \sum_{i=-1}^{2} (a_i T^i)$.

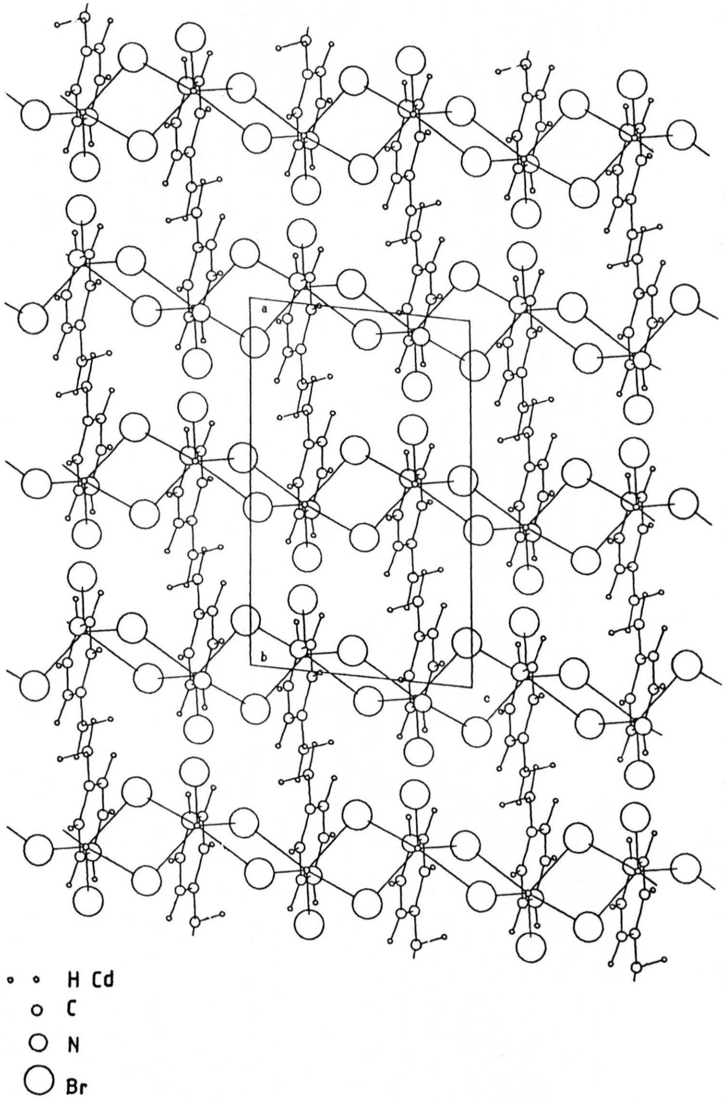


Fig. 2. Projection of the unit cell of 4-methylpyridinium tribromocadmate (**2**) along [010] onto the *ac* plane. The atoms for which the coordinates are given in Table 5 are marked by asterisks.

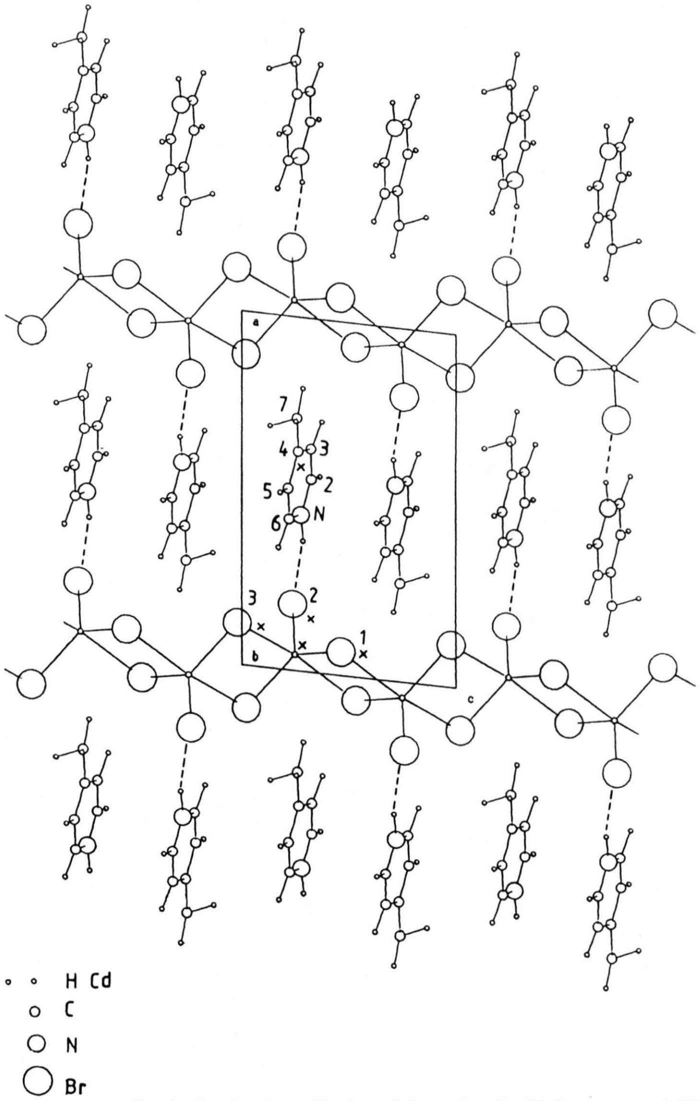


Fig. 3. Projection of halve of the unit cell of **2** from $y = -0.25$ to $y = +0.25$ along [010] onto the *ac* plane.

Table 6. Selected intra- and intermolecular (ionic) distances d (in pm) and angles (in degree) of **2**. Since the hydrogen atomic positions have not been found from Fourier projections, they have been fixed: C−H = 108 pm, N−H = 108 pm. Also the angles hydrogen atoms form with carbon and nitrogen have been fixed: C−C−H and C−N−H in the pyridine ring to 120°, C−C−H for the methyl group to 109°. These values are not given in the Table.

Connection	d/pm	Connection	Angle
$\mathrm{Br}^{(1)}-\mathrm{Cd}$	261.5(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}-\mathrm{Br}^{(2)}$	122.8(1)
$\mathrm{Br}^{(1')\,a}-\mathrm{Cd}$	288.4(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}-\mathrm{Br}^{(1')}$	82.7(1)
$\mathrm{Br}^{(2)}-\mathrm{Cd}$	256.4(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}-\mathrm{Br}^{(3)}$	88.7(1)
$\mathrm{Br}^{(3)}-\mathrm{Cd}$	284.9(2)	$\mathrm{Br}^{(2)}-\mathrm{Cd}-\mathrm{Br}^{(3)}$	96.4(1)
$\mathrm{Br}^{(3')\,b}-\mathrm{Cd}$	262.5(2)	$\mathrm{Br}^{(1)}-\mathrm{Cd}-\mathrm{Br}^{(3')}$	131.2(1)
$\mathrm{Br}^{(2)}\cdots\mathrm{Br}^{(1)}$	454.7(3)	$\mathrm{Br}^{(2)}-\mathrm{Cd}-\mathrm{Br}^{(1')}$	96.8(1)
$\mathrm{Br}^{(2)}\cdots\mathrm{Br}^{(1')}$	408.1(3)	$\mathrm{Br}^{(2)}-\mathrm{Cd}-\mathrm{Br}^{(3')}$	105.9(1)
$\mathrm{Br}^{(2)}\cdots\mathrm{Br}^{(3)}$	404.0(2)	$\mathrm{Br}^{(3)}-\mathrm{Cd}-\mathrm{Br}^{(1')}$	166.7(1)
$\mathrm{Br}^{(2)}\cdots\mathrm{Br}^{(3')}$	414.1(2)	$\mathrm{Br}^{(3)}-\mathrm{Cd}-\mathrm{Br}^{(3')}$	87.6(1)
$\mathrm{Br}^{(1)}\cdots\mathrm{Br}^{(1')}$	364.0(3)	$\mathrm{Br}^{(1')}-\mathrm{Cd}-\mathrm{Br}^{(3')}$	90.4(1)
$\mathrm{Br}^{(1)}\cdots\mathrm{Br}^{(3)}$	382.4(2)	$\mathrm{Cd}-\mathrm{Br}^{(1)}-\mathrm{Cd}^{(')\,c}$	97.3(1)
$\mathrm{Br}^{(3)}\cdots\mathrm{Br}^{(3')}$	379.2(3)	$\mathrm{Cd}-\mathrm{Br}^{(3)}-\mathrm{Cd}^{('')\,d}$	92.4(1)
$\mathrm{Br}^{(3')}\cdots\mathrm{Br}^{(1')}$	382.4(2)		
$\mathrm{C}^{(2)}-\mathrm{C}^{(3)}$	133.9(25)	$\mathrm{C}^{(2)}-\mathrm{C}^{(3)}-\mathrm{C}^{(4)}$	121.1(17)
$\mathrm{C}^{(3)}-\mathrm{C}^{(4)}$	140.7(22)	$\mathrm{C}^{(3)}-\mathrm{C}^{(4)}-\mathrm{C}^{(5)}$	116.0(16)
$\mathrm{C}^{(4)}-\mathrm{C}^{(5)}$	140.4(25)	$\mathrm{C}^{(4)}-\mathrm{C}^{(5)}-\mathrm{C}^{(6)}$	121.5(19)
$\mathrm{C}^{(5)}-\mathrm{C}^{(6)}$	134.6(30)	$\mathrm{C}^{(5)}-\mathrm{C}^{(6)}-\mathrm{N}$	120.0(18)
$\mathrm{C}^{(6)}-\mathrm{N}$	133.0(28)	$\mathrm{C}^{(6)}-\mathrm{N}-\mathrm{C}^{(2)}$	121.5(16)
$\mathrm{N}-\mathrm{C}^{(2)}$	136.7(25)	$\mathrm{N}-\mathrm{C}^{(2)}-\mathrm{C}^{(3)}$	119.8(17)
$\mathrm{C}^{(4)}-\mathrm{C}^{(7)}$	148.9(23)	$\mathrm{C}^{(3)}-\mathrm{C}^{(4)}-\mathrm{C}^{(7)}$	122.8(15)
		$\mathrm{C}^{(5)}-\mathrm{C}^{(4)}-\mathrm{C}^{(7)}$	121.2(15)

[a] $\mathrm{Br}^{(1')}$: $-x, 2-y, 1-z$; [b] $\mathrm{Br}^{(3')}$: $-x, 1-y, -z$; [c] Cd′: $1-x, 1-y, -z$; [d] Cd″: $x, 3/2-y, -1/2-z$.

Table 7. ^{79,81}Br NQR frequencies of **1** and **2** at 77 K and 285 K. Coefficients of the power series development $\nu_1 = f(T) = \sum_{i=-1}^{2} a_i\, T^i$. z is the number of experimental points used for the fitting of the respective curve and σ is the standard deviation. $T_1 = 77$ K, $T_2 = 298$ K. The power series development is valid from 77 K to 340 K.

ν_1	ν/MHz T_2 [a]	z	$\sigma \cdot 10^3$ / MHz	a_0 / MHz	$a_{-1} \cdot 10^2$ / MHz·K	$a_1 \cdot 10^3$ / MHz·K^{-1}	$a_2 \cdot 10^6$ / MHz·K^{-2}
$(\mathrm{C_6H_5NH_3})_4\mathrm{Cd_3Br_{10}}$ (**1**)							
$\nu_1\,(^{79}\mathrm{Br})$	75.36						
$\nu_1\,(^{81}\mathrm{Br})$	62.98	66	38.0	65.698	−1.225	−10.098	3.352
$\nu_2\,(^{79}\mathrm{Br})$	62.98	74	37.8	59.718	40.897	12.053	−3.992
$\nu_2\,(^{81}\mathrm{Br})$	52.59						
$\nu_3\,(^{79}\mathrm{Br})$	61.95						
$\nu_3\,(^{81}\mathrm{Br})$	43.39	70	38.7	43.416	−14.032	4.323	−9.106
$\nu_4\,(^{79}\mathrm{Br})$	50.00						
$\nu_4\,(^{81}\mathrm{Br})$	41.82	77	33.7	43.305	−62.455	−0.073	−16.577
$\nu_5\,(^{79}\mathrm{Br})$	48.56						
$\nu_5\,(^{81}\mathrm{Br})$	40.71	83	33.3	43.314	31.701	−12.989	13.710
$(4\text{-}(\mathrm{CH_3})\mathrm{C_5H_4NH})\mathrm{CdBr_3}$ (**2**)							
$\nu_1\,(^{79}\mathrm{Br})$	79.02						
$\nu_1\,(^{81}\mathrm{Br})$	66.01	47	22.4	66.997	13.784	−1.643	−5.819
$\nu_2\,(^{79}\mathrm{Br})$	66.40	48	33.5	66.007	13.513	2.900	−6.440
$\nu_2\,(^{81}\mathrm{Br})$	55.39						
$\nu_3\,(^{79}\mathrm{Br})$	60.75	57	16.6	60.852	21.463	−2.829	5.081
$\nu_3\,(^{81}\mathrm{Br})$	50.75						

[a] ν/MHz at $T_1 = 77$ K (same order for ν_i as for $T_2 = 298$ K): 77.60; 64.80; 60.72; 50.73; 50.00; 41.81; 51.62; 43.13; 50.92; 42.61 ‖ 79.97; 66.85; 66.29; 55.48; 60.78; 50.76.

Discussion

Crystal Structure and Bromine NQR of $(\mathrm{C_6H_5NH_3})_4\mathrm{Cd_3Br_{10}}$, (**1**)

From the composition of **1** one expects an interesting structure for the anion, adding to the variety of connections observed for bromocadmate compounds [4–7]. As one recognizes in the projection of the unit cell along [001], Fig. 1, the anion froms chains (respectively layers) in the *ab* plane, centered at $x = 0$ and $x = 0.5$. There is no connection Cd−Br−Cd in the [100] direction. That we do not deal with chains, but with two-dimensional networks with connection Cd−Br−Cd is shown in Fig. 6, a projection of the half of the unit cell along [100] from $x = 0.25$ to $x = 0.75$.

We consider the anionic unit with the center $\mathrm{Cd}^{(1)}$ at $x = 0.5$, $y = 0.5$, $z = 0$. Each unit is

$$[\mathrm{Br}^{(5)}\tfrac{1}{2}\mathrm{Br}^{(4,4)}\mathrm{Cd}^{(2)}\mathrm{Br}^{(1,2,3)}\mathrm{Cd}^{(1)} \cdot \mathrm{Br}^{(1,2,3)}\mathrm{Cd}^{2)}\tfrac{1}{2}\mathrm{Br}^{(4,4)}\mathrm{Br}^{(5)}].$$

It is composed of a quite regular centrosymmetric octahedron with $2\,\mathrm{Br}^{(1)}$, $2\,\mathrm{Br}^{(2)}$, and $2\,\mathrm{Br}^{(3)}$ around $\mathrm{Cd}^{(1)}$, face connected with two attached acentric neighboring octahedra with $\mathrm{Br}^{(2)}$, $\mathrm{Br}^{(3)}$, $\mathrm{Br}^{(1)}$, $\mathrm{Br}^{(5)}$, and $2\,\mathrm{Br}^{(4)}$ at the corners and $\mathrm{Cd}^{(2)}$ as center. The atom $\mathrm{Br}^{(5)}$ is solely connected to $\mathrm{Cd}^{(2)}$. The four atoms $\mathrm{Br}^{(4)}$ are shared with four neighbour units $[\mathrm{Cd_3Br_{10}}]$, Figure 6. In this way a two-dimensional network is formed, a puckered *bc* plane of Br and Cd, at $x = 0$ and $x = 0.5$. The octahedron $[\mathrm{Cd}^{(1)}\mathrm{Br}_6]$ is more densely packed than the octahedron $[\mathrm{Cd}^{(2)}\mathrm{Br}_6]$, see Table 4.

The $[\mathrm{Cd_3Br_{10}}]$-*bc* planes are separated from each other by layers of cations $(\mathrm{C_6H_5NH_3})^{\oplus}$. There are two crystallographically independent cations, labeled I and II, and they are connected to the $[\mathrm{Cd_3Br_{10}}]$ units by hydrogen bonds N−H ··· Br. All hydrogen atoms of both groups $\mathrm{N_IH_3}$ and $\mathrm{N_{II}H_3}$ are involved in hydrogen bonds. In Table 8 the hydrogen bond network (distances and angles) is listed and Fig. 7 shows the bonds graphically in a projection of part of the unit cell along [001].

Looking on the geometry of both anilinium ions $(\mathrm{C_6H_5NH_3})_{\mathrm{I}}^{\oplus}$ and $(\mathrm{C_6H_5NH_3})_{\mathrm{II}}^{\oplus}$, we shall not discuss

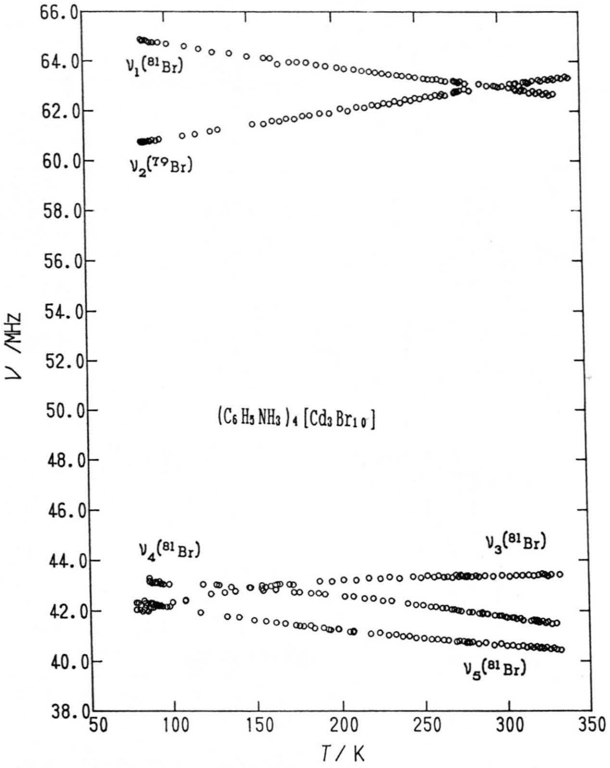


Fig. 4. $\nu(^{79,81}\mathrm{Br}) = f(T)$ of **1**.

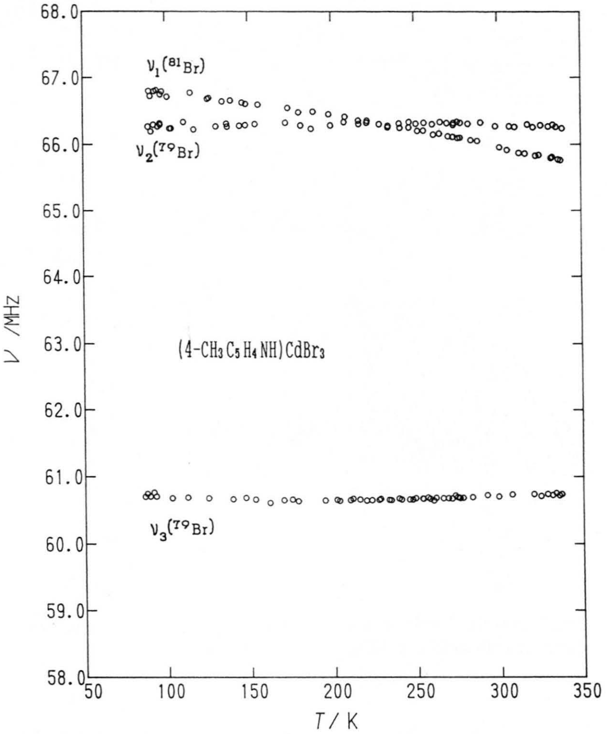


Fig. 5. $\nu(^{79,81}\mathrm{Br}) = f(T)$ of **2.**

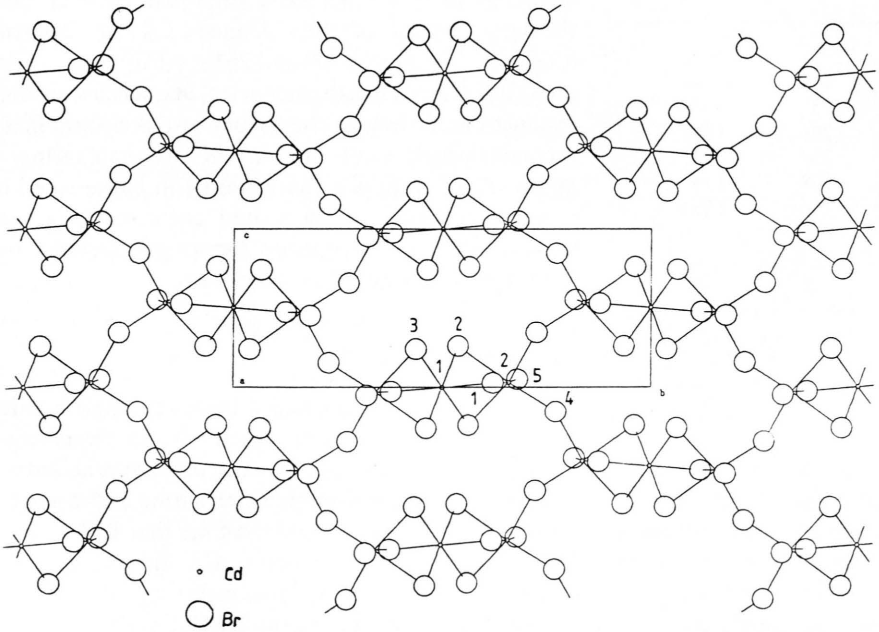


Fig. 6. Projection of half ($0.25 \leq x \leq 0.75$) of the unit cell of **1** along [100]. Only the anion frame is shown.

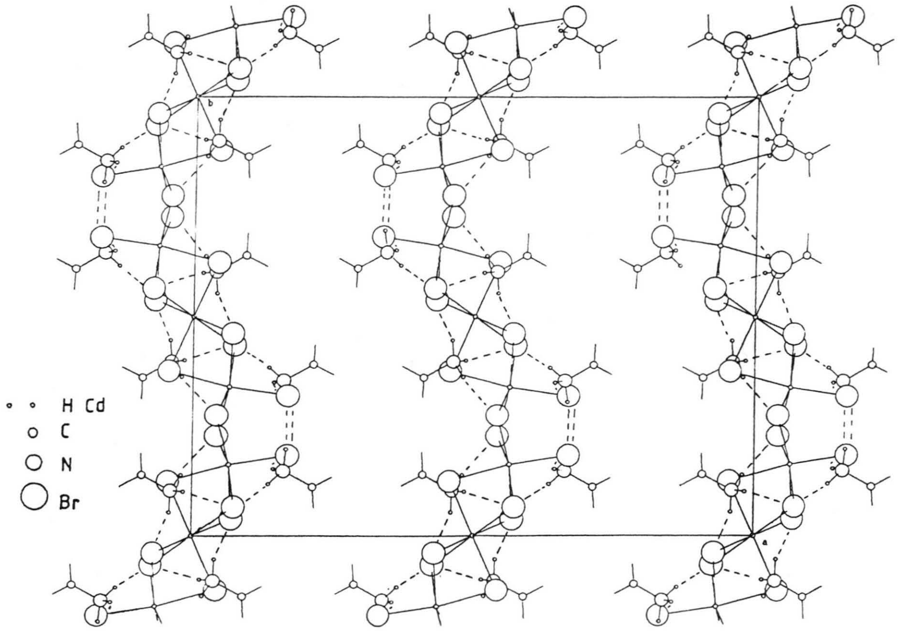


Fig. 7. Hydrogen bond scheme in **1**. The anion planes are shown in projection along [001] and the groups $-C^{(1)}NH_3$. The hydrogen bonds are marked by dashed lines.

Table 8. Hydrogen bond scheme in the structures of **1** and **2**. Bond distances $N-H\cdots Br$ (in pm) and angles $N-H\cdots Br$ (in degree).

Connection	$d(N-H\cdots Br)$	$d(H\cdots Br)$	Angle $N-H\cdots Br$
$(C_6H_5NH_3)_4Cd_3Br_{10}$ (**1**)			
$N_I-H_I^{(N,1)}\cdots Br^{(5')a}$	347.3	254	144
$N_I-H_I^{(N,2)}\cdots Br^{(3')b}$	341.0	239	157
$N_I-H_I^{(N,3)}\cdots Br^{(5'')c}$	343.1	241	158
$N_{II}-H_{II}^{(N,1)}\cdots Br^{(2)}$	342.3	303	102
$N_{II}-H_{II}^{(N,2)}\cdots Br^{(3)}$	351.0	268	134
$N_{II}-H_{II}^{(N,3)}\cdots Br^{(4')d}$	339.3	236	159
$(4\text{-}(CH_3)C_5H_4N)CdBr_3$ (**2**)			
$N-H^{(N)}\cdots Br^{(2)}$	328.1	228	154

[a] $Br^{(5')}$: $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; [b] $Br^{(3')}$: $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; [c] $Br^{(5'')}$: $\frac{1}{2}-x, \frac{1}{2}+y, z$; [d] $Br^{(4')}$: $1-x, 1-y, \frac{1}{2}-z$.

the distances C–H. Because of the heavy atom determined structure these distances have been fixed to 108.0 pm. We have furthermore fixed the distances N–H to 108.0 pm. Also the internal geometry of the cations is affected by the uncertainties of the positional coordinates of the carbon and nitrogen atoms. The mean distance C–C is 139.2 pm for cation I, 137.5 pm for cation II, equal within a mean error of 2.5 pm. For the C–N distances we find 147 pm (I) and 148 pm (II) pm.

The large spread of the five ^{81}Br NQR frequencies, $40.7 \le \nu(^{81}Br)/MHz \le 63$) (see Table 7) and the large spread of the distances Cd–Br, $269 \le d(Cd^{(1)}-Br^{(1,2,3)})/pm \le 300$ and $263 \le d(Cd^{(2)}-Br^{(1-5)})/pm \le 300$ offers an assignment of frequencies to the distances according to the theory of the electric field gradients which results in $\nu = a(1/d^3)$. In such a simple approach, often applied successfully in literature, the shortest distance Cd–Br would correspond to the highest ^{81}Br NQR frequency, the longest distance to the lowest frequency. For **1** we find:

$$\nu_1 \leftrightarrow Br^{(5)};\ \nu_2 \leftrightarrow Br^{(1)};\ \nu_3 \leftrightarrow Br^{(4)};$$
$$\nu_4 \leftrightarrow Br^{(2)};\ \nu_5 \leftrightarrow Br^{(3)}.$$

This approach works well if there are single bonds M-halogen (Cl, Br, I) only. However, as the crystal structure of **1** shows, there is only one bromine atom, ($Br^{(5)}$), in the complex anion which shows only a single bond (to Cd). In Figs. 1 and 6 we see that $Br^{(1-4)}$ are all involved in bridging bonds Cd–Br–Cd. In this situation the asymmetry parameter $\eta(^{81}Br)$ of the electric field gradient tensor, EFGT, with the principal axes ϕ_{xx}, Φ_{yy}, and Φ_{zz}, $|\Phi_{zz}| \ge |\Phi_{yy}| \ge |\Phi_{xx}|$,

$\eta = |\Phi_{xx} - \Phi_{yy}| / |\Phi_{zz}|$, may be much larger as 0.15, the upper limit one expects for a single bond Cd–Br. $\eta(^{81}\mathrm{Br})$ depends strongly on the bridging angle Cd–Br–Cd.

There is a further secondary influence on the Br-NQR frequencies, hydrogen bonds. Besides $\mathrm{Br}^{(1)}$ all bromines accept bonds N–H · · · Br, see Table 8. The distances N–H · · · Br we found are well within the range in which hydrogen bonds are expected since the ionic radii of $\mathrm{NH}_4^{\oplus}$ and $\mathrm{Br}^{\ominus}$ are 160 pm and 190 pm, respectively, $r(\mathrm{NH}_4)^{\oplus} + r(\mathrm{Br}^{\ominus}) = 350$ pm [11]. The hydrogen bond will lower the $(^{81}\mathrm{Br})$ NQR frequency because of the opposite direction of the EFGT main principle axis Φ_{zz} created by the bond $\mathrm{H}^{\oplus} \cdots \mathrm{Br}$ and the bond Br–Cd.

There are experiments which could give support for the assignment $\nu_i(^{81}\mathrm{Br}) \leftrightarrow \mathrm{Br}^{(j)}$, a) the exchange $\mathrm{H} \leftrightarrow \mathrm{D}$ which would change the hydrogen bond strength and thereby the resonance frequencies. This is, however, a qualitative experiment because such an exchange changes also the lattice dynamics and thereby influences the NQR frequencies. b) The hydrogen positions found from X-ray diffraction are too uncertain; neutron diffraction would have to be done, too, besides the large difficulties introduced by the strong interaction of Cd nuclei with the neutrons. c) The experiment of choice, but rather involved, would be a Zeeman NQR single crystal study of the Br-NQR spectrum.

Structure and Bromine NQR of 4-Methylpyridinium Tribromocadmate, (2)

The anion $\mathrm{CdBr}_3^{\ominus}$ of **2** forms a condensed system with chain structure. The $[\mathrm{CdBr}_3]_\infty$ are running along [001] at $x = 0$ and $x = 0.5$. Figure 8 gives the projection of the structure onto the *ab* plane, which is pseudotetragonal, centered. No two-dimensional links, neither in the *bc* plane nor in the *ab* plane are present (the *b* axis has a length of 1169 pm). The cation can form only one hydrogen bond which is directed to $\mathrm{Br}^{(2)}$, the bromine atom which is single bonded to Cd (see Figure 3). The most simple condensation of the anions would be a chain $\cdots \mathrm{Br}_3\mathrm{CdBr}_3\mathrm{CdBr}_3 \cdots$, face connected by three bromine atoms. It is the influence of the hydrogen bond between the rather basic 4-methylpyridinium hydrogen and bromine, which leads to a pentagonal coordination $[\mathrm{CdBr}_5]$ with one single bond $\mathrm{Cd{-}Br}^{(2)}$ and two bridging bonds $\mathrm{Cd{-}Br}^{(1)}{-}\mathrm{Cd}$ and $\mathrm{Cd{-}Br}^{(3)}{-}\mathrm{Cd}$. The bridges are quite asymmetric with distances $d(\mathrm{Cd{-}Br}^{(1)} = 262$ pm, $d(\mathrm{Cd{-}Br}^{(1')} = 288$ pm, $d(\mathrm{Cd{-}Br}^{(3)} = 285$ pm, and $d(\mathrm{Cd{-}Br}^{(3')} = 263$ pm. One of the bonds Cd–Br within a bridge is much shorter than the other, but the atoms $\mathrm{Br}^{(1)}$ and $\mathrm{Br}^{(3)}$ are very similar in their bridging power. The bridging angles $\mathrm{Cd{-}Br}^{(1)}{-}\mathrm{Cd}'$ and $\mathrm{Cd{-}Br}^{(3)}{-}\mathrm{Cd}''$ are 97° and 92°.

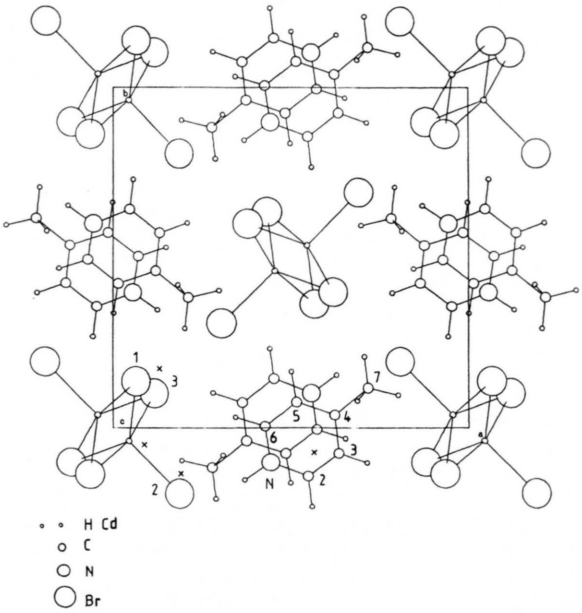
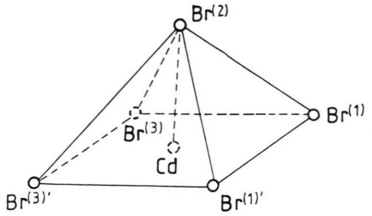


Fig. 8. Projection of the unit cell of **2** along [001] on the *ab* plane.

The pentagonal coordination of the cadmium is such that a fairly regular tetragonal pyramid is formed with $\mathrm{Br}^{(1)}$, $\mathrm{Br}^{(1')}$, $\mathrm{B}^{(3)}$, and $\mathrm{Br}^{(3')}$ as quadratic basis and $\mathrm{Br}^{(2)}$ at the top of the pyramid. This is shown by the sketch in Table 9. We have calculated the best plane through this basis (see Table 9) and the deviations of $\mathrm{Br}^{(1)}$ and $\mathrm{Br}^{(3)}$ is 40 pm at most. Cd is by 70 pm out of this plane (above). $\mathrm{Br}^{(2)}$ forms the top of the tetragonal pyramid, being 324 pm above the plane Br_4. The vector $\mathrm{Br}^{(2)}{-}\mathrm{Cd}$ forms an angle of 8° with the normal to the basis of the pyramid.

In total, the bridging action of the bromines $\mathrm{Br}^{(1)}$ and $\mathrm{Br}^{(3)}$ is weak. If we consider the three short distances Cd–Br, $d(\mathrm{Cd{-}Br}^{(2)}$, $-\mathrm{Br}^{(1)}$, and $-\mathrm{Br}^{(3')})$, 256 pm, 262 pm, and 263, respectively, and the corresponding angles $\mathrm{Br}^{(i)}{-}\mathrm{Cd}{-}\mathrm{Br}^{(j)}$, see Table 6, we find in first approximation a trigonal pyramid CdBr_3^- and a rather weak polymerisation tendency to the one-dimensional chain of pentagonal pyramids.

Table 9. Structure of the tetragonal pyramid $CdBr^{(1)'}Br^{(1)}Br^{(3)'}Br^{(3)}Br^{(2)}$ in the lattice of **2**.



Connection	Distance/pm	Connection	Angle/°
$Br^{(2)}-Br^{(1)}$	454.7(2)	$Br^{(1)}-Cd-Br^{(1)'}$	82.7(1)
$Br^{(2)}-Br^{(1)'}$	408.1(3)	$Br^{(1)}-Cd-Br^{(3)}$	88.7(1)
$Br^{(2)}-Br^{(3)}$	404.0(2)	$Br^{(3)}-Cd-Br^{(3)'}$	87.6(1)
$Br^{(2)}-Br^{(3)'}$	414.1(3)	$Br^{(3)'}-Cd-Br^{(1)'}$	90.4(1)
$Br^{(1)}-Br^{(1)'}$	364.0(3)	$Br^{(1)'}-Cd-Br^{(3)}$	166.7(1)
$Br^{(1)}-Br^{(3)}$	382.4(2)	$Br^{(1)}-Cd-Br^{(3)'}$	131.2(1)
$Br^{(3)}-Br^{(3)'}$	379.2(3)	$Br^{(2)}-Cd-Br^{(1)}$	122.8(1)
$Br^{(1)'}-Br^{(3)'}$	382.4(3)	$Br^{(2)}-Cd-Br^{(1)'}$	96.8(1)
$Cd-Br^{(2)}$	256.4(3)	$Br^{(2)}-Cd-Br^{(3)}$	96.4(1)
		$Br^{(2)}-Cd-Br^{(3)'}$	105.9

Equation of plane through $Br^{(1)}$, $Br^{(1)'}$, $Br^{(3)}$, $Br^{(3)'}$ (distances in Å):

$$9.4940\,x-7.3923\,y-0.0254\,z=-0.0064$$

Deviations from the plane (in pm): Cd, 70.05; $Br^{(2)}$, 323.95; $Br^{(1)}$, −39.58; $Br^{(1)'}$, 38.31; $Br^{(3)}$, 37.65; $Br^{(3)'}$, −36.38.

Angle between the direction $Cd-Br^{(2)}$ and the plane: 171.96°.

Three ^{81}Br NQR frequencies are observed over the whole temperature range investigated ($77 \leq T/K \leq 340$) for **2**, see Fig. 5 and Table 7, and the smooth curves $\nu = f(T)$ give no evidence of the occurrence of a phase transition. The line $\nu_1 = f(T)$ shows the normal NQR behavior, decreasing frequency with increasing T as predicted by Bayer [12]. It is the highest frequency in the spectrum at 298 K (and at 77 K, too). We assign it to the atom $Br^{(2)}$, single bonded to Cd, with the shortest distance Cd–Br (256 pm) in the structure. We expect that the hydrogen bond which attacks $Br^{(2)}$ will lower the frequency somewhat in comparison with an undisturbed single bond but will not change the temperature coefficient we expect from [12]. ν_1 (^{81}Br) and ν_3 (^{81}Br) are apart from ν_2 (^{81}Br), both showing a similar temperature dependence. We propose that these two resonance frequencies have to be assigned to $Br^{(1)}$ and $Br^{(3)}$, respectively.

From the arguments given, we propose the assignment

$$\nu_1(^{79,81}Br) \leftrightarrow Br^{(2)};\ \nu_{2,3}(^{79,81}Br) \leftrightarrow Br^{(1,3)}.$$

A further differentiation in the assignment of $\nu_{2,3}$ to $Br^{(1,3)}$ needs single crystal Zeeman NQR.

Acknowledgement

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