Isolated versus Condensed Anion Structure: the Influence of the Cation Size and Hydrogen Bond on Structure and Phase Transition in MX_4^{2-} Complex Salts. 2,2-Dimethyl-1,3-propanediammonium Tetrabromocadmate(II) Monohydrate, Dimethylammonium Tetrabromozincate(II), and Dimethylammonium Tetrabromocadmate(II)

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In the course of work on the anion condensation of Cd and Zn halides, the crystal structures and ^{79,81}Br NQR spectra of 2,2-dimethyl-1,3-propanediammonium tetrabromocadmate(II) monohydrate (**1**) and dimethylammonium tetrabromozincate(II) (**2**), and ^{79,81}Br NQR spectra of dimethylammonium tetrabromocadmate(II) (**3**) have been studied. An isolated $[CdBr_4]^{2-}$ ion of the salt $[H_3NCH_2C(CH_3)_2CH_2NH_3]CdBr_4 \cdot H_2O$ (**1**) is formed, with polar orthorhombic space group $Pbc2_1$, $Z = 4$, $a = 645.5(3)$, $b = 1628.3(8)$, $c = 1389.5(6)$ pm. $[(CH_3)_2NH_2]_2ZnBr_4$ (**2**) has also an isolated anion lattice, with monoclinic space group, $P2_1/c$, $Z = 4$, $a = 870.6(3)$, $b = 1195.6(4)$, $c = 1628.9(5)$ pm, $\beta = 121.84(1)°$. The ^{81}Br NQR spectrum of (**1**) is a quartet (ν in MHz, $T = 77$ K/303 K): $\nu_1 = 68.403/64.278$; $\nu_2 = 65.296/62.663$; $\nu_3 = 56.525/54.660$; $\nu_4 = 43.211/45.422$. The ^{81}Br NQR spectrum of (**2**) is a quartet too (ν in MHz, $T = 77$ K/300 K): $\nu_1 = 66.848/64.784$; $\nu_2 = 63.152/61.883$; $\nu_3 = 57.498/55.890$; $\nu_4 = 49.416/50.224$. The ^{81}Br NQR spectrum of $[(CH_3)_2NH_2]_2CdBr_4$ (**3**) is also a quartet (ν in MHz, $T = 77$ K/310 K): $\nu_1 = 68.606/67.272$; $\nu_2 = 65.806/63.296$; $\nu_3 = 58.096/57.369$; $\nu_4 = 55.757/53.393$. The change of NQR frequencies with temperature is smooth for all three compounds. One of the ^{81}Br NQR lines in both (**1**) and (**2**) increases slightly in frequency with increasing T. In the compound (**1**), the H_2O coordinates to NH_3^+ groups and to bromines forming a distorted tetrahedron $(Br\ldots)_2 \cdots H_2O \cdots (\ldots HN)_2$, the six angles lying between 69° and 131°. The relations between the bromine NQR and the crystal structures are discussed for the title compounds.

Introduction

Recently we became interested in the study of group II (Zn, Cd) halogeno complexes by crystal structure determination and observation of halogen nuclear quadrupole resonance (NQR), to get information about the condensation of the anions MX_3^-, and MX_4^{2-} (M = Zn, Cd; X = Cl, Br) under the influence of both the size and hydrogen bond ability of the respective counter cation [1–3]. Isolated anions, chains, and two-dimensional anion layers can be expected, and they are observed. Space filling (size) of the cations and hydrogen bonds between cation and halogen atoms of the anions play an important role in the condensation or polymerization of anions.

Here we report on the relation between the crystal structures and NQR results of 2,2-dimethyl-1,3-propanediammonium tetrabromocadmate(II) monohydrate, $[H_3NCH_2C(CH_3)_2CH_2NH_3]CdBr_4 \cdot H_2O$ (**1**), dimethylammonium tetrabromozincate(II) $[(CH_3)_2NH_2]_2ZnBr_4$ (**2**), dimethylammonium tetrabromocadmate(II), $[(CH_3)_2NH_2]_2CdBr_4$ (**3**).

Experimental

The compounds (**1**), (**2**), and (**3**) have been grown from stoichiometric mixtures of aqueous solutions of the respective amine, HBr, and $CdBr_2$ (commercial

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compounds, Aldrich) or $ZnBr_2$ at pH of 3. The results of the chemical analysis (in weight %, found/calculated) are as follows: (**1**): C, 10.81/10.83; H, 3.20/3.27; N, 5.04/5.05. (**2**): C, 10.05/10.06; H, 3.34/3.37; N, 5.88/5.87. (**3**): C, 9.13/9.16; H, 3.05/3.07; N, 5.36/5.34. Small single crystals of (**1**) and (**2**) were grown from aqueous solutions for the X-ray diffraction experiments. The structures were determined with a 4 circle X-ray diffractometer. The intensities were corrected for absorption and Lorentz-polarization factor. By the use of direct methods, Fourier synthesis and least squares analysis, the structures werde determined [4, 5]. The Br NQR studies were performed on a superregenerative-type spectrometer. For the title compounds the Br NQR signals were of good S/N ratios with line widths between 40 and 50 kHz, somewhat dependent on the temperature. (**1**) looses the H_2O molecules at 339 K according to the thermal analysis.

Results and Discussion

Crystal Structures: $[H_3NCH_2C(CH_2)_2CH_2NH_3]CdBr_4 \cdot H_2O$ (**1**)

(**1**) crystallizes orthorhombic with the polar space group $Pbc2_1$, $Z = 4$. The experimental conditions for the structure determination are listed in Table 1 together with those for (**2**) [6]. In Fig. 1, we show the formula unit with the numbering of the atoms used throughout this paper and with the 50% electron density of the thermal ellipsoids of the atoms. The hydrogen bond system is marked in Fig. 2, where the projection of the unit cell along the *a* axis onto the *bc* plane is drawn. The atomic coordinates are listed in

Table 1. Experimental conditions for the crystal structure determinations and crystallographic data of 2,2-dimethyl-1,3-diammoniumpropane tetrabromocadmate(II) monohydrate (**1**) and dimethylammonium tetrabromozincate(II) (**2**). Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoK_α); monochrometer: graphite (002); scan $2\theta/\omega$ (1): $C_5H_{18}Br_4CdN_2O$, $M = 554.24$; (2): $C_4H_{16}Br_4N_2Zn$, $M = 477.19$.

Compound	(1)	(2)
Crystal size/(mm^3)	$5 \times 0.3 \times 0.22$	$5 \times 0.37 \times 0.27$
Temperature/K	298	291
Absorption coefficient (μ/m^{-1})	12098	12510
θ-range for data collection	$2.50 \leq \theta/° \leq 29.97$	$2.29 \leq \theta/° \leq 22.5$
Index ranges	$0 \leq h \leq 9$, $-22 \leq k \leq 22$, $-19 \leq l \leq 19$	$0 \leq h \leq 9$, $-12 \leq k \leq 6$, $-17 \leq l \leq 14$
Lattice constants		
a/pm	645.5(3)	870.6(3)
b/pm	1628.3(8)	1195.6(4)
c/pm	1389.5(6)	1628.9(5)
α/°	90.00	90.00
β/°	90.00	121.84(1)
γ/°	90.00	90.00
$V \cdot 10^{-6}/(pm)^3$	1460.5(10)	1440.34(123)
Space group	$C_{2v}^5 - Pbc2_1$	$C_{2h}^5 - P2_1/C$
Formula units	4	4
$\varrho_{calc}/(Mg \cdot m^{-3})$	2.520(4)	2.200(2)
$F(000)$	1024	896
Reflections collected	8653	3365
Symmetry independent	4249	1884
$[R_{int}]$	0.0766	
Data	4248	1734
Restraints/Parameters	1/113	0/113
Goodnes of fit on F^2	1.020	
Final $R(I > 2\sigma(I))$	$R_1 = 0.0443$ $wR_2 = 0.1057$	$R_1 = 0.0711$ $wR_2 = 0.0687$
R (all data)	$R_1 = 0.0613$ $wR_2 = 0.1197$	
Largest diff: (Peak, Hole) /(10^{-6} e/(pm)^3)	1.751 and −2.374	
Max. and min. trans.	0.1541 and 0.0201	
Extinction coeff.	0.0034(2)	
Point positions	all atoms in 4a	all atoms in 4e

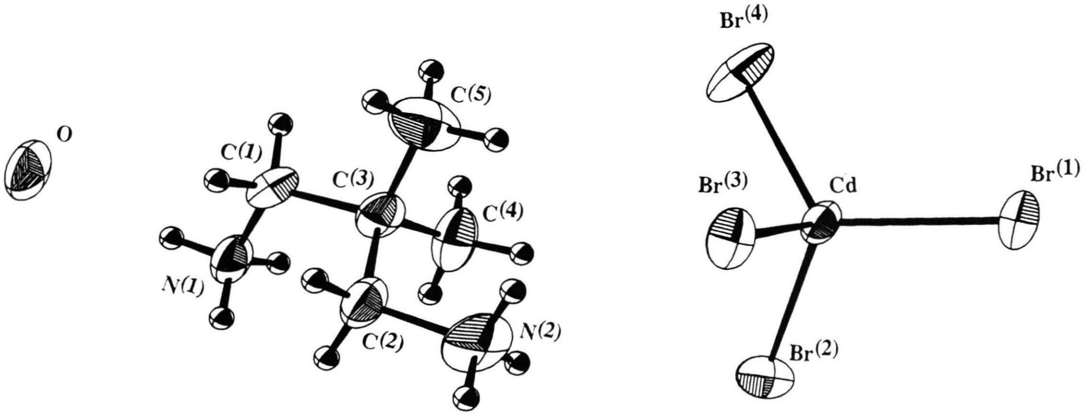

Fig. 1. Formula unit of 2,2-dimethyl-1,3-propanediammonium tetrabromocadmate(II) monohydrate (**1**) with the numbering of the atoms given in the Tables and thermal ellipsoids (50% of the electron density).

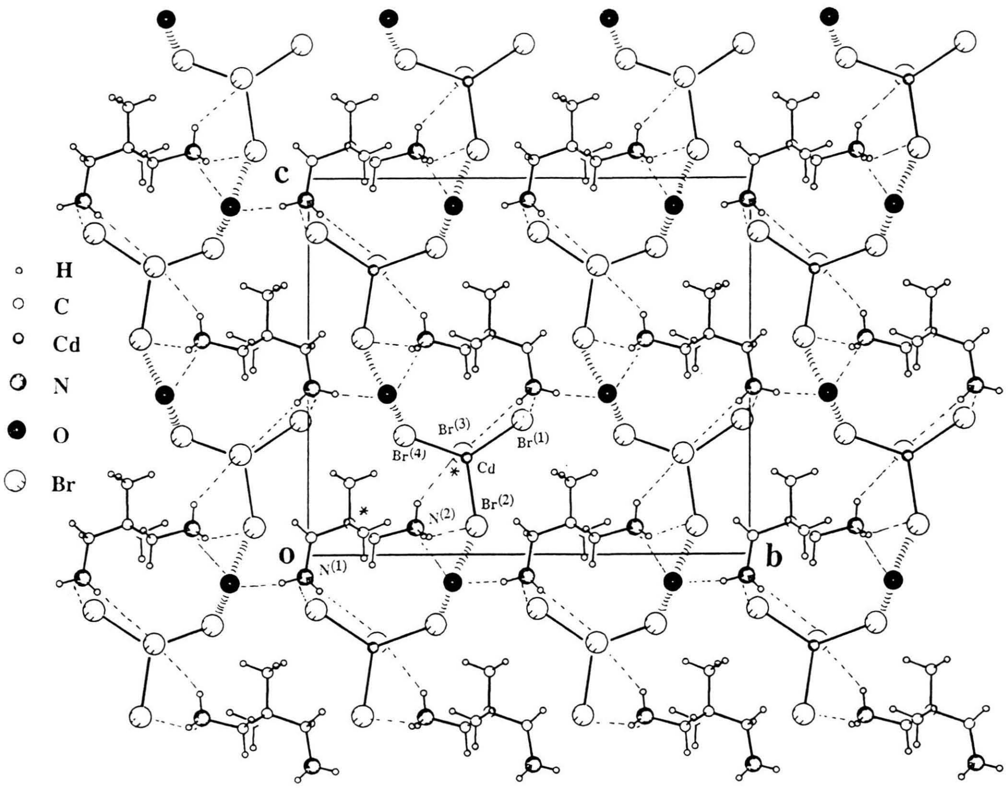

Fig. 2. Projections of the unit cell of (**1**) along [100] onto the *bc* plane. The hydrogen bonds are marked by dashed lines. The hydrogen bonds between O and Br are denoted by)))). The formula unit for which the atomic coordinates are given in Table 2 are marked by *.

Table 2, which includes displacement parameters. In Table 3, one finds the intramolecular (intraionic) distances and angles. Compared to the $[ZnBr_4]^{2-}$ tetrahedron of (**2**), the $[CdBr_4]^{2-}$ tetrahedron of (**1**) is much less regular, $255.2 \leq d(\text{Cd-Br})/\text{pm} \leq 264.6$ and also the scattering of the "tetrahedral" angles is quite large $102.9 \leq \angle(\text{Br-Cd-Br})/^\circ \leq 118.2$. This is due to the much more distorted hydrogen bond interaction in (**1**) compared to (**2**). Although the distances $d(\text{C-C})$ and angles $\angle(\text{C-C-C})$ of the cations are as expected, the dihedral angle $\angle(\text{N}^{(1)}\text{-C}^{(1)}\text{-C}^{(3)}\text{-C}^{(2)})$ is 75° and the angle $\angle(\text{N}^{(2)}\text{-C}^{(2)}\text{-C}^{(3)}\text{-C}^{(1)})$ 184°. As a result, the $H_3N^{(1)}$ group is close to the methyl group, $H_3C^{(4)}$. This conformation of the 2,2-dimethyl-1,3-propanediammonium dication is nearly identical to the anti-gauche conformation with respect to two NH_3^+ groups expected from the *ab initio* method [7]; the dihedral angles are 73.9° and 173.7°, although the anti-anti conformation of the dication is the most stable one in which both dihedral angles are 180°. This distortion of the dication in the crystal originates in the molecular packing through the hydrogen bonds. No layered structure appeared for the compound (**1**), whereas the structure of $[H_3N(CH_2)_3NH_3]CdBr_4$ is layered [1]. This might be due to the steric hindrance of two methyl groups at position 2 of dications in comparison to $[H_3N(CH_2)_3NH_3]CdBr_4$. A severe restriction is due to the cross-sectional area of the alkylene group which can be accommodated between the layers. This area is about 550 pm × 550 pm when considering the geometry of the layered $[CdBr_4]^{2-}$ ion in $[H_3N(CH_2)_3NH_3]CdBr_4$ [1]. The distance $d(\text{N}^{(1)}\text{-N}^{(2)})$ of 452 pm in (**1**) is almost identical to the distance between two N atoms of the dication in the crystal of $[H_3N(CH_2)_3NH_3]CdBr_4$. The distance between $C^{(5)}$ and $C^{(4)}$, which are carbon atoms of two methyl groups at position 2, is 238 pm. Taking into consideration the van der Waals radii of the methyl group, 200 pm [8], (**1**) can not have a layered structure like $[H_3N(CH_2)_3NH_3]CdBr_4$.

Table 2. Atomic coordinates ($\times 10^4$) and displacement parameters U_{eq} and U_{ij} (in (pm)^2) for $[H_3NCH_2C(CH_3)_2CH_2NH_3]CdBr_4 \cdot H_2O$ (**1**) and $[(CH_3)_2NH_2]_2ZnBr_4$ (**2**). U_{eq} is defined as 1/3 of the trace of the orthogonalized tensor U_{ij}. The temperature factor has the form: $T = \exp\{-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)\}$.

Compound (**1**)

Atom	x	y	z	U_{eq}
Cd	−0461(1)	3556(1)	2567(1)	369(1)
$\mathrm{Br}^{(1)}$	0489(1)	4823(1)	3569(1)	456(2)
$\mathrm{Br}^{(2)}$	0171(1)	3788(1)	0751(1)	506(2)
$\mathrm{Br}^{(3)}$	−4548(1)	3473(1)	2681(1)	486(2)
$\mathrm{Br}^{(4)}$	0731(2)	2151(1)	3163(1)	725(3)
$\mathrm{N}^{(1)}$	−4489(9)	−0075(5)	−0569(5)	420(14)
$\mathrm{H}^{(N1,1)}$	−4722(9)	−0597(5)	−0723(5)	504
$\mathrm{H}^{(N1,2)}$	−3154(9)	0041(5)	−0654(5)	504
$\mathrm{H}^{(N1,3)}$	−5252(9)	0250(5)	−0943(5)	504
$\mathrm{C}^{(1)}$	−5068(3)	0067(6)	0479(6)	407(16)
$\mathrm{H}^{(C1,1)}$	−6515(13)	−0077(6)	0564(6)	488
$\mathrm{H}^{(C1,2)}$	−4256(13)	−0302(6)	0875(6)	488
$\mathrm{N}^{(2)}$	−6137(9)	2390(4)	0720(5)	680(22)
$\mathrm{H}^{(N2,1)}$	−7162(9)	2689(4)	0473(5)	817
$\mathrm{H}^{(N2,2)}$	−4930(9)	2572(4)	0496(5)	817
$\mathrm{H}^{(N2,3)}$	−6153(9)	2432(4)	1359(5)	817
$\mathrm{C}^{(2)}$	−6438(13)	1476(5)	0437(6)	459(17)
$\mathrm{H}^{(C2,1)}$	−7769(13)	1287(5)	0674(6)	551
$\mathrm{H}^{(C2,2)}$	−6447(13)	1429(5)	−0259(6)	551
$\mathrm{C}^{(3)}$	−4750(10)	0935(5)	0840(5)	390(15)
$\mathrm{C}^{(4)}$	−2660(9)	1229(4)	0606(5)	568(21)
$\mathrm{H}^{(C4,1)}$	−2493(9)	1247(4)	−0080(5)	681
$\mathrm{H}^{(C4,2)}$	−1651(9)	0864(4)	0878(5)	681
$\mathrm{H}^{(C4,3)}$	−2469(9)	1770(4)	0867(5)	681
$\mathrm{C}^{(5)}$	−4908(10)	0922(4)	1916(4)	685(29)
$\mathrm{H}^{(C5,1)}$	−6257(10)	0731(4)	2101(4)	822
$\mathrm{H}^{(C5,2)}$	−4695(10)	1466(4)	2163(4)	822
$\mathrm{H}^{(C5,3)}$	−3872(10)	0560(4)	2174(4)	822
O	−5999(10)	−1760(4)	−0734(4)	652(17)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	470(2)	224(2)	412(2)	−21(2)	35(2)	−12(2)
$\mathrm{Br}^{(1)}$	438(3)	311(4)	618(4)	−47(3)	29(3)	−143(4)
$\mathrm{Br}^{(2)}$	567(4)	553(5)	399(3)	135(4)	9(3)	58(4)
$\mathrm{Br}^{(3)}$	419(3)	408(5)	631(5)	−62(3)	30(3)	−71(4)
$\mathrm{Br}^{(4)}$	585(5)	327(5)	1262(9)	49(4)	109(5)	290(6)
$\mathrm{N}^{(1)}$	493(32)	232(31)	535(32)	−30(28)	−12(24)	−56(28)
$\mathrm{C}^{(1)}$	481(32)	264(38)	476(33)	−14(32)	43(28)	100(31)
$\mathrm{N}^{(2)}$	986(54)	304(41)	752(44)	324(45)	12(45)	−59(39)
$\mathrm{C}^{(2)}$	496(39)	280(40)	602(38)	−44(34)	−52(31)	20(33)
$\mathrm{C}^{(3)}$	407(31)	269(36)	493(35)	68(31)	0(27)	10(32)
$\mathrm{C}^{(4)}$	490(38)	370(45)	844(58)	−13(40)	32(37)	−164(48)
$\mathrm{C}^{(5)}$	1025(69)	583(67)	449(36)	302(63)	−93(39)	−94(45)
O	740(38)	326(34)	889(44)	−81(35)	−124(34)	−52(36)

Compound (**2**)

Atom	x	y	z	U_{eq}
Zn	9043(3)	2043(2)	0785(1)	375(14)
$\mathrm{Br}^{(1)}$	12057(3)	2711(2)	1290(1)	493(14)
$\mathrm{Br}^{(2)}$	7991(4)	2874(2)	1732(2)	713(18)
$\mathrm{Br}^{(3)}$	9096(3)	0057(2)	0939(1)	481(10)
$\mathrm{Br}^{(4)}$	7158(3)	2613(2)	−0875(1)	479(14)
$\mathrm{N}^{(1)}$	10983(21)	1864(13)	3947(10)	628(130)
$\mathrm{H}^{(N1,1)}$	9935(21)	2251(13)	3287(10)	759
$\mathrm{H}^{(N1,2)}$	10957(21)	2205(13)	4553(10)	759
$\mathrm{C}^{(1)}$	13004(22)	2161(16)	4243(14)	1093(200)
$\mathrm{H}^{(C1,1)}$	12843(22)	3016(16)	4399(14)	994
$\mathrm{H}^{(C1,2)}$	13878(22)	2138(16)	3958(14)	994
$\mathrm{H}^{(C1,3)}$	13596(22)	1673(16)	4898(14)	994
$\mathrm{C}^{(2)}$	10392(38)	0586(20)	3855(20)	1337(267)
$\mathrm{H}^{(C2,1)}$	9580(38)	0551(20)	4177(20)	1101
$\mathrm{H}^{(C2,2)}$	11663(38)	0164(20)	4319(20)	1101
$\mathrm{H}^{(C2,3)}$	9681(38)	0180(20)	3158(20)	1101
$\mathrm{N}^{(2)}$	13706(18)	0044(14)	1603(9)	541(112)
$\mathrm{H}^{(N2,1)}$	13005(18)	−0709(14)	1225(9)	509
$\mathrm{H}^{(N2,2)}$	12822(18)	0755(14)	1275(9)	509
$\mathrm{C}^{(3)}$	14264(29)	−0000(14)	2635(10)	583(142)
$\mathrm{H}^{(C3,1)}$	13030(29)	0111(17)	2633(10)	683
$\mathrm{H}^{(C3,2)}$	15232(29)	0630(17)	3087(10)	683
$\mathrm{H}^{(C3,3)}$	14814(24)	−0820(17)	2913(10)	683
$\mathrm{C}^{(4)}$	15371(23)	0247(25)	1502(17)	1113(217)
$\mathrm{H}^{(C4,1)}$	14974(23)	0330(25)	0755(17)	1091
$\mathrm{H}^{(C4,2)}$	16343(23)	−0423(25)	1835(17)	1091
$\mathrm{H}^{(C4,3)}$	15972(23)	1020(25)	1880(17)	1091

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	411(15)	424(17)	290(12)	−8(12)	180(11)	−15(11)
$\mathrm{Br}^{(1)}$	420(13)	586(17)	418(12)	−106(12)	172(11)	−12(11)
$\mathrm{Br}^{(2)}$	895(20)	644(20)	600(14)	45(15)	523(15)	−100(13)
$\mathrm{Br}^{(3)}$	532(15)	424(16)	488(12)	11(12)	259(11)	58(10)
$\mathrm{Br}^{(4)}$	516(14)	579(18)	344(11)	69(12)	122(10)	110(10)
$\mathrm{N}^{(1)}$	965(201)	1253(49)	1060(182)	89(185)	753(169)	−82(168)
$\mathrm{C}^{(1)}$	693(152)	723(170)	333(105)	−49(130)	233(109)	−61(102)
$\mathrm{C}^{(2)}$	1770(316)	727(225)	1514(261)	117(237)	824(241)	111(201)
$\mathrm{N}^{(2)}$	332(103)	718(141)	573(105)	5(96)	106(86)	−76(93)
$\mathrm{C}^{(3)}$	693(152)	723(170)	333(105)	−49(130)	233(109)	−61(102)
$\mathrm{C}^{(4)}$	568(157)	1982(314)	790(181)	−171(176)	414(144)	−54(185)

Table 3. Intramolecular (intraionic) distance d (in pm) and angles (in degree) in 2,2-dimethyl-1,3-propanediammonium tetrabromocadamate(II) monohydrate (**1**) and dimethylammonium tetrabromozincate(II) (**2**).

Part I: Anions

Compound (**1**)

Connection	d/pm	Connection	Angle/°
$\mathrm{Cd-Br^{(1)}}$	256.4(1)	$\mathrm{Br^{(1)}-Cd-Br^{(2)}}$	112.03(4)
$\mathrm{Cd-Br^{(2)}}$	258.3(1)	$\mathrm{Br^{(1)}-Cd-Br^{(3)}}$	104.28(3)
$\mathrm{Cd-Br^{(3)}}$	264.6(2)	$\mathrm{Br^{(1)}-Cd-Br^{(4)}}$	118.20(5)
$\mathrm{Cd-Br^{(4)}}$	255.2(2)	$\mathrm{Br^{(2)}-Cd-Br^{(3)}}$	102.93(3)
$\mathrm{Br^{(1)}\cdots Br^{(2)}}$	426.8(2)	$\mathrm{Br^{(2)}-Cd-Br^{(4)}}$	113.63(5)
$\mathrm{Br^{(1)}\cdots Br^{(3)}}$	411.3(2)	$\mathrm{Br^{(3)}-Cd-Br^{(4)}}$	103.63(4)
$\mathrm{Br^{(1)}\cdots Br^{(4)}}$	439.0(2)		
$\mathrm{Br^{(2)}\cdots Br^{(3)}}$	409.1(2)		
$\mathrm{Br^{(2)}\cdots Br^{(4)}}$	430.0(2)		
$\mathrm{Br^{(3)}\cdots Br^{(4)}}$	408.6(2)		

Compound (**2**)

Connection	d/pm	Connection	Angle/°
$\mathrm{Zn-Br^{(1)}}$	243.4(5)	$\mathrm{Br^{(1)}-Zn-Br^{(2)}}$	110.9(2)
$\mathrm{Zn-Br^{(2)}}$	238.8(5)	$\mathrm{Br^{(1)}-Zn-Br^{(3)}}$	109.5(2)
$\mathrm{Zn-Br^{(3)}}$	238.5(5)	$\mathrm{Br^{(1)}-Zn-Br^{(4)}}$	105.2(2)
$\mathrm{Zn-Br^{(4)}}$	240.6(4)	$\mathrm{Br^{(2)}-Zn-Br^{(3)}}$	109.8(2)
$\mathrm{Br^{(1)}\cdots Br^{(2)}}$	397.2(5)	$\mathrm{Br^{(2)}-Zn-Br^{(4)}}$	110.0(2)
$\mathrm{Br^{(1)}\cdots Br^{(3)}}$	393.6(5)	$\mathrm{Br^{(3)}-Zn-Br^{(4)}}$	111.4(2)
$\mathrm{Br^{(1)}\cdots Br^{(4)}}$	384.4(5)		
$\mathrm{Br^{(2)}\cdots Br^{(3)}}$	390.5(5)		
$\mathrm{Br^{(2)}\cdots Br^{(4)}}$	392.6(5)		
$\mathrm{Br^{(3)}\cdots Br^{(4)}}$	395.8(5)		

Table 3. (continued).

Part II: Cations

Compound (**1**)

Connection	d/pm	Connection	Angle/°
$\mathrm{N^{(1)}-C^{(1)}}$	152.0(10)	$\mathrm{N^{(1)}-C^{(1)}-C^{(3)}}$	115.2(6)
$\mathrm{N^{(2)}-C^{(2)}}$	155.2(9)	$\mathrm{N^{(2)}-C^{(2)}-C^{(3)}}$	112.1(6)
$\mathrm{C^{(1)}-C^{(3)}}$	151.4(13)	$\mathrm{C^{(2)}-C^{(3)}-C^{(4)}}$	113.0(7)
$\mathrm{C^{(3)}-C^{(2)}}$	150.9(11)	$\mathrm{C^{(1)}-C^{(3)}-C^{(2)}}$	108.9(6)
$\mathrm{C^{(3)}-C^{(4)}}$	146.8(9)	$\mathrm{C^{(1)}-C^{(3)}-C^{(5)}}$	108.0(7)
$\mathrm{C^{(3)}-C^{(5)}}$	149.9(10)	$\mathrm{C^{(2)}-C^{(3)}-C^{(5)}}$	109.2(6)
		$\mathrm{C^{(4)}-C^{(3)}-C^{(5)}}$	106.8(6)
		$\mathrm{C^{(1)}-C^{(3)}-C^{(4)}}$	110.9(6)

The distances $\mathrm{N^{(1)}-H}$ and $\mathrm{N^{(2)}-H}$ have been fixed to 89 pm; the distances $\mathrm{C^{(1)}-H}$ and $\mathrm{C^{(2)}-H}$ to 97 pm; the distances $\mathrm{C^{(4)}-H}$ and $\mathrm{C^{(5)}-H}$ to 96 pm. The angles $\mathrm{C^{(1)}-N^{(1)}-H}$ and $\mathrm{C^{(2)}-N^{(2)}-H}$ have been fixed to 109.5(4)°; $\angle(\mathrm{N^{(1)}-C^{(1)}-H}) = 108.5°$, $\angle(\mathrm{N^{(2)}-C^{(2)}-H}) = 109.2°$. The angles $\mathrm{H-N-H}$ are fixed to 109.5° as fixed $\angle(\mathrm{C^{(3)}-C^{(1)}-H}) = 108.5(4)°$, $\angle(\mathrm{C^{(3)}-C^{(2)}-H}) = 109.2(4)°$, $\angle(\mathrm{C^{(3)}-C^{(4)}-H}) = 109.5°$, $\angle(\mathrm{C^{(3)}-C^{(5)}-H}) = 109.5°$, $\angle(\mathrm{H-C^{(1)}-H}) = 107.5°$, $\angle(\mathrm{H-C^{(2)}-H}) = 107.9°$, $\angle(\mathrm{H-C^{(4)}-H}) = 109.5°$, and $\angle(\mathrm{H-C^{(5)}-H}) = 109.5°$.

Compound (**2**)

Connection	d/pm	Connection	Angle/°
$\mathrm{N^{(1)}-C^{(1)}}$	160.0(10)	$\mathrm{H^{(N1,1)}-N^{(1)}-H^{(N1,2)}}$	109.5
$\mathrm{N^{(1)}-C^{(2)}}$	159.5(25)	$\mathrm{H^{(N1,1)}-N^{(1)}-C^{(1)}}$	115.0(9)
$\mathrm{N^{(2)}-C^{(3)}}$	148.5(21)	$\mathrm{H^{(N1,2)}-N^{(1)}-C^{(1)}}$	101.0(13)
$\mathrm{N^{(2)}-C^{(4)}}$	156.1(26)	$\mathrm{C^{(1)}-N^{(1)}-C^{(2)}}$	119.3(21)
		$\mathrm{H^{(N1,1)}-N^{(1)}-C^{(2)}}$	104.8(17)
		$\mathrm{H^{(N1,2)}-N^{(1)}-C^{(2)}}$	106.6(16)
		$\mathrm{C^{(3)}-N^{(2)}-C^{(4)}}$	110.9(20)
		$\mathrm{H^{(N2,1)}-N^{(2)}-C^{(3)}}$	111.4(15)
		$\mathrm{H^{(N2,2)}-N^{(2)}-C^{(3)}}$	108.1(15)
		$\mathrm{H^{(N2,1)}-N^{(2)}-H^{(N2,2)}}$	109.5
		$\mathrm{H^{(N2,1)}-N^{(2)}-C^{(4)}}$	110.3(18)
		$\mathrm{H^{(N2,2)}-N^{(2)}-C^{(4)}}$	106.6(18)

The distances $\mathrm{N^{(1)}-H^{(N1,1)}}$, $\mathrm{N^{(1)}-H^{(N1,2)}}$, $\mathrm{N^{(2)}-H^{(N2,1)}}$, $\mathrm{N^{(2)}-H^{(N2,2)}}$ have been fixed to 108 pm. Also the distances $\mathrm{C^{(1)}-H^{(C1,1,2,3)}}$, $\mathrm{C^{(2)}-H^{(C2,1,2,3)}}$, $\mathrm{C^{(3)}-H^{(C3,1,2,3)}}$, $\mathrm{C^{(4)}-H^{(C4,1,2,3)}}$ have been fixed to 108 pm. The angles $\mathrm{H^{(C1,1,2,3)}-C^{(1)}-H^{(C1,1,2,3)}}$, $\mathrm{H^{(C2,1,2,3)}-C^{(2)}-H^{(C2,1,2,3)}}$, $\mathrm{H^{(C3,1,2,3)}-C^{(3)}-H^{(C3,1,2,3)}}$, and $\mathrm{H^{(C4,1,2,3)}-C^{(4)}-H^{(C4,1,2,3)}}$ have been fixed to 109.5°.

$[(CH_3)_2NH_2]_2ZnBr_4$ (**2**)

(**2**) crystallizes monoclinic, $P2_1/c$, $Z = 4$ and the crystal structure of (**2**) is isostructural with the room temperature phase of $[(CH_3)_2NH_2]_2CdBr_4$ [9]. The experimental conditions for the structure determination and crystallographic data are given in Table 1; there are 2 cations in the asymmetric unit of the structure. In Fig. 3, the formula unit is shown with the numbering of the atoms used in this paper and with the thermal ellipsoids of the atoms. In Fig. 4, the projection of the unit cell of (**2**) along [100] onto the *bc* plane is presented. There is little deviation of the $[ZnBr_4]^{2-}$ tetrahedra from regularity. For $d(\mathrm{Zn-Br})$ we find $238.5 \le d/\mathrm{pm} \le 243.4$, the range of the angles $\angle(\mathrm{Br-Zn-Br})$ found is from 105.2 to 111.4°. As far as the cations are concerned, there is considerable differences for cation 1 ($\mathrm{N^{(1)}}$) and cation 2 ($\mathrm{N^{(2)}}$), as is seen in Table 3, the distances $d(\mathrm{N-C})$ for cation 1 being longer, and the angle $\angle(\mathrm{C-N-C})$ being larger than those of cation 2. Each of the two hydrogen atoms bound to the N atom in both cations forms the hydrogen bond with the $[ZnBr_4]^{2-}$ tetrahedron, as listed in Table 4. $\mathrm{Br^{(1)}}$ accepts two bonds, $\mathrm{N^{(1)}-H^{(N1,2)}\cdots Br^{(1')}}$ and $\mathrm{N^{(2)}-H^{(N2,2)}\cdots Br^{(1)}}$; $\mathrm{Br^{(2)}}$ and $\mathrm{Br^{(4)}}$ accept one hydrogen bond each, $\mathrm{N^{(1)}-H^{(N1,1)}\cdots Br^{(2)}}$ and $\mathrm{N^{(2)}-H^{(N2,1)}\cdots Br^{(4')}}$. The bromine atom $\mathrm{Br^{(3)}}$ is not involved in an $\mathrm{N-H\cdots Br}$ bond. This corresponds with the distances $d(\mathrm{Zn-Br})$, where $d(\mathrm{Zn-Br^{(1)}})$ is the longest one in the tetrahedron, $d(\mathrm{Zn-Br^{(3)}})$ the shortest one. However, the differences in $d(\mathrm{Zn-Br})$ are too small to be taken into consideration with respect to the hydrogen bonds. By the hydrogen bonds, $\mathrm{N^{(1)}}$ forms the tetrahedra which are loosely connected into chains along [001], and the chains are connected by bonds $\mathrm{N^{(2)}-H\cdots Br}$ along [010].

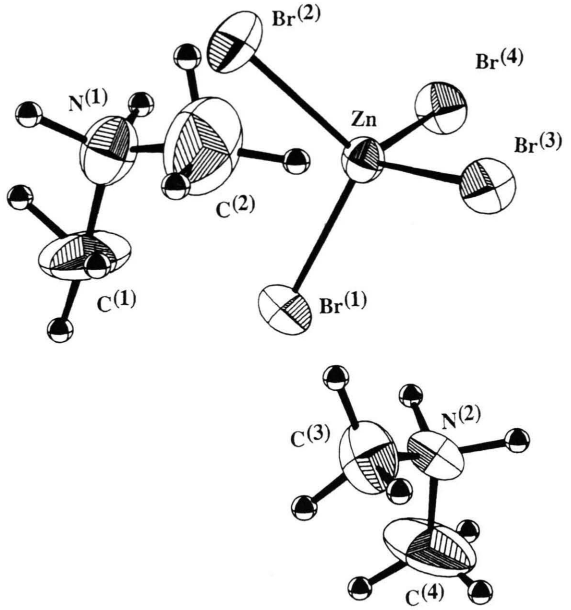

Fig. 3. Formula unit of dimethylammonium tetrabromozincate(II) (**2**) with the numbering of the atoms used in this paper and the thermal ellipsoids (50% of electron density).

^{79,81}*Br Nuclear Quadrupole Resonance:* $[H_3NCH_2C(CH_2)_2CH_2NH_3]CdBr_4 \cdot H_2O$ (**1**)

Four ^{81}Br NQR lines were observed for (**1**) with equal intensity, throughout the temperature range $77 \le T/\mathrm{K} \le 333$. No sign of a phase transition in this range can be deduced from the temperature-frequency curves as shown in Figure 5. Four NQR lines disappeared above 335 K. This is due to the dehydration. DTA and TG experiments showed that the dehydration started at 339 K in a closed condition and at 323 K in an open condition. The loss of weight observed corresponds to one molecule of H_2O.

^{81}Br NQR frequencies at selected temperature are found in Table 5. As common practice, the curves $\nu(^{81}\mathrm{Br}) = f(T)$ have been parameterized on the basis of the polynomial,

$$\nu = \sum_j a_j \cdot T^j \, (-1 \le j \le 2), \qquad (1)$$

and the coefficients a_j for (**1**) are found in Table 6, where those for compounds (**2**) and (**3**) are also given. The intensity ratio of four lines is in accordance with

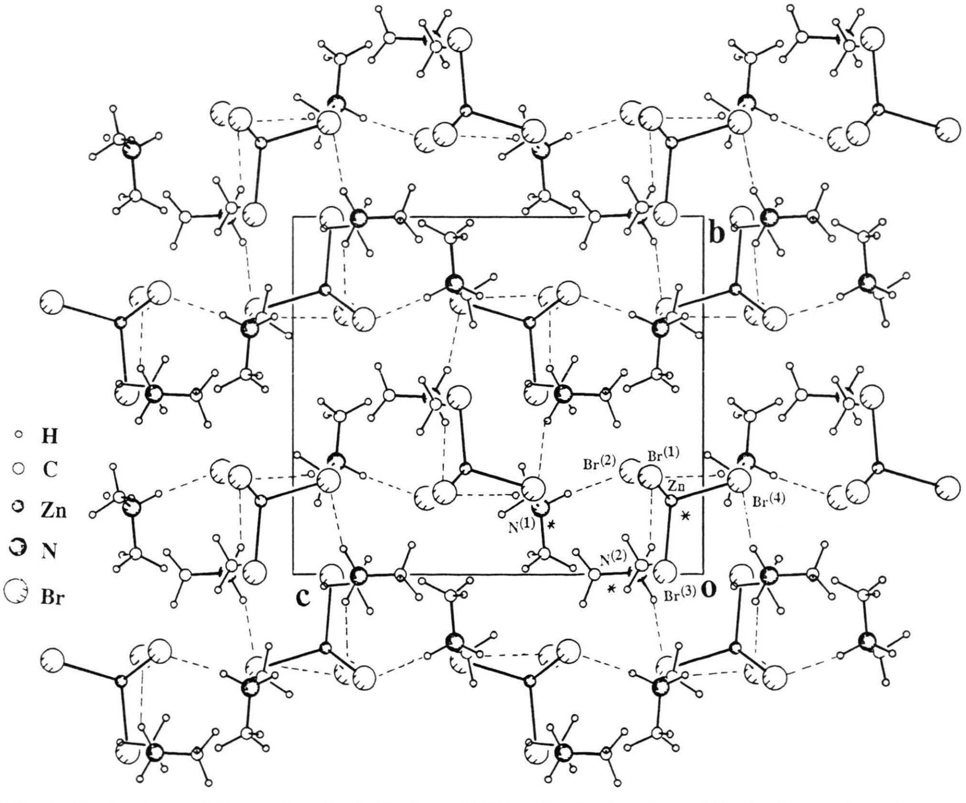

Fig. 4. Projections of the unit cell of (**2**) along [100] onto the *bc* plane. The hydrogen bonds are marked by dashed lines. The formula unit for which the coordinates of the atoms are given in Table 2 are marked by *.

Table 4. Intermolecular distances (in pm), angles (in degrees) and the hydrogen bond system in (**1**) and (2).

Compound (**1**)

Distorted tetrahedron $(\mathrm{Br}\cdots)_2\cdots\mathrm{H_2O}\cdots(\cdots\mathrm{HN})_2$

Connection	*d*/pm	Connection	Angle/°
$\mathrm{O^{(H_2O)}\cdots Br^{(2)}\_\$1}$	350.7(6)	$\mathrm{Br^{(2)}-O^{(H_2O)}-Br^{(4)}}$	68.4
$\mathrm{O^{(H_2O)}\cdots Br^{(4)}\_\$2}$	347.6(6)	$\mathrm{N^{(1)}-O^{(H_2O)}-N^{(2)}\_\$1}$	104.1
$\mathrm{O^{(H_2O)}\cdots N^{(1)}}$	292.1(9)	$\mathrm{Br^{(2)}-O^{(H_2O)}-N^{(1)}}$	88.35
$\mathrm{O^{(H_2O)}\cdots N^{(2)}\_\$1}$	281.0(9)	$\mathrm{Br^{(2)}-O^{(H_2O)}-N^{(2)}\_\$1}$	94.54
		$\mathrm{Br^{(4)}-O^{(H_2O)}-N^{(1)}}$	119.99
		$\mathrm{Br^{(4)}-O^{(H_2O)}-N^{(2)}\_\$1}$	131.13
Hydrogen bond			
$\mathrm{O^{(H_2O)}\cdots N^{(1)}}$	292.1(9)	$\mathrm{N^{(1)}-H^{(N1,2)}-Br^{(1)}}$	161.8
$\mathrm{O^{(H_2O)}\cdots H^{(N1,1)}}$	207	$\mathrm{N^{(1)}-H^{(N1,3)}-Br^{(3)}}$	137.2
$\mathrm{O^{(H_2O)}\cdots N^{(2)}\_\$1}$	281.0(9)	$\mathrm{N^{(1)}-H^{(N1,1)}-O^{(H_2O)}}$	161.0
$\mathrm{O^{(H_2O)}\cdots H^{(H2,2)}\_\$1}$	211	$\mathrm{N^{(2)}-H^{(N2,1)}-Br^{(2)}}$	147.0
$\mathrm{N^{(1)}\cdots Br^{(1)}\_\$3}$	345.4(6)	$\mathrm{N^{(2)}-H^{(N2,3)}-Br^{(3)}}$	136.13
$\mathrm{H^{(N1,2)}\cdots Br^{(1)}\_\$3}$	260	$\mathrm{N^{(2)}-H^{(N2,2)}-O^{(H_2O)}}$	134.69
$\mathrm{N^{(1)}\cdots Br^{(3)}\_\$3}$	356.5(7)		
$\mathrm{H^{(N1,3)}\cdots Br^{(3)}\_\$3}$	286		
$\mathrm{N^{(2)}\cdots Br^{(2)}\_\$4}$	329.6(6)		
$\mathrm{H^{(N2,1)}\cdots Br^{(2)}\_\$4}$	251		
$\mathrm{N^{(2)}\cdots Br^{(3)}}$	340.5(6)		
$\mathrm{H^{(N2,3)}\cdots Br^{(3)}}$	271		

Symmetry code: \$1: $-x-1$, $y-0.5$, z; \$2: $-x-1$, $-y$, $z-0.5$; \$3: x, $0.5-y$, $z-0.5$; \$4: $x-1$, y, z.

Compound (**2**)

Connection	*d*/pm	Connection	Angle/°
$\mathrm{N^{(1)}\cdots Br^{(2)}}$	336.8(10)	$\mathrm{N^{(1)}-H^{(N1,1)}-Br^{(2)}}$	167.7
$\mathrm{H^{(N1,1)}\cdots Br^{(2)}}$	231		
$\mathrm{N^{(1)}\cdots Br^{(1)}\_\$1}$	345.5(10)	$\mathrm{N^{(1)}-H^{(N1,2)}-Br^{(1)}\_\$1}$	151.9
$\mathrm{H^{(N1,2)}\cdots Br^{(1)}\_\$1}$	247		
$\mathrm{N^{(2)}\cdots Br^{(4)}\_\$2}$	333.5(8)	$\mathrm{N^{(2)}-H^{(N2,1)}-Br^{(4)}\_\$2}$	153.5
$\mathrm{H^{(N2,1)}\cdots Br^{(4)}\_\$2}$	233		
$\mathrm{N^{(2)}\cdots Br^{(1)}}$	342.3(8)	$\mathrm{N^{(2)}-H^{(N2,2)}-Br^{(1)}}$	151.2
$\mathrm{H^{(N2,2)}\cdots Br^{(1)}}$	244		

Symmetry code: \$1: x, $0.5-y$, $0.5+z$; \$2: $2-x$, $-y$, $-z$.

Table 5. ^{81}Br NQR frequencies, given in MHz, at selected temperatures, the signal to noise ratio, S/N in parenthese. The error in frequencies is ±15 kHz.

Compound	ν_i	*T*/K	ν/MHz	*T*/K	ν/MHz
(**1**)	ν_1	77	68.403(15)	303	64.278(13)
	ν_2	77	65.296(13)	303	62.663(11)
	ν_3	77	56.525(13)	303	54.660(11)
	ν_4	77	43.211(10)	303	45.422(10)
(**2**)	ν_1	77	66.848(40)	300	64.784(25)
	ν_2	77	63.152(35)	300	61.883(25)
	ν_3	77	57.498(37)	300	55.890(27)
	ν_4	77	49.416(38)	300	50.224(26)
(**3**)	ν_1	77	68.606(47)	310	67.272(13)
	ν_2	77	65.806(50)	310	63.296(15)
	ν_3	77	58.096(48)	310	57.369(17)
	ν_4	77	55.757(43)	310	53.393(17)

Table 6. Power series development of $\nu(^{81}\mathrm{Br}) = f(T)$ according to $\nu = \sum_j a_j \cdot T^j$. *Z* is the number of measurements taken σ is the mean deviation.

Compound	ν_i	*Z*	$\sigma \cdot 10^3$ / MHz	a_{-1} / MHz·K	a_0 / MHz	$a_1 \cdot 10^3$ / MHz·K^{-1}	$a_2 \cdot 10^6$ / MHz·K^{-2}
(**1**)	ν_1	28	33	−1.328	69.548	−12.702	−15.437
	ν_2	23	25	−1.727	66.176	−9.762	−6.138
	ν_3	28	29	1.186	57.452	−12.963	11.297
	ν_4	24	44	1.834	42.291	10.192	0.161
(**2**)	ν_1	84	26	−3.154	67.030	0.574	−27.635
	ν_2	83	22	44.195	62.381	5.031	−24.171
	ν_3	77	29	22.707	57.444	−6.928	1.173
	ν_4	69	27	−59.615	50.008	1.466	−0.575
(**3**)	ν_1	15	44	−2.970	68.649	0.371	−15.128
	ν_2	15	29	0.224	66.197	−4.242	−16.365
	ν_3	15	24	0.099	58.142	−0.665	−6.175
	ν_4	15	43	0.158	56.667	−10.904	1.404

the result of the crystal structure determination; there are four isolated $[\mathrm{CdBr_4}]^{2-}$ tetrahedra in the unit cell, and four bromine atoms of each tetrahedron are crystallographically inequivalent on the position 4a. The ^{81}Br NQR frequencies are spread over $45.42 \le \nu(^{81}\mathrm{Br})/\mathrm{MHz} \le 64.28$ at 303 K. On the other hand, the spread of Cd−Br distances, $255.2 \le d(\mathrm{Cd{-}Br})/\mathrm{pm} \le 264.6$ is not so large. However, $d(\mathrm{Cd{-}Br^{(3)}}) = 264.6$ pm is considerably longer than the others. We can assign the ν_4 line to the Br$^{(3)}$ atom according to the theory of the electric field gradients which results in the relation $\nu = f(1/d^3)$. In such a simple approach, the shortest Cd−Br distance would correspond to the highest ^{81}Br NQR frequency, the longest distance to the lowest frequency line. The Br$^{(3)}$ atom in the crystal has two hydrogen bonds with H$^{(N1,3)}$ and H$^{(N2,3)}$, as shown in Table 4. These two N−H···Br distances, $d(\mathrm{N^{(1)}\cdots Br^{(3)}}) = 356.5$ and $d(\mathrm{N^{(2)}\cdots Br^{(3)}}) = 340.5$ pm, are within the range in which hydrogen bonds are expected since the ionic radii of $\mathrm{NH_4^+}$ and $\mathrm{Br^-}$ are 160 and 190 pm, respectively [8]. The ν_4 line shows a positive temperature dependence in contrast to the normal temperature dependence expected from the Bayer theory [10]; the NQR frequency decreases with increasing temperature. We consider that this positive temperature dependence is due to the hydrogen bonds, as observed in several other cases [11]. The hydrogen bond will lower the Br NQR frequency be-

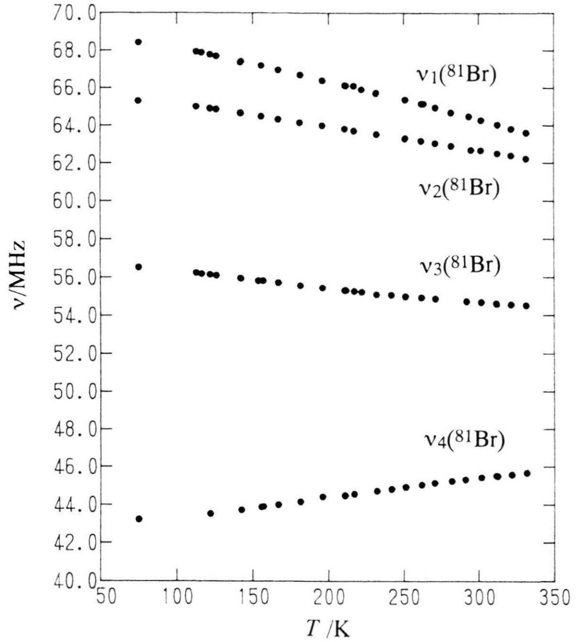

Fig. 5. ^{81}Br NQR frequencies (ν_1, ν_2, ν_3, ν_4) as a function of temperature for 2,2-dimethyl-1,3-propanediammonium tetrabromocadmate(II) monohydrate (**1**).

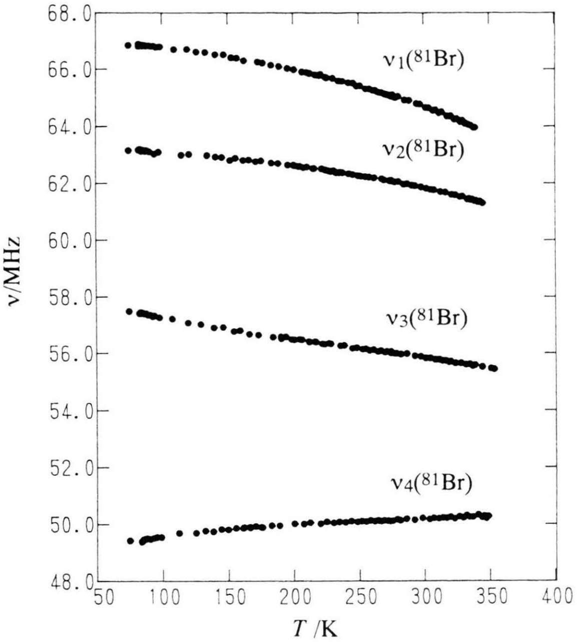

Fig. 6. ^{81}Br NQR frequencies (ν_1, ν_2, ν_3, ν_4) as a function of temperature for dimethylammonium tetrabromozincate(II) (**2**).

cause of the opposite contribution of the electric field gradient (EFG) at the Br atom created by the H · · · Br hydrogen bond and created by the Cd–Br bond. Some molecular motion will be activated with increasing temperature and then the breakage of the hydrogen bond will lead to the increase in the Br NQR frequency.

$[(CH_3)_2NH_2]_2ZnBr_4$ (2)

Four ^{81}Br NQR lines with equal intensity were observed for compound (**2**) at temperatures between 77 and 350 K, as is shown in Figure 6. ^{81}Br NQR frequencies at selected temperatures are found in Table 5, and the coefficients a_j of (1) are found in Table 6. Four NQR lines disappeared at temperatures above 355 K. DTA experiments did not show any heat anomaly either around 355 K or up to the melting point, 398 K. No evidence of a phase transition was seen in this temperature range. We are also interested in the phase transitions that occurred in a group of crystals expressed by R_2MX_4, where R, M, X denoted a monovalent cation, a divalent metal atom, and halogen, respectively. The chloride analogue of the compound (**2**) shows a 1st-order phase transition at ca. 270 K [12]. The structure of the chloride is similar to (**2**); space group $P2_1/n$, $a = 1329.7$, $b = 862.0$, $c = 1149.4$ pm, $\gamma = 89.8°$ [13], but on the basis of the number of NQR lines observed. Yamamoto et al. considered that the structure of the chloride is similar to Cs_2CdBr_4 [14], in which the tetrahedral $[CdBr_4]^{2-}$ ion has mirror symmetry. A group of compounds having R_2MX_4 formula, $[(CH_3)_4N]_2HgBr_4$ [15], and R_2ZnBr_4 (R = alkylammonium ion) [3], show phase transitions which have displacive character connected with the rotary mode of both the tetrahedral $[MX_4]^{2-}$ ions and cations, and order-disorder character of anions and/or cations, respectively.

All NQR lines disappeared at temperatures around 355 K. This is due to the reorientational motion of $[ZnBr_4]^{2-}$ tetrahedra and/or the thermal motion of $[(CH_3)_2NH_2]^+$ cations. The displacement parameters are a little high for the Br atoms of the $[ZnBr_4]^{2-}$ ion and considerably high for carbon and nitrogen atoms of cations, as shown in Table 2. The $[ZnBr_4]^{2-}$ tetrahedra are nearly regular, as mentioned above, and they are connected with the cations by N–H · · · Br hydrogen bonds. Therefore, the reorientational motion of $[ZnBr_4]^{2-}$ and/or the thermal motion of cations largely affect the EFG's at bromine sites. Although we can not assign NQR lines to the bromine atoms in the crystal due to identical Zn – Br distances, the positive temperature dependence of the ν_4 line is considered to be due to the hydrogen bond.

$[(CH_3)_2NH_2]_2CdBr_4$ (3)

Four ^{81}Br NQR lines were observed at temperatures between 77 and 350 K, as shown in Figure 7. ^{81}Br NQR frequencies at selected temperature are found in Table 5, and the coefficients a_j of (1) are found in Table 6. All NQR lines disappeared above 350 K. On the DTA curve there was neither heat anomaly around 350 K nor up to the melting point, 377 K. A first-order phase transition at 367 K was reported by Waskowska, using X-ray diffraction [9]. The hydrogen bond system of $[(CH_3)_2NH_2]_2ZnBr_4$ **(2)** is similar to the compound **(3)**. The cause of the disappearance of NQR lines in the compound **(3)** might be similar to the compound **(2)**, though the positive temperature dependence of NQR lines was not observed. The compound **(3)** has no layered structure like $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$ [1]. The restriction on the cross sectional area of the alkyl group is the same as in $[NH_3(CH_2)_3NH_3]CdBr_4$. In addition, the number of H atoms connected to the N atom is two in **(3)**. Therefore, the hydrogen bond scheme for **(3)** must be different from those of the two layered structures, $[H_3N(CH_2)_3NH_3]CdBr_4$ and $[n\text{-}H_3C(CH_2)_2NH_3]_2CdBr_4$, in which three H atoms per one N atom can be used to form three hydrogen bonds.

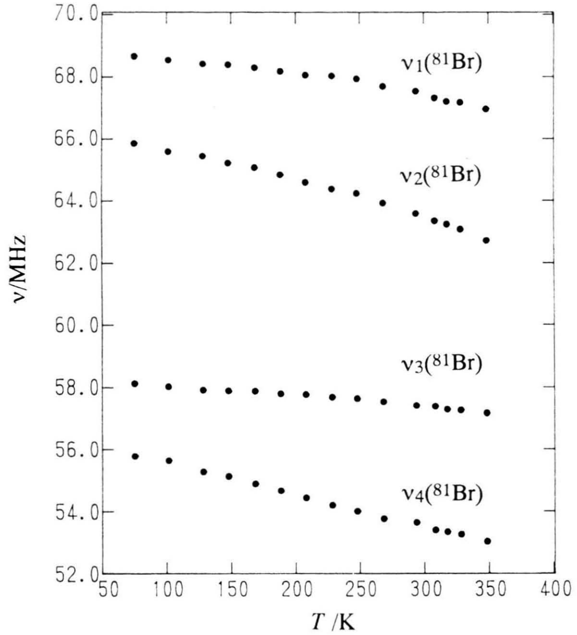

Fig. 7. ^{81}Br NQR frequencies (ν_1, ν_2, ν_3, ν_4) as functions of temperature for dimethylammonium tetrabromocadmate(II) **(3)**.

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[7] T. Okajima, to be published. *Ab initio* calculations were performed with the Gaussian 94 program system (i). Geometry optimizations were performed with the RHF/3-21G basis set (ii). Single-point energy calculations were then carried out on the RHF/3-21G optimized geometries using the 6-31G* basis set (iii) and second-order Moller Plesset (MP2) perturbation theory (iv).
The conformational profile calculated at the 3-21G level for the dication of **(1)** exhibits three minima **(a – c)**. The anti-anti conformation **(a)** is most stable. The anti-gauche **(b)** and gauche-gauche **(c)** conformers are less stable than the anti-anti **(a)** by 3.1 and 6.1 kcal/mol, respectively. This increase in conformer energy difference is consistent with the increase of gauche

arrangement of the C–N bond with respect to the C–C(–N) bond. It can be considered that each gauche (NH$_3$)C–C–C–N unit is destabilizing by about 3 kcal/mol due to electrostatic reason.
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