Tetraguanidium Hexabromocadmate, $[C(NH_2)_3]_4[CdBr_6]$. Crystal Structure and Bromine Nuclear Quadrupole Resonance *

V. G. Krishnan **, Shi-qi Dou, and Alarich Weiss
Institut für Physikalische Chemie, Technische Hochschule, D-64287 Darmstadt, Germany

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The ^{79,81}Br NQR spectra of tetraguanidinium hexabromocadmate, $[C(NH_2)_3]_4[CdBr_6]$ have been studied as a function of temperature from 77 K to 390 K and the crystal structure of the compound was determined at room temperature. The title compound crystallizes monoclinic, $P2_1/c$, with four formula units in the unit cell, $a = 839.2(3)$ pm, $b = 1895.8(6)$ pm, $c = 1527.4(5)$ pm, $\beta = 108.14(1)°$. The anion $[CdBr_6]^{4\ominus}$ is an isolated octahedron, with bond lengths $275 \leq d(Cd-Br)/pm \leq 281$, and bond angles $88 \leq (Br-Cd-Br)/° \leq 95$, slightly distorted by hydrogen bonds $N-H \cdots Br$. The ^{81}Br NQR sextet, in dependence from temperature, shows positive and negative temperature coefficients. At 77 K the ^{81}Br NQR frequencies have been found between 42.42 MHz and 31.99 MHz; the ^{79}Br NQR at the frequencies expected from the nuclear quadrupole moment ratio $Q(^{79}Br)/Q(^{81}Br)$. Relations between the ^{81}Br NQR spectrum, the crystal structure, and the hydrogen bonds are discussed.

Introduction

Halogeno complexes of Cd^{II} have the tendency to form Perovskite type structures with a variety of condensed $(CdBr_3)^-$ anions if the composition of the salt is $A^I CdBr_3$. Another quite stable and common composition is $A^I_2 CdBr_4$ with more or less distorted tetrahedral anions $[CdBr_4]^{2\ominus}$. Recently we have investigated a number of bromocadmate complexes by X-ray diffraction and bromine nuclear quadrupole resonance, NQR, and found several rather unusual types of polymer anions [1–3]. Besides the formation of polymer anions, Cd^{II} may exist in the solid state with Br ligands as isolated octahedral anion $[CdBr_6]^{4\ominus}$ and we have studied the bromine (^{79,81}Br) NQR in some complexes $A_4[CdBr_6]$ [4]. The crystal structures of these complexes are of high symmetry and if A is a simple cation such as an alkali metal ion, the octahedron $[CdBr_6]$ deviates only little from regularity. In the synthesis of Cd–Br-complexes with several organic cations, we were unable to produce an isolated octahedron $[CdBr_6]$, but recently this became possible with A = guanidinium ion, $(C(NH_2)_3)^{\oplus}$, and here we report the crystal structure and on bromine NQR of the complex salt $[C(NH_2)_3]_4[CdBr_6]$.

Experimental

Preparation

The compound was prepared from aqueous solutions of guanidinium carbonate, $CdBr_2$, and HBr. Colorless crystals were grown by concentrating the combined stoichiometric solutions (pH = 3) by evaporating the solvent at room temperature. The compound was dried over $CaCl_2$ in a dessicator. In Table 1 we give the results of the chemical analysis.

X-ray diffraction

A small crystal was selected for the diffraction experiment. X-ray diffraction intensities were collected on a 4- circle goniometer (see Table 2). The intensities were corrected for absorption and Lorentz-polarisation factor. By use of direct methods [5] and least squares refinement [6] the structure was determined. Due to the heavy atoms Cd and Br not all positions of the hydrogen atoms could be located by Fourier synthesis.

Nuclear Quadrupole Resonance, NQR

The bromine NQR spectra of the title compound were observed with CW methods on polycrystalline samples, using a superregenerative NQR spectrometer. To determine the NQR frequencies as function of temperature T, for $T = 77$ K the sample was immersed in liquid nitrogen and for temperatures between 77 K and room temperature (and above) the

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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, Petersenstr. 20, D-64287 Darmstadt, Germany.

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Table 1. Chemical analysis of the title compound $[C(NH_2)_3]_4[CdBr_6]$, $C_4H_{24}Br_6CdN_{12}$, $M = 832.2$. The data are given in weight % (obs/calc).

C:	5.69/ 5.77
H:	2.90/ 2.91
N:	20.50/20.20
Cd:	13.93/13.51
Br:	56.9 /57.62

Table 2. Experimental conditions for the crystal structure determination and crystallographic data of $[C(NH_2)_3]_4[CdBr_6]$. Diffractometer: Stoe Stadi 4; wavelength; 71.069 pm (MoKα); monochromator: Graphite (002); scan: $2\vartheta/\omega$; $M = 832.2$.

Formula	$C_4H_{24}Br_6CdN_{12}$
Crystal size (Habitus)	$(0.25 \times 0.4 \times 1.9)$ mm^3, colorless prism
Temperature/K	293
Absorption coefficient (μ/m^{-1})	11240
$(\sin\vartheta/\lambda)_{max}$/pm	0.00539
Reflexions	
Measured	5066
Symmetry independent	3010
Considered, $(F > 2\sigma(F))$	2555
Number of free parameters	245
F (000)	1560
$R(F)$	0.052
R_W (F)	0.039
R_M	0.035
Lattice constants	
a/pm	839.2(3)
b/pm	1895.8(6)
c/pm	1527.4(5)
β/°	108.14(1)
$V_{U\,Cell} \cdot 10^{-6}/(\mathrm{pm})^3$	2309.25(218)
Space group	$C_{2h}^5 - P2_1/c$
Formula units per V_E	$Z = 4$
$\varrho_{calc}/(\mathrm{Mg \cdot m^{-3}})$	2.393(2)
Point positions	All atoms in 4g: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$.

sample was in a stream of temperature and flow regulated nitrogen gas. T was measured via copper-constantan thermocouples to ±0.5°. The frequencies were found by counter technique to ±5 kHz, the accuracy limited determined by the width of the resonance lines.

Table 3. Positional and thermal parameters of the atoms in the crystal structure of $[C(NH_2)_3]_4[CdBr_6]$. The equivalent temperature factor U_{equ} is given in Å$^2 \cdot 1000$. Standard deviations are given in ( ).

Atom	x/a	y/b	z/c	U_{eq}
Cd	0.2135(1)	0.6170(1)	0.7640(1)	54(1)
$Br^{(1)}$	0.1670(1)	0.7556(1)	0.6948(1)	52(1)
$Br^{(2)}$	0.2696(1)	0.4779(1)	0.8253(1)	58(1)
$Br^{(3)}$	0.3591(1)	0.5858(1)	0.6274(1)	57(1)
$Br^{(4)}$	0.0696(2)	0.6578(1)	0.8978(1)	67(1)
$Br^{(5)}$	−0.0982(1)	0.5798(1)	0.6500(1)	59(1)
$Br^{(6)}$	0.5241(2)	0.6536(1)	0.8835(1)	68(1)
$C^{(1)}$	0.3690(15)	0.2598(6)	0.8679(9)	63(1)
$C^{(2)}$	0.2043(16)	0.5265(6)	1.1100(8)	62(9)
$C^{(3)}$	0.0405(14)	0.3670(6)	0.5947(8)	56(8)
$C^{(4)}$	0.4555(15)	0.6172(7)	0.3857(8)	65(9)
$N^{(C1,1)}$	0.2532(12)	0.2781(6)	0.9065(7)	74(8)
$N^{(C1,2)}$	0.3307(16)	0.2243(6)	0.7894(8)	85(8)
$N^{(C1,3)}$	0.5210(17)	0.2846(6)	0.9034(7)	72(7)
$N^{(C2,1)}$	0.2595(16)	0.4844(7)	1.1826(9)	86(10)
$N^{(C2,2)}$	0.0564(12)	0.5573(6)	1.0895(8)	74(8)
$N^{(C2,3)}$	0.3044(15)	0.5392(6)	1.0612(7)	78(8)
$N^{(C3,1)}$	0.0887(14)	0.4305(5)	0.5743(6)	69(7)
$N^{(C3,2)}$	0.0365(14)	0.3534(6)	0.6769(6)	80(8)
$N^{(C3,3)}$	−0.0033(14)	0.3194(5)	0.5281(6)	79(7)
$N^{(C4,1)}$	0.4029(15)	0.6712(6)	0.4223(7)	80(8)
$N^{(C4,2)}$	0.4963(15)	0.6227(5)	0.3113(6)	93(9)
$N^{(C4,3)}$	0.4676(27)	0.5590(6)	0.4266(9)	216(18)
$H^{1\,(N,C1,1)}$	0.2849(129)	0.3137(55)	0.9594(65)	100
$H^{2\,(N,C1,1)}$	0.1657(133)	0.2633(60)	0.8636(70)	100
$H^{1\,(N,C1,2)}$	0.2149(141)	0.2249(67)	0.7704(86)	100
$H^{2\,(N,C1,2)}$	0.3825(157)	0.1884(60)	0.7874(91)	100
$H^{1\,(N,C1,3)}$	0.6104(86)	0.2682(55)	0.8695(53)	100
$H^{2\,(N,C1,3)}$	0.5749(105)	0.2787(54)	0.9771(8)	100
$H^{1\,(N,C2,1)}$	0.3373(175)	0.4610(71)	1.1895(106)	100
$H^{2\,(N,C2,1)}$	0.2023(144)	0.4783(61)	1.2256(79)	100
$H^{1\,(N,C2,2)}$	−0.0126(108)	0.5496(53)	1.1384(49)	100
$H^{2\,(N,C2,2)}$	−0.0111(89)	0.5939(47)	1.0354(48)	100
$H^{1\,(N,C2,3)}$	0.3566(136)	0.4972(48)	1.0758(73)	100
$H^{2\,(N,C2,3)}$	0.2318(111)	0.5569(48)	0.9927(35)	100
$H^{1\,(N,C3,1)}$	0.1167(145)	0.4315(57)	0.5171(73)	100
$H^{2\,(N,C3,1)}$	0.0810(145)	0.4804(56)	0.5942(76)	100
$H^{1\,(N,C3,2)}$	−0.0357(111)	0.3158(46)	0.7022(51)	100
$H^{2\,(N,C3,2)}$	0.1029(113)	0.3887(45)	0.7317(39)	100
$H^{1\,(N,C3,3)}$	−0.0607(119)	0.3420(48)	0.4607(29)	100
$H^{2\,(N,C3,3)}$	0.0572(130)	0.2682(33)	0.5386(39)	100
$H^{1\,(N,C4,1)}$	0.4427(131)	0.6646(56)	0.4962(12)	100
$H^{2\,(N,C4,1)}$	0.3424(14)	0.7213(6)	0.4004(7)	100
$H^{1\,(N,C4,2)}$	0.5069(15)	0.6668(5)	0.2687(6)	100
$H^{2\,(N,C4,2)}$	0.4772(145)	0.5744(7)	0.2714(28)	100
$H^{1\,(N,C4,3)}$	0.4670(134)	0.5399(43)	0.4934(37)	100
$H^{2\,(N,C4,3)}$	0.4429(136)	0.5158(33)	0.3778(48)	100

Results

Crystal Structure

Tetraguanidinium hexabromocadmate(II), $[C(NH_2)_3]_4[CdBr_6]$, crystallizes monoclinic, space group $C_{2h}^5 - P2_1/c$, with $Z = 4$ $[C(NH_2)_3]_4[CdBr_6]$ in the elementary cell. The lattice constants are $a = 839.2(3)$ pm, $b = 1895.8(6)$ pm, $c = 1527.4(5)$ pm, $\beta = 108.14(1)°$. There is one hexabromocadmate ion in the asymmetric unit of the cell and consequently four cations $(C(NH_2)_3)^{\oplus}$. In Table 2 the experimental conditions for the structure determination are listed together with some crystallographic data. Table 3 re-

Table 4. Intramolecular (intraionic) distances *d*/pm in the unit cell of tetraguanidinium hexabromocadmate, $[C(NH_2)_3]_4[CdBr_6]$.

Connection	*d*/pm	Connection	*d*/pm
$\mathrm{Cd-Br^{(1)}}$	281.3(1)	$\mathrm{C^{(2)}-N^{(C2,1)}}$	132.7(16)
$\mathrm{Cd-Br^{(2)}}$	278.9(2)	$\mathrm{C^{(2)}-N^{(C2,2)}}$	131.8(14)
$\mathrm{Cd-Br^{(3)}}$	279.0(1)	$\mathrm{C^{(2)}-N^{(C2,3)}}$	130.7(15)
$\mathrm{Cd-Br^{(4)}}$	278.7(1)	$\mathrm{C^{(3)}-N^{(C3,1)}}$	133.7(13)
$\mathrm{Cd-Br^{(5)}}$	274.6(1)	$\mathrm{C^{(3)}-N^{(C3,2)}}$	129.2(13)
$\mathrm{Cd-Br^{(6)}}$	276.5(1)	$\mathrm{C^{(3)}-N^{(C3,3)}}$	132.3(12)
$\mathrm{C^{(1)}-N^{(C1,1)}}$	132.9(15)	$\mathrm{C^{(4)}-N^{(C4,1)}}$	130.7(14)
$\mathrm{C^{(1)}-N^{(C1,2)}}$	132.5(15)	$\mathrm{C^{(4)}-N^{(C4,2)}}$	128.8(14)
$\mathrm{C^{(1)}-N^{(C1,3)}}$	130.8(13)	$\mathrm{C^{(4)}-N^{(C4,3)}}$	125.8(14)

Table 5. Intramolecular (intraionic) angles, in degree, in the ions $[CdBr_6]^{4\ominus}$ and $[C(NH_2)_3]^{\oplus}$; angles C–N–H are not listed.

Connection	Angle/°	Connection	Angle/°
$\mathrm{Br^{(1)}-Cd-Br^{(2)}}$	176.7(1)	$\mathrm{N^{(C1,1)}-C^{(1)}-N^{(C1,2)}}$	121.9(12)
$\mathrm{Br^{(1)}-Cd-Br^{(3)}}$	87.7(1)	$\mathrm{N^{(C1,1)}-C^{(1)}-N^{(C1,3)}}$	118.4(12)
$\mathrm{Br^{(1)}-Cd-Br^{(4)}}$	88.6(1)	$\mathrm{N^{(C1,2)}-C^{(1)}-N^{(C1,3)}}$	119.2(12)
$\mathrm{Br^{(1)}-Cd-Br^{(5)}}$	90.5(1)	$\mathrm{N^{(C2,1)}-C^{(2)}-N^{(C2,2)}}$	121.5(12)
$\mathrm{Br^{(1)}-Cd-Br^{(6)}}$	90.3(1)	$\mathrm{N^{(C2,1)}-C^{(2)}-N^{(C2,3)}}$	117.9(13)
$\mathrm{Br^{(2)}-Cd-Br^{(3)}}$	89.0(1)	$\mathrm{N^{(C2,2)}-C^{(2)}-N^{(C2,3)}}$	120.5(12)
$\mathrm{Br^{(2)}-Cd-Br^{(4)}}$	94.7(1)	$\mathrm{N^{(C3,1)}-C^{(3)}-N^{(C3,2)}}$	120.6(11)
$\mathrm{Br^{(2)}-Cd-Br^{(5)}}$	89.9(1)	$\mathrm{N^{(C3,1)}-C^{(3)}-N^{(C3,3)}}$	117.1(11)
$\mathrm{Br^{(2)}-Cd-Br^{(6)}}$	89.4(1)	$\mathrm{N^{(C3,2)}-C^{(3)}-N^{(C3,3)}}$	121.3(11)
$\mathrm{Br^{(3)}-Cd-Br^{(4)}}$	176.2(1)	$\mathrm{N^{(C4,1)}-C^{(4)}-N^{(C4,2)}}$	122.1(13)
$\mathrm{Br^{(3)}-Cd-Br^{(5)}}$	91.4(1)	$\mathrm{N^{(C4,1)}-C^{(4)}-N^{(C4,3)}}$	117.4(12)
$\mathrm{Br^{(3)}-Cd-Br^{(6)}}$	90.3(1)	$\mathrm{N^{(C4,2)}-C^{(4)}-N^{(C4,3)}}$	120.4(13)
$\mathrm{Br^{(4)}-Cd-Br^{(5)}}$	89.5(1)		
$\mathrm{Br^{(4)}-Cd-Br^{(6)}}$	88.9(1)		
$\mathrm{Br^{(5)}-Cd-Br^{(6)}}$	178.2(1)		

ports the relative coordinates of the atoms within the unit cell and the equivalent thermal parameters. For the coefficients of the matrix of the temperature factors and for F_c, F_0 see [12]. In Fig. 1 we show the projection of the unit cell of the title compound along the *a* axis onto the *bc* plane. The existence of separated octahedra $[CdBr_6]^{4\ominus}$ is pointed out clearly. The hydrogen bonds are marked in the figure by broken lines. Table 4 lists the intramolecular (intraionic) distances and in Tab. 5 we report the intramolecular (intraionic) angles. An interesting feature of the structure of the title compound are the hydrogen bonds $\mathrm{N^{(1)}-H\cdots Br^{(k)}}$ and $\mathrm{N^{(1)}-H\cdots N^{(j)}}$. In Table 6 we have listed the short bonds $\mathrm{N-H\cdots Br}$ and $\mathrm{N-H\cdots N}$ (within the sum of the van der Waals radii of Br and $-NH_2$) and the angles $\mathrm{N-H\cdots Br}$ and $\mathrm{N-H\cdots N}$.

Table 6. Hydrogen bond scheme in $[C(NH_2)_3]_4[CdBr_6]$. Given are distances $d(\mathrm{N-H\cdots Br})$, $d(\mathrm{H\cdots Br})$ and angles $\langle(\mathrm{N-H\cdots Br}$, $\langle(\mathrm{N-H\cdots N})$; *d* in pm, angles in °.

Connection	$d(\mathrm{N\cdots Br})$	Connection	$d(\mathrm{H\cdots Br})$
$\mathrm{N^{(C1,1)}\cdots Br^{(1)a}}$	340.8	$\mathrm{H^{2(N,C1,1)}\cdots Br^{(1)}}$	265.8
$\mathrm{N^{(C1,3)}\cdots Br^{(1)b}}$	344.2	$\mathrm{H^{1(N,C1,3)}\cdots Br^{(1)}}$	237.7
$\mathrm{N^{(C3,2)}\cdots Br^{(1)a}}$	350.4	$\mathrm{H^{1(N,C3,2)}\cdots Br^{(1)}}$	246.5
$\mathrm{N^{(C2,2)}\cdots Br^{(2)c}}$	344.1	$\mathrm{H^{1(N,C2,2)}\cdots Br^{(2)}}$	244.4
$\mathrm{N^{(C2,3)}\cdots Br^{(2)d}}$	346.9	$\mathrm{H^{1(N,C2,3)}\cdots Br^{(2)}}$	306.6
$\mathrm{N^{(C3,2)}\cdots Br^{(2)}}$	343.1	$\mathrm{H^{2(N,C3,2)}\cdots Br^{(2)}}$	236.9
$\mathrm{N^{(C4,3)}\cdots Br^{(3)e}}$	332.8	$\mathrm{H^{2(N,C4,3)}\cdots Br^{(3)}}$	256.1
$\mathrm{N^{(C4,3)}\cdots Br^{(3)}}$	348.9	$\mathrm{H^{1(N,C4,2)}\cdots Br^{(3)}}$	263.1
$\mathrm{N^{(C4,1)}\cdots Br^{(3)}}$	364.6	$\mathrm{H^{1(N,C4,1)}\cdots Br^{(3)}}$	275.9
$\mathrm{N^{(C2,3)}\cdots Br^{(4)}}$	347.8	$\mathrm{H^{2(N,C2,3)}\cdots Br^{(4)}}$	252.7
$\mathrm{N^{(C3,3)}\cdots Br^{(4)f}}$	337.2	$\mathrm{H^{2(N,C3,3)}\cdots Br^{(4)}}$	266.6
$\mathrm{N^{(C2,2)}\cdots Br^{(4)}}$	352.4	$\mathrm{H^{2(N,C2,2)}\cdots Br^{(4)}}$	268.8
$\mathrm{N^{(C2,1)}\cdots Br^{(5)g}}$	346.5	$\mathrm{H^{2(N,C2,1)}\cdots Br^{(5)}}$	257.3
$\mathrm{N^{(C3,1)}\cdots Br^{(5)h}}$	345.6	$\mathrm{H^{1(N,C3,1)}\cdots Br^{(5)}}$	251.7
$\mathrm{N^{(C3,1)}\cdots Br^{(5)}}$	359.8	$\mathrm{H^{2(N,C3,1)}\cdots Br^{(5)}}$	270.9
$\mathrm{N^{(C1,1)}\cdots Br^{(6)i}}$	342.4	$\mathrm{H^{1(N,C1,1)}\cdots Br^{(6)}}$	251.3
$\mathrm{N^{(C1,2)}\cdots Br^{(6)k}}$	350.2	$\mathrm{H^{2(N,C1,2)}\cdots Br^{(6)}}$	302.3
$\mathrm{N^{(C2,1)}\cdots Br^{(6)i}}$	350.9	$\mathrm{H^{1(N,C2,1)}\cdots Br^{(6)}}$	285.1
$\mathrm{N^{(C2,2)}\cdots N^{(C2,2)e}}$	338.8		
$\mathrm{N^{(C1,3)}\cdots N^{(C4,1)b}}$	332.6	$\mathrm{H^{2(N,C1,3)}\cdots N^{(C4,1)}}$	252.5
$\mathrm{N^{(C4,3)}\cdots N^{(C4,3)e}}$	309.3	$\mathrm{H^{1(N,C4,3)}\cdots N^{(C4,3)}}$	221.1

Connection	Angle/°	Connection	Angle/°
$\mathrm{N^{(C1,1)}-H^2\cdots Br^{(1)a}}$	145.9	$\mathrm{N^{(C2,1)}-H^2\cdots Br^{(5)g}}$	160.1
$\mathrm{N^{(C1,3)}-H^1\cdots Br^{(1)b}}$	168.0	$\mathrm{N^{(C3,1)}-H^1\cdots Br^{(5)h}}$	162.3
$\mathrm{N^{(C3,2)}-H^1\cdots Br^{(1)b}}$	160.8	$\mathrm{N^{(C1,1)}-H^1\cdots Br^{(6)i}}$	148.0
$\mathrm{N^{(C3,2)}-H^2\cdots Br^{(2)}}$	167.0	$\mathrm{N^{(C2,1)}-H^1\cdots Br^{(6)i}}$	145.0
$\mathrm{N^{(C2,2)}-H^1\cdots Br^{(2)c}}$	151.6	$\mathrm{N^{(C1,2)}-H^2\cdots Br^{(6)k}}$	120.1
$\mathrm{N^{(C2,3)}-H^1\cdots Br^{(2)d}}$	109.2		
$\mathrm{N^{(C4,3)}-H^1\cdots Br^{(3)}}$	136.5	$\mathrm{N^{(C1,3)}-H^2\cdots N^{(C4,1)}}$	129.7
$\mathrm{N^{(C4,3)}-H^2\cdots Br^{(3)e}}$	127.1	$\mathrm{N^{(C4,3)}-H^1\cdots N^{(C4,3)e}}$	136.9
$\mathrm{N^{(C4,1)}-H^1\cdots Br^{(3)}}$	139.1		
$\mathrm{N^{(C2,3)}-H^2\cdots Br^{(4)}}$	145.7		
$\mathrm{N^{(C3,3)}-H^2\cdots Br^{(4)f}}$	122.3		
$\mathrm{N^{(C2,2)}-H^2\cdots Br^{(4)}}$	132.9		

[a] $\mathrm{Br^{(1)a}}$: $-x$, $1-y$, $3/2-z$; [b] $\mathrm{Br^{(1)b}}$: $1-x$, $1-y$, $3/2-z$; [c] $\mathrm{Br^{(2)c}}$: $-x$, $1-y$, $2-z$; [d] $\mathrm{Br^{(2)d}}$: $1-x$, $1-y$, $2-z$; [e] $\mathrm{Br^{(3)e}}$: $1-x$, $1-y$, $1-z$; [f] $\mathrm{Br^{(f)}}$: $-x$, $y-\frac{1}{2}$, $3/2-z$; [g] $\mathrm{Br^{(5)g}}$: x, $1-y$, $2-z$; [h] $\mathrm{Br^{(5)h}}$: $-x$, $1-y$, $1-z$; [i] $\mathrm{Br^{(6)i}}$: $1-x$, $1-y$, $2-z$; [k] $\mathrm{Br^{(6)k}}$: $1-x$, $y-\frac{1}{2}$, $3/2-z$.

Bromine Nuclear Quadrupole Resonance, ^{79,81}Br–NQR

The six crystallographically independent Br atoms, which form with Cd the $[CdBr_6]$ octahedron, must lead to six NQR lines for both, ^{79}Br and ^{81}Br, and the expected sextet spectrum was observed for each isotope. For orientation, in Table 7 we have given the resonance frequencies of the spectra at selected temperatures (77 K, 270 K, 388.7 K). The temperature dependence of the sextet spectra is complicated in so far as several of the lines show a change in sign of the slope $d\nu/dT$ within the temperature range covered by

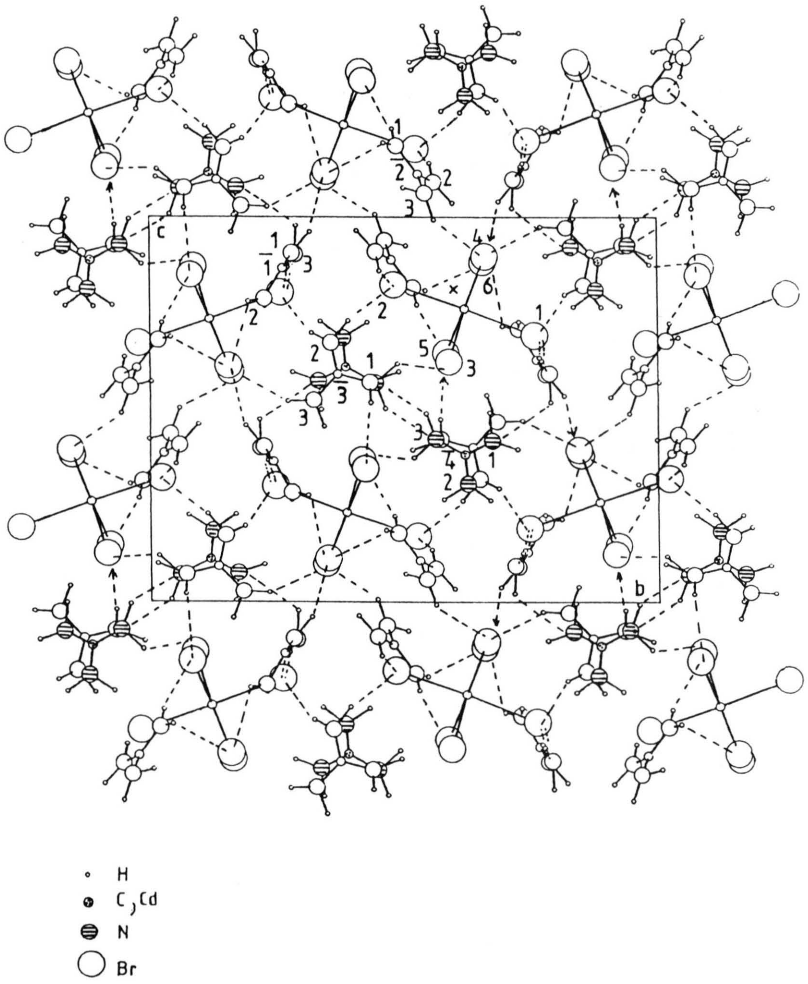

Fig. 1. Projection of the unit cell of $[C(NH_2)_3]_4[CdBr_6]$ along the *a* axis onto the *bc* plane. The hydrogen bonds are marked by broken lines. The numbered atoms correspond to the ones given in Table 3. The numbered carbon atoms of the guanidinium ions are marked by a bar.

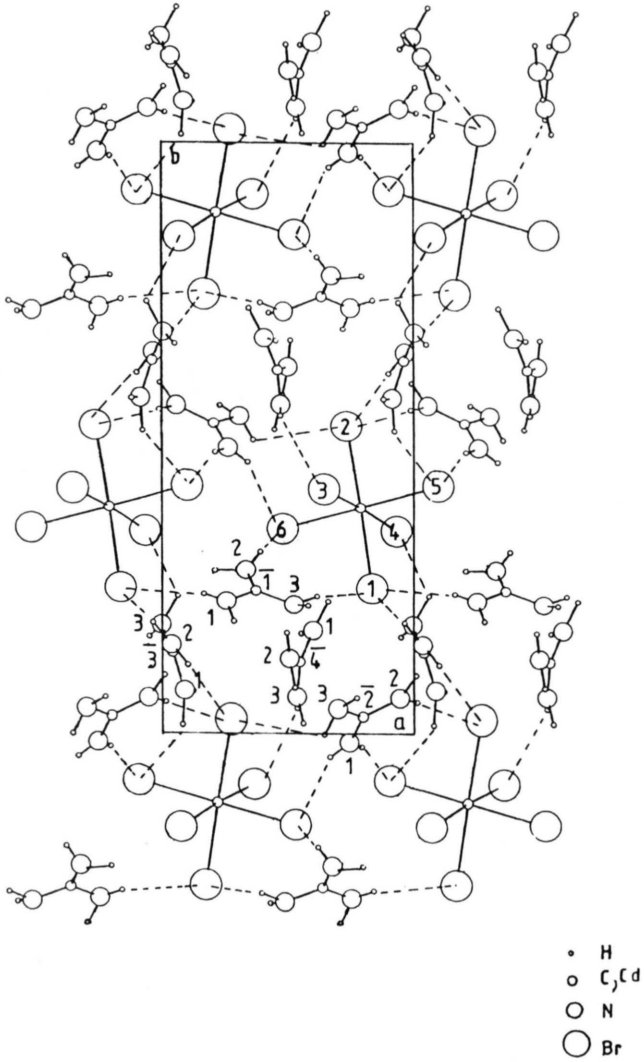

Fig. 5. Projection of half of the unit cell of tetraguanidinium hexabromocadmate along the *c* axis onto the *ab* plane. Hydrogen bonds are marked by dashed lines. The atoms for which the coordinates are given in Table 3 are numbered, carbon atoms of $(C(NH_2)_3)^{\oplus}$ additionally marked by a bar.

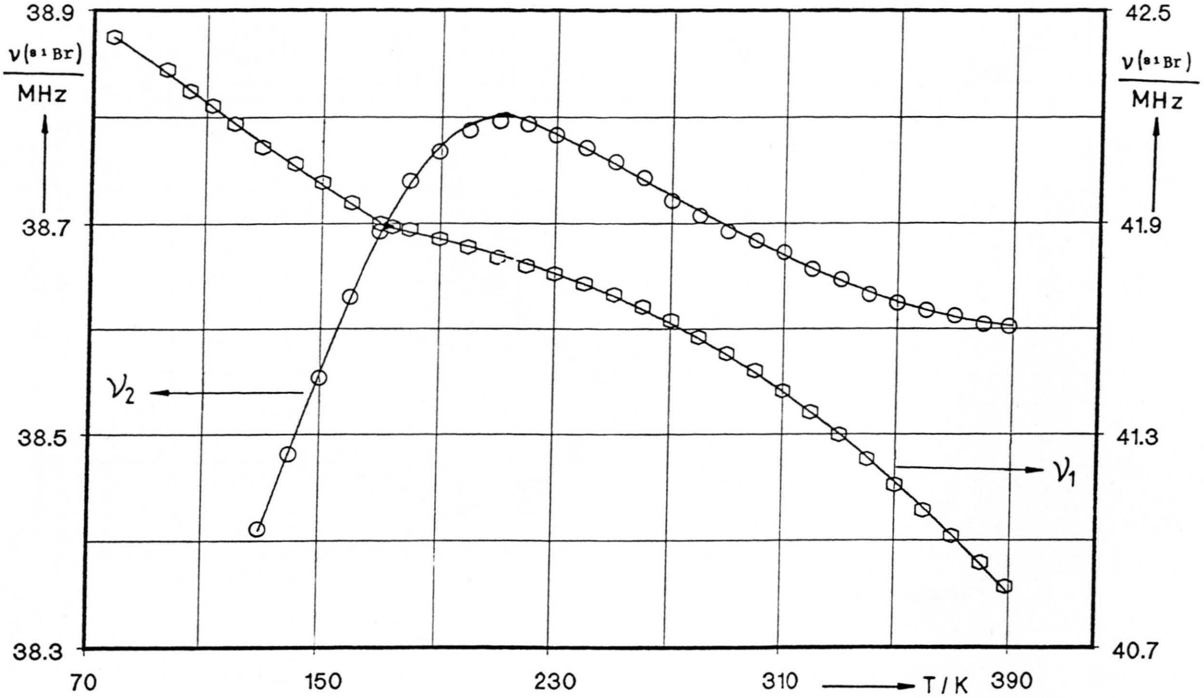

Fig. 2. Temperature dependence of the ^{81}Br NQR lines ν_1 and ν_2 of tetraguanidinium hexabromocadmate.

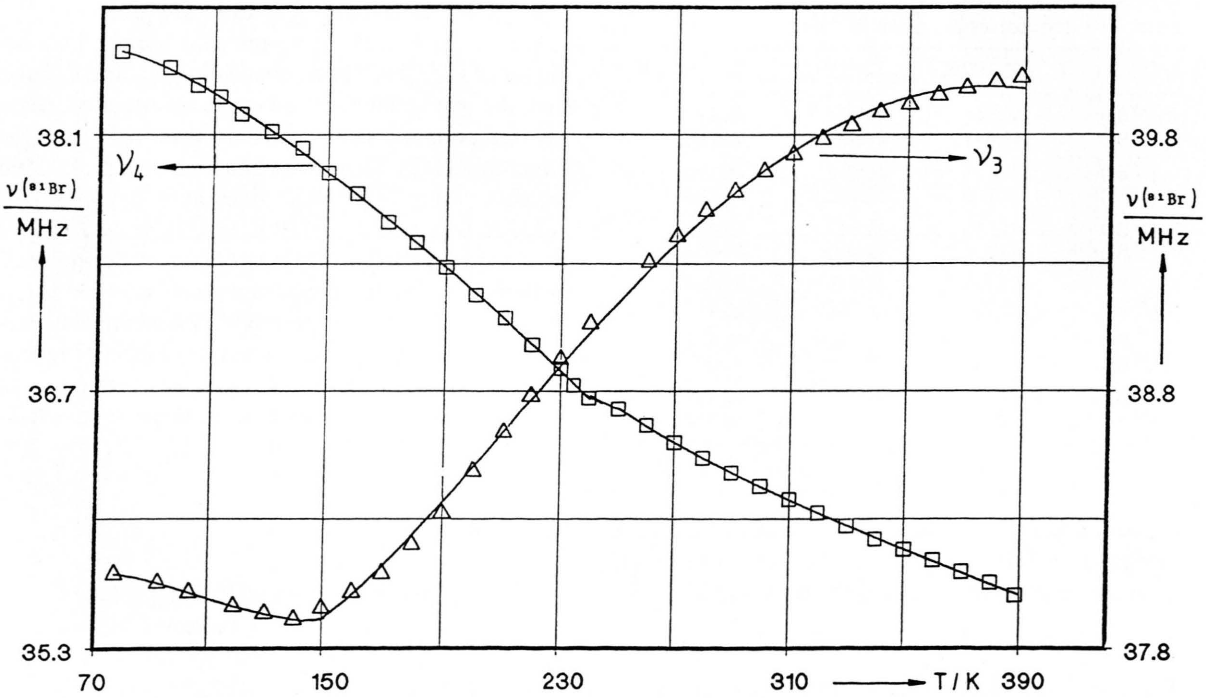

Fig. 3. $[C(NH_2)_3]_4[CdBr_6]$: ν_3 (^{81}Br) and ν_4 (^{81}Br)$= f(T)$.

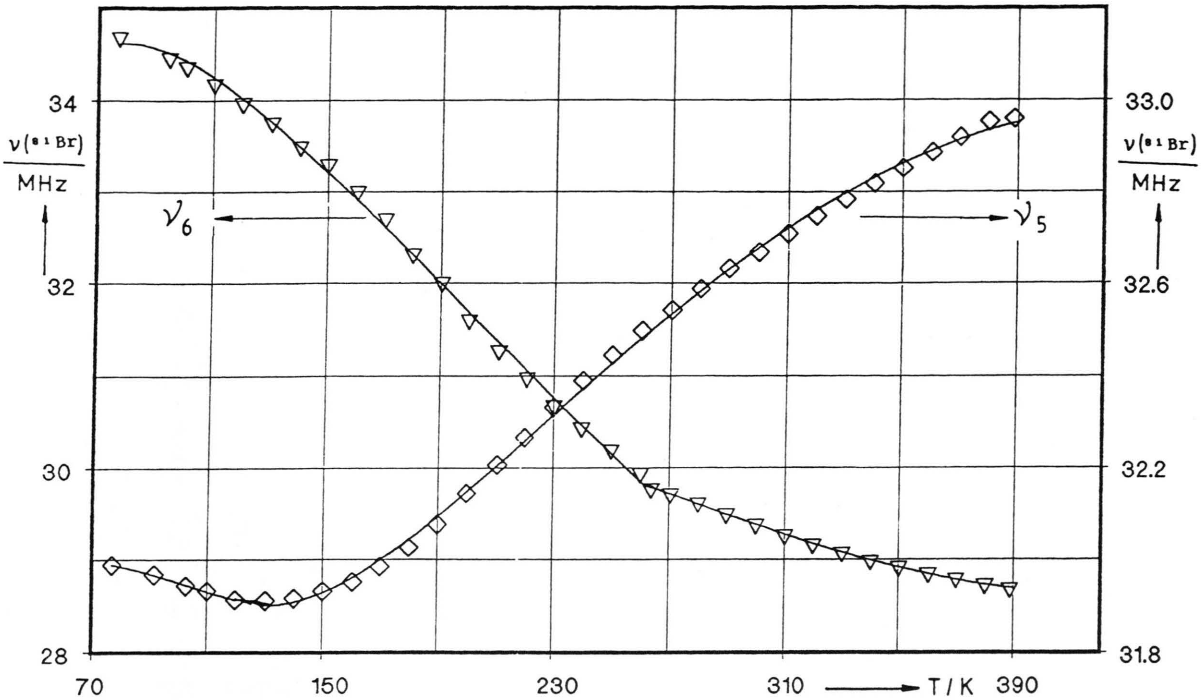

Fig. 4. Temperature dependence of the NQR lines ν_5 (^{81}Br) and ν_6 (^{81}Br) of tetraguanidinium hexabromocadmate.

Table 7. ^{79,81}Br NQR frequencies of tetraguanidinium hexabromocadmate, $[C(NH_2)_3]_4[CdBr_6]$, at selected temperatures. The frequencies are given in MHz.

ν_i	$T = 77$ K	$T = 270$ K	$T = 388.7$ K
ν_1 (^{79}Br)	50.766	49.804	48.909
ν_1 (^{81}Br)	42.421	41.623	40.868
ν_2 (^{79}Br)	45.254	46.341	46.196
ν_2 (^{81}Br)	37.806	38.722	38.603
ν_3 (^{79}Br)	48.019	46.187	45.483
ν_3 (^{81}Br)	40.124	38.596	38.005
ν_4 (^{79}Br)	42.729	44.931	45.967
ν_4 (^{81}Br)	35.703	37.547	38.413
ν_5 (^{79}Br)	38.281	38.939	39.461
ν_5 (^{81}Br)	31.988	32.541	32.977
ν_6 (^{79}Br)	41.504	35.569	34.327
ν_6 (^{81}Br)	34.681	29.722	28.684

the experiments. In Figs. 2–4 the results of the measurements $\nu(^{81}Br) = f(T)$ are shown. $\nu = f(T)$ has been parameterized by use of the polynomial

$$\nu(T) = a_{-1}\, T^{-1} + a\, T_0 + a_1\, T + a_2\, T^2 \,. \qquad (1)$$

The fitting was performed by dividing up the set of data in two temperature intervalls. In Table 8 the coefficients a_i and the temperature range in which the power series development is valid are given.

Figures 2–4 show quite unusual temperature behavior of ν_i (^{81}Br). The frequencies ν_1, ν_4, and ν_6 have, over the whole temperature range investigated, negative temperature coefficients as expected from the Bayer model [7]. There is a change in $d\nu/dT$ observed for these three ^{81}Br NQR lines at ~265 K (ν_6), at ~235 K (ν_4), and at ~170 K (ν_1). ν_3 and ν_5 behave also quite similarly in their temperature dependence. Both lines have a frequency minimum, at ~130 K (ν_5) and at ~145 K (ν_3), respectively. A positive temperature coefficient of ν_3 and ν_5 results at higher temperatures. Finally, ν_2 shows a frequency maximum at ~215 K above which temperature Bayer type behavior of $\nu_2 = f(T)$ is observed.

Discussion

The geometry of the isolated $[CdBr_6]$ octahedron is nearly regular. One finds (see Table 4) $274.6 \leq d(Cd-Br) \leq 281.3$, showing an overall spread of not more than 6 pm. Since the anion $[CdBr_6]^{4-}$ is acentric with respect to the central Cd atom, we expect deviations

Table 8. Coefficients of the power series development of ^{81}Br NQR frequencies $\nu(T) = \sum_{i=-1}^{2} (a_i T^i)$. The numbering of the frequencies follows Table 6 and Figures 3–5. Only the isotope ^{81}Br is considered. z is the number of points for the respective experimental curve. σ is the mean squares deviation, in kHz.

ν_i	(T_1-T_2) K	Z	σ / kHz	a_{-1} / MHz · K	a_0 / MHz	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^6$ / MHz · K^{-2}
ν_1	174–389	23	6	104.578	40.336	9.352	−22.000
ν_1	77–171	10	7	−26.945	43.587	−11.902	17.263
ν_2	220–389	18	3	−227.660	41.688	−11.069	11.934
ν_2	130–210	9	5	379.263	29.343	65.017	−136.070
ν_3	250–389	15	4	616.642	34.964	7.821	−10.450
ν_3	77–240	18	8	−37.588	41.283	−8.185	−6.782
ν_4	150–389	24	21	866.243	20.007	79.018	−96.609
ν_4	77–140	6	1	−113.253	39.339	−35.662	97.896
ν_5	130–389	27	14	253.861	27.647	20.577	−22.124
ν_5	77–120	5	3	−48.191	33.600	−16.558	48.777
ν_6	264–389	14	9	−1696.719	51.341	−79.003	82.225
ν_6	77–260	19	24	−307.328	42.593	−54.961	40.536

from 90° and 180° Br–Cd–Br angles. However the distortion is small; all intraoctahedral angles are found between 88° and 95°, 176° and 178°, respectively.

Besides an R-value of 5% ($R_w = 4\%$), see Table 2, due to the presence of the heavy atoms Cd and Br, the error in the determination of the bond distances C–N within the guanidinium ions is rather large, about ±1.5 pm on average (Table 4). For the intraionic angles N–C–N the error is ±1.3° (see Table 5). Within these limits the average bond distance C–N of the guanidinium ions is 131.2 pm for the four crystallographical independent cations, with a definite deviation of the mean value for the ion 4, with $\langle d(\mathrm{C-N})\rangle = 129.0$ pm. However, as seen from Table 5, the mean of the angles N–C–N is 120° for each of the four cations. In recent investigations, involving the crystal structure of guanidinium salts [8] we found for the distance d(C–N) in the ion $(\mathrm{C(NH_2)_3})^{\oplus}$ d(C–N) = 131.2 pm in the structure of $[\mathrm{C(NH_2)_3}]^{\oplus}$ $[\mathrm{ClF_2CCOO}]^{\ominus}$ and 132.2 pm in the structure of $[\mathrm{C(NH_2)_3}]^{\oplus}$ $[\mathrm{Cl_2HCCOO}]^{\ominus}$. The angles N–C–N in these two compounds are 119.9° and 120.0°, respectively. We don't report the equations of best planes for the atomic frame $\mathrm{CN_3}$ of the guanidinium ions in the title compound but for both, guanidinium chlorodifluoroacetate and guanidinium dichloroacetate the deviation of carbon and nitrogen from the best plane was ≤1 pm. In $[\mathrm{C(NH_2)_3}]^{\oplus}$ $[\mathrm{ClH_2COOH \cdots OOCCH_2Cl}]^{\ominus}$ [9] d(C–N) is 131.3 pm and the angle N–C–N 120°. For the ion $(\mathrm{C(NH_2)_3})^{\oplus}$, both, bond distances and bond angles of the $\mathrm{CN_3}$ frame are hard bond parameters [8, 9].

There are 24 hydrogen atoms per formula unit available and 18 possible hydrogen bond accepting atoms (6 bromine atoms and 12 nitrogen atoms). We can't expect a hydrogen bond saturated system; only part of the H-atoms will form bonds to neighboring atoms. (A hydrogen bond saturated system would, however, in principle be possible. Each Br atom may accept up to three hydrogen bonds and bonds N–H $\cdots$ H are possible, too). In the present discussion, we accept the following van der Waals and ionic radii: r_{vdW} (Br) = 185 pm; $r(\mathrm{Br}^{\ominus}) = 195$ pm [10], r_{vdW} $(\mathrm{NH_2}) = 175$ pm [11]. Following an empirical rule, hydrogen bonds should be considered if the distance of the H-atom donating group to the acceptor atom is within the sum of the vdW-radii of both atoms. In the present discussion we have to consider distances $d(\mathrm{N \cdots N})$ of ≤340 pm, $d(\mathrm{N \cdots Br})$ ≤350 pm as possible candidates. As Table 6 shows, there are many distances $d(\mathrm{N \cdots Br})$ within the limit given and also several $d(\mathrm{N \cdots N})$ are small enough to allow hydrogen bonds.

In Fig. 5 the projection of part of the unit cell of the title compound along the c axis onto the ab plane is shown and the hydrogen bonds N–H $\cdots$ N are given as broken lines. One recognizes, as proven by the distances given in Table 6 that there is no network of hydrogen bonds N–H $\cdots$ N, connecting the cation sublattice. The cation $(\mathrm{Gua})^{(4)}$ is connected to a neighboring $(\mathrm{Gua})^{(4)}$ ($d(\mathrm{N \cdots N}) = 309$ pm) and $\mathrm{Gua})^{(2)}$ may be interconnected with a neighbor $(\mathrm{Gua})^{(2)}$ ($d(\mathrm{N \cdots N}) = 339$ pm). A third bond N–H $\cdots$ N connects $(\mathrm{Gua})^{(1)}$ with $(\mathrm{Gua})^{(4)}$ ($d(\mathrm{N \cdots N})) = 333$ pm. No polymer cation hydrogen bond system is observed. There is no H bond interaction $(\mathrm{Gua})^{(1)} \cdots (\mathrm{Gua})^{(1)}$ as Fig. 6 shows (the ions are separated in the z-direction by $c/2 = 770$ pm) nor is such an interaction possible between $(\mathrm{Gua})^{(3)}$ and $(\mathrm{Gua})^{(4)}$ (see Fig. 2 and Table 6).

Considering the bond angles $N-H \cdots N$ we can neglect the possible bond $(Gua)^{(2)} \cdots (Gua)^{(2)}$. The most prominent hydrogen bond is found between $(Gua)^{(4)}$ and its opposite neighbor, created by the center of symmetry. The NH_2 groups involved are $N^{(C4,3)}H_2$, as seen in Table 6. The distance $N \cdots N$ is very short (309 pm) and the temperature factor U_{eq} is unusual high, $U_{eq}(N^{(C4,3)}) = 216 \cdot 10^{-3}$ Å^2. We have assumed the following model to explain the observations. The NH_2 group $N^{(C4,3)}$ is jumping between two positions $N^{(C4,3)a}$ and $N^{(C4,3)b}$. Consequently the "counter" cation (operation 1) is simultaneously moving. The two dynamical positions $N^{(C4,3\,a)}$ and $N^{(C4,3\,b)}$ have a distance of 100 pm and the distance $d(N^{(C4,3)} \cdots d(N^{(C4,3)\prime})$ splits into $d(N^{(C4,3\,a)} \cdots N^{(C4,3\,a)\prime}) = 325$ pm and $d(N^{(C4,3\,b)} \cdots N^{(C4,3\,b)\prime}) = 309$ pm. In the last squares calculations the distances $C-N$ of the group in question change from 126 pm to 138 pm for position a and to 130 pm for position b. The deviation of $N^{(C4,3\,a)}$ and $N^{(C4,3\,b)}$ from the best plane through $(CN_3)^{(4)}$ is -48 pm and $+50$ pm, respectively. There are also slight changes in the angles $N-C^{(4)}-N$, we shall not discuss here, see. The uncertainty in the hydrogen position and the fairly large errors in the positions of C and N, due to the heavy atoms Cd and Br prohibit further discussion of the $N-H \cdots N$ bonds.

Furthermore, the whole structure of the title compound and also the ^{79,81}Br NQR spectrum is strongly influenced by the librational motions of the guanidinium ions, which is reflected in the large U_{eq} of the nitrogen atoms (see Table 3). A structure determination at low temperatures, preferentially on the perdeuterated compound and with neutron diffraction should contribute to the solution of the problem.

In the discussion of the correlation: ^{79,81}Br NQR frequencies ↔ Br atom position within the octahedron $[CdBr_6]$ an interesting point are the hydrogen bond interactions $N-H \cdots Br$ which may have a considerable influence on the ^{79,81}Br NQR spectrum, on the frequencies as well their temperature dependence.

In the interpretation of the relation $\nu_i\,(^{81}Br) \leftrightarrow Br^{(j)}$, the first approximation is that the NQR frequencies should be proportional to the covalent character of the respective bond Br–Cd. More directly, the EFG at the bromine site created by the electron density distribution within the bond Cd–Br is given by $\Phi_{zz} = a(d(Cd-Br))^{-3}$. In straight foreward interpretation we assign Br–NQR data at $T = 77$ K and d(Cd–Br) data at room temperature according to this relation; using the data given in Tables 4 and 7 we find:

$$Br^{(1)} \leftrightarrow \nu_5;\; Br^{(2)} \leftrightarrow \nu_4;\; Br^{(3)} \leftrightarrow \nu_6;$$
$$Br^{(4)} \leftrightarrow \nu_2;\; Br^{(5)} \leftrightarrow \nu_1;\; Br^{(6)} \leftrightarrow \nu_3\,.$$

This approximation is too crude, as immediately seen from Table 7 and Figures 2–4. At 389 K the assignment would be $Br^{(j)} \leftrightarrow \nu_i$ (j/i): 1,6; 2/3; 3/5; 4/4; 5/1; 6/2 and at 270 K: 1/6; 2/4; 3/5; 4/3; 5/1; 6/2.

Generally, a single hydrogen bond, directed to a Br atom bonded to Cd atom, should lower the electric field gradient, EFG, at the bromine site. In a simple picture, the bromine experiences opposite action, from the positive central atom (in our case Cd) and from the hydrogen atom with partial positive charge. This leads to a lowering of the electric field and of the EFG at the bromine site. Two or more hydrogen bonds, acting on the bromine atom will enforce this compensation.

There is no pronounced influence of the hydrogen bonds $N-H \cdots Br$ on the bond distances $d(Cd-Br)$ as seen from Table 4 and Table 6. The later one shows that there are at least two hydrogen bonds directed to each of the 6 bromines within the "active" range, $d(Br \cdots N) < 350$ pm. Also the dynamical behavior of the Br–NQR frequencies gives no hint for the assignment of $\nu(^{79,81}Br)$ to $Br^{(1)}$.

Several ways are possible to approach the problem of correct assignment bromine NQR frequency to bromine position. An experiment, immediately coming in mind is a Zeeman-NQR experiment. However, since the bond angles Br–Cd–Br of the octahedron $[CdBr_6]$ deviate only a few degrees from 90° and 180°, respectively, and since we can expect a deviation of the main principal axis Φ_{zz} principal axis Φ_{zz} from being parallel to $r(Br-Cd)$ due to the influence of the hydrogen bonds, it is doubtful that one finds a solution of the problem by this way. As already mentioned, a precise structure determination by neutron diffraction at low temperatures and with deuterated samples would be of some help (there is, however, the problem of the strong neutron absorption of Cd, due to a nuclear reaction (Cd, *n*)). The most promising step, to our opinion, for solving the problem would be a spin echo double resonance experiment, SEDOR, using the pairs $^2H-^{79}Br$ and $^2H-^{81}Br$.

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