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Structure of Complex Bromides Crystallizing in MBr_2–NEt_4Br–H_2O Systems (M = Cd, Cu, Co) at 25°C

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Abstract—The crystalline structures of four tetraethylammonium salts, $[Et_4N]CdBr_3$, $[Et_4N]Cd_2Br_5$, $[Et_4N]_2CoBr_4$, and $[Et_4N]_2CuBr_4$ were determined by X-ray analysis of their single crystals. The $CdBr_x^{2-x}$ anions in the examined salts are linked to polymeric chains, and the coordination number of cadmium ion is 5 or 6. The *d*-metal ion in the copper and cobalt complexes has tetrahedral configuration, and the corresponding anions are discrete.

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Tetraalkylammonium ions are often considered to be analogs of alkali metal cations, which implies structural similarity of their compounds with similar compositions. However, this statement appears to be valid only for tetramethylammonium cation. Specificity of the reaction of tetraethylammonium and higher tetraalkylammonium salts with water is responsible for specific properties of the corresponding aqueous solutions [1–3] and probably for unusual structure of some salts crystallizing in MX_2–NEt_4X–H_2O systems. For example, the copper compound Et_4NCuCl_3 is not composed of planar Cu_2Cl_6 dimers (cf. $KCuCl_3$ [4]) or conjugated octahedron chain (cf. $CsCuCl_3$ [5]) but is a tetramer consisting of edge-connected two quadratic pyramids and two tetrahedra [6]. Though the structure of tetraethylammonium chlorometalates was studied in sufficient detail [7–9], there are almost no published data on the structure of tetraethylammonium bromometalates. The present article reports on the results of studying the structure of four tetraethylammonium salts crystallizing in ternary MBr_2–NEt_4Br–H_2O systems (M = Cd, Co, Cu) at 25°C: $[Et_4N]CdBr_3$ (**I**), $[Et_4N]Cd_2Br_5$ (**II**), $[Et_4N]_2CoBr_4$ (**III**), and $[Et_4N]_2CuBr_4$ (**IV**). The structure of bis(tetraethylammonium) tetrabromocadmate (**V**) was studied in [10].

The cadmium ion in complex **I** coordinates five bromine atoms, forming a distorted extended trigonal bipyramid (Table 1, Fig. 1). Such coordination polyhedron is quite unusual for halide cadmium complexes. Trigonal–bipyramidal coordination entity was reported for chlorocadmates [11], whereas no analogous configuration was reported previously for bromide cadmium complexes, so that we were likely to reveal it for the first time. The crystalline structure of tetramethyl-mmonium tribromocadmate $[Me_4N]CdBr_3$ having analogous composition consists of infinite $CdBr_6$ octahedron chains [12] and is similar to the

Table 1. Bond angles (*d*) and bond angles (φ) in the crystalline structure of complex **I**[a]

Bond	*r*, Å	Bond	*r*, Å
Cd–Br^1	2.5997(8)	N–C^3	1.525(6)
Cd–Br^2	2.6005(8)	N–C^4	1.508(6)
Cd–Br^3	2.5662(6)	C^1–C^{1A}	1.508(8)
Cd–Br^1#1	2.9276(9)	C^2–C^{2A}	1.522(8)
Cd–Br^2#2	2.9580(9)	C^3–C^{3A}	1.506(8)
N–C^1	1.524(6)	C^4–C^{4A}	1.519(7)
N–C^2	1.518(6)		
Angle	**φ, deg**	**Angle**	**φ, deg**
Br^3CdBr^1	120.85(3)	Br^3CdBr^2#2	92.87(3)
Br^3CdBr^2	115.99(3)	Br^1CdBr^2#2	90.37(2)
Br^1CdBr^2	123.15(2)	Br^2CdBr^2#2	86.07(2)
Br^3CdBr^1#1	93.66(3)	Br^1#1$CdBr^2$#2	172.97(2)
Br^1CdBr^1#1	84.04(2)	$CdBr^1Cd$#1	95.96(2)
Br^2CdBr^1#1	93.42(2)	$CdBr^2Cd$#2	93.93(2)

[a] Symmetry operations for equivalent atoms: #1 $-x + 1, -y + 2, -z + 1$; #2 $-x + 1, -y + 1, -z + 1$.

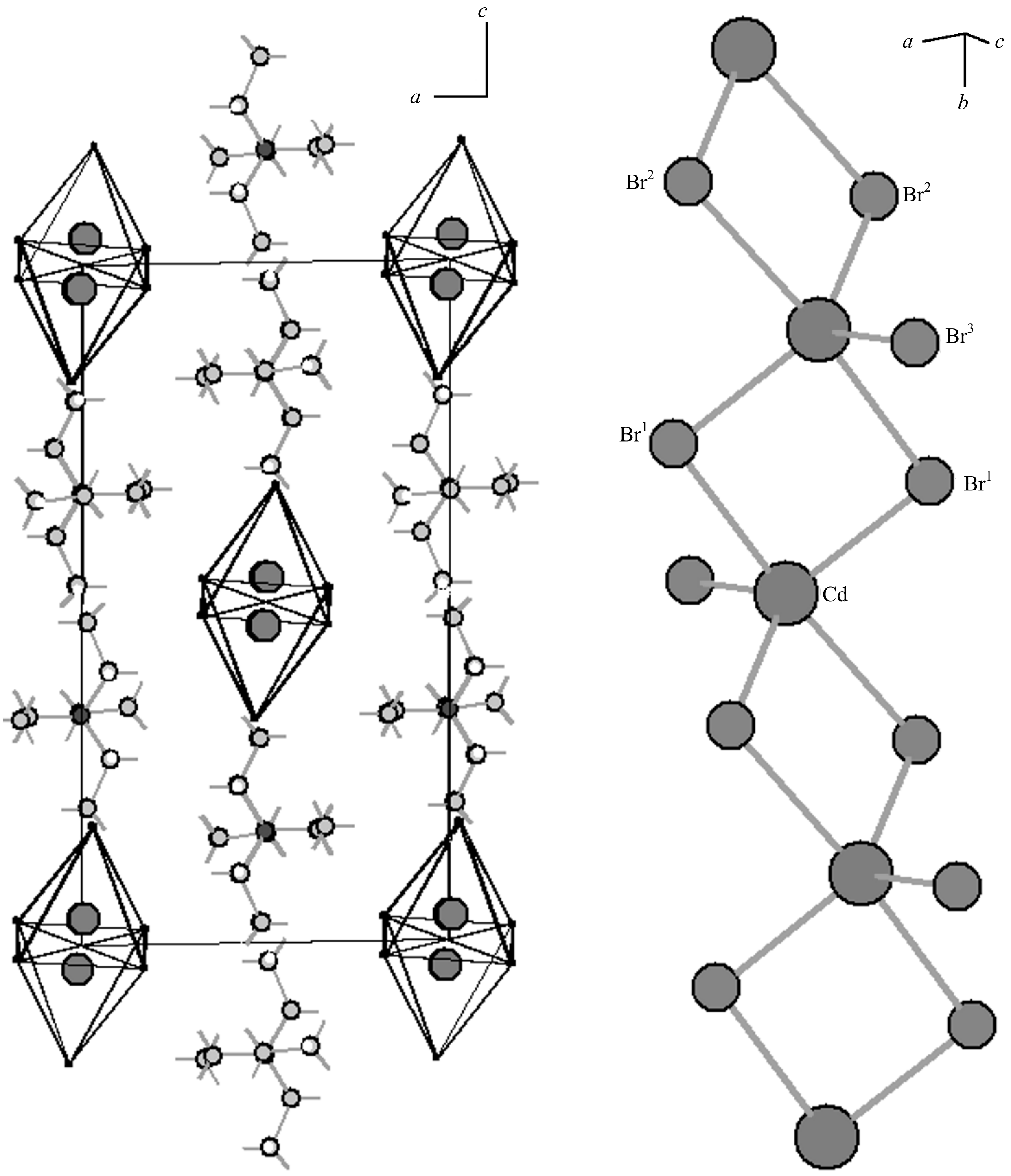

Fig. 1. A fragment of crystal packing of tetraethylammonium tribromocadmate (**I**). A polymeric anion fragment is shown separately.

structure of alkali metal tribromocadmates $MCdBr_3$ (M = K, Rb, Cs, NH_4) [13–15]. The $CdBr_5$ bipyramids in **I** are connected alternately at the Br^1–Br^1 (3.708 Å) and Br^2–Br^2 edges (3.802 Å), giving rise to isolated zigzag chains parallel to the *y* crystallographic axis. The space between the chains is occupied by isolated tetraethylammonium ions (Fig. 1).

Complex **II** in crystal is characterized by two modes of coordination to cadmium ions. The Cd^1 polyhedron is a distorted octahedron, and the Cd^2 coordination entity is a distorted extended trigonal bipyramid (Table 2, Fig. 2). The octahedrons surrounding Cd^1 are connected through the Br^1–Br^1 (3.738 Å) and Br^4–Br^4 edges (3.774 Å), thus forming chains parallel to the crystallographic *y* axis. The octahedron chains are coupled through the Br^2–Br^2 edge (3.677 Å) of the Cd^2 bipyramids to give layers parallel to the (100) plane. Here, each Cd^2 bipyramid is connected to two Cd^1 octahedrons at the Br^1–Br^3 edge (3.822 Å). The space between the layers is occupied by isolated tetraethylammonium ions with disordered CH$_2$ and CH$_3$ groups (Fig. 2).

Thus, decrease of the NEt$_4$Br-to-CdBr$_2$ ratio in the system NEt$_4$Br–CdBr$_2$–H$_2$O leads to gradual increase of the coordination number of cadmium in the complexes crystallized therefrom. The coordination number is 4 in [Et$_4$N]$_2$CdBr$_4$ [10] (CdBr$_4$ tetrahedra), 5 in [Et$_4$N]CdBr$_3$ (CdBr$_5$ trigonal bipyramids), 5 and 6 in [Et$_4$N]Cd$_2$Br$_5$ (CdBr$_5$ trigonal bipyramids and CdBr$_6$ octahedrons), and 6 in CdBr$_2\cdot$4H$_2$O [16] (CdBr$_4$(H$_2$O)$_2$ octahedrons).

Table 2. Bond angles (*d*) and bond angles (φ) in the crystalline structure of complex **II**[a]

Bond	*r*, Å	Bond	*r*, Å
Cd^1–Br^4#1	2.7293(9)	N–C^{3C}#4	1.447(10)
Cd^1–Br^4	2.7293(9)	N–C^{2B}#4	1.450(10)
Cd^1–Br^3	2.7991(8)	N–C^{2B}	1.450(10)
Cd^1–Br^3#2	2.7991(8)	N–C^{3B}	1.452(10)
Cd^1–Br^1	2.8898(9)	C^1–C^{1A}	1.531(10)
Cd^1–Br^1#3	2.8898(9)	C^2–C^{2A}	1.531(10)
Cd^2–Br^3	2.5917(8)	C^3–C^{3D}	1.525(10)
Cd^2–Br^3#4	2.5917(8)	C^3–C^{3C}	1.529(10)
Cd^2–Br^2	2.6048(13)	C^3–C^{3A}	1.534(10)
Cd^2–Br^2#5	2.8755(13)	C^3–C^{3B}	1.543(10)
Cd^2–Br^1	2.9220(13)	C^{2A}–C$^{2'}$	1.515(10)
N–C^{3A}	1.438(10)	C^{3A}–C$^{3'}$	1.517(10)
N–C^{3D}	1.441(10)	C^{3A}–C^{3C}	1.53(3)
N–C$^{1A'}$	1.443(10)	C^{3B}–C$^{3'}$	1.531(10)
N–C^{2A}#4	1.444(9)	C$^{1A'}$–C$^{1'}$	1.534(10)
N–C^{2A}	1.444(9)	C$^{2'}$–C^{2B}	1.538(10)
N–C^{3C}	1.447(10)		
Angle	φ, deg	Angle	φ, deg
Br^4#1Cd^{1}Br^4	87.49(4)	Br^3#2Cd^{1}Br^1#3	84.39(3)
Br^4#1Cd^{1}Br^3	94.05(3)	Br^{1}Cd^{1}Br^1#3	80.59(4)
Br^{4}Cd^{1}Br$_3$	88.13(3)	Br^{3}Cd^{2}Br^3#4	110.60(5)
Br^4#1Cd^{1}Br^3#2	88.13(3)	Br^{3}Cd^{2}Br^2	124.67(2)
Br^{4}Cd^{1}Br^3#2	94.05(3)	Br^3#4Cd^{2}Br^2	124.67(2)
Br^{3}Cd^{1}Br^3#2	176.99(4)	Br^{3}Cd^{2}Br^2#5	94.46(3)
Br^4#1Cd^{1}Br^1	96.45(2)	Br^3#4Cd^{2}Br^2#5	94.46(3)
Br^{4}Cd^{1}Br^1	171.77(3)	Br^{2}Cd^{2}Br^2#5	84.12(4)
Br^{3}Cd^{1}Br^1	84.39(3)	Br^{3}Cd^{2}Br^1	87.54(3)
Br^3#2Cd^{1}Br^1	93.31(3)	Br^3#4Cd^{2}Br^1	87.54(3)
Br^4#1Cd^{1}Br^1#3	171.77(3)	Br^{2}Cd^{2}Br^1	92.36(4)
Br^{4}Cd^{1}Br^1#3	96.45(2)	Br^2#5Cd^{2}Br^1	176.48(4)
Br^{3}Cd^{1}Br^1#3	93.31(3)		

[a] Symmetry operations for equivalent atoms: #1 –*x*, –*y*, –*z*; #2 –*x*, *y*, –*z*; #3 –*x*, –*y* + 1, –*z*; #4 *x*, –*y* + 1, *z*; #5 –*x*, –*y* + 1, –*z* + 1.

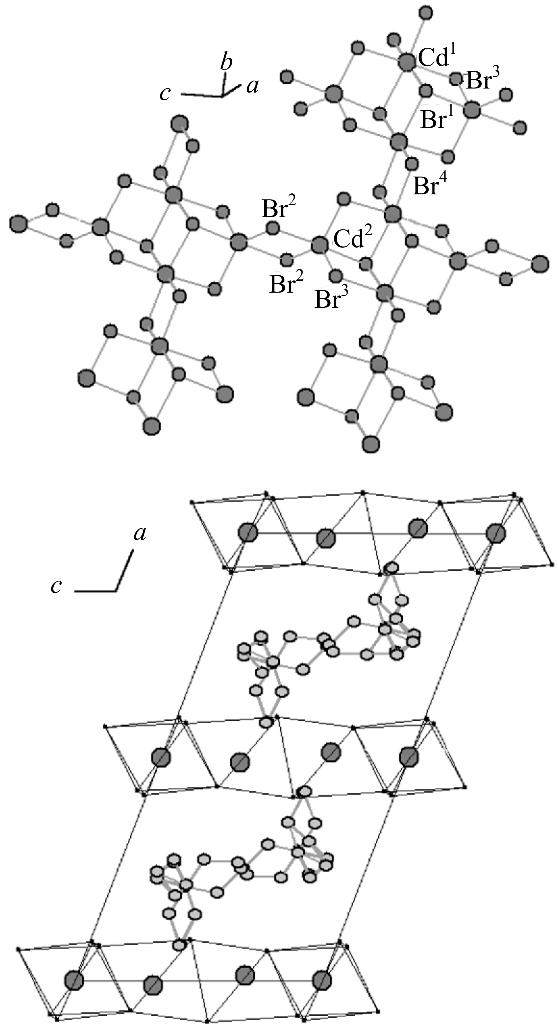

Fig. 2. A fragment of crystal packing of tetraethylammonium pentabromodicadmate (**II**). A polymeric anion fragment is shown separately.

Compounds **III** and **IV** in crystal are isostructural: isolated weakly distorted [CoBr$_4$]$^{2-}$ and [CuBr$_4$]$^{2-}$ tetrahedra are surrounded by isolated tetraethylammonium ions with disordered CH$_2$ and CH$_3$ groups (Table 3, Fig. 3). Such structure is typical of complexes like (NR$_4$)$_2$MX$_4$ [7–10]. The Co–Br bond length in complex **III** is 2.401 Å, which is almost equal to the corresponding distance in the tetrahedral CoBr$_4^{2-}$ anion in cesium pentabromocobaltate Cs$_3$CoBr$_5$ (2.399 Å,

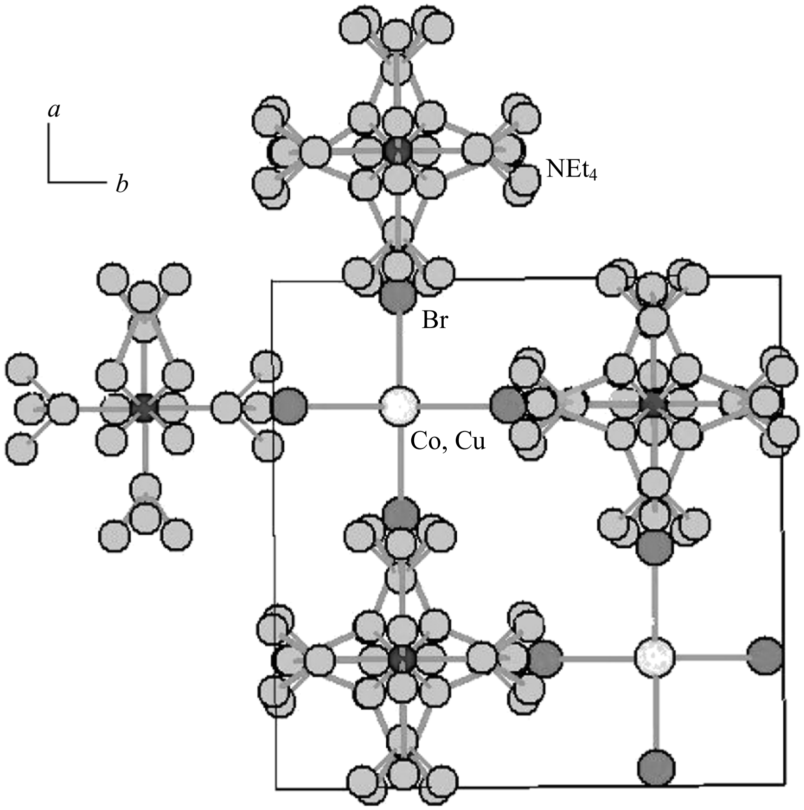

Fig. 3. A fragment of crystal packing of bis(tetraethylammonium) tetrabromocobaltate (**III**) and bis(tetraethylammonium) tetrabromocuprate (**IV**). A unit cell is framed.

[17]). The Cu–Br bond length in complex **IV** is 2.358 Å; it is very similar to the corresponding distances in cesium tetrabromocuprate (2.350 Å, [18]) and tetramethylammonium tetrabromocuprate (2.358 Å, [19]). These data indicate that the bond lengths in tetrahedral complex anions are weakly sensitive to the outer-sphere cation.

EXPERIMENTAL

Single crystals for X-ray diffraction study were obtained by slow evaporation of aqueous solutions of the corresponding salts. The X-ray diffraction data were acquired on an Xcalibur automatic diffractometer (MoK_α irradiation). All structures were solved by direct methods and were refined with account taken of anisotropy of thermal vibrations of non-hydrogen atoms. The calculations were performed with the aid of SHELX97 software package [20]. Hydrogen atoms in the crystalline structure of complex **I** were placed into calculated positions; the positions of hydrogen atoms in the structures of other complexes were not determined because of disordering of CH$_2$ and CH$_3$

Table 3. Bond angles (d) and bond angles (φ) in the crystalline structure of complexes **III** and **IV**[a]

Bond	d, Å		Angle	φ, deg	
	III	**IV**		**III**	**IV**
M–Br^1	2.4007(9)	2.3576(14)	Br#1MBr	109.97(3)	103.65(9)
M–Br^2	2.4007(9)	2.3576(14)	Br#1MBr#2	108.49(6)	112.46(5)
M–Br^3	2.4007(9)	2.3576(14)	BrMBr#2	109.97(3)	112.46(5)
M–Br^4	2.4007(9)	2.3576(14)	Br#1MBr#3	109.97(3)	112.46(5)
			BrMBr#3	108.49(6)	112.46(5)
			Br#2MBr#3	109.97(3)	103.65(9)

[a] Symmetry operations for equivalent atoms: #1 $-x + 3/2, -y + 1/2, z$; #2 $-y + 1, -x + 1, -z + 3/2$; #3 $y + 1/2, x - 1/2, -z + 3/2$.

Table 4. Crystallographic parameters and parameters of the X-ray diffraction experiments and structure refinement of compounds **I**–**IV**

Parameter	**I**	**II**	**III**	**IV**
Formula	$[NEt_4]CdBr_3$	$[NEt_4]Cd_2Br_5$	$[NEt_4]_2CoBr_4$	$[NEt_4]_2CuBr_4$
M	482.38	754.61	638.80	643.40
Crystal system	Monoclinic	Monoclinic	Tetragonal	Tetragonal
Space group	*P*21/*n*	*C*2/*m*	*P* 4(2)/*nmc*	*P*4(2)/*nmc*
a, Å	10.1020(3)	21.1074(13)	8.9856(6)	9.0383(4)
b, Å	7.6854(3)	8.3520(5)	8.9856(6)	9.0383(4)
c, Å	18.7384(6)	10.9010(13)	16.0006(8)	15.904(1)
α, deg	90	90	90	90
β, deg	90.971(3)	111.011(10)	90	90
γ, deg	90	90	90	90
V, Å^3	1454.60(9)	1794.0(3)	1291.90(14)	1299.24(12)
Z; D_x, g/cm^3	4; 2.213	4; 2.391	2; 1.651	2; 1.654
μ, mm^{-1}	9.708	13.486	13.661	6.977
Crystal habit	0.36×0.20×0.18	0.32×0.10×0.08	0.42×0.12×0.12	0.16×0.16×0.06
Range of θ, deg	3.86–32.16	3.89–32.25	4.10–32.26	4.09–29.94
Number of reflections with $I \geq 2\sigma(I)$	2940	2113	574	1008
R_1	0.0458	0.0623	0.0703	0.0690
wR_2	0.0997	0.1364	0.2084	0.2235
Residual electron density, max/min, e/Å^3	1.517/–1.037	1.163/–1.236	1.066/–0.677	0.631/–0.547

groups in tetraethylammonium ions. The principal crystallographic parameters and some parameters of the X-ray diffraction experiments and structure refinement are given in Table 4; the principal bond lengths and bond angles are collected in Tables 1–3; the coordinates of basis atoms and their thermal vibration parameters are available from the authors.

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