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Structural and vibrational studies of mixed potassium–ammonium chloromercurate(II) dihydrates $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$

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Abstract

The crystal structure of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_20$ has been determined by X-Ray single-crystal analysis. The title compound crystallises in the space group *Pmcm* and has the unit cell dimensions $a=4.5110(15)$Å, $b=14.489(2)$, $c=16.074(4)$ Å, $Z=2$. The refinement converged to $R=0.03$ 8 and $WR_2=0.105$. The structure may be described as consisting of alternating layers and chains built up from $HgCl_6$ octahedra. The ammonium groups (or K^+) and water molecules are located between the chains and layers. IR and RAMAN spectroscopic studies were performed to confirm results of the radiocristallographic method.

Keywords: Chloromercurates; Single-crystal; Structure; Raman spectra; IR spectra

1. Introduction

The compounds of general formula $AHgX_3$ (where A is monovalent cation and X a halide ion) exhibit structural phase transitions and interesting physical properties [1–3]. Crystalline α-NH_4HgCI_3 has a layer structure [4] and is known to undergo an order–disorder phase transition at 55 K [5]. X-Ray diffraction structure give tetragonal *P*4/*mmm* symmetry corresponding to the room temperature phase. $K_2HgCl_4.H_20$ contains distorted $HgCl_6$ octahedra form columns sharing two opposite edges [6,7].

The present investigation intends to study the solid state phase diagram with the border compounds $K_2HgCl_4.H_2O$ and α-NH_4HgCl_3.

2. Experimental details

2.1. Synthesis of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$

Single crystals of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$ were grown by slow evaporation from a mixture of water and acetone containing stoichiometric $KCl–NH_4Cl–HgCl_2$ at room temperature in the ratio 1 / 1/2. The formula is determined by refinement of the crystal structure and confirmed by chemical analysis.

2.2. Crystal data of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$

Crystal data collection procedure and structure refinement are given in Table 1. In total, 1529 reflections were collected with Enraf-Nonius CAD-4 diffractometer using the $\omega-2\theta$ scan technique. Corrections were made for Lorentz-Polarisation effects and absorption.

The positions of the mercury atoms were determined from a three dimensional Patterson synthesis, and the other non hydrogen atoms were located by three-dimensional Fourier function. Structure solution and refinement were carried out using SHELX programs [8,9]. The non hydrogen atoms were refined anisotropically. The H atoms were located geometrically, and attributed isotropic thermal factors equal to those of the atoms on which they are linked. The atomic coordinates are given in Table 2, the bond lengths and angles in Table 4, and the anisotropic displacement parameters in Table 3.

3. Discussion

The main feature of the structure of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$, is the coexistence of two

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Table 1
Summary of crystallographic data

Formula	$K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$
Formula weight	1117.33
Space group	*Pmcm*
a(Å)	4.5110(15)
b(Å)	14.489(2)
c(Å)	16.074(4)
V(Å^3)	1050.6(5)
Z	2
ρ_{calc} (g cm^3)	3.56
μ(mm^{-1})	23.635
Data collection instrument	Enraf-Nonius CAD-4 diffractometer
Radiation, graphite monochromator λ(Å)	Mo Kα(0.71069)
Temperature (°C)	20
Scan method	$\omega-2\theta$
Data collection range, 2θ(0)	$0<2\theta<56.59$
Transmission factors: max., min.	0.99, 0.53
No. unique reflections measured	1529
No. independent reflections	1477
No. reflections in refinement with $I>2\sigma(I)$	1298
R^a(%)	3.86
WR_2^b(%)	10.54
Calculated weights	$w=1/[\sigma^2(F_0^2)+(0.0674P)^2+1.29P]$ where $P=(F_0^2+2F_c^2)/3$

[a] $R=\Sigma\ \|F_0|-|F_c\|/\Sigma\ F_0$.

[b] $$WR_2=\left[\frac{\Sigma[w(|F_0|^2-|F_c|^2)]^2}{\Sigma[w(|F_0|^2)]^2}\right]^{1/2}$$

Table 2
Fractional atomic coordinates and equivalent thermal parameters

Atoms	Occup.	x	y	z	U_{eq}
Hg1	1	0.5	0.02095(3)	0.12529(3)	0.0583(2)
Hg2	1	0.5	0.5	0	0.0682(3)
K1	0.34(3)	0	0.5569(6)	0.25	0.064(3)
N1	0.66(3)	0	0.5549(6)	0.25	0.064(3)
K2	0.59(2)	0	0.2536(4)	0.25	0.061(2)
N2	0.41(3)	0	0.2536(4)	0.25	0.061(2)
K3	0.780(17)	0	0.23316(18)	0.52786(18)	0.0485(10)
N3	0.21(2)	0	0.23316(18)	0.52786(18)	0.0485(10)
Cl1	1	0	0.0333(2)	0.25	0.0423(6)
Cl2	1	0.5	0.18273(14)	0.11307(13)	0.0402(4)
Cl3	1	0.5	0.61818(15)	0.10079(14)	0.0448(5)
Cl4	1	1	0	0	0.0428(6)
Cl5	1	0.5	−0.13959(16)	0.13624(14)	0.0472(5)
Cl6	1	0	0.59436(17)	−0.09528(19)	0.0596(6)
O1	1	0	0.7474(10)	0.25	0.084(4)
O2	1	0.5	0.4028(11)	0.25	0.071(3)
H1	0.66(3)	0.1581	0.5923	0.25	0.06
H2	0.66(3)	0	0.521	0.2051	0.06
H3	0.41(3)	0.1581	0.2923	0.25	0.06
H4	0.41(3)	0	0.225	0.2051	0.06
H5	0.21(2)	0	0.1825	0.4956	0.05
H6	0.21(2)	0	0.2838	0.4956	0.05
H7	0.21(2)	0.1627	0.2331	0.5603	0.05
H8	1	0.1686	0.7879	0.25	0.08
H9	1	0.5	0.4392	0.2098	0.07

$$U_{eq}=\frac{1}{3}\Sigma_i\ \Sigma_j\ U_{ij}a_i^*a_j^*a_ia_j$$

Table 3
Anisotropic displacement parameters (in 10^{-3} Å^2)[a]

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg1	0.0914(4)	0.0288(3)	0.0547(3)	−0.00071(14)	0	0
Hg2	0.1058(5)	0.0453(4)	0.0535(4)	−0.0202(3)	0	0
K1/N1	0.063(4)	0.081(6)	0.048(4)	0	0	0
K2/N2	0.056(3)	0.081(4)	0.046(3)	0	0	0
K3/N3	0.0399(13)	0.0415(14)	0.0641(18)	0.0041(11)	0	0
Cl1	0.0435(13)	0.0444(16)	0.0391(14)	0	0	0
Cl2	0.0472(10)	0.0277(10)	0.0455(10)	0.0002(8)	0	0
Cl3	0.0527(10)	0.0343(10)	0.0474(11)	−0.0107(8)	0	0
Cl4	0.0488(14)	0.0403(14)	0.0392(14)	0.0011(12)	0	0
Cl5	0.0643(12)	0.0305(11)	0.0468(11)	−0.0032(8)	0	0
Cl6	0.0661(13)	0.0344(12)	0.0782(17)	−0.0048(11)	0	0
O1	0.041(5)	0.069(9)	0.141(13)	0	0	0
O2	0.074(6)	0.097(11)	0.042(5)	0	0	0

[a] The anisotropic displacement exponent takes the form $(-2\pi^2\ [h^2a^{*2}\ U_{11}+...+2hka^*b^*U_{12}])$.

Table 4
Selected bond lengths (Å) and angles (°)

Hg1	Cl5	2.333(2)	Cl5	Hg1	Cl2	179.54(4)
Hg1	Cl2	2.352(2)	Cl3[c]	Hg2	Cl3	180
Hg1	Cl1	3.0229(7)	H1	N1	H2	109.88(4)
Hg1	Cl4	3.0390(7)	H1	N1	H2	109.88(4)
Hg1	Cl4[a]	3.0390(7)	H5	N3	H6	109.5(3)
Hg1	Cl1[b]	3.0229(7)	H5	N3	H7	109.49(19)
Hg2	Cl3	2.357(2)	H6	N3	H7	109.57(19)
Hg2	Cl3[c]	2.357(2)	H3	N2	H4	107.90(8)
Hg2	Cl6	3.050(2)	K2[b]	O2	K1[b]	88.12(15)
Hg2	Cl6[b]	3.050(2)	K2	O2	H9[b]	115.9(4)
Hg2	Cl6[c]	3.050(2)	K1	O2	H9[b]	63.8(6)
Hg2	Cl6[d]	3.050(2)	Hg1[e]	Cl2	K3	106.24(7)
O1	H8	0.961(9)	Hg1[f]	Cl2	K3	106.24(7)
O2	K2[b]	3.124(12)	K3[f]	Cl2	K3[e]	86.92(9)
O2	K1[b]	3.154(13)	Hg1[b]	Cl2	K2	104.68(12)
O2	H9	0.834(10)	K3[b]	Cl2	K2[e]	149.06(13)
Cl2	K3[e]	3.279(3)	K3[b]	Cl2	K2[f]	85.51(5)
Cl2	K3[f]	3.279(3)	Hg2[g]	Cl3	K3	103.17(8)
Cl2	K2[b]	3.315(3)	Hg2[h]	Cl3	K3	103.17(8)
Cl3	K3[g]	3.332(3)	K3[h]	Cl3	K3[g]	85.21(9)
Cl3	K3[h]	3.332(3)	Hg2[b]	Cl3	K1	106.71(15)
N1	H1	0.895(6)	K3[b]	Cl3	K1[g]	88.48(11)
N1	H2	0.873(5)	K3[b]	Cl3	K1[h]	150. 12(15)
N1	H1[i]	0.895(6)	K3[k]	Cl4	K3[f]	180
N1	H2[e]	0.873(5)	Hg1[j]	Cl5	K3	112.75(8)
N2	H3	0.907(4)	Hg1[k]	Cl5	K3	112.75(8)
N2	H3[d]	0.907(4)	K3[k]	Cl5	K3[j]	91.23(9)
N2	H4	0.832(3)	K3[l]	Cl6	K1[h]	169.40(16)
N2	H4[e]	0.832(3)	K3[l]	Cl6	K2[h]	86.85(11)
N3	H5	0.899(3)	K1[l]	Cl6	K2[l]	82.54(16)
N3	H6	0.898(3)				
N3	H7	0.9003(17)				
N3	H7[d]	0.9003(17)				
Cl3	K1[b]	3.418(3)				
Cl4	K3[f]	3.408(3)				
Cl4	K3	3.408(3)				
Cl5	K3[j]	3.156(2)				
Cl5	K3[k]	3.156(2)				
Cl6	K3[h]	3.188(4)				
Cl6	K1[l]	3.296(7)				
Cl6	K2[l]	3.322(5)				

[a] $-1+x,\ y,\ z$; [b] $1+x,\ y,\ z$; [c] $x,\ 1-y,\ -z$; [d] $1+x,\ 1-y,\ -z$; [e] $x,\ y,\ -z+1/2$; [f] $x+1,\ y,\ -z+1/2$ [g] $-x+1,\ -y+1,\ z-1/2$; [h] $-x,\ -y+1,\ -z-1$; [i] $-x,\ y,\ z$; [j] $-x,\ -y,\ -1/2$; [k] $-x+1,\ -y,\ z-1-1/2$; [l] $-x,\ -y+1,\ -z$.

different structural motifs derived from the border compounds in the same crystal. The atomic arrangement of this structure may be considered as a succession of layers perpendicular to the *b* axis and chains along the *a* axis among which ammonium (or K^+) ions and water molecules are placed (Figs. 1 and 2). The Hg(2) atoms are surrounded by six Cl-atoms in the form of slightly distorted octahedron with the distances: 2.357(2) and 3.050(2)Å. The first two, shortest distances correspond to covalent bonds in the $HgCl_2$ molecule, while the other distances correspond to the coordination bonds. The $Hg(2)Cl_6$ octahedra are located on an inversion centre at (1/2, 1/2, 1/2) and form columns sharing two opposite edges. The layers consist of linked together $Hg(1)Cl_6$ octahedra. The coordination of Hg(1) atoms is best described as a $HgCl_2$ unit with Hg–Cl distances of 2.333(2) and 2.352(2)A. Four chlorine atoms complete the coordination to a slightly deformed octahedra. Their chlorine squares lie on the *ac* plane. The environment of the K atoms is as follows:

environment of K(1): six Cl atoms belonging to the $(Hg(2)Cl_4)_n^{-2n}$ chains and three water molecules. The K–Cl distances are: 3.296(7) and 3.418(3) Å, while the K–H_2O distances are 2.811(17) and 3.154(13) Å.

environment of K(2): five Cl atoms of Hg(1) octahedra, two Cl atoms of the others Hg(2) octahedra and two water molecules. The values of K–Cl bonds are: 3.192(7), 3.3 15(3) and 3.322(5) Å, while the values of K–H_2O bonds are: 3.124(12) Å.

environment of K(3): five Cl atoms corresponding to Hg(1) octahedra and three Cl atoms corresponding to Hg(2) octahedra. The bond distances range from 3.156(2) to 3.408(3) Å.

The interesting feature of this structure is the coexistence of two types of bonds ensuring the cohesion of the atomic arrangement:

– The H bonding contacts N–H... Cl, N–H...O and O–H...Cl (see Table 5) provide a linkage between cationic entities NH_4^+, water molecules H_2O and $[(HgCl_4)_n^{-2n}–(HgCl_3)_n^{-n}]$ anionic complexes.

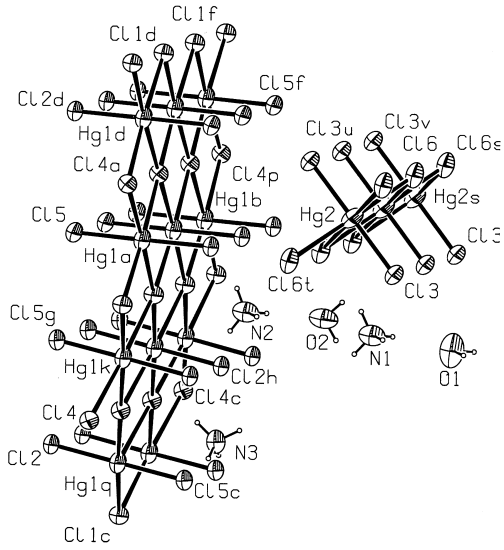

Fig. 1. Displacement ellipsoid plot (50% probability) of the title compound. H atoms are shown as small spheres of arbitrary radii.

– The ionic bonding between cationic entities K^+ and $[(HgCl_4)_n^{-2n}–(HgCl_3)_n^{-n}]$ anionic complexes.

Comparison with α-NH_4HgCl_3 and $K_2HgCI_4.H_2O$ compounds shows that the structure contains features of the two border compounds. The real formula is therefore that of the double-salt 4 $[K_{0.6275}(NH_4)_{0.33725}Cl].3HgCl_2.2H_2O$.

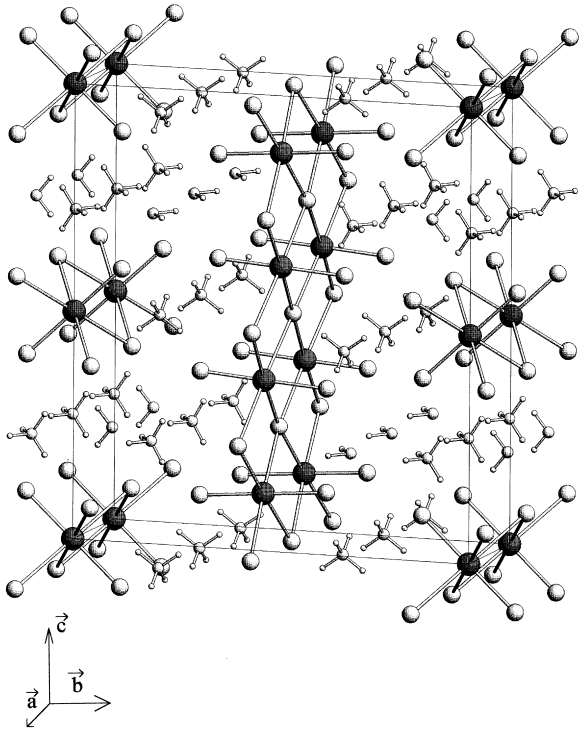

Fig. 2. Perspective view of the structure of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$.

Table 5
Hydrogen bonding lengths (Å) and bond angles (°) of type N–H–Cl, N–H–O and 0–H–Cl

D–H...A	D–H	H...A	D...A		DHA	
H1	0.895(6)	2.876(2)	3.418(3)	N1	120.40(13)	Cl3
H1	0.895(6)	2.358(14)	2.788(17)	N1	109.6(5)	O1
H2	0.873(5)	2.431(3)	3.296(7)	N1	170.8(5)	Cl6[a]
H2	0.873(5)	2.923(10)	3.154(13)	N1	97.2(4)	O2
H3	0.907(4)	2.223(12)	3.124(12)	N2	172.1(4)	O2
H4	0.832(3)	2.7660(14)	3.315(3)	N2	125.04(5)	Cl2
H4	0.832(3)	2.870(3)	3.192(7)	N2	105.3(4)	Cl1
H5	0.899(3)	2.8528(14)	3.279(3)	N3	110.63(10)	Cl2[b]
H6	0.898(3)	3.1567(18)	3.332(3)	N3	93.33(13)	Cl3[c]
H6	0.898(3)	2.292(3)	3.188(4)	N3	175.67(19)	Cl6[c]
H7	0.9003(17)	2.3752(17)	3.156(2)	N3	145.11(17)	Cl5[d]
H8	0.961(9)	2.585(2)	3.334(7)	O1	134.91(5)	Cl5[e]
H8	0.961(9)	2.585(2)	3.334(7)	O1	134.91(5)	Cl5[f]
H9	0.834(10)	2.952(2)	3.358(2)	O2	112.3(5)	Cl6[a]

[a] $-x, -y+1-z$; [b] $x, y, -z+1/2$; [c] $-x, -y+1, -z+1/2$; [d] $-x+1, -y, -z$; [e] $x, y+1, z$; [f] $-x+1, y+1, z$.

4. Raman and IR studies

Raman and IR spectroscopy at room temperature (293 K) were used to analyse the different observed bands of the mixed compound $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$ (Table 6).

The Raman bands associated with the NH_4^+ cation and those of $HgCl_6$ octahedra were assigned by comparison with the spectra of α-NH_4HgCl_3 [4].

The Raman lines observed at 25 cm^{-1} and 43 cm^{-1} are associated with $(HgCl_3)_n^{n-}$ layers and $(HgCl_4)_n^{2n-}$ chains translations. We have assigned the bands at 53 and 67 cm^{-1} to the translation mode of K^+. The shoulder at 88 and the band at 100 cm^{-1} correspond to the $HgCl_2$ libration of the layers and the chains. A well resolved band at 272 cm^{-1} corresponds to νHg–Cl. The librational mode of NH_4^+ appears at 123 and 190 cm^{-1}, where the translational mode appears at 150 cm^{-1} (Fig. 3).

Table 6
An attempt to assign the observed major bands

Raman (cm^{-1})	IR (cm^{-1})	Attribution
25 Sh		Translations $(HgCl_3)_n^{n-}$
43 m		Layers and chains
53 m		Translations K^+
67 m		
88 Sh		$HgCl_2$ librations of chains and
100 S		layers
123 Sh		Libration NH_4^+
150 W	222 W	Translation NH_4^+
190 W	279 m	Libration NH_4^+
272 S	305 m	νHgCl
	1401 S	νNH_4^+
	1611 S	νNH_4^+
	3006 Sh	νNH_4^+
	3135 m	νNH_4^+

S: Strong; W: Weak; Sh: Shoulder; m: Medium.

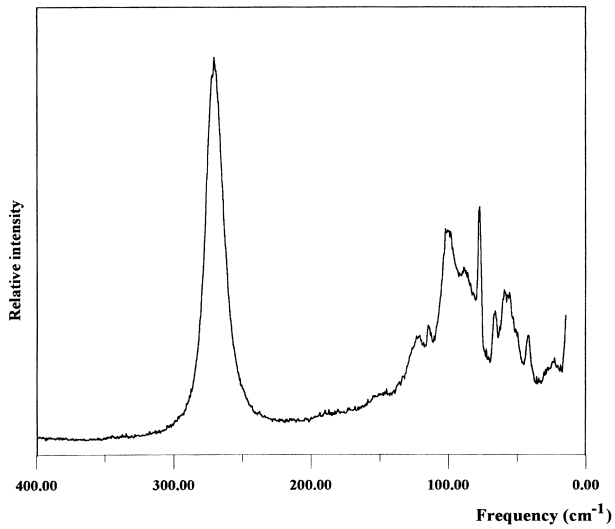

Fig. 3. Raman spectra at room temperature of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$ between 10 and 400 cm^{-1}.

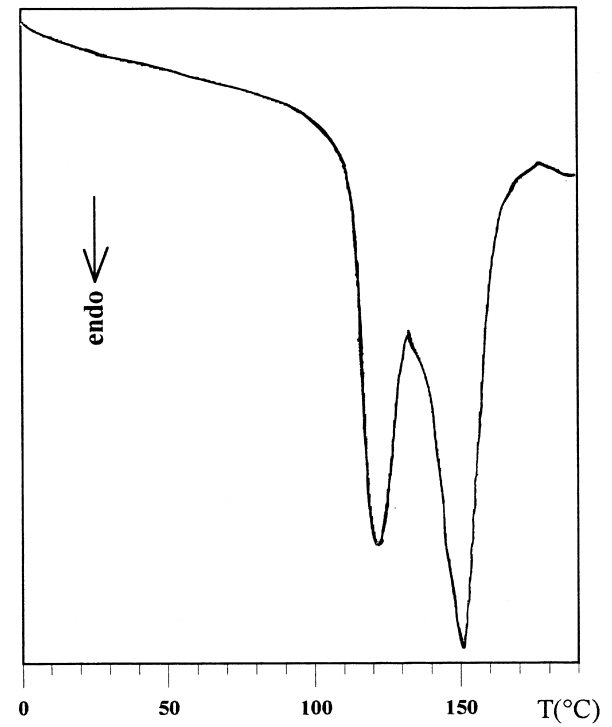

Fig. 4. DSC thermogram of $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}.2H_2O$ in the temperature range 273 K to 463 K.

5. Conclusion

The main feature of this structure is the coexistence of two types of structural motifs derived from the border compounds in the same crystal: it consists of $HgCl_6$ octahedra linked together into $(HgCl_3)_n^{-n}$ layers and $(HgCl_4)_n^{-2n}$ chains. The cohesion of the atomic arrangement is ensured by H bonding contacts (N–H...Cl, N–H...O and O–H...Cl) and ionic bonding between cationic K^+ and $[(HgCl_4)_n^{-2n}-(HgCl_3)_n^{-n}]$ anionic entities. We deduce that the cationic partial substitution disturbs the crystalline symmetry of the pure compounds and imposes the structure of the new solid solution. The mixed compound potassium–ammionium mercurate exhibits two phase transitions at $T_1=395$ K and $T_2=424$ K (Fig. 4). These transitions have been detected by differential scanning calorimetry and Raman Scattering. Additional studies on the nature of the phase transitions (Dielectric measurements, NQR) are under way and shall give more insight into the nature of the structural phase transitions.

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