Alkali metal halogenides coordination compounds with hexamethylenetetramine

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Abstract Six coordination compounds: $[\text{Li}(\text{H}_2\text{O})_4]^+ \cdot \text{hmta} \cdot \text{Cl}^-$, $[\text{Li}(\text{H}_2\text{O})_4]^+ \cdot \text{hmta} \cdot \text{I}^-$, $[\text{Na}(\text{H}_2\text{O})_4(\text{hmta})]_2^{2+} \cdot 2\text{H}_2\text{O} \cdot 2\text{Br}^-$, $[\text{Na}(\text{H}_2\text{O})_4(\text{hmta})]_2^{2+} \cdot 2\text{H}_2\text{O} \cdot 2\text{I}^-$, $[\text{K}(\text{H}_2\text{O})(\text{hmta})\text{I}]_n$ and $[\text{Rb}(\text{H}_2\text{O})(\text{hmta})\text{I}]_n$, have been synthesized and characterised by IR spectroscopy, thermogravimetry coupled with differential thermal analysis, elemental analysis and X-ray crystallography. Both the sodium compounds are isostructural in a solid state, an isostructurality is also observed between compounds containing potassium and rubidium iodides. The sodium compounds exist as dimers (dinuclear core of the complex ion is created by two sodium cations and two water molecules). The molecules of potassium and rubidium compounds are assembled to the two dimensional hybrid nets. The each potentially multifunctional ligand (the hmta) exists in the outer coordination sphere in lithium compounds, acts in a monodentate mode in sodium compounds and in bidentate-bridging modes in potassium and rubidium compounds. The lithium ions are four coordinated, and the sodium, potassium and rubidium ions are six coordinated. Thermal analyses show that the investigated compounds decompose gradually with the formation of alkali metal halides which, during the further heating, are totally removed or they undergo partial decomposition to oxides.

Keywords Alkali metal · Crystal structure · Hexamethylenetetramine · IR spectroscopy · Thermal decomposition

Introduction

The alkali metal ions play important roles in biological systems, for example they incorporate into important biological molecules such as enzymes [1] proteins and peptides [2–4], nucleotides [5] and membrane lipids [6]. The coordination chemistry of alkali metal cations and their interactions with ligands have been widely studied in the past years [7–10] including the chemistry of molecular clusters [11, 12] or macrocyclic compounds [13–15]. Many of the obtained complex compounds have potential applications in biological, inorganic, and synthetic chemistry [16, 17] and in biotechnology [18]. The coordination chemistry of cations such as Li^+ , Na^+ , and K^+ is of the utmost importance because of their significant role in different biological processes [19, 20] especially in the cell biology [21] and natural fluids biochemistry [22, 23]. For example potassium and sodium, together with proteins switching ion channels, are responsible for maintenance of the ionic equilibrium and these cations availability in intercellular fluids are responsible for electrochemical gradients across cell membranes and in consequence for transmitting nerve impulses and regulation of cell functions [21]. The research of compounds containing these cations, their ionic antagonists (like other alkaline metals) with anions existing in body fluids is thus of great importance, as they affect the sodium–potassium pump. In addition, recently, an increasing interest is put on construction of dinuclear, multinuclear and polymeric coordination compounds [24–27] created by self-assembly [28] of the components [29–32].

The present study is a continuation of investigations of the alkali metal salts properties with commercially used antiseptic drug [33], the hexamethylenetetramine which is a clathrate non-chelating neutral N-donor ligand. The hmta

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Table 1 Crystal data and structure refinement details for studied compounds

Compound	1a	1c	2b	2c	3c	4c
Empirical formula	C ₆ H ₂₀ ClLiN ₄ O ₄	C ₆ H ₂₀ LiN ₄ O ₄	C ₁₂ H ₄₄ Br ₂ N ₈ Na ₂ O ₁₀	C ₁₂ H ₄₄ I ₂ N ₈ Na ₂ O ₁₀	C ₆ H ₁₄ IKN ₄ O	C ₆ H ₁₄ IN ₄ ORB
Formula weight	254.65	346.10	666.35	760.33	324.21	370.58
Crystal system, space group	Trigonal, <i>R</i> 32 (No. 155)	Monoclinic, <i>P</i> 2 ₁ / <i>c</i> (No. 14)	Orthorhombic, <i>Pbca</i> (No. 61)	Orthorhombic, <i>Pbca</i> (No. 61)	Monoclinic, <i>C</i> 2/ <i>m</i> (No. 12)	Monoclinic, <i>C</i> 2/ <i>m</i> (No. 12)
Temperature (K)	291.0(3)	291.0(3)	291.0(3)	291.0(3)	291.0(3)	291.0(3)
Wavelength	$\lambda(\text{CuK}\alpha) = 1.54178$	$\lambda(\text{CuK}\alpha) = 1.54178$	$\lambda(\text{MoK}\alpha) = 0.71073$	$\lambda(\text{MoK}\alpha) = 0.71073$	$\lambda(\text{MoK}\alpha) = 0.71073$	$\lambda(\text{MoK}\alpha) = 0.71073$
Unit cell dimensions (Å, °)	$a = 12.5393(3)$ $b = 12.5393(3)$ $c = 43.3500(11)$ $\alpha = 90.00$ $\beta = 90.00$ $\gamma = 120.00$	$a = 9.5910(3)$ $b = 13.9313(12)$ $c = 10.8438(6)$ $\alpha = 90.00$ $\beta = 103.135(4)$ $\gamma = 90.00$	$a = 8.9863(4)$ $b = 17.7349(7)$ $c = 18.2487(8)$ $\alpha = 90.00$ $\beta = 90.00$ $\gamma = 90.00$	$a = 9.0277(9)$ $b = 18.0089(18)$ $c = 18.8356(17)$ $\alpha = 90.00$ $\beta = 90.00$ $\gamma = 90.00$	$a = 18.3370(16)$ $b = 6.7943(9)$ $c = 10.7385(13)$ $\alpha = 90.00$ $\beta = 122.691(9)$ $\gamma = 90.00$	$a = 18.4331(11)$ $b = 6.9396(4)$ $c = 10.9502(7)$ $\alpha = 90.00$ $\beta = 122.983(6)$ $\gamma = 90.00$
Volume (Å ³)	5902.9(2)	1410.99(15)	2908.3(2)	3062.3(5)	1126.0(2)	1174.98(15)
Z, calculated density (Mg/m ³)	18, 1.289	4, 1.629	4, 1.522	4, 1.649	4, 1.913	4, 2.095
Absorption coefficient (mm ⁻¹)	2.655	17.907	2.872	16.878	3.186	6.815
<i>F</i> (000)	2448	688	1376	1520	632	704
Crystal size (mm)	0.118 × 0.096 × 0.080	0.069 × 0.063 × 0.060	0.127 × 0.124 × 0.120	0.080 × 0.076 × 0.071	0.147 × 0.142 × 0.140	0.097 × 0.093 × 0.080
θ range for data collection (°)	3.06–66.09	4.73–69.98	2.23–25.02	4.70–67.98	2.25–25.01	2.22–25.00
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-51 \leq l \leq 51$	$-11 \leq h \leq 11$, $-16 \leq k \leq 16$, $-12 \leq l \leq 13$	$-10 \leq h \leq 10$, $-21 \leq k \leq 20$, $-21 \leq l \leq 21$	$-9 \leq h \leq 10$, $-21 \leq k \leq 21$, $-22 \leq l \leq 22$	$-21 \leq h \leq 21$, $-6 \leq k \leq 8$, $-11 \leq l \leq 12$	$-21 \leq h \leq 21$, $-8 \leq k \leq 7$, $-13 \leq l \leq 13$
Reflections collected/unique	22421/2348 [<i>R</i> _{int}] = 0.0249]	16140/2558 [<i>R</i> _{int}] = 0.0509]	27412/2567 [<i>R</i> _{int}] = 0.0283]	33337/2790 [<i>R</i> _{int}] = 0.0426]	5143/1082 [<i>R</i> _{int}] = 0.0656]	6024/1139 [<i>R</i> _{int}] = 0.0314]
Completeness	99.9% to $\theta = 67^\circ$	99.6% to $\theta = 67.7^\circ$	100% to $\theta = 25^\circ$	99.9% to $\theta = 67^\circ$	100% to $\theta = 25^\circ$	100% to $\theta = 25^\circ$
Min. and max. transmission	0.766–0.814	0.328–0.346	0.697–0.711	0.296–0.331	0.626–0.638	0.516–0.578
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2348/0/147	2558/0/145	2567/0/154	2790/0/154	1082/0/67	1139/0/70
Goodness-of-fit on <i>F</i> ²	1.124	1.127	0.989	1.083	1.090	1.207
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0339, <i>wR</i> ₂ = 0.0881	<i>R</i> ₁ = 0.0544, <i>wR</i> ₂ = 0.1318	<i>R</i> ₁ = 0.0280, <i>wR</i> ₂ = 0.0788	<i>R</i> ₁ = 0.0429, <i>wR</i> ₂ = 0.1175	<i>R</i> ₁ = 0.0301, <i>wR</i> ₂ = 0.0710	<i>R</i> ₁ = 0.0197, <i>wR</i> ₂ = 0.0473
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0340, <i>wR</i> ₂ = 0.0883	<i>R</i> ₁ = 0.0546, <i>wR</i> ₂ = 0.1321	<i>R</i> ₁ = 0.0388, <i>wR</i> ₂ = 0.0806	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.1192	<i>R</i> ₁ = 0.0308, <i>wR</i> ₂ = 0.0716	<i>R</i> ₁ = 0.0234, <i>wR</i> ₂ = 0.0639
Largest diff. peak and hole (e Å ⁻³)	0.329 and –0.407	0.558 and –0.760	0.268 and –0.527	1.332 and –1.035	0.689 and –1.513	0.759 and –0.750

in aqueous media can act as a multifunctional ligand (up to tetradentate mode) and as a multidentate acceptor of hydrogen bonds able to create versatile intramolecular networks [34, 35] and to create ligand–metal–ligand type supramolecular architectures [36–39]. The main goal of the present study was evaluation of the structural behaviour of the alkali metal halides in the presence of hmta in a solid state, and assessing the possibility of multinuclear species formation.

Experimental

Materials and synthesis

All chemicals (analytical grade) were obtained from POCH S.A. and used without further purification. The complex compounds $[\text{Li}(\text{H}_2\text{O})_4]^+\cdot\text{hmta}\cdot\text{Cl}^-$ (**1a**), $[\text{Li}(\text{H}_2\text{O})_4]^+\cdot\text{hmta}\cdot\text{I}^-$ (**1c**), $[\text{Na}(\text{H}_2\text{O})_4(\text{hmta})]_2^{2+}\cdot 2\text{H}_2\text{O}\cdot 2\text{Br}^-$ (**2b**), $[\text{Na}(\text{H}_2\text{O})_4(\text{hmta})]_2^{2+}\cdot 2\text{H}_2\text{O}\cdot 2\text{I}^-$ (**2c**), $[\text{K}(\text{H}_2\text{O})(\text{hmta})\text{I}]_n$ (**3c**) and $[\text{Rb}(\text{H}_2\text{O})(\text{hmta})\text{I}]_n$ (**4c**) were obtained in a direct reaction between the salt and the ligand. The lithium chloride, lithium iodide, sodium bromide, sodium iodide, potassium iodide and rubidium iodide (0.0420, 0.1338, 0.1030, 0.1499, 0.1660, and 0.2120 g, respectively, for **1a**, **1c**, **2b**, **2c**, **3c**, and **4c**) were dissolved in 5 cm³, for **1c**, **3** and **4**, in 3 cm³ for **2b** and **2c**, and in 4 cm³ for **1**, of water and then they were mixed with aqueous solutions of hexamethylenetetramine (molar ratio 1:1). The mixtures were stirred vigorously for 0.5 h, for **2b** and **3**, and 3 h, for **1a**, **1c**, **2c**, and **4c**, on a magnetic stirrer, placed in a refrigerator and left to crystallize at temperature of 5 °C). After 6 (**2b**) and 12 weeks (**1a**, **1c**, **2c**, **3c** and **4c**) the crystals grown. The products were filtered off and dried in air. The mixing of hmta with following salts: MF (M = Li, Na, K, Rb or Cs), NaCl, KCl, KBr, RbCl, RbBr or CsX (X = F, Cl, Br, I) at different proportions (2:1, 1:1 and 1:2) always leads to separate crystallisation (after 7–26 weeks) of pure hmta and pure inorganic salt (the compositions of these samples were confirmed by XRPD, identically as described below for thermal decomposition products). The compound $[\text{Li}(\text{H}_2\text{O})_4]^+\cdot\text{hmta}\cdot\text{Br}^-$ (**1b**) is formed in a solid state, however it always crystallises as fine crystalline powder changing to the amorphous powder outside the solution, and all attempts to obtain single crystals failed.

X-ray crystallography

Colourless rectangular prism shape crystals were mounted in turn on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated MoK α or CuK α radiation (Table 1) at temperature 291.0(3) K, with ω scan mode. The 11–36 s exposures times were used and

reflections inside Ewald sphere were collected up to $\theta = 25^\circ$ and $\theta = 67^\circ$, respectively, for MoK α and CuK α radiation. The unit cells parameters were determined from least-squares refinement of the 4615, 784, 3615, 3408, 836 and 4072 strongest reflections, respectively, for **1a**, **1c**, **2b**, **2c**, **3c** and **4c**. Details concerning crystal data and refinement are given in Table 1. Examination of reflections on two reference frames monitored after each 20 frames measured showed no loss of the intensity during measurements. Lorentz, polarization, and numerical absorption [40] corrections were applied. The structures were solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2 . All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as “riding” on the adjacent atom with individual isotropic displacement factor equal 1.2 times the value of equivalent displacement factor of the parent carbon atoms and 1.5 times for parent oxygen atoms. The carbon bonded hydrogen atom positions were idealised after each cycle of refinement. The SHELXS97, SHELXL97 and SHELXTL [41] software was used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. Selected interatomic bond distances and angles are listed in Table 2, and geometrical parameters of intermolecular interactions are listed in Table 3.

Physical measurements

IR spectra were recorded on a Jasco FT/IR 6200 spectrophotometer in the spectral range 4,000–400 cm^{−1} with the samples in the form of KBr pellets. The thermal analyses were carried out in a TG-DTA-SETSYS-16/18 thermoanalyser coupled with ThermoStar (Balzers) mass spectrometer. The samples were heated in corundum crucibles up to 1200 °C at a heating rate of 2 °C/min in air atmosphere. The processes temperature ranges were determined by means of thermoanalyser Data Processing Module [42]. The solid products of the thermal decomposition were determined from derivatographic curves and on the basis of IR spectra and elemental analyses of the sinters. The final and some transition products of the decomposition were confirmed by X-ray powder diffraction (XRPD) using the powder diffraction file [43]. Elemental analyses were carried out using a Vario EL III CHNOS Elemental Analyzer (C, H, N, O). The alkali metal contents were determined by flame spectrophotometry in mineralised samples. The content of the halogenide ions were determined by potentiometric titrations of mineralised samples with AgNO₃ used as a titrant. Elemental analyses for studied compounds [Calculated/Found (%)] (**1a**): C 28.30/28.22, H 7.92/7.99, O 25.13/25.00, N 22.00/21.97, Li 2.73/2.74, Cl 13.92/14.06; (**1b**): C 24.09/23.95, H 6.69/6.98, O 21.42/22.16, N

Table 2 Selected structural data for studied compounds (Å, °)

1a	1c	2b	2c	3c	4c				
Li1–O2	1.934(4)	Li1–O4	2.3166(19)	Na1–O2	2.335(6)	K1–I1	3.4896(5)	Rb1–I1	3.5904(3)
Li1–O3	1.937(4)	Li1–O3	2.3496(18)	Na1–O3	2.352(7)	K1–O1	2.7834(19)	Rb1–O1	2.963(4)
Li1–O4	1.942(3)	Li1–O2	2.4124(19)	Na1–O4	2.407(8)	K1–O1 ⁱⁱ	2.8285(19)	Rb1–N1	3.190(4)
Li1–O1	1.946(4)	Li1–O1	2.4282(18)	Na1–O1 ^{viii}	2.451(6)	K1–N1	3.105(2)	Rb1–N3 ⁱ	3.338(4)
O2–Li1–O3	115.93(18)	O4–Li1–O2	2.5202(18)	Na1–O1	2.504(6)	K1–N2	3.308(3)	Rb1–O1 ^v	2.898(4)
O2–Li1–O4	110.75(17)	O4–Li1–O3	2.5930(19)	Na1–N1	2.599(6)	K1–I1–K1 ^{vi}	153.56(3)	Rb1–I1–Rb1 ^{vi}	150.22(2)
O3–Li1–O4	98.03(16)	O2–Li1–O3	92.04(6)	Na1–O1–Na1 ^{viii}	94.24(18)	K1–O1–K1 ⁱⁱ	95.00(6)	Rb1–O1–Rb1 ^{vi}	92.72(10)
O2–Li1–O1	110.88(17)	O4–Na1–O3	90.12(6)	O2–Na1–O3	94.0(2)	O1–K1–O1 ⁱⁱ	85.00(6)	O1 ^v –Rb1–O1	87.28(10)
O3–Li1–O1	114.02(18)	O4–Na1–O2	161.60(7)	O2–Na1–O4	94.8(3)	O1–K1–N1	82.69(5)	O1 ^v –Rb1–N1	79.68(10)
O4–Li1–O1	106.05(16)	O3–Na1–O2	98.39(7)	O3–Na1–O4	163.6(3)	O1 ⁱⁱ –K1–N1	167.69(3)	O1–Rb1–N1	166.96(10)
		O4–Na1–O1	80.29(7)	O2–Na1–O1 ^{viii}	101.5(2)	O1–K1–N2 ⁱⁱⁱ	176.86(7)	O1 ^v –Rb1–N3 ⁱ	173.11(11)
		O3–Na1–O1	104.57(7)	O3–Na1–O1 ^{viii}	82.0(2)	O1 ⁱⁱ –K1–N2 ⁱⁱⁱ	98.15(7)	O1–Rb1–N3 ⁱ	99.61(10)
		O2–Na1–O1	81.79(6)	O4–Na1–O1 ^{viii}	82.8(2)	N1–K1–N2 ⁱⁱⁱ	94.17(6)	N1–Rb1–N3 ⁱ	93.43(10)
		O4–Na1–O1 ⁱ	74.83(6)	O2–Na1–O1	165.6(2)	O1–K1–I1	99.551(17)	O1–Rb1–I1	101.640(15)
		O3–Na1–O1 ⁱ	158.69(6)	O3–Na1–O1	74.5(2)	O1 ⁱⁱ –K1–I1	99.859(16)	O1 ^v –Rb1–I1	99.702(18)
		O2–Na1–O1 ⁱ	100.45(7)	O4–Na1–O1	98.5(3)	N1–K1–I1	82.244(15)	N1–Rb1–I1	80.754(18)
		O1–Na1–O1 ⁱ	87.96(6)	O1 ^{viii} –Na1–O1	85.76(18)	N2 ⁱⁱⁱ –K1–I1	79.962(16)	N3 ⁱ –Rb1–I1	79.013(16)
		O4–Na1–N1	109.85(7)	O2–Na1–N1	84.9(2)	I1 ^{iv} –K1–I1	153.56(3)	I1–Rb1–I1 ^{vii}	150.22(2)
		O3–Na1–N1	84.27(7)	O3–Na1–N1	105.0(3)				
		O2–Na1–N1	87.31(6)	O4–Na1–N1	89.5(2)				
		O1–Na1–N1	166.83(7)	O1 ^{viii} –Na1–N1	170.3(2)				
		O1 ⁱ –Na1–N1	86.75(6)	O1–Na1–N1	89.64(18)				

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y, -z$; (iii) $-x, -y, -z$; (iv) $x, y + 1, z$; (v) $-x + 1, -y, -z$; (vi) $x, y - 1, z$; (vii) $x, y + 1, z$; (viii) $-x + 1, -y + 2, -z$

Table 3 Hydrogen bonds in studied compounds (Å, °)

	D–H	H...A	D...A	D–H...A
1a				
O1–H1O...C11 ⁱ	0.95	2.20	3.1493(14)	175.0
O1–H1P...N12 ⁱⁱ	0.87	2.07	2.907(2)	159.5
O2–H2O...N2 ⁱⁱⁱ	0.94	1.95	2.883(2)	175.2
O2–H2P...C13	0.97	2.21	3.1777(16)	174.0
O3–H3O...N1 ^{iv}	0.90	1.91	2.783(2)	163.0
O3–H3P...C12	0.93	2.33	3.2346(16)	167.1
O4–H4O...N11	0.90	1.92	2.801(2)	165.8
O4–H4P...C12	0.94	2.33	3.2000(15)	154.8
1c				
O1–H1O...N2 ^v	0.87	1.95	2.799(4)	166.9
O1–H1P...I1 ^{vi}	0.91	2.69	3.590(4)	172.1
O2–H2O...N3	0.92	1.98	2.886(4)	167.2
O2–H2P...N4 ^{vii}	0.96	1.91	2.861(4)	167.5
O3–H3O...I1 ^{viii}	0.97	2.60	3.563(3)	172.1
O3–H3P...I1	0.95	2.64	3.555(3)	163.9
O4–H4O...O1 ^{vii}	0.83	2.12	2.936(4)	169.3
O4–H4P...N1 ^{ix}	0.94	1.89	2.820(4)	170.3
2b				
O1–H1O...N4 ^v	0.90	1.95	2.846(2)	171.9
O1–H1P...Br1 ^x	0.87	2.90	3.7099(16)	156.5
O2–H2O...O11	0.89	2.03	2.900(3)	166.2
O2–H2P...O11 ^{xi}	0.97	1.98	2.933(3)	167.9
O3–H3O...Br1 ^{xii}	0.90	2.53	3.4232(16)	174.9
O3–H3P...N2 ^{xi}	0.91	1.94	2.849(2)	174.1
O4–H4O...O2 ^x	0.92	2.07	2.974(3)	166.6
O4–H4P...N3 ^{xii}	0.89	1.91	2.799(2)	175.6
O11–H11O...Br1 ^{xiii}	0.92	2.42	3.2935(19)	158.6
O11–H11P...Br1 ^{xiv}	0.94	2.38	3.2625(19)	156.6
2c				
O1–H1O...N2 ^{xv}	0.80	2.06	2.857(7)	168.7
O2–H2O...N4 ^{xvi}	0.72	2.17	2.877(8)	169.5
O2–H2P...I1 ^{xvii}	0.89	2.69	3.584(6)	179.6
O3–H3O...O4 ^{xviii}	0.90	2.13	3.028(12)	178.2
O3–H3P...N3 ^{xix}	0.86	1.98	2.833(8)	177.7
O4–H4O...O99	0.96	2.01	2.968(13)	174.4
O4–H4P...O99 ^{xvi}	0.99	2.00	2.992(14)	175.7
O99–H99P...I1 ^{xxi}	0.86	2.60	3.456(9)	177.3
O99–H99O...I1 ^{xi}	0.90	2.58	3.419(9)	155.8
C4–H4B...O99	0.97	2.58	3.543(12)	171.3
3c				
O1–H1O...N3 ^{xxi}	0.92	1.97	2.876(2)	169
4c				
O1–H1O...N2 ^{xxii}	0.87	1.99	2.863(4)	173.4

Symmetry codes: (i) $x - 1, y, z$; (ii) $x - y - 1/3, -y + 1/3, -z + 1/3$; (iii) $-x, -x + y, -z$; (iv) $-x + y, -x + 1, +z$; (v) $x + 1, y, z$; (vi) $-x + 2, y - 0.5, -z + 0.5$; (vii) $x, -y + 0.5, z - 0.5$; (viii) $-x + 2, -y + 1, -z$; (ix) $-x + 1, -y, -z$; (x) $-x + 1, -y, -z + 1$; (xi) $x + 0.5, y, -z + 0.5$; (xii) $x + 0.5, -y + 0.5, -z + 1$; (xiii) $-x, -y, -z + 1$; (xiv) $-x + 0.5, -y, z - 0.5$; (xv) $-x + 2, -y + 2, -z$; (xvi) $x - 0.5, y, -z + 0.5$; (xvii) $-x + 0.5, y + 0.5, z$; (xviii) $-x + 1, -y + 2, -z$; (xix) $x - 0.5, -y + 2.5, -z$; (xx) $x + 1, y, z$; (xxi) $-x + 0.5, -y + 0.5, -z + 1$; (xxii) $x + 0.5, y - 0.5, z$

18.74/18.50, Li 6.69/6.23, Br 26.74/26.22; (**1c**): C 20.82/20.76, H 5.82/5.93, O 18.49/18.54, N 16.19/16.11, Li 2.01/2.24, I 36.66/36.98; (**2b**): C 24.61/24.69, H 6.60/6.51, N 16.81/16.68, Na 6.90/6.95, Br 23.98/23.54; (**2c**): C 18.94/19.01, H 5.79/5.67, N 14.73/14.70, Na 6.04/5.97, I 33.38/33.30; (**3c**): C 22.21/22.18, H 4.32/4.39, N 17.27/17.22, K 12.06/11.87, I 39.14/39.30; (**4c**): C 19.42/19.32, H 3.78/3.85, N 15.11/15.00, Rb 23.06/23.62, I 34.24/34.01.

Results and discussion

The perspective views of the studied compounds are shown in Figs. 1, 2, 3, 4, 5, and 6. The compounds **2b** and **2c** are isostructural in a solid state and the isostructurality is also observed for compounds **3c** and **4c**. The four carbon atoms of two hmta molecules of compound **1** lie on the two-fold rotation axis (special position *d* of the *R32* space group at

Fig. 1 The molecular conformation of compound **1a** with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are drawn as spheres of arbitrary radii. The symmetry generated atoms (indicated by dashed lines) are obtained by $y, x, -z$ and $-x + 2/3, -x + y + 1/3, -z + 1/3 - x, -y + 1, -z + 1$ symmetry transformation, respectively for atoms with “A” and “B” suffix letters

Fig. 2 The molecular conformation of compound **1c** with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are drawn as spheres of arbitrary radii

$-x, -x, 0$, for C1 and C4 atoms and at $0, x, 0$, for C11 and C41 atoms) and three chloride ions occupy special positions c with site symmetry 3 (three-fold rotation axis) at $0, 0, z$. Thus, the asymmetric unit of **1a** contains one $[\text{Li}(\text{H}_2\text{O})_4]^+$ complex cation, a half of two hmta molecules and one-third of three chloride anions. All atoms of

compound **1c** lie in general positions and thus, the asymmetric unit is composed from one $[\text{Li}(\text{H}_2\text{O})_4]^+$ complex cation, one hmta molecule and one iodide anion. All atoms of compound **2b** and **2c** also lie in general positions, but the complex molecules have the internal inversion centres at $0.5, 0, 0$ (special position b of the $Pbca$ space group) and thus each of them occupies the two asymmetric units. In compounds **3c** and **4c** the iodide anions, metal cations, water molecules, two nitrogen and two carbon atoms of each hmta molecule are located on the mirror plane (special position j of the $C2/m$ space group at $x, 0, z$), therefore, the asymmetric unit contains half of the $\text{M}_3(\text{H}_2\text{O})(\text{hmta})\text{I}$ ($\text{M}_3 = \text{K}$ and Rb) moiety. The above mentioned mirror plane expands the asymmetric unit to the two dimensional hybrid compound extending along crystallographic (100) plane (Fig. 7). The metal centres of **3c** and **4c** create the 4-c uninodal sql/Shubnikov tetragonal plane net, described by $\{4^4.6^2\}$ Schläfli symbol and $[4.4.4.4.6(2)0.6(2)]$ extended point symbol. Some atoms (especially uncoordinated water molecules oxygen atoms and uncoordinated anions) of presented compounds show minor symptoms of disorder what manifests in slightly prolate displacement ellipsoids. Each lithium cation is four coordinated by the four oxygen atoms of water molecules, each sodium cation is six coordinated by one monodentate hmta molecule, three terminal water molecules and two bridging water molecules (analogically to the sodium thiocyanate coordination compound with hmta [44]), and the potassium and rubidium cations are six coordinated by two bridging bidentate

Fig. 3 The molecular conformation of compound **2b** with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are drawn as spheres of arbitrary radii. The

symmetry generated atoms indicated by *dashed lines* are obtained by $-x + 1, -y, -z + 1$ symmetry transformation

Fig. 4 The molecular conformation of compound **2c** with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are drawn as spheres of arbitrary radii. The

symmetry generated atoms indicated by *dashed lines* are obtained by $-x + 1, -y + 2, -z$ symmetry transformation

Fig. 5 The molecular conformation of compound **3c** with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are drawn as spheres of arbitrary radii. The symmetry generated atoms indicated by *dashed lines* are obtained by symmetry transformations (C2A, C3A, H2AA, H2BA, H3AA, H3BA, IA1: $x, -y, z$; N2A: $-x, y, -z$; K1A: $-x, -y, -z$; K1B, O1A: $-x, -y, -z + 1$)

hmta molecules, two bridging iodide ions and two bridging oxygen atoms of water molecules. All bridging water molecules are asymmetrically bonded to the metal ions (Table 2). The coordination polyhedra of the lithium cations can be described as slightly distorted tetrahedra (the sum of the polyhedra internal interbond angles are 655.7 and 656.8°, respectively for **1a** and **1c**, what is close to the ideal value of 656.8°) and sodium, potassium and rubidium cations as distorted tetragonal bipyramids (Fig. 8, Table 4). In both sodium complex compounds the least deformed is

the polyhedron base containing one bridging water molecule, one nitrogen atom and two terminal water molecules, whilst in compounds **3c** and **4c** the polyhedron bases containing two nitrogen and two oxygen atoms are planar by symmetry (Table 4, Fig. 8). The sodium cations are placed close to the polyhedra centres, and potassium and rubidium cations are slightly displaced from such centres (Table 4).

The bond valences were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/b]$ [45, 46], where R_{ij} is the bond-valence parameter (in

Fig. 6 The molecular conformation of compound **4c** with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are drawn as spheres of arbitrary radii. The symmetry generated atoms indicated by dashed lines are obtained by symmetry transformations (C1A, C2A, N2A, H1AA, H1BA, H2AA, H2BA, H1O: $x, -y, z$; N3A, Rb1A: $-x + 1, -y, -z + 1$; Rb1B, O1A: $-x + 1, -y, -z$)

Fig. 7 A part of molecular packing of compounds **3c** and **4c** showing the two dimensional hybrid net. The hydrogen atoms are omitted for clarity

the formal sense R_{ij} can be considered as a parameter equal to the idealised single-bond length between i and j atoms for given b) and b was taken as 0.37 Å [47–50]. The $R_{\text{Li-O}}$, $R_{\text{Na-O}}$, $R_{\text{Na-N}}$, $R_{\text{K-N}}$, $R_{\text{K-O}}$, $R_{\text{K-I}}$, $R_{\text{Rb-N}}$, $R_{\text{Rb-O}}$, and $R_{\text{Rb-I}}$ were taken as 1.466, 1.80, 1.93, 2.26, 2.13, 2.28, 2.37, 2.26 and 3.01, respectively [51]. The computed bond valences of the metal ions (Table 5) show that amongst the studied compounds the Li–O bonds are the strongest ones (as expected, due to lower coordination number of lithium cation in comparison to other used cations, and, in

consequence, sharing valence amongst smaller number of ligands). The all water molecules are bonded to the lithium cation with comparable strengths, whilst in sodium compounds the strongest ones are the two bonds between the metal ions and terminal water molecules, one of Na–O(bridging water) bonds is the weakest one and the Na–N bonds have strength comparable to the other, above unspecified, Na–O bonds. In the potassium and caesium compounds the strongest are $M_3\text{--I}$ bonds, the $M_3\text{--N}$ are the weakest ones, and the $M_3\text{--O}$ bonds have the medium strength in comparison to other coordination bonds. The computed total valences of central atoms are 1.112, 1.137, 1.158, 1.140, 0.868 and 0.927, respectively for compounds **1a**, **1c**, **2b**, **2c**, **3c**, and **4c**. The small overestimating of the formal oxidation states of lithium and sodium originates from relative unimpeded coordination spheres of these metals compounds and underestimation of the formal oxidation states of potassium and rubidium originates from constraints imposed by the relatively rigid hybrid net. The both lithium compounds are assembled by intermolecular hydrogen bonds [52, 53] to the three dimensional supra-molecular networks, however, in compound **1a** each water molecule creates one O–H $\cdots$ N and one O–H $\cdots$ Cl hydrogen bond whilst in compound **1c** the three different hydrogen bonds acceptors (N, I, O) are involved into interactions and two water molecules are hydrogen-bonded to the homo-atomic acceptors (i.e., one water molecule to two N atoms and one water molecule to two I atoms, Table 3). Due to isostructurality the hydrogen bonding scheme in **2b** and **2c** is analogous and multiple O–H $\cdots$ N, O–H $\cdots$ O and O–H $\cdots$ X₂ (X₂ = Br, I) interactions assemble the molecules to the

Fig. 8 The coordination polyhedra of the central atoms. The symmetry generated atoms indicated by *dashed lines* are obtained by symmetry transformations described in Fig. 1, 2, 3, 4, 5, and 6

three dimensional hydrogen-bonded network. In addition, the dinuclear compounds **2b** and **2c** are interlinked by intramolecular O–H···O hydrogen bonds. In compounds **3c** and **4c** only O–H···N intermolecular hydrogen bonds exist, and these ones link neighbouring hybrid nets to the three dimensional network. The analysis of the intermolecular short contacts (the shortest C–H···A contact exists in

compound **2c** for C4–H4B···O99 atoms with H···A and C···A distances 2.58 and 3.54 Å, respectively) shows absence of the interaction which can be classified as weak hydrogen bonds [53, 54].

The characteristic very broad bands observed at a range of 3,448–3,482 cm^{-1} (Table 6) in all of the presented compounds originate from asymmetric O–H vibrations of

Table 4 The geometric properties of weighted least-squares internal polyhedra planes in studied compounds (Å,°)

Plane A	Plane B	Maximum deviating atom within plane A	Deviation of the metal atom from plane A	Dihedral angle between planes A and B
2b				
O1/N1/O2/O4	O1/N1/O3/O1 ⁱ	0.0352(10) for O1	0.1417(12)	85.95(3)
O1/N1/O3/O1 ⁱ	O2/O4/O3/O1 ⁱ	0.3319(11) for N1	0.0719(10)	86.12(4)
O2/O4/O3/O1 ⁱ	O1/N1/O2/O4/	0.3604(11) for O4	0.0469(12)	85.66(4)
2c				
O1 ^{viii} /N1/O2/O1	O1 ^{viii} /N1/O3/O4	0.2282(34) for N1	0.0483(34)	84.33(14)
O1 ^{viii} /N1/O3/O4	O2/O1/O3/O4	0.0020(44) for O1 ^{viii}	0.1395(46)	85.09(14)
O2/O1/O3/O4	O1 ^{viii} /N1/O2/O1	0.2512(40) for O3	0.0735(43)	87.22(15)
3c				
N1/O1 ⁱⁱ /I1/I1 ^{iv}	N2 ⁱⁱⁱ /O1/I1/I1 ^{iv}	0.5141(02) for N1	0.1303(09)	88.04(4)
N2 ⁱⁱⁱ /O1/I1/I1 ^{iv}	N2 ⁱⁱⁱ /O1/N1/O1 ⁱⁱ	0.2476(10) for N2 ⁱⁱⁱ	0.3038(12)	90.00(1)
N2 ⁱⁱⁱ /O1/N1/O1 ⁱⁱ	N1/O1 ⁱⁱ /I1/I1 ^{iv}	0.0000(0)	0.0000(00)	90.00(1)
4c				
N1/O1/I1/I1 ^{vii}	N3 ⁱ /O1 ^v /I1/I1 ^{vii}	0.5840(17) for N1	0.1404(15)	88.04(6)
N3 ⁱ /O1 ^v /I1/I1 ^{vii}	N3 ⁱ /O1 ^v /N1/O1	0.2649(17) for N3 ⁱ	0.4168(16)	90.00(1)
N3 ⁱ /O1 ^v /N1/O1	N1/O1/I1/I1 ^{vii}	0.0000(0)	0.0000(0)	90.00(1)

Symmetry codes as in Table 2

Table 5 Bond valences (v.u.)

1a		1c		2b		2c		3c		4c	
Li1–O2	0.282	Li1–O4	0.304	Na1–O4	0.248	Na1–O2	0.236	K1–I1/I1 ^{iv}	0.193	Rb1–I1/I1 ^{iv}	0.208
Li1–O3	0.280	Li1–O2	0.288	Na1–O3	0.226	Na1–O3	0.225	K1–O1	0.171	Rb1–O1	0.150
Li1–O4	0.276	Li1–O3	0.278	Na1–O2	0.191	Na1–O4	0.194	K1–O1 ⁱⁱ	0.151	Rb1–O1 ^v	0.178
Li1–O1	0.273	Li1–O1	0.266	Na1–O1	0.183	Na1–O1 ^{viii}	0.172	K1–N1	0.102	Rb1–N1	0.109
				Na1–O1 ⁱ	0.143	Na1–O1	0.149	K1–N2	0.059	Rb1–N3 ⁱ	0.073
				Na1–N1	0.167	Na1–N1	0.164				

Symmetry codes as in Table 2

water molecules. The C–N stretching vibrations of the hmta molecules existing at 815 cm^{−1} for pure and outer coordination sphere (compounds **1a** and **1c**) hmta molecules are split into two bands (mostly lower shifted, Table 6) in compounds **2b**, **2c**, **3c** and **4c** due to formation of metal–N coordination bonds [55]. The two bands at 1,670 and 1,640 cm^{−1} (Table 6) existing in compounds **2b** and **2c** spectra proof that these compounds contain two types of water molecules located in outer and inner coordination sphere (Table 6) [56]. For other compounds (**1a**, **1c**, **3c**, **4c**) only bands originating from the inner coordination sphere water molecules are observed (Table 6). The bands at about 700 cm^{−1} of $\nu_{\text{M–H}_2\text{O}}$ vibrations (Table 4) proof coordination of water molecules to the metal ions [33, 55, 57]. The band at about 1,240 cm^{−1} is not split in the studied compounds what proofs that in all cases at least one nitrogen atom is not coordinated to the metal ion [33]. In all analysed compounds the stretching vibrations of

hmta methylene groups are distinctly shifted and slightly broadened in comparison to the pure ligand due to different surrounding of the CH₂ groups in the crystal nets of the studied compounds and pure hmta [56, 58, 59].

The thermal decomposition of the studied compounds is a gradual process (Scheme 1). In all compounds the decomposition begins with endothermic removal of water molecules. In general, water molecules are lost in two steps apart from compounds **3c** and **4c** where they are removed in a single process. For each compound the water evolution starts at different temperatures. In **2b** water evaporation starts at 23 °C whilst in **3c** and **4c** the process begins at 73 and 58 °C, respectively. Next, the anhydrous coordination compounds lose hmta molecules. In **2b**, **2c**, **3c**, and **4c** the whole amine is released during its one-step endothermic sublimation process. It is a quick process and after this, the sublimated hmta molecules are oxidised to volatile products—the ion current signals corresponding to C⁺, CO⁺,

Table 6 Vibrational frequencies (cm^{-1}) and their assignment in studied compounds

1a	1c	2b	2c	3c	4c	hmta [65, 66]	Assignment
	3481bb	3486bb	3480bb	3482bb			$\nu_{\text{as}}(\text{O-H})$
3452w		3448bb	3453bb	3463bb			$\nu_{\text{as}}(\text{O-H})$
2964w		2951vw	2963vw	2954vw	2956w	2955	$\nu_{\text{s}}(\text{CH}_2)$
2937w	2936w	2938w	2936w			2949	$\nu_{\text{as}}(\text{CH}_2)$
				2923w	2926w	2934	$\nu_{\text{s}}(\text{CH})$
				2905vw		2909	$\nu_{\text{s}}(\text{CH}_2)$
2888w	2893w	2890w	2893w	2874w	2879w	2874	$\nu_{\text{s}}(\text{CH}_2)$
		1669m	1669w				$\delta(\text{O-H})_{\text{outer coordination sphere water molecules}}$
1617vw		1637vw	1636w	1637vw	1608vw		$\delta(\text{O-H})_{\text{inner coordination sphere water molecules}}$
	1487vw	1488vw	1481vw	1482w	1483w	1485	$\rho(\text{CH}_2)$, $\rho(\text{CH}_2)$, CNC deformation
1463m	1465m	1465s	1466s	1461s	1461s	1460	$\sigma(\text{CH}_2)$, CH_2 deformation
	1448vw	1448vw	1448vw			1440	$\sigma(\text{CH}_2)$
1381m	1381m	1379s	1380m	1379s	1383s	1370	$\tau(\text{CH}_2)$
	1353w	1350w	1349w	1351w	1337w	1346	$\omega(\text{CH}_2)$
1320vw	1339vw	1323vw	1319vw	1322w		1324	$\tau(\text{CH}_2)$
		1314vw	1313vw			1306	$\omega(\text{CH}_2)$, $\tau(\text{CH}_2)$
1240s	1238s	1237vs	1238vs	1239vs	1241vs	1240	$\rho(\text{CH}_2)$, $\nu(\text{C-N})$
1185vw	1187vw	1183vw	1198vw	1207w		1192	$\omega(\text{CH}_2)$
	1122vw	1121vw	1127vw	1129vw		1129	CNC deformation
	1053w	1058w	1052w	1047w		1048	$\tau(\text{CH}_2)$, CNC deformation, $\delta(\text{NCN})$
1007vs	1008vs	1008vs	1008vs	1007vs	1008vs	1007	$\nu(\text{C-N})$
	947w	937w	935w			933	$\rho(\text{CH}_2)$
938w			920vw	929w	929w	925	$\nu(\text{C-N})$, $\rho(\text{CH}_2)$
815m	815m	817m, 794w	814m, 797w	812s, 782w	805m, 784m	815	$\nu(\text{C-N})$, $\rho(\text{CH}_2)$
		783w				779	$\nu(\text{C-N})$
688m	688m	738m	720m	681m	682m		$\nu(\text{M-O})$
		691s	668m	672s	670m	673	$\delta(\text{N-C-N})$, CNC deformation
	531vw	512vw		512vw	510vw	512	$\tau(\text{NCN})$
	462vw		458vw			463	$\delta(\text{NCN})$

vw very weak, w weak, m medium strength, s strong, vs very strong, ν stretching, δ bending, ρ rocking, σ scissoring, τ wagging, ω twisting, s symmetric, as asymmetric, bb broad band

CO_2^+ , N^+ , NO^+ and HCOOH^+ are observed [60] in generated gases. The increase of ion currents is observed at higher temperatures comparing to the temperature of the amine sublimation due to crystallization of the sublimated hmta molecules inside the mass spectrometer system [61]. In **1a** and **1c** the amine molecules are removed in two substages. First, similarly to above described compounds, the hmta molecules sublimate. In the second substage, the remaining amine molecules are combusted within the sample in an exothermic process [62]. At this point the decomposition of the investigated compounds decelerates and the alkali metal halides are formed. Next the salts begin to decompose, at first this is a slow process with almost negligible mass loss—the exception is compound **1c** where significant mass loss is seen earlier, at lower temperatures (lithium iodide melts at about 460 °C). The further thermal decomposition accelerates when the

temperature reaches the melting point of the formed halides. In case of **1a**, **1c**, **2c**, and **3c** the salts are totally removed. In **2b** and **4c** the salts undergo partially evaporation and partially decomposition to the alkali metal oxides and the final, stable products are Na_2O and Rb_2O (respectively, for **2b** and **4c**).

Conclusion

The reaction of alkali metal halogenides with hmta (performed in molar ratio 1:1) leads to the formation of coordination complex compounds, mononuclear in case of lithium compounds, dinuclear sodium compounds and polymeric potassium and rubidium compounds, thus the ability to formation of multinuclear species depends only on the type of metal and it increases with increasing atomic

Scheme 1 Stages of the thermal decomposition of studied compounds (*m.l.* experimental mass loss/theoretical mass loss, *v.p.* volatile products, *product was confirmed by XRPD)

Anion/Cation	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs
F ⁻			coordination compounds		
Cl ⁻	[Li(H ₂ O) ₄] ⁺ ·hmta·Cl ⁻				
Br ⁻	[Li(H ₂ O) ₄] ⁺ ·hmta·Br ⁻	[Na(H ₂ O) ₄ (hmta)] ₂ ²⁺ ·2H ₂ O·2Br ⁻			
I ⁻	[Li(H ₂ O) ₄] ⁺ ·hmta·I ⁻	[Na(H ₂ O) ₄ (hmta)] ₂ ²⁺ ·2H ₂ O·2I ⁻	[K(H ₂ O)(hmta)] _n	[Rb(H ₂ O)(hmta)] _n	
		Total decomposition		are not formed	Partial decomposition

Fig. 9 The reactivity of hmta towards alkali metal halogenides, together with demarcation of differences in thermal decomposition

number (Fig. 9). In lithium compounds the hmta molecules are located in the outer coordination sphere and in sodium, potassium and rubidium compounds in the inner coordination sphere. The thermal decomposition of studied compounds proceeds via halogenides or metal oxides with evolving halogens [62–64] (Fig. 9).

Supplementary data

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No CCDC859820, CCDC859821, CCDC859822, CCDC859823, CCDC859824, and CCDC859825, respectively for compounds **1a**, **1c**, **2b**, **2c**, **3c**, and **4c**.

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