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Ureates and hydrates of magnesium chloride, nitrate and tetrafluoroborate

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Five magnesium complexes two of which with tetrafluoroborate anion $[U_6Mg]^{2+}.2BF_4^-$ – **1**, $[(H_2O)_6Mg]^{2+}.2BF_4^-$ – **2**, two with chloride anion – $[U_6Mg]^{2+}.2Cl^-.4U$ – **3**, $[U_4Mg(H_2O)_2]^{2+}.2Cl^-$ – **4** and one with nitrate anion – $[U_6Mg]^{2+}.2NO_3^-$ – **5**, have been synthesized. Crystals suitable for X-ray diffraction have been obtained by slow evaporation from aqueous solutions. The single crystal X-ray studies showed that compounds **1** and **2** crystallize in orthorhombic $P2_12_12$ (a = 9.964(5), b =11.979(6), c = 9.638(5)) and in orthorhombic $Pnnm$ (a = 5.4322(6), b = 13.2050(12), c = 7.6786(6)) space groups respectively. Compounds **3** and **4** crystallize in the monoclinic $P2_1/c$ space group with unit cell parameters a = 9.6317(8), b = 7.2241(7), c = 23.506(3), β = 94.045(9) and a = 8.0168(16), b = 14.844(2), c = 28.662(4), β= 94.194(16) respectively. Compound **5** crystallizes in the triclinic P–1 space group with a = 7.1917(6), b = 8.279(3) c = 9.555(9), α = 71.01(6), β = 89.17(3), γ = 84.158(19).

Keywords: magnesium tetrafluoroborate, magnesium chroride, magnesium nitrate, ureate, hydrate, single crystal.

INTRODUCTION

It is well known that Mg^{2+} coordinates with ligands containing urea moiety. Up to now single crystal studies of magnesium complexes with formamide [1], DMF [2], methylurea [3] and dimethylurea [4] have been conducted. Such studies exploit the Mg^{2+} bioavailability and its role as co-factor in many enzymes [5], for energy production in the transformation of adenosine triphosphate (ATP) and adenosine diphosphate (ADP) [6], in the DNA extension by Polymerase and for the building of the chlorophyll center [7]. From the above mentioned magnesium complexes, those involving urea are extensively characterized including bromide [8, 9], sulfate [10, 11], formate [12, 13], dihydrogen phosphate [14], chlorate [15] and nitrate [16] salts. The diversity of the Mg^{2+}-urea complexes (excluding the formate and dihydrogen phosphate salts) can be generalized in two main structural types: $[U_6Mg]^{2+}$ and $[U_4Mg(H_2O)_2]^{2+}$. In all cases the magnesium is octahedrally coordinated [17, 18]. Here we report the synthesis and crystal structure analysis of five magnesium complexes: two with tetrafluoroborate anion $[U_6Mg]^{2+}.2BF_4^-$ – **1**, $[(H_2O)_6Mg]^{2+}.2BF_4^-$ – **2**, two with chloride anion – $[U_6Mg]^{2+}.2Cl^-.4U$ – **3**, $[U_4Mg(H_2O)_2]^{2+}.2Cl^-$ – **4** and one with nitrate anion – $[U_6Mg]^{2+}.2NO_3^-$ – **5**.

MATERIALS AND METHODS

Single crystal samples of the synthesized complexes were obtained by slowly evaporation from aqueous solution of the corresponding magnesium salt and urea in equimolar proportions at room temperature. All compounds (except MgO – Merck) were purchased from Sigma-Aldrich and were used with no further purification.

*Synthesis of hexakis(urea-O) magnesium bis(tetrafluoroborate), $[U_6Mg]^{2+}.2BF_4^-$, **1***

Magnesium tetrafluoroborate was prepared according to a modified methodology [19] by reacting magnesium oxide and tetrafluoroboric acid in an equilibrium manner.

MgO (4.03 g, 0.1 mol) was mixed in 10 ml distilled water and 13 ml (8.78 g, 0.1 mol) of 48%

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HBF_4 were added dropwise with stirring. After one hour a clear solution of magnesium tetrafluoroborate was formed. The water was removed in vacuo to give a quantitative yield of $[(H_2O)_6Mg]^{2+}2BF_4^-$ as a microcrystalline phase.

Hexaaqua magnesium tetrafluoroborate (305.9 mg, 0.001 mol) and urea (360.4 mg, 0.006 mol) were dissolved in 10 ml distilled water and after slow evaporation of the aqueous solution single crystal samples of **1** were obtained.

*Synthesis of hexakis(aqua) magnesium bis(tetrafluoroborate), $[(H_2O)_6Mg]^{2+}.2BF_4^-$, **2***

Hexaaqua magnesium tetrafluoroborate (305.9 mg, 0.001 mol) was dissolved in 10 ml distilled water and after slow evaporation single crystal samples of **2** were obtained.

*Synthesis of hexakis(urea-O) magnesium dichloride tetraurea, $[U_6Mg]^{2+}.2Cl^-.4U$, **3***

Anhydrous magnesium chloride (95.21 mg, 0.001 mol) and urea (600.6 mg, 0.02 mol) were dissolved in 10 ml distilled water and after slow evaporation of the aqueous solution single crystal samples of **3** were obtained.

*Synthesis of bis(aqua) tetrakis(urea-O) magnesium dichloride, $[U_4Mg(H_2O)_2]^{2+}.2Cl^-$, **4***

Anhydrous magnesium chloride (95.21 mg, 0.001 mol) and urea (240.2 mg, 0.004 mol) were dissolved in 5 ml distilled water and after slow evaporation of the aqueous solution single crystal samples of **4** were obtained.

*Synthesis of hexakis (urea-O) magnesium dinitrate, $[U_6Mg]^{2+}.2NO_3^-$, **5***

MgO (4.03 g, 0.1 mol) was dissolved in 5 ml distilled water and 6.5 ml (6.04 g, 0.1 mol) of 65% HNO_3 were added dropwise. The mixture was then stirred for one hour. The excess water was removed by heating. After the reaction mixture cool down colorless crystals of Hexaaqua magnesium nitrate $[(H_2O)_6Mg]^{2+}.2NO_3^-$ were obtained.

Hexaaqua magnesium nitrate (256.4 mg, 0.001 mol) and urea (360.4 mg, 0.006 mol) were dissolved in 10 ml distilled water and after slow evaporation of the aqueous solution single crystal samples of **5** were obtained.

Single crystal X-ray diffraction

Suitable single crystals of compounds **1-5** were mounted on a glass capillaries. The intensity and diffraction data for compound **1** were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a scintillation detector and using graphite monochromated Mo Kα radiation (λ = 0.71073). Diffraction data for compounds **2–5** were collected on an Agilent SupernovaDual diffractometer equipped with an Atlas CCD detector using micro-focus Mo Kα radiation (λ = 0.71073). Collection and data reduction program was CrysAlisPro, Rigaku Oxford Diffraction, 2017, version 1.1.171.37.35 [20]. Due to the thermal instability (i.e. high hygroscopicity, lack of diffraction after 10–15 min) of compounds **2–4** at ambient conditions data collection were performed by flash freezing the crystals at 150 K in N_2 stream using Cobra, Oxford cryosystem. The crystal structures were solved by direct methods with ShelxS and refined by the full-matrix least-squares method of F^2 with ShelxL programs [21, 22]. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. Hydrogen atoms were placed at calculated positions using a riding scheme (*Ueq* = 1.2 for N-H = 0.86 Å). The ORTEP [23] drawings of the molecules present in the asymmetric unit and the most important crystallographic parameters from the data collection and refinement are shown in Figure 1–5 and Table 1 respectively. The figures concerning crystal structure description and comparison were prepared using Mercury software (version 3.9) [24]. Selected bonds lengths, angles and torsion angles are given in Tables 2 and 3.

RESULTS AND DISCUSSION

Crystal structures of magnesium tetrafluoroborate ureates or hydrates have not been previously reported. The conducted search in the ICDD and ICSD databases returned only a powder diffractogram of anhydrous magnesium tetrabluorobate. Subsequent search for crystal structure data of magnesium chlorides urea salts also did not return results. The case of magnesium nitrate ureas is a little bit different as such compounds have been investigated since the 1930s [25]. The authors managed to define the space group and unit cell parameters of $[U_4Mg\ (H_2O)_2]^{2+}.2NO_3^-$. Later, other authors report the isolation of ureas of magnesium nitrate with variable urea and water content in the crystal structure [26–28]. Interestingly, there are data for only one crystal structure: $[U_4Mg(H_2O)_2]^{2+}.2NO_3^-$ [16]. Among the magnesium halides only two crystal structures of two urea complexes of magnesium

Table 1. Most important data collection and refinement parameters for compounds **1–5**

Compound	1	2	3	4	5
Empirical formula	$C_6H_{24}B_2F_8MgN_{12}O_6$	$B_2F_8H_{12}MgO_6$	$C_{10}H_{40}Cl_2MgN_{20}O_{10}$	$C_4H_{20}Cl_2MgN_8O_6$	$C_6H_{24}MgN_{14}O_{12}$
Formula weight	558.30	306.03	695.83	371.49	508.70
Temperature/K	290	150	150	150.0	290
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_12_12$	*Pnnm*	$P2_1/c$	$P2_1/c$	P–1
a/Å	9.964(5)	5.4322(6)	9.6317(8)	8.0168(16)	7.1917(6)
b/Å	11.979(6)	13.2050(12)	7.2241(7)	14.844(2)	8.279(3)
c/Å	9.638(5)	7.6786(6)	23.506(3)	28.662(4)	9.555(9)
α/°	90	90	90	90	71.01(6)
β/°	90	90	94.045(9)	94.194(16)	89.17(3)
γ/°	90	90	90	90	84.158(19)
Volume/Å^3	1150.3(10)	550.80(9)	1631.5(3)	3401.7(10)	535.0(6)
Z	2	2	2	8	1
ρ_{calc} (g/cm^3)	1.612	1.845	1.416	1.451	1.579
μ/mm^{-1}	0.192	0.288	0.292	0.454	0.171
F(000)	572.0	308.0	732.0	1552.0	266.0
Crystal size/mm^3	0.2×0.15×0.1	0.3×0.25×0.25	0.25×0.2×0.2	0.35×0.3×0.3	0.25×0.2×0.2
Radiation, λ [Å]	Mo*K*α λ = 0.71073	Mo*K*α λ = 0.71073	Mo*K*α λ = 0.71073	Mo*K*α λ = 0.71073	Mo*K*α λ = 0.71073
2Θ range for data collection/°	4.226 to 55.922	6.17 to 55.912	5.902 to 56.832	5.67 to 57.068	7.33 to 56.866
Reflections collected	5745	1442	6794	14528	3595
Reflections independent	2777	606	3332	7093	2173
R_{int}/ R_{sigma}	0.0466/0.0575	0.0244/0.0232	0.0673/0.1073	0.1143/ 0.1854	0.0205/0.0333
Data/restraints/ parameters	2777/0/159	606/0/72	3332/0/196	7093/0/383	2173/0/151
Goodness-of-fit on F^2	1.041	1.077	1.051	1.133	1.058
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.0416 wR_2 = 0.0975	R_1 = 0.0530 wR_2 = 0.1420	R_1 = 0.0647 wR_2 = 0.1096	R_1 = 0.1398 wR_2 = 0.3503	R_1 = 0.0438 wR_2 = 0.1028
Final *R* indexes [all data]	R_1 = 0.0681 wR_2 = 0.1087	R_1 = 0.0717 wR_2 = 0.1613	R_1 = 0.1494 wR_2 = 0.1491	R_1 = 0.2545 wR_2 = 0.4473	R_1 = 0.0555 wR_2 = 0.1127
Largest diff. peak/ hole /e Å^{-3}	0.29/–0.23	0.35/–0.25	0.27/–0.25	1.39/–1.09	0.50/–0.34

Table 2. Selected bonds for structures **1–5**

Compounds	1	2	3	5	4		4	
Bonds	Å	Å	Å	Å	Bonds	Å	Bonds	Å
Mg1—O1	2.059(2)	2.065(2)	2.057(3)	2.067(2)	Mg11—O11	2.092(7)	Mg12—O12	2.064(8)
Mg1—O2	2.052(2)	2.061(3)	2.074(3)	2.0414(16)	Mg11—O21	2.015(7)	Mg12—O22	2.063(7)
Mg1—O3	2.105(2)	–	2.078(2)	2.0907(14)	Mg11—O31	2.096(7)	Mg12—O32	2.083(8)
O1—C1	1.250(4)	–	1.242(4)	1.246(3)	Mg11—O41	2.066(7)	Mg12—O42	2.056(7)
O2—C2	1.250(3)	–	1.240(5)	1.236(3)	Mg11—O51	2.100(8)	Mg12—O52	2.040(9)
O3—C3	1.254(4)	–	1.256(5)	1.253(2)	Mg11—O61	2.038(8)	Mg12—O62	2.096(8)
C1—N11	1.316(5)	–	1.338(5)	1.339(3)	O11—C11	1.240 (12)	O12—C12	1.247(12)
C1—N12	1.328(5)	–	1.344(5)	1.331(3)	O21—C21	1.247(13)	O22—C22	1.249(13)
C2—N21	1.332(4)	–	1.319(5)	1.332(3)	O31—C31	1.261(12)	O32—C32	1.241(12)
C2—N22	1.317(4)	–	1.339(6)	1.334(3)	O41—C41	1.238(13)	O42—C42	1.210(12)
C3—N31	1.336(4)	–	1.327(5)	1.327(3)	N21—C11	1.319(13)	C42—N82	1.289(17)
C3—N32	1.328(5)	–	1.325(4)	1.329(3)	C31—N51	1.345(17)	C21—N41	1.314(18)

Table 3. Selected Angles and Torsion angles for structures **1**–**5**

Compounds	1	2	3	5	Compound	4
Angles	°	°	°	°	Angles	°
O2—Mg1—O1	84.11(9)	89.22(9)	86.92(10)	88.45(8)	O22—Mg12—O32	93.5(3)
O2—Mg1—O3	95.54(9)	–	88.03(10)	90.65(6)	O12—Mg12—O22	88.5(3)
C1—O1—Mg1	139.8(2)	–	135.1(3)	143.52(14)	C11—O11—Mg11	162.3(7)
C2—O2—Mg1	141.89(19)	–	133.8(2)	140.78(14)	C12—O12—Mg12	155.6(7)
C3—O3—Mg1	132.9(2)	–	133.8(3)	133.56(14)	C31—O31—Mg11	138.0(7)
N11—C1—N12	117.6(3)	–	116.9(4)	117.4(2)	N32—C22—N42	117.9(12)
N22—C2—N21	117.5(3)	–	116.9(4)	118.3(2)	N52—C32—N62	115.3(10)
N32—C3—N31	117.1(3)	–	117.4(4)	117.76(19)	N81—C41—N71	118.2(11)
Torsion angles	°	°	°	°	Torsion angles	°
Mg1—O1—C1—N12	12.9(6)	–	175.6(2)	–175.21(17)	Mg12—O42—C42—N72	–149.60(15)
Mg1—O2—C2—N22	16.5(6)	–	–157.3(3)	–179.17(17)	Mg12—O32—C32—N62	178.51(15)
Mg1—O3—C3—N32	4.1(5)	–	–176.0(2)	158.97(16)	Mg11—O11—C11—N11	103.68(12)

bromide: hexaurea magnesium bromide tetra urea $[U_6Mg]^{2+}$ $2Br^-.4U$ [8] and diaqua tetraurea magnesium dibromide $[U_4Mg(H_2O)_2]^{2+}2Br^-$ [9] have been reported. Following the synthesis by using the technique of slow evaporation from an aqueous solution, we were able to grow single crystals of five magnesium salts: two with tetrafluoroborate anion $[U_6Mg]^{2+}.2BF_4^-$ – **1**, $[(H_2O)_6Mg]^{2+}.2BF_4^-$ – **2**, two with chlorine anion – $[U_6Mg]^{2+}.2Cl^-.4U$ – **3**, $[U_4Mg(H_2O)_2]^{2+}.2Cl^-$ – **4** and one with nitrate anion – $[U_6Mg]^{2+}.2NO_3^-$ – **5**. The problem with the crystal structure determination of urea complexes of magnesium chlorides is associated with their relative instability at ambient temperature. Actually, the performed room temperature data collection resulted in good diffraction of the crystals for 10–15 minutes after what diffraction disappeared almost instantly. The attempted X-ray powder data collection was also unsuccessful. Thus we performed single crystal data collection by flash freezing the crystals in N_2 at 150 K.

Compound 1, $[U_6Mg]^{2+}.2BF_4^-$ crystallizes in orthorhombic $P2_12_12$ space group with one BF_4^- molecule and ½ of the $[U_6Mg]^{2+}$ moiety in the asymmetric unit. The Mg–O and urea bond lengths and angles are comparable to those analogous com-

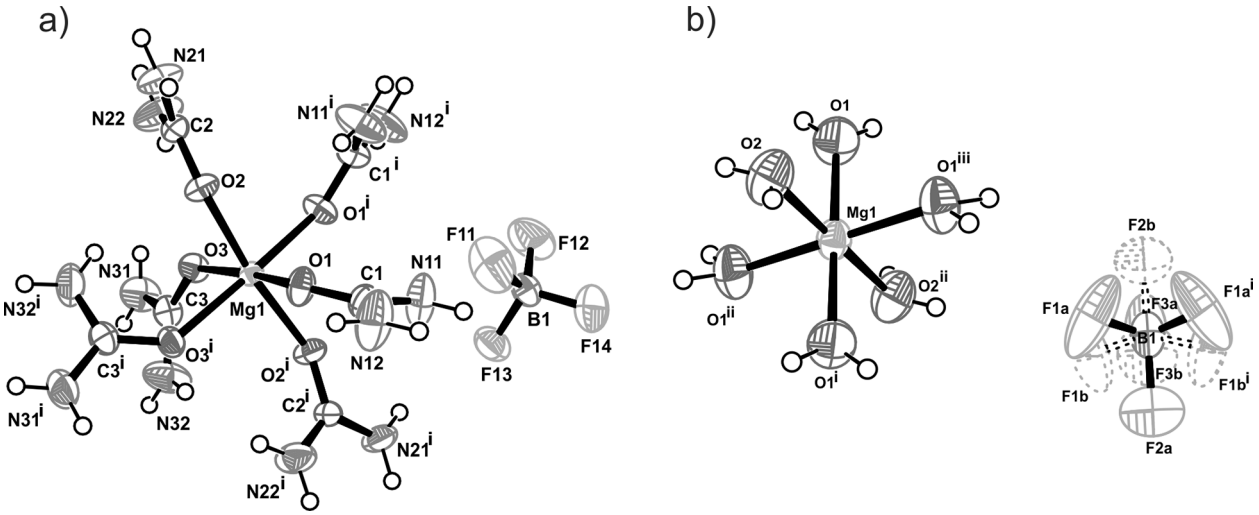

Fig. 1. View of the molecular structures of compounds **1** – a) (symmetry operation: i: *1-x*,1-*y*,*z*) and **2** – b) (symmetry operations: (i): *x*,*y*,*1-z*; (ii): *2-x*,1-*y*,*z* (iii): *2-x*,1-*y*,*1-z* with atomic numbering scheme. Atomic displacement parameters for the non-H atoms are drawn at the 50% probability level; the H atoms are presented with spheres with arbitrary radii. The minor disordered component (44%) of the BF_4^- is shown as dashed lines.

pounds [10, 11, 14, 16] Table 2 and 3. Magnesium coordination is octahedral, very slightly distorted, with four Mg–O distances of ~2.0 Å and two longer distances 2.1 Å. The four oxygen atoms exhibiting shorter bond distances with Mg are nearly planar (the mean plane defined by the four oxygen has an *rms* of 0.103 Å). The Mg–O geometry is stabilized trough six N-H…O intramolecular hydrogen bonds (Table 4). The BF_4^- moiety tetrahedral geometry is close to the expected ideal geometry: three of the bond lengths are nearly identical (~1.37 Å) and one is shorter 1.349 Å, while the angles F-B-F vary from 107.7 to 110.5°. All of the F atoms are involved in halogen bonding F…N with NH from urea (Table 3).

Compound 2, $[(H_2O)_6Mg]^{2+}.2BF_4^-$, crystallizes in orthorhombic *Pnnm* space group. The magnesium octahedral coordination is completed by six water molecules. The octahedra is "perfect" as Mg, O1 and O2 atoms are situated on special positions. The two Mg–O distances have comparable values (~2.06 Å) and are intermediate to those of compound **1** where Mg is coordinated by six urea oxygens. The BF_4^- molecule is disordered over two position with a major component of 56%. For compound **2** no intramolecular hydrogen bond interactions could be located. Similarly to compound **1** the all F atoms (from BF_4^-) are involved in halogen bonding interactions of O–H…F type (Table 5).

Table 4. Hydrogen bonded geometry (Å, °) for compound **1**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21*A*···F1^{3}i	0.86	2.34	3.092 (4)	147
N21—H21*B*···O^{3i}i	0.86	2.40	3.108 (4)	141
N21—H21*B*···O^{1ii}i	0.86	2.42	3.157 (4)	144
N32—H32*A*···O^{3}i	0.86	2.46	3.065 (4)	128
N32—H32*A*···O^{2}i	0.86	2.63	3.156 (5)	121
N32—H32*A*···F1^{2i}v	0.86	2.64	3.055 (4)	111
N32—H32*B*···F1^{1}v	0.86	2.24	3.056 (5)	158
N32—H32*B*···F1^{4}v	0.86	2.53	3.278 (5)	146
N22—H22*A*···O3	0.86	2.53	3.263 (4)	143
N22—H22*A*···F1^{3i}i	0.86	2.38	2.936 (4)	123
N22—H22*B*···O^{2ii}i	0.86	2.52	3.297 (4)	150
N22—H22*B*···O^{1ii}i	0.86	2.51	3.224 (4)	142
N31—H31*A*···F1^{3i}i	0.86	2.42	3.152 (4)	143
N31—H31*B*···F1^{2}v	0.86	2.64	3.444 (5)	157
N12—H12*B*···F1^{4v}i	0.86	2.25	3.073 (5)	159
N11—H11*A*···F11	0.86	2.19	2.825 (4)	130
N11—H11*B*···F1^{2v}i	0.86	2.18	3.027 (4)	170

Symmetry operations: (i) −*x*+1, −*y*+1, *z*; (ii) −*x*+3/2, *y*−1/2, −*z*+1; (iii) *x*+1/2, −*y*+1/2, −*z*+1; (iv) *x*−1/2, −*y*+3/2, −*z*+1; (v) *x*, *y*, *z*+1; (vi) *x*−1/2, −*y*+3/2, −*z*.

Table 5. Hydrogen bonded geometry (Å, °) for compound **2**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···F1*A*^{i}	0.94	2.02	2.888(13)	153
O1—H1*A*···F1*B*^{i}	0.94	2.26	3.106(11)	149
O1—H1*A*···F1*B*^{ii}	0.94	2.63	3.219(10)	121
O1—H1*B*···F2*A*^{ii}	0.87	2.42	3.011(7)	126
O1—H1*B*···F3*A*^{iii}	0.87	2.26	2.967(9)	139
O1—H1*B*···F3*B*^{iii}	0.87	2.27	2.984(7)	140
O1—H1*B*···F2*B*^{iv}	0.87	2.54	3.055(8)	119
O2—H2···F1*A*^{v}	0.80	2.28	3.075(14)	169
O2—H2···F1*B*^{v}	0.80	2.24	2.974(10)	153

Symmetry operations: (i) −*x*+1, −*y*+1, *z*; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) *x*+1/2, −*y*+1/2, *z*−1/2; (iv) −*x*+3/2, *y*+1/2, −*z*+1/2; (v) *x*+1/2, −*y*+1/2, *z*+1/2.

Compound 3 $[U_6Mg]^{2+}.2Cl^-.4U$, crystallizes in monoclinic $P2_1/c$ space group (Fig. 2) and features the same $[U_6Mg]^{2+}$ cations as compound **1**. Here the counterion is Cl^- instead of the BF_4^- present in compound **1**. In **3** along with the cationic $[U_6Mg]^{2+}$ and anionic (Cl^-) parts two additional urea molecules can be located. The Mg–O values are similar to those of **1**, around 2.07 Å and similarly to **1** the $[U_6Mg]^{2+}$ octahedra is stabilized by intramolecular hydrogen bonds (Table 6). Halogen bonding N-H… Cl is also observed. Due to the presence of the additional urea molecules the three-dimensional packing is stabilized by a multitude of hydrogen bonding interactions (Table 6). The three-dimensional arrangement of the $[U_6Mg]^{2+}$ cations in the crystal structure leads to the formation of "cavities" (voids,

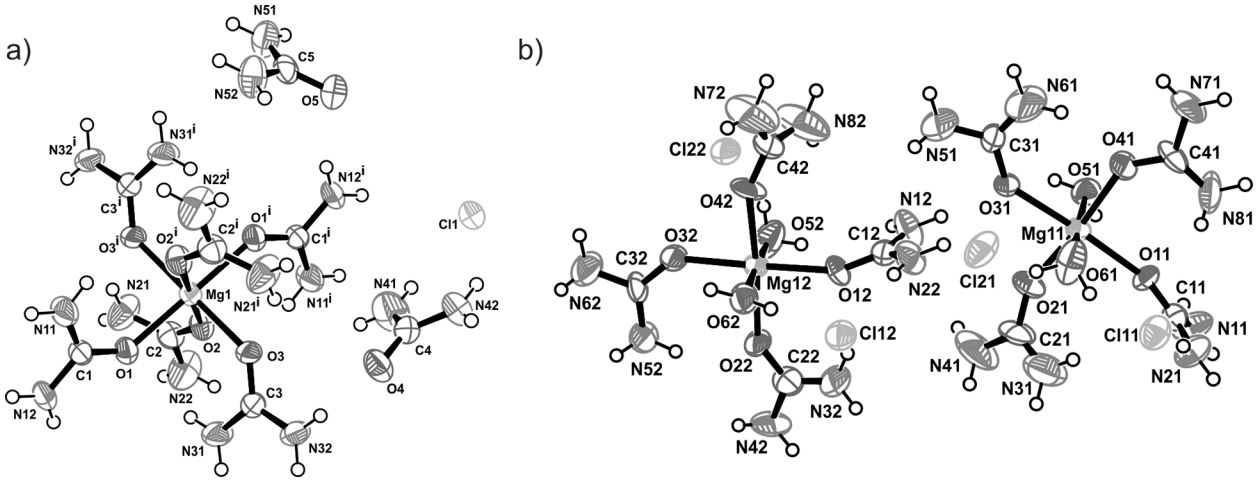

Fig. 2. ORTEP view of the molecular structures of compounds **3** – a) and **4** – b) with atomic numbering scheme. Atomic displacement parameters for the non-H atoms are drawn at the 50% probability level; the H atoms are presented with spheres with arbitrary radii.

Table 6. Hydrogen bonded geometry (Å, º) for compound **3**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N31—H31*A*···O2	0.86	2.59	3.150 (4)	124
N31—H31*A*···O1	0.86	2.36	2.983 (4)	129
N31—H31*B*···Cl1^{i}	0.86	2.49	3.317-(4)	162
N21—H21*A*···O3^{ii}	0.86	2.19	2.949 (5)	146
N21—H21*B*···N12^{iii}	0.86	2.60	3.282 (5)	137
N32—H32*A*···O4	0.86	2.10	2.955 (5)	175
N32—H32*B*···O4^{iv}	0.86	2.35	2.999 (4)	133
N51—H51*A*···O5^{v}	0.86	2.08	2.932 (4)	172
N51—H51*B*···Cl1^{vi}	0.86	2.63	3.430 (3)	156
N42—H42*A*···Cl1^{vii}	0.86	2.60	3.419 (4)	159
N42—H42*B*···Cl1^{viii}	0.86	2.82	3.333 (4)	120
N52—H52*A*···O5^{ix}	0.86	2.24	3.076 (5)	163
N52—H52*B*···Cl1^{vi}	0.86	2.92	3.661 (3)	145
N22—H22*A*···N42^{i}	0.86	2.52	3.329 (5)	157
N22—H22*B*···O5^{x}	0.86	2.63	3.261 (5)	131
N41—H41*B*···Cl1	0.86	2.57	3.433 (4)	177
N12—H12*A*···O5^{ii}	0.86	2.18	3.019 (5)	165
N12—H12*B*···Cl^{1i}i	0.86	2.77	3.404 (3)	132
N11—H11*A*···O^{2i}i	0.86	2.22	2.934 (4)	141
N11—H11*B*···O^{4x}i	0.86	2.15	2.930 (4)	151

Symmetry operations: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*, *y*−1, *z*; (iv) −*x*, −*y*+2, −*z*+1; (v) −*x*+1, *y*−1/2, −*z*+3/2; (vi) *x*+1, *y*, *z*; (vii) *x*, *y*+1, *z*; (viii) −*x*, *y*+1/2, −*z*+3/2; (ix) −*x*+1, *y*+1/2, −*z*+3/2; (x) *x*, −*y*+1/2, *z*−1/2; (xi) −*x*+1, −*y*+2, −*z*+1.

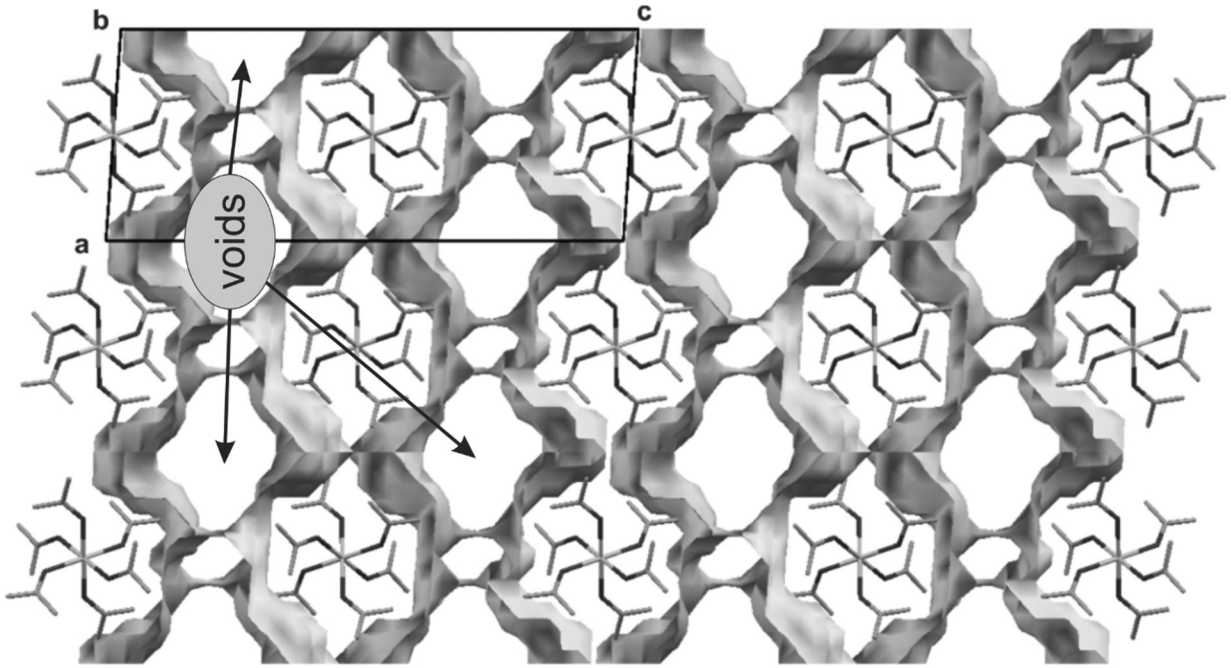

Fig. 3. Observed formation of "cavities" (voids) in the crystal structure of **3** (note that the urea molecules and Cl^- have been omitted from the illustration).

Fig. 3) that occupy 42.6% of the unit cell volume (e.g. 695.47 from 1631.5(3) Å^3, the urea molecule have been omitted from this calculation). Due to the smaller size of the monoatomic Cl^- (compared to the BF_4^-), the stabilization of the crystal structure of **3** requires the inclusion of urea to fill the empty spaces.

Compound 4, crystallizes in monoclinic $P2_1/c$ space group (Fig. 2b) with two molecules $[U_4Mg(H_2O)_2]^{2+}.2Cl^-$ in the asymmetric unit and is nearly isostructural to $[U_6Mg]^{2+}.2Br^-.4U$ reported in ref. [8]. The bond lengths and angles for the two molecules are nearly identical and are comparable with those of compounds **1–3**, **5** (Tables 2 and 3). The geometry of the two molecules differs slightly, mainly due to the different orientation of the urea to the mean plane formed by the $O\text{-}_{UREA}$ participating in Mg coordination (Fig. 4).

Again, as for compounds **1–3**, the $[U_4Mg(H_2O)_2]^{2+}$ octahedra is stabilized by intramolecular hydrogen bonds (Table 7). The three-dimensional packing of the molecules stabilizing the crystal structure generates a significant number of intermolecular halogen and hydrogen bonds (Table 7). The "inclusion" of additional urea/water molecules (to fill the gaps in the structure) is not necessary as the presence of the two water molecules in the Mg coordination sphere permits denser packing of $[U_4Mg(H_2O)_2]^{2+}$ moieties (closer contact, nearly interpenetration, Fig. 5).

Fig. 4. Overlay of the molecules present in the asymmetric unit of **4** (*rms* 0.604 Å).

Table 7. Hydrogen bonded geometry (Å, °) for compound **4**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O51—H51*A*···Cl21^{i}	0.91	2.25	3.096 (8)	156
O51—H51*B*···Cl11^{i}	0.90	2.29	3.122 (8)	154
O61—H61*A*···Cl11	0.88	2.41	3.067 (8)	132
O61—H61*B*···Cl21	0.88	2.46	3.044 (9)	124
O52—H52*A*···Cl12^{i}	0.88	2.38	3.193 (9)	153
O52—H52*B*···Cl22	0.88	2.40	3.076 (9)	134
N22—H22*A*···Cl12	0.88	2.52	3.396 (10)	171
N22—H22*B*···O31	0.88	2.23	3.019-(11)	150
N12—H12*A*···Cl12^{i}	0.88	2.58	3.416 (10)	158
N12—H12*B*···O31	0.88	2.37	3.128 (11)	144
N21—H21*A*···Cl11	0.88	2.49	3.365 (10)	179
N21—H21*B*···O32^{ii}	0.88	2.53	3.294 (11)	145
N11—H11*A*···Cl11^{i}	0.88	2.46	3.328 (10)	172
N11—H11*B*···O32^{ii}	0.88	2.37	3.163 (12)	150
N52—H52*C*···O22	0.88	2.11	2.896 (12)	148
N52—H52*D*···Cl22^{iii}	0.88	2.57	3.413 (10)	161
N42—H42*A*···Cl11^{iv}	0.88	2.75	3.576 (13)	156
N42—H42*B*···Cl21^{iv}	0.88	2.49	3.254 (10)	146
N71—H71*A*···Cl22^{v}	0.88	2.77	3.647 (12)	173
N71—H71*B*···Cl12^{vi}	0.88	2.73	3.376 (9)	132
N71—H71*B*···Cl2^{1v}i	0.88	2.99	3.684 (12)	137
N31—H31*B*···O6^{2i}v	0.88	2.56	3.434 (14)	171
N72—H72*A*···Cl2^{2vi}i	0.88	2.99	3.771 (15)	149
N62—H62*D*···Cl2^{2ii}i	0.88	2.67	3.489 (12)	155
N41—H41*B*···Cl1^{2i}v	0.88	2.41	3.260 (12)	163
N32—H32*A*···O12	0.88	2.11	2.872 (14)	145
N32—H32*B*···Cl1^{2i}v	0.88	2.46	3.319 (11)	166
N82—H82*B*···O5^{1vii}i	0.88	2.33	3.198 (13)	171
N61—H61*C*···O41	0.88	2.06	2.842 (17)	148
N61—H61*D*···Cl2^{2}v	0.88	2.76	3.273 (13)	118
N61—H61*D*···Cl1^{1i}x	0.88	2.74	3.558 (14)	154
N51—H51*C*···Cl1^{1i}x	0.88	2.53	3.375 (13)	160
N51—H51*D*···N22	0.88	2.74	3.319 (16)	124
N81—H81*A*···O11	0.88	2.05	2.862 (14)	152
N81—H81*B*···Cl2^{1v}i	0.88	2.25	3.119 (12)	169

Symmetry operations: (i) x−1, y, z; (ii) *x*, *y*−1, *z*; (iii) −*x*+1, −*y*+2, −*z*+1; (iv) −*x*+2, −*y*+1, −*z*+1; (v) −*x*+1, *y*−1/2, −*z*+1/2; (vi) −*x*+2, *y*−1/2, −*z*+1/2; (vii) *x*+1, *y*, *z*; (viii) −*x*+1, *y*+1/2, −*z*+1/2; (ix) −*x*+2, *y*+1/2, −*z*+1/2.

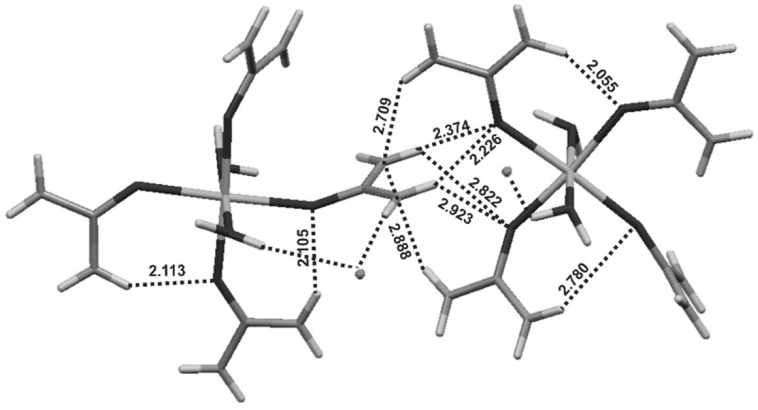

Fig. 5. Representation of the dense packing of the $[U_4Mg(H_2O)_2]^{2+}$ moieties observed in **4** (hydrogen bonds are shown as dotted lines, distances are in Å).

Compound 5, $[U_6Mg]^{2+}.2NO_3^-$, crystallizes in the triclinic *P*–1 space group with 1/2 molecule in the asymmetric unit (Fig. 6).The bond lengths and angles of the nitro group and $[U_6Mg]^{2+}$ fragment are comparable to those of compounds **1–4** (Tables 2 and 3). Here the difference is in the anion – the nitro group – which is more bulky than the Cl^- and more compact than BF_4^-. As for compounds **1–4** the intramolecular and intermolecular hydrogen bonds stabilizing the molecular geometry of the $[U_6Mg]^{2+}$ and the three-dimensional packing are also observed (Table 8).

According to the structural data obtained from compounds **1**–**5** the Mg octahedral coordination is very conservative. The Mg–O distances are not affected by the change coordinating moiety urea *vs* water (Table 9) or by the change of anion moiety (Cl^-, $NO3^-$, BF_4^-). The rotation of the urea around the $Mg–O_{UREA}$ bond is not hampered and allows the

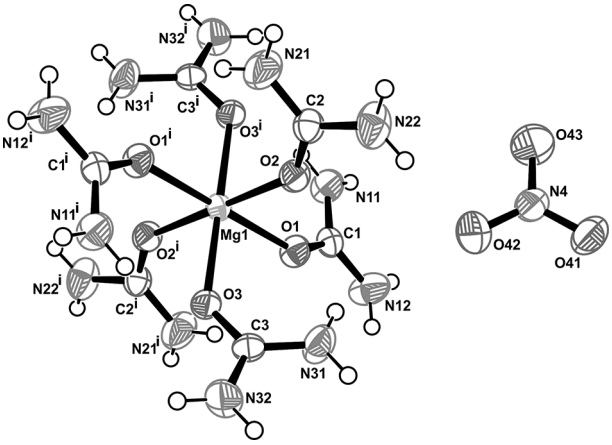

Fig. 6. ORTEP view of compound **5** with atomic numbering scheme (symmetry operation (i); *x*,*y*,*z*). Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The H atoms are presented with spheres with arbitrary radii.

Table 8. Hydrogen bonded geometry (Å, °) for compound **5**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N22—H22*A*···O42	0.86	2.31	3.107 (4)	153
N22—H22*B*···N32^{i}	0.86	2.65	3.502 (4)	174
N31—H31*A*···O1	0.86	2.35	3.035 (3)	137
N31—H31*B*···O43^{ii}	0.86	2.34	3.091 (3)	146
N21—H21*A*···O1^{iii}	0.86	2.43	3.082-(3)	133
N21—H21*A*···O41^{iv}	0.86	2.33	2.953 (4)	130
N21—H21*B*···O43^{v}	0.86	2.36	3.157 (4)	155
N32—H32*A*···O2^{ii}	0.86	2.53	3.114 (3)	126
N32—H32*A*···O3^{vi}	0.86	2.51	3.267 (3)	148
N32—H32*B*···O43^{ii}	0.86	2.19	2.975 (4)	152
N11—H11*A*···O3^{iii}	0.86	2.29	3.031 (4)	145
N11—H11*B*···O41^{vii}	0.86	2.30	3.064 (3)	148
N12—H12*A*···O41^{viii}	0.86	2.64	3.307 (3)	136
N12—H12*A*···O42^{viii}	0.86	2.17	3.018 (3)	169
N12—H12*B*···O41^{ix}	0.86	2.63	3.345 (3)	142
N12—H12*B*···O43^{vii}	0.86	2.39	3.029 (3)	131

Symmetry operations: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, *y*, *z*+1; (v) −*x*+2, −*y*, −*z*+1; (vi) −*x*, −*y*+1, −*z*+1; (vii) −*x*+2, −*y*+1, −*z*; (viii) −*x*+1, −*y*+1, −*z*; (ix) *x*, *y*+1, *z*.

Table 9. Average Mg–O distances and negative and positive deviations from average for compounds **1**–**5**

Compound	Bond Mg—O (Å)	Angle O—Mg1—O (°)
1	2.072 (–0.013; +0.028)	90 (–5.9; +5.54)
2	2.063 (–0,002; +0.002)	90 (–0.06; +0.68)
3	2.070 (–0.003; +0.012)	90 (–3.08; +1.42)
4	2.071 (–0.028; +00.33)	90 (–2.5; +3.5)
5	2.067 (–0.024; +0.025)	90 (–1.55; +0.65)

formation of intermolecular halogen and hydrogen bonds that stabilize the three-dimensional packing of the crystal structures. Both the cation and anion "sizes" are affecting the crystal packing.

CONCLUSIONS

The crystal structure of five magnesium complexes have been determined. The structures reveal the traditional octahedral coordination of Mg. The change of anion (Cl^-, NO_3^-, BF_4^-) does not induce changes in the octahedral Mg coordination. When magnesium chloride forms a complex with six molecules of urea, additional urea molecules are included in the crystal structure. No such "inclusion" is observed for the other magnesium salts BF_4^- and NO_3^-. This is explained by the large size of the coordinated cation $[U_6Mg]^{2+}$ and the small size of the anion (Cl^-). The three-dimensional packing of the cation produces voids in the structure that cannot be completely filled by the small anion. In order to minimize the "free spaces" additional urea molecules are required. Therefore, the crystal structure is stabilized by incorporating two additional urea molecules with each chlorine anion and the compound crystallizes as $[U_6Mg]^{2+}.2Cl^-.4U$.

SUPPLEMENTARY MATERIALS

ICSD No XX1, XX1, xx4 xx3 and XX1 contains the supplementary crystallographic data for compounds **1–5** respectively. Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata(at)fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number.

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УРЕАТИ И ХИДРАТИ НА МАГНЕЗИЕВ ХЛОРИД, НИТРАТ И ТЕТРАФЛУОРОБОРАТ

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(Резюме)

Получени са пет комплекса на магнезий и е определен кристалният им строеж. Два с тетрафлуороборатен анион – $[U_6Mg]^{2+}.2BF_4$ – **1** и $[(H_2O)_6Mg]^{2+}.2BF_4$ – **2**, два с хлориден – $[U_6Mg]^{2+}.2Cl^-.4U$ – **3** и $[U_4Mg(H_2O)_2]^{2+}.2Cl$ – **4**, както и един с нитратен – $[U_6Mg]^{2+}.2NO_3^-$ – **5**. Образци за монокристален рентгеноструктурен анализ са израстнати чрез бавно изпарение от воден раздвор на съответната магнезиева сол и карбамид. Два от тях кристализират в моноклинна сингония $[U_6Mg]^{2+}$ $2Cl^-.4U$ и $[U_4Mg(H_2O)_2]^{2+}$ $2Cl^-$, пространствена група – $P\ 2_1/c$ с параметри на елементарната клетка a = 9.6317(8), b = 7.2241(7), c = 23.506(3), β =94.045(9) и a = 8.0168(16), b = 14.844(2), c = 28.662(4), β= 94.194(16) съответно, един в триклинна – $[U_6Mg]^{2+}$ $2NO_3^-$ пространствена група – P–1 с параметри на елементарната клетка a = 7.1917(6), b = 8.279(3) c =9.555 (9), α = 71.01(6), β = 89.17(3), γ = 84.158(19) и два в орторомбична $[U_6Mg]^{2+}2BF_4^-$ кристализира в пространствена група – $P2_12_12$, с параметри на елементарната клетка a = 9.964(5), b = 11.979(6), c = 9.638(5)), а $[(H_2O)_6Mg]^{2+}2BF_4^-$ в пространствена група – Pnnm с параметри на елементарната клетка a = 5.4322(6), b = 13.2050(12), c = 7.6786(6).