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Crystal Structures of Hexaaquamagnesium Diliturate Dihydrate, $Mg(H_2O)_6^{2+}(C_4H_2N_3O_5^-)_2 \cdot 2H_2O$ and the Isomorphous Calcium Salt

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The crystal structures of the two isomorphous title compounds were determined by single-crystal X-ray diffraction. The space group for the monoclinic crystals is $P2_1/c$, No. 14, $Z=2$. At 293 K, $a=12.039(1)$, $b=12.096(1)$, $c=6.741(2)$ Å, $\beta=97.86(1)°$ and $V=972.4(5)$ Å^3 for hexaaquamagnesium 5-nitrobarbiturate dihydrate. The cell parameters for the isomorphous calcium compound are $a=12.349(1)$, $b=12.167(1)$, $c=6.818(1)$ Å, $\beta=97.08(1)°$, $V=1016.6(3)$ Å^3. In the crystals the cations and the anions are stacked in alternating layers. The crystal structures are extensively stabilized by hydrogen bonds some of which link the anions to infinite chains. The hydrogen bonds in these chains are significantly shorter when the cation is hexaaquamagnesium.

Dilituric acid (5-nitrobarbituric acid) has been investigated as a reagent for the isolation of naturally occurring bases and some metal ions.[1] In this context Redemann and Niemann observed that magnesium diliturate has a very low solubility in water (0.1 mmol l^{-1}, 25 °C) and accordingly is an excellent reagent for the isolation of magnesium. Calcium diliturate is more soluble (5.7 mmol l^{-1}, 25 °C).

In the present investigation the crystal structures of hexaaquamagnesium diliturate dihydrate **1** and the isostructural hexaaquacalcium diliturate dihydrate **2** have been determined in the hope that the crystal structures could tell something about the solubilities of the title compounds.

Results and discussion

General description of the crystal structures. In the crystal structures of **1** and the isomorphous **2**, the metal–hexaaqua cations and the diliturate anions are stacked in alternating layers (Fig. 1). The metal ions are situated at the centre of symmetry (special position b), and thus occupy the plane $x=1/2$. Four of the water molecules in the metal–hexaaqua ion are situated near to this plane.

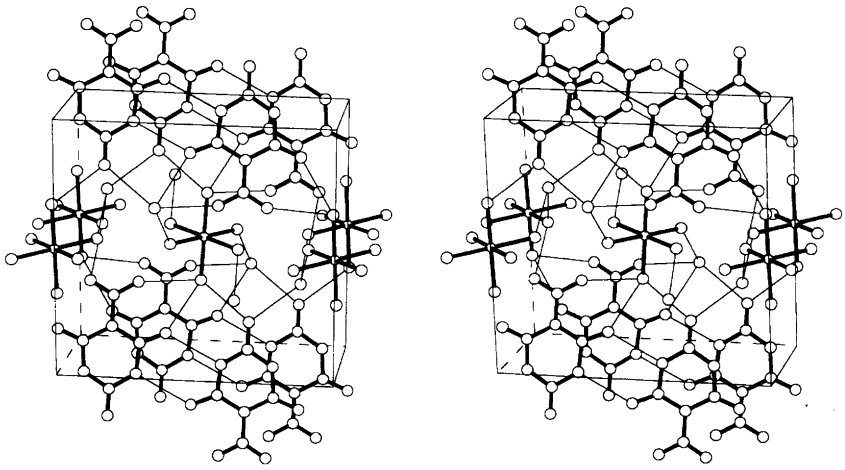

Fig. 1. Stereo drawing of one unit cell of **1**. The thin lines represent the intermolecular hydrogen bonds. The direction of the *a*-axis is vertical, downwards; the direction of the *b*-axis is horizontal from the left to the right.

Table 1. Coordination distances (Å) and angles (°) for $[Mg(H_2O)_6]^{2+}$ in **1** and $[Ca(H_2O)_6]^{2+}$ in **2**.

Mg^{2+}–O(10)	2.047(2)	O(10)–Mg^{2+}–O(20)	87.23(8)
Mg^{2+}–O(20)	2.062(2)	O(10)–Mg^{2+}–O(30)	89.68(7)
Mg^{2+}–O(30)	2.060(2)	O(20)–Mg^{2+}–O(30)	88.23(9)
Ca^{2+}–O(10)	2.302(2)	O(10)–Ca^{2+}–O(20)	83.66(7)
Ca^{2+}–O(20)	2.312(2)	O(10)–Ca^{2+}–O(30)	89.98(7)
Ca^{2+}–O(30)	2.344(2)	O(20)–Ca^{2+}–O(30)	88.57(8)

The (100) plane cuts through the six-membered rings of all anions. The planar dilurate anions are nearly coincident with ($\bar{3}04$) and accordingly I ($\bar{3}04$) is one of the strongest reflections.

The stable octahedral $Mg(H_2O)_6^{2+}$ ion is well represented among reported crystal structures,[2] whereas rather few structures incorporating the $Ca(H_2O)_6^{2+}$ ion are described. The dimensions of the metal–hexaaqua ions are given in Table 1. The relative stability of the hexaaqua ions $Mg(H_2O)_6^{2+}$, $Ca(H_2O)_6^{2+}$ is reflected in the results from thermogravimetric investigations of **1** and **2**. On heating of **1**, a loss of 4 mol equiv. of water is observed in the temperature range 100–140 °C,[3] whereas **2** loses 6 mol equiv. of water in the range 33–100 °C. The coordination distances in the metal–hexaaqua ions are in agreement with corresponding distances found in related compounds $[Mg(H_2O)_6^{2+}$,[5–8] $Ca(H_2O)_6^{2+}$[9]]. The water molecule [O(40)], which is not part of the metal–hexaaqua ion, links the cations and the anions via hydrogen bonds.

Discussion of hydrogen bonds. The crystal structures of **1** and **2** are to a great extent stabilized by hydrogen bonds (Table 2) which can be categorized as (a) hydrogen bonds between the anions, (b) hydrogen bonds involving the water molecule O(40) which is not part of the metal hexaaqua ions and (c) hydrogen bonds between the cations and the anions. The atom numbering of the anion is given in Fig. 2.

In the hydrogen bonds (c) the oxygen atoms O(2), O(6), O(51), O(52) are acceptors for hydrogen bonds from the water molecules in the metal–hexaaqua ion.

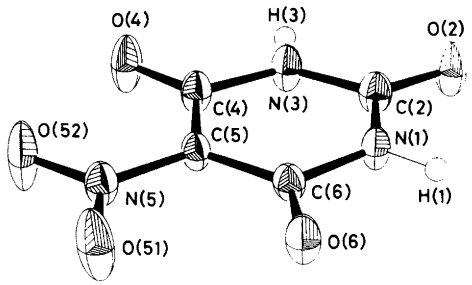

Fig. 2. Displacement ellipsoid drawing of the dilurate anion in **1** with ellipsoids drawn at the 50% probability level. The atom numbering is valid for both **1** and **2**.

The average value D···A of the hydrogen bonds (c) and (b) is shortened a little when Mg^{2+} is replaced by Ca^{2+}. Within category (a), the anions are linked to infinite chains by the hydrogen bonds O(4)···HN(1) and O(6)···HN(3). This type of hydrogen bond probably plays an important role in the crystal structures of dilurates, as a related linkage has been observed for ammonium dilurate **3**[10] and dilituric acid trihydrate[11] (Fig. 3). Hydrogen bonds (a) are considerably elongated by the transition **1** → **2**.

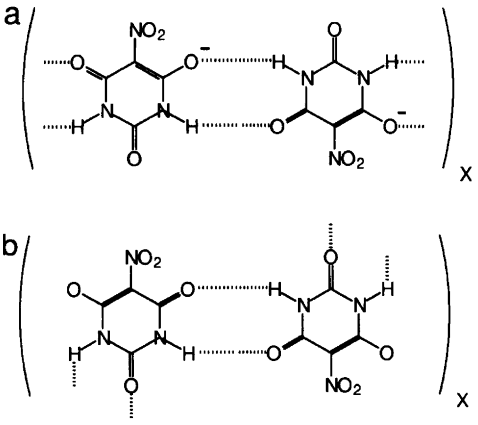

Fig. 3. Intermolecular hydrogen bonds (dashed lines) between the anions in (a) **1** and **2**; (b) ammonium dilurate[10] and dilituric acid trihydrate.[11]

Table 2. Distances/Å and angles/° in the hydrogen bonds in **1** and **2**.

	D···A		D–H		H···A		∠(D–H···A)	
D–H···A; D = O/N; A = O	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
N(1)($-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$)–H(1)···O(4)[a]	2.826(2)	2.863(2)	0.90(2)	1.01(2)	1.93(2)	1.85(2)	174(2)	178(2)
N(3)($-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)–H(3)···O(6)[a]	2.834(2)	2.874(2)	0.84(2)	0.92(2)	2.00(2)	1.96(2)	177(2)	172(2)
O(40)–H(41)···O(2)($-x$, $1-y$, $-z$)[b]	2.854(2)	2.836(2)	0.82(2)	0.83(2)	2.07(2)	2.01(2)	159(2)	174(2)
O(40)–H(42)···O(4)(x, $\frac{3}{2}-y$, $-\frac{1}{2}+z$)[b]	2.850(2)	2.836(2)	0.81(2)	0.83(2)	2.09(2)	2.08(2)	156(2)	152(2)
O(40)–H(42)···O(52)(x, $\frac{3}{2}-y$, $-\frac{1}{2}+z$)[b]	2.782(2)	2.804(2)	0.81(2)	0.83(2)	2.19(2)	2.19(2)	130(2)	131(2)
O(20)–H(21)···O(40)[b]	2.784(2)	2.757(3)	0.68(2)	0.75(2)	2.11(2)	2.04(2)	167(3)	162(2)
O(30)–H(32)···O(40)($1-x$, $1-y$, $-z$)[b]	2.744(3)	2.756(3)	0.82(2)	0.75(2)	1.94(2)	1.99(2)	166(2)	176(2)
O(10)–H(11)···O(2)($-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)[c]	2.834(2)	2.816(2)	0.84(2)	0.82(2)	2.02(2)	2.01(2)	163(2)	172(2)
O(10)–H(12)···O(6)[c]	2.858(2)	2.794(2)	0.74(2)	0.81(2)	2.20(2)	2.08(2)	148(2)	147(2)
O(10)–H(12)···O(51)[c]	2.833(2)	2.831(2)	0.74(2)	0.81(2)	2.22(2)	2.19(2)	140(2)	137(2)
O(30)–H(31)···O(52)(x, $\frac{3}{2}-y$, $-\frac{1}{2}+z$)[c]	2.782(3)	2.801(3)	0.68(2)	0.76(2)	2.11(2)	2.05(2)	175(3)	171(2)

[a,b,c]The categories of hydrogen bonds are described under 'Results and discussion'.

A comparison between the crystal structures **1** and **2** suggests some reasons for the low solubility of **1**; apparently the ions in **1** have a size well adapted for relatively dense packing in the crystals (**1**, 1.751; **2**, 1.726 g cm^{-1}). The shorter hydrogen bonds (a) in **1** need more energy to be broken than do the same bonds in **2**.

Most of the corresponding bond distances in the anions of **1**, **2** and **3** have insignificant bond differences. Exceptions are some bonds connected with the nitro group [N(5)–O(52): **1**, 1.226(2); **2**, 1.225(2); **3**, 1.246(2) Å; N(5)–C(5): **1** and **3**, 1.404(2), **2**, 1.420(3) Å]. A possible explanation for this might be

Table 3. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Formula	$Mg(H_2O)_6^{2+}(C_4H_2N_3O_5^-)_2 \cdot 2H_2O$	$Ca(H_2O)_6^{2+}(C_4H_2N_3O\text{-})_2 \cdot 2H_2O$
Formula weight	512.581	528.356
λ/ Å	0.71069	0.71069
T/K	293	293
Crystal dimension/mm	0.16 × 0.16 × 0.52	0.16 × 0.26 × 0.46
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/ Å	12.039(1)	12.349(1)
b/ Å	12.096(1)	12.167(1)
c/ Å	6.741(2)	6.818(1)
β/°	97.86(1)	97.08(1)
V/ $Å^3$	972.4(5)	1016.6(3)
Z	2	2
D_c/g cm^{-3}	1.751	1.726
μ/cm^{-1}	1.878	3.978
Transmission factor min./max.	0.962 0.977	0.878 0.945
No. of independent reflections	2821	2962
No. of observed reflections[a]	2112	2186
Standard intensity reflection every 180 min	$I(60\bar{2})$	$I(53\bar{3})$
Standard intensity variation	2%	2%
$R(F_o)$[b]	0.044	0.044
$R_w(F_o)$[c]	0.036	0.037
Weighting w	$1/\sigma^2(F)$	$1/\sigma^2(F)$
No. of parameters refined	181	181
Max. and min. $\Delta\rho$/e $Å^{-3}$	0.3/−0.4	0.4/−0.4

[a]Criteria for observed reflections $I > 2.5\sigma(I)$. [b]$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c]$R_w = [\Sigma w|F_o - F_c|^2/\Sigma wF_o^2]^{1/2}$.

Table 4. Fractional atomic coordinates and equivalent isotopic displacement parameters ($Å^2$) for **1** and **2**. $U_{eq} = (\frac{1}{3})\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	Atom	*x/a*	*y/b*	*z/c*	U_{eq}
1					**2**				
Mg^{2+}	½	½	½	0.0334(3)	Ca^{2+}	½	½	½	0.0362(2)
O(2)	−0.1813(1)	0.8279(1)	0.1178(2)	0.0386(5)	O(2)	−0.1739(1)	0.8242(1)	0.1164(3)	0.0418(7)
O(4)	0.1273(1)	1.0251(1)	0.3434(3)	0.0428(6)	O(4)	0.1240(1)	1.0216(1)	0.3440(3)	0.0440(7)
O(6)	0.1266(1)	0.6307(1)	0.3545(2)	0.0335(5)	O(6)	0.1245(1)	0.6290(1)	0.3473(3)	0.0365(6)
O(10)	0.3288(1)	0.5093(1)	0.4702(3)	0.0449(6)	O(10)	0.3123(1)	0.5064(1)	0.4691(4)	0.0521(7)
O(20)	0.4800(2)	0.3640(2)	0.3141(3)	0.0520(8)	O(20)	0.4704(1)	0.3494(1)	0.2935(4)	0.0624(9)
O(30)	0.4996(1)	0.6056(2)	0.2603(3)	0.0450(6)	O(30)	0.4986(1)	0.6113(1)	0.2190(3)	0.0463(7)
O(40)	0.3296(1)	0.3556(1)	−0.0383(3)	0.0444(6)	O(40)	0.3170(1)	0.3570(1)	−0.0361(4)	0.0486(7)
O(51)	0.3059(1)	0.7415(1)	0.5031(3)	0.0572(7)	O(51)	0.3032(1)	0.7393(2)	0.4724(4)	0.0675(9)
O(52)	0.3073(1)	0.9159(1)	0.4829(3)	0.0619(8)	O(52)	0.3019(1)	0.9127(1)	0.4703(4)	0.0574(8)
N(1)	−0.0239(1)	0.7330(1)	0.2375(3)	0.0262(6)	N(1)	−0.0210(1)	0.7306(1)	0.2337(3)	0.0280(7)
N(3)	−0.0231(1)	0.9226(1)	0.2314(3)	0.0300(6)	N(3)	−0.0211(1)	0.9194(1)	0.2321(4)	0.0318(7)
N(5)	0.2570(1)	0.8282(1)	0.4517(3)	0.0285(5)	N(5)	0.2542(1)	0.8254(2)	0.4349(4)	0.0328(7)
C(2)	−0.0823(2)	0.8281(2)	0.1911(3)	0.0272(6)	C(2)	−0.0777(2)	0.8250(2)	0.1896(4)	0.0301(8)
C(4)	0.0886(2)	0.9313(2)	0.3157(3)	0.0271(7)	C(4)	0.0875(2)	0.9281(2)	0.3140(4)	0.0291(8)
C(5)	0.1445(2)	0.8280(2)	0.3630(3)	0.0239(6)	C(5)	0.1425(2)	0.8257(2)	0.3548(4)	0.0266(7)
C(6)	0.0881(2)	0.7250(2)	0.3221(3)	0.0236(6)	C(6)	0.0883(2)	0.7225(2)	0.3159(4)	0.0263(7)

that the positive charge of the cation is nearer to the nitro group O-atoms in **1** and **3**. The mesometric form $>C(5)=N(5)^{+}-[O(51)^{-}, O(52)^{-}]$ is thus better stabilized for these compounds.

Experimental

Crystal preparation. The crystals used in the structure determinations were prepared by allowing aqueous solutions of 5-nitrobarbituric acid and $MgSO_4$ (0.5 M)/$CaCl_2$ (0.1 M) to diffuse slowly into each other in the horizontal part of an H-shaped tube. A satd. soln. of commercially available 5-nitrobarbituric acid was used.

Structure determination. Crystal data and parameters of the data collection are compiled in Table 3. Unit cell parameters were determined by accurate centring of 25 reflections for **1** and 23 reflections for **2**. The data were collected on an Enraf–Nonius CAD4-F diffractometer, using graphite-monochromated Mo Kα radiation and $\omega/2\theta$ scan. The reflections were collected within the range **1**, $(2\leqslant\theta\leqslant30°, +h, +k, \pm l)$; **2**, $(2\leqslant\theta\leqslant30°, \pm h, +k, +l)$ and corrected for Lp-effects and absorption.[12]

1 was solved by direct methods using the SHELXS86 program;[13] initial coordinates for **2** were taken from the structure of **1**. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Positional parameters for all H-atom are from $\Delta\rho$ maps. They were refined isotropically with a common fixed H temperature factor. Refinements and geometric calculations were performed with the Xtal3.2 program system.[14] The least-squares refinement was based on *F*. The atomic scattering factors were from *International Tables for X-Ray Crystallography*.[15] Atomic coordinates and thermal parameters are given in Table 4.

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