

Hemi[hexaaquamagnesium(II)] (μ -2,6-bis[[bis(carboxylatomethyl)amino]-methyl]-4-chlorophenolato)bis[di-aquamagnesium(II)] decahydrate

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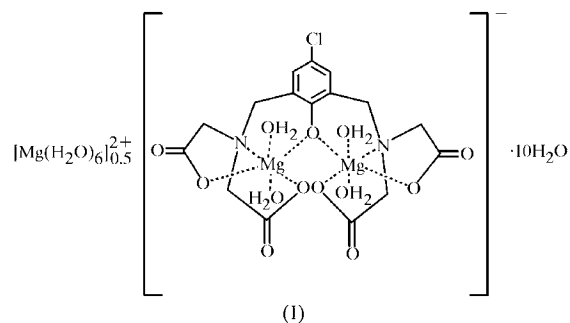
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The crystal structure of the title compound, $[\text{Mg}(\text{H}_2\text{O})_6]_{0.5}^{2+}[\text{Mg}_2(\text{C}_{16}\text{H}_{14}\text{ClN}_2\text{O}_9)(\text{H}_2\text{O})_4] \cdot 10\text{H}_2\text{O}$, shows that this binuclear complex consists of two Mg centres in distorted octahedral geometry, joined by an oxo bridge which is a derivative of the deprotonated hydroxy group of the phenolate in the ligand molecule. In the anion, the coordination sphere of each Mg^{II} ion is completed by two carboxylates, a tertiary N atom and two water molecules. The inner coordination spheres for the Mg^{II} ions are very similar, both in ligand sets and in geometry. Each unit of the binuclear complex has one negative charge neutralized by a neighbouring hydrated cation, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, in which the Mg atom lies on an inversion centre. In each cell, there are 34 water molecules and most of them participate in the formation of hydrogen bonds, which contribute greatly to the stability of the whole structure.

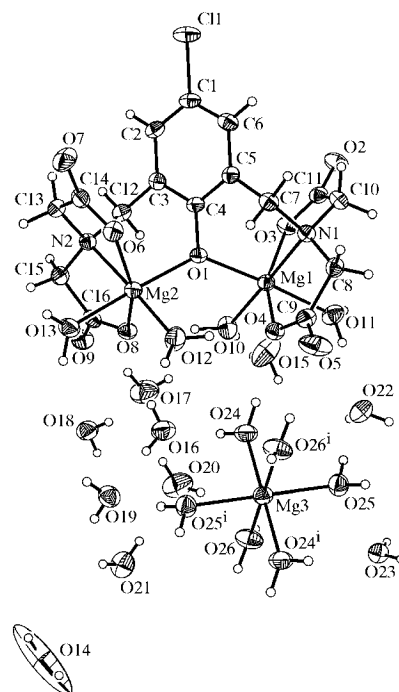
Comment

It is well known that Mg arises out of the active centres in many nucleases (Wilcox, 1996; Sam & Perona, 1999). However, the usage has not been reported to date of simple complexes of Mg to mimic the nucleases to hydrolyse DNA. Recently, we synthesized the title novel complex, (I), of Mg with Cl-HXTA (Cl-HXTA is 5-chloro-2-hydroxy-1,3-xylene- α,α -diamine- N,N,N',N' -tetraacetic acid), and found that this complex is able to cleave DNA in a hydrolytic path. Cl-HXTA is an acyclic dinucleating ligand with a phenolate bridge (Murch *et al.*, 1987). As a pentavalent anionic ligand, it has four methoxycarbonyl chelating arms, with two sets of donor atoms, namely one N and three O atoms, as the coordination sites. One of the advantages of Cl-HXTA is that most of its dinuclear metal complexes are soluble in water and it is thus convenient to carry out experiments on biological activity.

The main features of the molecular geometry of (I) are listed in Table 1, and the molecular configuration and crystal packing are illustrated in Figs. 1 and 2, respectively.



From Fig. 1, it can readily be seen that the inner coordination spheres for the two Mg^{II} ions are similar in geometry and donor atoms. Each metal ion adopts a distorted octahedral coordination geometry comprised of two carboxylates, a tertiary N atom, two water molecules and the bridging phenolate (atom O1). The $\text{Mg1} \cdots \text{Mg2}$ separation is 3.787 (1) Å, suggesting no obvious bonding. There is only one oxo bridge formed in (I), which is quite different from the structure of $[\text{Fe}_2(\text{HXTA})(\text{OH})(\text{H}_2\text{O})_2]$ (Murch *et al.*, 1987), where there are two oxo bridges (one O stems from the phenolate and the other from a hydroxide group in a water molecule). For (I), the average Mg—O bond length in the


Figure 1

The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $-x, 1-y, 1-z$].

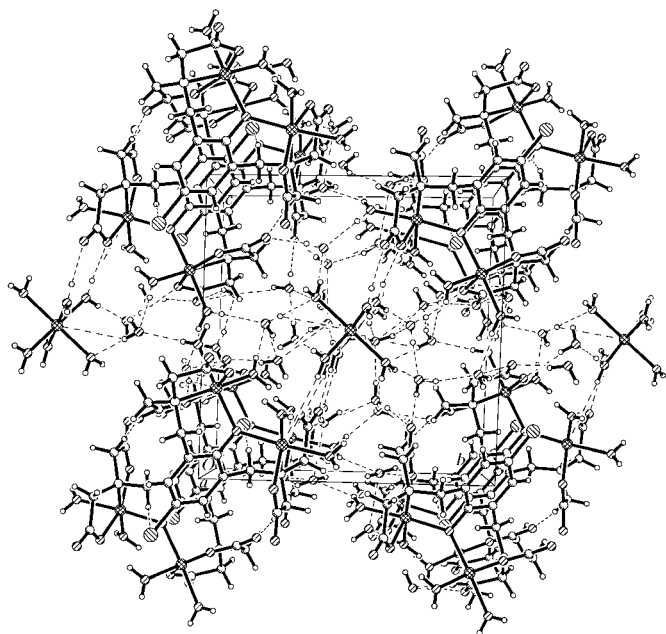


Figure 2
The crystal packing of (I), viewed along the *a* direction. The hydrogen bonds are shown as dashed lines.

phenolate bridge is 2.067 (5) Å, in accordance with that of the metal–phenolate bonds in other reported dinuclear complexes, such as $[\text{Fe}_2(\text{sal})_3\text{trien}(\text{OMe})]\text{Cl}_2$ and $[\text{Fe}_2(\text{sal})_3\text{trien}(\text{OH})]\text{Cl}_2$ (Chiari *et al.*, 1983). The coordination spheres of the two Mg^{II} ions possess evident similarity, both in ligand sets and in geometry. More specifically, in each coordination sphere, the tertiary N, the bridging O and two O atoms from water molecules make up the equatorial plane, while two carboxylate O atoms occupy two polar positions and thus complete a distorted octahedral geometry. The complex anion as a whole has a pseudo- C_2 axis along C11/C1/C4/O1, which has been reported previously by Sakiyama *et al.* (1999).

The $\text{Mg1}–\text{O1}–\text{Mg2}$ angle in (I) is $132.72(9)^\circ$, which is obviously larger than the analogous $\text{Fe1}–\text{O}–\text{Fe2}$ angle in the $[\text{Fe}_2(\text{HXTA})\text{OH}(\text{H}_2\text{O})_2]$ complex (102.56° ; Murch *et al.*, 1987), perhaps due to the different numbers of oxo bridges formed between the two metal ions. The axial coordination atoms perpendicular to the equatorial plane of the Mg core lean away from the core somewhat, as demonstrated by the two largest angles at each Mg, *viz.* $\text{O10}–\text{Mg1}–\text{O3}$ [$105.62(9)^\circ$] and $\text{O6}–\text{Mg2}–\text{O12}$ [$104.57(9)^\circ$]. In addition, the four angles in the equatorial plane for each Mg core, taking the metal as the common apex, are close to right angles, being in the range $86.59(8)–91.58(9)^\circ$ for atom Mg1 and $86.54(9)–92.74(9)^\circ$ for Mg2. In addition, the least-squares plane of the aromatic ring of Cl-HXTA and the plane defined by atoms Mg1, Mg2 and O1 are twisted, with a dihedral angle of $56.23(7)^\circ$.

Interestingly, each unit of this binuclear complex has one negative charge neutralized by a neighbouring hydrated cation, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, which is shared by another complexing

unit. From another viewpoint, in the two faces of the cell in the *c* direction, there are two hydrated Mg^{II} ions, to achieve charge balance.

In each cell there are 34 water molecules, contributing greatly to the stability of the whole structure by forming hydrogen bonds. Some of these intra- and intermolecular hydrogen bonds are illustrated in Fig. 2 and their numerical values are given in Table 2.

Experimental

All chemicals were of AR grade, commercially available from the Beijing Chemical Reagents Company in China, and were used without further purification. The ligand Cl-HXTA was synthesized following a modification of the published procedures of Murch *et al.* (1987) and Branum *et al.* (2001). To an aqueous solution (100 ml) of iminodiacetic acid (16.7 g, 0.125 mol) and *p*-chlorophenol (8.07 g, 0.063 mol) was added NaOH (10.5 g, 0.25 mol) in water (40 ml) in an ice–water bath. Upon dissolution, formaldehyde (15 ml, 37%) was added dropwise at 273 K. The solution was stirred for 30 min, heated at 343 K for 4 h and then concentrated to dryness. Recrystallization of the solid from methanol produced light-yellow crystals of $\text{Na}_4(\text{Cl-HXTA})$ (yield 90%). $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.4929 g, 2 mmol) and $\text{Na}_4(\text{Cl-HXTA})$ (0.5165 g, 1 mmol) were each dissolved in H_2O (5.0 ml). The two solutions were mixed at 323 K with stirring and kept agitating for 2 h. The resulting colourless solution was filtered and the filtrate was used to grow crystals at room temperature over anhydrous CaCl_2 in a desiccator. Colourless crystals of (I) suitable for X-ray crystallography were obtained after 10 d by slow evaporation of the solvent.

Table 1
Selected geometric parameters (Å, °).

Mg1–O10	2.015 (2)	O1–Mg2	2.072 (2)
Mg1–O1	2.062 (2)	Mg2–O12	1.992 (2)
Mg1–O3	2.063 (2)	Mg2–O6	2.071 (2)
Mg1–O4	2.088 (2)	Mg2–O13	2.075 (2)
Mg1–O11	2.114 (2)	Mg2–O8	2.111 (2)
Mg1–N1	2.210 (2)	Mg2–N2	2.201 (2)
O10–Mg1–O1	86.59 (8)	O12–Mg2–O1	89.45 (8)
O10–Mg1–O3	105.62 (9)	O6–Mg2–O1	94.33 (8)
O1–Mg1–O3	99.82 (8)	O12–Mg2–O13	86.54 (9)
O10–Mg1–O4	97.90 (9)	O6–Mg2–O13	85.07 (8)
O1–Mg1–O4	93.27 (8)	O1–Mg2–O13	175.66 (9)
O3–Mg1–O4	153.61 (9)	O12–Mg2–O8	99.64 (9)
O10–Mg1–O11	91.51 (9)	O6–Mg2–O8	154.89 (9)
O1–Mg1–O11	175.96 (9)	O1–Mg2–O8	92.44 (8)
O3–Mg1–O11	84.13 (8)	O13–Mg2–O8	89.88 (8)
O4–Mg1–O11	83.45 (8)	O12–Mg2–N2	176.46 (10)
O10–Mg1–N1	174.52 (9)	O6–Mg2–N2	78.81 (8)
O1–Mg1–N1	90.04 (8)	O1–Mg2–N2	91.36 (8)
O3–Mg1–N1	79.20 (8)	O13–Mg2–N2	92.74 (9)
O4–Mg1–N1	77.97 (8)	O8–Mg2–N2	76.89 (8)
O11–Mg1–N1	91.58 (9)	O24–Mg3–O26	88.02 (8)
Mg1–O1–Mg2	132.72 (9)	O24–Mg3–O25	86.88 (8)
O12–Mg2–O6	104.57 (9)	O26–Mg3–O25	90.82 (8)
O10–Mg1–O1–Mg2	50.67 (13)	Mg1–O1–Mg2–O12	40.50 (14)
O3–Mg1–O1–Mg2	155.95 (12)	Mg1–O1–Mg2–O6	145.07 (12)
O4–Mg1–O1–Mg2	–47.05 (13)	Mg1–O1–Mg2–O13	63.1 (12)
O11–Mg1–O1–Mg2	–11.4 (13)	Mg1–O1–Mg2–O8	–59.12 (13)
N1–Mg1–O1–Mg2	–125.01 (13)	Mg1–O1–Mg2–N2	–136.05 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O10—H10C...O8	0.89	1.97	2.828 (3)	160
O10—H10D...O15	0.80	1.92	2.714 (3)	169
O11—H11A...O14 ⁱ	0.82	2.23	2.932 (4)	143
O11—H11B...O22	0.83	1.93	2.743 (3)	164
O12—H12C...O18 ⁱⁱ	0.81	1.93	2.723 (3)	170
O12—H12D...O4	0.88	1.88	2.712 (3)	157
O13—H13C...O18 ⁱⁱⁱ	0.82	2.03	2.812 (3)	158
O13—H13D...O23 ⁱ	0.87	1.93	2.789 (3)	171
O24—H24A...O4	0.88	2.03	2.897 (3)	171
O24—H24B...O16	0.82	1.92	2.742 (3)	176
O25—H25A...O22	0.83	1.91	2.734 (3)	171
O25—H25B...O19 ^{iv}	0.90	1.82	2.712 (3)	170
O26—H26A...O5 ^{iv}	0.85	1.96	2.805 (3)	177
O26—H26B...O20 ⁱ	0.83	1.98	2.807 (3)	177
O14—H14A...O3 ^v	0.84	2.21	2.796 (4)	127
O15—H15C...O21 ⁱ	0.89	1.90	2.759 (3)	163
O15—H15D...O5 ^{vi}	0.85	1.87	2.716 (3)	175
O16—H16A...O8	0.79	2.11	2.893 (3)	171
O16—H16B...O19	0.83	1.93	2.754 (3)	172
O17—H17A...O9	0.93	1.78	2.695 (3)	166
O18—H18A...O17	0.89	1.85	2.722 (4)	166
O18—H18B...O25 ⁱ	0.84	2.03	2.869 (3)	179
O19—H19A...O2 ^v	0.82	1.92	2.737 (3)	179
O19—H19B...O23 ⁱ	0.82	1.96	2.760 (3)	164
O20—H20A...O20 ⁱ	0.82	1.98	2.770 (6)	162
O20—H20B...O16	0.92	2.27	3.008 (3)	138
O21—H21A...O2 ^v	0.81	1.96	2.762 (3)	170
O21—H21B...O20	0.81	1.97	2.761 (4)	164
O22—H22A...O21 ⁱ	0.91	1.87	2.769 (3)	173
O22—H22B...O7 ^{vii}	0.80	1.87	2.662 (3)	173
O23—H23A...O6 ^{viii}	0.81	2.03	2.812 (3)	162
O23—H23B...O9 ^{vii}	0.82	2.05	2.803 (3)	151

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

Crystal data

[Mg(H₂O)₆]_{0.5}[Mg₂(C₁₆H₁₄ClN₂O₉)(H₂O)₄].10H₂O

$M_r = 780.79$

Triclinic, $P\bar{1}$

$a = 9.871$ (2) Å

$b = 13.119$ (3) Å

$c = 13.438$ (3) Å

$\alpha = 88.421$ (3)°

$\beta = 84.029$ (2)°

$\gamma = 84.050$ (3)°

$V = 1721.2$ (6) Å³

Data collection

Bruker SMART 1K CCD area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2000)

$T_{\min} = 0.928$, $T_{\max} = 0.951$

7116 measured reflections

$Z = 2$

$D_x = 1.507$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 3324 reflections

$\theta = 2.2$ – 26.4 °

$\mu = 0.25$ mm⁻¹

$T = 183$ (2) K

Block, colourless

$0.30 \times 0.20 \times 0.20$ mm

5921 independent reflections

4743 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25.0$ °

$h = -11 \rightarrow 11$

$k = -15 \rightarrow 14$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.137$

$S = 1.05$

5921 reflections

430 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0783P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 1.22$ e Å⁻³

$\Delta\rho_{\text{min}} = -1.12$ e Å⁻³

H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^3-H = 0.97$ Å (for methylene) and $Csp^2-H = 0.93$ Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. H atoms attached to O atoms (in water molecules) were located in difference Fourier maps and constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(O)$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: SHELXTL/PC.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1658). Services for accessing these data are described at the back of the journal.

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