Structure of Magnesium Diacetate Tetrahydrate

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Abstract. Tetraaquabis(acetato-O)magnesium, [Mg(C$_2$H$_3$O$_2$)$_2$(H$_2$O)$_4$], $M_r = 214.49$, monoclinic, $P2_1/c$, $a = 4.8084$ (4), $b = 11.9943$ (13), $c = 8.5548$ (8) Å, $\beta = 95.355$ (7)°, $V = 491.24$ (8) Å^3, $Z = 2$, $D_x = 1.45$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å (graphite monochromator), $\mu = 1.86$ cm^{-1}, $F(000) = 228$, $T = 295$ K, final $R = 0.0423$ and $wR = 0.0579$ for 1905 observed reflections. A new, more precise determination of the structure of magnesium acetate tetrahydrate has been performed which allows significant distinctions between the various Mg—O and C—O bonds to be made. Details of the hydrogen-bonding scheme are also more reliably determined.

Introduction. The structure of magnesium acetate tetrahydrate was originally obtained by Shankar, Khubchandani & Padmanabhan (1957) using a multiple film projection technique. However, the need for a more precise determination, especially of the hydrogen positions, has been pointed out, for example by Padmanabhan & Srinivasan (1973), to facilitate spectroscopic work. To some extent the deficiencies in the original publication have been circumvented because of a more recent and more refined X-ray determination of the structure of the isomorphous nickel acetate (Downie, Harrison, Raper & Hepworth, 1971) which has aided various spectroscopic studies on solid magnesium acetate (Raghuvanshi, Khandelwal & Bist, 1982, 1985). We have recently carried out an extensive Raman investigation of aqueous solutions of magnesium acetate (Semmler, 1989; Semmler, Irish & Ozeki, 1990) during which we hoped to determine the structures of the various complexes which exist in solution. To complement this work a new X-ray determination of the structure of crystalline magnesium acetate tetrahydrate was carried out and is reported here. During the review process we have become aware of a more recent determination (Trunov & Endeladze, 1986). This is a considerable improvement on the earlier

work of Shankar *et al.*, but its precision is significantly less than that of the work presented here. In particular we are able to distinguish different Mg—O and C—O bonds.

Experimental. Colorless needle-like crystals of the title compound were obtained by slow evaporation of water from a saturated aqueous solution of magnesium acetate. From one of these needles a prism (0.42 × 0.40 × 0.46 mm) was cut and used for X-ray work. Accurate unit-cell parameters were derived from the refined angles of 30 general reflections (22 $< 2\theta < 32$°), well distributed in reciprocal space, on a Siemens $R3m/V$ diffractometer. The data were collected by 2θ–θ scans (3.5 $< 2\theta < 70.0$°) using variable scan speeds, the rates (2.93–29.30° min^{-1}) being determined from a quick preliminary scan; scan width 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Background measurements were made at the beginning and end of each scan for a total time equal to one quarter of the scan time. Crystal stability was checked by monitoring two reflections (080; 006) every 100 measurements (only ± 2% variation). Empirical absorption corrections were derived from ψ-scan data (transmission factors 0.82–0.90). From 2160 total reflections, 1905 were considered observed [$F \geq 6\sigma(F)$, h:0→7, k:0→19, l:−13→13]. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares methods, the function minimized being $\Sigma w(F_o - F_c)^2$, using Nicolet–Siemens *SHELXTL-Plus* software (Sheldrick, 1987). Hydrogen atoms were located from a difference Fourier synthesis and included in the refinement with isotropic thermal parameters. The number of parameters refined was 90 (data-to-parameter ratio 21.2:1). In the final cycle of refinement an extinction correction $\chi = 0.041$ (8) {where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$} was used. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0037F^2$. The goodness of fit parameter, S, was 1.24 and the largest and mean Δ/σ values were 0.191 and 0.008, respectively. The maximum and minimum residual electron densities were +0.32 and −0.31 e Å^{-3}. The source of atomic scattering factors was *International Tables for X-ray Crystallography* (1974, Vol. IV).

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Table 1. *Atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *and isotropic or equivalent isotropic displacement parameters* ($\text{Å}^2 \times 10^4$; *for* H $\times 10^3$)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U/U_{eq}
Mg	0	0	0	230 (2)
O(1)	2302 (2)	−1452·8 (7)	−165 (1)	304 (2)
O(2)	−660 (3)	−2529·4 (9)	−1623 (2)	451 (3)
O(3)	2699 (2)	839·9 (7)	−1411 (1)	292 (2)
O(4)	2499 (2)	448·6 (9)	1984 (1)	320 (3)
C(1)	1434 (3)	−2404·8 (9)	−664 (2)	283 (3)
C(2)	3001 (4)	−3413 (1)	−34 (2)	466 (5)
H(21)	491 (7)	−327 (3)	6 (3)	75 (9)
H(22)	291 (7)	−331 (3)	111 (3)	87 (9)
H(23)	292 (7)	−396 (3)	−70 (3)	73 (8)
H(31)	219 (5)	121 (2)	−212 (3)	51 (6)
H(32)	420 (5)	114 (2)	−101 (2)	39 (5)
H(41)	419 (6)	40 (2)	192 (3)	45 (5)
H(42)	237 (6)	105 (2)	203 (3)	56 (7)

Table 2. *Bond lengths, bond angles and hydrogen-bond parameters* ($\text{Å},^\circ$)

Mg—O(1)	2·0761 (8)	Mg—O(3)	2·1091 (8)
Mg—O(4)	2·0577 (9)	O(1)—C(1)	1·2754 (14)
O(2)—C(1)	1·2467 (17)	C(1)—C(2)	1·4981 (20)

O(1)—Mg—O(3)	90·09 (3)	O(1)—Mg—O(4)	90·10 (3)
O(3)—Mg—O(4)	90·24 (3)	O(1)—Mg—O(1a)	180·00 (3)
O(1)—Mg—O(3a)	89·91 (3)	O(3)—Mg—O(3a)	180·00 (3)
O(1)—Mg—O(4a)	89·90 (3)	O(3)—Mg—O(4a)	89·76 (3)
O(4)—Mg—O(4a)	180·00 (3)	Mg—O(1)—C(1)	127·92 (5)
O(1)—C(1)—O(2)	123·11 (6)	O(1)—C(1)—C(2)	117·68 (8)
O(2)—C(1)—C(2)	119·20 (9)		

O(4)—H(42)	0·73 (3)	H(42)···O(2a)	1·97 (3)
O(4)···O(2a)	2·6562 (15)	O(3)—H(31)	0·78 (2)
H(31)···O(2d)	1·96 (2)	O(3)···O(2d)	2·7035 (14)
O(3)—H(32)	0·85 (2)	H(32)···O(1b)	1·92 (2)
O(3)···O(1b)	2·7446 (12)	O(4)—H(41)	0·82 (3)
H(41)···O(3b)	2·18 (3)	O(4)···O(3b)	2·8588 (13)

O(3)—H(31)···O(2d)	162 (2)	O(4)—H(42)···O(2a)	157 (2)
O(4)—H(41)···O(3b)	140 (2)	O(3)—H(32)···O(1b)	166 (2)

Symmetry code: (*a*) $-x$, $-y$, $-z$; (*b*) $1-x$, $-y$, $-z$; (*d*) $-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$.
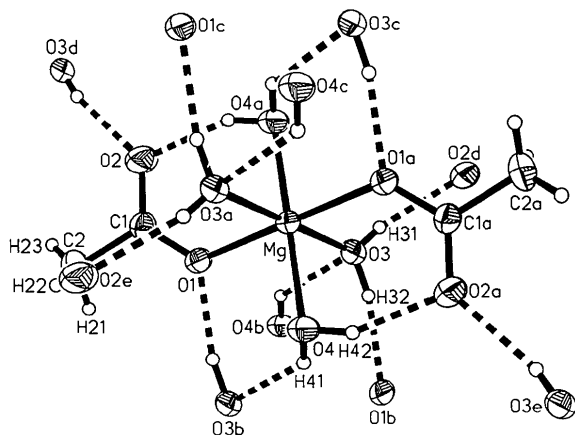

Fig. 1. Magnesium acetate tetrahydrate showing details of hydrogen bonding. The symmetry translations are: (*a*) $-x$, $-y$, $-z$; (*b*) $1-x$, $-y$, $-z$; (*c*) $-1+x$, y, z; (*d*) $-x$, $-\frac{1}{2}+y$, $-\frac{1}{2}-z$; (*e*) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

Discussion. Final positional parameters are listed in Table 1.* The essential structural features described by Shankar *et al.* and Trunov & Endeladze have been confirmed (Fig. 1); however, the molecular parameters are more precisely determined. The structure is analogous to that of the isomorphous nickel compound (Downie *et al.*). The differences that there are reflect the slightly larger size of Mg^{2+} (0·72 Å) compared to Ni^{2+} (0·69 Å) (Tackett, 1989). Each magnesium atom is attached to six atoms in an essentially octahedral fashion though there is some distortion, as is evident in the variety of Mg—O bond lengths in Table 2. This is due to the different ligands, acetate and water, and to differences between the hydrogen-bonding environments of the water molecules. Two of these (type 1) are intramolecularly hydrogen bonded to acetate ions attached to the same magnesium atom, whereas the other two (type 2) are only involved in intermolecular hydrogen bonds. The shortest Mg—O bonds are those to type 1 water molecules, which are about 0·05 Å less than those to type 2. The former are also noticeably shorter than those to the coordinated acetate oxygen atoms, a feature not clear from the work of Trunov & Endeladze. Owing to the *trans* arrangement of the different ligand pairs the distortion due to differing Mg—O bond lengths is not reflected in the bond angles about magnesium, all of which are essentially 90 or 180°. Bond lengths and angles within the acetate ions, and general details of the hydrogen-bonding scheme, are discussed in the papers by Downie *et al.* and Trunov & Endeladze. Our data for the magnesium compound are shown in Table 2. The consequences of the greater precision in the present work can be seen especially clearly in the context of the differences (or lack thereof) of the C—O distances within individual acetate groups. Whereas the Russian workers have indicated that the two distances are 'equalized', from our study it is clear that they are different (by at least 0·02 Å), the bond to the oxygens also attached to magnesium being the longer.

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Structure of *cis*-Diaquabis(1,10-phenanthroline)zinc Sulfate Hexahydrate

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Abstract. $[Zn(C_{12}H_8N_2)_2(H_2O)_2]SO_4.6H_2O$, $M_r = 665.98$, triclinic, $P\bar{1}$, $a = 10.070$ (4), $b = 12.280$ (3), $c = 13.358$ (2) Å, $\alpha = 109.12$ (2), $\beta = 92.58$ (2), $\gamma = 110.85$ (2)°, $V = 1433.9$ (7) Å³, $Z = 2$, $D_x = 1.54$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.1$ cm⁻¹, $F(000) = 692,$. $T = 293$ K, $R = 0.044$ for 3985 observed reflections. The Zn atom is coordinated in a distorted octahedral geometry by four N atoms from two 1,10-phenanthroline (phen) ligands and two water molecules. The intermolecular ring-stacking interactions between the phen ligands occur in two forms: infinite chains and discrete dimers. Hydrogen bonds further stabilize the structure.

Introduction. Phenanthroline, as an excellent planar π system, has often been involved in model compounds to mimic non-covalent interactions in biological processes. Transition-metal complexes of phenanthroline and its substituted derivatives have been found to be probes for examining distinctive conformations along the DNA helix (Barton, 1989). These cationic complexes bind to DNA through weak interactions such as the π stacking associated with intercalation of the aromatic heterocyclic groups between the base pairs, and exhibit a high level of specificity in the recognition of different sites (Pyle, Rehmann, Meshoyrer, Kumar, Turro & Barton, 1989). It is of interest, therefore, to understand the structural features of these compounds. We describe here the structure of *cis*-diaquabis(1,10-phenanthroline)zinc sulfate hexahydrate.

Experimental. The complex was obtained from an aqueous acetone solution of $ZnSO_4.7H_2O$ and 1,10-phenanthroline monohydrate. Crystal $0.48 \times 0.36 \times$

0.32 mm; Nicolet *R3m/E* diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω scan, scan speed $7.32°$ min⁻¹, scan width $1.4°$; $3 < 2\theta < 56°$, h $-12 \rightarrow 12$, k $-15 \rightarrow 15$, l $0 \rightarrow 17$; lattice parameters from 20 reflections within the range $12 < 2\theta < 24°$; Lp and empirical absorption corrections, minimum and maximum transmission coefficients 0.87 and 0.96; two intensity monitors varied <2%; total 6748 unique reflections, 3985 with $I > 3\sigma(I)$. Structure solved by direct methods and Fourier synthesis; block-diagonal least-squares refinement on F for non-H atoms (anisotropic thermal parameters); H atoms were located on a difference map, except some from the water molecules, and were fixed with $U = 0.06$ Å². $R = 0.044$, $wR = 0.062$, $S = 1.13$, where $w = 1/[\sigma^2(F_o) + 0.0017(F_o)^2]$, $(\Delta/\sigma)_{max} = 0.06$, maximum and minimum heights in final difference map 0.55 and -0.36 e Å⁻³, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were performed with the *SHELXTL* program system (Sheldrick, 1983) on an Eclipse S/140 computer.

Discussion. Final atomic coordinates with their e.s.d.'s are listed in Table 1.* Bond lengths and angles are given in Table 2. The compound consists of a discrete $[Zn(phen)_2(H_2O)_2]^{2+}$ cation, sulfate anion and six water molecules. Figs. 1 and 2 show the structure of the cation and the crystal packing.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54269 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.