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The Crystal and Molecular Structure of Bis(diacetamide) diaquomagnesium(II) Didiacetamide Perchlorate

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The crystal structure of bis(diacetamide)diaquomagnesium(II) didiacetamide perchlorate, $[Mg(OH_2)_2(DA)_2](DA)_2(ClO_4)_2$*, has been determined from three-dimensional X-ray data. The unit cell is triclinic, space group* $P\bar{1}$*, with dimensions* $a = 10.614(2)$ Å, $b = 10.050(2)$ Å, $c = 7.655(2)$ Å, $\alpha = 75.69(7)°$, $\beta = 70.49(8)°$, $\gamma = 83.04(8)°$, *and* $Z = 1$. *The structure was solved by the heavy atom method and refined by block-diagonal least squares to a conventional unweighted R of 0.088.*

The coordination sphere about the magnesium can be described as a slightly distorted octahedron formed by the carbonyl oxygens of two diacetamide ligands in the equatorial plane and the oxygen atoms of two water molecules at the apices. In addition, two uncomplexed diacetamide molecules are hydrogen bonded to the coordinated water molecules. Other hydrogen bonds between the amide nitrogens and perchlorate oxygens cause the formation of infinite chains. Magnesium–oxygen bond distances are in the range 2.026(7) to 2.048(6) Å.

Introduction

The complex $[Mg(OH_2)_2(DA)_2](DA)_2(ClO_4)_2$, bis(diacetamide)diaquomagnesium(II) didiacetamide perchlorate (DA = diacetamide), indicated through stoichiometry that it was ten-coordinate. In view of the unusually high coordination numbers found for $[Ba(DA)_5](ClO_4)_2$ and $[Sr(OH_2)(DA)_4](ClO_4)_2$, ten [1] and nine [2] respectively, it was desired to resolve the coordination number of magnesium in this complex.

Experimental

Preparation

$[Mg(OH_2)_2(DA)_2](DA)_2(ClO_4)_2$ was prepared by a modification of the method previously described [3]. Stoichiometric quantities of recrystallized diacetamide, anhydrous magnesium perchlorate, and deionized water were dissolved in the minimum amount of pure methanol. Slow evaporation of the solvent yielded small, colorless crystals that had to be sealed in quartz capillaries for all X-ray measurements.

X-ray Study

Preliminary studies indicated that the crystals belonged to the triclinic system. Lattice parameters as determined on an Enraf–Nonius CAD-4 automated diffractometer were $a = 10.614(2)$ Å, $b = 10.050(2)$ Å, $c = 7.655(2)$ Å, $\alpha = 75.69(8)°$, $\beta = 70.49(7)°$, and $\gamma = 83.04(8)°$. Density measurements by flotation showed there was one molecule per unit cell ($d_{obs} = 1.483$ g/cm^3, $d_{calc} = 1.477$ g/cm^3).

Intensity data were collected on the CAD-4 using graphite monochromatized copper Kα radiation. All values were scaled to a single intensity control reflection which was measured every thirty minutes. A total of 1319 observed reflections ($I \geqslant 1.5\ \sigma_I$) was collected within the range $0° < \theta < 65°$.

Solution and Refinement

The structure was solved by the heavy atom method using computer programs obtained from the National Research Council of Canada [4]. A chlorine atom was initially placed at the origin and the remaining non-hydrogen atoms were located from Fourier maps calculated for the space group P1. From normalized structure factor calculations, it appeared as if the space group were centrosymmetric. Examination of the spatial distribution of the atomic coordinates helped confirm the presence of a center of symmetry. The unit cell was then translated so that the center of symmetry (Mg atom) was placed at

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TABLE I. Fractional Atomic Coordinates and Isotropic Thermal Parameters.

Atom	x/*a*	y/*b*	z/*c*	B
Mg	0.0	0.0	0.0	2.9
N_1	0.2787(6)	–0.0901(8)	0.1166(11)	2.8
N_2	0.1876(7)	–0.4503(8)	0.4668(11)	3.3
O_1	0.1856(5)	–0.0860(6)	–0.1126(8)	3.1
O_2	0.0807(5)	0.0289(6)	0.1947(8)	3.2
O_3	–0.0615(6)	–0.1864(7)	0.1650(10)	3.7
O_4	0.1462(7)	–0.3931(7)	0.1858(10)	4.5
O_5	0.0175(7)	–0.2918(8)	0.5005(10)	4.7
C_1	0.4026(10)	–0.1893(13)	–0.1556(17)	4.5
C_2	0.2792(8)	–0.1191(9)	–0.0475(13)	2.5
C_3	0.1840(8)	–0.0167(9)	0.2303(13)	3.3
C_4	0.2125(10)	0.0073(12)	0.3950(15)	3.4
C_5	0.3136(14)	–0.5663(15)	0.2168(20)	5.8
C_6	0.2059(10)	–0.4596(10)	0.2843(15)	3.8
C_7	0.0961(10)	–0.3673(10)	0.5678(14)	4.1
C_8	0.1014(15)	–0.3766(14)	0.7601(18)	4.8
Cl	0.5794(3)	–0.2608(3)	0.2842(4)	4.8
O_6	0.5872(17)	–0.1786(15)	0.1204(22)	11.5
O_7	0.4510(11)	–0.2816(19)	0.4021(30)	20.6
O_8	0.6427(13)	–0.2121(22)	0.3860(19)	11.2
O_9	0.6366(22)	–0.3794(20)	0.2744(28)	15.9
H_1	0.44	–0.23	–0.06	
H_2	0.39	–0.24	–0.22	
H_3	0.48	–0.12	–0.25	
H_4	0.34	–0.12	0.19	
H_5	0.29	0.03	0.31	
H_6	0.21	–0.07	0.46	
H_7	0.16	0.07	0.42	
H_8	0.00	–0.25	0.21	
H_9	–0.14	–0.21	0.22	
H_{10}	0.36	–0.57	0.08	
H_{11}	0.30	–0.67	0.35	
H_{12}	0.39	–0.57	0.25	
H_{13}	0.26	–0.50	0.54	
H_{14}	0.10	–0.48	0.85	
H_{15}	0.04	–0.38	0.85	
H_{16}	0.18	–0.33	0.79	

the origin. The structure was refined anisotropically by block-diagonal least squares in both P1 and $P\bar{1}$. Since the estimated standard deviations in the atomic coordinates were significantly smaller for the centrosymmetric case, the possibility of the crystal belonging to space group P1 was elimated at this point and all further calculations were done for $P\bar{1}$. The hydrogen atoms were located from a difference Fourier map, but attempts to refine on their positions proved unsuccessful since C–H, N–H, and O–H bond distances became shorter with successive cycles of refinement. The hydrogen atom coordinates given in Table I represent the unrefined positions as read directly from the difference map. A final R-factor of 0.088 was obtained.

The mean atomic scattering factors were corrected for both real and imaginary dispersion effects [5]. The function minimized in the least squares calculation was $R = \Sigma w(|F_o|-k|F_c|)^2$. All observed reflections were given unit weight and unobserved reflections were not included in the summations. A table of observed and calculated structure factors is available from the Editor. Fractional atomic coordinates and anisotropic thermal parameters are given in Tables I and II respectively.

Results and Discussion

Magnesium atoms have been shown to be capable of forming complexes in which uncoordinated molecules are held by hydrogen bonding. In the complex $MgEDTAH_2 \cdot 6H_2O$ the magnesium atoms are totally coordinated by the six water molecules [6]. These moieties in turn form hydrogen bonds to the uncomplexed H_2EDTA. Passer *et al.* [7] report a magnesium complex with water and EDTA in which the anion is similarly held by hydrogen bonds to a hexa-aquomagnesium cation.

In $[Mg(OH_2)_2(DA)_2](DA)_2(ClO_4)_2$, the magnesium is coordinated to six oxygens that form a slightly distorted octahedron. Four of the oxygen atoms are contributed by two bidentate diacetamides (Fig. 1), forming the equatorial plane of the octahedron, and the two oxygen atoms in the apical positions are contributed by the two water molecules. Magnesium–oxygen bond distances range from 2.026 (7) to 2.048(6) Å (Fig. 2) and are very close to the sum of the atomic radii [8] (Mg = 1.50 Å, O = 0.60 Å).

Both the complexed and the uncomplexed diacetamides are in the *anti–anti* conformation and are very nearly planar (r.m.s. deviation < 0.2 Å). The hydrogen bond between the water molecule and the uncomplexed diacetamide may be considered to involve one hydrogen atom and both carbonyl oxygens. The hydrogen to carbonyl oxygen distances are less than the sum of the van der Waals radii [9] of hydrogen (1.2–1.45 Å) and oxygen (1.5 Å). Similar interactions also exist between the amide groups and the perchlorate. H_4 forms hydrogen bonds between N_1 and perchlorate oxygens O_6 and O_7. Based on the H——O distances and the N–H——O angles, these bonds should be of approximately equal strength. The hydrogen bond between N_2 and O_9 is probably stronger than that between N_2 and O_8 because of the shorter H——O distance and the angle N_2–H_{13}——O_9 being closer to 180°. In all cases, the H——O distances are within the range of the sum of the van der Waals radii of hydrogen and oxygen. The effect of the N–H——O bonding is to form infinite chains.

The packing is shown in Figure 1. Interatomic distances and bond angles are given in Figure 2.

TABLE II. Anisotropic Thermal Parameters as Mean Square Amplitude.[a]

Atom	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{23} \times 10^4$	$U_{13} \times 10^4$	$U_{12} \times 10^4$
Mg	–	–	–	–	–	–
N_1	286(37)	579(51)	583(51)	−140(42)	−241(36)	199(34)
N_2	503(48)	472(51)	624(54)	−84(42)	−290(42)	68(38)
O_1	297(30)	581(41)	451(37)	−180(32)	−129(27)	141(28)
O_2	300(30)	584(42)	519(39)	−235(33)	−196(28)	149(28)
O_3	395(35)	626(45)	697(47)	−31(37)	−237(34)	38(31)
O_4	820(52)	684(50)	607(48)	−256(40)	−293(41)	336(40)
O_5	826(53)	733(53)	708(52)	−317(43)	−325(43)	371(42)
C_1	401(56)	1191(104)	875(88)	−537(80)	−221(57)	416(62)
C_2	284(44)	472(58)	477(56)	−96(46)	−95(40)	150(40)
C_3	363(48)	415(56)	544(61)	−143(47)	−157(44)	−4(40)
C_4	539(63)	970(89)	605(71)	−302(65)	−334(56)	65(58)
C_5	988(101)	1134(116)	1021(108)	−371(93)	−73(84)	775(90)
C_6	554(61)	475(63)	619(69)	−131(53)	−174(53)	185(48)
C_7	585(62)	445(60)	550(65)	−148(50)	−203(51)	−36(47)
C_8	1388(124)	927(101)	642(82)	−229(74)	−466(84)	7(87)
Cl	446(13)	775(19)	844(20)	−72(15)	−331(13)	128(12)
O_6	3392(210)	1953(140)	2274(155)	1272(122)	−2197(161)	−1517(141)
O_7	486(68)	3274(222)	4180(273)	−766(200)	−434(112)	−363(101)
O_8	1285(105)	5072(294)	1270(106)	−980(145)	−416(86)	−993(143)
O_9	4066(289)	2806(214)	2650(212)	−1433(176)	−1212(198)	2441(212)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

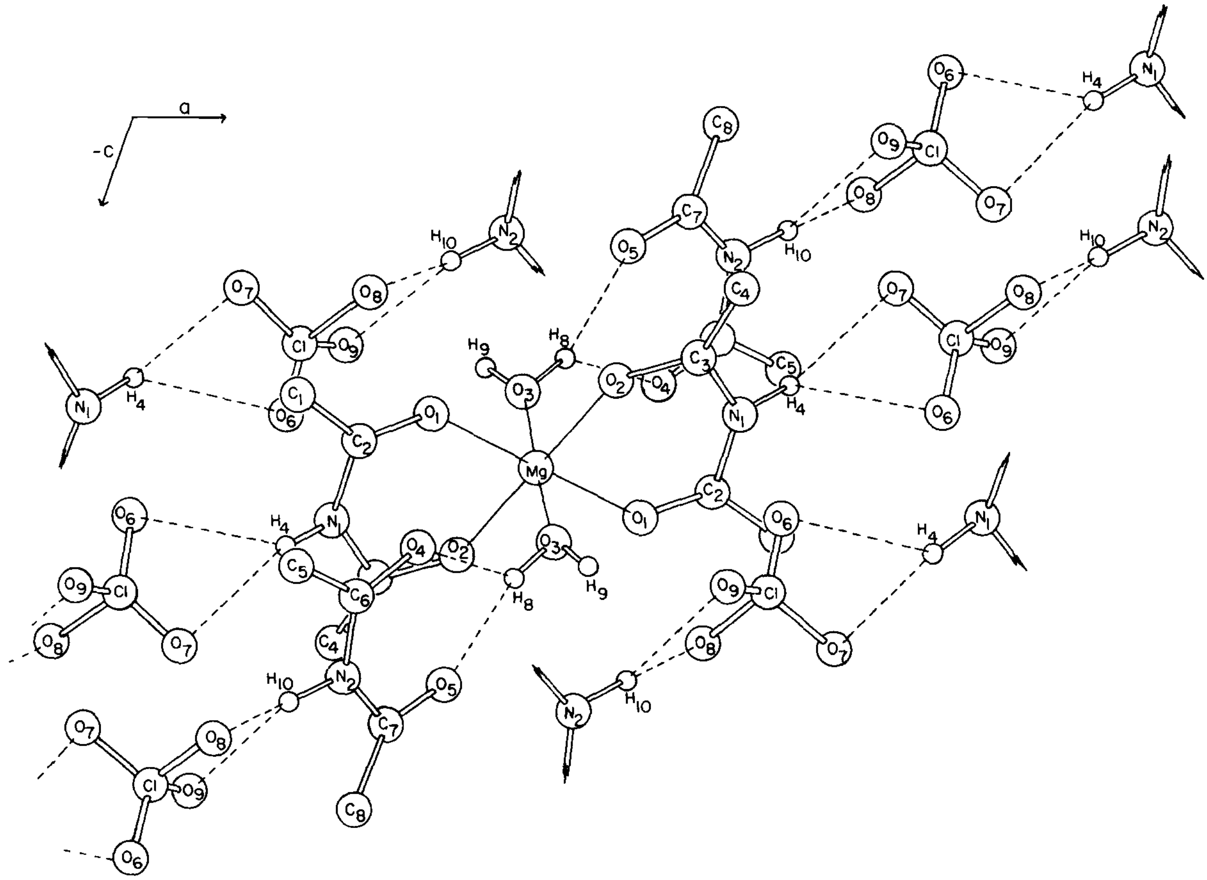

Fig. 1. Structure of $[Mg(OH_2)_2(DA)_2](DA)_2(ClO_4)_2$.

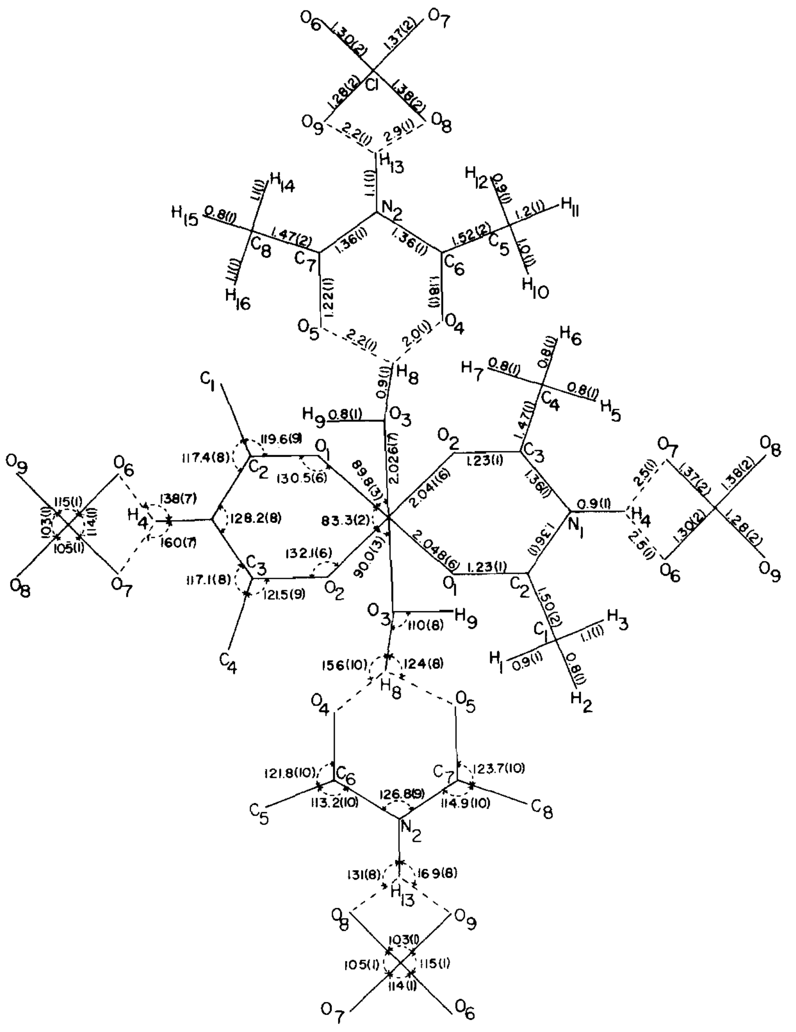

Fig. 2. Interatomic distances and bond angles.

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