average. The absence of any significant deviation from the average among the four C-O bond lengths provides further evidence for weak complexing; in the cobalt[3] and iron[8,11] chelates, by contrast, the division of the C-O bond lengths into two distinctive subgroups is quite in accord with the relatively strong complexing. By comparison with the data from earlier structure determinations for EDTA chelates, the C-C and C-N bond lengths in both the ethylenediamine and glycinato rings reported herein are notable only for their higher precision; these newer results are, however, especially useful for comparison with the corresponding data reported in the accompanying paper[12] for the extended uncomplexed $[H_2EDTA]^{2-}$ ion as it exists in crystalline $Mg(OH_2)_6[H_2EDTA]$.

Departures from planarity are smaller in a glycinato ring (Figure 2) which is closed through a short (2.08 Å) $Mg-O_1$ bond than in a ring which is closed through a long (2.27 Å) $Mg-O_3$ bond; the sums of the interior angles in these rings are 534.9 and 528.1°, respectively. Associated with the stronger complexing in a ring of the first type is a more favorable bond angle at the magnesium atom, $O_1MgN = 74.2°$ as compared with $O_3MgN = 70.2°$, along with the apparent capacity to enforce significant deviations of $|2.2|$ to $|3.6|°$ from the ideal values in the remaining bond angles (Table IV). Angular strain in a glycinato ring of the second type is largely confined to the unduly small angle O_3MgN.

The C_2 twisting of the ethylenediamine ring from planarity reduces the sum of the interior angles to 515.6°. Apart from the Mg-N bond length, the bond parameters differ immaterially from those obtained in earlier studies of EDTA chelates; they are principally of interest for comparison with corresponding parameters in the uncomplexed $[H_2EDTA]^{2-}$ ion.[12]

From the further examination of Figure 1 and Table IV, we see that the coordination polyhedron surrounding a sodium ion is a very irregular octahedron of no required symmetry. Three carboxylate oxygen atoms from two adjacent $[H_2OMgEDTA]^{2-}$ ions define one triangular face of the octahedron, and three water molecules define the opposite face. The sodium ion in the first octant (Figure 1) and four of its ligand atoms, O_3, O_{w2}, O_{w3}, and O_{w4} have precisely the coordinates listed in Table I; the other two ligands are O_1' from the complex anion centered at the origin and O_4' from a complex which is derived from the first by unit translation along *z*. Sodium ions are tightly bridged in pairs by O_{w3} atoms of water molecules lying on twofold axes at $0, y, n/2$ with $n = \pm1, \pm2$, etc. These structural subunits $(O_{w3} + 2Na^+)$ alternate with the complex anions along *z* to give distinctive linear chains (Figure 1). Intrachain hydrogen bonds are identified as $O_{w1} \cdots O_{w4} = 2.718$ (4) Å with $O_{w4}O_{w1}O_{w4}' = 112.9$ (3)° and $O_2 \cdots O_{w2} = 2.851$ (4) Å with $C_1O_2O_{w2} = 107.4$ (2)°. The network of interchain hydrogen bonding involves $O_2 \cdots O_{w3} = 2.704$ (6) Å with $C_1O_2O_{w3} = 121.9$ (2)°, $O_2 \cdots O_{w4} = 2.910$ (5) Å with $C_1O_2O_{w4} = 116.2$ (2)°, and $O_4 \cdots O_{w4} = 2.964$ (6) Å with $C_3O_4O_{w4} = 108.6$ (2)°. It is clear that interactions between chains are very much smaller than those within the chains.

Registry No. $Na_2[H_2OMgEDTA]\cdot5H_2O$, 40025-62-5.

Contribution from the Department of Chemistry,
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Structure of Hexaaquomagnesium Dihydrogenethylenediaminetetraacetate, $Mg(OH_2)_6H_2EDTA$. Stereochemistry of the Uncomplexed H_2EDTA^{2-} Ion[1]

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$Mg(OH_2)_6H_2EDTA$ (H_4EDTA = ethylenediaminetetraacetic acid) crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.781$ (1), $b = 13.478$ (2), $c = 8.385$ (1) Å, $\cos\beta = -0.0269$ (2) or $\beta = 91.55°$, and $Z = 2$. Diffracted intensities were recorded from a spherical specimen of 0.42-mm diameter with Mo Kα radiation on a computer-controlled four-circle diffractometer. Of the 2840 independent reflections scanned for $(\sin\theta)/\lambda \lesssim 0.743$ Å^{-1}, the 2529 retained as observed gave a data/parameter ratio of 20.4 for the anisotropic, full-matrix, least-squares refinement of structure. The centrosymmetric $Mg(OH_2)_6{}^{2+}$ and H_2EDTA^{2-} species are tied into a three-dimensional network through an elaborate pattern of hydrogen bonding. The presence of the N-H bonds in H_2EDTA^{2-} leads to an averaged C-N bond length of 1.498 (2, 4) Å as compared with 1.471 (3, 2) Å in the $[H_2OMgEDTA]^{2-}$ chelate (the first figure in parentheses is the esd of an individual determination and the second is the mean deviation from the average). Variations in the C-C and C-O bond lengths, both within and between the two species, are quite trivial.

Introduction

As pointed out in the preceding paper[2] and amplified below, a crystalline phase of empirical composition, $MgH_2EDTA\cdot6H_2O$ (H_4EDTA = ethylenediaminetetraacetic acid), is the initial product of crystallization at pH <6.8 from aqueous solutions which might otherwise be expected to provide crystalline salts containing an anionic chelate of Mg(II), *e.g.*, the $[H_2OMgEDTA]^{2-}$ species.[2] The X-ray analysis of structure reported herein was undertaken to ascertain whether this ubiquitous phase is correctly formulated as the acid salt, $Mg(OH_2)_6H_2EDTA$, containing the uncomplexed H_2EDTA^{2-} ion or as the crystalline hydrate of a chelate, *e.g.*, the quadridentate octahedral $(H_2O)_2MgH_2EDTA$ molecule with two uncomplexed glycine arms. That the phase is the acid salt was fully established by M. O'D. J. through a structure determination based upon photographically recorded data.[3] It was recognized, however, that certain quantitative deficiencies in the preliminary study could be rectified through structure refinement based upon the more accurate

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(1) Research supported in part by National Science Foundation Grant GP-6710X, by Public Health Research Grant 2-R01-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

(2) J. J. Stezowski, R. Countryman, and J. L. Hoard, *Inorg. Chem.*, 12, 1749 (1973).

(3) M. M. O'Donnell, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1966.

Table I. Atomic Coordinates in the Asymmetric Unit of Structure[a]

Atom type[a]	Fractional coordinates[b]		
	10^4x	10^4y	10^4z
Mg	0	0	0
O_{w1}	−2659 (1)	133 (1)	189 (2)
O_{w2}	249 (2)	1409 (1)	−1001 (1)
O_{w3}	326 (1)	634 (1)	2214 (1)
O_1	5037 (2)	1662 (1)	270 (2)
O_2	3562 (2)	1407 (1)	2480 (2)
O_3	9645 (1)	3170 (1)	801 (1)
O_4	7731 (1)	3446 (1)	−1195 (1)
N	5054 (1)	3655 (1)	684 (1)
C_1	4423 (2)	4701 (1)	540 (2)
C_2	3758 (2)	3043 (1)	1522 (2)
C_3	4176 (2)	1944 (1)	1416 (2)
C_4	6804 (2)	3567 (1)	1476 (2)
C_5	8175 (2)	3383 (1)	245 (2)

[a] O_{wi} and O_i denote oxygen atoms in water molecules and carboxylate groups, respectively. [b] The figure in parentheses following each coordinate is the estimated standard deviation in the last significant figure.

intensity data obtainable by counter measurement—that, indeed, the extraordinarily high quality of the crystals would make it feasible to determine very precise stereochemical parameters. The realization of this program (by V. W. D.) is reported herein; the comparison of the structural parameters in the extended and (apart from hydrogen bonding) uncomplexed H_2EDTA^{2-} ion with those observed in $[H_2OMgEDTA]^{2-}$ and other chelated species commands special interest.

Experimental Section

An aqueous slurry containing equimolar amounts of magnesium carbonate and ethylenediaminetetraacetic acid gave, upon warming, a clear stock solution (pH ~3). The addition to an aliquot of this stock solution of an equimolar amount of the carbonate of lithium, sodium, potassium, calcium, or magnesium, with subsequent warming, led in each case to a clear solution ($5 < pH < 6$). When subjected to slow isothermal evaporation, every such solution—as also a portion of the stock solution—gave initially crystals of the $Mg(OH_2)_6H_2EDTA$ phase.[4]

The brilliant transparent crystals displayed a face development and optical behavior consistent with the monoclinic holohedral crystal class C_{2h}-$2/m$. Sensitive tests for piezoelectricity, made with a Geibe-Schiebe detector, were negative. Systematically absent reflections from the Weissenberg and precession X-ray diffraction patterns given by a single crystal were those uniquely demanded by the monoclinic space group[5] $P2_1/c$-$C_{2h}{}^5$. Use of the accurate lattice constants given below and an assumed cell content of 2 $[Mg(OH_2)_6H_2EDTA]$ led to a calculated density at 20° of 1.597 g/cm³ in agreement with that measured by flotation, 1.60 (1) g/cm³.

The simple atomic arrangement in the crystal was determined by the straightforward application of statistically "direct" methods to photographically recorded three-dimensionally correlated data.[3] Fourteen interpenetrating layers of equiinclination Weissenberg intensity data, seven each along *a* and *c*, were recorded using multiple-film techniques and Ni-filtered Cu Kα radiation. But it then turned out that photometric measurement of the diffracted intensities with a Joyce-Loebl Flying Spot microdensitometer was beset with a host of problems which, as detailed in the referenced thesis,[3] were never quite satisfactorily solved. The 1211 independent data which came out of the three-dimensional correlation of the relative $|F_o|^2$ values did lead without difficulty to a physically rational structure, but least-squares refinement of the structural parameters led to a conventional residual (R_1) of 0.103, to a weighted residual (R_2) of 0.176, and to nonpositive definite assignments to several thermal parameters. Taking these results as convincing evidence for unreliable intensities, we proceeded to collect an entirely new set of data on a computer-controlled four-circle Picker FACS-I diffractometer using Zr-filtered Mo Kα radiation.

A large well-shaped crystal of $Mg(OH_2)_6H_2EDTA$ was ground to a sphere of 0.42-mm diameter and was mounted on a glass fiber having a tip diameter of 0.1 mm. Least-squares refinement of the diffraction geometry recorded with automated centering of 12 fully resolved reflections ($44° \lesssim |2\theta| \lesssim 57°$) on the diffractometer led to the lattice parameters (λ 0.70926 Å) $a = 7.7812$ (11), $b = 13.4777$ (17), $c = 8.3848$ (8) Å, and $\cos\beta = -0.0269$ (2) or $\beta = 91.55°$ at 20 ± 1°. Intensity measurements utilized the θ-2θ scanning technique at a takeoff angle of ~2° with a scanning rate of 1°/min, a scanning range for each reflection of $(2.60 + 0.692 \tan\theta)°$, and a counting period of 40 sec for background at each end of the scan. During the scanning of the 2840 independent reflections having $(\sin\theta)/\lambda \lesssim 0.743$ Å^{-1}, the intensities of three standard reflections displayed no observable trend with time.

Since the absorption of X-rays in the spherical specimen with $\mu R = 0.040$ (μ (the linear absorption coefficient) = 0.191 mm^{-1}, $R = 0.42/2 = 0.21$ mm) was virtually independent of scattering angle, the intensity data were reduced directly to relative squared amplitudes, $|F_o|^2$, by application of the Lorentz and polarization factor. Of the 2840 reflections scanned, just 311 were rejected as objectively unobserved through application of the low-rejection criterion, $|F_o| < 0.5\sigma_F$ wherein σ_F is defined as in the preceding paper.[2] The remaining 2529 reflections were then employed in successive stages of structure refinement as follows: (1) isotropic full-matrix least-squares refinement of the parameters for all atoms save hydrogen; (2) difference Fourier synthesis to give approximate positions for all 13 hydrogen atoms; (3) full-matrix least-squares refinement of all structural parameters, anisotropically save for the isotropic thermal parameters of the hydrogen atoms. Atomic form factors, all computing programs, and the weighting scheme employed during final least-squares refinement were those specified in the preceding paper.[2] With the data/parameter ratio of 2529/124 = 20.4 corresponding to the rejection as unobserved of just 10.9% of all scanned reflections, the final values of the conventional and weighted residuals were 0.045 and 0.057, respectively.[6]

The coordinates of the carbon and all heavier atoms in the asymmetric unit of structure and the associated anisotropic thermal parameters are listed in Tables I and II, respectively; "refined" structural parameters of the hydrogen atoms are given in Table III.

Additional cycles of least-squares refinement, characterized by the exclusion of the 598 "low-angle" reflections having $(\sin\theta)/\lambda < 0.437$ Å^{-1} (and the inclusion *pro forma* of hydrogen contributions with fixed values of the parameters), led to residuals of 0.048 and 0.058 for R_1 and R_2, respectively. These computations were designed to make the structural model, which assumes spherical symmetry in the atomic form factors, a better approximation to physical reality for the carbon and all heavier atoms.[7] Possibly significant alterations in the bond lengths calculated from the data in Table I were limited to the C-C bonds, but even for these bonds the averaged increase in length of 0.004 Å amounted only to two standard deviations.

Discussion

Tables IV and V are listings of bond lengths and bond angles, respectively, within the hexaaquomagnesium ion, $Mg(OH_2)_6{}^{2+}$, and the dihydrogenethylenediaminetetraacetate ion, H_2EDTA^{2-}, the structural subunits employed for development of the three-dimensional crystalline arrangement. Table VI provides the quantitative description of the elaborate pattern of hydrogen bonding which ties the $Mg(OH_2)_6{}^{2+}$ and H_2EDTA^{2-} ions into the three-dimensional network; we note, in this connection, that it is the nitrogen atoms of H_2EDTA^{2-} which are protonated (Table IV) to give the anion its acidic character.

Figure 1 is a computer-drawn diagram in perspective, as viewed along *a*, of (slightly more than) the contents of one unit cell in the crystalline arrangement. Magnesium ions of the $Mg(OH_2)_6{}^{2+}$ species are positioned at the inversion centers

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(4) See also G. Brunisholz, *Chimia*, 11, 363 (1957); *Helv. Chim. Acta*, 40, 2004 (1957).

(5) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 99.

(6) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1754.

(7) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, 94, 6689 (1972).

Table II. Thermal Parameters of Atoms in the Asymmetric Unit of Structure

Atom type[a]	Anisotropic parameters,[b] Å^2						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
Mg	1.36 (2)	1.48 (2)	1.58 (2)	0.13 (2)	0.04 (2)	−0.26 (2)	1.45
O_{w1}	1.48 (4)	1.76 (4)	4.10 (6)	0.23 (3)	0.05 (4)	−0.73 (4)	2.13
O_{w2}	2.93 (5)	1.69 (4)	2.13 (4)	0.28 (3)	0.03 (4)	0.02 (3)	2.18
O_{w3}	1.91 (4)	2.70 (4)	2.02 (4)	−0.32 (3)	0.31 (3)	0.84 (3)	2.06
O_1	4.84 (7)	1.92 (4)	2.37 (5)	1.39 (4)	−0.17 (4)	−0.35 (4)	2.57
O_2	2.48 (5)	2.16 (4)	4.00 (6)	−0.78 (4)	−0.73 (4)	1.54 (4)	2.39
O_3	1.45 (4)	3.24 (5)	2.44 (4)	0.54 (3)	−0.04 (3)	−0.37 (4)	2.20
O_4	1.88 (4)	2.90 (5)	1.57 (4)	0.26 (3)	0.33 (3)	0.03 (3)	2.02
N	1.23 (3)	1.01 (3)	1.22 (4)	0.06 (3)	0.10 (3)	0.01 (3)	1.15
C_1	1.70 (4)	0.98 (4)	1.80 (5)	0.12 (3)	0.37 (3)	0.10 (3)	1.41
C_2	1.44 (4)	1.20 (4)	2.02 (5)	−0.10 (3)	0.40 (4)	0.20 (4)	1.48
C_3	2.01 (5)	1.19 (4)	2.19 (5)	−0.16 (4)	−0.80 (4)	0.20 (4)	1.64
C_4	1.23 (4)	1.88 (5)	1.39 (4)	0.09 (3)	−0.01 (3)	0.09 (4)	1.47
C_5	1.39 (4)	1.48 (4)	1.87 (5)	0.04 (3)	0.30 (3)	−0.07 (4)	1.55

[a] O_{wi} and O_i denote oxygen atoms in water molecules and carboxylate groups, respectively. [b] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Parameters for Hydrogen Atoms in the Asymmetric Unit of Structure

Atom type[a]	Fractional coordinates[b]			Thermal
	10^3x	10^3y	10^3z	B,[c] Å^2
H_{w11}	−326 (4)	62 (2)	30 (3)	2.1 (5)
H_{w12}	−329 (4)	−35 (2)	−14 (3)	2.3 (6)
H_{w21}	4 (4)	155 (2)	−192 (4)	2.5 (6)
H_{w22}	9 (4)	194 (2)	−46 (3)	2.1 (6)
H_{w31}	−50 (4)	99 (2)	270 (3)	2.2 (5)
H_{w32}	127 (4)	93 (2)	240 (3)	1.7 (5)
H_N	513 (3)	340 (2)	−28 (2)	0.2 (3)
H_{C11}	438 (3)	500 (2)	163 (3)	0.6 (4)
H_{C12}	327 (3)	468 (2)	9 (2)	0.4 (4)
H_{C21}	373 (3)	322 (2)	260 (3)	1.1 (4)
H_{C22}	267 (3)	314 (2)	100 (3)	0.9 (4)
H_{C41}	706 (3)	417 (2)	208 (3)	0.6 (4)
H_{C42}	680 (3)	300 (2)	221 (3)	0.6 (4)

[a] Each symbol for a hydrogen atom carries, as subscripts, the literal symbol and subscripted number of the atom to which it is directly bonded. A third subscript is used to distinguish between hydrogens bonded to the same atom. [b] The figure in parentheses following each coordinate is the estimated standard deviation in the last significant figure. [c] Isotropic thermal parameter from refinement.

Table IV. Bond Lengths in $Mg(OH_2)_6H_2EDTA$

Bond class[a]	Length,[b] Å	Bond class[a]	Length,[b] Å
$Mg-O_{w1}$	2.087 (1)	$O_{w1}-H_{w11}$	0.82 (3)
$Mg-O_{w2}$	2.087 (1)	$O_{w1}-H_{w12}$	0.86 (3)
$Mg-O_{w3}$	2.053 (1)	$O_{w2}-H_{w21}$	0.80 (3)
C_1-C_1'	1.524 (2)	$O_{w2}-H_{w22}$	0.86 (3)
C_2-C_3	1.519 (2)	$O_{w3}-H_{w31}$	0.91 (3)
C_4-C_5	1.524 (2)	$O_{w3}-H_{w32}$	0.84 (3)
$N-C_1$	1.496 (2)	C_1-H_{C11}	1.00 (2)
$N-C_2$	1.493 (2)	C_1-H_{C12}	0.97 (2)
$N-C_4$	1.504 (2)	C_2-H_{C21}	0.93 (2)
C_3-O_1	1.246 (2)	C_2-H_{C22}	0.95 (2)
C_3-O_2	1.254 (2)	C_4-H_{C41}	0.98 (2)
C_5-O_3	1.257 (2)	C_4-H_{C42}	0.98 (2)
C_5-O_4	1.250 (2)	$N-H_N$	0.89 (2)

[a] Atoms identified as in Tables I–III. [b] Figure in parentheses following each length is the estimated standard deviation in the last significant figure.

Table V. Bond Angles in $Mg(OH_2)_6H_2EDTA$[a]

Angular class[b]	Value,[c] deg	Angular class[b]	Value,[c] deg
$O_{w1}MgO_{w2}$	93.18 (5)	NC_1C_1'	110.4 (1)
$O_{w1}MgO_{w3}$	89.64 (5)	NC_2C_3	111.3 (1)
$O_{w2}MgO_{w3}$	88.54 (5)	NC_4C_5	110.8 (1)
$C_2C_3O_1$	117.6 (1)	C_1NC_2	109.5 (1)
$C_2C_3O_2$	115.8 (1)	C_1NC_4	113.7 (1)
$C_4C_5O_3$	115.6 (1)	C_2NC_4	111.3 (1)
$C_4C_5O_4$	117.6 (1)	H_NNC_1	109 (1)
$O_1C_3O_2$	126.6 (1)	H_NNC_2	106 (1)
$O_3C_5O_4$	126.8 (1)	H_NNC_4	107 (1)

[a] Three types of angles subtended at carbon atoms, HCH, CCH, and NCH, are not entered in this table; the averaged value of these 15 angles is 109 (1, 1, 3)°, wherein the first figure in parentheses is the esd of an individual determination, while the second and third figures are the respective mean and maximum deviations from the average. [b] Atoms identified as in Tables I–III. [c] Figure in parentheses following each value is the esd in the last significant figure.

Table VI. Parameters Relating to Hydrogen Bonding

Hydrogen bond[a] D–H···A	Interatomic distance,[b] Å		Angle DHA, deg
	D···A	H···A	
$O_{w1}-H_{w11}\cdots O_1{}^c$	2.733 (2)	1.93 (3)	169
$O_{w1}-H_{w12}\cdots O_1{}^d$	3.064 (2)	2.23 (3)	164
$O_{w1}-H_{w12}\cdots O_2{}^d$	3.119 (2)	2.43 (3)	138
$O_{w2}-H_{w21}\cdots O_3{}^e$	2.769 (2)	1.97 (3)	176
$O_{w2}-H_{w22}\cdots O_3{}^c$	2.860 (2)	2.00 (3)	178
$O_{w3}-H_{w31}\cdots O_4{}^f$	2.746 (2)	1.84 (3)	172
$O_{w3}-H_{w32}\cdots O_2$	2.728 (2)	1.90 (3)	168
$N-H_N\cdots O_4$	2.660 (2)	2.18 (2)	113
$N-H_N\cdots O_2{}^g$	2.899 (2)	2.22 (2)	132
$N-H_N\cdots O_1$	2.708 (2)	2.38 (2)	102

[a] The notation identifying each structural *class* of atom is that employed in all other tables. Donor (D) and hydrogen atoms have the coordinates (*x*, *y*, *z*) listed in Tables I and III. Superscripts *c–g* specify the symmetry-related positions of those aceptor (A) atoms which lie outside the asymmetric unit. [b] The number in parentheses following each distance is the esd in the last significant figure. [c] $x - 1, y, z$. [d] $\bar{x}, \bar{y}, \bar{z}$. [e] $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$. [f] $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$. [g] $x, \frac{1}{2} - y, z - \frac{1}{2}$.

0, 0, 0 and 0, 1/2, 1/2, and the pair of extended H_2EDTA^{2-} ions each observe the required C_i-$\bar{1}$ symmetry by being centered at 1/2, 0, 1/2 and 1/2, 1/2, 0. The generally small thermal ellipsoids in Figure 1 reflect the low values of the thermal parameters (Table II) which, isotropically, range from 2.57 Å^2 for one carboxylate oxygen atom downward to 1.15 Å^2 for a nitrogen atom; indeed, these data provide nonspecific, but quite convincing, evidence for high stability of the crystalline arrangement.

More specific evidence for rather strong interaction of the $Mg(OH_2)_6{}^{2+}$ cation with its environment is to be seen in the departure of the MgO_6 octahedron from dimensional regularity. Significant variations among the $Mg-O_w$ bond lengths (Table IV), the O_wMgO_w angles (Table V), and the $O_w\cdots O_w$ packing contacts (2.869 (2)–3.032 (2) Å) are all to be noted.

The N-H bond distance of 0.89 (2) Å (Table IV) and the

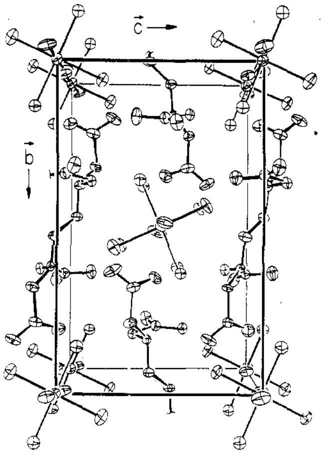

Figure 1. Computer-drawn diagram of one unit cell in the crystalline arrangement. The atoms are represented as ellipsoids in agreement with the thermal parameters listed in Table II.

averaged O-H and C-H bond lengths of 0.85 and 0.97 Å, respectively, are, of course, fictitiously short each by roughly 0.10 Å relative to the true internuclear separations. This approximate positioning of the hydrogen atoms does contribute, nevertheless, to clarification of the pattern of hydrogen bonding and of the special role played by the acidic N-H groups.

From study of the data listed in Table VI, particularly the D· · ·A (donor· · ·acceptor) separations and the DHA angles, it is seen that five of the six hydrogen atoms of the three water molecules are effectively used in conventional hydrogen bonding to five neighboring carboxylate oxygen atoms. Furthermore, the sixth of these hydrogen atoms, H_{w12}, is positioned so as to be in somewhat stabilizing interaction with two carboxylate oxygen atoms of the O_1 and O_2 types, rather more so with the first. The averaged value, 1.93 Å, of the H· · ·A (of $H\cdots O_i$) distances in the five fully constituted bond systems presumably is ~0.10 Å longer than the averaged internuclear distance by reason of the underestimation of the O_{wi}-H internuclear distance (*vide supra*).

We then note (Table VI) that while all three of the $H_N\cdots O_i$ separations surely correspond to stabilizing interactions, only the NH_NO_2 angle of 132° is the least suggestive of conventional hydrogen bonding.

Turning now to the precisely determined bond lengths (Table IV) in the H_2EDTA^{2-} anion of $\bar{1}$ symmetry, we see that the four C-O distances average to 1.252 (2, 4, 6) Å, the three C-C distances to 1.522 (2, 2, 3) Å, and the three C-N distances to 1.498 (2, 4, 6) Å, wherein the first figure within the parentheses following an averaged length is the esd of an individual determination and the second and third figures are the respective mean and maximum deviations from the average.[8] The corresponding averaged bond lengths in the $[H_2OMgEDTA]^{2-}$ chelate of required C_2 symmetry are C-O = 1.255 (3, 3, 5), C-C = 1.518 (5, 2, 3)[9], and C-N = 1.471 (3, 2, 3) Å. The data suggest that the C-O bond lengths are not materially altered either by the rather weak complexing[2] of the carboxylate oxygen atoms to a metal cation such as Mg^{2+} or by the involvement of the oxygen atoms in fairly strong hydrogen bonding.

We note also that the structure determination for $Mg(OH_2)_6H_2EDTA$ provides compelling evidence for an aliphatic C-C bond in the ethylenediamine entity of the uncomplexed H_2EDTA^{2-} ion (the C_1-C_1' bond in Table IV) which is closely comparable in length with the C-C bond formed between methylene carbon and trigonally hybridized carboxylate carbon atoms. There is, consequently, no reason to suppose that this phenomenon, which has frequently been observed (at a lower level of precision) in chelated ethylenediamine rings, is uniquely associated with ring formation.

Certainly the most interesting feature of the comparative data cited above is the significant increase of ~0.027 Å in the C-N bond distance when protonation of the nitrogen atom is substituted for the Mg-N complexing bond. Protonation allows the stripped hydrogen nucleus to penetrate the electron cloud associated with the "inert" electron pair to within about 1.00 Å of the nitrogen nucleus. The formation of the N-H bond requires some stretching of the C-N bonds to new equilibrium distances primarily, we suppose, as the consequence of the coulombic repulsion of the proton for the nuclei of the carbon atoms.

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[8] Exclusion of the low-angle data from the least-squares refinement of structure (*vide supra*) leads to C-C = 1.526 (2, 2, 3) Å (and to alterations <0.001 Å in the averaged C-O and C-N distances). Refinement procedures used in obtaining the data listed in Tables I-VI more nearly parallel those employed in the preceding paper.[2]

[9] The rather large esd of 0.005 Å is the root-mean-square of the three values 0.004, 0.004, and 0.006 Å.