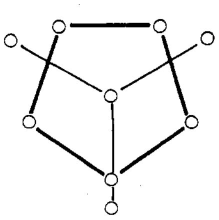
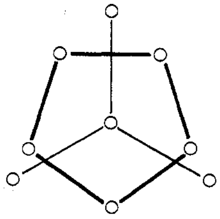


π-$C_5H_5Fe(CO)_3^+$



π-$C_5H_5Mn(CO)_3$

is a 12° rotation of the carbon monoxide ligands relative to the cyclopentadienyl ring. This transition, a 12° rotation, which may or may not be the result of packing forces in the crystal, gives the two compounds different geometrical configurations, but it would be difficult to say whether this would affect their relative reactivities.

Registry No. π-$C_5H_5Fe(CO)_3PF_6$, 12079-61-7.

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850

Structure of the Ethylenediaminetetraacetatoaquomagnesate(II) Ion in a Crystalline Sodium Salt. Comparative Stereochemistry of the Seven-Coordinate Chelates of Magnesium(II), Manganese(II), and Iron(III)[1]

JOHN J. STEZOWSKI, RACHEL COUNTRYMAN, and J. L. HOARD*

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The salt, $Na_2[H_2OMgEDTA]\cdot 5H_2O$ ($EDTA^{4-}$ = ethylenediaminetetraacetate), crystallizes in the monoclinic space group C_2 with $a = 11.504$ (3), $b = 9.801$ (3), $c = 8.816$ (3) Å, $\cos\beta = -0.3565$ (3) or $\beta = 110.88°$, and $Z = 2$. Diffracted intensities were recorded with Zr-filtered Mo Kα radiation on a computer-controlled four-circle diffractometer. Of the 3800 independent reflections scanned for $(\sin\theta)/\lambda \lesssim 0.98$ Å,$^{-1}$ the 2791 retained as objectively observed gave a data/parameter ratio of 21 for the anisotropic, full-matrix, least-squares refinement of structure. The seven-coordinate $[H_2OMgEDTA]^{2-}$ ion of required C_2 symmetry carries two pairs of very long bonds, Mg–N = 2.378 (2) and Mg–O = 2.270 (3) Å, along with a fairly short pair, Mg–O = 2.078 (2) Å, and the unique $Mg-OH_2$ bond at 2.060 (3) Å. All coordination polyhedra in the EDTA chelates of Mg(II), Mn(II), and Fe(III), as also in $[H_2OFeDCTA]^-$ ($DCTA^{4-}$ = 1,2-diaminocyclohexane-*N,N'*-tetraacetate), are C_2 hybrids between a C_{2v} pentagonal bipyramid and the C_{2v} monocapped trigonal prism, but with one or the other predominating in the ratio ∿3:1; only $[H_2OFeEDTA]^-$ is better classified as pentagonal bipyramidal. The quantitative differences between the qualitatively similar $[H_2OMgEDTA]^{2-}$ and $[H_2OFeDCTA]^-$ ions may be summed up as follows. The bonding in $[H_2OFeDCTA]^-$ (and in $[H_2OFeEDTA]^-$) enforces very tight packing of the ligands, whereas the bonding pattern in $[H_2OMgEDTA]^{2-}$ is tailored to a pattern of easy packing relations. The large difference in the stability constants of the magnesium and manganese chelates is mostly attributable to the difference in size of the cations; the larger manganese ion is well-adapted to observe the geometrical constraints imposed by the multiply bridged ring system.

Introduction

The equilibrium reaction in aqueous solution for the complexing of a bivalent cation by the quadruply charged ethylenediaminetetracetate anion ($EDTA^{4-}$) is conveniently written as

$$M(OH_2)_h^{2+} + EDTA^{4-} \rightleftarrows [(H_2O)_qMEDTA]^{2-} + (h-q)H_2O$$

For the usual case of sexadentate chelation by the $EDTA^{4-}$ ion, the coordination number of the metal ion in the complexed species becomes 6, 7, 8, 9, · · · accordingly as q = 0, 1, 2, 3, · · · water molecules are retained in the coordination group. Reported values[2] of log K at 20° for the equilibria in which M^{2+} is in turn Mg^{2+}, Ca^{2+}, and Mn^{2+} are 8.7, 10.6, and 14.0, respectively. The stability constants for the Ca(II) and Mn(II) chelates may appear to be anomalously high relative to that of the Mg(II) complex, but only on the assumption—long since discredited[3,4]—that sexadentate octahedral coordination is freely accessible to, and preferred for, all such species. Existing evidence[4-7] strongly supports a sexadentate seven-coordinate formulation for the manganese chelate, both in crystals and in solution. And, as pointed out elsewhere,[8] a nine-coordinate $[(H_2O)_3CaEDTA]^{2-}$ anion, with a stereochemistry similar to that of the $[(H_2O)_3Ln\text{-}EDTA]^-$ chelates[9] (Ln = lanthanide), seems likely to be the most characteristic form of the Ca(II) complex. Neither eight- nor ten-coordinate species, however, should be dismissed from consideration.[10]

An abnormally low value for the stability constant of the Mg-EDTA complex is, by contrast, fully consistent with our earlier stereochemical studies of octahedral[3,4] and seven-

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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) *Cf.* S. Chabarek and A. E. Martell, "Organic Sequestering Agents," Wiley, New York, N. Y., 1959, pp 572-573, for a comprehensive tabulation of stability constants with listed references, predominantly to studies by Schwarzenbach and his collaborators.

(3) *Cf.* (a) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, 81, 549 (1959); (b) G. S. Smith and J. L. Hoard, *ibid.*, 81, 556 (1959).

(4) J. L. Hoard, G. S. Smith, and M. Lind in "Advances in the Chemistry of the Coordination Compounds," Macmillan, New York, N. Y., 1961, pp 296-302.

(5) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 3, 27 (1964).

(6) M. Ciampolini, P. Paoletti, and L. Sacconi in "Advances in Chemistry of the Coordination Compounds," Macmillan, New York, N. Y., 1961, p 303.

(7) M. S. Zetter, M. W. Grant, E. J. Wood, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 11, 2701 (1972).

(8) G. H. Cohen and J. L. Hoard, *J. Amer. Chem. Soc.*, 83, 3228 (1966).

(9) (a) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 87, 1611 (1965); (b) J. L. Hoard, B. Lee, and M. D. Lind, *ibid.*, 87, 1612 (1965). We note that the terbium chelate has also been shown to be nine-coordinate.

(10) See V. A. Uchtman, Abstracts, 162nd National Meeting of the American Chemical Society, Sept 1971, No. INORG 58, for a brief description of the stoichiometrically constrained structure of crystalline $Ca_2EDTA\cdot 7H_2O$.

coordinate[4,5,11] EDTA chelates. All of these analyses lend their support to the view that neither of the sexadentate formulations, the octahedral $[MgEDTA]^{2-}$ and the seven-coordinate $[H_2OMgEDTA]^{2-}$, could be free from substantial stereochemical disability. The one other plausible alternative, the quinquedentate, monoaquo, octahedral formulation having one uncomplexed glycinate arm, also would be expected to yield an abnormally low stability constant for the complex anion.

The determination of structure reported herein for crystalline $Na_2[H_2OMgEDTA]\cdot 5H_2O$ demonstrates that, at least in this phase, the complex anion is both sexadentate and seven-coordinate but that the observed values of the stereochemical parameters are not conducive to high stability (see Discussion).

A useful by-product of this study is the very precise determination of structure for excellent crystals of the salt $Mg(OH_2)_6H_2EDTA$, which is briefly reported in the accompanying paper.[12] The accurate parameters thus derived for the H_2EDTA^{2-} anion in its extended and (apart from hydrogen binding) uncomplexed form are presumably quite representative of the species in aqueous solution.

Experimental Section

Monoclinic crystals of $Na_2[H_2OMgEDTA]\cdot 5H_2O$ were prepared following Sawyer and Paulsen.[13] This phase crystallized during the slow cooling of an ethanol–water solution at an adjusted pH of 6.8–7.0. Such upward adjustment of the pH from ∿6.0 was required to repress hydrolysis of the complex anion and to preclude the otherwise invariable crystallization of $Mg(OH_2)_6H_2EDTA$ as the primary product from solutions in which the solute composition was empirically $M_2MgEDTA$, M = Na, K, or Li.[12]

Weissenberg and precession photographs from an approximately 0.5 × 0.5 × 0.5 mm specimen crystal afforded sharply defined diffraction patterns which were virtually free of streaking or other indication of disorder. The crystal was wedged within a sealed glass capillary to minimize loss of water of crystallization. Joint consideration of the diffraction symmetry, the pattern of systematic extinctions, and the positive test for piezoelectricity obtained with a Geibe-Schiebe detector narrowed the choice of space group to $C2$ or Cm. Least-squares refinement of the diffraction geometry recorded with automated centering of 38 reflections on a Picker FACS-1 diffractometer led to the lattice parameters $a = 11.504$ (3), $b = 9.801$ (3), and $c = 8.816$ (3) Å; $\cos\beta = -0.3565$ (3) or $\beta = 110.88°$. The experimental density, 1.66 g/cm³, agreed well with that calculated, 1.668 g/cm³, for $Z = 2$.

Diffracted intensities from the crystal specified above were measured with Zr-filtered Mo Kα radiation at a takeoff angle of ∿2° on the four-circle automated diffractometer. A scanning rate of 1°/min, a scanning range for each reflection of $(1.75 + 0.692 \tan\theta)°$, and a counting period of 40 sec for background at each end of the scan were employed. All symmetry-independent reflections, ∿3800 in all, for $(\sin\theta)/\lambda \lessapprox 0.98$ were thus scanned. The intensities of three periodically monitored reflections displayed no observable trend; random variations were in the range of ±3%. Inasmuch as corrections for absorption in the crystal were not needed ($\mu = 0.22$ mm^{-1} for Mo Kα radiation), the net intensities were reduced to relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factor (Lp). Retention as objectively observed of those data for which $|F_o| > 1.35\sigma_F$ wherein σ_F is the standard deviation computed from $\sigma_F^2 = [Ct + k^2B]/4|F_o|^2(Lp)^2$, with Ct the total count from the scan, k the ratio of scanning time to background counting time, and B the background count, left 2791 independent data for the determination and refinement of structure.

In undertaking structure determination we first noted that (since $Z = 2$) the twofold axis required of the complex anion in a crystalline arrangement based upon the space group $C2$ is precisely the one symmetry element which an externally unconstrained sexadentate (or quadridentate) EDTA chelate, whether six- or seven-coordinate, is expected to display, whereas the mirror plane required of the complex in an arrangement based upon Cm is highly improbable, if not impossible, of fulfillment.[3-5,11] Partial interpretation of the three-dimensional Patterson synthesis led to placement of the sodium ions in general positions of $C2$ with values of x, y, z assigned relative to the position of a magnesium atom on a twofold axis at $0, y, 0$ with, arbitrarily, $y = 0$. The positions of all other atoms were subsequently determined from Fourier and difference Fourier syntheses.[14] Following anisotropic, full-matrix, least-squares refinement[14] of the coordinates and thermal parameters of all atoms save hydrogen, a difference Fourier synthesis revealed concentrations of electron density, with peak values of 1–2 e/Å³, in positions near those theoretically anticipated for all of the hydrogen atoms in the asymmetric unit of structure. Subsequent least-squares refinement included contributions from the hydrogen atoms placed to approximate theoretical geometry with C–H and O–H distances fixed at ∿1.08 and 0.99 Å, respectively; each hydrogen atom was assigned an isotropic thermal parameter equal to that of the atom to which it was attached and no further refinement of the hydrogen parameters was attempted. Empirical weights, $w = 1/\sigma^2$, calculated from $\sigma = \Sigma_0{}^3 a_n|F_o|^n$, with the a_n from the least-squares fitting of the curve $\||F_o| - |F_c|\| = \Sigma_0{}^3 a_n|F_o|^n$, were employed during final refinement.

Shifts in parameters during the final cycle of refinement were generally less than 5% of their estimated standard deviations. A final difference Fourier synthesis displayed a small residual peak having approximately 10% of the full peak height for an uncomplexed water molecule on a twofold axis; all other residuals were substantially smaller. The data/parameter ratio was 2791/132 = ∿21, the final values of the conventional R_1 and the weighted R_2 were 0.065 and 0.090, respectively, and the estimated standard deviation of an observation of unit weight was 1.35. Probably the principal source of error in the measurement of hkl intensity data was the geometry-dependent absorption of the X-rays in the glass capillary enclosing the crystal specimen.[15]

Coordinates and the associated thermal parameters for all atoms save hydrogen are presented in Tables I and II, respectively; the parameters assigned to the hydrogen atoms are given in Table III.

Discussion

Figure 1 is a diagram of the crystalline arrangement as viewed along the crystallographic b axis of twofold rotational symmetry; the associated bond distances and angles are listed in Table IV. Figure 2 is a diagram in perspective of the seven-coordinate $[H_2OMgEDTA]^{2-}$ anion as it exists with required C_2-2 symmetry in the crystal; the Mg–O_{w1} bond to the water molecule lies on the twofold axis. As a consequence of the ring structure, the coordination polyhedron is geometrically a C_2 hybrid between the monocapped trigonal prism and the pentagonal bipyramid. That the geometry is better described in first approximation as monocapped trigonal prismatic is readily seen from a detailed examination of Figures 1–3.

We first direct attention in Figure 1 to the skeleton of the anion wherein the magnesium and O_{w1} atoms lie on the y axis and the pattern of ring connexities is fully delineated. Were dimensionally exact C_{2v} geometry for the monocapped trigonal prism preserved in the inner coordination group, the four complexed carboxylate oxygen atoms would lie at the vertices of a rectangle and the lowest edge of the polyhedron, N· · ·N′, would be perpendicular to the longer edges of the rectangle. This geometry, however, cannot be fully achieved

(11) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).

(12) M. O'D. Julian, V. W. Day, and J. L. Hoard, *Inorg. Chem.*, **12**, 1754 (1973).

(13) D. T. Sawyer and P. T. Paulsen, *J. Amer. Chem. Soc.*, **80**, 1597 (1958).

(14) Computer programs employed in this study were as follows: (a) A. Zalkin's Fourier program FORDAP; (b) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962; (c) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(15) 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-73-1749.

Table I. Atomic Coordinates in the Unit Cell of the Crystal

Atom type	Coordinates with standard deviations[a]		
	10^4x	10^4y	10^4z
Mg	0	0	0
Na	1230 (1)	1127 (2)	4197 (2)
N	−1207 (2)	−1920 (2)	181 (2)
O_1	−1617 (2)	87 (3)	−2042 (2)
O_2	−3622 (2)	−388 (3)	−3263 (3)
O_3	−767 (2)	332 (2)	2013 (3)
O_4	−1499 (2)	−588 (3)	3818 (3)
O_{W1}	0	2102 (3)	0
O_{W2}	3365 (2)	1802 (3)	5249 (3)
O_{W3}	0	2525 (8)	5000
O_{W4}	840 (4)	3634 (7)	2747 (7)
C_1	−2579 (2)	−576 (3)	−2180 (3)
C_2	−2496 (2)	−1634 (3)	−892 (4)
C_3	−1154 (2)	−652 (3)	2614 (3)
C_4	−1164 (2)	−2049 (3)	1863 (3)
C_5	−707 (3)	−3141 (3)	−335 (3)

[a] The number in parentheses following each coordinate is the estimated standard deviation in the last significant figure.

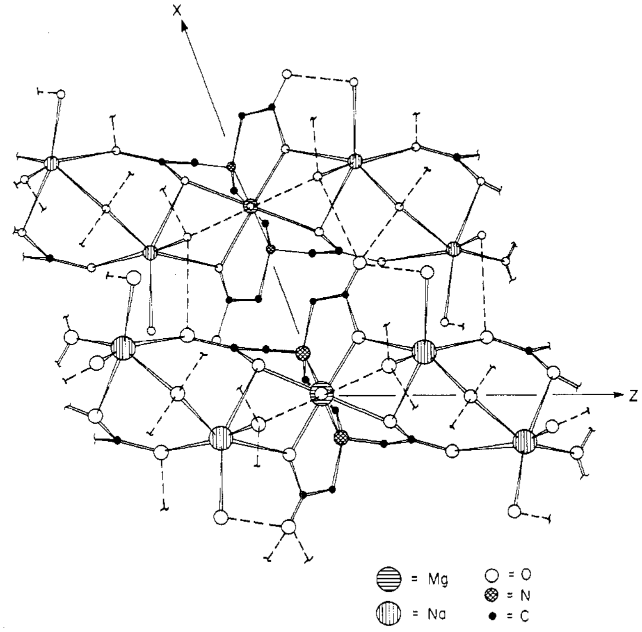

Figure 1. Diagram of the crystalline arrangement as viewed along the twofold (y) axis normal to the plane $y = 0$. The arrows along x and z correspond in magnitude and direction to the lattice constants a and c, respectively. Two complex anions, those in which the magnesium atoms lie at 0, 0, 0 and 0, $-^1/_2$, 0, are fully delineated.

because it would require the ethylenediamine ring system to be planar—a physically improbable, if not to say impossible, constraint. The usual, most natural, C_2 twisting of the ethylenediamine ring, as seen in Figure 1, is propagated through the nitrogen bond systems and the glycinato rings to give a C_2 twisted complex.

Equally unattainable is the pentagonal-bipyramidal coordination of dimensionally exact C_{2v} geometry wherein the water molecule, the two nitrogen atoms, and two of the four carboxylate oxygen atoms form an exactly planar girdle around the metal atom. Generally, however, the observed C_2 hybrid of these hypothetical limiting configurations has one or the other predominating in a ratio lying between 2:1 and 3:1, as estimated from the angle of twist. To this approximation, the observed geometries of the $[H_2OMgEDTA]^{2-}$, $[H_2OMnEDTA]^{2-}$, and $[H_2OFeDCTA]^-$ chelates[5,8] ($DCTA^{4-}$ = 1,2-diaminocyclohexane-*N,N'*-tetraacetate) are classified as monocapped trigonal prismatic, while that of the $[H_2OFeEDTA]^-$ species is pentagonal bipyramidal.[11] These observations, all from determinations of crystalline structure, are suggestive of stereochemically nonrigid behavior for the EDTA chelates in aqueous solution. As pointed out earlier,[8] however, the detailed comparison of structural parameters for the $[H_2OFeEDTA]^-$ and $[H_2OFeDCTA]^-$ complexes is compatible with some preference for pentagonal-bipyramidal coordination in the EDTA chelate, whereas this geometry is quite probably destabilized in the DCTA species by serious steric interaction between two unduly tight pairings of cyclohexane hydrogen atoms with neighboring glycinato hydrogen atoms. The stereochemical parameters of these high-spin iron(III) chelates are especially pertinent to our further discussions of the $[H_2OMgEDTA]^{2-}$ anion because, for standard octahedral coordination, Mg-O bond lengths involving carboxylate oxygen atoms or water molecules are expected to be only slightly longer (<0.05 Å) than the analogous Fe-O distances.[16,17]

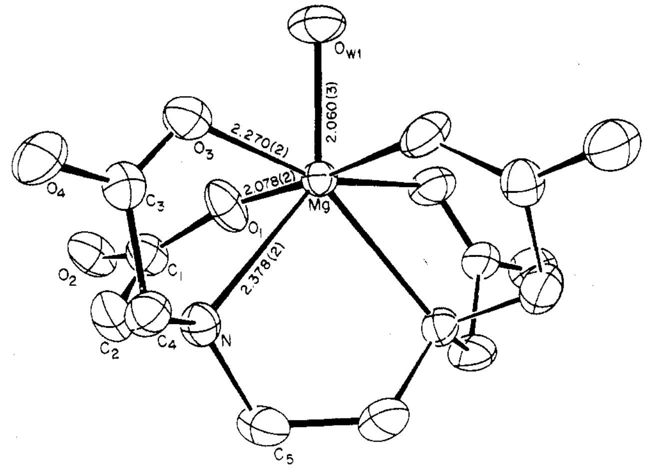

Figure 2. Diagram of the complex anion in which the atoms are drawn as ellipsoids in agreement with the thermal parameters listed in Table II. Atoms are numbered as in Tables I-V. Not shown are the hydrogen atoms carried by the O_{W1}, C_2, C_4, and C_5 atoms.

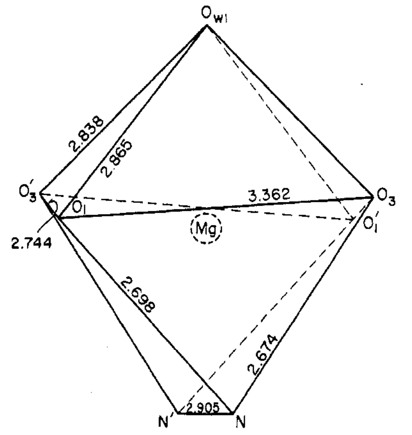

Figure 3. Projection of the coordination polyhedron in the complex anion along a direction perpendicular to the twofold axis and to the pair, $O_1 \cdots O_3$ and $O_3' \cdots O_1'$, of symmetry-equivalent edges. Glycinato rings span the edges $N \cdots O_1$, $N \cdots O_3$, $N' \cdots O_1'$, and $N' \cdots O_3'$.

Figure 3 is a projection of the coordination polyhedron of $[H_2OMgEDTA]^{2-}$ along a direction which is perpendicular both to the twofold axis and to the pair of structurally equivalent $O_1 \cdots O_3$ and $O_3' \cdots O_1'$ edges. Were we dealing with

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[16] Pauling's tabulation of ionic radii[17] gives Mg-O = 2.05 Å, Fe-O = 2.04 Å.

[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

Table II. Thermal Parameters of the Atoms in the Crystal

Atom type	Anisotropic parameters with standard deviations,[a] Å^2						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[b] Å^2
Mg	1.62 (3)	1.45 (3)	1.87 (3)	0.0	0.44 (3)	0.0	1.70
Na	3.05 (4)	3.06 (5)	2.52 (4)	−0.11 (4)	1.31 (4)	−0.16 (4)	2.76
N	1.87 (5)	2.06 (6)	1.84 (5)	−0.02 (4)	0.73 (4)	0.29 (5)	1.88
O_1	2.20 (5)	3.10 (8)	2.39 (6)	−0.79 (6)	0.21 (4)	1.01 (6)	2.40
O_2	2.23 (5)	3.20 (8)	3.55 (9)	−0.60 (6)	−0.59 (5)	1.01 (6)	2.90
O_3	3.29 (8)	2.05 (6)	3.45 (9)	−0.42 (6)	1.62 (7)	−0.06 (6)	2.71
O_4	4.1 (1)	3.12 (8)	3.37 (9)	−0.24 (8)	2.33 (8)	−0.75 (6)	3.01
O_{W1}	3.9 (1)	1.64 (8)	2.9 (1)	0	1.5 (1)	0	2.58
O_{W2}	3.7 (1)	3.6 (1)	2.2 (1)	−0.6 (1)	0.9 (1)	−0.1 (1)	3.11
O_{W3}	8.4 (4)	4.4 (2)	9.7 (5)	0	3.8 (4)	0	6.94
O_{W4}	4.8 (2)	9.4 (3)	9.3 (3)	2.2 (2)	−1.6 (2)	−6.8 (3)	5.83
C_1	1.80 (6)	2.17 (7)	2.17 (7)	−0.24 (6)	0.29 (6)	0.22 (6)	2.10
C_2	1.72 (6)	3.14 (10)	3.02 (10)	−0.42 (6)	0.63 (6)	0.90 (8)	2.44
C_3	2.11 (7)	2.08 (7)	2.42 (8)	−0.04 (6)	0.99 (6)	0.11 (6)	2.14
C_4	2.72 (8)	1.85 (6)	2.15 (7)	0.12 (6)	1.24 (6)	0.36 (6)	2.07
C_5	3.00 (8)	1.90 (6)	2.34 (8)	−0.58 (6)	1.26 (7)	−0.30 (6)	2.23

[a] Numbers in parentheses are the estimated standard deviations. [b] Isotropic thermal parameter.

Table III. Parameters Assigned to Hydrogen Atoms

Atom[a]	Coordinates			B,[b] Å^2
	10^3x	10^3y	10^3z	
H_1 (C_2)	−297	−257	−141	2.7
H_2 (C_2)	−296	−109	−20	2.7
H_3 (C_4)	−205	−244	184	2.1
H_4 (C_4)	−41	−262	272	2.1
H_5 (C_5)	−100	−404	13	2.3
H_6 (C_5)	−105	−309	−168	2.3
H_7 (O_{W1})	77	257	69	2.6
H_8 (O_{W2})	381	92	544	3.1
H_9 (O_{W2})	355	250	456	3.1
H_{10} (O_{W3})	50	329	563	9.0
H_{11} (O_{W4})	39	432	314	7.5
H_{12} (O_{W4})	130	415	228	7.5

[a] The notation in this column indicates the carbon or oxygen atom to which each hydrogen atom is attached. [b] Isotropic thermal parameter.

Table IV. Bond Parameters in the Crystalline Structure[a]

Bond class	Length, Å	Angular class	Value, deg	Angular class	Value, deg
Mg-O_{W1}	2.060 (3)	O_1MgO_3	101.19 (9)	$O_4C_3C_4$	117.1 (2)
Mg-O_1	2.078 (2)	O_1MgO_{W1}	87.64 (7)	C_1C_2N	113.1 (2)
Mg-O_3	2.270 (2)	$O_3'MgO_1$	78.12 (9)	C_3C_4N	110.7 (2)
Mg-N	2.378 (2)	O_3MgO_{W1}	81.76 (6)	C_2NC_4	109.1 (2)
C_1-O_1	1.252 (3)	O_1MgN	74.16 (8)	C_2NC_5	111.8 (2)
C_3-O_3	1.255 (3)	O_3MgN	70.22 (8)	C_4NC_5	111.5 (2)
C_1-O_2	1.253 (3)	NMgN′	75.35 (10)	C_2NMg	106.5 (2)
C_3-O_4	1.260 (3)	$O_{W1}MgN$	142.32 (5)	C_4NMg	109.0 (1)
C_1-C_2	1.515 (4)	O_1MgO_1'	175.27 (25)	C_5NMg	108.8 (2)
C_3-C_4	1.519 (4)	O_3MgO_3'	163.52 (13)	NC_5C_5'	111.3 (2)
C_5-C_5'	1.520 (6)	MgO_1C_1	123.3 (2)	O_1NaO_3	68.4 (1)
C_2-N	1.473 (3)	MgO_1Na	110.6 (1)	O_1NaO_4	106.2 (1)
C_4-N	1.472 (3)	MgO_3C_3	121.0 (2)	O_1NaO_{W2}	88.2 (1)
C_5-N	1.469 (3)	MgO_3Na	97.9 (2)	O_1NaO_{W4}	93.4 (1)
Na-O_1	2.334 (2)	NaO_1C_1	124.5 (2)	O_3NaO_4	100.8 (1)
Na-O_3	2.537 (3)	NaO_4C_3	131.4 (2)	O_3NaO_{W3}	85.7 (1)
Na-O_4	2.366 (3)	NaO_3C_3	106.1 (2)	O_3NaO_{W4}	82.2 (1)
Na-O_{W2}	2.389 (3)	$O_1C_1O_2$	124.8 (2)	O_4NaO_{W2}	93.7 (1)
Na-O_{W3}	2.257 (5)	$O_1C_1C_2$	117.8 (2)	O_4NaO_{W3}	97.5 (1)
Na-O_{W4}	2.732 (8)	$O_2C_1C_2$	117.4 (2)	$O_{W2}NaO_{W3}$	112.5 (1)
		$O_3C_3O_4$	125.6 (3)	$O_{W2}NaO_{W4}$	84.7 (1)
		$O_3C_3C_4$	117.2 (2)	$O_{W3}NaO_{W4}$	65.4 (2)

[a] Figures in parentheses are the estimated standard deviations.

seven chemically identical ligands in the "hard-sphere" approximation of C_{2v} geometry and a complexing bond length of 2.08 Å (as observed for Mg-O_1), the metal atom would lie 0.45 Å below the plane of the rectangular girdle formed by four of the ligands. In the C_2 twisted polyhedron of Figure 3, the magnesium atom lies just 0.205 Å below the mean plane of the four carboxylate oxygen atoms; the O_1,O_1' and O_3,O_3' pairings of oxygen atoms lie respectively 0.120 Å below and 0.120 Å above the mean plane. Although the small out-of-plane displacement of the magnesium atom correlates with both the extraordinarily long Mg-N bond distance of 2.378 (2) Å and the easy O· · ·O contacts in the pyramidal MgO_5 cap (Figure 3), these contacts are in large measure eased by the gross stretching of the Mg-O_3 bond distance to 2.270 (2) Å. Thus the arbitrary reduction of this bond length to the 2.078 (2) Å observed for Mg-O_1, while preserving all bond angles at the magnesium atom (Table IV), yields calculated distances for O_3· · ·O_{W1}, O_1· · ·O_3', and N· · ·O_3 contacts of 2.707, 2.625, and 2.574 Å, respectively—all reduced by $\gtrsim$0.100 Å below the observed values entered on Figure 3. Furthermore, the observed N· · ·O_1 and N· · ·O_3 separations (2.698 and 2.674 Å), which are substantially less than the sum of the van der Waals radii[17] (2.90 Å), together with the fairly tight N· · ·N′ separation (2.095 Å), require the nitrogen atoms to lie 2.087 (3) Å below the mean plane of the carboxylate oxygen atoms. In these circumstances, the Mg-N bond distance is necessarily long because the achievement of a rational stereochemistry for the pyramidal MgO_5 cap takes precedence in determining the equilibrium position of the magnesium atom on the twofold axis.

Table V is a listing of comparative stereochemical data for the coordination polyhedra in all four of the seven-coordinate EDTA and DCTA chelates of determined structures. We note first that, with the single exception of the M-O_{W1} distance, the purely qualitative orderings of the bond lengths and of the packing spearations within each species conform to a common pattern. Inasmuch as the qualitative similarities between the coordination polyhedra in the $[H_2OMgEDTA]^{2-}$ and $[H_2OFeDCTA]^-$species are especially striking, an examination of the quantitative differences is quite illuminating. The M-N, M-O_1, and M-O_3 distances in the iron chelate are shorter by 0.088, 0.061, and 0.178 Å than the corresponding values in the magnesium complex; the averaged difference of 0.109 Å is more than twice that anticipated for standard octahedral coordination and the gross reduction of 0.178 Å in M-O_3 is especially noteworthy. All classes of packing contents which, in the magnesium chelate, fall somewhat below the van der Waals values are further reduced in the iron species. The resistance of the Fe-O_3 bond to undue stretching is largely responsible for the very tight O_3· · ·O_{W1} and N· · ·O_3 contacts of 2.535 and 2.576 Å, respectively. Thus it appears that the bonding in $[H_2OFeDCTA]^-$ is quite strong enough to enforce tight packing of the ligands, whereas the bonding pattern in $[H_2OMgEDTA]^{2-}$ is tailored to the requirement of easy packing relations. The shortness of the $Mg-O_{w1}$ bond [2.060 (3) Å] is an interesting, if incidental, consequence of the constraints put on the other complexing bonds.

In the coordination group of the $[H_2OFeEDTA]^-$ chelate, the O_3 and O_3' atoms join the water molecule and the nitrogen atoms in forming the quasipentagonal girdle around the iron atom. Tight-packing contacts within this girdle but very easy contacts with the axial O_1 and O_1' atoms are anticipated and are observed (Table V). Lengthenings of the $Fe-O_w$ and $Fe-O_3$ distances by ∿0.015 Å and of Fe-N by ∿0.03 Å from the values in $[H_2OFeDCTA]^-$ are observed in $[H_2OFeEDTA]^-$; the concomitant shortening of the $Fe-O_1$ distance is ∿0.04 Å. In appraising the relative stabilities of the monocapped trigonal-prismatic and pentagonal-bipyramidal forms of the EDTA chelate, the fact that the latter is the species found in crystals[11] of both $Rb[H_2OFeEDTA] \cdot H_2O$ and $Li[H_2OFeEDTA] \cdot 2H_2O$ should not be given undue weight; it is quite conceivable that packing relations in the crystal dictate the choice between the anionic configurations.

From examination of the parameters listed in Table V for the $[H_2OMnEDTA]^{2-}$ ion, we see at once that the effective size of the high-spin Mn^{2+} cation is very well suited to the formation of a stereochemically sound seven-coordinate chelate of monocapped trigonal-prismatic geometry. The pyramidal MnO_5 cap of the coordination polyhedron is characterized by nearly uniform bond lengths and very easy, if rather varied, $O \cdots O$ packing contacts. Relative to an averaged Mn-O distance of 2.235 Å, the Mn-N bond length of 2.377 Å probably differs little from the optimum value.[18] We note further that the $N \cdots N$, $N \cdots O_3$, and $N \cdots O_1$ contacts are quite like those in the loosely packed magnesium chelate and are definitely more favorable than those in either of the iron(III) species.

A few summarizing remarks in regard to this family of seven-coordinate chelates are in order. The structural nonequivalence required by the C_2 symmetry between the two sets of glycinato rings is either minimized or maximized accordingly as the limiting approximation to monocapped trigonal-prismatic or pentagonal-bipyramidal coordination is utilized. M-N distances are necessarily long and are restricted to a rather narrow range of variation, 2.29-2.38 Å. M-O distances, by contrast, range from 1.98 to 2.27 Å. The averaged M-O distance in each seven-coordinate species is significantly larger than the value anticipated for standard octahedral coordination but is grossly larger only in the least stable complex—the $[H_2OMgEDTA]^{2-}$ ion. A substantial increase in the already large difference (0.19 Å) between the $Mg-O_3$ and $Mg-O_1$ bond lengths in $[H_2OMgEDTA]^{2-}$ should be expected in the pentagonal-bipyramidal form. The much greater stability of the analogous manganese complex is for the most part attributable to the excellent fitting of the larger manganese ion with the geometrical constraints imposed by the multiply bridged, chelated ring system.

Table V. Quantitative Data for the Seven-Coordination Polyhedra

Type of parameter[a]	Length (Å) in the EDTA chelate of			Length (Å) in $[H_2OFe\text{-}DCTA]^-$ [e]
	Mg(II)[b]	Mn(II)[c]	Fe(III)[d]	
$M-N$	2.378 (2)	2.377	2.323	2.290
$M-O_1$	2.078 (2)	2.226	1.977	2.017
$M-O_3$	2.270 (3)	2.246	2.104	2.092
$M-O_{w1}$	2.060 (3)	2.235	2.107	2.090
$N \cdots N$	2.905 (3)	2.902	2.797	2.834
$N \cdots O_3$	2.674 (3)	2.652	2.598	2.576
$N \cdots O_1$	2.698 (3)	2.703	2.739	2.639
$O_3 \cdots O_{w1}$	2.838 (3)	2.825	2.495	2.535
$O_1 \cdots O_{w1}$	2.865 (3)	3.319	3.053	2.987
$O_1 \cdots O_3'$	2.744 (3)	2.955	2.897	2.700
$O_1 \cdots O_3$	3.362 (4)	3.430	2.989	3.133

[a] Notations employed in earlier papers[5,8,11] are altered to agree with that used for $[H_2OMgEDTA]^{2-}$. [b] Figure in parentheses following each datum is the esd in units of 0.001 Å; 40-50% higher values apply to the data for the other chelates. [c] Averaged values.[5] [d] Averaged values[11] with the data from $Li[H_2OFeEDTA] \cdot 2H_2O$ given twice the weight of that from $Rb[H_2OFeEDTA] \cdot H_2O$. [e] Averaged values.[8]

In order to achieve a fair approximation to *regular* octahedral geometry in the coordination group of a sexadentate EDTA chelate, it is necessary that there be little difference between the lengths of the M-N and M-O bonds and, furthermore, that these bond lengths be rather small.[3,4] These conditions, which are conspicuously violated by all of the seven-coordinate chelates discussed herein, are best observed by the low-spin cobalt(III) complex,[3] $[CoEDTA]^-$; wherein all complexing bond lengths are confined to the range from 1.88 to 1.92 Å. Apart from the inevitable C_2 twisting of the coordination octahedron, the principal departure from geometrical regularity is the opening to 104.0° of the OCoO angle between the pair of Co-O bonds which are trans to the M-N bonds. For a sufficient increase in the size of the central atom, achieved the more readily whenever the increase in the M-N bond length is disproportionately large, the concomitant opening of the OMO bond angle trans to the M-N bonds becomes so large as to encourage the coordination of a water molecule in the "hole" thus formed. An octahedral sexadentate $[FeEDTA]^-$ complex would be expected[18,19] to have $Fe-O \approx 2.00$ Å, but $Fe-N > 2.20$ Å. Thus, it is probable that the preference for seven-coordination exhibited by the EDTA chelates of both the magnesium and the high-spin ferric[20] ions is largely attributable, albeit indirectly, to the disproportionately low affinities of these cations for amino nitrogen relative to their affinities for carboxylate oxygen.

The structural nonequivalence of the two sets of glycinato rings in the $[H_2OMgEDTA]^{2-}$ ion is reflected in objectively significant differences between several pairings of corresponding bond angles (Table IV and Figure 2) and in the large difference (0.192 Å) between the $Mg-O_3$ and $Mg-O_1$ distances, but not at all in the C-C, C-N, and C-O bond lengths. Averaged values of these nearly invariant bond lengths are C-C = 1.517 (4, 2), C-N = 1.473 (3, 1), and C-O = 1.255 (3, 3) Å, wherein the first figure in parentheses is the estimated standard deviation (esd) of each individual determination and the second figure is the mean deviation from the

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(18) In the quinquedentate six-coordinate $H_2OFeHEDTA$ molecule,[19] which carries a neutral, uncomplexed glycine arm, the Fe-N distance is 2.20 Å as compared with an averaged Fe-O distance of 2.00 Å. Given the considerable relaxation in the ring constraints and the associated packing relations which accompany the elimination of one ring in favor of a water molecule,[3b] this result suggests that the complexing bonds formed by the isoelectronic high-spin Fe^{3+} and Mn^{2+} ions with amines must always be much longer than the bonds formed with carboxylate oxygen atoms. In these terms, the observed difference of 0.14 Å between the Mn-N and Mn-O bond lengths in the manganese chelate might even represent some tightening of the M-N bonds as a consequence of the multiply bridged ring structure.

(19) J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *Inorg. Chem.*, 2, 1316 (1963).

(20) A low-spin $[FeEDTA]^-$ species, were it formed, would be expected to be both isostructural and nearly isodimensional with the $[CoEDTA]^-$ ion. Comparison of the data cited above for $[CoEDTA]^-$ with that given in Table V for $[H_2OFeEDTA]^-$ is illustrative of the stereochemical dependence of ferric complexes on the spectroscopic state of the iron atom.

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 $n = \pm 1, \pm 2$, 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.

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Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850

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

MAUREEN O'DONNELL JULIAN, V. W. DAY, and J. L. HOARD*

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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 $(\sin \theta)/\lambda \overline{<} 0.743$ 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, $MgH_2EDTA \cdot 6H_2O$ (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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(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.