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Stereochemistry of Ethylenediaminetetraacetato Complexes. I. The Structure of Crystalline $Mn_3(HY)_2 \cdot 10H_2O$ and the Configuration of the Seven-Coordinate $Mn(OH_2)Y^{-2}$ Ion(1–3)

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Analysis of $\{hkl\}$ X-ray data for $0 < (\sin \theta)/\lambda < 0.95$ from monoclinic crystals of $Mn_3(HY)_2 \cdot 10H_2O$ yields definitive structure determination. The unit cell contains two $Mn_3(HY)_2 \cdot 10H_2O$; all atoms, save two Mn at inversion centers, occupy fourfold general positions of C^5_{2h}-$P2_1/n$ (Table I). The atomic arrangement can be put together as follows: Sexadentate seven-coordinate $Mn(OH_2)Y^{-2}$ ions (Fig. 1) are distributed in general positions (Fig. 2) and are converted into quasi-infinite chains $[Mn(OH_2)YH]_n^{-n}$ parallel to b (Fig. 2) by the addition of protons (the acid hydrogens) to hydrogen bond contiguous pairs of O_5 and O_7 atoms (Fig. 1) along the sequence. This bonding is very tight, O_5--H--O_7 = 2.469 ± 0.010 Å., and is at least quasi-symmetric. Manganese occupying inversion centers displays octahedral coordination; the coordination group comprises two carboxylate oxygens of O_8 type (Fig. 1), two water molecules which are hydrogen bonded at 2.708 ± 0.019 Å. to carboxylate O_6 atoms, and two water molecules which are hydrogen bonded at 2.698 ± 0.010 Å. to carboxylate O_2 atoms. All water molecules, including two sets not complexed to manganese, are involved in hydrogen bonding (Table IV). C–N and C–C bond lengths average 1.471 ± 0.007 and 1.519 ± 0.008 Å. and are otherwise notable for the internal consistency displayed by the individual data (Table II). C–O bond lengths seem to reflect quantitative variations in the strength of the bidentate complexing displayed by carboxylate. Ring bond angles conform rather well to the quasi-symmetry C_2-2 for the sexadentate seven-coordinate $Mn(OH_2)Y$ group (Table V). Departure from this ideal symmetry is manifest in the loosely packed inner coordination group (Table VI) and in the weak Mn–O and Mn–N complexing bonds (Table III). Table VII and Fig. 1 and 3 describe the coordination group of the idealized $Mn(OH_2)Y^{-2}$ ion which is regarded as the most probable species in solutions of appropriate pH.

Introduction

Inasmuch as the existence of sexadentate *seven*-coordinate $[Fe(OH_2)Y]^-$, Y^{-4} = ethylenediaminetetraacetate, as sensibly discrete anions in crystalline $RbFe(OH_2)Y \cdot H_2O$[4,5] and $LiFe(OH_2)Y \cdot 2H_2O$[6] is in accord with *a priori* analysis[7] which should apply equally to the anionic Mn(II) complex, a similarly formulated $[Mn(OH_2)Y]^{-2}$ for a similar environment becomes the more plausible. In the *acid* chelates formed by EDTA,[7] however, one usually expects to find uncomplexed $\cdot CH_2COOH$ "arms." The crystalline "acid salt" $Mn_3(HY)_2 \cdot 10H_2O$ captured our interest through its failure[7] to exhibit any semblance of the infrared absorption reliably attributable to uncomplexed $\cdot COOH$. We inferred that $\cdot COOH$ must be involved in extraordinarily cogent hydrogen bonding, abetted by the promotion of acid strength concomitant with complexing of $\cdot COOH$ to Mn(II). Structure determination by analysis of three-dimensional X-ray data confirms[8] the first of these expectations. The acid hydrogens are used for extraordinarily tight linking (*vide infra*) of seven-coordinate $Mn(OH_2)Y^{-2}$ into "infinite" strings $[Mn(OH_2)YH]_n^{-n}$ extending parallel to one axis. Further complexing and bridging which puts the remaining one-third of the Mn(II) ions into octahedral coordination, and fully utilizes the water molecules and carboxylate oxygen atoms to form a three-dimensional network, are of comparable interest. The role of carboxylate as a bidentate bridging agent is quantitatively displayed.

Experimental

Reaction of solid $MnCO_3$ with a warmed solution of EDTA proceeds smoothly in accordance with the stoichiometry $3MnCO_3 + 2H_4Y = Mn_3(HY)_2 + 3H_2O + 3CO_2$. Crystalline $Mn_3(HY)_2 \cdot 10H_2O$, obtained by evaporation of the resulting solution, is rather less soluble than most EDTA-complexed materials and is readily purified by recrystallization from aqueous solution. Chemical analysis is in excellent agreement with the composition $Mn_3(HY)_2 \cdot 10H_2O$, excepting some understandable uncertainty as to the precise water content.

Thorough preliminary study of single crystals by photographic methods using Cu Kα radiation preceded counter measurement of three-dimensional intensity data using Mo Kα radiation. The monoclinic unit of structure containing two $Mn_3(HY)_2 \cdot 10H_2O$ has $a = 9.212 \pm 0.005$, $b = 16.16 \pm 0.01$, $c = 11.88 \pm 0.01$ Å., $\beta = 90° 36' \pm 3'$; the calculated and measured densities are 1.73 and 1.72 g./cc., respectively. The systematic vanishings of spectra, $\{h0l\}$ for $h + l$ odd and $[0k0]$ or k odd, are demanded only by the space group[9] C^5_{2h}-$P2_1/n$; the absence of detectable piezoelectricity supports this centrosymmetric choice.

Three-dimensional diffraction intensities were recorded with Mo Kα radiation on our General Electric spectrometer assembly by the procedures described earlier.[10] With a linear absorption

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(2) Publication as numbered contributions under a common generic title begins with this paper (*cf.* ref. 4, 7, 8, 18, and 19 for earlier work published elsewhere).

(3) The abbreviations EDTA and short formula H_4Y are used throughout for ethylenediaminetetraacetic acid. No quasi-structural formula simple enough to be written in linear form is accurately descriptive of the partially three-dimensional complexing in the "acid salt," $Mn_3(HY)_2 \cdot 10H_2O$.

(4) J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

(5) M. D. Lind and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).

(6) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **3**, 34 (1964).

(7) J. L. Hoard, G. S. Smith, and M. D. Lind in "Advances in the Chemistry of the Coordination Compounds," the Macmillan Company, New York, N. Y., 1961, pp. 296–302. (Reprints of this paper are available.)

(8) J. L. Hoard, B. Pedersen, S. Richards, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 3533 (1961).

(9) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, pp. 98–99.

(10) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

coefficient of 1.2 mm.$^{-1}$ for a crystal averaging 0.25 mm. in diameter (maximum deviation *ca.* 20%), correction for variation of absorption with either scattering angle or specimen shape was not required. Intensity data were reduced to approximately absolute $|F|^2$ values for structure analysis with the aid of the computational program already described.[10] The range of intensity measurement, $0 < 2\theta < 85°$, was that used also in the study[11] of $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$. Data from the two substances, of generally comparable quality, were handled throughout by rather similar procedures, including corrections for spectral dispersion[12] and the entry of half the minimum observable intensity count for each "unobserved" $\{hkl\}$ within the range of measurement for inclusion in final difference synthesis.[13] More than 85% of all reflections having $2\theta < 85°$ were recorded above background for both $Mn_3(HY)_2 \cdot 10H_2O$ and $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$. The number of independent reflections was about four times as large for the manganese compound (a factor of two from monoclinic *vs.* orthorhombic symmetry, another factor of about two from the volume ratio of the respective primitive units).

Determination of Structure

A Patterson synthesis,[13] $P(uvw)$, of those $|F|^2$ data lying within the equivalent Cu Kα limiting sphere led immediately to the arrangement of manganese atoms; the pattern of major peaks, in respect to both magnitudes and positions, was in virtually perfect agreement with the assignment of four Mn to general positions[9] of $P2_1/n$, $\pm(x, y, z)$ and $\pm(^1/_2 + x, {^1/_2} - y, {^1/_2} + z)$, and two Mn to inversion centers, $^1/_2, 0, 0$ and $0, {^1/_2}, {^1/_2}$. The value of $R = \Sigma||F_o| - |F_c||/\Sigma||F_o|$ was 0.54 for manganese contributions[14] alone. The full structure then was developed by Fourier synthesis[13] in successive approximations during which an averaged thermal parameter B was employed, all light atoms were assigned the form factor of nitrogen, only peaks having a maximum density $\geqq 8$ electrons/Å.^{3} were treated as real in setting up the next stage of computation, and no structural criteria having to do with bond distances or ring connexity were applied. The completed electron density function, $\rho_0(xyz)$, although synthesized with the aid of only a qualitative chemical analysis, was notably free of worrisome small peaks or other extraneous factors. Use of the further qualitative information that the crystal was a hydrated EDTA complex of Mn(II) was more than sufficient to characterize the structure and to establish the exact chemical composition.

The structurally distinct classes of atoms then were assigned their proper form factors and first approximations to characteristic thermal parameters, B_i, preparatory to refinement of structure by difference synthesis.[13] Refinement procedures similar to (but lacking the noncentrosymmetric complications of) those employed for $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$ were applied to the $\{hkl\}$ data having $(\sin\theta)/\lambda \leqq 0.673$, comprising about 13% more reflections than are recordable with Cu Kα radiation; "back-shift" corrections were found to be significant. Cycling was continued until the 78 positional coordinates and the 27 thermal parameters approached stable values. Indications of several reasonably situated hydrogen atoms on ρ_0 were insufficiently decisive to justify detailed study. R, computed for the 4440 independent reflections, including those unobserved (*ca.* 5%), is 0.098, as compared with 0.078 for (the Cu Kα range of) $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$. The $Mn_3(HY)_2 \cdot 10H_2O$ structure is fundamentally more complex (78 as against 46 positional parameters) and gets a smaller fractional contribution to the total scattering from "heavy" atoms. Extinction, moreover, was less pronounced in the $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$ data, probably a consequence of the cutting and grinding operations to which the specimen was subjected.

Further refinement through three cycles of difference synthesis with all data for $2\theta < 85°$ included produced no startling change. Apparent back-shift corrections for the most part became very small, less than 0.006 Å. excepting for three of the ten carbon atoms. Shifts in atomic positions given by this further refinement approach probable significance in the statistical sense only for the four structural classes of atoms having large thermal parameters ($B_i > 3$Å.^{2}); all but one of these classes comprise oxygen atoms of water molecules. The more extensive data give, in agreement with earlier observations,[10,11] less spread in such presumably well-defined bonds as C–C and C–N, and an electron density function ρ_0 which, in large measure, speaks for the structural study. R for all of the data, 14–25% of which represent "unobservable" or weakly observable reflections, is 0.155, as compared with 0.139 for the same range of 2θ in $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$.

Table I lists the atomic coordinates with associated standard deviations estimated by Cruickshank's procedure,[13] the individual thermal parameters, and the peak values of electron densities—all as obtained from refinement of the complete data. The peak densities and thermal parameters of this study correlate satisfactorily with one another and with the corresponding data for chemically similar atoms reported[11] for $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$.

Discussion of Results

We present first a brief descripiton of the principal structural features as a guide to quantitative discussion. The model (Fig. 1) for the sexadentate seven-coordinate $Mn(OH_2)Y^{-2}$ ion emerges from our data as detailed later. Although the resemblance of the inner coordination group, MnN_2O_5, to that of the idealized (C_{2v}-mm2) NbF_7^{-2} ion[15] is real, an appropriately idealized $Mn(OH_2)Y^{-2}$ is restricted to the lesser symmetry C_2-2, *i.e.*, to a twofold axis passing through (Fig. 1) the mid-point of the C_I–C_{II} bond, the manganese atom, and oxygen of the water molecule. The $Mn(OH_2)Y$ grouping in $Mn_3(HY)_2 \cdot 10H_2O$, moreover, does

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(11) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

(12) L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962).

(13) *cf.* H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, London, 1953.

(14) The atomic form factor used for manganese was that of L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957), corrected for dispersion following C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955). Form factors for other atoms were those of J. Berghuis, *et al.*, *ibid.*, **8**, 478 (1955).

(15) J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939).

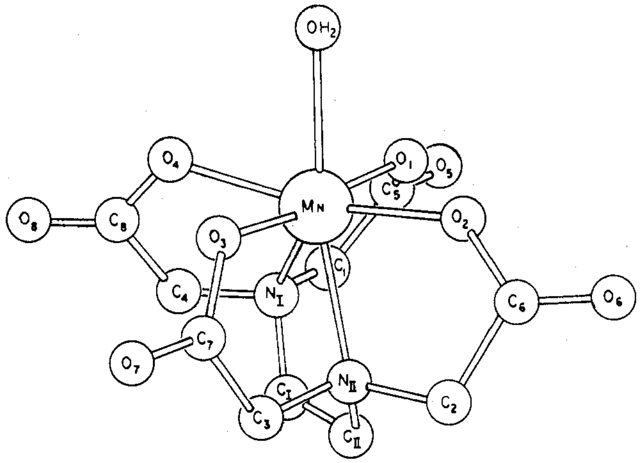

Fig. 1.—Idealied model of the sexadentate seven-coordinate $Mn(OH_2)Y^{-2}$ with the twofold axis vertical. Arabic subscripts are even or odd for atoms lying, respectively, within glycinate rings G_e or G_o.

not correspond to the sensibly discrete, doubly charged anion. Every carboxylate group functions as a bidentate bridging agent, and the atoms O_5, O_7, and O_8 (Fig. 1) form bonds fully comparable in strength with the Mn–O linking within the $Mn(OH_2)Y$ group. The twofold screw axis (Fig. 2) along $^1/_4$, y, $^1/_4$ operates on the $Mn(OH_2)Y$ group centered (Table I) at 0.15977, 0.22325, 0.22096 to generate an infinite "chain" of these groups; inasmuch as the separation between O_5 and O_7 oxygen atoms of contiguous groups is 2.469 ± 0.010 Å. (*vide infra*), we infer that the acid hydrogens are used in extraordinarily strong hydrogen bonds O_5--H--O_7 to give quasi-infinite anionic chains, $[Mn(OH_2)YH]_n^{-n}$, parallel to b. The charge attributed to an anionic chain represents an upper limit in view of the following cross linking.

Oxygen atoms O_8 (Fig. 1) are directly coordinated to manganese atoms (Mn_i), one-third of the total, occupying inversion centers. Octahedral coordination for Mn_i is completed with four water molecules, $2w_2$ and $2w_3$ of Table I. The O_8–Mn_i–O_8 axis (Fig. 2) is nearly parallel to the b-axis of the crystal, the octahedral edges defined by paired w_2 and w_3 water molecules are nearly parallel to either a or c. Each oxygen atom O_6 (Fig. 1) forms a good hydrogen bond (2.708 ± 0.019 Å.) with a water molecule w_3, but is not otherwise deeply involved in cross linking. All water molecules, including those (w_4 and w_5) not coordinated directly to either structural class of manganese, contribute to the general pattern of hydrogen bonding and, consequently, to the three-dimensional linking which lends stability to the crystalline arrangement.

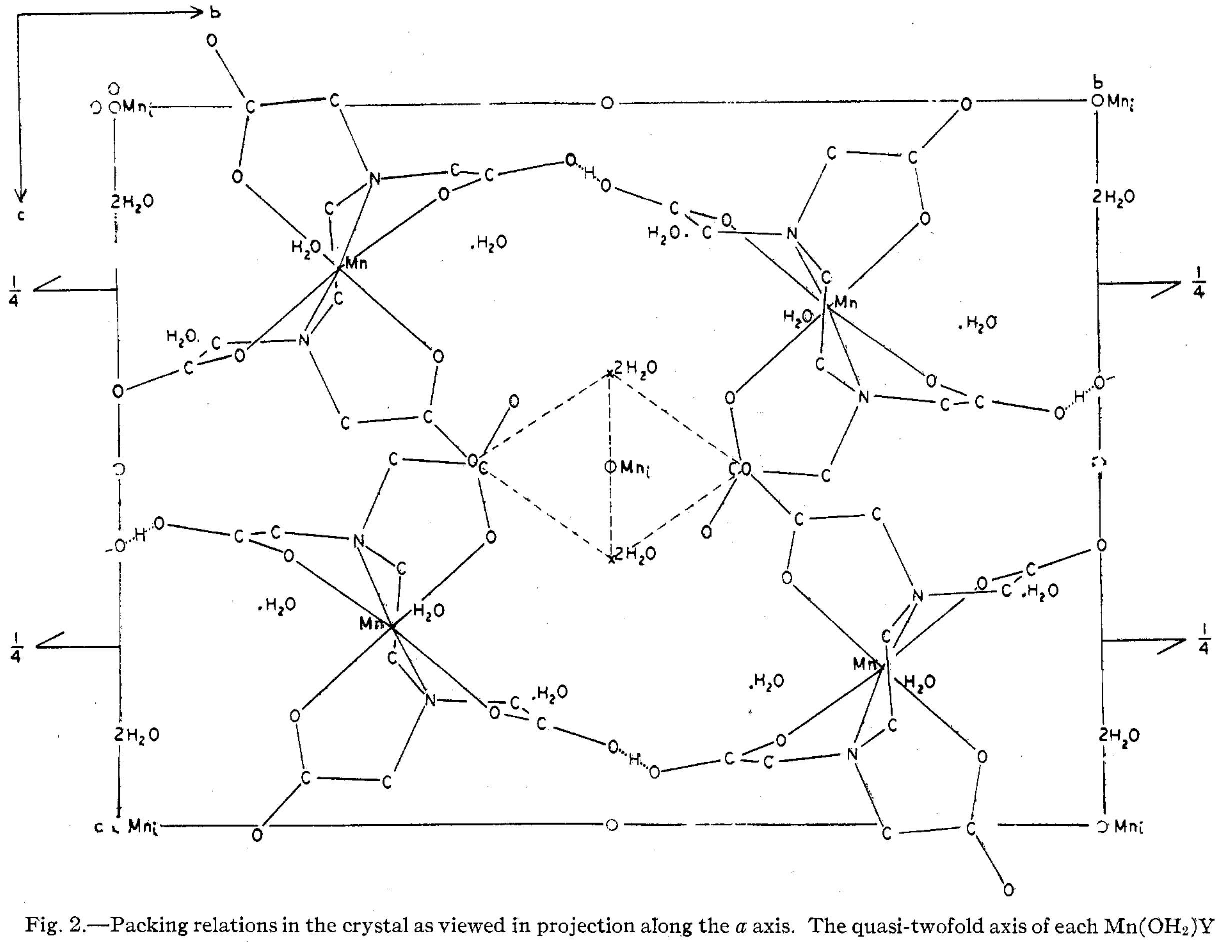

Fig. 2.—Packing relations in the crystal as viewed in projection along the a axis. The quasi-twofold axis of each $Mn(OH_2)Y$ group is roughly parallel to a. The $O_5 \cdot\cdot H \cdot\cdot O_7$ hydrogen bonds giving infinite strings $[Mn(OH_2)YH]_n^{-n}$ along b are explicitly indicated; the numerous hydrogen bonds formed by water molecules (Table IV) are omitted. Octahedral coordination about Mn_i is best seen at the center of the diagram.

TABLE I

PARAMETER DATA[a] FOR $Mn_3(HY)_2 \cdot 10H_2O$

Atom type	(Coordinate ± std. dev.) × 10^4			B, Å.^{2}	ρ_{max}, e/Å.^{3}
	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$		
O_1	2122 ± 3	1196 ± 2	3431 ± 2	2.18	23.9
O_2	1403 ± 4	1231 ± 2	942 ± 2	2.25	22.9
O_3	2106 ± 3	3338 ± 2	1165 ± 2	2.01	25.0
O_4	1245 ± 3	3245 ± 2	3489 ± 2	2.11	23.9
O_5	1246 ± 4	−35 ± 3	3935 ± 3	2.55	21.1
O_6	1032 ± 7	971 ± 4	−884 ± 5	3.33	16.0
O_7	1189 ± 4	4573 ± 2	754 ± 3	2.50	21.1
O_8	5032 ± 4	1366 ± 2	25 ± 3	2.36	22.8
N_I	−488 ± 3	1886 ± 1	3234 ± 2	1.54	26.6
N_{II}	−396 ± 3	2541 ± 1	960 ± 2	1.62	25.9
C_1	−457 ± 4	976 ± 2	3330 ± 2	1.93	20.0
C_2	−16 ± 4	2183 ± 2	−136 ± 3	2.20	17.9
C_3	−480 ± 4	3449 ± 2	909 ± 3	1.97	19.0
C_4	−324 ± 3	2271 ± 2	4348 ± 2	1.85	20.6
C_5	1096 ± 3	706 ± 2	3577 ± 2	1.73	21.3
C_6	867 ± 4	1393 ± 2	−16 ± 3	2.16	17.8
C_7	1062 ± 3	3797 ± 2	942 ± 2	1.68	22.2
C_8	362 ± 3	3124 ± 2	4270 ± 2	1.68	21.6
C_I	−1806 ± 4	2216 ± 2	2668 ± 3	1.94	21.0
C_{II}	−1720 ± 3	2144 ± 2	1396 ± 3	1.99	20.4
w_1	3995 ± 3	2103 ± 2	2015 ± 2	2.12	24.5
w_2	3353 ± 5	4 ± 3	1280 ± 4	2.90	18.9
w_3	−3369 ± 10	−5 ± 6	1310 ± 7	4.37	12.9
w_4	5662 ± 6	785 ± 4	3221 ± 4	3.23	16.6
w_5	5444 ± 6	3575 ± 4	1948 ± 5	3.31	16.3
Mn_i	$^1/_2$ ..	0 ..	0 ..	1.88	126.1

Mn_g: $10^5x = 15977 \pm 4$; $10^5y = 22325 \pm 2$; $10^5z = 22096 \pm 2$; $B = 1.48$ A.^{2}; $\rho_{max} = 149.6$ A.^{3}

[a] Complete amplitude data have been submitted as Document No. 7708 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $11.25 for photoprints or $3.75 for 35-mm. film in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

TABLE II

AVERAGED BOND LENGTHS

Bond type	Mean length, Å.	Deviations, Å. Mean	Max.	Std.
C–N	1.471	0.004	0.009	0.007
C–C[a]	1.519	0.004	0.008	0.008
C–O	1.257	0.011	0.019	0.009
Mn_g–O	2.236	0.017	0.025	0.005
Mn_g–N	2.377	0.025	0.025	0.004
Mn_i–w	2.155	0.004	0.004	0.013

[a] Includes the C–C bond at 1.518 ± 0.008 Å. in the ethylenediamine ring.

TABLE III

INDIVIDUAL BOND LENGTHS

Bond	Length, Å.	σ, Å.	Bond	Length, Å.	σ, Å.
C_5–O_1	1.244	0.007	Mn–N_I	2.352	0.004
C_5–O_5	1.274	0.009	Mn–N_{II}	2.402	0.004
C_7–O_3	1.239	0.007	Mn–w_1	2.232	0.005
C_7–O_7	1.276	0.008	Mn–O_1	2.261	0.005
C_6–O_2	1.263	0.009	Mn–O_2	2.212	0.006
C_6–O_6	1.245	0.013	Mn–O_3	2.223	0.005
C_8–O_4	1.255	0.008	Mn–O_4	2.254	0.006
C_8–O_8	1.257	0.008	Mn_i–O_8	2.199	0.006

TABLE IV

HYDROGEN BOND PARAMETERS

Bond[a]	Length ± σ, Å.	Angles,[b] degrees	
$O_5 \cdots O_7$	2.469 ± 0.010	$O_5O_7C_7$, 108.2	$O_7O_5C_5$, 112.9
$O_2 \cdots w_2$	2.698 ± 0.010	$O_2w_2Mn_i$, 111.3	$w_2O_2C_6$, 122.9
$O_6 \cdots w_3$	2.708 ± 0.019	$O_6w_3Mn_i$, 115.3	$w_3O_6C_6$, 124.6
$w_1 \cdots w_5$	2.722 ± 0.011	$w_5w_1w_4$, 112.6	$w_3w_1O_8$, 99.9
$w_3 \cdots w_4$	2.758 ± 0.019	$w_4w_3Mn_i$, 111.9	$w_4w_3O_6$, 132.3
$O_8 \cdots w_1$	2.820 ± 0.008	$O_8w_1w_4$, 112.6	$w_1O_8C_8$, 113.2
$O_7 \cdots w_4$	2.869 ± 0.012	$O_7w_4w_3$, 102.9	$w_4O_7C_7$, 80.8
$O_4 \cdots w_2$	2.869 ± 0.011	$O_4w_2Mn_i$, 89.3	$w_2O_4C_8$, 92.5
$O_5 \cdots w_5$	2.915 ± 0.012	$O_5w_5w_1$, 114.9	$w_5O_5C_5$, 123.3
$w_1 \cdots w_4$	2.977 ± 0.011	$w_4w_1Mn_g$, 121.5	$w_4w_1O_8$, 85.8

[a] O···O contacts less than 3.00 Å. listed. [b] Standard deviations in range 0.2–0.4°.

Bond length data are presented in Tables II–IV. The averaged bond lengths, each accompanied by its mean, maximum, and standard deviations from the mean, as listed in Table II, give direction to the subsequent discussion. Table III contains pertinent data for individual bonds. In dealing with hydrogen bonding it is most convenient to consider distances and angles together; the data needed are given in Table IV.

Inspection of Table II tells us that it is pointless to look at individual values for the C–N, C–C, and Mn_i–w bond lengths. We note that 1.47 Å. is the standard value for a C–N single bond and that 1.52 Å. is a good value for a C–C bond in which one of the carbon atoms is in trigonal hybridization. We would expect, however, a C–C bond nearer 1.54 Å. in the ethylenediamine ring.

The relatively small spread indicated for C–O bond lengths reflects the bidentate role of carboxylate in the structure and, more specifically, the weakness of Mn(II)–O complexing bonds. Such spread, however, is notably present in four C–O bonds involving just two carbon atoms, C_5 and C_7 (Table III). Recalling that O_5 and O_7 are the oxygen atoms (from contiguous Mn-$(OH_2)Y$ groups) which are hydrogen bonded at 2.469 ± 0.010 Å. (Table IV), whereas O_1 and O_3 are complexed to Mn_g, we note that the nearly identical C_5–O_5 and C_7–O_7 distances average to 1.275 Å., the C_5–O_1 and C_7–O_3 distances to 1.242 Å.; the difference, 0.033 Å., is about four times the standard deviation, 0.008 Å. It would appear that the oxygen atoms complexed to Mn_g have assumed additional carbonyl character, while O_5 and O_7 each partially simulate the state of an oxygen atom forming two single bonds. The structural quasi-equivalence of O_5 with O_7 and of O_1 with O_3 extends (Table I) to the respective peak electron densities and thermal parameters. All of these data testify to the cogency of the O_5--H--O_7 bond (*cf.* Table IV for the bonding angles) and to the probability that it is quasi-symmetrical. Although about 0.07 Å. longer than the probably symmetric hydrogen bond in nickel dimethylglyoxime,[16] the O_5--H--O_7 bond has more nearly the character of a freely formed intermolecular linkage than that of an intramolecular tie which is both demanded and reinforced by a special internal geometry.

The near identity (Table III) of the C_8–O_4 and C_8–O_8 bond lengths is consistent with the observation that

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(16) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 7555 (1959).

each oxygen atom is complexed to manganese and that each forms also a comparatively weak hydrogen bond with a water molecule (Table IV). That C_6–O_2 is longer than C_6–O_6 by a possibly significant 0.018 Å. (Table III) is consistent with the observation that, while each oxygen atom forms a good hydrogen bond (2.70–2.71 Å.), O_2 is complexed also to Mn_g. The over-all pattern of C–O distances within the flat (*vide infra*) carboxylate groups is highly satisfactory.

The Mn–O and Mn–N bond lengths are notably large in agreement with the limited complexing capacity of Mn^{+2} in the stable sextet state, *i.e.*, with each 3d-orbital occupied by an unpaired electron. The bonding remains weak whether one views it wholly in electrostatic terms or calls upon the $4sp^3$ (and, just possibly, the 4d) orbitals of Mn^{+2} for construction of an overlay of covalent bonding. Such an overlay in the anionic complex would be sensibly restricted to the five Mn–O bonds (including Mn–w_1), as these are much shorter, 0.13 Å. on the average, than are the Mn–N bonds; a difference of about 0.04 Å. in the covalent radii of nitrogen and oxygen is expected[17] and is confirmed for two EDTA complexes, the CoY^- ion[18] and the $Ni(OH_2)HY$ acid,[19] in which the importance of covalent bonding to nitrogen scarcely can be doubted. One notes that, as expected on an electrostatic basis, the averaged Mn–O bond length is longer in the seven-coordination group than in the octahedron. Although large enough to attain probable statistical significance, the observed variations among the four bond lengths involving carboxylate oxygen in the anionic complex follow no quasi-symmetric pattern and seem to be the result of the stresses exerted on the complex by its highly asymmetric environment; when averaged in agreement with C_2-2, the two Mn_g–O bond lengths obtained differ by only 0.010 Å.

Of greater concern is the observation that the four Mn_i–OH_2 bonds in the octahedral coordination group are certainly as short as, and probably are significantly shorter (0.042 Å.) than, the two Mn_i–O_8 bonds involving carboxylate oxygen, a quite unexpected result in terms of electrostatic bonding. Inasmuch as the bond angles at Mn_i (an inversion center) are $O_8Mnw_2 = 89.8 \pm 0.2°$, $O_8Mnw_3 = 90.9 \pm 0.3°$, $w_2Mnw_3 = 91.1 \pm 0.3°$, the approximation to full tetragonal bipyramidal symmetry, D_{4h}-4mmm, is excellent. One sees a quite plausible bonding scheme which calls upon all four of the stable $4sp^3$ orbitals of Mn^{+2} for the construction of digonal sp_y hybrids for the attachment of carboxylate oxygen, and, through combination of p_x and p_z each with p-orbitals of two oxygen atoms of water molecules, two sets of the three-center four-electron delocalized orbitals described by Rundle[20]; but as just one of the three delocalized orbitals directed along x (or z) contributes directly to bonding,[20] the over-all scheme calls again for shorter bonds to carboxylate oxygen than to water. It does not seem feasible to devise a simple bonding scheme, free of arbitrary features, which would require shorter bonds to the four water molecules than to carboxylate oxygen. We must appeal again to the highly asymmetric packing stresses, which need have little effect on the individually coordinated water molecules, but are critical to the specification of carboxylate bridging and complexing. This conclusion seems to be required whether covalent bonding is or is not consequential.

Treatment of possible covalent bonding in the quasi-pyramidal MnO_5 cap of the anionic complex could use two sets of three-center four-electron bonding systems for tying carboxylate oxygen atoms in pairs to Mn^{+2} (although there would be significant departures from linearity in both systems—*vide infra*) and the remaining p-orbital (with admixture of s) of Mn^{+2} for attaching the water molecule. This scheme has much less appeal than that proposed for the formally analogous FeO_5 cap from the $Fe(OH_2)Y^-$ complex, but this is a necessary consequence of real stereochemical differences.[5,6]

Carboxylate groups of every structural class are flat within the experimental accuracy: the sum of the bond angles at the central carbon atom is in every case 360° within the accuracy of formal computation on the computer.

The sum of the interior angles in the ethylenediamine ring is 518.1°, a good deal short of the 540° corresponding to planarity. The required distortion[21] is taken very nearly in agreement with a twofold axis passing through manganese and the mid-point of the C_I–C_{II} bond (Fig. 1); a symmetrical twisting displaces the carbon atoms from the mean plane defined by manganese and the two nitrogen atoms. Approximate preservation of tetrahedral bond angles at nitrogen requires simultaneous rotations of the ring systems branching from nitrogen atoms around the respective N–Mn bonds, thus dividing the four glycinate rings into structurally distinct pairs; one such pair, the G_o set, is identified (Fig. 1) by the odd (Arabic) subscripts carried by carbon and oxygen atoms, the other, G_e, by even subscripts on C and O. In the crystalline environment of no required symmetry the $Mn(OH_2)Y$ group, as shown below, maintains a quasi-twofold axis.

The mean value, with mean deviation, of the sum of the interior angles for the pair of glycinate rings, G_o, is $518.9 \pm 0.9°$, and for the pair, G_e, $526.8 \pm 0.4°$. Table V lists mean bond angles, each with maximum (or mean) and standard deviations from the mean, for the three structural classes of rings obtained by averaging on the assumption of a quasi-twofold axis. Observed deviations from the mean are uniformly $\lesssim 0.9°$, too

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(17) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

(18) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

(19) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

(20) R. E. Rundle, *ibid.*, **85**, 112 (1963). Of the three orbitals comprising a three-center four-electron bonding system (with either x or z as symmetry axis), the antibonding orbital remains unfilled and the nonbonding orbital places its two electrons back upon the ligands (whence they came). All electrons for the bonding pattern above are supplied by the ligands.

(21) If nearly regular tetrahedral angles be maintained at carbon and nitrogen, planarity of the ethylenediamine ring requires a bond angle NMN $\gtrsim 100°$ and—what appears to be impossible of practical attainment for any choice of M—a bond distance M–N $\lesssim 1.65$ Å. A realistic value of this latter is accompanied by a bond angle NMN $< 90°$ and kinking of the ring.

TABLE V

RING BOND ANGLES[a]

Ring type[b]	Bond angle	Mean value, deg.	Deviations, deg. Max.	Deviations, deg. Std.	Ring type[b]	Bond angle	Mean value, deg.	Deviations, deg. Max.	Deviations, deg. Std.
G_o	MnNC	105.5	0.3	0.2	G_e	MnNC	106.5	0.3	0.2
	NCC	108.5	0.1	0.3		NCC	111.9	0.3	0.4
	CCO	120.5	0.0	0.4		CCO	117.3	0.1	0.4
	COMn	114.5	0.9	0.3		COMn	119.2	0.2	0.3
	OMnN	70.0	0.3	0.1		OMnN	71.7	0.7	0.1
	OCO	124.7	0.3	0.5		OCO	125.9	0.2	0.7
E	MnNC	109.7	0.8	0.2	G_o-G_e	CNC	111.0	0.6	0.3
	NCC	111.8	0.2	0.3	G_o-E	CNC	113.9	0.2	0.4
	NMnN	75.3	...	0.1	G_e-E	CNC	109.9	0.4	0.3

[a] The quasi-symmetry of C_2-2 assumed in averaging. [b] G_o and G_e identify glycinate rings (Fig. 1) carrying, respectively, odd and even subscripts on C and O. E identifies the ethylenediamine ring.

TABLE VI

PARAMETERS OF THE INNER COORDINATION GROUP

Observed data				Av. configuration		
Edge	Length, Å.	Edge	Length, Å.	Edge	Length, Å.	σ, Å.
N_I–O_1	2.657	N_{II}–O_3	2.647	N–O_o	2.652	0.007
N_I–O_4	2.723	N_{II}–O_2	2.683	N–O_e	2.703	0.007
N_I–N_{II}	2.902	...	...	N–N	2.902	0.006
O_1–O_2	3.024	O_3–O_4	2.885	O_o–O_e	2.955	0.008
O_2–O_3	3.463	O_1–O_4	3.397	O_o–O_e	3.430	0.008
w_1–O_1	2.829	w_1–O_3	2.822	w_1–O_o	2.825	0.007
w_1–O_2	3.038	w_1–O_4	3.600	w_1–O_e	3.319	0.008
Angle	Value, deg.	Angle	Value, deg.	Angle	Value, deg.	σ, deg.
O_1MnO_2	85.1	O_3MnO_4	80.3	O_oMnO_e	82.7	0.1
O_3MnO_2	102.7	O_1MnO_4	97.6	O_oMnO_e	100.1	0.2
$O_1N_IO_4$	78.3	$O_3N_{II}O_2$	81.1	O_oNO_e	79.7	0.1
O_4Mnw_1	106.7	O_2Mnw_1	86.2	O_eMnw	96.5	0.2
O_3Mnw_1	78.6	O_1Mnw_1	78.0	O_oMnw	78.3	0.1
O_1MnO_3	154.8	...	...	O_oMnO_o	154.8	0.5
O_2MnO_4	194.1	...	...	O_eMnO_e	194.1	0.6

[a] Averaged in accord with C_2-2. O_o and O_e are oxygen atoms in glycinate rings carrying, respectively, odd and even subscripts in Fig. 1.

small to encourage detailed analysis, and are clearly attributable to asymmetric stresses from the environment. The inter-ring CNC bond angles, G_o–G_e, etc., in Table V also are in agreement with quasi-twofold symmetry. All twelve bond angles at nitrogen in the structure lie within the range 109.5 ± 4.5°, in good agreement with published data[18,19] for simpler EDTA complexes. Differences between the two classes of glycinate rings show up primarily in the bond angles; thus (Table V) the corresponding NCC, CCO, and COMn angles differ, for G_o and G_e, by 3–5°.

Table VI lists distances and angles not previously cited which are descriptive of the inner coordination group of the anionic complex. Data related by the quasi-twofold axis are given in the same row with the averaged value at the right. Of the thirteen edges of the coordination polyhedron, the four corresponding to N–O contacts (and to intra-ring spans) are fairly short, but the remaining nine correspond to packing relations which range from easy to quite loose. The approximation to quasi-twofold symmetry of the deformable complex is seen (Table VI) to be better where the tighter interatomic contacts are involved. Consider, for example, the packing relations which concern the water molecule. The reasonably short w_1–O_1 and w_1–O_3 edges together with the bond angles subtended at manganese conform to a quasi-twofold axis, whereas the long w_1–O_2 and w_1–O_3 edges differ materially from one another. Formation by w_1 of hydrogen bonds of various strengths (2.72, 2.82, 2.98 Å.; *cf.* Table IV) with other water molecules in the markedly asymmetric environment is quite sufficient to account for the observed displacement of w_1 from the quasi-twofold axis.

The quantitative description in Cartesian coordinates of the inner coordination group of the $Mn(OH_2)Y^{-2}$ anion, as presented in Table VII, assumes a twofold axis and a single bond length each for Mn–O and Mn–N.

TABLE VII

CARTESIAN COORDINATES OF THE IDEALIZED (C_2-2) COORDINATION GROUP[a]

Atom	Position	*X*, Å.	*Y*, Å.	*Z*, Å.
Mn	Origin	0	0	0
w_1	On 2	0	0	2.236
O_o	General	1.649	1.430	0.485
O_e	General	−1.696	1.430	−0.275
N	General	0.459	1.376	−1.884

[a] Twofold axis along 00*Z*. General positions: XYZ, $\bar{X}\bar{Y}Z$, Mn–O = 2.236 Å.; Mn–N = 2.377 Å.

This idealization is a greatly simplified, but quite faithful, representation of the averaged data which have been presented; it is intended to reproduce the more important distances and angles with high precision. A projection of this idealized model parallel to the Y-axis, *i.e.*, perpendicular both to the twofold (2) axis and the longer O–O edges, is shown[22] in Fig. 3.

Within the appropriate pH range in aqueous solution the sexadentate anionic Mn(II) complex might be thought to exist in one or more of the following forms: (1) six-coordinate MnY^{-2}, either octahedral or trigonal prismatic; (2) seven-coordinate $Mn(OH_2)Y^{-2}$, either as specified herein (Table VIII, Fig. 1 and 3) or with the configuration described for $Fe(OH_2)Y^{-}$; (3) eight-coordinate $Mn(OH_2)_2Y^{-2}$, with an inner coordination group of quasi-$Mo(CN)_8^{-4}$ type.[23] We appraise first the six-coordinate possibilities, assuming that there are no special restrictions on the bond angles at sextet Mn^{+2}. It is readily seen, by direct calculation or from sufficiently rigid and accurate models, that ring constraints are better served by the octahedron whenever the bond distance is sufficiently small, $\overline{<}$ *ca.* 2.05 Å. For a bond distance $\overline{>}$2.15 Å., the octahedral configuration is quite bad, whereas an approximately trigonal prismatic configuration provides a superior geometry for minimizing ring strain; but, inasmuch as the face opposite the nitrogen atoms is sufficiently open to permit easy coordination of a water molecule, we should confidently expect the seven-coordinate $Mn(OH_2)Y^{-2}$, as described herein, in preference to any six-coordinate species.

The eight-coordinate possibility of $Mo(CN)_8^{-4}$ type is the obvious extrapolation from a sexadentate octahedral complex in which the central atom has swelled until space for two water molecules becomes available at the open end of the complex. This configuration has greater appeal for an electrostatically bonded complex than has the closely related alternative obtained by adding a single water molecule (at the mean position on the twofold axis) to give a roughly planar girdle of 2N, 2O, and H_2O around the central atom, but it is the latter which is adopted by $Fe(OH_2)Y^{-}$ in crystals thus far studied—perhaps for reasons set forth in the accompanying papers.[5,6] In both configurations, moreover, it would seem that ring strain must increase fairly rapidly with increasing size of the central atom, and that, for a bond distance greater than about 2.15 Å., ring constraints would favor the seven-coordinate geometry exemplified in Fig. 1. It is plausible, consequently, that minimization of ring strain controls the selection of configuration for the weakly complexing sextet Mn^{+2}, to make the $Mn(OH_2)Y^{-2}$ of Table VII and Fig. 1 and 3 the principal complex species in solutions of appropriate pH.

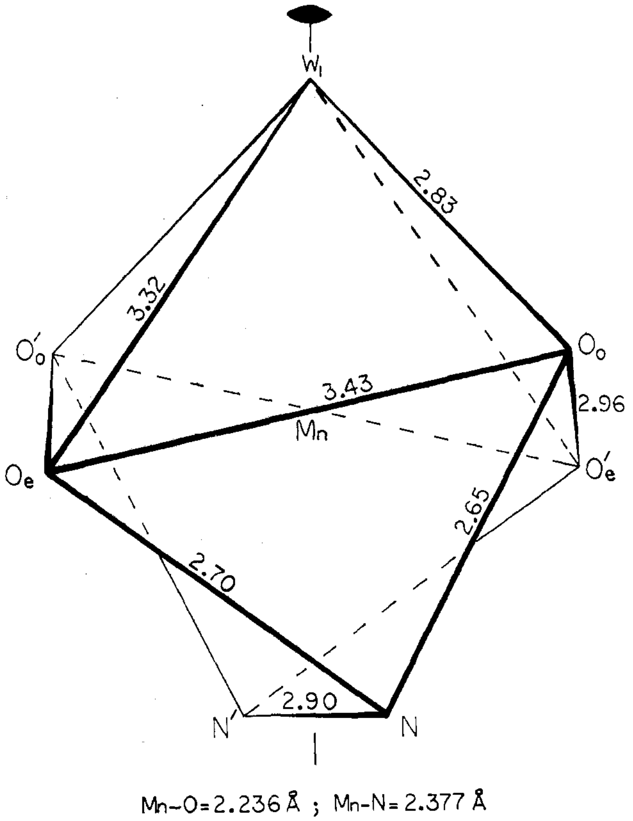

Fig. 3.—The idealized (C_2-2) coordination polyhedron of $Mn(OH_2)Y^{-2}$ as viewed parallel to the Y-axis following Table VII.

Calorimetrically determined values[24] of ΔH for the exothermic reaction in solution of $M(OH_2)_6^{+2}$, M = Mn, Fe, Co, Ni, with each of several complexing agents, including Y^{-4}, are qualitatively interpretable on a structural basis. When either ethylenediamine (en) or diethylenetriamine (dien) is employed to give six-coordinate $M(en)_3^{+2}$ or $M(dien)_2^{+2}$, the plot of $-\Delta H$ *vs.* atomic number of M is virtually linear (and strongly increasing) throughout the sequence, Mn, Fe, Co, Ni. When, on the other hand, either the sexadentate "penten" [N,N′,N″-tetrakis(2-aminoethyl)ethylenediamine] or Y^{-4} is the complexing agent, the value of $-\Delta H$ is "anomalously" high for formation of the Mn(II) complex considered as the end member in a six-coordinate sexadentate series. The effect is especially large for the EDTA complex; the experimental value of $-\Delta H$ is roughly 10 kcal./mole larger than that estimated by extrapolation for six-coordinate MnY^{-2}. The corresponding anomaly is about half as large for the pentene complex. Clearly these thermochemical data are most readily interpretable in terms of $[Mn(OH_2)penten]^{+2}$, $Mn(OH_2)Y^{-2}$, and perhaps some $Mn(OH_2)_2Y^{-2}$ as the complexed products of the reactions.

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(22) Were the higher symmetry, C_{2v}-mm2, of the NbF_7^{-2} configuration to be assumed, Table VII of Fig. 3 would be altered as follows: the four oxygen atoms would have the same (somewhat positive) Z and the same absolute values, $|X|$ and $|Y|$, for the other coordinates; the nitrogen atoms would have $X = 0$; the projection parallel to Y would then show these six atoms as three superposed pairs.

(23) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(24) M. Ciampolini, P. Paoletti, and L. Sacconi in "Advances in the Chemistry of the Coordination Compounds," the Macmillan Co., New York, N. Y., 1961, *cf.* Fig. 1, p. 304. The authors of this paper drew our attention to its bearing on our own studies during discussion at the VIth International Conference on Coordination Chemistry.