The Structure of the Seven-Coordinate *trans*-1,2-Diaminocyclohexane-N,N′-tetraacetatoaquoferrate(III) Ion in Crystals of the Calcium Salt[1,2]

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Abstract: A quantitative stereochemical description of the *trans*-1,2-diaminocyclohexane-N,N′-tetraacetatoaquoferrate(III) ion, written as $[Fe(OH_2)Z]^-$, comes from a three-dimensional X-ray analysis of the crystalline structure of the calcium salt, $Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$. The monoclinic cell containing four formula units of the salt has $a = 34.34$, $b = 8.844$, $c = 13.527$ A, and $\beta = 91.02°$; the space group is C2/c. The $[Fe(OH_2)Z]^-$ ion is stereochemically akin to the anionic ethylenediaminetetraacetato chelates of Fe(III) and Mn(II), written as $[Fe(OH_2)A]^-$ and $[Mn(OH_2)A]^{2-}$; all three are sexadentate, seven-coordinate, monaquo complexes in which the constraints on the formation of complex ring systems assume first importance. The coordination polyhedron and the ring foldings in $[Fe(OH_2)Z]^-$ resemble those in $[Mn(OH_2)A]^{2-}$, but the division of Fe–O bonds into classes with significantly different lengths is a feature of both iron complexes. The stereochemical role of the cyclohexane ring in $[Fe(OH_2)Z]^-$ is illuminated by the study.

The complexed species formed by ethylenediaminetetraacetic acid (hereafter written as EDTA or H_4A) with a variety of transition period[5a–f] and rare earth[6a,b] ions have been shown to utilize a distinctive stereochemistry that is, in large measure, controlled by the constraints attendant upon the formation of the continuously joined, multiply branched, ring systems.[5,6] In all of the anionic complexes and in half or more of the neutral species thus far studied, the complexing agent is actively sexadentate, but coordination numbers greater than six are commonplace.[5,6] The ring constraints, indeed, are incompatible with a quasi-octahedral configuration except for a central cation of relatively small size; with larger central ions, aquo complexes such as the seven-coordinate[5e,f] $[Mn(OH_2)A]^{2-}$ and $[Fe(OH_2)A]^-$, the nine-coordinate[6b] $[La(OH_2)_3A]^-$, and the ten-coordinate[6a] $La(OH_2)_4AH$ are observed.

Inasmuch as 1,2-diaminocyclohexane-N,N′-tetraacetic acid (hereafter written as DCTA or H_4Z) and EDTA form parallel series of complexes with the same broad spectrum of cations, but with stability constants that are quite generally more favorable (by one to three powers of ten[7]) to the DCTA complexes, comparative studies of the stereochemistry of corresponding pairs are of manifest interest. Transformation of the chelating agent from a 1,2-ethane derivative (EDTA) to a 1,2-cyclohexane derivative (DCTA) materially reduces the number of configurations which are available to the EDTA sub-unit contained within DCTA. The structural and thermodynamic consequences of this constraint, important both for the complexed species and for the free chelating agent in solution, are illuminated by the study now reported of the complex anion formed by *trans*-DCTA with ferric ion. A detailed stereochemical description of this complex anion comes from a determination by X-ray diffraction analysis of crystalline structure for the calcium salt, written as $Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$; the $[Fe(OH_2)Z]^-$ anion is found to be seven-coordinate with bond distances similar to those observed[5f] for $[Fe(OH_2)A]^-$, but with a configuration rather more like that recorded[5e] for $[Mn(OH_2)A]^{2-}$.

Experimental Section

Single crystals of $Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$ of usable quality for X-ray diffraction analysis were obtained by the following procedure. An aqueous slurry containing stoichiometric equivalents of solid H_4Z and freshly precipitated $Fe(OH)_3$ was held at 70–80° with continuous agitation until all solid material had reacted to leave a strongly acid amber-colored solution of the complex acid. To a portion of this solution was then added, bit by bit, the stoichiometric equivalent of finely powdered $CaCO_3$; slight effervescence produced by the escaping carbon dioxide was noted. Very slow evaporation at room temperature of the resulting solution furnished rod-like crystals of $Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$. Similar procedures along with a number of variations thereof were employed in unsuccessful attempts to prepare single crystals of comparable quality of the salts of Li^+, Na^+, K^+, Rb^+, NH_4^+, $N(CH_3)_4^+$, Mg^{2+}, Mn^{2+}, and Cu^{2+}.

Oscillation, Weissenberg, and precession photographic techniques were utilized to establish that crystals of $Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$ are monoclinic, to give approximate lattice constants, and to determine the probable space group[8] as either $C2/c\text{-}C_{2h}^6$ or $Cc\text{-}C_s^4$. The choice of C2/c was supported by the absence of detectable piezoelectricity and by the subsequently successful determination of structure based upon the centrosymmetric space group. Cell constants, as measured on a GE spectrometer assembly, are $a = 34.34 \pm 0.02$, $b = 8.844 \pm 0.011$, $c = 13.527 \pm 0.017$ A, and $\beta = 91.02 \pm 0.05°$. The measured density, 1.65 g/cc, is in reasonable

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[2] The abbreviation, DCTA, and short formula, H_4Z, are used throughout for *trans*-1,2-diaminocyclohexane-N,N′-tetraacetic acid. EDTA and H_4A are similarly employed for ethylenediaminetetraacetic acid.

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[7] S. Chabarek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959, pp 572–576.

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Table I. Structural Parameters for Crystalline $Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$

Atom type	Coordinate ± standard deviation			B, A^2	Amplitude,[a] A
	$(x \pm \sigma_x)$ × 10^5	$(y \pm \sigma_y)$ × 10^4	$(z \pm \sigma_z)$ × 10^4		
O_1	43473 ± 6	8306 ± 4	7424 ± 3	2.6	0.18
O_2	36178 6	8106 4	5061 3	2.7	0.19
O_3	42358 6	5984 4	6183 3	2.2	0.17
O_4	40531 6	10447 4[b]	5785 3	2.0	0.16
w_1	44767 6	8313 4	5238 3	2.7	0.19
N_1	36543 6	9594 4	7280 3	1.8	0.15
N_2	35319 6	6546 4	6705 3	1.9	0.15
C_1	33860 6	8623 6	7868 3	2.4	0.17
C_2	32143 6	7379 6	7211 4	2.5	0.18
C_3	39462 6	10319 6[b]	7956 4	2.5	0.18
C_4	43068 6	9338 5	8066 3	2.1	0.16
C_5	33746 16	5860 6	5772 4	2.2	0.17
C_6	33882 16	6987 6	4921 4	2.7	0.19
C_7	37415 6	5396 5	7323 4	2.1	0.16
C_8	41330 6	5079 5	6854 4	1.9	0.16
C_9	34587 6	10746 6[b]	6641 4	2.1	0.17
C_{10}	37542 16	11300 5[b]	5888 4	1.7	0.15
O_5	45398 6	9572 4	8761 2	3.0	0.20
O_6	31945 16	6787 7	4161 4	5.1	0.25
O_7	43266 6	4000 4	7174 3	2.9	0.19
O_8	37025 6	12502 4[b]	5452 3	2.5	0.18
C_{11}	29461 16	6328 7	7811 5	3.5	0.21
C_{12}	26229 16	7232 9	8304 6	4.5	0.24
C_{13}	27970 16	8446 9	8958 5	4.6	0.24
C_{14}	30595 16	9513 7	8371 5	3.6	0.21
Ca	$^1/_2$	3549 2	$^3/_4$	2.5	0.18
w_2	$^1/_2$	6282 7	$^3/_4$	3.5	0.21
w_3	48059 6	3950 5	9179 3	3.6	0.21
w_4	47855 6	1318 5	6612 4	3.5	0.21
w_5	44904 16	6643 6	9686 4	4.1	0.23
w_6	25881 64	8627 25	5462 18	9.2[c]	0.34
Fe	40037 1	$10^5 y = 81657 \pm 2$	$10^5 z = 61863 \pm 2$	1.4	0.13

[a] Root-mean-square amplitude in angstroms = $\sqrt{B/8\pi^2}$. [b] These coordinates exceed $y = 1$ in order that a discrete complex unit might be described. [c] Assuming only half an atom.

agreement with that calculated, 1.64 g/cc, for a cell content of $4Ca[Fe(OH_2)Z]_2 \cdot 8H_2O$.

Three-dimensional intensity data from a specimen of approximately cubical shape (0.35 × 0.37 × 0.37 mm) were taken with Mo Kα radiation for $0 < 2\theta < 55°$ on a GE spectrometer assembly carrying a scintillation counter. The applicable linear absorption coefficient being just 0.95 mm^{-1}, absorption corrections were deemed unnecessary. Intensity measurement utilized the divergent beam with stationary crystal and counter technique, the background for each reflection being evaluated as the mean of the counts taken at $2\theta \pm 1.2°$. Several standard reflections, well distributed in the limiting sphere, were employed for periodic checking of alignments. A slow decline with time in the intensities of the standard reflections, but at nearly the same fractional rate in all cases, suggested a slow decomposition of the crystals that gradually progressed from the surface inward. The periodically measured intensities of the standard reflections were used to scale all of the intensity data to a common basis in time. Intensity counts were then reduced to relative $|F|$ values by means of the BASIC[9] program for the Control Data Corp. 1604 computer.

Of a total of 4708 independent reflections accessible in the Cu Kα limiting sphere, 4329 were recorded above background. The amplitude data, scaled to a quasi-absolute basis, are characterized as follows. About 4100 reflections have $|F| > 6$ and a group of 3720 for which intensity estimates were reasonably quantitative has $|F| > 10$. Just ten reflections have $|F| > 300$, but some 287 have $|F| > 100$; F_{000}, for comparison, is 2128.

A moderately sharpened Patterson synthesis of the stronger 45% of the three-dimensional $|F|^2$ data led at once to placement of the iron atoms in the eightfold general positions[8] of C2/c, *i.e.*, in $\pm(x, y, z)$, $\pm(x, \bar{y}, {}^1/_2 + z)$, and each of these translated by $({}^1/_2, {}^1/_2, 0)$. Assignment of phases based on the calculated contributions of the iron atoms to the structure amplitudes sufficed to develop the complete structure by Fourier synthesis in successive approximation.[10]

Refinement of structure utilized diagonal least-squares[11] minimization of the function, $\Sigma w(|F_o| - |F_c|)^2$, with $w = 4F_{\min}/|F_o|$ for $|F_o| \geq 4F_{\min}$, $w = 1$ for $|F_o| \leq 4F_{\min}$, and $F_{\min}$ taken as 3.9; $|F_c|$ and $|F_o|$ are, respectively, the absolute values of the calculated and observed structure amplitudes. Individual anisotropic thermal parameters and positional coordinates for all atoms except hydrogen, and an over-all scale factor—a total of 281 variable parameters for the asymmetric unit—were refined; the ratio of variable parameters to independent $\{hkl\}$ data was ~1:15. A difference synthesis based upon the final results of the least-squares refinement was essentially flat to within 0.5 e/A^3. Values of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.105 for the 4708 independent $\{hkl\}$, observed and unobserved, having $(\sin \theta)/\lambda < 0.65$ and 0.094 for the 4329 reflections recorded as above background were obtained.

The atomic coordinates of the structure, with associated standard deviations estimated by *doubling* the values given by the diagonal least-squares refinement, are listed in Table I. This arbitrary procedure facilitates the direct comparison of stereochemical parameters for the $[Fe(OH_2)Z]^-$, $[Fe(OH_2)A]^-$, and $[Mn(OH_2)A]^{2-}$ complexes because, in the earlier studies,[5e,5f] the estimated standard deviations also were doubled. One may bear in mind that in all three studies (but perhaps least so for that now reported) the standard deviations cited for all bond parameters are conservatively large. Quasi-isotropic thermal parameters for individual atoms, estimated following Rossman, *et al.*,[12] from the anisotropic values, and the corresponding root-mean-square amplitudes of vibration also are

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[9] B. T. Gorres and R. A. Jacobson, "Data Processing, Least Squares Preparation, and Patterson Sharpening Programs for the Control Data Corporation 1604," Frick Chemical Laboatory, Princeton University, Princeton, N. J., Technical Report No. 4, Aug 1, 1963.

[10] The atomic form factors used for all atoms were taken from the "International Tables for X-Ray Crystallography, Vol. 3, Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962, p 201.

[11] F. A. Muller and R. A. Jacobson, "Full Matrix Least Squares and General Fourier Programs for the Control Data Corporation 1604," Frick Chemical Laboratory, Princeton University, Princeton, N. J., Technical Report No. 1, June 17, 1963.

[12] M. G. Rossman, R. A. Jacobson, F. L. Hirshfeld, and W. N. Lipscomb, *Acta Cryst.*, 12, 530 (1959).

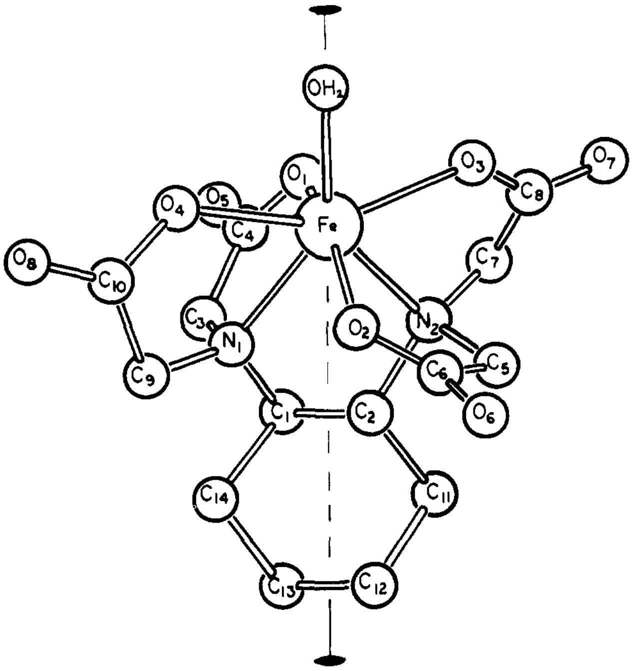

Figure 1. Model in perspective of the seven-coordinate aquo complex, $[Fe(OH_2)Z]^-$, as described quantitatively by Tables II–V.

listed in Table I.[13] The numbering of atoms and of water molecules (w_i) is maintained in Figures 1 and 3.

Stereochemistry of the Complex Anion

The $[Fe(OH_2)Z]^-$ ion, illustrated in Figure 1, is both sexadentate and seven-coordinate, with a water molecule, w_1, filling the seventh position. The configuration assumed by the complex anion, its asymmetric environment in the crystal notwithstanding, approximates rather closely to the maximum allowable symmetry, C_2-2, of such a group. The effective twofold axis (Figure 1) that passes through the oxygen of the water molecule, the iron atom, and the center of the cyclohexane ring classifies the four glycinate rings into two sets of two. Thus the $FeO_1C_4C_3N_1$ and $FeO_2C_6C_5N_2$ rings comprise one such pair, designated as the L type (to suggest *less* strained), and the $FeO_3C_8C_7N_2$ and $FeO_4C_{10}C_9N_1$ rings the other pair, designated the M type (to suggest *more* strained, *vide infra*). CH and E are used as symbols for the cyclohexane and the pseudo-ethylenediamine ($FeN_1C_1C_2N_2$) rings, respectively. Also, independently of ring type, O_c is used for carboxylate oxygen atoms (O_1, . . ., O_4) that are complexed to the iron atom and O_u for carboxylate oxygen atoms (O_5, . . ., O_8) that are not.

Ring bond angles, averaged in agreement with an effective twofold axis, are listed in Table II. Comparison of the maximum deviations from the averaged values with the corresponding standard deviations shows that the mean values of the ring bond angles give a quantitatively adequate and objectively significant representation of the data. The cyclohexane ring is in the "chair" form and, judging from the clustering of the six bond angles near the regular tetrahedral value, is sensibly unstrained. The carboxylate groups with attached carbon atoms, *i.e.*, the CCO_cO_u groupings, are each flat within the accuracy of the determination.

Table II. Ring Bond Angles in the Complex Anion[a,b]

Ring type	Bond angle	Mean value, deg	Deviations, deg	
			Max	Std
E	FeNC	111.1	0.0	0.2
	NCC	110.0	0.2	0.4
	NFeN	76.5	. . .	0.2
L	FeOC	122.4	0.2	0.4
	OCC	115.7	0.7	0.6
	CCN	110.8	0.1	0.5
	CNFe	105.1	1.0	0.3
	NFeO	75.3	0.4	0.2
	CCO_u	120.2	0.8	0.7
	OCO_u	124.1	0.1	0.8
M	FeOC	118.1	0.1	0.5
	OCC	115.7	0.5	0.5
	CCN	108.1	0.2	0.5
	CNFe	104.5	0.7	0.3
	NFeO	71.8	0.3	0.2
	CCO_u	119.2	1.2	0.6
	OCO_u	125.1	0.7	0.8
E–L[c]	CNC	109.5	0.1	0.5
E–M[c]	CNC	115.3	0.1	0.6
L–M[c]	CNC	110.9	0.8	0.6

[a] Averaged assuming twofold (C_2) symmetry. [b] Bond angles in the cyclohexane ring range from 110.2 to 111.4° and average 110.8°. [c] Angle at junction of two rings.

It is seen, however, that every bond angle in an L ring is apparently as large as, or larger than, the corresponding angle in a ring of M type. Observed differences of 4.3 and 3.5° in the respective FeO_cC and $NFeO_c$ angles are, by objective criteria, highly significant. The sum of the interior angles in an L ring (529.3°) exceeds that in an M ring (518.2°) by some 11°; rings of L type are less sharply folded and carry less angular strain than those of M type. Further, the CNC angle between E and M rings (115.3 ± 0.6°) implies a constraint on the formation of M rings that is equalled (or perhaps exceeded) among EDTA complexes only by an analogous stereochemical limitation on the formation and stability of the family of quasi-octahedral sexadentate anions.[5a–d]

Bond lengths within the $[Fe(OH_2)Z]^-$ ion, averaged either in agreement with an effective twofold axis or, for certain bond types, on a still wider basis, are listed in Table III. The C–N, C–O_c, C–O_u, and glycinate ring C–C bond distances are seen to be virtually independent of ring type. Averaged lengths for C–O_c (1.273 A), C–O_u (1.233 A), and glycinate C–C (1.523 A) bonds each agree within 0.001–0.004 A with the corresponding datum reported[5f] for $[Fe(OH_2)A]^-$. The C–N distance (1.492 ± 0.006 A) is a possibly significant 0.020 A larger than that in $[Fe(OH_2)A]^-$; 1.479 ± 0.005 A is cited[14] as expected for a single C–N bond involving "4-covalent nitrogen." The C_{12}–C_{13} bond in the cyclohexane ring is a possibly significant 0.033 A shorter than the "paraffinic" 1.541 A.[14] It is objectively less probable that the C_1–C_2 bond (1.526 ± 0.007 A) is significantly shorter than the standard 1.541 A;

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(13) A complete listing of amplitude data for the Cu Kα sphere and of anisotropic thermal parameters has been deposited as Document No. 8870 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $5.00 for photoprints or $2.25 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

(14) *Cf.* ref 10, p 276.

one notes, however, that the analogous bond (though not shared with a CH ring) in $[Fe(OH_2)A]^-$ and $[Mn(OH_2)A]^{2-}$ has the respective lengths, 1.502 ± 0.006 and 1.518 ± 0.008 A. The remaining C–C distances in the CH ring, 1.538 ± 0.009 A, are quite normal.

Table III. Averaged Bond Lengths within the Complex Anion

Bond Type	No. of bonds	Ring type(s)	Av length, A	Deviations, A Mean	Std[a]
C_1–C_2	1	E, CH	1.526	...	0.007
C_{12}–C_{13}	1	CH	1.508	...	0.011
C–C	4	CH	1.538	0.009	0.009
C–C	4	L, M	1.523	0.004	0.006
C–N	6	E, L, M	1.492	0.002	0.006
C–O_c	4	L, M	1.273	0.007	0.006
C–O_u	4	L, M	1.233	0.006	0.005
Fe–O	2	L	2.017	0.017	0.004
Fe–O	2	M	2.092	0.005	0.004
Fe–w_1	1	...	2.090	...	0.003
Fe–N	2	E	2.290	0.008	0.004

[a] Root mean square of the individual standard deviations. The individual standard deviations in Tables II, III, IV, VI, and VII were calculated by the "Errors Program for the Control Data Corporation 1604" of B. T. Gorres and R. A. Jacobson, Frick Chemical Laboratory, Princeton University, Princeton, N. J., March 1963, as revised by G. H. Cohen in July 1964.

One objectively significant departure from C_2 symmetry in the pattern of bond distances (Table III) is provided by the Fe–O bonds in the L rings; these differ from one another by 0.034 ± 0.004 A. As emphasized earlier,[5e,f] it is natural that most of the strains produced in the complex anion by the asymmetric stresses from its environment should accumulate in the complexing bonds and, more generally, in the coordination group; the $[Fe(OH_2)Z]^-$, $[Fe(OH_2)A]^-$, and $[Mn(OH_2)A]^{2-}$ ions in their respective crystalline environments are all thus affected. The Fe–N bond length in $[Fe(OH_2)Z]^-$, 2.290 ± 0.004 A, is 0.035 A shorter than in $[Fe(OH_2)A]^-$; in both cases the Fe–N distance is so long as to bespeak weak bonding. Fe–O bonds in M rings (2.092 ± 0.004 A) are significantly longer than in L rings (2.017 ± 0.004 A), a phenomenon that, as discussed later, has its parallel in $[Fe(OH_2)A]^-$, but not in $[Mn(OH_2)A]^{2-}$. That the Fe–w_1 bond (2.090 ± 0.003 A) should be as short as the Fe–O bonds of M rings in $[Fe(OH_2)Z]^-$ is what one would expect from consideration of the stereochemical data characterizing $[Fe(OH_2)A]^-$ and $[Mn(OH_2)A]^{2-}$.

Significant deviations from the symmetry of C_2-2 are evident in the parameters of the coordination polyhedron as listed in Table IV. In each line of Table IV the observed data are paired at the left in accordance with the quasi-twofold axis and the averaged datum of primary chemical interest is given, using the general symbolism, at the right. Observed deviations from the C_2 configuration, attributable wholly to the asymmetric stresses exerted by the crystalline environment, are comparable with those reported for $[Fe(OH_2)A]^-$ and $[Mn(OH_2)A]^{2-}$ in analogous circumstances.

Cartesian coordinates of the averaged coordination group of C_2-2 symmetry are given in Table V. The origin is taken at the iron atom, and the coordinate system is oriented to make the twofold axis coincide with the Cartesian Z axis and to give O_L and O_M atoms the same value of Y. The geometries of this coordination group and, interestingly enough, of the CaO_7 grouping in the crystalline arrangement (*vide infra*) are both readily derivable from the more symmetric (C_{2v}-mm2) configuration described long ago for the

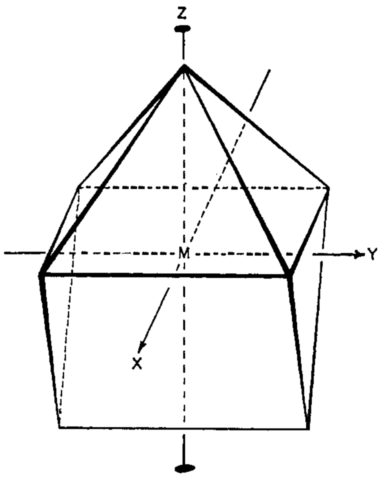

Figure 2. The coordination polyhedron of reference (C_{2v} symmetry, NbF_7^{2-} type[15]) for discussion of the FeN_2O_5 and CaO_7 coordination groups (C_2 symmetry) of this report. Mutually perpendicular mirror planes (of which one is the plane of the paper) intersect in the twofold axis.

Table IV. Parameters of the Inner Coordination Group in $Fe(OH_2)Z^-$

Observed data: Edge	Length, A	Edge	Length, A	Averaged data[a]: Edge[b]	Length, A	σ, A
O_1–N_1	2.642	O_2–N_2	2.636	$(O_L$–$N)$[c]	2.639	0.005
O_1–N_2	3.333	O_2–N_1	3.275	$(O_L$–$N)$[d]	3.304	0.005
O_1–O_4	3.072	O_2–O_3	3.195	$(O_L$–$O_M)$[e]	3.133	0.005
O_1–O_3	2.675	O_2–O_4	2.724	$(O_L$–$O_M)$[f]	2.700	0.006
O_1–w_1	2.996	O_2–w_1	2.960	O_L–w	2.987	0.005
O_3–N_2	2.578	O_4–N_1	2.574	O_M–N	2.576	0.004
O_3–w_1	2.568	O_4–w_1	2.502	O_M–w	2.535	0.006
N_1–N_2	2.834	...	...	N–N	2.834	0.006
Angle	**Value, deg**	**Angle**	**Value, deg**	**Angle[b]**	**Value, deg**	**σ, deg**
O_1FeN_1	74.9	O_2FeN_2	75.7	(O_LFeN)[c]	75.7	0.2
O_1FeN_2	101.0	O_2FeN_1	99.1	(O_LFeN)[d]	100.0	0.3
O_1FeO_4	96.1	O_2FeO_3	102.8	(O_LFeO_M)[e]	99.5	0.3
O_1FeO_3	80.9	O_2FeO_4	83.3	(O_LFeO_M)[f]	82.1	0.3
O_1Few_1	93.2	O_2Few_1	92.7	O_LFew	92.9	0.3
O_3FeN_2	72.2	O_4FeN_1	71.5	O_MFeN	71.8	0.2
O_3Few_1	75.8	O_4Few_1	73.4	O_MFew	74.6	0.3
N_1FeN_2	76.5	...	...	NFeN	76.5	0.2
O_1FeO_2	173.8	...	...	O_LFeO_L	173.8	0.8
O_3FeO_4	148.9	...	...	O_MFeO_M	148.9	0.7

[a] In agreement with a twofold axis. [b] O_L and O_M are in rings of L and M type, respectively. [c] O_L and N in same ring. [d] O_L and N in different rings touching only at Fe. [e] O_L and O_M in rings sharing an Fe–N bond. [f] O_L and O_M in rings touching only at Fe.

Table V. Cartesian Coordinates of the Idealized (C_2-2) Coordination Group[a]

Atom	Position	X, A	Y, A	Z, A
Fe	Origin	0	0	0
w_1	On 2	0	0	2.090
O_M	General	−1.533	1.309	0.554
O_L	General	1.531	1.309	−0.104
N	General	−0.487	1.331	−1.799

[a] Twofold axis along 0, 0, Z. General positions: X, Y, Z; $\bar{X}, \bar{Y}, Z$. Fe–O_M = 2.092 A, Fe–O_L = 2.017 A, Fe–N = 2.290 A.

NbF_7^{2-} and TaF_7^{2-} ions.[15] This configuration, illustrated in Figure 2, has symmetry planes ($X = 0$ and $Y = 0$) that intersect in the twofold (Z) axis. The central atom (M) at the origin, the single ligand on the Z axis, and the two ligands at the bottom of the diagram lie in one symmetry plane ($X = 0$). The four remaining ligands form a rectangular array with the shorter pair of edges parallel to the Y axis and with the common Z coordinate significantly greater than zero.

From the data of Table V it is seen that the projected positions on the XY plane of the two O_L and the two O_M atoms delineate a nearly perfect rectangle with alternate edges nearly or exactly parallel to the respective X and Y axes; it is clear, however, that significantly different values of Z for O_L and O_M prevent the four-atom grouping from approximating closely to C_{2v} geometry. Further, the plane of the iron and the two nitrogen atoms does not coincide with the axial plane, $X = 0$, as required by C_{2v}, but corresponds rather to a counterclockwise rotation around the Z axis of 20.2°. The N–C and C–C bonds of the (necessarily) ruffled pseudo-ethylenediamine ring cross back and forth through the axial plane; the plane of the iron and the two carbon atoms of the E ring corresponds to a clockwise rotation around Z of some 5° from $X = 0$. Although the mere existence of the pattern of ring connexities (Figure 1) restricts the $[Fe(OH_2)Z]^-$ ion to C_2 symmetry, it is the cogent physical constraints attending ring formation that require the obvious dimensional departures from the pseudo-symmetry of C_{2v}.

Except for the lengths of the complexing bonds, the detailed geometry of the inner coordination group in the $[Fe(OH_2)Z]^-$ ion is remarkably similar to that of the $[Mn(OH_2)A]^{2-}$ complex.[16] The departures from C_{2v} geometry in the coordination group of $[Mn(OH_2)A]^{2-}$ correspond to torsional strains that are similar both in kind and in degree to those just described for the $[Fe(OH_2)Z]^-$ ion; thus the orientation of the plane containing the iron and two nitrogen atoms in $[Mn(OH_2)A]^{2-}$ corresponds to a counterclockwise rotation around Z of 18.5° from the axial plane, $X = 0$. The glycinate ring types in $[Mn(OH_2)A]^{2-}$, symbolized as G_e and G_o, are analogous to the respective L and M types in $[Fe(OH_2)Z]^-$. Sums of interior ring angles are: G_e, 526.8°; G_o, 518.9°; L, 529.2°; M, 518.2°; E in $[Mn(OH_2)A]^{2-}$, 518.1°; and E in $[Fe(OH_2)Z]^-$, 518.7°.

Although the patterns of complexing bond lengths are generally similar for $[Fe(OH_2)Z]^-$ and $[Fe(OH_2)A]^-$, the geometries of the inner coordination groups are rather different. The coordination polyhedron in $[Fe(OH_2)A]^-$ is realized by moderate deformation of a pentagonal bipyramid, a geometrical configuration that is sterically inferior to that (Figure 2) of NbF_7^{2-} type. Over-all compensation for this steric inferiority would seem to be fully provided by the easing of ring strains in $[Fe[OH_2)A]^-$; the glycinate ring types[5f] R and G, for which the respective sums of the interior angles are 535.1 and 524.8°, are less strongly folded and have more nearly standard bond angles than do the corresponding L and M rings in $[Fe(OH_2)Z]^-$. Strain in the R rings and those steric repulsions involving O_R atoms are both effectively minimized[5f] in the $[Fe(OH_2)A]^-$ configuration; consequently, one expects the Fe–O_R bond lengths (1.969 ± 0.003 A) to be significantly shorter than the short Fe–O_L bond lengths (2.017 ± 0.004 A) in $[Fe(OH_2)Z]^-$. The crowding, on the other hand, of a water molecule, two O_G, and two N atoms into a five-membered girdle around the iron atom[5f] presumably is the dominant factor in making the Fe–O_G (2.119 ± 0.003 A) and Fe–w_I (2.107 ± 0.003 A) bonds in the EDTA complex slightly longer than the corresponding Fe–O_M (2.092 ± 0.004 A) and Fe–w_I (2.090 ± 0.003 A) bonds in the DCTA chelate. The mean plane of the ruffled ethylenediamine ring in $[Fe(OH_2)A]^-$ nearly coincides with a plane of reference that contains the iron and two O_G atoms (and the water molecule). Relative to this reference plane, the iron and the two nitrogen atoms determine a plane that corresponds to a clockwise rotation around the twofold axis of 10.2°, whereas the iron and the two carbon atoms of the E ring determine a plane that corresponds to a counterclockwise rotation of 12°. For the same pattern of ring connexities in the EDTA and DCTA complexes—presumably, that is, for corresponding optical isomers—the ruffling or kinking of the E rings is taken in opposite senses; otherwise put, the required twisting around the twofold axis is left-handed in the one case, right-handed in the other.

The structural considerations thus far advanced make it clear that both configurations are accessible to the EDTA complex, but they further suggest that the geometry observed for the $[Fe(OH_2)A]^-$ ion is energetically somewhat better. Evidence which indicates that the $[Fe(OH_2)Al^-$ configuration is not accessible to the DCTA complex was obtained as follows. A calculation that utilized the expected positions of the hydrogen atoms in $[Fe(OH_2)Z]^-$ gave no H–H separations below 2.2 A.[17] It was then estimated from scaled models that imposition of the $[Fe(OH_2)A]^-$ configuration on $[Fe(OH_2)Z]^-$ would make two sets of H–H separations fall below 1.5 A. Hydrogen atoms attached to glycinate carbons C_7 and C_9 (Figure 1) would interfere with hydrogen atoms attached to cyclohexane carbons C_{11} and C_{14}, respectively. The mirrored ruffling of the E ring, *i.e.*, the reversed direction of twist about the twofold axis, in $[Fe(OH_2)Z]^-$ as compared with $[Fe(OH_2)A]^-$, is accompanied by a mirrored ruffling of the cyclohexane ring and other configurational adjustments that eliminate impossibly small H–H distances.

Stability constants of $10^{25.1}$ and $10^{28.6}$ are reported for respective EDTA[7] and DCTA[18] chelates as formed in aqueous solution by the reaction

$$[Fe(OH_2)_6]^{3+} + A^{4-} \text{ or } Z^{4-} \rightleftharpoons 5H_2O + [Fe(OH_2)A]^- \text{ or } [Fe(OH_2)Z]^-$$

That very large entropies of formation carry primary responsibility for the large magnitudes of the formation constants is an established and partly understood fact.[7] One sees, nonetheless, that the partial molar entropy

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

[16] The Cartesian coordinates of the coordination group in $[Mn(OH_2)A]^{2-}$ are given for an arbitrary choice of optical isomer.[5e] A reversal in sign for all X coordinates gives the optical isomer wanted for comparison with that described for the $[Fe(OH_2)Z]^-$ ion.

[17] Hydrogen atoms were placed 1.00 A from the carbon atoms to which they were attached with observance of regular tetrahedral bond angles. The calculation is described in the Ph.D. Thesis of G. H. Cohen from whom a machine language coding for the Control Data Corp. 1604 compatible with the Princeton series of crystallographic programs is available.

[18] A. E. Martell, private communication.

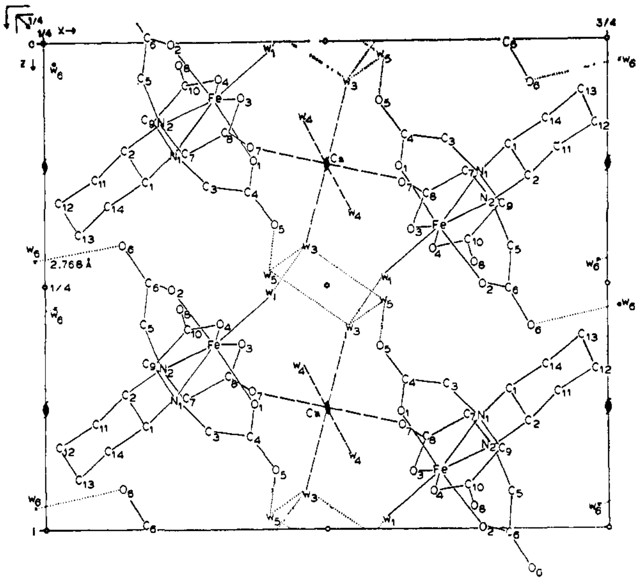

Figure 3. Diagram of the crystalline arrangement in projection parallel to the *b* (or *y*) axis. The complex anion in the lower left-hand quadrant has the coordinates (x, y, z) listed in Table I; the other three, reading clockwise, are at x, $1 - y$, $z - {}^1/_2$; $1 - x$, $1 - y$, $1 - z$; $1 - x$, y, ${}^3/_2 - z$. A water molecule of w_2 type is located above Ca^{2+} on the twofold axis at ${}^1/_2$, y, ${}^3/_4$, but below Ca^{2+} at ${}^1/_2$, y, ${}^1/_4$. Solid lines show bonds within the complex anion, dashed lines bonds to Ca^{2+}, and dotted lines the hydrogen bonds (not all of which are indicated).

of the complexing agent must decrease during complex formation, the consequence of the drastic reduction in the number of configurations accessible to this species. Further, the presence of the cyclohexane ring in the free DCTA species materially reduces the number of configurations accessible to the EDTA sub-unit therein as compared with the free EDTA species, whereas the same constraint in the complexed species is relatively unimportant in determining the change in entropy. Consequently, one expects the decrease in partial molar entropy of the complexing agent during chelation to be smaller in magnitude, therefore less unfavorable or relatively more favorable to the over-all ΔS for DCTA then for EDTA. This analysis should apply more generally to the DCTA and EDTA chelates formed with other cations as long as the paired complexes have the same coordination number, multidentate character, and chemical constitution of the inner coordination group.

Although stereochemical comparison of the $[Fe(OH_2)A]^-$ and $[Fe(OH_2)Z]^-$ configurations suggests that the former is energetically superior for EDTA and, consequently, for the EDTA sub-unit of DCTA, one does not conclude thereform that the change in partial molar enthalpy of the complexing agent attending chelation is necessarily more favorable for EDTA than for DCTA. It may be, for example, that some of the energetically most favored configurations accessible to the uncomplexed A^{4-} species are among those excluded for Z^{4-}.

The Crystalline Arrangement

A diagram of the crystal structure as projected parallel to the unique *b* axis of C_2 symmetry is displayed in Figure 3. The particularly interesting features of the arrangement are the coordination polyhedron defined by the seven ligands of the calcium ion and the rather varied utilization of six structural classes of water molecules. The quantitative data of Table VI together with Figures 2 and 3 afford a full description of the cationic coordination group; the data of Table VII along with Figure 3 serve to illuminate the role of hydrogen bonding in the crystal.

Table VI. Parameters of the Cation Coordination

Bond	No.	Length, A	σ, A
$Ca\text{-}w_2$	1	2.379	0.006
$Ca\text{-}w_3$	2	2.402	0.005
$Ca\text{-}O_7$	2	2.417	0.005
$Ca\text{-}w_4$	2	2.417	0.007
Edge[a]	**No.**	**Length, A**	**σ, A**
$w_2\text{-}w_3$	2	3.146	0.007
$w_2\text{-}O_7$	2	3.094	0.005
$w_3\text{-}O_7$	2	3.145	0.006
$w_3'\text{-}O_7$	2	3.522	0.004
$O_7\text{-}w_4$	2	2.954	0.006
$w_3\text{-}w_4'$	2	2.929	0.006
$w_4\text{-}w_4'$	1	2.794	0.007
Angle[a]	**No.**	**Value, deg**	**σ, deg**
w_2Caw_3	2	81.5	0.3
w_2CaO_7	2	80.4	0.1
O_7Caw_3	2	82.3	0.2
O_7Caw_3'	2	94.9	0.3
O_7Caw_4	2	76.0	0.1
w_3Caw_4'	2	74.9	0.3
w_4Caw_4'	1	70.6	0.3
O_7CaO_7'	1	160.7	0.4
w_3Caw_3'	1	163.0	0.8

[a] The primed water molecules refer to those generated by the operation of the twofold axis through Ca and w_2 on the unprimed water molecules of the same subscript.

Table VII. Hydrogen Bond Parameters

Bond	Length ± σ, A	Angle	Value ± σ, deg
$w_2\text{-}O_1$	2.869 ± 0.005	O_1w_2Ca	128.6 ± 0.4
		$C_4O_1w_2$	121.3 ± 0.4
		FeO_1w_2	115.6 ± 0.2
$w_3\text{-}w_5$	2.709 ± 0.008	$w_3w_5O_5$	130.8 ± 0.5
		Caw_3w_5	119.2 ± 0.5
$w_3\text{-}w_5'$[a]	2.887 ± 0.006	$w_3w_5'O_5'$	109.8 ± 0.3
		Caw_3w_5'	103.4 ± 0.4
$w_3\text{-}w_1'$[b]	2.719 ± 0.006	$w_3w_1'Fe'$	127.7 ± 0.4
		Caw_3w_1'	120.9 ± 0.4
$w_4\text{-}O_4'$[c]	2.841 ± 0.003	$w_4O_4'Fe'$	103.5 ± 0.2
		$w_4O_4'C_{10}'$	120.1 ± 0.4
		Caw_4O_4'	132.6 ± 0.3
$w_4\text{-}O_5'$[d]	2.836 ± 0.004	$w_4O_5'C_4'$	118.2 ± 0.4
		Caw_4O_5'	106.9 ± 0.3
$w_5\text{-}O_5$	2.882 ± 0.007	$w_5O_5C_4$	97.9 ± 0.4
		$w_3w_5O_5$	130.8 ± 0.5
$w_1\text{-}O_5'$[e]	2.746 ± 0.006	$w_1O_5'C_4'$	127.3 ± 0.8
		Few_1O_5	124.1 ± 0.4

[a] Primed group generated by inversion center at (${}^1/_2$, ${}^1/_2$, 1). [b] Primed group generated by *c* glide at $y = {}^1/_2$. [c] Primed group generated by translation along y one cell length. [d] Primed group generated by twofold axis and translation along y of one cell length. [e] Primed group generated by *c* glide at $y = 1$.

Each calcium ion, positioned on a twofold axis, coordinates five water molecules and two carbonyl oxygen atoms. The geometry of the CaO_7 group approximates closely to that of the ideal NbF_7^{2-} configurational type, discussed earlier and illustrated in Figure 2. The coordination group as viewed along the twofold axis is to be seen in Figure 3. The water molecule, w_2, on the twofold axis coincides in projection with the calcium ion. Two water molecules of w_3 type and two carbonyl oxygen atoms of O_7 type outline a (slightly ruffled) four-sided figure that becomes, in projection, a nearly perfect rectangle; the calcium ion lies 0.34 A below the mean plane, *i.e.*, opposite to the w_2 molecule. Two water molecules of w_4 type lie in a quasi-mirror plane of the grouping and define (Figure 2) the bottom edge of the polyhedron.

It is seen (Table VI) that the Ca–w_2 bond length, 2.379 ± 0.006 A, is apparently a little shorter than the averaged value, 2.412 ± 0.006 A, of the other six bonds. Relative edge lengths of the coordination polyhedron are consistent with approximate minimization of the destabilizing energy arising from the mutual repulsions of the closed-shell ligands. All edge lengths save one, w_4–w_4' at 2.794 ± 0.007 A (Table VI), are a good deal longer than the van der Waals diameter for an oxide oxygen atom; a Ca–O bond length of 2.41 A is in fact better suited to a coordination number of nine. A discrete sexadentate EDTA chelate of calcium ion is expected to be an aquo complex with a stereochemistry and a composition akin to those of the EDTA chelates of the rare earth ions.[6a,b]

The interatomic distances and angles listed in Table VII suggest that hydrogen bonding which involves several structural classes of carboxylate oxygen atoms and all classes of water molecules is instrumental in stabilizing the crystalline arrangement.[19] It is seen (Table VII and Figure 3) that water molecules of types w_2, w_3, and w_4 are used for direct bridging between calcium ions and complex anions and, further, that w_3 molecules couple with w_5 molecules to provide bridging by more devious routes. The ligand water molecule, w_1, in the complex anion forms two strong hydrogen bonds, one to a w_3 molecule, the other to a carbonyl oxygen atom of a neighboring anion.

The hydrogen bonding, except as noted below, is confined to thick parallel layers that center in the planes, $x = 0, \pm 1/2, \pm 1$, etc., containing the twofold axes; these layers are tied together across the planes, $x = \pm 1/4, \pm 3/4$, etc., containing the twofold screw axes by the van der Waals interactions of (principally) the cyclohexane rings with one another, and by the set of w_6–O_6 hydrogen bonds (Figure 3). Although the w_6–O_6 separation of 2.77 A corresponds to a hydrogen bond of fair strength, the structure determination shows (Table I) that half at most of the positions assigned to the w_6 water molecules are filled; more than half-occupancy would indeed put pairs of w_6 molecules related by an inversion center only 2.42 A apart. One then notes, however, that the packing relations in the neighborhood of the inversion center apparently would permit adjustment of the w_6–w_6' separation to an acceptably higher value while retaining satisfactory hydrogen bonding to O_6 atoms. Hence it seems possible that the salt crystallized from solution with a full quota of w_6 molecules, corresponding to $Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$, but that half or more of these escaped during subsequent experimental study. The diffraction data and the crystalline arrangement derived therefrom correspond to half-occupancy of w_6 positions and the formula, $Ca[Fe(OH_2)Z] \cdot 8H_2O$, for the salt. The experimentally measured density is in slightly, but not decisively, better agreement with the latter formula.

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[19] Oxygen–oxygen separations that might be construed as involving weak hydrogen bonds are absent for the range 2.89–3.19 A.