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Stereochemistry of Ethylenediaminetetraacetato Complexes.

II. The Structure of Crystalline Rb[Fe(OH$_2$)Y]·H$_2$O[1-3]

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III. The Structure of Crystalline Li[Fe(OH$_2$)Y]·2H$_2$O[1-3]

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Structure determinations for monoclinic (P2/a) crystals of RbFe(OH)$_2$Y·H$_2$O and for orthorhombic (Pbca) crystals of LiFe(OH$_2$)Y·2H$_2$O, in each case derived from the $\{hkl\}$ X-ray data recordable for $0 < (\sin\theta)/\lambda < 0.76$, yield concordant stereochemical descriptions of the aquoethylenediaminetetraacetatoferrate(III) anion, Fe(OH$_2$)Y$^-$. The sexadentate seven-coordinate aquo complex (Fig. 1), with an inner coordination group of roughly pentagonal bipyramidal shape, approximates in both crystals to the maximum symmetry allowable for the isolated anion—a single twofold axis passing through OH$_2$, Fe(III), and the mid-point of the C–C bond in the ethylenediamine ring. Stabilization is mostly attributable to the five Fe–O bonds of averaged length 2.056 Å., as against 2.325 Å. for Fe–N (Table IV); the observed disproportionation (Table IV) between the C–O bond lengths of each carboxylate group fits the pattern of strong complexing. As an overlay to the primary electrostatic stabilization, a suggested pattern of covalent bonding utilizing the 4sp^3 orbitals of Fe^{+3} to strengthen the attachment of the five oxygen atoms seems to provide the most convincing reason why the observed configuration is preferred to either the seven-coordinate alternative exemplified by Mn(OH$_2$)Y^{-2} of the accompanying paper or the eight-coordinate bisaquo Fe(OH$_2$)$_2$Y$^-$ of Mo(CN)$_8{}^{-4}$ type. The evidence for the observed Fe(OH$_2$)Y as the dominant anionic species in solution is rather convincing.

Introduction

In an earlier paper[6] we have analyzed the indirect evidence which suggests that the ethylenediaminetetraacetatoferrate(III) ion is a fully chelated *aquo*-complex, perforce a *seven*-coordinate Fe(OH$_2$)Y$^-$ (or, possibly, an *eight*-coordinate Fe(OH$_2$)$_2$Y^{-2}). A subsequent communication[7] announced proof, to be documented herein, of the existence of *seven*-coordinate Fe(OH$_2$)Y$^-$ in crystalline RbFe(OH$_2$)Y·H$_2$O. Determination of structure for RbFe(OH$_2$)Y·H$_2$O, the first study in which the recently described procedures[8,9] for three-dimensional X-ray analysis were fully employed, gave definitive stereochemical data, but suggested other stereochemical possibilities which led to the independent study of LiFe(OH$_2$)Y·2H$_2$O.

The configuration established for Fe(OH$_2$)Y$^-$ in the rubidium salt and that described for Mn(OH$_2$)Y^{-2} in the accompanying paper[10] belong to the same symmetry class—a highly desirable twofold axis is all that can be permitted—but the respective coordination groups have markedly different shapes; the Mn(OH$_2$)Y^{-2} configuration is much more like that anticipated from *a priori* considerations which emphasized electrostatic bonding and the minimization of ring strain. In Fe(OH$_2$)Y$^-$, as found in the rubidium salt, the six "claws" of the chelate occupy formally the positions corresponding to six-eighths completion of an eight-coordination group of Mo(CN)$_8{}^{-4}$ type.[11,12] On a purely electrostatic basis the coordination of two water molecules to give Fe(OH$_2$)$_2$Y$^-$ ought to be preferred energetically to a single molecule in the (actually more crowded) mean position in the observed Fe(OH$_2$)Y$^-$. We had then to consider two further possibilities: (1) that a molecule of water is lost from eight-coordinate Fe(OH$_2$)$_2$Y$^-$ in order to make possible the crystallization of the rubidium salt—the only polymorphic form obtained under a variety of conditions[13]—and (2) that a distortion from the electrostatically preferred seven-coordinate configuration (of Mn(OH$_2$)Y^{-2} type) is a condition for crystallization of RbFe(OH$_2$)Y·H$_2$O.

Of six salts containing the Fe(III) complex which were subjected to preliminary X-ray study (by Gordon S. Smith and M. D. Lind during 1958), LiFe(OH$_2$)Y·2H$_2$O provides the best crystals, with all atoms occupying eightfold positions in the space group Pbca. The apparently difficult structural problem is readily handled by three-dimensional analysis to give a quantitatively improved description of the same configura-

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[1] Supported by the National Science Foundation, the U. S. Army Research Office (Durham), and the Advanced Research Projects Agency. The study of LiFe(OH$_2$)Y·2H$_2$O, III above, received major support from the National Institutes of Health, United States Public Health Service. We thank also the Staff of the Cornell Computing Center, Mr. Richard C. Lesser, Director.

[2] The abbreviation, EDTA, and short formula, H$_4$Y, are used throughout for ethylenediaminetetraacetic acid. Thus Fe(OH$_2$)Y$^-$ represents the sexadentate seven-coordinate complex of Fig. 1.

[3] For earlier studies of EDTA complexes published elsewhere without benefit of a generic title see ref. 6, 7, 21, 25, and 28; *cf.* also ref. 10.

[4] Predoctoral Fellow of the Monsanto Chemical Company, 1960–1961; National Science Foundation Summer Fellow, 1961.

[5] Fellow of the John Simon Guggenheim Memorial Foundation, 1960.

[6] J. L. Hoard, G. S. Smith, and M. 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 for distribution.

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

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

[9] G. L. Glen, J. V. Silverton, and J. L. Hoard, *ibid.*, **2**, 250 (1963).

[10] S. N. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *ibid.*, **3**, 27 (1964).

[11] J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).

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

[13] Particularly cogent evidence that crystallization does not involve the addition of water to predominantly sexadentate *six*-coordinate FeY$^-$ is cited later.

tional type for Fe(OH_2)Y^- as that earlier established by study of the rubidium salt. This concordance has led us to look more diligently for a *rationale* indicating a preference for the observed stereochemical type; it is responsible also for the form taken by this report on the results of two independent studies.

Experimental

Crystalline salts conforming to the empirical formula MFeY·$n$$H_2O$, with $M^+ = Li^+$, Na^+, K^+, Rb^+, or NH_4^+, and n never less than 1.5, were obtained by essentially the procedure to be described for RbFe(OH_2)Y·H_2O. All salts carried a distinctively amber color which deepened into a dark brown for sufficiently large crystals; such coloration, indeed, was characteristic of all solutions containing complexed Fe(III) throughout the pH range (~1–7) with which we had occasion to deal. Crystalline RbFe(OH_2)Y·H_2O was obtained as follows. An aqueous slurry containing stoichiometric equivalents of freshly precipitated $Fe(OH)_3$ and solid H_4Y was held at 60–80° with regular stirring until a clear amber-colored solution having a pH of ~1 was obtained. Subsequent titration with the stoichiometric equivalent of aqueous Rb_2CO_3 raised the pH to 5–6. Slow evaporation at room temperature of the resulting solution gave finally the very soluble RbFe(OH_2)Y·H_2O as transparent plates with good face development. Crystals of similar habit giving identical X-ray data were grown also for the pH range 2–3 from a solution obtained by adding half the equivalent amount of Rb_2CO_3 to a solution of the complex acid of pH ~1. The behavior of our solutions was similar to that described by Schwarzenbach and Heller.[14]

Thorough X-ray examination by means of oscillation, Weissenberg, and precession photographs provided the space group and cell data for the several crystalline compounds which led us originally to select the rubidium salt as most likely to be amenable to structure determination using only zonal data. The sole plausible alternative, the potassium salt of empirical formula KFeY·2.5H_2O, provided X-ray data which were strongly suggestive of a close structural relationship, definitely short of isomorphism, with RbFe(OH_2)Y·H_2O. All of the other salts were found to crystallize either with larger unit cells or in noncentrosymmetric space groups.

The monoclinic unit cell of RbFe(OH_2)Y·H_2O has $a = 14.17 \pm 0.02$, $b = 7.73 \pm 0.01$, $c = 14.63 \pm 0.02$ Å., $\beta = 90.4 \pm 0.1°$, and contains 4RbFe(OH_2)Y·H_2O; calculated and measured densities are equal at 1.93 g./cc. The space group[15] is P2/a. The othorhombic unit cell of LiFe(OH_2)Y·2H_2O has $a = 9.68 \pm 0.01$, $b = 18.10 \pm 0.02$, $c = 17.64 \pm 0.02$ Å. and contains eight LiFe(OH_2)Y·2H_2O; calculated and measured densities are, respectively, 1.74 and 1.72 g./cc. The space group[15,16] is Pbca. The choice of space group for each crystal is supported by the regular vanishings[15] of spectra, the absence of detectable piezoelectricity, the character of the Patterson function[17] $P(uvw)$, and all subsequent developments leading to structure determination.

Three-dimensional intensity data were taken with Mo Kα radiation for the range $2\theta < 65°$ on a General Electric spectrometer assembly by procedures already described.[8] With this radiation the linear absorption coefficient of RbFe(OH_2)Y·H_2O is 4.4 mm.$^{-1}$ (>75% attributable to Rb^+) and just 1.1 mm.$^{-1}$ for LiFe(OH_2)Y·2H_2O. A roughly cubical specimen approximately 0.25 mm. on an edge was cut from a crystalline plate of RbFe(OH_2)Y·H_2O and was then rolled about on a carborundum block to round off corners and edges. Correction of the intensity data for variation of absorption with either scattering angle or specimen shape thus became unimportant and was ignored. Because crystals of RbFe(OH_2)Y·H_2O had been observed to undergo a slow surface decomposition when exposed to air (presumably from loss of the loosely held water not complexed to Fe(III)), the specimen was given a protective coating of polystyrene. A crystal specimen of perhaps 25–50% larger volume was employed in the case of LiFe(OH_2)Y·2H_2O. This specimen was not shaped to the desirable quasi-spherical form and may have been too long in one dimension to meet fully, for some orientations, the requirements of the convergent beam technique. The systematic trend in the intensities of a particular group of reflections thus implied is not apparent in our final comparisons of calculated with observed amplitudes.

Some 3022, *ca.* 52%, of the 5818 forms $\{hkl\}$ corresponding to $2\theta < 65°$ were recordable above background for the monoclinic RbFe(OH_2)Y·H_2O; the time spent in extending the measurements beyond the equivalent Cu Kα limiting sphere, $2\theta = 55°$, or even beyond $2\theta = 50°$, was largely wasted. Some 5027, *ca.* 89%, of the 5632 forms $\{hkl\}$ having $2\theta < 65°$ were recorded above background for LiFe(OH_2)Y·2H_2O. Intensity counts were reduced to $|F|^2$ data by means of the machine program for the Burroughs 220 computer described earlier.[8] Programs used for the computation of three-dimensional Patterson and Fourier syntheses and for the objective evaluation of atomic positions from Fourier syntheses were simply related to those employed in other recent studies[8–10] from this laboratory.

Two years of inconclusive attempts to determine structure for RbFe(OH_2)Y·H_2O through analysis of zonal X-ray data preceded solution of the problem by the three-dimensional procedures outlined herein. Our experience with this study, and subsequently with two others in analogous circumstances, suggests that prior zonal analysis is not only unnecessary, but, as a general rule, is best ignored during three-dimensional analysis.

Determination of Structures

The Patterson synthesis $P(uvw)$ of the three-dimensional $|F|^2$ data for RbFe(OH_2)Y·H_2O led unambiguously to the arrangement of rubidium and iron atoms in the crystal: 4Rb^+ and 4Fe(III) each were placed in general positions[15] of P2/a, *i.e.*, in $\pm(x, y, z)$, $\pm(^1/_2 + x, \bar{y}, z)$, with coordinates only slightly altered during the subsequent determination and refinement of the complete structure. Making use of the combined phase-determining properties of Rb^+ and Fe(III), the complete structure was developed in cycles of Fourier synthesis[17] by successive approximation.[18] This procedure was slowed, but not unduly complicated, by the circumstance that reflection amplitudes for $h + k$ odd were much weaker on the average than those for $h + k$ even—a feature clearly produced by having $y \sim {}^1/_4$ for Rb^+. An averaged thermal parameter of 3.25 Å.^{2} (which was none too large) was employed during the initial stage of fixing the approximate structure with qualitative certainty. Individual thermal parameters for the several structural classes of atoms then were introduced and refined simultaneously with the positional coordinates (and scale factor for the observed data) through successive cycles of difference synthesis[17] until no further changes of significance were indicated. The

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[14] G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

[15] "International Tables for X-Ray Crystallography, Vol. I. Symmetry Groups," the Kynoch Press, Birmingham, 1952.

[16] We have departed from the conventional ordering of the axes according to magnitude in order to retain the cyclic permutation of glide plane translations achieved in the description Pbca.

[17] *Cf.* H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, London, 1953.

[18] The atomic form factor used for Rb^+ 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). The form factor for Fe was that of A. J. Freeman and J. H. Wood, *ibid.*, **12**, 271 (1959). Form factors for C, N, and O were from J. Berghuis, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

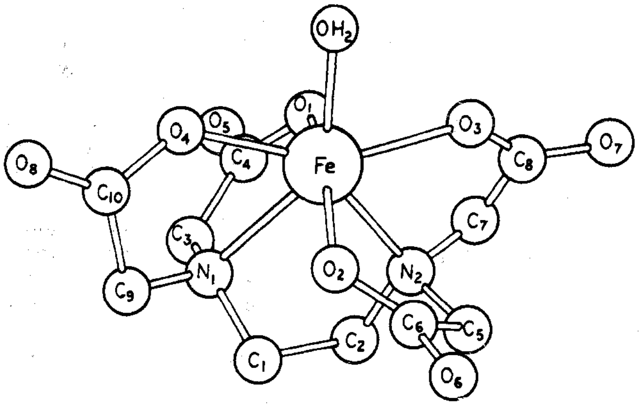

Fig. 1.—Model in perspective of the sexadentate seven-coordinate $Fe(OH_2)Y^-$ with the twofold axis vertical. OH_2, O_3, N_2, N_1, and O_4 define the five-sided and roughly planar girdle in the crudely pentagonal bipyramidal coordination group. Chelate rings containing either O_3 or O_4 are of G type, those containing O_1 or O_2 are of R type (*cf.* text).

procedures used for refinement, as subsequently generalized for the case of noncentrosymmetric structures, have been described in the published study[9] of $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$. The value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, initially 0.43 for just the contributions of the heavy atoms Rb^+ and Fe(III) to observed reflections within the range $2\theta < 65°$, was reduced to 0.126 for the final structure based upon the 3022 observed forms $\{hkl\}$; a large fraction of these latter were only weakly observable.

The atomic coordinates with associated standard deviations estimated by Cruickshank's procedure,[17] the individual thermal parameters, and the peak values of the electron densities are listed in Table I. Labeling of atoms within the complex anion is the same as that of the model represented by Fig. 1. We note that the peak electron densities are nearly identical for Fe(III) and Rb^+, a consequence of the much larger thermal motion of the latter. The thermal parameter (3.57 $Å.^2$) of Rb^+ is, indeed, substantially exceeded only by that (4.2 $Å.^2$) of one uncomplexed carboxylate oxygen, O_5, and by that (*ca.* 5.8 $Å.^2$) of the water molecules, w_2 and w_3, which are not complexed to Fe(III). The data of Table I and the character of the difference syntheses suggest a loose three-dimensional network in which fairly rigid $Fe(OH_2)Y^-$ ions undergo combined translatory and libratory vibrations; the effect of libration on an individual thermal parameter becomes more readily evident as the distance of the atom from the center of the complex increases.

Determination of structure for $LiFe(OH_2)Y \cdot 2H_2O$, with no time wasted upon zonal analysis, was achieved without difficulty. The Patterson synthesis $P(uvw)$ of three-dimensional $|F|^2$ data placed eight Fe in general positions[15] of Pbca, *i.e.*, in $\pm(x, y, z)$, $\pm(^1/_2 - x, {}^1/_2 +$ $, z)$, $\pm(x, {}^1/_2 - y, {}^1/_2 + z)$, $\pm(^1/_2 + x, y, {}^1/_2 - z)$. The phase-determining power of the eight Fe atoms was fully adequate to initiate development of the complete structure in cycles of Fourier synthesis[17] by successive approximation. Refinement of structure was carried through cycles of difference synthesis, with use of individual thermal parameters for atoms of the several structural types, to yield generally very satisfactory results. At this point (early 1963) we were enabled to carry out least squares refinements on the newly installed Control Data 1604 computer at the Cornell Computing Center, using programs kindly furnished by Dr. R. A. Jacobson's group[19] at Princeton University. Diagonal least squares refinements which minimized (I), $\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$, and (II), $\Sigma w^2(|F_o|^2 - |F_c|^2)^2/\Sigma w^4|F_o|^4$, were employed with $w^{1/2} = 1$ for $|F_o| < 4|F_{\min}|$, $w^{1/2} = 4|F_{\min}|/|F_o|$ for $|F_o| > 4|F_{\min}|$. (Both programs scale the F_c values, so the denominators in I and II are constants.)

Table I

Structural Parameters for Crystalline $RbFe(OH_2)Y \cdot H_2O$[a]

Atom type	(Coordinate ± std. dev.) × 10^4 $x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	B, $Å.^2$	$\rho_{\max}$, $e/Å.^3$
O_1	1360 ± 4	64 ± 8	3136 ± 4	2.6	15.5
O_2	658 ± 5	3817 ± 8	1440 ± 5	2.6	15.4
O_3	2452 ± 5	2445 ± 9	1884 ± 4	2.6	14.8
O_4	−69 ± 5	596 ± 9	1450 ± 5	2.6	15.5
w_1	1601 ± 4	−69 ± 8	1174 ± 4	2.6	16.9
N_1	−247 ± 6	1962 ± 10	3068 ± 6	2.5	12.6
N_2	1447 ± 4	3863 ± 7	3163 ± 4	2.5	15.1
Fe	1065 ± 1	1696 ± 1	2136 ± 1	1.94	86.7
C_1	−163 ± 7	3490 ± 10	3684 ± 6	2.8	10.5
C_2	845 ± 6	3754 ± 13	3979 ± 6	2.8	10.4
C_3	−245 ± 7	296 ± 11	3571 ± 6	2.8	10.4
C_4	698 ± 8	−428 ± 13	3713 ± 9	2.8	9.5
C_5	1318 ± 7	5463 ± 9	2652 ± 5	2.8	10.4
C_6	935 ± 5	5347 ± 10	1681 ± 5	2.8	12.9
C_7	2467 ± 6	3561 ± 11	3380 ± 6	2.8	10.1
C_8	2974 ± 7	3113 ± 9	2517 ± 4	2.8	10.4
C_9	−1057 ± 6	2124 ± 12	2464 ± 10	2.8	12.1
C_{10}	−920 ± 7	1125 ± 19	1586 ± 7	2.8	10.8
O_5	877 ± 7	−1500 ± 13	4290 ± 7	4.2	12.7
O_6	901 ± 5	6592 ± 10	1177 ± 5	3.6	14.0
O_7	3840 ± 5	3298 ± 10	2440 ± 5	3.6	13.2
O_8	−1571 ± 5	881 ± 9	1048 ± 6	3.6	14.2
Rb	951 ± 1	2513 ± 1	−433 ± 1	3.57	87.2
w_2	$^1/_4$	5320 ± 20	0	5.8	7.1
w_3	$^1/_4$	3155 ± 20	$^1/_2$	5.8	8.4

[a] Complete amplitude data are given in the thesis of M. D. Lind, "The Crystal Structure of Rubidium Ethylenediaminetetraacetatoaquoferrate(III) Monohydrate," Cornell University, 1962, available either on loan from the Cornell University Library or from University Microfilms, Inc., 113 North First St., Ann Arbor, Mich.

The range of variation in the results given by difference synthesis and the two least squares refinements was gratifyingly small, notably so for the stereochemical parameters of the complex anion. We report herein the results of the least squares refinement (I) inasmuch as these come nearest to providing a median description of the crystalline arrangement and carry generally a very slightly superior air of internal consistency. One may say that the chemically significant results are independent of the choice of refinement procedure. The value of the conventional R is 0.095 for the 5027 observed $\{hkl\}$ having $2\theta < 65°$.

The atomic coordinates with associated standard deviations (estimated by *doubling* the values claimed by

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(19) We are especially indebted to Mr. Fredrik A. Muller in this connection.

TABLE II

STRUCTURAL PARAMETERS FOR CRYSTALLINE $LiFe(OH_2)Y \cdot 2H_2O$[a]

Atom type	(Coordinate ± std. dev.) × 10^4			B, Å.²
	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	
O_1	2034 ± 3	1151 ± 2	2287 ± 2	2.57
O_2	1986 ± 3	1781 ± 1	171 ± 2	2.55
O_3	993 ± 3	2502 ± 2	1628 ± 2	1.93
O_4	1206 ± 3	398 ± 2	906 ± 2	2.52
w_1	−409 ± 3	1412 ± 2	1172 ± 2	1.88
N_1	3756 ± 3	765 ± 2	1112 ± 2	2.01
N_2	3594 ± 3	2279 ± 2	1336 ± 2	1.79
C_1	4977 ± 4	1224 ± 2	961 ± 2	1.79
C_2	4903 ± 4	1884 ± 2	1472 ± 2	1.93
C_3	3856 ± 5	365 ± 2	1843 ± 3	2.65
C_4	2724 ± 4	562 ± 2	2408 ± 2	2.16
C_5	3610 ± 4	2671 ± 2	609 ± 2	2.37
C_6	2821 ± 4	2290 ± 2	−22 ± 2	2.17
C_7	3298 ± 4	2781 ± 2	1958 ± 2	2.03
C_8	1770 ± 4	2961 ± 2	1960 ± 2	2.04
C_9	3493 ± 5	249 ± 2	483 ± 3	2.40
C_{10}	2004 ± 5	−8 ± 2	527 ± 3	2.82
O_5	2573 ± 5	169 ± 2	2957 ± 2	4.84
O_6	2994 ± 4	2484 ± 2	−683 ± 2	3.51
O_7	1351 ± 4	3528 ± 2	2287 ± 2	2.70
O_8	1683 ± 5	−587 ± 2	215 ± 4	4.55
Li	2922 ± 8	−854 ± 4	3140 ± 4	2.21
w_2	1156 ± 4	−1225 ± 2	3522 ± 2	2.77
w_3	4153 ± 4	−934 ± 2	3982 ± 2	3.13
Fe:	$10^5x = 17570 \pm 3$;	$10^5y = 14791 \pm 2$;	$10^5z = 12529 \pm 2$;	$B = 1.59$ Å.²

[a] Complete amplitude data including the coefficients of the anisotropic thermal parameters have been deposited as Document No. 7709, 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 $5.00 for photoprints or $2.25 for 35-mm. film in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

the least squares program) and isotropic thermal parameters calculated from the anisotropic coefficients of the least squares refinement are listed for $LiFe(OH_2)Y \cdot 2H_2O$ in Table II. The labeling of atoms within the complex anion agrees with that of Fig. 1. The generally much lower level of thermal motion in $LiFe(OH_2)Y \cdot 2H_2O$, in contrast with $RbFe(OH_2)Y \cdot H_2O$, is made evident by comparing the B values of Tables I and II.

Stereochemistry of the Complex Anion

We present first stereochemical parameters for the sexadentate seven-coordinate $Fe(OH_2)Y^-$ as derived from both crystalline structures. Inspection of the somewhat idealized model (Fig. 1) shows that the inner coordination group is roughly of pentagonal bipyramidal shape,[20] although the complex cannot in fact have greater symmetry than C_2-2. In agreement with earlier observations[10,21] on EDTA chelates, $Fe(OH_2)Y^-$ occurs in a position of no required symmetry in either crystal, but retains, nonetheless, a highly useful approximation to C_2. This axis passes through the central atom and the mid-point of the C–C bond (C_1–C_2 of Fig. 1) in the ethylenediamine ring. The stereochemistry of the complex is more or less modified by its asymmetric environment according to the following pattern.

Certain bond lengths, notably those of C–C and C–N bonds, practically ignore symmetry considerations by conforming rather closely to "standard" chemical types. C–O bond lengths within a carboxylate group differ accordingly as the oxygen atoms, O_c and O_u, respectively, are or are not complexed to the central atom; the difference between the C–O_c and C–O_u bond lengths, a maximum in the free complex, decreases as O_u atoms interact more strongly with environmental species (*cf.* the accompanying paper). The ring architecture tends to conform in its most essential aspects to the requirements of C_2. The inner coordination group, including the complexing bonds, is the principal repository for asymmetric packing strains and thus displays the most obvious departure from twofold symmetry. We shall follow this outline in discussing the stereochemistry of $Fe(OH_2)Y^-$.

Table III lists the averaged bond length together with the mean, maximum, and standard deviations from the mean, for each of the several bond types as derived from the data for (A) $RbFe(OH_2)Y \cdot H_2O$ and (B) $LiFe(OH_2)Y \cdot 2H_2O$. The classification of bond type is chemical for bonds between light atoms and is in accordance with a quasi-twofold axis for bonds involving Fe(III); the number of individual values contributing to the average is indicated parenthetically for each bond type. The short Fe–O_R bonds involve O_1 and O_2 of Fig. 1, the longer Fe–O_G bonds are to O_3 and O_4; the subscripts R and G refer to ring type as defined later.

The data (A) from the rubidium salt provide no in-

TABLE III

AVERAGED BOND LENGTHS WITHIN THE COMPLEX ANION

Bond type	Averaged length, Å.	Deviations, Å. Mean	Deviations, Å. Max.	Deviations, Å. Std.[a]
	(A) From $RbFe(OH_2)Y \cdot H_2O$			
C_1–C_2(1)	1.503	...	...	0.022
C–C(4)	1.497	0.018	0.036	.025
C–N(6)	1.475	.015	.027	.022
C–O_c(4)	1.299	.012	.024	.021
C–O_u(4)	1.222	.011	.020	.022
Fe–O_R(2)	1.993	.019	.019	.011
Fe–O_G(2)	2.078	.007	.007	.012
Fe–w_1(1)	2.106	...	...	.011
Fe–N(2)	2.317	.005	.005	.012
	(B) From $LiFe(OH_2)Y \cdot 2H_2O$			
C_1–C_2(1)	1.502	...	...	0.006
C–C(4)	1.519	0.003	0.006	.006
C–N(6)	1.472	.007	.017	.005
C–O_c(4)	1.272	.007	.010	.005
C–O_u(4)	1.230	.010	.019	.007
Fe–O_R(2)	1.969	.030	.030	.003
Fe–O_G(2)	2.119	.009	.009	.003
Fe–w_1(1)	2.107	...	...	.003
Fe–N(2)	2.325	.021	.021	.003

[a] Root-mean-square of the individual standard deviations.

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(20) Were the hard sphere model an adequate approximation for setting the minimum steric requirements, the pentagonal bipyramid could receive no consideration for seven-coordination. By use of a more realistic model, *e.g.*, with a Born type repulsive energy ($U \sim R_{ij}^{-n}$) summed over all ligand pairings (R_{ij}) and an n of 7–9, the bipyramidal configuration gains steric *a priori* probability fairly comparable with that of two other configurations. Ring constraints in EDTA complexes restrict the competition to the configurational types exemplified by $Mn(OH_2)Y^{-2}$ and $Fe(OH_2)Y^-$.

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

TABLE IV

SOME INDIVIDUAL BOND LENGTHS IN $Fe(OH_2)Y^-$ FROM $LiFe(OH_2)Y \cdot 2H_2O$

Bond	Length ± σ, Å.	Bond	Length ± σ, Å.	Bond	Length ± σ, Å.
$Fe–O_1$	1.938 ± 0.003	$O_1–C_4$	1.281 ± 0.005	$C_4–O_5$	1.213 ± 0.005
$Fe–O_2$	1.999 ± 0.002	$O_2–C_6$	1.276 ± 0.005	$C_6–O_6$	1.231 ± 0.005
$Fe–O_3$	2.110 ± 0.003	$O_3–C_8$	1.267 ± 0.005	$C_8–O_7$	1.249 ± 0.005
$Fe–O_4$	2.128 ± 0.004	$O_4–C_{10}$	1.262 ± 0.006	$C_{10}–O_8$	1.228 ± 0.008
$Fe–w_1$	2.107 ± 0.003	$Fe–N_1$	2.346 ± 0.003	$Fe–N_2$	2.304 ± 0.003

stance in which the maximum deviation from the averaged bond length is sufficiently large, relative to the standard deviation, to attain statistical significance. The data (B) from the lithium salt, on the other hand, require individual consideration of certain bond lengths. Application of statistical criteria to the comparison of corresponding averages from (A) and (B) tells us that the objective evidence for significant differences between the two averaged configurations has little substance, at least in respect to bond lengths.

From the $LiFe(OH_2)Y \cdot 2H_2O$ data we obtain C–N = 1.472 ± 0.005 Å., C–C = 1.519 ± 0.006 Å. in glycinate rings, 1.502 ± 0.006 Å. in the ethylenediamine ring, and from the $Mn_3(HY)_2 \cdot 10H_2O$ data[10] the corresponding values 1.471 ± 0.007 Å., 1.519 ± 0.008 Å., and 1.518 ± 0.008 Å. The 1.47 Å. is standard for a C–N single bond and the 1.52 Å. is a good value for a C–C bond in which one atom is trigonally hybridized. We are not aware of any convincing theoretical basis for supposing that the C–C bond in the ethylenediamine ring should be significantly less than 1.54 Å.

Table IV lists individual bond lengths, excepting those of C–C and C–N, for $Fe(OH_2)Y^-$ as derived from the $LiFe(OH)_2Y \cdot 2H_2O$ structure. The data are arranged to display an apparent correlation of C–O with Fe–O bond lengths.

Inasmuch as each row (except the last) of Table III deals with the Fe–O, O_c–C, and C–O_u bonds of a particular carboxylate, the order of listing Fe–O bonds in the first column determines the orders for O_c–C and C–O_u bonds in their respective columns. It is seen that as the Fe–O bond length increases (bond strength decreasing), the O_c–C bond length decreases (double bond character increasing) and, excepting the C_{10}–O_8 bond,[22] the C–O_u bond length increases (double bond character decreasing). The existence of a (nearly) consistent over-all pattern, although carrying little statistical significance, is reassuring.

The Fe–O bonds, which are classified into three groups (Table III) by a quasi-twofold axis, divide practically into just two. The group of three longer bonds, averaging 2.115 Å. in the more accurate $LiFe(OH_2)Y \cdot 2H_2O$ data, are to O_3, O_4, and the oxygen of w_1; these atoms, along with the two nitrogens, are squeezed into a staggered five-sided girdle (Fig. 1) around Fe(III). The O_1 and O_2 atoms are bonded to iron at 1.97 Å. with minimum interference from other ligands. We are dealing with high spin (sextet) Fe^{+3}, the averaged length of the five Fe–O bonds is 2.056 Å., and the sum of the ionic radii[23] (for octahedral coordination) is 2.04 Å. But whereas the covalent radii of oxygen and nitrogen differ[23–25] by no more than 0.04 Å., the Fe–N bonds (2.325 Å.) in $Fe(OH_2)Y^-$ are 0.20 Å. longer than the longest Fe–O bond, and are 0.27 Å. longer than the average of all Fe–O bonds. The significance of these data and the probable character of the bonding will be discussed later in connection with the detailed geometry of the coordination group, the merits of alternative configurations, and the probable species in aqueous solution.

The numerous bond angle data for the complex lend themselves to simple presentation in terms of the quasi-symmetry of C_2. First we note that all carboxylate groups are essentially planar; formal calculation of the sum of the bond angles subtended at the central carbon atom gives invariably, in both sets of data, 360° within 0.1°. The quasi-twofold axis divides the glycinate rings into two groups: the rings $FeO_1C_4C_3N_1$ and $FeO_2C_6C_5N_2$ will be designated by the class symbol R, the rings $FeO_3C_8C_7N_2$ and $FeO_4C_{10}C_9N_1$ by G, and the ethylenediamine ring by E, in close analogy with a symbolism used earlier[21,26] in discussing the octahedral CoY^-. The departure from 540° in the sum of the interior angles is a gross measure of folding and kinking in a five-membered ring. The mean value, with mean deviation, of this sum for each ring type is as follows: (A) $RbFe(OH_2)Y \cdot H_2O$: 534.5 ± 3.1° for R, 524.3 ± 2.3° for G, 516.6° for E; (B) $LiFe(OH_2)Y \cdot 2H_2O$: 535.1 ± 1.6° for R, 524.8 ± 0.6° for G, 514.1° for E. The character of the approximation to C_2 symmetry of $Fe(OH_2)Y^-$ as it occurs in both salts is exhibited in a more detailed fashion by the data of Table V; averaged values of the ring bond angles, each with the maximum (or mean) and standard deviation from the mean, are listed therein for each ring type. Bond angles in carboxylate which involve the uncomplexed atoms O_u are included, although these angles are fairly sensitive to the asymmetric environment; the restrictions, roughly, are that the carboxylate group must remain virtually planar with individual bond angles of 120 ± *ca.* 5°. The last three rows of Table V refer to branching angles at nitrogen between rings.

The descriptions provided by the two sets of data are

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[22] The large thermal motions (Table II) of O_5 and especially O_8 and the peripheral location of these atoms on the complex probably means that both C_4–O_5 and C_{10}–O_8 are underestimated—perhaps by as much as 0.02 Å.

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

[24] In CoY^- (ref. 21), Co(III)–O = 1.88, 1.90 Å., Co(III)–N = 1.92 Å.

[25] In $Ni(OH_2)YH_2$, Ni–O = 2.05 Å., Ni–N = 2.08 Å. in the "square" girdle around nickel. G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959).

[26] The complexing bonds ($Fe–O_3$, $Fe–O_4$) in the G-ring lie nearly in the plane defined by the central atom and the two nitrogens. The complexing bonds ($Fe–O_1$, $Fe–O_2$) in an R-ring effect ring closure roughly along the normal to the plane MNN.

TABLE V

RING BOND ANGLES[a] IN THE COMPLEX ANION

		$RbFe(OH_2)Y\cdot H_2O$			$LiFe(OH_2)Y\cdot 2H_2O$		
		Mean value,	Deviations, deg.		Mean value,	Deviations, deg.	
Ring type	Bond angle	deg.	Max.	Std.	deg.	Max.	Std.
E	FeNC	111.0	0.5	0.6	111.5	0.1	0.2
	NCC	109.9	0.4	0.9	108.7	0.8	0.3
	NFeN	74.8	...	0.3	73.7	...	0.1
R	FeOC	121.1	0.4	0.8	120.4	1.2	0.2
	OCC	115.6	1.2	1.1	117.4	0.2	0.3
	CCN	116.0	2.3	1.1	114.2	0.3	0.3
	CNFe	103.6	1.1	0.5	104.3	0.7	0.2
	NFeO	78.2	0.5	0.3	78.9	0.4	0.1
	CCO_u	122.8	0.5	1.5	118.9	0.8	0.3
	OCO_u	121.6	1.7	1.4	123.7	0.6	0.4
G	FeOC	121.3	0.1	0.8	121.9	0.8	0.3
	OCC	114.9	0.1	1.2	115.6	0.2	0.4
	CCN	110.3	1.2	1.4	109.0	0.3	0.3
	CNFe	105.4	1.1	0.5	106.9	0.1	0.2
	NFeO	72.5	0.1	0.3	71.3	0.9	0.1
	CCO_u	121.9	0.2	1.4	119.3	0.5	0.4
	OCO_u	123.2	0.4	1.4	125.1	0.8	0.4
E–R	CNC	113.0	0.2	1.0	112.1	0.4	0.3
E–G	CNC	111.8	0.7	1.0	111.0	0.4	0.3
R–G	CNC	111.6	0.5	1.0	110.8	0.2	0.3

[a] Averaged assuming a quasi-twofold axis.

notably similar, with that from the lithium salt both more accurate and more nearly in conformity with a twofold axis. FeO_1C_4 (119.1°) and FeO_2C_6 (121.6°) bond angles of the R-rings in the lithium salt probably differ significantly as a means of relieving asymmetric strain, but the difference of 0.06 Å. between the $Fe–O_1$ and $Fe–O_2$ bond lengths is of more consequence in this connection. Although the difference of 7° in the NFeO bond angles, as between R- and G-rings, is superficially striking, it probably has little energetic significance in a complex with sextet Fe^{+3} as the central ion and the nitrogen atoms holding aloof. Variations from the standard tetrahedral value in the CNFe angles are surely unimportant. The (114.2°) angle at methylene carbon in the R-rings and the (115.6°) angle at carboxylate carbon in the G-rings probably represent the most serious angular strains.

The distances and angles not previously cited which are descriptive of the inner coordination group of $Fe(OH_2)Y^-$ as derived (A) from $RbFe(OH_2)Y\cdot H_2O$ and (B) from $LiFe(OH_2)Y\cdot 2H_2O$ are listed in Table VI. Data related by the quasi-twofold axis are given in the same row with the averaged value and the (root-mean-square) standard deviation at the right. On the basis of twofold symmetry there are two classes each of O_R–N and O_R–O_G edges of the coordination polyhedron: $(O_R–N)_R$ signifies those which lie within R-rings, whereas the others represent just packing contacts.

The data of Table VI show that deviations from twofold symmetry are occasionally substantial, especially in (A), and that the qualitative patterns of distortion are somewhat different as between (A) and (B). The averaged parameters from (A) and (B) provide, nevertheless, consistent descriptions of the coordination group in $Fe(OH_2)Y^-$. Two of the eight edge types correspond to very tight packing, whereas four others are notably loose; thus the complex lends itself to considerable distortion under moderate asymmetric stressing, most clearly apparent in the ease with which the water molecule is pulled (or pushed) out of the plane defined by Fe(III) and the two O_G atoms.

The quantitative description in Cartesian coordinates of the coordination group in an $Fe(OH_2)Y^-$ of C_2-2 symmetry, as presented in Table VII, is based upon the data from the lithium salt. This description reproduces exactly the averaged bond lengths from Table III while giving with high accuracy the averaged edge lengths and angles of (B) in Table VI. The twofold axis is taken coincident with Z, Fe(III) is at the origin, and N_1 and N_2 are in the XZ plane. O_G atoms are just 0.36 Å. from the XZ plane, O_R atoms are 0.30 Å. from YZ, and the angle between the vertical planes which intersect in the twofold axis and pass, respectively, through O_G and O_R is 91.1° when O_G and O_R are in rings branching from the same nitrogen atom (Fig. 1).

That two salts crystallizing in such different structural types as do $LiFe(OH_2)Y\cdot 2H_2O$ and $RbFe(OH_2)Y\cdot H_2O$ provide a common description of the complex anion suggests that this stereochemical species takes precedence, both in crystals and in solution, over any of the following alternatives: (1) the "standard" sexadentate octahedral FeY^-, (2) the sexadentate seven-coordinate configuration of $Mn(OH_2)Y^{-2}$ type, and (3) the sexadentate, eight-coordinate, bisaquo complex, $Fe(OH_2)_2Y^-$, of $Mo(CN)_8^{-4}$ configurational type. We cite first evidence against the standard octahedral configuration (1) in order to narrow the field for the more tenuous discussion of (2) and (3).

Were octahedral FeY^- a fairly plentiful species in solution, it should crystallize with either Rb^+ or NH_4^+

Table VI

Parameters of the Inner Coordination Group in $Fe(OH_2)Y^-$

Observed data				Averaged datum		
Edge	Length, Å.	Edge	Length, Å.	Edge	Length, Å.	σ, Å.
(A) From $RbFe(OH_2)Y\cdot H_2O$						
O_1-N_1	2.709	O_2-N_2	2.750	$(O_R-N)_R$	2.730	0.018
O_1-N_2	2.939	O_2-N_1	3.068	$(O_R-N)_P$	3.004	0.017
O_1-O_4	3.206	O_2-O_3	2.826	$(O_R-O_G)_1$	3.016	0.017
O_1-O_3	3.030	O_2-O_4	2.694	$(O_R-O_G)_2$	2.862	0.016
O_1-w_1	2.896	O_2-w_1	3.312	O_R-w	3.054	0.016
O_3-N_2	2.602	O_4-N_1	2.606	O_G-N	2.604	0.017
O_3-w_1	2.509	O_4-w_1	2.459	O_G-w	2.484	0.016
N_1-N_2	2.816	...	...	N–N	2.816	0.017
(B) From $LiFe(OH_2)Y\cdot 2H_2O$						
O_1-N_1	2.753	O_2-N_2	2.734	$(O_R-N)_R$	2.744	0.004
O_1-N_2	3.052	O_2-N_1	3.019	$(O_R-N)_P$	3.036	0.004
O_1-O_4	2.908	O_2-O_3	3.043	$(O_R-O_G)_1$	2.976	0.005
O_1-O_3	2.900	O_2-O_4	2.930	$(O_R-O_G)_2$	2.915	0.004
O_1-w_1	3.113	O_2-w_1	2.992	O_R-w	3.053	0.005
O_3-N_2	2.604	O_4-N_1	2.585	O_G-N	2.595	0.004
O_3-w_1	2.536	O_4-w_1	2.463	O_G-w	2.500	0.004
N_1-N_2	2.788	...	...	N–N	2.788	0.004
Angle	Value, deg.	Angle	Value, deg.	Angle	Value, deg.	σ, deg.
(A) From $RbFe(OH_2)Y\cdot H_2O$						
O_1FeN_1	77.7	O_2FeN_2	78.6	$(O_RFeN)_R$	78.2	0.3
O_1FeN_2	86.2	O_2FeN_1	89.8	$(O_RFeN)_P$	88.0	0.3
O_1FeO_4	104.8	O_2FeO_3	87.2	$(O_RFeO_G)_1$	96.0	0.4
O_1FeO_3	96.5	O_2FeO_4	82.6	$(O_RFeO_G)_2$	89.6	0.3
O_1Few_1	90.4	O_2Few_1	107.1	O_RFew	98.8	0.4
O_3FeN_2	72.4	O_4FeN_1	72.5	O_GFeN	72.5	0.3
O_3Few_1	73.5	O_4Few_1	72.1	O_GFew	72.8	0.3
N_1FeN_2	74.8	...	...	NFeN	74.8	0.3
O_1FeO_2	162.6	...	...	O_RFeO_R	162.6	1.8
O_3FeO_4	139.2	...	...	O_GFeO_G	139.2	1.6
(B) From $LiFe(OH_2)Y\cdot 2H_2O$						
O_1FeN_1	79.3	O_2FeN_2	78.5	$(O_RFeN)_R$	78.9	0.1
O_1FeN_2	91.6	O_2FeN_1	87.7	$(O_RFeN)_P$	89.7	0.1
O_1FeO_4	91.2	O_2FeO_3	95.5	$(O_RFeO_G)_1$	93.4	0.1
O_1FeO_3	91.4	O_2FeO_4	90.4	$(O_RFeO_G)_2$	90.9	0.1
O_1Few_1	100.6	O_2Few_1	93.5	O_RFew	97.1	0.2
O_3FeN_2	72.2	O_4FeN_1	70.4	O_GFeN	71.3	0.1
O_3Few_1	73.9	O_4Few_1	71.1	O_GFew	72.5	0.1
N_1FeN_2	73.7	...	...	NFeN	73.7	0.1
O_1FeO_2	165.6	...	...	O_RFeO_R	165.6	0.3
O_3FeO_4	144.8	...	...	O_GFeO_G	144.8	0.3

Table VII

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

Atom	Position	X, Å.	Y, Å.	Z, Å.
Fe	Origin	0	0	0
w	On 2	0	0	2.107
N	General	1.395	0	−1.860
O_R	General	0.303	−1.930	−0.250
O_G	General	1.988	0.358	0.640

[a] Twofold axis along 00Z. General positions: XYZ, $\bar{X}\bar{Y}Z$. $Fe-O_R$ = 1.969, $Fe-O_G$ = 2.119, Fe–w = 2.107, Fe–N = 2.325 Å.

in the structural type[21] of proven merit which characterizes the isomorphous series[6] $AMY\cdot 2H_2O$, with $A^+ = Rb^+$ or NH_4^+, M(III) = Al, Cr, or Co. One doubts that octahedral FeY^- coordinates a water molecule to further crystallization of the decidedly inferior packing arrangement (*vide infra*) of $RbFe(OH_2)Y\cdot H_2O$, but this latter is the product obtained over wide ranges of pH and cationic concentration. The ammonium salt crystallizes in an undetermined arrangement of greater complication, presumably stabilized relative to the $RbFe(OH_2)Y\cdot H_2O$ structural type through utilization of NH_4^+ for hydrogen bonding. (The $AMY\cdot 2H_2O$ arrangement allows hydrogen bonding[21] by NH_4^+ *in situ*.)

In solution at low pH one must expect, at equilibrium, a mixture of sexadentate anions and quinquedentate neutral species. The crystalline acid[27,28] generally obtained is a bright yellow phase, containing, as proved by X-ray analysis,[28] molecules of the quinquedentate octahedral $Fe(OH_2)YH$ with a free $\cdot CH_2COOH$ arm.

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[27] J. L. Lambert, C. E. Godsey, and L. M. Seitz, *Inorg. Chem.*, **2**, 127 (1963).

[28] J. L. Hoard, C. H. L. Kennard, and G. M. Smith, *ibid.*, **2**, 1316 (1963).

It has been pointed out,[28] however, that the excessively large solubility of this phase in conjunction with the solution behavior suggests that such octahedral $Fe(OH_2)YH$ is a less important species in solution than a quinquedentate, seven-coordinate, bisaquo $Fe(OH_2)_2YH$ with a free $\cdot CH_2COOH$ arm. The averaged bond data obtained for the octahedral $Fe(OH_2)YH$ are Fe–O = 2.00, Fe–N = 2.22 Å., each smaller than the corresponding averaged value in $Fe(OH_2)Y^-$, but retaining a large difference between Fe–N and Fe–O distances.[29] Given rather inconsequential contributions from nitrogen in either case, the over-all energetic advantage of adding a fifth tightly held oxygen atom would seem easily to outweigh the increased ligand repulsions (limited to four contacts). Available log K values of $[MY^-]/[M^{+3}][Y^-]$ for pertinent choices of M(III) are: Fe(III),[14] 25.1; Al(III),[30] 16.1; Ga(III),[30] 20.3. Inasmuch as the Ga–O and Ga–N bond lengths[28] in $Ga(OH_2)YH$, 1.948 and 2.123 Å., respectively, are substantially shorter than the corresponding values for $Fe(OH_2)YH$, sexadentate octahedral GaY^-, analogous to AlY^-, appears to be the most probable anionic species in solution. The "anomalously" high stability constant for the anionic Fe(III) complex is expected for

$$Fe(OH_2)_6^{+3} + Y^- = Fe(OH_2)Y^- + 5H_2O$$

allowing retention in the anion of one water molecule of the hexaaquo complex.

We consider the case for a sexadentate seven-coordinate $Fe(OH_2)Y^-$ as the dominant anionic species in solution to be pretty well established. It is more difficult to see why the observed $Fe(OH_2)Y^-$ is preferred to the alternative $Mn(OH_2)Y^{-2}$ configuration and to an eight-coordinate $Fe(OH_2)_2Y^-$ of $Mo(CN)_8^{-4}$ type.

In the Mn(II) complex[10] quasi-equivalence is preserved in the five Mn–O bond lengths at the very large value 2.235 Å., and the still longer Mn–N bonds (2.377 Å.) remain relatively consequential; the observed configuration is the obvious choice for an electrostatic complex, and it occurs as a somewhat formal geometrical entity in a crystalline arrangement describable throughout in electrostatic terms. The $Fe(OH_2)Y^-$ ion carries by contrast the air of a stable discrete complex having inherent peculiarities. Stabilization is largely attributable to the five Fe–O bonds, two of which are very short, but averaging over-all to the rather tight value of 2.056 Å.; further, the observed disproportionation of the C–O bond lengths within each carboxylate group fits the pattern of strong complexing. Computation suggests (but hardly proves) that shrinkage of the $Mn(OH_2)Y^{-2}$ configurational type to accommodate M–O bonds as short as 2.06 Å. might give more ring strain than in the observed $Fe(OH_2)Y^-$ ion. Were this factor decisive, the bond parameters for $Fe(OH_2)Y^-$ would still be compatible with electrostatic bonding suitably modified by ligand repulsions. One looks, nevertheless, for a possible overlay of covalent bonding which might contribute to the stability and the accompanying peculiarities of the observed configuration.

Inasmuch as the half-filled 3d-subshell of sextet Fe^{+3} must remain intact, and we exclude from consideration the high-lying 4d-orbitals,[31] it remains to see what might be done with the four orbitals, $4sp^3$; all electrons for bonding to Fe^{+3} are to be supplied by the ligands. Rotation of the complex, as described in Table VII, by about 9° around Z brings O_G and O_R atoms nearly into the XZ and YZ planes, respectively. The use of sp_y digonal hybrids on Fe^{+3} for bonding the pair of O_R atoms would help to account for the very short (1.97 Å.) Fe–O_R bonds; the departure from linearity of 15° in the O_R–Fe–O_R bond system probably is not serious. Assignment of the $4p_z$-orbital of Fe^{+3} for attachment of the water molecule at 2.107 Å. is equally straightforward. We then suppose that the $4p_x$-orbital of Fe^{+3} is used along with two 2p-orbitals of O_G atoms in a three-center four-electron bonding system analogous to that described by Rundle[32] and Wiebenga, *et al.*[33] Of the three delocalized orbitals thus obtained, the bonding and the nonbonding orbitals are filled, and the antibonding orbital is unoccupied; the nonbonding orbital, however, places its electrons back onto the ligands whence they came. Bonding of this type is somewhat compromised in the present instance by the departure from linearity of 35° in the O_G–Fe–O_G angle. That the Fe–O_G bond length (2.12 Å.) is not significantly longer than that of Fe–OH_2 is ascribable to the dominant ionic contribution from the charged O_G atom which the electrostatic interaction of Fe^{+3} with OH_2 cannot match.

The preceding bonding scheme utilizes all four of the stable orbitals on Fe^{+3} in a pattern which correlates reasonably well with the observed peculiarities of the coordination group. We have seen no alternative scheme for the $Mn(OH_2)Y^{-2}$ configuration nor for an FeO_6 grouping in an eight-coordinate $Fe(OH_2)Y^-$, which could make as efficient, or as nearly complete, use of the $4sp^3$ orbitals on Fe^{+3}. It is primarily on this point that we see a basis for preference of the observed seven-coordinate $Fe(OH_2)Y^-$ over an eight-coordinate $Fe(OH_2)_2Y^-$. Formation of the latter surely would require the short Fe–O_G bonds to be increased, probably to about 2.10 Å., but the additional water molecule would then be coordinated with little increase in ligand repulsive energy.

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(29) It is evident that (ammonia) nitrogen contributes substantially less to ligand field splitting in sextet Fe^{+3} (or Mn^{+2}) than does water, carboxylate oxygen, or (quite certainly) fluoride. The ordering of the ligands thus derived is very different from that of the usual spectrochemical series, yet it is the sextet Fe^{+3} complexes, as representative of a class displaying no "crystal field stabilization" in octahedral or tetrahedral fields, which afford a reasonable prospect of physical conformity with the semantics of pure crystal field theory.

(30) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

(31) For a tetragonal pyramidal configuration of five bonds, to which the FeO_6 cap roughly conforms, a minimum of two d-orbitals are required by symmetry for the construction of five σ-bonds. *Cf.* G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(32) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

(33) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961).

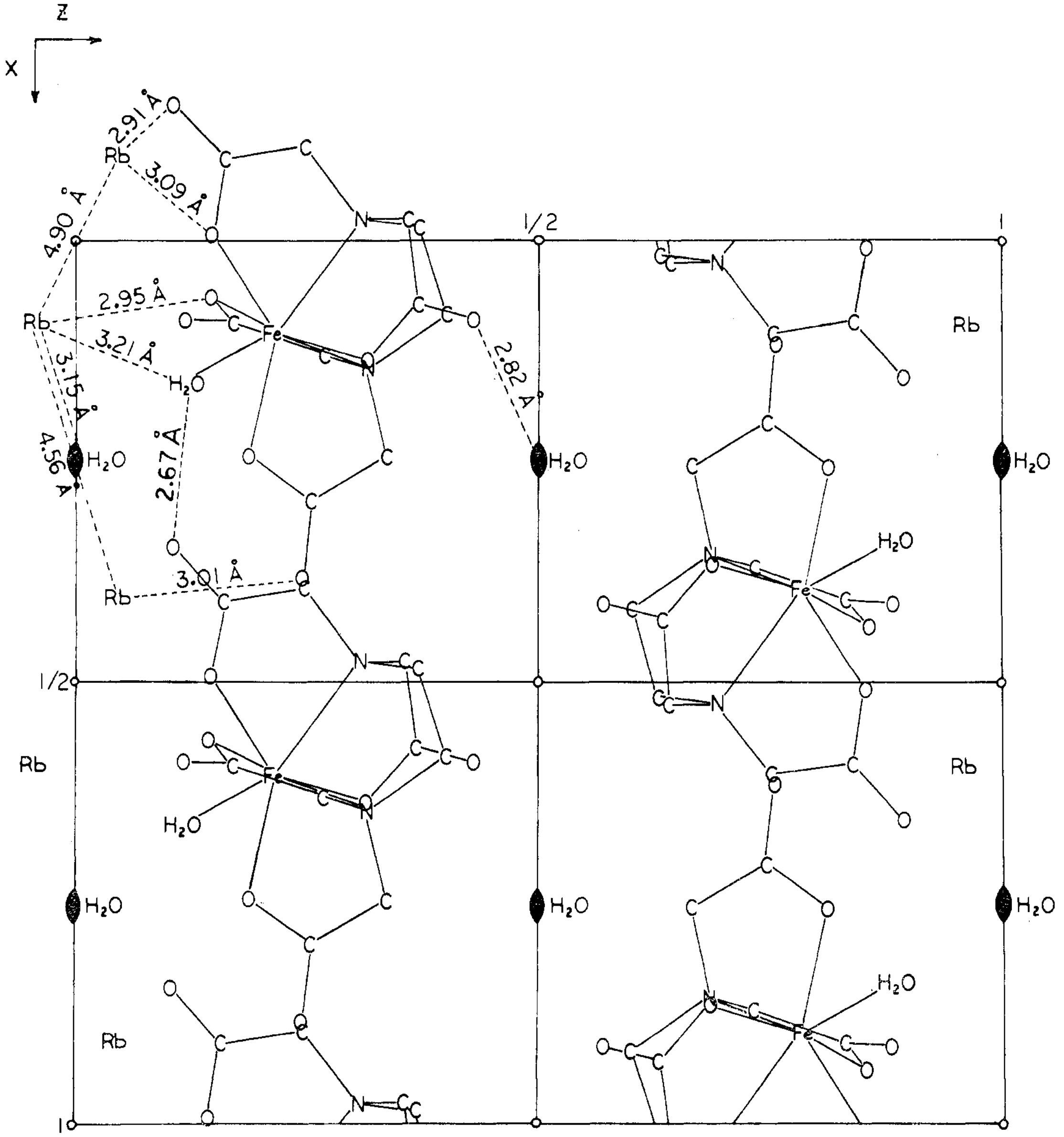

Fig. 2.—Packing relations in RbFe(OH$_2$)Y·H$_2$O illustrated in projection upon (010). General positions in P2/a are ±(x, y, z); ±($^1/_2$ + x, $\bar{y}$, z). The coordinates of Table I are those for the complex (and for other atoms) which lie nearest to the origin in the figure.

Packing Relations in the Crystals

Figure 2 displays the packing relations in crystalline RbFe(OH$_2$)Y·H$_2$O as viewed parallel to the short b axis. The anions form layers one complex thick along c, with approximate median planes $z = \pm {}^1/_4, \pm {}^3/_4$, etc. Single layers are loosely tied by the cations into electrically neutral double layers with median planes z = 0, ±1, etc. Cohesion between double layers across the planes $z = \pm {}^1/_2, \pm {}^3/_2$, etc., depends largely upon van der Waals attraction supplemented by rather weak hydrogen bonds (just two in each cell) formed by water molecules (w$_3$) with carboxylate oxygen (O$_5$). Thus w$_3$–O$_5$ = 2.82 Å., O$_5$w$_3$O$_5^c$ = 126°. All intermolecular contacts across $z = {}^1/_2$ which fall below 4.00 Å. involve O$_5$: C$_3$–O$_5^c$ = 3.39, C$_1$–O$_5^c$ = 3.50, C$_2$–O$_5^c$ = 3.94, C$_4$–O$_5^c$ = 3.98, and O$_5$–O$_5^c$ = 3.99 Å.

The Rb–O distances of significance are just six in number, and average to 3.05 Å., which is at least 0.15 Å. larger than the sum of the ionic radii for six-coordination.[23] Individual Rb–O distances are 2.91 Å. to O$_8$, 2.95 Å. to O$_2$, 3.01 Å. to O$_7$, 3.09 Å. to O$_4$, 3.15 Å. to w$_2$, and 3.21 Å. to w$_1$. These data account fully for the extraordinarily large thermal parameter of Rb$^+$ relative to most of the lighter atoms (Table I).

Some additional stabilization within each anionic layer is provided by hydrogen bonds formed by the water molecule, w$_1$, which also is firmly tied to Fe^{+3}. Thus w$_1$–O$_8^a$ = 2.67 Å., w$_1$–O$_6^b$ = 2.77 Å., and O$_8^a$w$_1$-O$_6^b$ = 97.4°. (Because O$_6^b$ lies one b-translation below O$_6$, the bond w$_1$–O$_6^b$ is not shown in Fig. 2.) We note that the water molecules, w$_2$, play the limited role of dielectric filler.

The molecular volume in the crystal of RbFe(OH$_2$)-Y·H$_2$O is 8% greater than that of the ammonium salt (of undetermined structure).

Figure 3 illustrates the packing relations in crystalline LiFe(OH$_2$)Y·2H$_2$O by projection of the cell contents

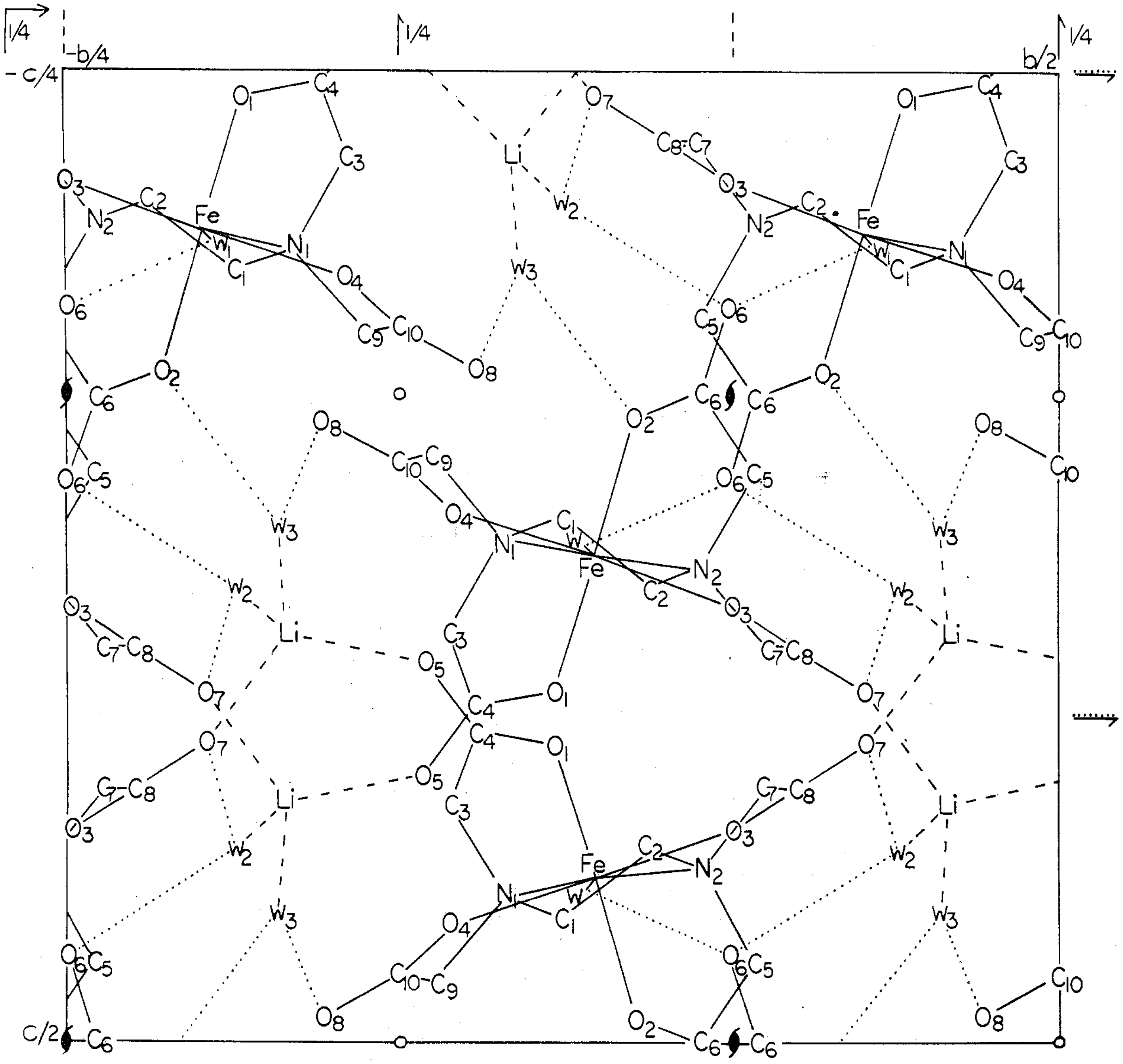

Fig. 3.—Packing relations in $LiFe(OH_2)Y\cdot 2H_2O$ displayed in projection on (100). The complex anion in the middle of the diagram is centered at x, y, z (Table I), the anion near the bottom at $^1/_2 + x, y, ^1/_2 - z$. The pair of C_1 atoms (or of O_1, etc.) which nearly coincide on projection are separated by at least $a/2 = 4.84$ Å. As the quasi-twofold axis of $Fe(OH_2)Y^-$ is nearly parallel to a, the anions mentioned point down, the other two shown (at $\bar{x}, \bar{y}, \bar{z}$ and $^1/_2 + x, ^1/_2 - y, \bar{z}$) point up.

onto (100). The quasi-twofold axis of each $Fe(OH_2)Y^-$ is nearly parallel to a with, as required by Pbca, the opposite polarities equally represented in the structure. The arrangement, in contrast with that of $RbFe(OH_2)\cdot H_2O$, makes rather efficient use of the cations to acquire a three-dimensional salt-like character. The cation is tetrahedrally coordinated with carboxylate oxygens O_5 and O_7 and water molecules w_2 and w_3. Bond angles at Li^+ lie in the range 103.7–118.6°. Bond lengths are $Li–w_3 = 1.911$ Å., $Li–O_5 = 1.920$ Å., $Li–w_2 = 1.959$ Å., $Li–O_7 = 2.006$ Å., averaging to 1.949 ± 0.008 Å.; this latter is 0.05 Å. less than the sum of the ionic radii for six-coordination,[23] but may be as much as 0.05 Å. too large for ideal four-coordination.

The probable hydrogen bonds, corresponding to O--H--O separations $\lesssim 2.90$ Å., are indicated in Fig. 3; the cut-off at 2.90 Å. is sharp because the range 2.90–3.13 Å. is unrepresented in our data. Hydrogen bond distances are $w_1–O_6$, 2.680 Å.; $w_2–O_6$, 2.810 Å.; $w_2–O_7$, 2.853 Å., $w_3–O_2$, 2.827 Å., $w_3–O_8$, 2.901 Å., with standard deviations $\lesssim 0.010$ Å. The more pertinent bond angles are O_6w_1Fe, 123.6°; $O_6w_2O_7$, 111.8°, and $O_2w_3O_8$, 95.0°.

The thermal parameters of the atoms in a crystalline EDTA complex give some idea of the quality of the three-dimensional linking or, alternatively, of the packing density. Of six different structural types thus far reported, that of $LiFe(OH_2)Y\cdot 2H_2O$ stands second to the $Mn_3(HY)_2\cdot 10H_2O$ arrangement (which exhibits complexing in three dimensions) in such a quality rating. At the bottom is the $RbFe(OH_2)Y\cdot 2H_2O$ structural type, with those of the complex acids, $Ni(OH_2)YH_2$ and $Fe(OH_2)YH$, and of the salt, $RbCoY\cdot 2H_2O$, occupying intermediate positions. The existence of two or more isomorphs for each of the three structural types last listed has been proved.