CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS 66044

# Classification of Conformational Types of Metal Ethylenediaminetetraacetato Complexes

BY B. LEE

*Received November 2, 1971*

Any five-membered ring can have four and only four conformations when all of its five bond lengths and four of its five bond angles are specified. Simple formulas can be derived which give the coordinates of the atoms in terms of the five bond lengths and four bond angles. For the ethylenediamine ring of a metal–ethylenediaminetetraacetato (EDTA) complex, only two of these four conformations occur, these two being a mirror-image pair. For the glycinate rings, the four conformations can effectively be classified into two categories, the difference in the two conformational types in one category being relatively minor. For a given optical isomer corresponding to a given choice of conformation of the ethylenediamine ring, there are then $2^4 = 16$ conformational types. Six of these types are equivalent to six other types by a twofold symmetry, leaving 10 pairs as the number of distinct conformational types available for the EDTA moiety of any of its fully chelated metal complexes. Some characteristic features of each of these 10 conformational types are described.

A number of metal–ethylenediaminetetraacetato (EDTA) complexes were subject to accurate three-dimensional X-ray crystallographic investigations[1] and shown to exhibit a wide variety of structures. In addition, the characteristic behavior of thermodynamic quantities in the formation of the lanthanide–EDTA complexes[2] has been suggested to be related to a discrete conformational change of the EDTA moiety of the complexes.[3] It was deemed of interest to determine if the conformations of the EDTA moiety in these complexes can be systematically cataloged into distinct conformational types. In order to do this, a general study of the conformation of a single isolated five-membered chelate ring is first made. The results are then applied to the EDTA moiety of the fully chelated complex, which forms a fused five-membered ring system.

## A General Five-Membered Ring

Consider a five-membered ring $MB_1A_1A_2B_2$ (Figure 1). When this is a chelate ring and M is the metal ion, one can usually make fairly good estimates of the values of the bond lengths $a$, $b_1$, $b_2$, $c_1$, and $c_2$ and of the bond angles $\alpha_1$, $\alpha_2$, $\beta_1$, and $\beta_2$ from the standard bond lengths and bond angles and the size of the metal ion. In terms of these parameters, one can derive the atomic coordinates, the bond angle $\gamma$, some dihedral angles, and the parameters that measure the degree of nonplanarity of the ring. The derivation is outlined in this section. The method is somewhat analogous to the general method given by Corey and Sneen.[4]

Let us choose the coordinate system as follows. As indicated in Figure 1, the $x$ axis runs along the $A_1A_2$ bond and the $y$ axis runs perpendicular to it, passing through M. The $z$ axis is then chosen so as to complete a right-handed cartesian coordinate system. Let $C_1$ be the circle that atom $B_1$ traces when the bond $A_1B_1$ is rotated around the $x$ axis, keeping the bond angle $\alpha_1$ constant. Let $\phi_1$ be the angle that the projection of the bond $A_1B_1$ onto the plane of the circle $C_1$ makes with the $x$–$y$ plane. Define $C_2$ and $\phi_2$ similarly. Choose the sign of $\phi_1$ and $\phi_2$ such that a positive $\phi_1$ or $\phi_2$ rotation corresponds to the right-handed screw motion advancing in the positive $x$ direction.

The lengths $l_1 = \overline{MA_1}$ and $l_2 = \overline{MA_2}$ are determined from the quantities $b_1$, $c_1$, $\beta_1$, $b_2$, $c_2$, and $\beta_2$. Since $a$ is also given, the triangle $MA_1A_2$ is completely determined and the coordinates of M, $A_1$, and $A_2$ can readily be derived. The position of the atoms $B_1$ and $B_2$ may be found as follows. Since $b_1$ and $\alpha_1$ are given, atom $B_1$ must lie on circle $C_1$. Similarly atom $B_2$ must lie on circle $C_2$. Therefore the position of the atoms $B_1$ and $B_2$ and hence the geometry of the entire ring are completely defined by giving the values of $\phi_1$ and $\phi_2$ in addition to the nine bond lengths and angles. The angles $\phi_1$ and $\phi_2$ may be regarded as ruffling parameters, being zero when the ring is planar. The values of these angles may be determined by computing the bond lengths $c_1$ and $c_2$ or the bond angles $\beta_1$ and $\beta_2$ in terms of these angles.

Atomic coordinates and some useful formulas thus derived are given in Table I. It is seen that the nine bond lengths and angles are sufficient to determine only the magnitude of the angles $\phi_1$ and $\phi_2$. Thus four conformations are equally compatible with each given set. These conformations are designated as $(++)$, $(+-)$, $(-+)$, and $(--)$, where the two signs in a parentheses refer to the signs of $\phi_1$ and $\phi_2$. The third and the fourth conformations are the mirror images of the second and the first conformations, respectively. When the ring is symmetrical, the subscript $i$ may be dropped; the first conformation is then the "envelope" form and the second the "half-chair" form.

The magnitudes of $\phi_1$ and $\phi_2$ or, specifically, $|\phi_1| + |\phi_2|$ may be used as a measure of the degree of ruffling of a ring. It should be noted that $|\phi_1| + |\phi_2|$ is a completely defined function of the five bond lengths and the four bond angles. To increase or decrease the degree of ruffling would require a change of one or more of the nine bond length and angle parameters.

---

[1] (a) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959); (b) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959); (c) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964); (d) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **3**, 34 (1964); (e) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, **87**, 1611 (1965); (f) J. L. Hoard, B. Lee, and M. D. Lind, *ibid.*, **87**, 1612 (1965); (g) B. Lee, M. D. Lind, and J. L. Hoard, paper presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] J. L. Mackey, J. E. Powell, and F. H. Spedding, *J. Amer. Chem. Soc.*, **84**, 2047 (1962).

[3] (a) B. Lee, Ph.D. Dissertation, Cornell University, Ithaca, N. Y., Feb 1967; (b) B. Lee, M. D. Lind, and J. L. Hoard, to be submitted for publication.

[4] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **77**, 2505 (1955).

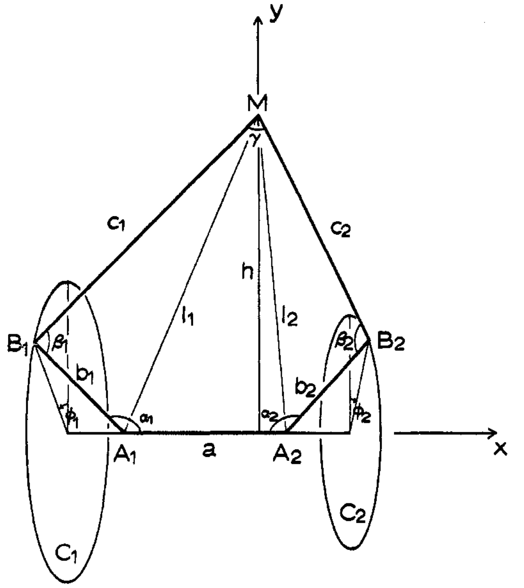

Figure 1.—Geometry of a general five-membered ring.

TABLE I
FIVE-MEMBERED RING GEOMETRY[a]

Coordinates

| | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| M | $0$ | $h$ | $0$ |
| $A_i$ | $\mp t_i$ | $0$ | $0$ |
| $B_i$ | $\mp(t_i - b_i \cos \alpha_i)$ | $b_i \sin \alpha_i \cos \phi_i$ | $b_i \sin \alpha_i \sin \phi_i$ |

Dihedral Angles and Ruffling Parameter

$$\cos \tau_i{}^b = \frac{t_i - b_i \cos \alpha_i + c_i \cos \alpha_i \cos \beta_i}{c_i \sin \alpha_i \sin \beta_i}$$

$$\phi_{21}{}^b = \phi_2 - \phi_1$$

$$\cos \phi_i{}^c = \frac{b_i - c_i \cos \beta_i - t_i \cos \alpha_i}{h \sin \alpha_i}$$

Bond Angle and Ring Span[d]

$$\cos \gamma = \frac{c_1{}^2 + c_2{}^2 - s_0{}^2}{2c_1c_2} - \frac{b_1b_2}{c_1c_2} \sin \alpha_1 \sin \alpha_2(1 - \cos \phi_{21})$$

$$s^2 = s_0{}^2 + 2b_1b_2 \sin \alpha_1 \sin \alpha_2(1 - \cos \phi_{21})$$

Auxiliary Relations

$$h^2 = l_i{}^2 - t_i{}^2$$

$$l_i{}^2 = b_i{}^2 + c_i{}^2 - 2b_ic_i \cos \beta_i$$

$$t_i = (a/2) \pm (l_1{}^2 - l_2{}^2)/2a$$

$$s_0{}^2 = [a - (b_1 \cos \alpha_1 + b_2 \cos \alpha_2)]^2 + [b_1 \sin \alpha_1 - b_2 \sin \alpha_2]^2$$

[a] $i = 1$ or 2. When a double sign occurs the upper and lower signs are for $i = 1$ and 2, respectively. [b] $\tau_i$ and $\phi_{21}$ are the dihedral angles around the bonds $A_i$–$B_i$ and $A_1$–$A_2$, respectively. [c] The angles $\phi_i$ may be regarded as ruffling parameters; $\phi_1 = \phi_2 = 0°$ for a planar ring. [d] The ring span $s$ is the distance between the two ligand atoms $B_1$ and $B_2$ in the same ring. The parameter $s_0$ is the distance between the $B_1$ and $B_2$ atoms when the four atoms $B_1$, $A_1$, $A_2$, and $B_2$ are on a plane.

## Five-Membered Rings in EDTA Complexes

For the chelate rings in EDTA complexes, we consider the atom M in Figure 1 to be the metal ion, $B_i$ the chelating ligand atoms oxygen or nitrogen, and $A_i$ the carbon atoms. For the ethylenediamine ring (E ring), we arbitrarily label the two sides with subscripts 1 and 2. The atoms $B_1$, $A_1$, $A_2$, and $B_2$ will be designated as $N_1$, $C_1$, $C_2$ and $N_2$. For the glycinate ring (G ring), the nitrogen side is chosen to be the side 1, the atoms $B_1$, $A_1$, $A_2$, and $B_2$ being designated as N, C, C′, and O.

In order to obtain some general idea of the structural parameters involved, a survey is made of the bond lengths and angles occurring in a number of EDTA complexes and related compounds. Some of the results are given in Table II.[5] The carbon–carbon and the carbon–nitrogen bond lengths are constants within the accuracy of the experiments. The C′–O distance shows a slight tendency to decrease as the complexing bond length M–O is increased; the slope of a least-squares line gives 0.05-Å decrease in the C′–O length per 1-Å increase in the M–O length. The bond angle MNC in the E ring is constant within experimental error. The bond angles NCC of the E ring and MNC, CC′O, and NCC′ of the G rings show a tendency to increase with increasing M–O bond length at a rate ranging from 3.5 to 7.5° per 1 Å. For simplicity, all these trends were neglected and only the average and the root-mean-square (rms) deviations from the average are given in Table II. The angle MOC′, however, shows a large dependence on the M–O bond length that cannot be neglected. The equation of a least-squares line is given in this case. Both the M–O and M–N distances increase with increase in the size of the metal ion. Again for simplicity, the M–N distance is regarded as a linear function of the M–O distance and the equation of the least-squares line is given. Since the fit is relatively poor (rms $\sigma = 0.09$ Å), this relation is to be used only for obtaining rough numbers.

TABLE II
"STANDARD" CHELATE RING BOND LENGTHS AND ANGLES IN EDTA CHELATES[a]

| | E ring | | G ring | | | |
|---|---|---|---|---|---|---|
| $a$ | C–C | 1.53 (1) | C–C′ | 1.52 (1) | | |
| $b$ | N–C | 1.48 (1) | N–C | 1.48 (1) | C′–O | 1.27 (2) |
| $c^b$ | | | | | | |
| $\alpha$ | NCC | 111 (2) | NCC′ | 111 (2) | CC′O | 118 (2) |
| $\beta$ | MNC | 110 (1) | MNC | 107 (2) | MOC′[b] | |

[a] Lengths are given in ångströms; angles, in degrees. Numbers in parentheses are the rms deviations given for the last significant digit of the mean values. [b] The M–N distance $c_N$ and the MOC′ angle $\beta_2$ are given in terms of the M–O distance $c_O$ by $c_N = c^0{}_N + p(c_O - c^0{}_O)$ and $\beta_2 = \beta^0{}_2 + p'(c_O - c^0{}_O)$, respectively, where $c^0{}_N = 2.45$ Å, $p = 1.207$, $c^0{}_O = 2.23$ Å, $\beta^0{}_2 = 121°$, and $p' = 14.55$. The rms deviations of the observed values from the values calculated from these formulas are 0.09 Å and 3°, respectively, for $c_N$ and $\beta_2$.

With the data given in Table II and the formulas given in Table I, all the structural parameters of a chelate ring can be computed as a function of the distance M–O. The calculated and observed values of the complexing bond angle $\gamma$ and of the ring span $s$ are plotted in Figures 2 and 3, respectively. The marked decrease in $\gamma$ with increasing complexing bond lengths is evident. It is noted that the decreasing tendency is nearly independent of the ring type. The ring span generally increases with increasing complexing bond length but the tendency is seen to be much smaller for the G rings than for the E ring.

All the chelate rings in EDTA complexes that have been investigated are significantly ruffled (see below). Ruffling of a ring is geometrically accomplished by rota-

---

(5) Compounds included in compiling the data given in this table are $NH_4CoEDTA$,[1a] $LiFe(OH_2)EDTA$,[1d] $Ca[Fe(OH_2)DCTA]_2$,[5a] $Mn[Mn(OH_2)HEDTA]_2$,[1c] $K_2Zr(NTA)_2$,[5b] $Na_4[(MoO_3)_2EDTA]$,[5c] $NaTb(OH_2)_3EDTA$,[3] $KLa(OH_2)_3EDTA$,[3] and $La(OH_2)_4HEDTA$.[3] A unit weight was assigned to each compound in computing the average: (a) G. H. Cohen and J. L. Hoard, *J. Amer. Chem. Soc.*, **88**, 3228 (1966) [DCTA is for *trans*-1,2-diaminocyclohexane-*N*,*N*′-tetraacetate]; (b) J. L. Hoard, E. W. Silverton, and J. V. Silverton, *ibid.*, **90**, 2300 (1968) [NTA is for nitrilotriacetate; this structure was used for computing the G-ring parameters only]; (c) J. J. Park, M. D. Glick, and J. L. Hoard, *ibid.*, **91**, 301 (1969) [this structure was used for computing the G-ring parameters only].

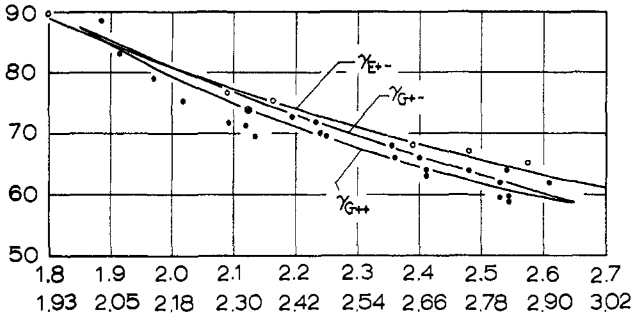

Figure 2.—The complexing bond angle $\gamma$ as a function of the bond length M–O. The lower abscissa scale gives the corresponding M–N bond length according to the equation given in footnote *b* of Table II. With the structural parameters given in Table II, the G ring does not close when the M–O length is smaller than 1.85 Å or greater than 2.65 Å. Points are the observed values for the compounds listed in footnote 5. When a pseudo-twofold symmetry exists, the data used are the appropriately averaged values: ●, for G ring; ○, for E ring. The $E^{+-}$, $G^{+-}$, and $G^{++}$ designations are for the (+ –) type E ring, the (+ –) type G ring, and the (+ +) type G ring.

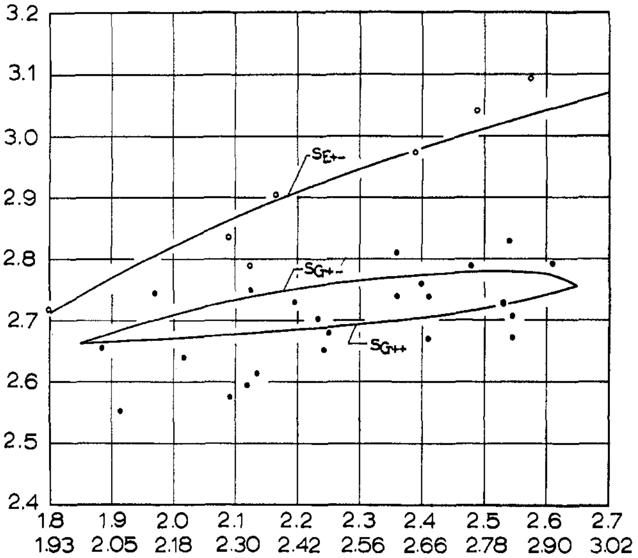

Figure 3.—The ring span *s* as a function of the bond length M-O. The lower abscissa scale is as in Figure 2 and points are the observed values for the same set of compounds: ●, for G ring; ○, for E ring. The $E^{+-}$, $G^{+-}$, and $G^{++}$ designations are as in Figure 2.

tion around one or more of the ring bonds such that the dihedral angle around the bond is nonzero. These rotations are energetically favored or disfavored according to the steric effect they produce among the side groups that are attached to the atoms of the ring. Rotation around the C′–O bond may be expected to be especially disfavored because of its partial double-bond character. When the ring ruffling is energetically disfavored, deformation of bond lengths and angles will occur to reduce the ruffling. The ring is then in a strained state.

TABLE III
RUFFLING PARAMETERS OF EDTA AND OTHER AMINOPOLYCARBOXYLIC ACID COMPLEXES[a]

| | $\phi_1$ | $\phi_2$ | Type | | $\phi_1$ | $\phi_2$ | Type | | $\phi_1$ | $\phi_2$ | Type |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $NH_4CoEDTA$ | | | | $Ni(OH_2)H_2EDTA$ | | | | $LiFe(OH_2)EDTA$ | | | |
| E | −25 | 23 | | E | −31 | 29 | | E | −28 | 29 | |
| $G_1$ | 2 | 10 | aλ | $G_1$ | 0 | 7 | aλ | $G_1$ | 1 | 18 | aλ |
| $G_2$ | 26 | 6 | eλ | $G_2$ | 28 | 5 | eλ | $G_2$ | 28 | 8 | eλ |
| $G_3$ | 10 | 1 | aλ | $G_3$ | 12 | 0 | aλ | $G_3$ | 15 | −1 | aλ |
| $G_4$ | 24 | 11 | eλ | $G_4$ | Uncomplexed | | | $G_4$ | 28 | 6 | eλ |
| $RbFe(OH_2)EDTA$ | | | | $Ca[Fe(OH_2)DCTA]_2$ | | | | $Mn[Mn(OH_2)$-$HEDTA]_2$ | | | |
| E | −30 | 24 | | E | −26 | −27 | | | | | |
| $G_1$ | 3 | 11 | aλ | $G_1$ | −32 | −14 | aδ | E | −26 | 28 | |
| $G_2$ | 31 | 6 | eλ | $G_2$ | −22 | −6 | eδ | $G_1$ | −31 | −16 | aδ |
| $G_3$ | 24 | 0 | aλ | $G_3$ | −28 | −15 | aδ | $G_2$ | −28 | 3 | eδ |
| $G_4$ | 24 | 12 | eλ | $G_4$ | −25 | −7 | eδ | $G_3$ | −28 | −18 | aδ |
| | | | | | | | | $G_4$ | −25 | −11 | eδ |
| $K_2Zr(NTA)_2$ | | | | $Na_4(MoO_3)_2EDTA$ | | | | | | | |
| Ga | 24 | 8 | λ | $G_1$ | −25 | −8 | δ | $La(OH_2)_4HEDTA$ | | | |
| Gg | −19 | 17 | δ | $G_2$ | 16 | −7 | λ | E | −38 | 25 | |
| Gm | −27 | 2 | δ | | | | | $G_1$ | −31 | −18 | aδ |
| | | | | | | | | $G_2$ | −22 | 4 | eδ |
| $NaTb(OH_2)_3EDTA$ | | | | $KLa(OH_2)_3EDTA$ | | | | $G_3$ | 23 | 7 | aλ |
| E | −31 | 31 | | E | −33 | 33 | | $G_4$ | −27 | −7 | eδ |
| $G_1$ | −26 | −1 | aδ | $G_1$ | −29 | 2 | aδ | | | | |
| $G_2$ | 22 | −14 | eλ | $G_2$ | 23 | −13 | eλ | | | | |
| $G_3$ | 19 | 6 | aλ | $G_3$ | 19 | 6 | aλ | | | | |
| $G_4$ | −28 | −6 | eδ | $G_4$ | −32 | −6 | eδ | | | | |

[a] Numbers are given in degrees. References are given in footnotes 1 and 5. $G_1$ and $G_2$ are respectively the axial and equatorial rings that share the same nitrogen atom. $G_3$ and $G_4$ are similarly the axial and equatorial rings that share the other nitrogen atom. Ga, Gg, Gm refer to the three different types of G rings that occur in the $K_2Zr(NTA)_2$ species. See ref 5b.

The values of $\phi_1$ and $\phi_2$ observed in various complexes are given in Table III. The E ring is always very much ruffled and $\phi_1$ and $\phi_2$ take opposite sign.[6] Since the two sides of the ring are chemically equivalent, $\phi_1$ and $\phi_2$ are roughly the same in magnitude. For the G rings, on the other hand, the bond lengths and angles of the two sides are very different and a substantial disparity in the magnitudes of $\phi_1$ and $\phi_2$ generally occurs. These values are plotted in Figure 4 in order to compare them with the geometrically expected values shown as curves calculated from the data given in Table II. The large scatter of points from the calculated curves indicates sensitivity of these values to the variation of the bond length and angle parameters. Nevertheless one can clearly see that $\phi_1$ is substantially larger than $\phi_2$ with only a few exceptions involving relatively planar rings. That $\phi_1$ be larger than $\phi_2$ is compatible with the expected stereochemical preferences. The partial double-bond character of the C′–O bond will tend to make the atoms M, O, C′, and C lie on a plane and tend to keep the angles $\phi_2$ and $\tau_2$, the dihedral angle around the C′–O bond, small. When $\tau_1$, the dihedral angle around the N–C bond, or

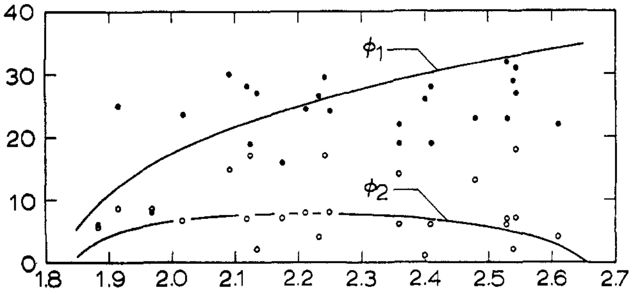

Figure 4.—The ruffling parameters for a G ring as a function of the bond length M–O. The points are the observed values for the same set of compounds as for Figure 2: ●, for $\phi_1$; ○, for $\phi_2$.

---

(6) See, for example, R. D. Gillard and H. M. Irving, *Chem. Rev.*, **65**, 603 (1965). Notice that the ruffling will occur even if the complexing bond lengths are of the exact length for a perfect planar ring, since the disposition of the two pairs of hydrogen atoms attached to the carbon atoms is more favorable when the ring is puckered. See, for example, E. L. Eliel, "Elements of Stereochemistry," Wiley, New York, N. Y., 1969, p 33.

$\phi_1$ is zero, on the other hand, the atoms around C and N are eclipsed. Large values of $\tau_1$ and $\phi_1$ are thus expected. When $\phi_2$ is small and $\phi_1$ is large, the dihedral angle around the C–C′ bond given by $\phi_{21} = \phi_2 - \phi_1$ becomes large. According to the idea presented by Dunitz and Strickler,[7] this is again to be expected for the anionic G rings since the C′–$O_u$ bond, where $O_u$ is the uncomplexed oxygen atom, is expected to be largely of double-bond character.

It is convenient to introduce symbols to designate the different glycinate ring types. A glycinate ring may be designated as equatorial (e) or axial (a) according to whether the atom C of the ring is equatorial or axial to the ethylenediamine ring. This classification is possible because the E ring is always very much puckered. Each of these ring types may further be divided into λ or δ classes according to whether $\phi_1$ and hence $\tau_1$ are positive or negative.[8] We will not further subdivide the ring types according to the sign of $\phi_2$. These symbols are used to indicate the ring types in Table III.

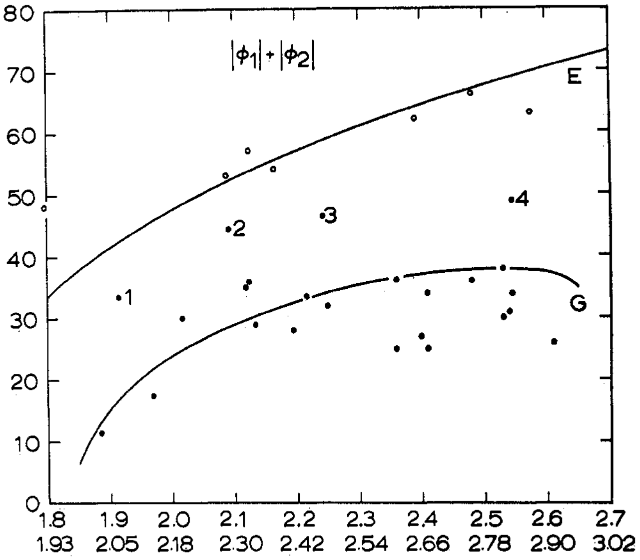

Figure 5.—The degree of ruffling $|\phi_1| + |\phi_2|$ as a function of the bond length M–O. The lower abscissa scale is as in Figure 2 and the points are the observed values for the same set of compounds: ●, for G ring; ○, for E ring. The exceptional G rings are labeled (see the text).

We note, here, in passing, a few more conspicuous features of the ring ruffling. In Figure 5 are plotted the degrees of ruffling, $|\phi_1| + |\phi_2|$, as a function of the complexing bond lengths. We note first that the E ring is always more ruffled than the G rings. The ruffling of the E ring generally increases with increasing complexing bond lengths. A similar general trend is apparent for the G rings when the M–O distance is less than about 2.1 Å; for longer M–O distances the tendency appears to be much less. To the extent that the calculated curves represent the degree of ruffling expected of a ring that has the "standard" bond lengths and angles obtained as averages observed in many similar structures, an exceptional ruffling is an indication of a large deviation of the bond lengths and angles from the "standard" values and thus represents either an exceptional stability or an exceptional strain associated with the formation of the ring. The four G rings that are exceptionally more ruffled are labeled. The first three are the equatorial λ (eλ) or the axial δ (aδ) type rings of the $[CoEDTA]^-$, $[Fe(OH_2)DCTA]^-$, and $[Mn(OH_2)HEDTA]^-$ species. The increased ruffling in these cases is probably brought about in order to meet the symmetry requirement. It is interesting in the light of the discussion to be given later that the highly ruffled eλ rings of the $[Fe(OH_2)EDTA]^-$ species do not appear exceptional in this plot. The fourth exceptional ruffling occurs for the aδ ring of the $[La(OH_2)_4HEDTA]$ species and is probably the result of a deformation that appears to occur in this complex to avoid a very short interligand contact.[8]

## Conformational Types of EDTA Complexes

Conformational types of the whole EDTA complex may be derived by specifying that of each of the five chelate rings. There are only two possibilities for the ethylenediamine ring since $\phi_1$ and $\phi_2$ always have opposite sign. Since these two possibilities are optical isomers, we may arbitrarily choose one conformation.

When the E ring is thus completely defined in space, the positions of the atoms M, N, and C of the four G rings are also completely fixed. These atoms are M, $B_1$, and $A_1$ in Figure 1 when the figure refers to a G ring. The angle $\phi_1$ is positive or negative according to whether the triangle $MA_1B_1$ is before or behind the plane $MA_1A_2$ as it is flipped back and forth along the line $MA_1$. However, since the $MA_1B_1$ triangle is now space-fixed, we obtain positive and negative $\phi_1$ by flipping, instead, the figure $MA_1A_2B_2$ around the line $MA_1$. Once one mode of flipping is chosen, we have a further flipping to do of the triangle $MA_2B_2$ around the line $MA_2$. This flipping corresponds to a positive or negative choice of the angle $\phi_2$. Thus in general four different types of a glycinate ring result. The total number of types of conformations available to an EDTA moiety is then $4^4 = 256$ optically isomeric pairs. However, for the purposes of delineating gross shapes of the EDTA complexes, we may neglect differences between the two types generated by the second flipping (the flipping around $MA_2$). This is because the angle $\phi_2$ is usually small as was pointed out in the previous section and because the effect of the second flipping should be relatively inconsequential compared to that of the first flipping because of the difference in the size of the group flipped. The second flipping may then be viewed as a relatively minor adjustment made by the ring system to ease local crowding, ligand repulsion, etc., without causing a major change in the shape of the complex. This consideration makes the number of major conformational types $2^4 = 16$ optically isomeric pairs.

The 16 conformational types with a given E-ring conformation are diagrammatically represented in Figure 6. It is noted from the figure that the conformations that possess a twofold symmetry are unique but that the asymmetric ones always occur in pairs related by a twofold symmetry. There are, therefore, 10 pairs of distinct major conformational types to an EDTA moiety when it is fully complexed to a metal

---

[7] J. D. Dunitz and P. Strickler, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 595.

[8] When $|\phi_1| > |\phi_2|$, as is usually the case with only few exceptions involving nearly planar rings, this convention makes a ring λ when $\phi_{21} < 0°$ and δ when $\phi_{21} > 0°$.

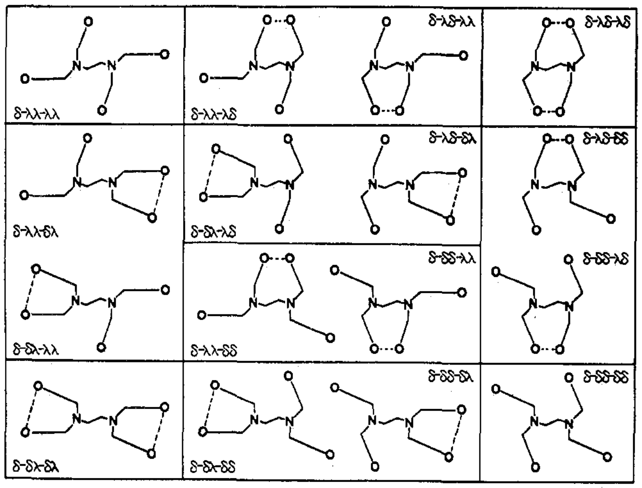

Figure 6.—Schematic diagrams of the conformational types of sexadentate EDTA complexes. Each diagram shows a rather accurate stereographic projection (where the plane of projection touches the reference sphere rather than passing through its center) of the ligand atoms of the chelating agent of the complex. The geometries of the $[Fe(OH_2)EDTA]^-$ and the $[Fe(OH_2)DCTA]^-$ complexes were used for this construction. The viewing direction is from the metal ion to the center of the $C_1$–$C_2$ bond of the E ring. Lines are drawn between the atoms only to indicate the connectivity and the signs of $\phi_1$ (and $\phi_2$ for the E ring) angle. Two types related by a twofold axis are enclosed in a box. Dotted lines indicate expected short interligand contacts.

ion. Symbols given to each of these types are also given in Figure 6.[9]

## Discussion

The five five-membered rings in EDTA complexes are continuously joined and fused together. Many of them are severely ruffled. It is therefore unlikely that these rings undergo the type of pseudorotation observed in cyclopentane[10] and its analogs. While minor conformational fluctuations undoubtedly exist within each type, nevertheless it seems plausible that the 10 pairs of conformational types derived in the previous section represent discrete, identifiable species.[11] When more than one type is available to a metal complex, its solution will contain a mixture of two or more distinct types in dynamic equilibrium. A transition from one conformational type to another may be induced by replacing one metal ion for another or by simply changing the equilibrium conditions, such as pH and temperature, of a solution containing a mixture of two or more types. Such transitions may involve a change in coordination number even when the chelation remains sexadentate throughout the process because, as expounded by Hoard and coworkers,[12] the sexadentate EDTA complexes of all but the smallest of the metal ions are expected to have one or more of water molecules complexed to the metal ion in their aqueous solution. Such transitions should be amenable to the usual kinetic and thermodynamic studies.

An interesting and important question is this: "Given a metal ion, what type of complex will it form and what coordination number will it have?" The answer to this question will depend in part on the type of symmetry requirements imposed on the system by the electronic orbitals of the central metal ion and on the stereochemical properties of the additional ligands that are available to the complex. These factors will not be dealt with here. Whenever additional ligands are considered, we will assume them to be the water molecules. What we will discuss in the following section are some of the geometric characteristics of each conformational type and the interplay of these characteristics and the size of the metal ions in influencing the answer to the above question. For concreteness, we will consider the δ isomers (those with a δ-type E ring) diagrammed in Figure 6.

Four of the 10 conformational types are symmetrical. Two of these symmetrical types, the δ-λλ-λλ and the δ-δδ-δδ types, have been found in nature. Comparison of these two types is useful because examples of all four ring types—aλ, eλ, aδ, and eδ—are provided by these two types. Even superficial examination reveals that these four types can be grouped into two classes of two—eλ and aδ in one class and aλ and eδ in another. For quantitative comparison of these two classes, we will take two examples whose structures have been established accurately by X-ray studies. The monoaquo sexadentate seven-coordinate Fe(III) complex of EDTA[1d] which is of a δ-λλ-λλ type[11,20] and that of the similar chelating agent DCTA[5a] which is of a δ-δδ-δδ type will serve the purpose. It is seen that the oxygen atoms of the ring type eλ and, to a much less extent, of the type aδ lie near the plane $MN_1N_2$. Thus in $[Fe(OH_2)EDTA]^-$ the angle between the planes $MN_1N_2$ and $MO_{e\lambda}O_{e\lambda}$ is 10° compared with 81° between the $MN_1N_2$ and $MO_{a\lambda}O_{a\lambda}$ planes; in $[Fe(OH_2)DCTA]^-$, the angle between the $MN_1N_2$ and $MO_{a\delta}O_{a\delta}$ planes is 30° compared with 70° between the $MN_1N_2$ and $MO_{e\delta}O_{e\delta}$ planes. Related to this property is the fact that eλ-aδ types can reach farther around the metal ion than can the aλ-eδ types. If we define the central plane of the complex as the plane passing through the metal ion and perpendicular to the effective twofold axis, the $O_{e\lambda}$ atoms of $[Fe(OH_2)EDTA]^-$ are above (*i.e.*, on the opposite side of the nitrogen atoms) and the $M$–$O_{e\lambda}$ bonds make an angle of 17° with this plane. The $O_{a\lambda}$ atoms, on the other hand, are below this plane with an angle of 7°. Similarly the $O_{a\delta}$ atoms in $[Fe(OH)_2)DCTA]^-$ complex are above the central plane with an angle of 15°, and the $O_{e\delta}$ atoms are below the plane by 3°. Examination of stereomodels reveals quite convincingly that these distinctions between the eλ-aδ types and the aλ-eδ types are inherent properties of the geometry of the chelating agent rather than the exceptional properties of the examples chosen. As we will see later, these properties of the two classes of ring types appear to have some striking effects on the geometry of the nine- and ten-coordinate lanthanide–EDTA complexes.

The facts that the $O_{e\lambda}$ atoms are so close to the

---

[9] The symbols are constructed in the following manner. The first letter is δ or λ according to whether the dihedral angle $\phi_{21}$ around the $C_1$–$C_2$ bond of the E ring is positive ($\phi_2 > \phi_1$) or negative ($\phi_2 < \phi_1$), respectively. The following two letters refer to the types of the two G rings attached to the same nitrogen, the first one for the axial ring and the second for the equatorial ring. The last two letters similarly refer to the types of two the G rings attached to the other nitrogen atom, the first letter being for the axial ring. According to this system, a symbol refers to the same conformational type after its two middle letters are interchanged with its last two letters.

[10] W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).

[11] *Exceptions occur when relatively small metal ions are involved and hence some rings are quite flat. In these cases the distinction between two conformational types disappears. See footnote 20.*

[12] J. L. Hoard, G. S. Smith, and M. D. Lind, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan Co., New York, N. Y., 1961, pp 296–302.

$MN_1N_2$ plane and that the $O_{a\lambda}$ atoms are on an axis that is nearly perpendicular to the $MN_1N_2$ plane make the δ-λλ-λλ type suitable for an octahedral coordination when the γ angles are close to 90°. The Co(III),[1a] Cr(III),[12] and Al(III)[12] ions form the sexadentate octahedral complex salts of this type. The average Co–O distance is found to be 1.905 Å.

The γ angles of the eλ rings in $[CoEDTA]^-$ species average to 83°, which is substantially smaller than 90°. Since the γ angles decrease quite markedly as the size of the metal ion is increased (Figure 2), the suitability of the δ-λλ-λλ type conformation for a sexadentate octahedral geometry will decrease rapidly with increase in the size of the metal ion. Protonation of a G ring increases its M–O distance and thus will have quite detrimental effects as pointed out by Hoard, Smith, and Lind.[12] All the acid complexes of Cr(III), Fe(III), Ni(II), Cu(II), and Ga(III) are found to be monoaquo pentadentate octahedral complexes[1b,13] derivable from the δ-λλ-λλ type $[CoEDTA]^-$ species by opening an eλ ring.[14,15] The average M–O distances in these complexes are found or expected to range roughly from 1.95 to 2.15 Å.

The anionic Fe(III) complex[1d] has an interesting pentagonal-bipyramidal geometry utilizing the δ-λλ-λλ type of EDTA conformation. The $M-O_{e\lambda}$ and the $M-O_{a\lambda}$ distances in this species average to about 2.10 and 1.98 Å, respectively. These distances are near the two extremes of the range cited above. The long $M-O_{e\lambda}$ distance makes the $\gamma_{e\lambda}$ angle approach 72° (= 360°/5), at which point the two $O_{e\lambda}$ and the two nitrogen ligands are placed near the four corners of a pentagon. The fifth site is left open for a water molecule. The short $M-O_{a\lambda}$ distance on the other hand helps increase the $\gamma_{a\lambda}$ angle toward 90° which is required for an ideal pentagonal-bipyramidal geometry. The pattern of long equatorial and short axial bond distances, on the other hand, is what one should expect for this coordination geometry from a consideration of the interligand repulsions.[16] Albeit the coordination geometry realized is still much distorted, the fortunate compatibility between the geometry of the coordination polyhedron and that of the chelating agent in the δ-λλ-λλ type conformation should be expected to render this complex exceptionally stable (see ref 1d and the references cited therein).

Let us now turn to the other symmetrical conformational type observed—the δ-δδ-δδ type. If one tries to build an octahedron using this conformational type, one immediately meets a number of problems. The $O_{a\delta}$ ligands are much closer to the $MN_1N_2$ plane than the $O_{e\delta}$ ligands but not close enough to regard the two $O_{a\delta}$ and the two nitrogen atoms to lie even approximately on a plane if the relation between the M–N and the M–O distances are to be maintained even roughly as given in Table II. Also the $O_{e\delta}$ atoms are too far from the axis that is normal to the $MN_1N_2$ plane. These distortions may be described more conveniently in the following terms. One may view an octahedron as a trigonal antiprism. The three atoms that form a triangular base in this case are the nitrogen atom and the two oxygen atoms of the two G rings that share the same nitrogen. The two bases are staggered in an octahedron and eclipsed in a trigonal prism. The combined effect of the distortions outlined above is to twist the two bases so that they are between these ideal cases. The angle of this twist in the $[Fe(OH_2)DCTA]^-$ and the $[Mn(OH_2)HEDTA]^-$ species, which are both based upon the δ-δδ-δδ type conformation (Table III), are both about 26° measured from the eclipsed position. The resulting geometry looks rather more like a trigonal prism. The distortions from this ideal geometry take the form of poor definition of the plane formed by the four oxygen atoms and the deviation from parallelism of the prism axis and the line joining the two nitrogen atoms.

The greater extent of eclipsing of the two triangular bases in this conformational type causes a decrease in interligand contact distances while at the same time leaving a large open space above the plane of the four oxygen atoms. This conformational type therefore becomes favorable for large metal ions for which the interligand distances are large enough to compensate for the decrease produced by the partial eclipsing and for the case where the open space above the four oxygen atoms becomes large enough to attract a water molecule. Two examples of the species that fit this description are, as indicated above, the seven-coordinate sexadentate monoaquo complexes of $[Fe(OH_2)DCTA]^-$ and $[Mn(OH)_2HEDTA]^-$. Examination of the interligand contacts present in these two species[1c,5a] indicates that the Fe(III) ion is just large enough to form this type of complex whereas the Mn(II) ion is perhaps larger than necessary, there being no short contacts. The critical interligand contact distances are $O_{a\delta}$–w = 2.535, 2.825 Å and $O_{a\delta}-O_{e\delta}$ = 2.700, 2.755 Å, respectively, for the Fe(III) and the Mn(II) complexes, where w stands for the oxygen atom of the water ligand and the $O_{a\delta}-O_{e\delta}$ contact is between those of the two G rings that do *not* share the same nitrogen. The average M–O distances for these two complexes are 2.07 and 2.24 Å, respectively. Possible reasons for the $[Fe(OH_2)DCTA]^-$ species to form this type of complex rather than the δ-λλ-λλ type observed for the $[Fe(OH_2)EDTA]^-$ species have been put forward by Cohen and Hoard.[5a]

No X-ray studies of an eight-coordinate EDTA complex have been reported.[16a] Two coordination geometries appear to be about equally favorable for an eight-coordination:[17] the $D_{4d}$ square antiprism and the $D_{2d}$ dodecahedron. The former geometry may be derived from the δ-δδ-δδ type geometry of the $[Fe(OH_2)DCTA]^-$ and the $[Mn(OH_2)HEDTA]^-$ structures in the following manner. The two triangular bases in these two structures (see above) are approximately isosceles but

---

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

[14] Evidences have been reported in the literature[15] that the monoaquo- and the mononitroethylenediaminetetraacetato complexes of Co(III) in solution have an axial ring open. This is at variance with the conclusion reached by Hoard and his coworkers after detailed examination of the sexadentate $[Co^{III}EDTA]^-$ structure and is supported by the existence and the structure of the many acid complexes listed in the text. Single-crystal X-ray studies of the mononitro complex have been started in this laboratory in the hope of resolving this ambiguity.

[15] (a) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966); (b) B. B. Smith and R. H. Betts, *ibid.*, **9**, 2585 (1970).

[16] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 507 ff.

[16a] NOTE ADDED IN PROOF.—An X-ray study of the Ca(II) complex of EDTA has recently been called to my attention (V. A. Uchtman, Abstracts, 162nd National Meeting of the American Chemical Society, No. INOR 58, Washington, D. C., 1971). The complex was described as a sexadentate, diaquo, eight-coordinate, species.

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

not equilateral; the O–O distance is much larger than the two O–N distances that are about equal. Average values are O–O = 3.13, 3.43 Å and O–N = 2.61, 2.68 Å, respectively, for the iron and manganese complexes. A water molecule may be placed between the two oxygen atoms in the plane of each triangular base to make it an approximate square. The resulting coordination geometry will be an approximation to a square antiprism. The major distortion in this structure is expected to be that the two square bases are not completely staggered. The twist angle of the trigonal bases in the two seven-coordinate $\delta$-$\delta\delta$-$\delta\delta$ complexes is $\sim$26° as noted above. This angle probably cannot be increased much more. The major difficulty of this structure will then appear as a relatively short contact between the two additional water molecules. A bidentate ligand may be preferable, although Hoard and Silverton's "most favorable" square antiprism[17] has this length (one of their *l* edges) greater than the ring bite of any G rings (their *s* edges) by $\sim$6%.

The dodecahedral geometry can be derived from the $\delta$-$\lambda\lambda$-$\lambda\lambda$ type monoaquo seven-coordinate $[\mathrm{Fe(OH_2)EDTA}]^-$ species by replacing the lone water molecule with two water molecules disposed symmetrically on the plane of $\mathrm{MO_{a\lambda}O_{a\lambda}}$. The structural merits and shortcomings of this structure have been discussed by Hoard and coworkers.[1c,1d] Again a bidentate ligand is expected to favor the formation of this complex type. An eight-coordinate complex of either of the above two types should be expected to have the M–O distances in the range of 2.15–2.35 Å.[18,19]

The two other symmetrical types $\delta$-$\delta\lambda$-$\delta\lambda$ and $\delta$-$\lambda\delta$-$\lambda\delta$ have not been observed. Both of these types are expected to have two short contacts. One of each of these types of short contacts is observed in the lanthanide–EDTA complexes which will be described shortly. In the $\delta$-$\lambda\delta$-$\lambda\delta$ type, the e$\lambda$-a$\delta$ type rings are absent and the entire EDTA group will be far below the central plane (see above), simultaneously generating the two impossibly short contacts. It can be confidently expected that this type of complex will never occur even for the largest of the metal ions. The $\delta$-$\delta\lambda$-$\delta\lambda$ type is made entirely of the e$\lambda$-a$\delta$ ring types. In the direction roughly parallel to the line joining the atoms $N_1$ and $N_2$, the chelating rings will reach around the metal ion very effectively; the four oxygen atoms will be in the central plane when the $\gamma$ angles are down near 60° (=180°/3). Along the direction perpendicular to the plane of the E ring, there will be a large open space. This conformational type is the best candidate for a 12-coordinate icosahedral complex with two additional ligands more or less directly above the two nitrogen atoms and four additional ligands in a plane that is roughly perpendicular to the line $N_1$–$N_2$ so that an overall symmetry of $C_{2v}$ is approximately retained. For an ideal icosahedral geometry with the four oxygen atoms perfectly on the central plane, the metal–ligand distance *c* is given in terms of the $O_{e\delta}$–$O_{a\delta}$ separation *s* by $c = 0.952s$. At $s = 2.8$ Å, $c = 2.66$ Å, which gives the correct range of $\gamma$ angles according to Figure 2. Again three bidentate ligands, rather than six monodentate ligands, will be preferable for the formation of this complex type. However, the required M–O distance of $\sim$2.66 Å is a good deal longer than the average M–O distance of 2.54 Å observed in the $\mathrm{La(OH_2)_4HEDTA}$ species (see below). The problem of ring closure becomes acute at this long complexing bond length and significant distortions of ring bond lengths and angles are to be expected (see the caption for Figure 2). In any case, the possibility of a 12-coordinate EDTA complex must be looked for using metal ions that are even larger than La(III) or Th(IV). Stable complexes of such large metal ions as Ba(II) or Tl(I) are, however, so rare that the prospect of ever synthesizing such species must be regarded as dim at present.

The 10-coordinate $\mathrm{La(OH_2)_4HEDTA}$ complex[1e,3] is of the $\delta$-$\delta\delta$-$\lambda\delta$ type. A physical model of this type with a symmetrical E-ring shows an impossibly short contact between the atoms $O_{e\delta}$ and $O_{a\lambda}$. This problem is accommodated in the lanthanum acid complex by a counterclockwise rotation of the atoms attached to the $N_2$ atom around the M–$N_2$ bond where $N_2$ is the nitrogen atom from which the two rings $G_{a\lambda}$ and $G_{e\delta}$ branch. This rotation can be detected by the fact that the atom $C_2$ lies perfectly on the plane $\mathrm{MN_1N_2}$ within experimental error while the atom $C_1$ lies 0.64 Å out of the plane.[3a] (In the lanthanum salt complex below, the $C_1$ and $C_2$ atoms are +0.44 and −0.35 Å out of the plane, respectively.) Large differences between the E-ring $\phi_1$ and $\phi_2$ angles (Table III) and between the M–$N_1$ and M–$N_2$ bond lengths are also observed[3a] consistent with this rotation. The $O_{e\delta}$–$O_{a\lambda}$ distance after this adjustment is 2.76 Å. The best symmetrical polyhedron that approximates the disposition of the ten ligand atoms in this complex is the bicapped square antiprism.[3] Two water molecules and the two oxygen atoms of the G rings that branch at $N_1$ form an approximate square, which is "capped" by another water molecule, while the fourth water molecule, the atom $N_1$, and the two oxygen atoms of the other two G rings form another square, "capped" by the $N_2$ atom. Three M–O distances (O refers to the EDTA oxygens and not those of the water molecules) average to 2.54 Å. The fourth M–O distance, that of one M–$O_{e\delta}$, is long at 2.61 Å due to the protonation of the $G_{e\delta}$ ring involving $N_1$.

The nine-coordinate anions $[\mathrm{La(OH_2)_3EDTA}]^-$ and $[\mathrm{Tb(OH_2)_3EDTA}]^-$ are of the $\delta$-$\delta\lambda$-$\lambda\delta$ type.[1f,3] This type differs from the $\delta$-$\delta\delta$-$\lambda\delta$ type of the lanthanum acid complex in only one respect; one e$\delta$ ring of the acid complex has changed to an e$\lambda$ type in the anions. This change effectively removes the short contact in the acid complex described above—the $O_{e\lambda}$–$O_{a\lambda}$ distances in the anions are 3.16 and 2.98 Å, respectively, for the lanthanum and the terbium complexes. The shortest inter-ring ligand–ligand contact occurs between the $O_{a\delta}$ and $O_{e\lambda}$ atoms (the contact indicated by a dotted line in Figure 6). The distances observed are 2.86 and 2.79 Å, respectively, for the lanthanum and the terbium complexes. The coordination geometry approximates a monocapped square antiprism derivable from the bicapped square antiprism of the acid complex by removing a water molecule that served as the cap to a square base. The M–O distances (excluding the M–$\mathrm{H_2O}$ distances) average to 2.50 and 2.38 Å, respectively, for the lanthanum and the terbium complexes.

---

[18] Intorre and Martell[19] reported properties of the mixed Zr(IV)–chelate systems involving EDTA or DCTA and a number of bidentate ligands. Their suggestion of eight-coordination for these systems is in complete accord with the expectations presented here. It should be interesting to see which of the two types envisioned here actually occurs in these systems.

[19] B. J. Intorre and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 3618 (1961).

It should be noted that there is one aδ ring in the ten-coordinate acid species and the mean plane of the four oxygen atoms is some 0.78 Å below the metal ion.[3a] In the nine-coordinate anionic species there are two eλ-aδ type rings. The four oxygen atoms are still below the metal ion but the separation decreases to 0.62 and 0.49 Å in the lanthanum and the terbium complexes, respectively. Concomitant with this change in conformational type is the shrinkage of the free space (*i.e.*, free from the chelating agent) around the metal ion and the resulting ejection of one water molecule out of the coordination sphere. An interesting possibility may be noted here in connection with this kind of discrete change in the conformational types. The lanthanide ions have closely similar chemical properties and have ionic sizes that vary in a systematic and successive manner. The EDTA chelate of, say, the largest ion will belong to a certain conformational type. As successively smaller ions along the series are substituted, the complexing bond lengths will decrease and the complex will become more and more compact. It is possible that at a certain point along the series, overcrowding of ligands will force a change in conformational type. Just before such a change, the ligands of the EDTA moiety will be in a most compact state so as to provide enough space for a maximum number of water molecules. After the change, the EDTA moiety will adopt a more spacious conformation and the space available to the water ligands will shrink, resulting in an ejection of one or more of the water molecules from the coordinate sphere. The reported thermodynamic behavior of lanthanide–EDTA complexes[2] is in qualitative agreement with that expected from this type of transition occurring in the region of Sm–Gd. A fuller discussion relating to this possibility will be presented in a report currently under preparation.[3b]

The conformational types δ-δλ-λλ and δ-δλ-δδ contain three of the eλ-aδ type rings. These types are therefore probably not very suitable for forming complexes with high coordination number. For complexes with coordination numbers of 8 or less, on the other hand, the types δ-λλ-λλ and δ-δδ-δδ will be preferable because of their symmetric nature.[20] The types δ-λλ-λδ and δ-λλ-δδ contain one or two eλ-aδ type rings and each contains one short contact. Plausibility of occurrence of these types is difficult to assess because of their highly unsymmetric character.

**Acknowledgment.**—Part of this work was done while I was a postdoctoral fellow at Cornell University, supported by NSF Grant No. GP-6710X. I thank Professor J. L. Hoard for initiating me into this field, for reading the original rough draft, and for making several valuable comments. The financial support by the National Institutes of Health *via* the Health Science Advancement Award to the University of Kansas is very gratefully acknowledged.

---

(20) It should, however, be noted that the $\phi_1$ angles of one of the axial rings of the species $[\mathrm{CoEDTA}]^-$ and $[\mathrm{Fe(OH_2)EDTA}]^-$ are essentially 0° (Table III). These species may thus be regarded as an intermediate of the types δ-λλ-λλ and δ-δλ-λλ. Whether the dissymmetry between the two axial rings is an inherent property of this type of complexes or is a result of packing forces in the solid state is a difficult question to settle unambiguously. There is no *a priori* reason that the system should be unsymmetrical and hence the latter possibility is assumed throughout this discussion. The fact that this phenomenon occurs in all three complexes which crystallize in very different space groups and also in the $\mathrm{Ni(OH_2)H_2EDTA}$ species would, however, favor the former possibility. If it is indeed the case that the $\phi_1$ angle of one of the aλ rings of the δ-λλ-λλ type must remain near zero, then it becomes fairly certain that the diaquo eight-coordinate dodecahedral complex based on the δ-λλ-λλ type will never be realized since this geometry requires large ruffling of both of the axial rings and thus an increase in $\phi_2$ angle to 25–30° if the $\phi_1$ angle is to remain 0°.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SIMON FRASER UNIVERSITY,
BURNABY 2, BRITISH COLUMBIA, CANADA

# The Crystal Structure of Ammonium Oxodiperoxoamminevanadate(V)

BY R. E. DREW AND F. W. B. EINSTEIN*

*Received September 1, 1971*

The crystal structure of the compound $\mathrm{NH_4[VO(O_2)_2(NH_3)]}$ has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the orthorhombic space group *Pnma* with four formula units in a cell of dimensions $a$ = 8.370 (2) Å, $b$ = 6.877 (1) Å, and $c$ = 9.244 (2) Å. Refinement by full-matrix least-squares methods has given a conventional $R$ value of 3.1% for the 566 observed reflections. The coordination of the vanadium atom can best be described in terms of a pentagonal pyramid, the four oxygens of the two peroxo groups and the ammonia nitrogen atom forming the distorted base of the pyramid, while the vanadyl oxygen occupies the apical position. Each ion has crystallographic mirror symmetry, the peroxy groups being the only nonhydrogen atoms lying off the mirror plane. Analysis of the motion of the anion as a rigid body yields interatomic distances of 1.883 (3) and 1.882 (3) Å for the V—O peroxo bonds, 1.606 (3) Å for the V═O bond, 2.110 (4) Å for the V—$\mathrm{NH_3}$ distance, and 1.472 (4) Å for the O—O peroxo bond.

## Introduction

An extensive investigation of the chemistry of the transition metal–peroxy complexes has been carried out,[1] but relatively little structural chemistry of peroxo complexes which do not involve chromium, molybdenum, and cobalt has been elucidated. The only previous structural work known to us on peroxovanadates was the demonstration of the isomorphism of the compounds $\mathrm{K_3[M^V(O_2)_4]}$ ($\mathrm{M^V}$ = V, Cr, Nb, or Ta) by X-ray powder photographic methods,[2] the chromium compound having been shown to have a quasidodecahe-

---

(1) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964).

(2) J. E. Fergusson, C. J. Wilkins, and J. F. Young, *J. Chem. Soc.*, 2136 (1962).