Stereochemistry of Discrete Eight-Coordination. IV. The Structure of the Bis(nitrilotriacetato)zirconate(IV) Ion in Crystals of the Potassium Salt[1,2]

J. L. Hoard,[3] Enid W. Silverton,[4] and J. V. Silverton

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received October 5, 1967*

Abstract: A quantitative description of the bis(nitrilotriacetato)zirconate(IV) ion, $Zr[N(CH_2COO)_3]_2^{2-}$ (written as ZrA_2^{2-}), comes from a three-dimensional X-ray analysis of crystalline structure for the potassium salt, $K_2ZrA_2 \cdot H_2O$. The orthorhombic unit cell containing $4K_2ZrA_2 \cdot H_2O$ has $a = 14.84$, $b = 14.83$, and $c = 8.67$ Å; the space group is Ccc2-$C_{2v}{}^{13}$. The coordination group is unmistakably dodecahedral with two nitrogen and two oxygen atoms at *A* vertices, and four oxygen atoms at *B* vertices (the notations are from part I, "Basic Analysis," in this series). Complexing bond lengths of $Zr-O^B = 2.13$, $Zr-O^A = 2.25$, and $Zr-N = 2.44$ Å, each with an estimated standard deviation below 0.01 Å, are pertinent to the discussion of the bonding pattern. The observed stereoisomeric form of the complex anion appears to handle the problems of ring structure and nonbonding repulsions in a superior manner, better, indeed, than any competing form whether this be based upon the dodecahedron, the antiprism, or the cube.

Studies carried out by Intorre and Martell[5] led them to conclude that the bis(nitrilotriacetato)zirconate(IV) complex, $Zr[N(CH_2COO)_3]_2^{2-}$ (to be written[2] ZrA_2^{2-}), exists in aqueous solutions as a multidentate eight-coordinate species. Several stereoisomeric forms of an eight-coordinate ZrA_2^{2-} ion in which the quadridentate chelating agent uses all of its "teeth" or "claws" are formally possible, but all are subject to the geometrical and energetic constraints imposed by branching ring structure and multiple ring formation. The character of these constraints is displayed in existing structural data for the ethylenediaminetetraacetato (EDTA) chelates of a wide variety of metal ions.[6] Of primary importance in delimiting the choice of coordination polyhedron for the ZrA_2^{2-} ion is the branching of three glycinate rings from each nitrogen atom coupled with the requirement that the six bond angles at this bridgehead (three within rings and three between rings) must all lie within the range 109.5 ± 5°. Furthermore, the "bite" of a glycinate ligand that spans an edge of the coordination polyhedron, more elegantly described as the ring-span or N–O separation in the five-membered chelate ring, may vary within the range 2.61–2.80 Å, but with an evidently strong preference for a value near to the 2.67 Å that corresponds to the use of standard bond angles and distances in a flat glycinate moiety. With the notable exception of the complexes formed with low-spin Co(III),[6a] the metal–oxygen and, particularly, the metal–nitrogen bonds are quite generally much too long to be compatible with a planar glycinate ring in which ideal bond angles are maintained at the nitrogen and the two carbon atoms; a significant puckering and/or folding of the ring together with modest relaxations from the requirement of ideal bond angles allows the ring span to remain within structurally acceptable bounds.[7]

It was earlier pointed out[8] that maintenance of exact threefold symmetry in the disposition of the three glycinate rings branching from each nitrogen atom leads quite naturally to a configuration for a ZrA_2^{2-} complex that, while taking account of ring constraints, is based upon a quasi-cubic coordination group; but it was simultaneously reported[8] that the ZrA_2^{2-} ion, as it exists in crystals of the potassium salt, utilizes the superior coordination geometry[9] of the triangular dodecahedron within a molecular configuration that handles most satisfactorily the constraints attending chelation. Indeed, it will subsequently appear that the observed stereoisomer handles the problems of ring structure better, and those of nonbonding repulsions not less well, than any competing form, whether this be based upon the triangular dodecahedron, the square antiprism, or the cube.

Documentation of the structure determination for $K_2ZrA_2 \cdot H_2O$ and a full account of the interpretations accorded to the structural results are presented at this time. The interesting, but ill-defined, role of π bonding in favoring one set of Zr–O complexing bonds over the other receives special attention.

Experimental Section

Zirconium(IV) chloride, solid nitrilotriacetic acid, and the carbonates of potassium and rubidium were the starting materials for prep-

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[2] The abbreviation, NTA, and the short formula, H_3A, are used throughout for nitrilotriacetic acid, $N(CH_2COOH)_3$.

[3] Author to whom correspondence should be addressed.

[4] Gulf Research and Development Predoctoral Fellow, 1962–1963; Proctor and Gamble Summer Fellow, 1961.

[5] B. I. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 358 (1960).

[6] (a) H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959); (b) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959); (c) J. L. Hoard, G. S. Smith, and M. D. Lind in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 296; (d) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964); (e) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **3**, 34 (1964); (f) M. D. Lind, B. Lee, and J. L. Hoard, *J. Am. Chem. Soc.*, **87**, 1611 (1965); (g) J. L. Hoard, B. Lee, and M. D. Lind, *ibid.*, **87**, 1612 (1965); (h) G. H. Cohen and J. L. Hoard, *ibid.*, **88**, 3228 (1966).

[7] The interdependent roles played by coordination number, complexing bond lengths, ring constraints, and nonbonding repulsions in determining chelate stereochemistry are appraised in a paper now in preparation.

[8] J. L. Hoard, E. Willstadter, and J. V. Silverton, *J. Am. Chem. Soc.*, **87**, 1610 (1965).

[9] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963), give comprehensive descriptions and critical appraisals of the eight-coordination polyhedra.

Table I. Unit Cell Data for the Potassium and Rubidium Salts

Salt	Lattice constant ± std dev $a \pm \sigma$, Å	 $b \pm \sigma$, Å	 $c \pm \sigma$, Å	Density ρ_o, g/cc
$K_2ZrA_2 \cdot H_2O$	14.843 ± 0.005	14.83 ± 0.01	8.673 ± 0.005	1.984
$Rb_2ZrA_2 \cdot 2H_2O$	14.93 ± 0.01	14.83 ± 0.01	8.94 ± 0.01	2.28

aration of the crystalline salts $K_2ZrA_2 \cdot H_2O$ and $Rb_2ZrA_2 \cdot 2H_2O$. Procedures adapted from those described by Intorre and Martell[5] gave the complexed species in aqueous solution at pH 6; isothermal evaporation of these solutions furnished single crystals of the salts for structure determination by X-ray diffraction analysis.

A preliminary X-ray study of the crystals utilized oscillation and Weissenberg photographs taken with Cu Kα radiation. The salts crystallize, nearly isomorphously, in the orthorhombic system; the pattern of systematically absent spectra in conjunction with positive tests for piezoelectricity point uniquely to C_{2v}^{13}-Ccc2 as the space group.[10] Lattice constants derived from data taken with Mo Kα radiation on a General Electric XRD-5 spectrometer assembly, and densities calculated in each case for a cell content of $4M_2ZrA_2 \cdot nH_2O$, are given in Table I. Approximately measured densities of 2.03 and 2.24 g/cc for the respective potassium and rubidium salts are indicative, for both substances, of a water content intermediate between the monohydrate and dihydrate formulations; the water content assigned to each salt in Table I is that established by structure determination. It is to be noted, however, that X-ray data of the quality required for an accurate structure determination were furnished only by the potassium salt, and that the crystal specimen used for the counter recording of the diffracted intensities displayed no evidence of deterioration during the entire period of measurement (*vide infra*).

Three-dimensional intensity data for both salts were measured on a G.E. spectrometer assembly with Mo Kα radiation by the stationary-crystal–stationary-counter procedures described earlier.[11] Data for the rubidium salt, recorded in 1961 from a crystal specimen having a volume less than 10% of the optimum value prescribed for the experimental technique, proved to be adequate for a qualitatively certain determination of structure. The semiquantitative stereochemical description thus provided of the complex anion was only suggestive of the more detailed conclusions that were subsequently based upon the structure determination for the potassium salt. Success in the preparation of usable crystals of $K_2ZrA_2 \cdot H_2O$, achieved some 2 years later, led to the results presented in this paper. The single crystal of the potassium salt used for structure determination was in block form with edges about 0.35 × 0.40 × 0.40 mm. Throughout the period of counter measurement of diffracted intensities, periodically checked reference reflections gave reproducible intensities. Of a possible 2300 independent reflections having $(\sin \theta)/\lambda < 0.81$, 1900 gave intensities which were surely above background. With a linear absorption coefficient of the crystal for Mo Kα radiation of but 1.1 mm^{-1}, no corrections for absorption were deemed necessary. The intensity data for both salts were reduced by usual procedures to the relative squared amplitudes, $|F_{hkl}|^2$, needed for structure determination.

Interpretation of the Patterson syntheses $P(uvw)$ of the $|F_{hkl}|^2$ squared amplitudes obtained from the crystals of both salts led to placement of zirconium atoms on twofold axes in the special positions[10] 4(c): $^1/_4, ^1/_4, z;\ ^1/_4, ^3/_4, ^1/_2 + z;\ ^3/_4, ^3/_4, z;\ ^3/_4, ^1/_4, ^1/_2 + z$ of Ccc2, with z conveniently chosen as zero, and rubidium or potassium ions in the general positions[10] 8(d): $x, y, z;\ \bar{x}, \bar{y}, z;\ \bar{x}, y, ^1/_2 + z;\ x, \bar{y}, ^1/_2 + z;$ etc. The heavy atom vectors of the Patterson syntheses were compatible with either of two closely related choices of numerical coordinates for the alkali cations, but it turned out that the correct combination of cation and zirconium coordinates gave from the outset a lower value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, with F_o and F_c the respective observed and calculated[12] reflection amplitudes. Positions of light atoms were then developed from the amplitude data by Fourier synthesis in cycles of successive approximation.

Detailed refinement of the $K_2ZrA_2 \cdot H_2O$ structure utilized anisotropic thermal parameters for individual atoms and diagonal least-squares minimization of each of the functions: $\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$, with $\sqrt{w} = 1$ for $|F_o| < 8$, $8/|F_o|$ for $|F_o| > 8$; $\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$, with $\sqrt{w} = 1$ for $|F_o| < 8$, $64/|F_o|$ for $|F_o| > 8$. The alternative procedures gave generally consistent results with values of the residual, R, of 0.082 and 0.087. Parameters given by the first procedure were then used as input for the first of two cycles of difference synthesis; only quite small and mostly oscillatory shifts in parameters were indicated. The atomic coordinates listed in Table II were obtained by averaging the results of the least-squares refinement with those of the final difference synthesis; the accompanying standard deviations were estimated by Cruickshank's procedures[13] for the noncentrosymmetric case. Inasmuch as the thermal parameters are neither very large nor unduly anisotropic, the more immediately useful isotropic values given by the final cycle of isotropic least-squares refinement are listed in Table II.

Table II. Parameter Data[a] for the $K_2ZrA_2 \cdot H_2O$ Structure

Atom type	(Coordinates ± std dev) × 10^4 $x \pm \sigma_x$	 $y \pm \sigma_y$	 $z \pm \sigma_z$	B, Å^2
N	3238 ± 2	1173 ± 2	1080 ± 3	1.4
O_1	1881 ± 1	1233 ± 1	−958 ± 2	1.5
O_2	3474 ± 2	2086 ± 2	−1650 ± 3	1.9
O_3	3461 ± 2	2884 ± 1	1711 ± 3	1.8
O_4	1454 ± 2	−201 ± 2	−549 ± 3	2.3
O_5	4420 ± 2	2622 ± 2	3654 ± 3	2.4
O_6	4226 ± 2	913 ± 2	−2645 ± 3	2.5
C_1	2576 ± 2	414 ± 2	1100 ± 4	1.9
C_2	3538 ± 2	1392 ± 2	2672 ± 3	1.8
C_3	4010 ± 2	958 ± 2	91 ± 4	1.8
C_4	3886 ± 2	1310 ± 2	−1556 ± 4	1.5
C_5	1935 ± 2	486 ± 2	−228 ± 3	1.4
C_6	3843 ± 2	2356 ± 2	2705 ± 3	1.3
OH_2	0	0	−2429 ± 7	3.4
Zr	$^1/_4$	$^1/_4$	0	0.91
K	694 ± 0.4	1553 ± 0.3	−3577 ± 1	2.42

[a] Complete amplitude data have been submitted as Document No. 9777 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20450 A copy may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Stereochemistry of the Complex Anion

The twofold axis required of the ZrA_2^{2-} complex in the crystal is also the sole element of symmetry that the free stereoisomer could have. The coordination polyhedron, nonetheless, is unmistakably of the triangular dodecahedral type.[9,14] It is most efficiently described by specifying wherein the shape parameters expected[9] for a ZrO_8 dodecahedron of maximum symmetry, D_{2d}-

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(10) "International Tables for X-ray Crystallography," Vol. I, "Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, p 123.

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

(12) The atomic form factors used for zirconium, potassium, and rubidium were from L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957), corrected, when required, for dispersion following C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955). Form factors for lighter atoms were those of J. Berghuis, *et al.*, *ibid.*, **8**, 478 (1955).

(13) D. W. J. Cruickshank, *ibid.*, **9**, 747 (1956).

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

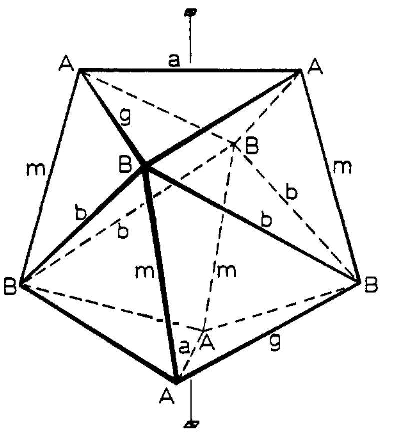

Figure 1a. The D_{2d}-$\bar{4}m2$ dodecahedron. Equivalent trapezoids, BAAB, lie in the two orthogonal mirror planes that intersect in the unique $\bar{4}$ (or z) axis. The polyhedron center is the point of intersection of the $\bar{4}$ and two twofold axes. Each twofold axis passes through the midpoints of a pair of opposite b edges. The labeling of vertices and of edges shows how these sort into symmetry-equivalent groups.

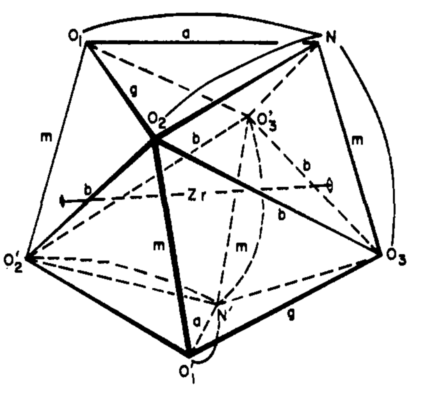

Figure 1b. Diagram of the coordination group and the chelation pattern in the dodecahedral bis(nitrilotriacetato)zirconate(IV) ion. Polyhedron vertices are labeled in agreement with Tables II–VII in the text. Primed and unprimed symbols distinguish each pair of atoms that are related through the single twofold axis retained in the complex.

$\bar{4}m2$,[15] are modified by the substitution in two positions of nitrogen atoms for oxygen and by ring formation. A dodecahedral ZrO_8 group of D_{2d} symmetry is properly written as $ZrO^A{}_4O^B{}_4$ or MA_4B_4 in recognition of the fact that ligand classes O^A and O^B (or A and B) necessarily are nonequivalent (see Figure 1). No meaningful quantum mechanical estimate of the energetic difference between the two bond types exists; it appears, however, that M–B bonds are favored through feeling much less strongly the adverse effects of the mutual (closed-shell) repulsions of the ligands and by a net contribution from π bonding (*vide infra*). A significant lengthening of the eight edges g at the expense of the two edges a and the four edges m (Figure 1), as observed in several complexes, is attributable to a general minimization of nonbonding repulsions—and, perhaps in part, to a marked preference for a unique set of bond angles at the central atom.

The predicted parameters for a ZrO_8 dodecahedron of D_{2d} symmetry are[9]: average Zr–O = 2.198 ± 0.005 Å; M–A/M–B = 1.03; $a = m = 2.57, g = 2.73, b = 3.28$ Å; $\Theta_A = 35.2°$, $\Theta_B = 73.5°$. The average Zr–O bond length is essentially the mean value from five accurate studies of zirconium(IV) in both antiprismatic and dodecahedral coordination with oxygen. However, the bond-length ratio, M–A/M–B = 1.03, from the study of the tetrakis(oxalato)zirconate(IV) ion,[16] is thought to be conservatively small for reasons cited earlier.[9] Θ_A and Θ_B are the respective angles made by bonds M–A and M–B with the unique $\bar{4}$ axis.

In the $ZrA_2{}^{2-}$ complex, a nitrogen atom is placed at an A site (Figure 1), and the three glycinate rings which branch from this nitrogen atom span edges a, g, and m to place oxygen atoms O_1, O_2, and O_3 at sites of types A, B, and B, respectively. The twofold axis which $ZrA_2{}^{2-}$ retains then generates the second of the chelated nitrilotriacetato groups from the first, *i.e.*, N → N′, $O_1 \rightarrow O_1'$, etc. This description applies equally to either of a pair of optical isomers. In the systematic notation subsequently to be used for discussing stereoisomerism, the observed stereoisomer is represented as (*Aagm; A′a′g′m′*) or, more simply, as $(Aagm)^2$; the capital letter identifies the type of site occupied by nitrogen, small letters the edges spanned by the branching glycinate rings.

We see from Table III that the Zr–O_2 and Zr–O_3 bonds, both formally of M–B type, differ in length by an apparent 0.012 Å, and average to 2.130 Å, whereas the Zr–O_1 bond, of M–A type, comes out to be 2.251 Å. A Zr–O bond length of 2.191 Å, the mean for M–A and M–B bond types, compares favorably with the 2.198 Å cited from earlier studies. The M–A/M–B ratio of 2.251/2.130 = 1.057 in $ZrA_2{}^{2-}$ is significantly larger than the 1.03 found[16] in $Zr(C_2O_4)_4{}^{4-}$; differences in the magnitude and in the distribution of resultant charge carried by the two complexes probably are pertinent in this connection. Considering that the appropriate covalent radii[17] of nitrogen and oxygen differ by only 0.04 Å and that the Zr–N bond in $ZrA_2{}^{2-}$ is of M–A type, one might then expect Zr–N = 2.29 Å; it is in fact (Table III) some 0.15 Å larger still. Differences of 0.15–0.30 Å in the M–N and M–O bond lengths of the ethylenediaminetetraacetato (EDTA) chelates of Fe(III),[6e] Mn(II),[6d] and La(III)[6f,g] are well established, whereas "normal" differences (≃0.04 Å) in the EDTA chelates of Co(III)[6a] and Ni(II)[6b] are observed. If one ignores chemical experience in favor of qualitative bonding theory, the long and presumably weak Zr–N bonds in $ZrA_2{}^{2-}$ are rather surprising. It might be supposed that Zr(IV), with its full panoply of eight $4d^45sp^3$ orbitals available for σ bonding, could provide the strong quantum mechanical deformation of amino nitrogen needed to render this ligand strongly complexing.

The principal factors requiring distortion of the coordination polyhedron from the symmetrical D_{2d} form are the constraints attending ring formation, the large discrepancy in the length of the Zr–N and Zr–O bonds, and the larger (by about 0.10 Å) packing radius of nitro-

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[15] The $\bar{4}m2$ description of D_{2d} places the equivalent pair of secondary (x, y) axes in the mutually perpendicular mirror planes (see Figure 1). In the alternative $\bar{4}2m$ description x and y coincide with the twofold axes.

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

[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 224, 246.

Table III. Parameters of the Coordination Dodecahedron

A. Polyhedron Edges and Bond Lengths

Bond or edge	Type in Figure 1	Length ± σ, Å	Bond or edge	Type in Figure 1	Length ± σ, Å
Zr–N	M–A	2.439 ± 0.009	N–O_3'	*g*	2.936 ± 0.012
Zr–O_1	M–A	2.251 ± 0.007	O_1–O_2'	*m*	2.619 ± 0.011
Zr–O_2	M–B	2.124 ± 0.009	O_1–O_2	*g*	2.747 ± 0.011
Zr–O_3	M–B	2.136 ± 0.008	O_1–O_3'	*g*	2.708 ± 0.011
N–O_1	*a*	2.681 ± 0.012	O_2–O_3	*b*	3.145 ± 0.012
N–O_2	*g*	2.749 ± 0.012	O_2–O_2'	*b*	3.140 ± 0.012
N–O_3	*m*	2.616 ± 0.012	O_3–O_3'	*b*	3.072 ± 0.011

B. Angles Subtended at Zr(IV) by Dodecahedral Edges

Type		Angle ± σ,	Type		Angle ± σ,
Angle	Edge	deg	Angle	Edge	deg
$NZrO_2$	*g*	73.7 ± 0.3	$NZrO_1$	*a*	69.5 ± 0.2
O_1ZrO_2	*g*	77.7 ± 0.3	$NZrO_3$	*m*	69.4 ± 0.3
O_1ZrO_3'	*g*	76.3 ± 0.3	O_1ZrO_2	*m*	73.5 ± 0.3
$NZrO_3'$	*g*	79.5 ± 0.4	(OZrO)[a]	*b*	94.3 ± 0.3[a]

[a] Averaged value for four angles reported.

gen as compared with oxygen. Explicit consideration of this last factor is required, however, only for interring packing contacts between nitrogen and oxygen. The general pattern of edge lengths displayed in Table III is quite surprisingly like that of the D_{2d} dodecahedron. All polyhedron edges *g*, including the two of N–O_2 type which are simultaneously ring spans, are above 2.70 Å. Displacement of the nitrogen atom by ~0.08 Å from the O_1O_3Zr plane allows the N–O_2 ring span of *g* type to be shorter at 2.75 Å than the N–O_3' inter-ring separation at 2.94 Å; the sum of the van der Waals radii[17] is 2.90 Å. O–O contacts between rings are large (2.71, 2.75 Å) as *g* edges, small (2.62 Å) as *m* edges. The two other *m* edges are also ring spans, N–O_3 = 2.616 ± 0.012 Å. Indeed, the ring spans N–O_3 at 2.62 Å and N–O_2 at 2.75 Å are near the extreme values of the range observed for glycinate rings in some nine different structural types of EDTA complexes studied in this laboratory. In view of the long Zr–N and Zr–O_1 bonds, the ring span N–O_1 of edge type *a* is about as small at 2.68 Å as can reasonably be anticipated. The bond angles subtended at Zr(IV) by the short ring spans N–O_1 of *a* type and N–O_3 of *m* type are, respectively, 69.5 and 69.4° (Table III), both significantly smaller than the angle of 73.5° subtended by the short edge (not a ring span) O_1–O_2' of *m* type.

Some averaged parameters of the coordination group in ZrA_2^{2-}, for comparison with those of the D_{2d} dodecahedron listed earlier, are the following: $Zr\text{–}O^A/Zr\text{–}O^B = 1.057$; Zr–O = 2.191 ± 0.008 Å as the average of bond types; $Zr\text{–}L^A/Zr\text{–}L^B = 1.101$ (L includes both O and N); average Zr–L = 2.238 Å; $a = 2.68$, $m = 2.62$, $g = 2.785$, $b = 3.13$ A; $2\theta_A = 69.5 \pm 0.4°$, $2\theta_B = 147.6 \pm 0.6°$.

The characteristic isosceles trapezoid BAAB (Figure 1) in the D_{2d} dodecahedron becomes in ZrA_2^{2-} the somewhat irregular figure $O_3NO_1O_2'$ for which the principal dimensions have been given. Distortion from planarity in this trapezoidal figure is small. Atoms N and O_2' lie 0.06 Å above the mean plane, O_3 and O_1, an equal distance below. The dihedral angle between the mean planes of the two trapezoidal figures, $O_3NO_1O_2'$ and $O_3'N'O_1'O_2$, is 88.4°. Distortion of the dodecahedral coordination group in ZrA_2^{2-} from the symmetrial D_{2d} polyhedron is small enough that one tends to overlook it upon cursory examination of an accurately scaled model of the complex.

Bond lengths and bond angles within the complex anion, Tables IV and V, are tabulated in vertical arrays which, as indicated by the subheadings, correspond each to a particular ring type. The first five entries in each column take one around the five-membered ring; additional entries complete the description of the carboxylate group and give the other ring parameters specified in the footnotes to Tables IV and V. Any row of data in either table affords a direct comparison of corresponding parameters for the three ring types. A glycinate ring is illustrated in Figure 2.

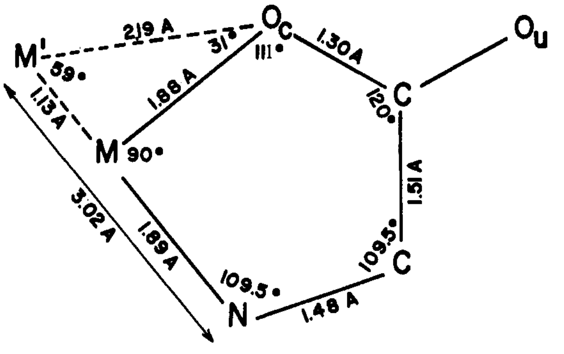

Figure 2. Diagram of a planar glycinate ring that uses ideal N–C, C–C, and C–O bond lengths and ideal bond angles at nitrogen and carbon atoms. M and M′ correspond, respectively, to Co(III) and Zr(IV) as discussed in the text.

Inasmuch as the C–C and C–N bond lengths are expected[6d–f] to be nearly independent of variations in configuration of the glycinate ring, we look first at the third and fourth rows of Table IV. The degree of internal consistency in each set of bond lengths is just fair and the standard deviations are rather large: consequently, we concentrate attention on suitably taken averaged values for C–C, C–N, and C–O bond lengths. Averaged lengths with mean deviations for C–C and

Table IV. Bond Lengths in the Complex Anion

In ring *Aa*		In ring *Ag*		In ring *Am*	
Bond	Length ± σ, Å	Bond	Length ± σ, Å	Bond	Length ± σ, Å
Zr–O_1	2.251 ± 0.007	Zr–O_2	2.124 ± 0.009	Zr–O_3	2.136 ± 0.008
O_1–O_5	1.278 ± 0.013	O_2–C_4	1.306 ± 0.014	O_3–C_6	1.295 ± 0.013
C_5–C_1	1.497 ± 0.016	C_4–C_3	1.532 ± 0.015	C_6–C_2	1.499 ± 0.015
C_1–N	1.495 ± 0.015	C_3–N	1.467 ± 0.014	C_2–N	1.486 ± 0.014
N–Zr	2.439 ± 0.009	N–Zr	2.439 ± 0.009	N-Zr	2.439 ± 0.009
O_5–O_4	1.275 ± 0.014	C_4–O_6	1.222 ± 0.015	C_6–O_5	1.251 ± 0.014
N–O_1[a]	2.681 ± 0.012	N–O_2[a]	2.749 ± 0.012	N–O_3[a]	2.616 ± 0.012

[a] The *ring span* defining an edge of the coordination polyhedron.

Table V. Bond Angles in the Complex Anion

In ring *Aa*		In ring *Ag*		In ring *Am*	
Type	Angle ± σ, deg	Type	Angle ± σ, deg	Type	Angle ± σ, deg
$NZrO_1$	69.5 ± 0.2	$NZrO_2$	73.7 ± 0.3	$NZrO_3$	69.4 ± 0.3
ZrO_1C_5	121.0 ± 0.3	ZrO_2C_4	122.2 ± 0.4	ZrO_3C_6	126.4 ± 0.4
$O_1C_5C_1$	118.8 ± 0.4	$O_2C_4C_3$	114.5 ± 0.7	$O_3C_6C_2$	115.5 ± 0.5
C_5C_1N	110.8 ± 0.6	C_4C_3N	112.2 ± 0.7	C_6C_2N	108.5 ± 0.5
C_1NZr	108.5 ± 0.4	C_3NZr	107.6 ± 0.5	C_2NZr	108.3 ± 0.4
$O_1C_5O_4$	123.3 ± 0.7	$O_2C_4O_6$	124.8 ± 0.7	$O_3C_6O_5$	123.1 ± 0.6
$O_4C_5C_1$	117.8 ± 0.7	$O_6C_4C_3$	120.5 ± 0.6	$O_5C_6C_2$	121.3 ± 0.6
C_2NC_3[a]	110.9 ± 0.5	C_1NC_2[a]	110.6 ± 0.5	C_3NC_1[a]	110.9 ± 0.6

[a] Angle at nitrogen for junction of two rings.

C–N bonds are, respectively, 1.509 ± 0.015 and 1.483 ± 0.010 Å, of which the first happens to be just 0.010 Å smaller, the second just 0.010 Å larger, than the C–C and C–N bond lengths obtained from the more accurate structure determinations for EDTA chelates of Fe(III)[6e] and Mn(II).[6d] Our results, indeed, are in good agreement with other accurate determinations of these bond lengths.[18]

Using O_c and O_u to represent oxygen atoms accordingly as these are or are not complexed to Zr(IV), we obtain from the second and sixth rows of Table IV averaged C–O_c and C–O_u bond lengths, with their mean deviations, of 1.293 ± 0.011 and 1.249 ± 0.018 Å, respectively. This difference in bond lengths is indicative of rather strong complexing to Zr(IV), comparable with that in the EDTA chelate of Fe(III).[6e] We should, however, distinguish two cases: more strongly modified C–O distances are expected for the rings *Ag* and *Am* with their short Zr–O complexing bonds of M–B type than for the ring *Aa* with its significantly longer Zr–O bond of M–A type. Averaged C–O_c and C–O_u bond lengths, with their mean deviations, are 1.301 ± 0.006 and 1.237 ± 0.015 Å, respectively, for the *Ag* and *Am* rings, whereas the C–O_c (C_5–O_1) length at 1.278 Å and the C–O_u (C_5–O_5) length at 1.275 Å in the *Aa* ring are equal within the accuracy of the structure determination. A contributing factor to this apparent equalization of the C_5–O_1 and C_5–O_5 bond lengths, which is absent from the other ring systems, is the rather short hydrogen bond at 2.721 ± 0.010 Å formed by the "uncomplexed" O_5 with a water molecule. Although one supposes that the C_5–O_1 bond should be, and probably is, somewhat longer than C_5–O_5, present data are inadequate to settle this point. Relative weakness of the Zr–O_1 bond of M–A type is, nonetheless, consistently indicated.

The sum of the three bond angles subtended at the central carbon atom in a carboxylate group is in no case (Table V) less than 359.8°, and every carboxylate group is flat within experimental error. Angles at carboxylate carbon of the O_cCO_u class (sixth row in Table V) show the minimum of variation with ring type; the averaged O_cCO_u angle, with mean deviation, is 123.7 ± 0.8°. Angles of the O_uCC class (seventh row in Table V) cluster about the ideal 120° value, but with a significant difference of 4.3° between the largest and the smallest values. The detailed configuration of each carboxylate group is primarily dependent upon the bond angle of O_cCC class which, as a ring angle, is itself subject to the constraints imposed by chelation and all that this implies. Angles of the O_cCC class (third row in Table V) all are below 120°, with 4.3° as the difference between the largest (118.8°) and smallest (114.5°) values.

The spread (3.7°) in the ring bond angles at methylene carbon (fourth row in Table V) also is substantial; the angle O_4C_3N (112.2°) in the *Ag* ring of maximum ring span (2.75 Å) shows the largest deviation from the regular tetrahedral value (109.5°). It is, indeed, only the bond angles at nitrogen that, as two distinct classes, are essentially preserved irrespective of ring type. The ring angles of the CNZr class (fifth row in Table V) average to 108.1° with a mean deviation of but 0.4°, and the external angles at nitrogen between rings (last row in Table V) average to 110.8° with a mean deviation of just 0.1°; further, these averaged values lie 1.3–1.4° to either side of the regular tetrahedral angle. Thus the bond parameters of the nitrogen atom conform effectively to C_{3v}-3m symmetry; with the exception of the weak complexing bond to Zr(IV), the approximation to regular tetrahedral symmetry is not bad.[19]

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(18) *Cf.* "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

The sum of the five interior angles in a glycinate ring gives, when compared with the 540° maximum, a useful measure of the over-all departure from planarity. Sums of 528.6° for *Aa*, 530.2° for *Ag*, and 528.1° for *Am* in ZrA_2^{2-} suggest a quasi-equivalent over-all treatment of the three rings tending to minimize the effect of differences in detailed configuration. It is easily demonstrated that, even in the free stereoisomer, these rings cannot be planar. Figure 2 is useful in this connection.

Taking ideal bond angles of 120° at carboxylate carbon and 109.5° at methylene carbon together with $C\text{–}O_c$, C–C, and C–N bond lengths of 1.30, 1.51, and 1.48 Å, respectively, the ideal ring span, $O_c\text{–}N$, comes out at 2.67 Å (or less if there be any departure from planarity), a value which lies a little below the midpoint of the range, 2.60–2.80 Å, observed for glycinate rings. Simultaneous maintenance of a 109.5° bond angle at nitrogen within a fully planar ring gives for the length of the complexing bond to oxygen, $M\text{–}O_c = (2.67 \sin 44.8°)/\sin O_cMN$. The minimum value of $M\text{–}O_c$, corresponding to 90° for the angle O_cMN, is 1.88 Å, and the M–N bond length becomes 1.89 Å. Only a trivial relaxation of the assumed restraints is needed to accommodate the $M\text{–}O_c$ and M–N bond lengths of 1.88 and 1.92 Å observed in the two nearly planar glycinate rings of the EDTA complex of cobalt(III).[6a] If, however, M be taken to be Zr(IV) with Zr–O as 2.19 Å, one obtains 3.02 Å for Zr–N, 59.0° for the angle O_cZrN, and 142° for CO_cZr. A sufficiently pronounced folding of the ring along the line connecting the nitrogen and the oxygen atoms, *i.e.*, along an edge of the coordination polyhedron, is the most obvious means by which—with maintenance of the regular tetrahedral angle at nitrogen—the Zr–N and Zr–O bond distances and the NZrO and ZrOC bond angles may be allowed to assume acceptable values. However, the more general foldings and/or puckerings of the glycinate rings that are commonly observed in the ECTA chelates[6] are also exemplified in the ZrA_2^{2-} ion.

For the ZrA_2^{2-} ion specified by the data in Table II the equation of the mean plane for each type of glycinate ring is as follows

$$\text{ring } Aa\text{:}\quad 0.6632x - 0.1823y - 0.7259z = 1.9489$$

$$\text{ring } Ag\text{:}\quad -0.6897x - 0.6179y - 0.3774z = -4.8409$$

$$\text{ring } Am\text{:}\quad 0.7790x - 0.0281y - 0.6007z = 2.9955$$

Computed displacements of the atoms in each glycinate ring from the mean plane are listed in Table VI.

A pronounced folding along the polyhedron edge defined by the N–O line represents the largest distortion from planarity in the *Aa* ring. In the *Ag* ring, referring again to Figure 2, the outstanding feature is a folding along the line ($C_3\text{–}O_2$) through the methylene carbon and complexed oxygen atoms; virtual planarity, of course, is maintained by the four-atom moiety that includes the methylene carbon and the three carboxylate atoms. The *Am* ring, of minimum ring span (2.62 Å), is not well-characterized in first approximation by specifying a single folding.[7]

Table VI. Out-of-Plane Displacements of the Atoms in the Glycinate Rings

Ring *Aa*		Ring *Ag*		Ring *Am*	
Atom type	Displacement, Å	Atom type	Displacement, Å	Atom type	Displacement, Å
Zr	0.16	Zr	0.01	Zr	0.13
O_1	−0.17	O_2	0.09	O_3	−0.10
C_5	0.03	C_4	−0.17	C_6	−0.05
C_1	0.22	C_3	0.17	C_2	0.25
N	−0.24	N	−0.10	N	−0.23
O_4[a]	0.12	O_6[a]	−0.54	O_5[a]	−0.23

[a] An O_u atom not included in the derivation of the mean plane.

Each type of glycinate ring in the ZrA_2^{2-} ion is subject to rather distinctive constraints that, however, are interdependent; the fusion of the three rings along the N–Zr complexing bond is overriding. The observed fact that the three CNC angles between rings have virtually identical values, 110.6–110.9°, that are only slightly larger than the ideal 109.5° is, perhaps, the best single bit of evidence that residual strains are quite uniformly distributed among the three types of rings. This does not mean that the *Aa* ring, with its long $Zr\text{–}O_1$ bond (2.25A) of M–A type, is fundamentally as stable as the *Am* and *Ag* rings, with their short Zr–O bonds (2.13 Å) of M–B type.

The difference between the averaged $Zr\text{–}O^A$ and $Zr\text{–}O^B$ bond lengths in ZrA_2^{2-}, 0.12 ± 0.01 Å, is just twice that observed in the $Zr(C_2O_4)_4^{4-}$ ion[16] and, indeed, is not significantly smaller than the 0.14 Å reported for the zircon structure[20] (an atomic arrangement that has Zr(IV) in D_{2d} dodecahedral coordination). From the plausible assumption that the large resultant charge of $Zr(C_2O_4)_4^{4-}$ is apportioned equally among the eight uncomplexed carbonyl-oxygen atoms on the periphery of the anion, it follows that the effect of the internal Coulombic repulsions is strongly directed toward minimization of the difference between $Zr\text{–}O^A$ and $Zr\text{–}O^B$ bond lengths.[16,21] The resultant charge of ZrA_2^{2-} is only half that of $Zr(C_2O_4)_4^{4-}$; it is desirable, nonetheless, to examine the packing relations in the crystalline arrangement specified by the data of Table II for indirect evidence of particularities in the charge distribution that might affect the complexing Zr–O bond lengths.

The significantly short interatomic distances that illuminate the roles played by the potassium ion and the water molecule in the crystalline structure are given in Table VII. The largest value listed is only 2.97 Å,

[19] The assertive character of the tertiary amino-nitrogen atom in respect to bond angles is fully apparent in the EDTA chelates of various metal ions[6] wherein the additional constraint on configuration imposed by formation of the necessarily nonplanar ethylenediamine ring is highly restrictive. The external angles at nitrogen between rings in fully sexadentate complexes based upon seven-,[6c–e] nine-,[6f] and ten-coordination[6g] polyhedra lie in the range from 110 to 114°, mostly between 110 and 112°. Extreme values, 108.6 and 116.1°, for these external angles are observed in what is surely the most favorable circumstance for sexadentate octahedral coordination (the EDTA complex of Co(III)[6a]) wherein two glycinate rings are readily closed as nearly flat and virtually unstrained systems, but the two other glycinate rings are closed in stereochemically difficult circumstances with considerable residual strain.[6a–c]

[20] I. R. Krstanović, *Acta Cryst.*, **11**, 896 (1958).

[21] The geometric configuration of the four O_u^A atoms is nearly regular tetrahedral, while that of the four O_u^B atoms is approximately square planar; consequently, the partial Coulombic energy from $O_u^B\text{–}O_u^B$ repulsions is significantly larger than that from $O_u^A\text{–}O_u^A$ repulsions. Further examination of the structure of the crystalline sodium salt[16] suggests that particularly strong interactions of two O_u^A and of two O_u^B atoms with the sodium ions are to be correlated with nontrivial alterations of 0.03–0.04 Å in the lengths of the corresponding $Zr\text{–}O_c^A$ and $Zr\text{–}O_c^B$ complexing bonds.

Table VII. Bonds to the Potassium Ion and the Water Molecule

Bond	Length,[a] Å	Comments
$K–O_5$[b]	2.701	Oxygen of O_u type in *Am* ring
$K–O_4$[c]	2.867	Oxygen of O_u type in *Aa* ring
$K–O_2$[d]	2.897	Oxygen of O_c type in *Ag* ring
$K–O_1$	2.914	Oxygen of O_c type in *Aa* ring
$K–O_5$[e]	2.969	Oxygen of O_u type in *Am* ring
$H_2O–K$[f]	2.713	Each H_2O is bonded to two K^+ ions
$H_2O–O_4$[g]	2.721	Each H_2O is bonded to two O_u atoms

[a] Estimated standard deviations in the range 0.007–0.010 Å. [b–e] Oxygen atoms with coordinates related to those in Table II as [b] $(^1/_2 - x, {}^1/_2 - y, z - 1)$, [c] $(x, \bar{y}, \bar{z} - {}^1/_2)$, [d] $(^1/_2 - x, {}^1/_2 - y, z)$, [e] $(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. [f] Second bond to K^+ in $\bar{x}\bar{y}z$. [g] Second bond to O in $\bar{x}\bar{y}z$.

reflecting the fact that the next nearest neighbor of a potassium ion is a carboxylate carbon atom at 3.38 Å and the next nearest neighbors of the water molecule are two carboxylate oxygen atoms at 3.47 Å. Apart from those lying within the complex anion, interatomic distances between 2.97 and 3.24 Å are lacking in the crystalline structure; the 3.24-Å distance, an O–O separation, is at once the closest contact between a pair of contiguous ZrA_2^{2-} ions and an edge length of the irregular coordination polyhedron around the potassium ion.

The data of Table VII show that the direct interaction of the potassium ion with ring oxygen atoms is weakest for an *Ag* ring, strongest for an *Am* ring; indeed, the fact that each O_u (O_5) atom of an *Am* ring forms two bonds with potassium ions, one very short at 2.70 Å, might suggest that the larger part of the resultant charge of the ZrA_2^{2-} ion (as it exists in the crystal) is concentrated in the O_u atoms of the two *Am* rings. It is more probable, however, that the concentration of charge on the O_u (O_4) atom of an *Aa* ring is comparable with that on the O_u atom of an *Am* ring. We observe that the water molecule forms simultaneously two short bonds (2.71 Å) with K^+ ions and two short hydrogen bonds (2.72 Å) with O_u atoms of *Aa* rings; the respective bond angles subtended at H_2O are 136.9 and 106.4°, and the bonding pattern approximates to C_{2v} symmetry. The compact nature of the bonding suggests that the water molecule is strongly polarized in the combined fields of the potassium ions and of O_u atoms that carry significant negative charges; the $K–O_4$ distance of 2.87 Å is also compatible with this interpretation.

We conclude that a difference of the order of 0.10 Å between the $Zr–O^A$ and $Zr–O^B$ bond lengths in a dodecahedral ZrO_8 coordination group is the usual expectation. Not all nor even the larger part of this difference is necessarily attributable to differences in the direct bonding interactions. Thus for a dodecahedral ZrO_8 group involving only monodentate ligands, the nonbonding repulsions of the $O^A–O^A$ subclass give rise to a destabilizing energy estimated[9] to be ~8 kcal/mole larger than that from repulsions of the $O^B–O^B$ subclass. It is clear that eight d^4sp^3 orbitals in the valence shell of Zr(IV) are used in σ bonding,[22] but this neither requires nor implies the energetic equivalence of the σ-bonding contributions to the respective $Zr–O^A$ and $Zr–O^B$ bond types.[23] The most stable of the Zr(IV) valence-shell orbitals, d_{xy} in a $\bar{4}m2$ representation of D_{2d}, has the axes of its four lobes passing through the midpoints of the four *b* edges of the dodecahedron (Figure 1). Barred from σ bonding, the d_{xy} orbital is available for π bonding with, primarily, the O^B ligands; such bonding enhances the concentration of electron density in the equatorial layer that encompasses the four O^B ligands and the four *b* edges of the coordination group. A realistic theoretical estimate of the net benefit to the $Zr–O^B$ bonds from the π contribution requires the simultaneous consideration of the σ bonding and of the usually neglected effects of electron repulsions and correlations on the combined patterns of σ and π bonding. The probability that such a realistic estimate can be made is essentially the probability that the entire bonding problem can be handled in a satisfactorily fundamental manner.

Some further illumination of the bonding problem is provided by comparing the stereochemical data cited for dodecahedral oxozirconate(IV) complexes with that given in a forthcoming paper[24] for the octacyanomolybdate(IV) ion as this exists in the crystalline potassium salt. In the dodecahedral $Mo(CN)_8^{4-}$ ion, by contrast with the typical dodecahedral oxozirconate(IV) complex, there is no measurable difference between the bond lengths of M–A and M–B types: Mo–C = 2.164 Å with a mean deviation of 0.005 Å for all eight bonds as compared with an estimated standard deviation of 0.007 Å for an individual bond length.[24] Lacking an absolute basis for deciding whether, in the absence of nonbonding repulsions and of π bonding, the σ contributions to M–A and M–B bonds in dodecahedral complexes should be quasi-equivalent, it appears as experimental fact that in the Zr(IV) complexes the M–B bonds are the stronger, but that in $Mo(CO)_8^{4-}$ the presence of the pair of electrons in the d_{xy} orbital of Mo(IV) is responsible for modifying the strength of the M–B bonds to approximate equivalence with that of the M–A bonds. The net benefits from π bonding in the Zr(IV) complexes cannot be separately assessed, but they are evidently more favorable than any corresponding benefit from π bonding in the $Mo(CN)_8^{4-}$ ion.[25]

Whether, as has sometimes been assumed,[26] the net benefits from π bonding are larger for the dodecahedron than for the antiprism is a matter that receives detailed consideration elsewhere.[24] Empirically, however, there is little reason to suppose that π bonding is ever the dominant factor in the selection of coordination geometry for a discrete eight-coordinate oxo complex of Zr(IV); the oxozirconate(IV) complexes of known stereochemistry are distributed more or less equally between dodecahedral and antiprismatic coordination. The several factors that influence the choice of coordination polyhedron, as set forth in an earlier discussion of discrete eight-coordination,[9] receive further consideration in the following section.

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(22) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(23) G. H. Duffey, *ibid.*, **18**, 746 (1950).

(24) J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Am. Chem. Soc.*, in press.

(25) This conclusion carries no surprise. In the oxozirconate(IV) complexes, whether utilizing the dodecahedron or the antiprism as coordination polyhedron, π bonding transfers charge from the $p\Pi$ orbitals of oxygen to the lowest lying d orbital of Zr(IV), whereas in $Mo(CN)_8^{4-}$ the "back" π bonding transfers charge from the filled, most stable, d orbital of Mo(IV) to the unfilled $p\Pi^*$ antibonding orbitals of the cyanide groups.

(26) *Cf.* L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

Possible Stereoisomeric Forms of the Complex Anion

The conceivable stereoisomeric forms of the bis(nitrilotriacetato)zirconate(IV) complex that are based upon quasi-cubic coordination are not so evidently implausible as to be dismissed without consideration. Every such stereoisomer has the nitrogen atoms at opposite vertices of an arbitrarily chosen body diagonal of the quasi-cube, and this diagonal can be (and, presumably, would be) retained as an axis of threefold symmetry to bestow structural equivalence on the three glycinate rings that are fused along a common Zr–N bond. The point group symmetries of the theoretical stereoisomers retaining a threefold axis are C_3, C_{3i}, D_3, C_{3v}, and D_{3d}. Both C_{3v} and D_{3d}, however, require planarity of the glycinate rings, a condition that is incompatible with the large Zr–N and Zr–O bond lengths and the simultaneous maintenance of even moderately satisfactory bond angles at carbon and nitrogen atoms (*vide supra*). Of the three remaining possibilities, the C_{3i} isomer necessarily puts the six oxygen atoms coordinated to Zr(IV) at the vertices of a trigonal antiprism (or flattened octahedron) in which the six short edges have the same length. Only trivial relaxations from this coordination geometry are plausible for the D_3 and the C_3 isomers, and the following calculation, based upon C_{3i}, should serve for all three.

The combination of Zr–N = 2.44 Å with Zr–O = 2.20 Å yields a rhombohedron (quasi-cube) for the coordination polyhedron with edges of 2.61 Å and rhombohedral angle of 85.2°. These data then correspond to six close O–O inter-ring distances of 2.61 Å, a ring span of 2.61 Å for all rings, and OZrN bond angles of only 68.0° in the ZrA_2^{2-} ion. The experimentally observed stereoisomer (Table III) has, by contrast, just two close inter-ring contacts, O–O = 2.62 Å, has ring spans that average to the more natural value, 2.68 Å, and has OZrN bond angles that are certainly more favorable. Thus the steric inferiority of the C_{3i} isomer is exposed.

If, however, the Zr–N distance in the C_{3i} isomer were increased to ~2.64 Å (if, that is, the importance of the Zr–N bonds were further deprecated), the ring spans and the inter-ring O–O separations would become ~2.68 Å, the flattened octahedral ZrO_6 would become the heart of the complex, and neither the practical unavailability nor the otherwise doubtful merits of the Zr(IV) f orbitals needed for quasi-cubic bonding[22] would be of vital concern. But the ZrO_6 octahedron would depart so far from regularity (OZrO bond angles would be ~75 and 105°) that the normally efficient use of d^5sp^3 orbitals of Zr(IV) for combined σ and π bonding would be strongly impaired. Quasi-regularity of the ZrO_6 octahedron, even with the shorter Zr–O distance of 2.10 Å, implies a Zr–N separation of ~3.5 Å. Thus the C_{3i} isomer might be stable in a strictly six-coordinate version, but not, apparently, as a recognizable eight-coordinate species.

The number of stereoisomeric forms of the bis(nitrilotriacetato)zirconate(IV) complex that can be based upon dodecahedral coordination is limited to three if we exclude those which would require glycinate rings to span the long *b* edges ($\gtrsim$3.10 Å) connecting B vertices (see Figure 1 and the earlier discussion). One of these stereoisomers retains the symmetry of a mirror plane, C_s-m; the two others, of which one is the observed $(Aagm)^2$ isomer, retain the symmetry of C_2-2 and, consequently, are optically active. Using the symbolism introduced earlier (which does not distinguish between pairs of optical isomers), the dodecahedral stereoisomers take the representations listed in Table VIII.

Table VIII. Stereoisomeric Forms of the ZrA_2^{2-} Complex[a]

Dodecahedral class			Antiprismatic class		
I^d	*Bmgg*; *Amgg*	C_s-m	I^a	$(ssl)^2$	C_2-2
II^d	$(Aagg)^2$	C_2-2	II^a	$(sll)^2$	C_2-2
III^d	$(Aagm)^2$	C_2-2	III^a	$(sll)^2$	C_2-2 ($\bar{8} \rightarrow 2$)

[a] The twofold axis in the III^a isomer replaces the $\bar{8}$ axis in the D_{4d} antiprism. Every other isomer retains a simple element of twofold symmetry that is present as such in the coordination polyhedron of maximum symmetry.

Consideration of the dodecahedral stereoisomers I^d and II^d suggests that neither of them can meet the generally high level of structural merit that characterizes the observed isomer III^d. I^d is the only isomer listed in Table VIII that does not accord equivalent treatment to the two nitrilotriacetate groups; both the placement of the nitrogen atoms and the pattern of ring connexities call for particularly strong deformations of the coordination polyhedron. The positioning of a weakly complexing nitrogen atom at a B vertex appears to be energetically and structurally unsound; the nitrogen atom has no capacity for π bonding to Zr(IV) and a $Zr-N^B$ bond length more than 0.20 Å longer than that of the $Zr-O^B$ bonds is to be expected.

The simultaneous spanning of two of the rather long *g* edges required of two glycinate rings in each ligand system of *Bmgg*, *Amgg*, or *Aagg* type must produce undue strain in the bond angles at nitrogen and/or undue deformation of the coordination polyhedron; such strains are especially significant when the nitrogen atom is at an A vertex, as is the case for both ligand systems $(Aagg)^2$ in the II^d isomer. The II^d stereoisomer is subject also to the serious objection that the two inter-ring N–O contacts (that come out to be 2.94 Å in the observed III^d isomer) must be made along two of the relatively short *m* edges. Inasmuch as none of the shortcomings cited for the I^d and the II^d stereoisomers is to be found in the observed isomer, it is very probable that in solution, the undoubtedly high lability of the complex anion notwithstanding, the III^d $(Aagm)^2$ stereoisomer is the favored species, at least among those that utilize dodecahedral coordination.

The square antiprism as coordination polyhedron for the bis(nitrilotriacetato)zirconate(IV) complex gives rise to just three stereoisomeric forms, all with C_2-2 symmetry. Using an earlier symbolism,[9] *s* denotes the edge of a square face and *l* a lateral edge connecting the square faces in the antiprism. Two *s* and two *l* edges join at each vertex and, neglecting optical isomerism, there are two distinguishable combinations of *s* and *l* edges to be spanned by the three glycinate rings of the first nitrilotriacetate group: *ssl* and *sll*. The geometrically allowed combinations of *ssl* and *sll* that give possible stereoisomeric forms of ZrA_2^{2-} are those listed in Table VIII.

The four angles subtended by the four pairings of adjacent edges at each vertex of the D_{4d} antiprism are, in the hard-sphere approximation ($l = s$), 90° for the s–s pairing, 60° for each of the other three. Neither the *ssl* nor the *sll* choice of the three edges to be spanned by a nitrilotriacetate group seems well suited to the preservation, simultaneously, of a quasi-regular tetrahedral bonding pattern for the nitrogen atom, of acceptable ring geometry, and of a recognizable approximation to antiprismatic coordination. A square face of the antiprism, with an area ~2.3 times that of a triangular face, is readily folded along one diagonal by stresses of small intensity.[27] Multidentate chelation in general, and chelation by nitrilotriacetate in particular, imposes stress patterns that are quite unlikely to be compatible with preservation of the square faces or, even approximately, of antiprismatic coordination. The antiprism, moreover, is readily transformed into the dodecahedron by way of comparatively small movements of just half of the coordinated atoms; in a ZrO_8 group, four oxygen atoms must each be shifted by ~0.75 Å to achieve this transformation.[9] The known antiprismatic examples of discrete eight-coordinate complexes utilize monodentate or simple bidentate ligands. The superior adaptibility of the dodecahedron to a wide spectrum of complicating features, such as those which arise with mixed ligands, multidentate chelation, and asymmetric charge distributions, seems to be a natural phenomenon[9,28] that, in many of the more complicated species of established stereochemistry, can be traced to rather obvious sources.[9]

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

(28) E. L. Muetterties and C. M. Wright, *Quart Rev.* (London), 31, 109 (1967).