

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORKStereochemistry of Discrete Eight-Coördination. III.
Tetrasodium Tetrakisoxalatozirconate(IV) Trihydrate¹

BY G. L. GLEN, J. V. SILVERTON, AND J. L. HOARD

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Three-dimensional $\{hkl\}$ X-ray data in the range $0 < (\sin \theta)/\lambda < 0.95$ from orthorhombic crystals of $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ yield a definitive determination of structure. The tetrakisoxalatozirconate(IV) ion, required by the space group (B2₂,2) to have a single twofold axis, belongs in fact to the dodecahedral $(\text{Mo}(\text{CN})_6)^{-4}$ stereoisomeric type having $D_{2d}-42m$ ideal symmetry and designated *mmmm* in the first paper (HS) of this series. The complicated crystalline arrangement is determined primarily by direct interaction of sodium ions with oxalato oxygen (water molecules are relegated to the role of filler), and the $\text{Zr}(\text{C}_2\text{O}_4)_4^{-4}$ ion departs significantly from $\bar{4}2m$ symmetry. This distortion is limited, well within the probable experimental accuracy, to the inner coördination group, *i.e.*, to the chemically least stable and structurally least rigid part of the complex. The structurally non-equivalent oxalato rings are flat and, barring some variation in Zr-O bond lengths, are virtually isodimensional. Bond parameters, including an averaged Zr-O bond length of 2.199 Å., are in excellent agreement with a composite of other reported data. A structurally significant difference of 0.06 Å. between averaged bond lengths for Zr-O_A and Zr-O_B types (*cf.*, HS) overlies the distortion of the inner coördination group.

Introduction

The approximate stereochemistry of the tetrakisoxalatozirconate(IV) ion, $\text{Zr}(\text{C}_2\text{O}_4)_4^{-4}$, as it exists in the sodium salt, $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$, is described in an earlier communication.² That the inner coördination group of this eight-coördination complex occurs in the dodecahedral $\text{Mo}(\text{CN})_6^{-4}$ configurational type, rather than the antiprismatic, seems to have occasioned some surprise. In the first paper³ (HS) of this series we provide a frame of reference which may be helpful in assessing the *a priori* probabilities of the various stereoisomeric types based on both configurations for a complex of specified chemical type. In so doing we have made use of quantitative stereochemical data drawn from the structure determination for $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ to be described in this paper.

We have chosen to study the oxalatozirconate(IV) complex in preference to alternatives containing heavier M(IV) elements, and, as in the study of zirconium acetylacetonate,⁴ have depended primarily on Fourier methods in analyzing very extensive three-dimensional X-ray data provided by a single crystal. Although we would have preferred to base our study on a centrosymmetric crystal containing $\text{Zr}(\text{C}_2\text{O}_4)_4^{-4}$ so as ultimately to have the phase assignment for reflection amplitudes less dependent upon details of the theoretical model, we were able to obtain crystals suitable for X-ray analysis only in the case of the non-centrosymmetric sodium salt.

Experimental

Crystals of $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ and of the isomorphous $\text{Na}_4\text{Hf}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ were prepared as recommended by Johnson.⁵

(1) Supported in part by the U. S. Army Research Office (Durham), the National Science Foundation, and the Advanced Research Projects Agency. We thank also the Staff of the Cornell Computing Center, Mr. Richard C. Lesser, Director.

(2) J. L. Hoard, G. L. Glen, and J. V. Silvertton, *J. Am. Chem. Soc.*, **83**, 4293 (1961).

(3) J. L. Hoard and J. V. Silvertton, *Inorg. Chem.*, **2**, 235 (1963).

(4) J. V. Silvertton and J. L. Hoard, *ibid.*, **2**, 243 (1963).

Thorough preliminary study by photographic methods using $\text{CuK}\alpha$ radiation preceded the counter measurement of $\{hkl\}$ intensity data using $\text{MoK}\alpha$ radiation. The orthorhombic unit cell containing $4\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ has $a = 7.42 \pm 0.01$, $b = 11.81 \pm 0.02$, $c = 19.74 \pm 0.02$ Å.; the calculated and measured densities are 2.262 and 2.27 g./cc., respectively. The hafnium compound has $a = 7.43 \pm 0.01$, $b = 11.85 \pm 0.02$, $c = 19.76 \pm 0.02$ Å., with calculated and measured densities of 2.583 and 2.57 g./cc., respectively. The systematic vanishings of spectra, $\{hkl\}$ for $h + l$ odd, $\{0k0\}$ for k odd, and positive tests for piezoelectricity make B2₂,2 the unique choice as space group.

Three dimensional X-ray intensity data for the zirconium compound were measured on our G.E. spectrometer assembly as described earlier.⁴ The specimen employed, cut from a larger crystal, had initially the shape of a rectangular parallelepiped 0.18 mm. along a , 0.22 mm. along b , and 0.25 mm. along c ; prior to use, rough edges and corners of the specimen were removed by gently rolling it about on a fine-grained carborundum block. The size and shape of this specimen together with a linear absorption coefficient of but 9.2 cm^{-1} for $\text{MoK}\alpha$ radiation made it quite unnecessary to correct for absorption. Within the range of measurement, $2\theta < 85^\circ$, some 3442 independent $\{hkl\}$ were examined, of which 2978 were above background. The 464 "unobserved" $\{hkl\}$ were assigned each an intensity count of half the minimum observable, and were included in the final stage of refinement by difference synthesis. The fraction of reflections having measurable intensity was larger for $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ at $2\theta = 85^\circ$ than for zirconium acetylacetonate⁴ at the cut-off of $2\theta = 65^\circ$. For a variety of more or less evident reasons, $2\theta = 85^\circ$ seemed a good place to stop; a sufficient reason was that spectral dispersion, for which the correction at cut-off was still only 16%, would have required substantial alterations in experimental procedures had the measurements been extended to significantly higher 2θ .

The measurements just described were preceded by an equally extensive series carried out on a similar specimen of the isomorphous hafnium analog. These measurements were the unplanned result of a blunder whereby specimens of the zirconium and hafnium compounds were interchanged. Being available, however, the $\{hkl\}$ data for $\text{Na}_4\text{Hf}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ can be used to establish virtual isodimensionality with $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$. Corrections for absorption, no longer negligible with $\mu = 69.4 \text{ cm}^{-1}$ for $\text{MoK}\alpha$ radiation, were not made on the $\{hkl\}$ intensity data for $\text{Na}_4\text{Hf}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$.

Still earlier, *i.e.*, during the extended period required for prep-

(5) F. A. Johnson, Ph.D. Thesis, University of Wisconsin, 1958. We are indebted to Professor E. M. Larsen for advice in this connection.

aration of good crystals of $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$, intensity data were recorded for two zones of reflection from carefully shaped specimens of the hafnium compound. These data sufficed for the determination of hafnium positions within the crystal, in complete agreement with the subsequent analysis of three-dimensional data, but were of little use in the further elucidation of structure.

Determination of Structure

Inasmuch as but two $\text{M}(\text{C}_2\text{O}_4)^{-4}$ ions are present within a primitive unit cell, the M(IV) atoms must lie upon one or the other sets of non-equivalent twofold axes in the space group^{6a} B22₁2. A Patterson synthesis^{6b} of general $|F|^2$ data from $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ was unambiguously in favor of the axes parallel to c with Zr in the $4b$ positions,⁶ $0 \frac{1}{4}z$, $0 \frac{3}{4}z$, etc., and $z = 0.107$. In this description, the contribution of zirconium to the complex structure amplitude is either wholly real (k even) or wholly imaginary (k odd). It is necessary, indeed, to include the contribution from at least one set of atoms lying in the general positions before any value of the complex phase other than 0 , $\pm\pi/2$, or π can be assigned to a general structure amplitude. An approximately correct assignment of positions to the oxygen atoms bonded to zirconium made with the help of the Patterson function $P(uvw)$ sufficed to initiate the cyclic process of Fourier approximation leading to the construction of the electron density function $\rho(xyz)$ for the structure.

The pattern of vectors emanating from the origin of $P(uvw)$ with termini on or near a sphere of 2.2 Å radius includes, in superposition, the vector patterns of a ZrO_8 group in both orientations which occur in the crystal together with the inversions of these through the origin. Lacking the complete analysis⁸ of HS, we had an initial bias in favor of the antiprismatic coordination group deriving from its known occurrence in zirconium acetylacetonate.⁴ We thus were enabled to see in $P(uvw)$ two symmetry-independent possibilities for rather distorted antiprismatic ZrO_8 groups. Calculation of contributions to the structure amplitudes⁷ based upon these possibilities gave, upon comparison with the observed amplitudes, a somewhat better value for one (0.416) than the other (0.446) of $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. The model giving the better R naturally was chosen to initiate the cycle of structure determination by successive approximation to the Fourier synthesis, $\rho(xyz)$. Several cycles of calculation led to the following situation.

The value of R , after an initial drop, had leveled off at 0.33. There were more peaks of comparable prominence in $\rho(xyz)$ than were needed to account for all of the lighter atoms and, for the most judicious identification

of peaks with atomic positions, there remained at least two unacceptable interatomic separations.

Proceeding still on the basis of internal evidence, two of the oxygen atoms coordinated to zirconium in the asymmetric unit of structure were assigned new coordinates which (1) agreed with two hitherto unused peaks in $\rho(xyz)$, (2) were fully compatible with $P(uvw)$, and (3) gave contributions to the structure amplitudes which, interestingly, were just the complex conjugates of those given by the atoms replaced. Some re-interpretation of the positions of carbon and outer oxygen atoms, all in the direction of giving recognizable oxalato groups, was then in order, and a supposed sodium ion was eliminated as being too close to the reconstituted complex. In one additional cycle of computation, the new atomic positions were reproduced and enhanced in $\rho(xyz)$, most of the extraneous peaks had disappeared, and R had dropped to 0.24.

At this point the $\text{Zr}(\text{C}_2\text{O}_4)_4^{-4}$ complex had assumed for the first time an unreservedly recognizable form: it displayed the connectivity, and approximated rather closely to the maximum symmetry, $D_{2d}-\bar{4}2m$, of the dodecahedral stereoisomeric type designated as *mmmm* in HS. Two more cycles of computation sufficed for the identification of all atoms. Deduction of the approximate structure made use of amplitude data limited to the range $2\theta < 55^\circ$, along with an averaged thermal parameter, $B = 1.2 \text{ \AA}^2$. These restrictions were relaxed during subsequent refinement through many cycles of difference synthesis.

The electron density functions ρ_0 and ρ_c were computed during each cycle of refinement by the synthesis, respectively, of observed (F_o) and calculated (F_c) reflection amplitudes. Objective evaluation of a peak position was achieved (on the Burroughs 220) through the least squares fitting of a gaussian to 27 points surrounding the peak.⁸ The input coordinates for a cycle were obtained as described by Shoemaker, *et al.*⁸ Each coordinate from ρ_0 was subjected to a *back-shift* correction for finite termination of series and an *n-shift* correction ($1 \lesssim n \lesssim 2$) to handle residual errors in the complex phase angles; $n = 2$ was used in every cycle except the last, for which n was set at 1.9. Thermal parameters for each structural class of atom were adjusted following Atoji⁹ during each cycle of refinement. Periodic redetermination of scale factor and of the averaged thermal parameter served to keep observed and calculated amplitudes on a mutually compatible "absolute" basis; this meant also that individual thermal parameters were connected by one useful general restriction. Most of the cited operations, when assembled into a refinement cycle, were programmed for, and carried out on, the Burroughs 220.

Refinement proceeded in stages determined as follows: stage 1 made use of all experimental amplitudes for reflections lying within the $\text{CuK}\alpha$ sphere ($2\theta < 55^\circ$), stage 2 utilized all amplitude data within the range of

(6) (a) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1952, Vol. I, p. 106; (b) Cf. H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, London, 1953.

(7) The atomic form factor used for zirconium was that of L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957), for other atoms, those of J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955). Zirconium form factors were corrected for dispersion following C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(8) D. P. Shoemaker, J. Donahue, V. Schomaker, and R. B. Corey, *J. Am. Chem. Soc.*, **72**, 2328 (1950).

(9) M. Atoji, *Acta Cryst.*, **10**, 291 (1957).

TABLE I
 PARAMETER DATA FOR $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}^a$

Atom type	(Coordinate \pm std. dev.) $\times 10^4$						B , \AA^2	ρ Max., $\text{e}/\text{\AA}^3$
	x	$\pm \sigma_x$	y	$\pm \sigma_y$	z	$\pm \sigma_z$		
Zr	0	..	1/4	..	1066 ^b	0	0.82	307.3
O ₁	1670	12	2875	6	163	4	1.58	27.5
O ₂	967	11	810	5	785	3	1.51	28.3
O ₃	2451	14	3290	7	1394	4	1.82	26.3
O ₄	810	11	1568	5	2009	3	1.41	30.2
O ₅	4138	17	3722	10	-224	5	2.38	21.3
O ₆	1833	11	-905	7	1147	5	2.02	23.9
O ₇	5102	21	4038	17	1117	7	3.17	17.5
O ₈	2104	21	25	9	2441	5	2.44	20.3
C ₁	3147	12	3419	7	229	4	1.59	20.6
C ₂	1414	12	88	7	1231	3	1.54	22.5
C ₃	3651	13	3613	8	977	4	1.72	20.7
C ₄	1460	12	562	6	1964	3	1.35	23.7
Na ₁	2013	12	3153	6	2760	4	2.56	32.6
Na ₂	3392	10	0	..	0	..	2.33	36.9
Na ₃	1/2	..	1/4	..	4117	3	2.15	39.7
O _I	1/2	..	1/4	..	2489	7	3.31	16.3
O _{II}	2338	63	1565	31	3541	12	4.18	13.0

^a Following submission with the manuscript for examination by referees, complete amplitude data have been submitted as Document No. 7390 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting \$3.75 for photoprints or \$2.00 for 35-mm. film in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress. ^b For Zr, $z = 0.10658 \pm 1 \times 10^{-5}$.

measurement ($2\theta < 85^\circ$) except for the class of 464 unobserved or doubtfully observable reflections, and stage 3 included these latter also. We had virtually completed the refinement in stage 2, and were doubting the probable utility of stage 3, when our attention became refocused on a persistent extraneous peak lying on the twofold axis near enough to the complex to be interpreted (as it had been for a time during initial analysis) in terms of a sodium position. On the basis of stage 2 amplitudes, the peak appeared on ρ_0 , ρ_c , and a synthesis of zirconium contributions, with a peak density of about 6 electrons/ \AA^3 . We thereupon added the 464 missing reflections to the syntheses, with use in the case of ρ_0 of amplitudes corresponding to the initial assignment of half-minimum intensity counts noted earlier, and found the extraneous peak to be reduced below 2 electrons/ \AA^3 in every case. Hence we assumed that inclusion of these reflections generally would benefit ρ_0 , at least statistically, through providing a truer picture of peak shape and apparent position; the resolving power of the synthesis, of course, had been set already by using reflections out to $2\theta = 85^\circ$.

The effect of the additional refinement cycles of stage 3 on the apparent dimensions of the complex was in continuation of a trend evident from the outset: namely, to reduce the spread in bond lengths within any set of quasi-chemically equivalent bonds in the oxalato group while increasing the spread in the (by comparison) weak Zr-O bonds. Averaged values, however, were little affected during the later stages of refinement, trivially so (ca. 0.002 \AA .) for Zr-O. Table I lists the atomic coordinates with associated standard deviations estimated by Cruickshank's procedure^{6b} for the non-centrosymmetric case, the individual thermal parameters, and the peak values of electron densities—all as obtained from the last cycle of refinement. Values of R based on the parameters of Table I, but

computed, respectively, for the amplitude data specified for each stage of refinement, are: I, 0.078; II, 0.129; III, 0.139.

With substitution of the form factor of hafnium for that of zirconium, but use otherwise of the parameters (including the B for Zr) of Table I in computing amplitudes F_o for comparison with the measured amplitudes of $\text{Na}_4\text{Hf}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$, the values of R obtained are 0.066 for I (CuK α sphere data) and 0.147 for III. The virtual isodimensionality of the two complexes thus is assured.

The large values of the peak electron densities (Table I) are notable, e.g., for carbon the range is from 20.6 to 23.7 electrons/ \AA^3 . Measurement of reflection intensities for $0 < 2\theta < 85^\circ$ with MoK α radiation corresponds to complete measurement ($0 < 2\theta < 180^\circ$) with a radiation of about 1.04 \AA . wave length. Ibers¹⁰ has computed for carbon the curves of peak electron density, $\rho(0)$, vs. thermal parameter, B , based upon theoretically complete data for each of three standard radiations (CrK α , CuK α , MoK α). Our mean values for carbon, $\rho(0) \cong 22$ electrons/ \AA^3 , $B \cong 1.5 \text{\AA}^2$, give a point which seems about right to fall on an interpolated curve for $\lambda = 1.04 \text{\AA}$. on Ibers's diagram.

Discussion of Results

In presenting the quantitative stereochemical description of the $\text{Zr}(\text{C}_2\text{O}_4)_4^{-4}$ ion, we discuss first the idealized configuration of $D_{2d}-42m$ symmetry (Fig. 1) with bond data obtained by averaging; we then discuss all bond data for which deviations from the averaged configuration approach or exceed possible significance.

The single twofold axis required of the complex in the crystal coincides with the (vertical) $\bar{4}$ axis of the idealized configuration of Fig. 1. (Atoms are identified in ac-

(10) J. A. Ibers, *Acta Cryst.*, **14**, 538 (1961).

TABLE II
 STEREOCHEMICAL PARAMETERS^a OF THE RINGS

Bond type	Mean length, Å.	Deviations, Å.		Bond Angle	Mean values	Deviations	
		Max.	Std.			Max.	Std.
C _A -O _A	1.281	0.004	0.019	O _A ZrO _B	71.3°	0.17°	0.27°
C _B -O _B	1.271	.000	.021	ZrO _A C _A	119.8°	.03°	.72°
C _A -C _B	1.545	.006	.021	ZrO _B C _B	121.7°	.27°	.81°
C _A -O _A ^e	1.222	.009	.025	O _A C _A C _B	112.7°	.26°	.97°
C _B -O _B ^e	1.222	.002	.027	O _B C _B C _A	114.1°	.10°	1.02°
O _A -O _B ^b	2.563	.017	.020	O _A C _A O _A ^e	125.5°	.85°	1.56°
				O _B C _B O _B ^e	127.2°	.74°	1.80°
Zr-O _A	2.230	.014	.014	C _A C _B O _B ^e	118.7°	.81°	1.40°
Zr-O _B	2.168	.024	.014	C _B C _A O _A ^e	121.8°	.62°	1.20°

^a The quasi-symmetry of S₄- $\bar{4}$ assumed in averaging. ^b The ring span or dodecahedral edge *m* (HS)—not a bond distance.

cordance with Table I, and each pair of primed and unprimed atoms carrying the same subscript, *e.g.*, O₄' and O₄, are structurally equivalent in the crystal.) The full symmetry of $\bar{4}2m$ places all atoms with even-numbered subscripts in one mirror plane, all atoms with odd-numbered subscripts in the perpendicular mirror plane, with zirconium lying on the axis of intersection, *i.e.*, the $\bar{4}$ axis. The interlocking pair of perpendicular trapezoids, O₂O₄O₄'O₂' and O₃O₁O₁'O₃', define the inner coordination group of the complex. Atoms O₁, O₁', O₄', and O₄, equivalent in $\bar{4}2m$, are A-type ligands in the symbolism of HS³; these atoms define a bisphenoid elongated along $\bar{4}$. The B-type³ atoms O₂, O₂', O₃', and O₃ similarly define a bisphenoid flattened along $\bar{4}$; the mutual orientation of the bisphenoids is that of the "positive" and "negative" tetrahedra inscribed within a cube.¹¹

Figure 2 gives dimensions, averaged in agreement with the symmetry of $\bar{4}2m$, sufficient to define the complex of presumably greatest chemical interest. (A general rounding-off of all lengths to 0.005 Å. is indicated; *vide infra*.) When the dotted trapezoid of Fig. 2 (which corresponds to *a* = 2.570 Å., *m* = 2.563 Å. on Fig. 1 of HS) interlocks with another such to give the inner coordination group of D_{2d} symmetry, the lengths of the remaining edges of the dodecahedron become 2.735 Å. for the eight of O_A-O_B or *g* type, 3.19 Å. for the four of O_B-O_B or *b* type (HS).

As we examine the stereochemical data for the complex in detail, we shall see that real deviations from $\bar{4}2m$ symmetry in the inner coordination group are accompanied by a remarkable lack of significant dimensional variation between the non-equivalent oxalato groups carrying odd and even subscripts, respectively, in Fig. 1. The sums of the bond angles at carbon atoms range between 359.94 and 360.05° for the four structurally distinct cases; inasmuch as each result is 360° within the accuracy of formal computation from the data fed into the Burroughs 220, it follows that every CCO₂ subunit is flat within experimental accuracy. Similarly the computed sums of the interior angles of the five-membered ring systems are 539.44 and 539.65°, respectively, for rings carrying odd and even subscripts; the essential planarity of the ring systems is thereby as-

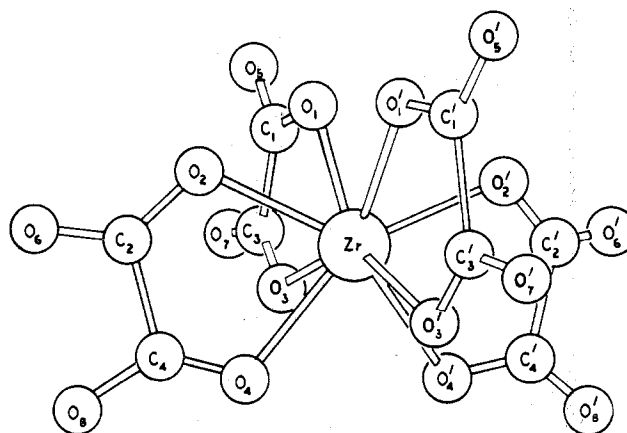


Fig. 1.—Perspective drawing of the idealized (D_{2d}- $\bar{4}2m$) Zr(C₂O₄)₄⁻⁴ ion. Odd subscripts identify atoms lying in one mirror plane, even subscripts those lying in the perpendicular plane; these planes intersect in the vertical $\bar{4}$ symmetry axis. The mutually interpenetrating trapezoids, O₂O₄O₄'O₂' and O₃O₁O₁'O₃', are equivalent through the operation $\bar{4}$ and, together, define the dodecahedral coordination group.

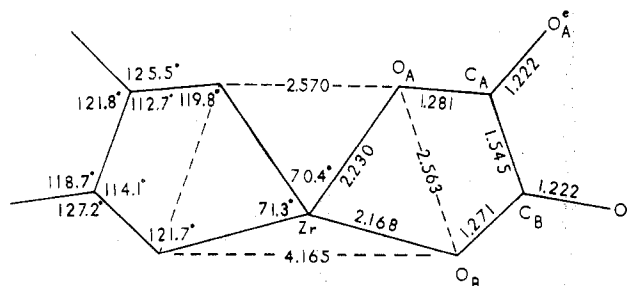


Fig. 2.—Bond parameters averaged in accordance with D_{2d}- $\bar{4}2m$ (or S₄- $\bar{4}$ since the ring systems are flat). "Chemically identical" atoms carrying subscripts A and B are structurally distinct in $\bar{4}2m$; the difference between Zr-O_A and Zr-O_B bond lengths is significant. Distortion from $\bar{4}2m$ symmetry is limited to the inner coordination group, as shown by Fig. 3.

sured. In Table II we give values for ring bond lengths and angles averaged in agreement with $\bar{4}2m$ (or the sub-group $\bar{4}$), each with maximum (which is also the mean) deviation and standard deviation from the mean. The symbols used to identify atom types are as in Fig. 2.

We see from Table II that, excepting only the Zr-O bond lengths, the observed deviation from the mean for any bond length or angle within the ring is well below the formally computed standard deviation; on the

(11) Cf. J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **51**, 2853 (1939).

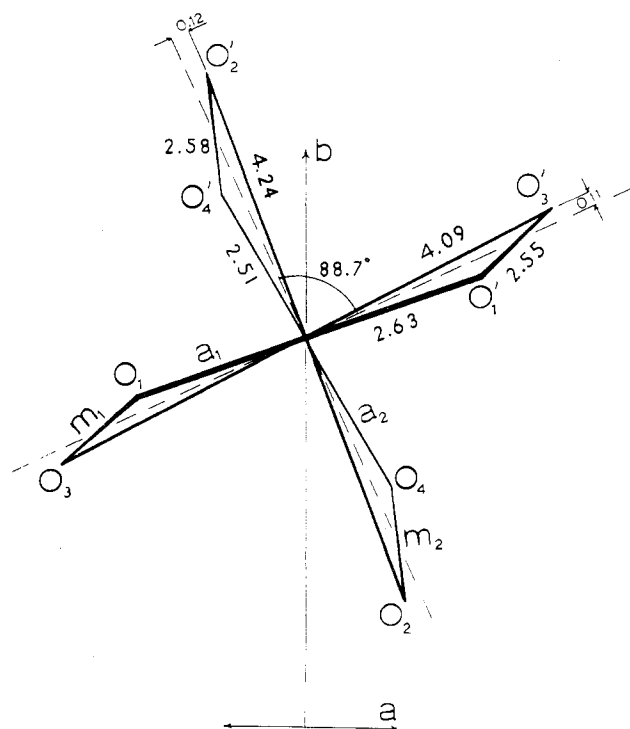


Fig. 3.—View along the twofold (quasi- $\bar{2}$) axis of the two “trapezoids” defining the inner coordination group. Most of the distortion is the product of rotational twisting at zirconium of the flat rings. The first twisting maintains nearly D_2 symmetry, the second gives polar character to the true twofold axis, *i.e.*, makes $a_1 > a_2$, etc. (see text).

average, indeed, the ratio of maximum to standard deviation is about 0.40 for bond angles, only 0.18 for bond lengths. Further, we can take the bond length as 1.276 Å. for all C–O bonds involving the oxygen atoms complexed to zirconium, 1.222 Å. for the remaining C–O bonds, and have in each case a maximum deviation from the mean of just 0.009 Å., as compared with the respective standard deviations of 0.020 and 0.026 Å. These bond length data are compared with results obtained by other investigators in Table III.

The compounds are listed in Table II in the order of decreasing divergence between the two types of carbon–oxygen bonds; the anticipated and the observed orderings are identical. The results for the oxalatochromate(III) complex¹⁴ must be weighted lightly—*cf.*, the improbably small C–C bond distance. For the carboxyl-

TABLE III
BOND LENGTHS IN OXALATES AND OXALATO COMPLEXES

Compound	(C–O) _I , Å.	(C–O) _{II} , Å.	C–C, Å.
α -Oxalic Acid ¹²	1.29	1.19	1.56
Oxalic acid dihydrate ¹³	1.28	1.19	1.53
$K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ ¹⁴	1.31	1.24	1.39
$Na_4Zr(C_2O_4)_4 \cdot 3H_2O$	1.275	1.22	1.545
$(NH_4)_2C_2O_4 \cdot H_2O$ ¹⁵	1.25	1.23	1.56
Sodium oxalate ¹⁶	1.23	1.23	1.54

(12) E. G. Cox, M. W. Dougill, and G. A. Jeffrey, *J. Chem. Soc.*, 4854 (1952).

(13) F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.*, **6**, 385 (1953).

(14) J. N. van Niekerk and R. R. L. Schoening, *ibid.*, **4**, 35 (1951).

(15) G. A. Jeffrey and G. S. Parry, *J. Chem. Soc.*, 4864 (1952).

(16) G. A. Jeffrey and G. S. Parry, *J. Am. Chem. Soc.*, **76**, 5283 (1954).

ate group in the ethylenediaminetetraacetatocobaltate(III) ion,¹⁷ C–O bond lengths of 1.22 and 1.30 ± 0.018 Å. and a C–C distance of 1.53 ± 0.02 Å. are reported.

Even though determined from data bearing the imprint of the strongly scattering zirconium, our bond parameters for the oxalato group seem not less plausible than those of the most accurately studied member (whichever this may be) of the cited group of simpler compounds. In the light of all that has been said the formally computed standard deviations of Table II assume an even more definite air of unreality than those computed for zirconium acetylacetonate.⁴ The absence of a center of inversion in the present structure somewhat beclouds the comparison and we shall not pursue the matter further at this time. We do suggest, however, that in dealing with the inner coordination group of $Zr(C_2O_4)_4^{4-}$, the focus of interest for this study, differences of >0.025 Å. in Zr–O bond lengths, and >0.04 Å. in O–O distances, are to be taken seriously.

Deviations from the maximum possible symmetry, mostly insignificant for the zirconium acetylacetonate molecule in the crystal,⁴ are quite real for the $Zr(C_2O_4)_4^{4-}$ ion in the salt-like aggregate. The principal distortions are indicated in Fig. 3 with identification of the two sets of trapezoidal oxygen atoms as in Fig. 1. The projection of Fig. 3 is along the twofold (quasi- $\bar{2}$) axis which also is the line of intersection at 88.7° of the mean planes of the structurally independent pair of trapezoidal groups. These latter are twisted at zirconium very nearly in agreement with D_2 symmetry while retaining flat rings; each oxalato group is inclined about 5° to the mean trapezoidal plane, and each oxygen atom of the coordination group is 0.11–0.12 Å. from the plane. The twisting, which boils down to a small redirection of Zr–O bonds with concomitant small alterations in inter-ring OZrO bond angles, should require little energy. The preservation of a nearly constant OZrO angle within the rings is demanded, of course, by the ring character.

A superimposed distortion of the inner coordination group, which makes the required twofold axis somewhat polar and, thereby, a poorer approximation to quasi- $\bar{2}$ symmetry, also is illustrated by Fig. 3. A pair of equivalent oxalato rings rotates about zirconium either toward the twofold axis (even subscripts) or away from it (odd subscripts). Thus the inter-ring distance O_1-O_1' , a dodecahedral edge of *a*-type (HS), is lengthened to 2.63 Å., while the analogous O_4-O_4' is shortened to 2.51 Å. The longer bases of the “trapezoids,” which are not dodecahedral edges, simultaneously are altered as shown in Fig. 3.

The structurally independent Zr–O bond distances, each occurring twice within one or the other trapezoidal group (Fig. 1), are: Zr– O_4 , 2.244; Zr– O_1 , 2.216; Zr– O_2 , 2.192; Zr– O_3 , 2.144 Å. In terms of $\bar{4}2m$ (or just $\bar{4}$) symmetry, the first two are of A-type, the latter pair of B-type (HS), with the respective averaged bond distances and mean deviations, Zr– $O_A = 2.230 \pm 0.014$,

(17) H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

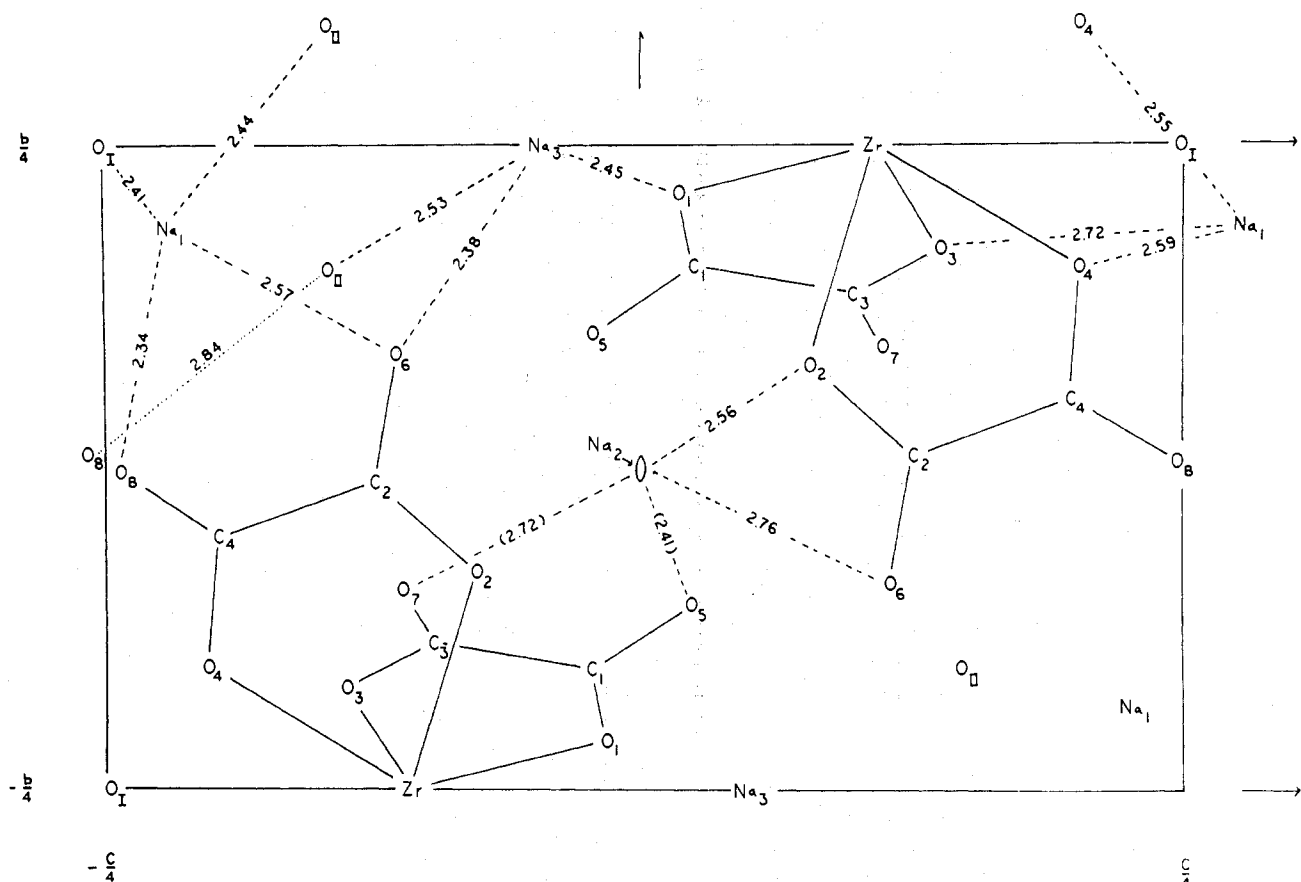


Fig. 4.—Diagram to illustrate the packing arrangement within the crystal. The pertinent Na-O and O-O distances are indicated. General positions in B22₁2 are xyz ; $x\bar{y}\bar{z}$; $\bar{x}, 1/2 - y, z$; $\bar{x}, 1/2 + y, \bar{z}$, and each of these plus $1/2, 0, 1/2$.

$Zr-O_B = 2.168 \pm 0.024 \text{ \AA}$. The variation in the second case is somewhat larger than the maximum deviation from the mean (0.019 \AA .) obtained for $Zr-O$ in zirconium acetylacetonate,⁴ a reflection of gross differences in packing stresses for the two crystalline arrangements. In both cases, however, the data are clear in their insistence that the inner coordination group is the principal repository for packing strains. We consider the observed difference of 0.06 \AA . between the averaged $Zr-O_A$ and $Zr-O_B$ bond lengths to be a highly significant empirical result; it is, moreover, in qualitative agreement³ with the much larger distance, 0.14 \AA ., obtained by refinement of the zircon structure.¹⁸ Interesting connotations of differing M-A and M-B bond lengths in the dodecahedral configuration are discussed in HS.

The averaged (all bonds) $Zr-O$ bond lengths, 2.199 \AA . in $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$, 2.198 \AA . in zirconium acetylacetonate,⁴ are near the mean of values obtained in other studies of zirconium in eight-coordination. Thus in $Zr(SO_4)_2 \cdot 4H_2O$,¹⁹ $Zr(IO_3)_4$,²⁰ and $ZrSiO_4$,¹⁸ the averages of the reported $Zr-O$ bond lengths are, respectively, 2.180, 2.206, and 2.22 \AA .

About 75% of the close Na-O contacts in the crystal involve oxygen of oxalato groups; the coordination groups of sodium ions are completed, as needed, by

water molecules, and hydrogen bonding is relegated to a very minor role. Pertinent Na-O distances are given in Table IV. The diagram of Fig. 4, with the aid of Tables I and IV, enables one to follow, albeit laboriously, the details of the packing.

A sodium ion, Na_1^+ , in the general position^{6a} is in seven-coordination with Na_1-O distances ranging from 2.34 to 2.72 \AA .; just two of the coordinated oxygen atoms belong to water molecules. A sodium ion, Na_2^+ , lying on a twofold axis parallel to a is in eight-coordination with Na_2-O distances (in four equivalent pairs) ranging from 2.41 to 2.76 \AA .; none of the coordinated oxygen atoms belong to water molecules. A sodium ion, Na_3^+ , lying on a twofold axis parallel to c is in six-coordination with Na_3-O distances in the range 2.38 to 2.53 \AA .; the pair of oxygen atoms, O_{II} , at 2.53 \AA . belong to water molecules. All three coordination figures are notably irregular, and every structural class of oxa-

TABLE IV
SODIUM-OXYGEN DISTANCES

Type	Dist., \AA .	Type	Dist., ^a \AA .
Na_1-O_8	2.34	Na_2-O_5	2.41
Na_1-O_I	2.41	Na_2-O_2	2.56
Na_1-O_{II}	2.44	Na_2-O_7	2.72
Na_1-O_4	2.55	Na_2-O_6	2.76
Na_1-O_6	2.57	Na_3-O_6	2.38
Na_1-O_4	2.59	Na_3-O_I	2.45
Na_1-O_8	2.72	Na_3-O_{II}	2.53

^a Each distance in this column occurs twice for each Na^+ .

(18) I. R. Krstanović, *Acta Cryst.*, **11**, 896 (1958).

(19) J. Singer and D. T. Cromer, *ibid.*, **12**, 719 (1959).

(20) A. C. Larson and D. T. Cromer, *ibid.*, **14**, 128 (1961).