

- MCMMASTER, W. H., KERR DEL GRANDE, N., MALLET, J. H. & HUBBEL, J. H. (1969). *Compilation of X-ray Cross Sections*. Natl. Bur. Stand. (URCL-50 174 Sec. II Rev. 1) (TID 4500 UC-34 Physics).
- MARSH, R. E. (1958). *Acta Cryst.* **11**, 654–663.
- METZLER, D. E., IKAWA, M. & SNELL, E. E. (1954). *J. Am. Chem. Soc.* **76**, 648–652.
- NASSIMBENI, L. R., PERCY, G. C. & RODGERS, A. L. (1976). *Acta Cryst.* **B32**, 1252–1256.
- PERAULT, A. M., PULLMAN, B. & VALDEMORO, C. (1961). *Biochim. Biophys. Acta*, **46**, 555–575.
- UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). *Acta Cryst.* **22**, 870–878.
- UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1968). *Acta Cryst.* **B24**, 1361–1369.
- UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1969). *Acta Cryst.* **B25**, 328–335.
- VOZNIAK, M., NICOLE, J. & TRIDOT, G. (1972). *Chim. Anal. (Paris)*, **54**, 147–154.
- WILLSTADTER, E., HAMOR, T. A. & HOARD, J. L. (1963). *J. Am. Chem. Soc.* **85**, 1205–1206.

Acta Cryst. (1978). **B34**, 2110–2115

The Crystal and Molecular Structure of Tetrakis(tropolonato)zirconium(IV)–Chloroform: Zr(C₇H₅O₂)₄·(CHCl₃)_{2.25}

BY ALAN R. DAVIS AND FREDERICK W. B. EINSTEIN*

Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

(Received 20 August 1977; accepted 10 January 1978)

The title compound crystallizes in the triclinic space group $P\bar{1}$, with cell constants $a = 11.714$ (3), $b = 15.163$ (4), $c = 10.317$ (3) Å, $\alpha = 91.74$ (2), $\beta = 73.91$ (3), $\gamma = 100.94$ (2)°, and $Z = 2$. 4527 reflections were measured by counter methods using monochromatized Mo $K\alpha$ radiation [$\lambda(\alpha) = 0.70926$ Å]. Full-matrix least-squares refinement of the 2774 reflections classed as observed (*i.e.* $\geq 2.3\sigma$) gave a final R factor of 7.5%. The geometry about the Zr atom is very nearly dodecahedral, with an average Zr–O bond distance of 2.177 Å, and an average O···O intraligand donor-atom separation of 2.493 Å. The two shortest O···O interligand distances in the ‘ZrO₈’ polyhedron occur between adjacent ligands which are approximately coplanar, providing a further example of what appears to be a trend in high-coordinate chelate complexes. One tropolone ligand is disordered between two positions as a result of close contact with a partially occupied chloroform molecule. However, this disorder does not affect the essential geometry of the ‘ZrO₈’ polyhedron.

Introduction

The tropolonato ligand (hereon abbreviated to T), has been shown to form high-coordinate complexes with a wide variety of metals (Muetterties & Wright, 1967). Previous structural studies have shown it to be a compact, planar ligand with a fairly constant inter-donor-atom separation (Guggenberger & Muetterties, 1972; Davis & Einstein, 1974, 1975). This paper reports the crystal and molecular structure of an eight-coordinate complex of this ligand with Zr^{IV}, which may be compared to other similarly coordinated metal complexes, and its geometry is discussed in relation to the existing theory of high coordination.

Experimental

ZrT₄(CHCl₃)_{2.25} was prepared according to the method described by Muetterties & Wright (1967). Zirconium

tetrachloride (0.25 g, 0.001 mol) was dissolved in chloroform (20 ml) and added with stirring to a solution of tropolone (0.6 g, 0.0045 mol) in chloroform (10 ml). A further 10 ml of chloroform was added to this mixture, which was then refluxed for $\frac{1}{4}$ h. Slow evaporation of the resulting brown solution gave brown/orange crystals which became yellow and amorphous when stored in the absence of chloroform. Rapid loss of chloroform of solvation and the accompanying loss of crystalline character made accurate thermogravimetric analysis impossible, and the mounting of a single crystal somewhat difficult. Finally, a single crystal of approximate dimensions 0.9 × 0.13 × 0.06 mm was sealed under an atmosphere of chloroform in a Lindemann-glass tube, and mounted along the needle axis. Cu radiation ($\lambda = 1.5418$ Å) was used in a preliminary photographic investigation which established triclinic Laue symmetry, with the a axis approximately coincident with the needle axis of the crystal. Accurate cell dimensions were determined from the counter measurement of 12 of the strongest reflections having $2\theta > 20^\circ$ using a Picker FACS-1

* To whom correspondence should be addressed.

computer-controlled four-circle diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.70926 \text{ \AA}$), with a take-off angle of 1.0° .

Crystal data

Zr(C₇H₅O₂)₄·(CHCl₃)_{2.25}, FW 844.3, crystallizes in the triclinic space group $P1$, with $a = 11.714 (3)$, $b = 15.163 (4)$, $c = 10.317 (3) \text{ \AA}$, $\alpha = 91.74 (2)$, $\beta = 73.91 (3)$, $\gamma = 100.94 (2)^\circ$, $V = 1683.3 \text{ \AA}^3$, $d_m = 1.60$ (by flotation), $Z = 2$, $d_x = 1.67 \text{ g cm}^{-3}$, $\mu(\text{Mo } K\alpha) = 9.23 \text{ cm}^{-1}$, $t = 22 (\pm 1)^\circ\text{C}$.

Reflections for the unique set of data were collected in two shells using a scintillation detector with pulse-height analysis, with a symmetric θ - 2θ scan at a speed of 2° min^{-1} . For data where $\sin \theta < 0.2164$, a scan

base width of 1.5° was used, with background counts of 10 s made at both scan limits; for data where $0.2164 < \sin \theta < 0.3826$, a scan base of 0.9° was used with background counts of 4 s made at both scan limits. After each seventy reflections, two standard reflections were measured; their variation was $\pm 5\%$ over the entire data collection. The measured intensities were corrected for Lorentz and polarization effects; absorption was neglected since it was estimated to produce an extreme error of $\pm 6\%$ in I . 4527 reflections were measured, of which 2774 were classed as observed (*i.e.* greater than $2.3\sigma_I$, where $\sigma_I = [\text{TC} + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$ and where TC is the total count, B_1 and B_2 are background counts at either end of the scan range, t_s is the scan time, t_b is the total background count time, k is a constant set to 0.03, and I is the net count}.

Table 1. Fractional atomic coordinates ($\times 10^4$, for Zr $\times 10^5$) in crystalline ZrT₄·(CHCl₃)_{2.25}

Least-squares estimated errors in this and other tables are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Zr	-22056 (8)	18206 (7)	7586 (11)	C(33')	514 (22)	5262 (15)	1103 (24)
Cl(1)	4221 (3)	3422 (2)	3829 (4)	C(34')	1662 (21)	5118 (16)	711 (24)
Cl(2)	6211 (3)	4830 (3)	3399 (4)	C(35')	2058 (18)	4360 (15)	245 (23)
Cl(3)	4788 (23)	4305 (18)	1509 (26)	C(36')	1438 (19)	3496 (15)	157 (24)
Cl(3')	5362 (24)	4475 (15)	1270 (21)	C(37')	168 (21)	3210 (16)	483 (26)
Cl(4)	709 (4)	1362 (3)	-4078 (4)	C(41)	-3535 (16)	2620 (7)	-1972 (15)
Cl(5)	2106 (3)	1451 (3)	-2197 (4)	C(42)	-4517 (11)	2888 (6)	-1248 (15)
Cl(6)	1610 (4)	3063 (3)	-3096 (5)	C(43)	-4589 (19)	3193 (12)	-2455 (24)
Cl(7)	-20 (17)	3356 (12)	3778 (16)	C(44)	-3803 (27)	3334 (16)	-3684 (28)
Cl(8)	-505 (17)	5020 (15)	4726 (26)	C(45)	-2632 (23)	3135 (12)	-4043 (18)
Cl(9)	1675 (25)	4625 (20)	4539 (40)	C(46)	-2043 (12)	2790 (9)	-3245 (20)
O(1)	-1137 (5)	830 (4)	-236 (6)	C(47)	-2396 (12)	2532 (8)	-1894 (16)
O(2)	-3376 (5)	611 (4)	364 (6)	C(1)	5504 (10)	3982 (8)	2619 (12)
O(3)	-1796 (6)	1258 (4)	2436 (7)	C(2)	1096 (10)	1936 (8)	-2728 (11)
O(4)	-3711 (6)	1735 (5)	2570 (9)	C(3)	270	4246	4744
O(5)	-2027 (13)	3089 (10)	1859 (16)	H(12)	-65	-3308	-143
O(5')	-1846 (13)	3279 (10)	1160 (16)	H(13)	-563	-1564	-2480
O(6)	-1272 (5)	2398 (5)	382 (7)	H(14)	-2367	-2213	-2696
O(7)	-3634 (6)	2384 (5)	1248 (9)	H(15)	-4145	-1833	-1716
O(8)	-1670 (6)	2245 (5)	-1346 (8)	H(16)	-4556	-726	-415
C(11)	-1625 (8)	87 (7)	-708 (10)	H(22)	-1481	588	4416
C(12)	-1905 (7)	-492 (7)	-1395 (10)	H(23)	-2519	190	6468
C(13)	-1213 (8)	-1266 (7)	-2036 (11)	H(24)	-4364	409	7537
C(14)	-2345 (8)	-1693 (7)	-2140 (11)	H(25)	-5617	979	6741
C(15)	-3458 (7)	-1446 (7)	-1541 (11)	H(26)	-5386	1489	4727
C(16)	-3708 (7)	-739 (7)	-756 (10)	H(32)	-1580	4574	2966
C(17)	-2944 (8)	-37 (7)	-362 (10)	H(33)	105	5534	3023
C(21)	-2539 (9)	1108 (7)	3601 (13)	H(34)	2009	5299	2363
C(22)	-2281 (9)	720 (8)	4652 (14)	H(35)	2730	4288	1019
C(23)	-2928 (11)	479 (8)	5960 (13)	H(36)	1788	3064	426
C(24)	-4090 (12)	602 (8)	6603 (11)	H(32')	-1275	4889	1504
C(25)	-4854 (10)	960 (9)	6106 (15)	H(33')	435	5866	1377
C(26)	-4698 (9)	1293 (8)	4851 (13)	H(34')	2284	5623	764
C(27)	-3687 (9)	1396 (7)	3689 (13)	H(35')	2929	4435	-119
C(31)	-956 (18)	3576 (14)	1856 (22)	H(36')	1923	3045	-169
C(32)	-835 (20)	4388 (16)	2501 (23)	H(42)	-5232	2857	-515
C(33)	210 (26)	4973 (18)	2565 (29)	H(43)	-5356	3340	-2426
C(34)	1407 (27)	4841 (20)	2114 (30)	H(44)	-4044	3592	-4391
C(35)	1854 (21)	4199 (17)	1338 (27)	H(45)	-2179	3256	-4976
C(36)	1276 (22)	3457 (16)	930 (27)	H(46)	-1240	2711	-3725
C(37)	-11 (23)	3131 (18)	1112 (27)	H(1)	6044	3574	2254
C(31')	-736 (19)	3737 (14)	914 (23)	H(2)	338	1896	-1954
C(32')	-547 (19)	4641 (15)	1197 (22)	H(3)	-24	3991	5627

Structure determination and refinement

A three-dimensional Patterson synthesis based on all the data gave the position of the Zr atom; refinement of these atomic parameters and two scale factors (for the inner and outer shells of data) gave $R = 0.439$, where $R = \sum (|F_o| - |F_c|) / \sum |F_o|$. A Fourier synthesis gave the positions of the eight O and the three Cl atoms of one molecule of chloroform. Several cycles of refinement and subsequent electron density difference maps gave the positions of a further molecule of chloroform and all tropolonato C atoms. With all these atoms assigned anisotropic thermal parameters, full-matrix least-squares refinement gave an R factor of 0.101, though it was clear that one tropolonato ligand (ligand 3) was irregular. The seven C atoms and one O at this ligand had very large components of thermal motion in a direction approximately perpendicular to the general plane of the ring, suggesting that the ring was disordered between two positions. Further, there were some large peaks still unaccounted for in the electron density difference map which were close to this disordered ring. The disorder in ligand 3 was accommodated by arranging the seven C atoms and one O atom [O(5)] in two positions, each with half occupancy. Upon refinement of alternate occupancy factors and isotropic thermal-motion parameters, this model behaved well, with refined occupancy factors remaining at 0.5. The peaks thus far unaccounted for in the difference map suggested another molecule of chloroform. However, since this molecule was extremely close to a centre of symmetry, and since in either position it had close contact with one position of ligand 3, it was assigned an occupancy of 0.25. A list of the short contacts which led to our model is given in Table 4 and the resulting packing within the unit cell can be seen in Fig. 4. Two further ramifications of the

presence of the partially occupied, disordered chloroform should be mentioned. When the molecule is present, ligand 3 is bent away to relieve short contacts that occur. The alternative position adopted by this ligand creates several short contacts with a further chloroform molecule of crystallization [notably atom Cl(3)], with subsequent disorder imparted to this

Table 2. Bond lengths (Å) and angles (°) within the 'ZrO₈' polyhedron of crystalline ZrT₄·(CHCl₃)_{2.25}

Zr—O(1)	2.188 (6)	O(1)ZrO(2)	69.4 (2)
Zr—O(2)	2.172 (6)	O(3)ZrO(4)	69.0 (3)
Zr—O(3)	2.161 (7)	O(5)ZrO(6)	71.5 (5)
Zr—O(4)	2.172 (8)	O(5')ZrO(6)	66.6 (5)
Zr—O(5)	2.197 (6)	O(7)ZrO(8)	68.8 (3)
Zr—O(5')	2.220 (14)	O(1)ZrO(3)	78.2 (2)
Zr—O(6)	2.208 (14)	O(1)ZrO(6)	70.7 (2)
Zr—O(7)	2.206 (7)	O(1)ZrO(8)	77.1 (3)
Zr—O(8)	2.168 (8)	O(2)ZrO(3)	95.9 (2)
O(1)—O(2)	2.480 (7)	O(2)ZrO(4)	79.8 (2)
O(3)—O(4)	2.457 (9)	O(2)ZrO(7)	78.2 (2)
O(5)—O(6)	2.574 (15)	O(2)ZrO(8)	91.6 (3)
O(5')—O(6)	2.425 (15)	O(3)ZrO(5)	84.4 (5)
O(7)—O(8)	2.471 (10)	O(3)ZrO(5')	101.4 (6)
O(1)—O(3)	2.743 (9)	O(3)ZrO(6)	78.6 (3)
O(1)—O(6)	2.538 (9)	O(4)ZrO(5)	70.5 (5)
O(1)—O(8)	2.713 (10)	O(4)ZrO(5')	85.4 (5)
O(2)—O(3)	3.218 (8)	O(4)ZrO(7)	72.5 (3)
O(2)—O(4)	2.786 (9)	O(5)ZrO(7)	81.5 (5)
O(2)—O(7)	2.772 (9)	O(5')ZrO(7)	73.7 (5)
O(2)—O(8)	3.111 (9)	O(5)ZrO(8)	104.2 (5)
O(3)—O(5)	2.936 (16)	O(5')ZrO(8)	84.9 (5)
O(3)—O(5')	3.390 (16)	O(6)ZrO(8)	76.9 (3)
O(3)—O(6)	2.759 (10)	O(5)ZrO(5')	19.3 (5)
O(4)—O(5)	2.529 (17)		
O(4)—O(5')	2.979 (18)		
O(4)...O(7)	2.589 (12)	O(5')...O(8)	2.961 (16)
O(5)...O(7)	2.882 (17)	O(6)...O(8)	2.713 (10)
O(5')...O(7)	2.655 (16)	O(5)...O(5')	0.743 (18)
O(5)...O(8)	3.452 (17)		

Table 3. Parameters used to describe the 'ZrO₈' polyhedron

(a) Values of δ and φ (as defined by Porai-Koshits & Aslanov, 1972) for regular polyhedra of the dodecahedra class, and for tetrakis(tropolonato) complexes of Sc^{III}, Nb^V and Zr^{IV}

	δ (°)				φ (°)	
Dodecahedron	29.5	29.5	29.5	29.5	0	0
Bicapped trigonal prism	0	21.7	48.2	48.2	16.1	16.1
Square antiprism	0	0	52.5	52.5	24.5	24.5
ScT ₄ ⁻	13.4	29.0	42.3	43.0	10.8	10.8
ZrT ₄ ⁻	22.9	31.8	32.4	40.1	6.6	1.9
NbT ₄ ⁺	19.4	21.0	42.9	45.1	11.5	13.9

(b) Angular parameters (°) which define the geometry of ZrT₄⁻, ScT₄⁻ and NbT₄⁺ compared with those generated by calculation

	φ_A	φ_B	θ_A	θ_B	$M - A/M - B$
D_{2d} dodecahedron ($b = 1.15$)	39.2	112.3	45.0	40.6	1.0
D_2 square antiprism ($b = 1.15$)	37.5	107.1	33.4	52.5	1.0
ScT ₄ ⁻ ($b = 1.13$)	36.3	105.5	37.8	48.3	1.01
ZrT ₄ ⁻ ($b = 1.145$)	35.8	105.6	44.3	47.9	1.01
NbT ₄ ⁺ ($b = 1.16$)	35.7	106.3	37.8	49.7	1.01

molecule (see Table 4). The disorder is manifested in the large Cl atom thermal-motion parameters; in particular, the extreme motion exhibited by Cl(3) in one direction (z) implied two alternative positions, a model which was adopted (each position being assigned an occupancy factor of 0.5), and which behaved well during further refinement. Some minor disorder is also imparted to ligand 4, which is apparent from the rather high thermal parameters for the C atoms of this ring. All H atom positions were calculated. Full-matrix least-squares refinement of all non-hydrogen atomic parameters, with all atoms assigned anisotropic thermal-motion parameters except the C atoms of ligand 3, atom O(5), and chloroform C atoms, gave a final R factor of 0.075.

Constant unit weights were used in the early stages of refinement; in the final stages, weights $\{= 1/[\sigma^2(F)]\}$ where $\sigma(F) = \sigma_f / (Lp)(2F_o)$ were used. Atomic scattering factors used were taken from Cromer & Waber (1974). Crystallographic computer programs used in this determination have been cited elsewhere (Einstein & Jones, 1972). Atomic positional coordi-

nates are listed in Table 1.* Table 2 shows the bond lengths and angles of the 'ZrO₈' polyhedron, and Table 3 lists the parameters used to describe this polyhedron. Table 4 gives selected intermolecular contacts relevant to the model used to describe the disorder present in the structure. Fig. 1 is a perspective view of the ZrT₄ moiety, Fig. 2 outlines the ZrO₈ coordination polyhedron, Fig. 3 shows the generalized eight coordination relevant to the discussion, and Fig. 4 illustrates the packing within the unit cell.

Discussion

The 'ZrO₈' polyhedron

The procedure described by Porai-Koshits & Aslanov (1972) is used to describe the coordination

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33336 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Shortest intermolecular contacts (Å) in crystalline ZrT₄(CHCl₃)_{2.25} which determine the model used to describe the structure (see text and Fig. 4)

Cl(8*) is the centrosymmetrically related alternative position of Cl(8) in the disordered CHCl₃ molecule of solvation.

H(32)—Cl(8)	2.49	C(33)—Cl(9)	2.89
H(33)—C(3)	2.34	C(33)—C(3)	2.92
H(33)—Cl(8)	1.79	C(34)—C(3)	2.58
H(33)—Cl(9)	2.72	C(35)—Cl(7)	2.97
H(33)—H(3)	1.52	C(36)—Cl(7)	2.90
H(34)—Cl(9)	2.33	C(37)—Cl(7)	2.79
C(31)—Cl(7)	2.59	H(35')—Cl(3')	2.40
C(32)—Cl(7)	2.56	H(46)—H(3)	2.18
C(32)—Cl(8)	2.56	H(45)—Cl(7)	2.50
C(33)—Cl(7)	2.62	H(46)—Cl(7)	2.70
C(33)—Cl(8)	2.03	C(46)—H(3)	2.70
C(33)—Cl(8*)	2.83		

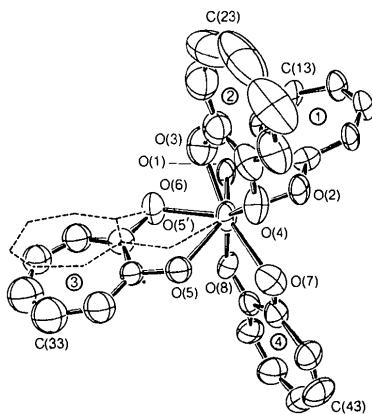


Fig. 1. A perspective view of the ZrT₄ molecule, illustrating the thermal-motion ellipsoids (50%) and labelling. The alternative position of ligand 3 (as explained in the text) is shown in outline.

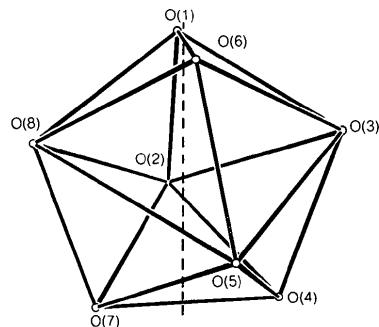


Fig. 2. A perspective view of the distorted dodecahedron formed by the eight O donor atoms in ZrT₄. The direction of the approximate 4 axis is shown by the broken line.

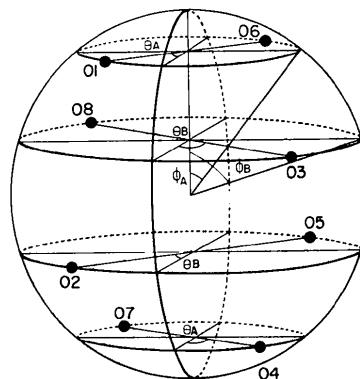


Fig. 3. A diagram of the generalized eight coordination used in the discussion, showing labelling of the angular parameters. [The labelling of the angular parameters used in this discussion differs from those used previously by us. The change has been made to make the labelling consistent with similar work on six coordination (Kepert, 1978).]

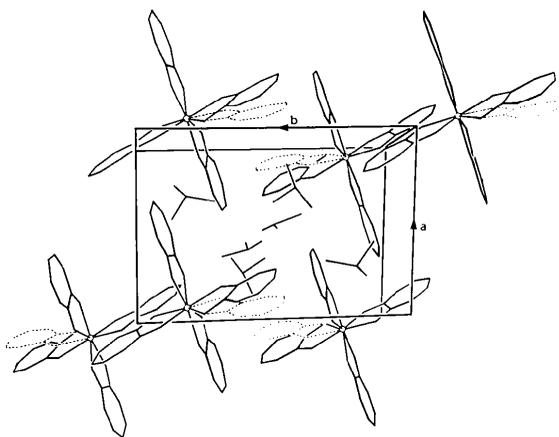


Fig. 4. A view (along *c*) of the unit cell of $ZrT_4 \cdot (CHCl_3)_{2.25}$, illustrating the packing and the disorder in ligand 3 (as described in the text).

polyhedron formed by the eight O atoms. [In this discussion, the position adopted by ligand 3 when the nearby chloroform molecule is present is ignored; the atomic coordinates of atom O(5) are used, rather than O(5').] The polyhedron is described by the four values of σ , the angle between pairs of faces which intersect along those edges which connect vertices at which five edges are joined. These vertices are seen in Fig. 2 as O(5), O(2), O(8) and O(3). Also, the angles φ which indicate the degree of nonplanarity of the intersecting trapezoids O(1), O(2), O(5), O(6) and O(3), O(4), O(7), O(8) are given with the σ values for ZrT_4 , NbT_4^+ , ScT_4^- and idealized polyhedra in Table 3(a). A comparison of these values shows that the ZrO_8 polyhedron is best described as a dodecahedron, distorted slightly towards a bicapped trigonal prism.

Calculations of eight-coordinate geometry for tetrakis-chelate complexes have been made (Blight & Kepert, 1972; Hoard & Silverton, 1963) which are based on the minimization of the total repulsion energy obtained by summing over all donor-atom-donor-atom repulsions. The interaction between the donor atoms of each bidentate ligand is assumed to be constant. The angular parameters of a generalized eight-coordinate stereochemistry (illustrated in Fig. 3) are varied to give the most stable geometry (or geometries) at various values of the normalized bite (*b*): the ratio of the ligand inter-donor-atom separation to the metal-donor-atom distance.

The calculations indicate that at low values of *b* (0.5 → 1.16), the most stable geometry corresponds to the D_{2d} dodecahedron; as the bite increases (1.14 → 1.23), two geometries of equal stability corresponding to the D_{2d} dodecahedron and D_2 square antiprism are obtained. At large normalized bites (1.17 → 1.24), the most stable geometry corresponds to a D_4 square antiprism. Two areas of uncertainty occur where a

Table 5. Bond lengths (Å) and angles (°) in the tropolonato ligands of $ZrT_4 \cdot (CHCl_3)_{2.25}$

Ligand	1	2	3	3'	4
	[O(1), O(2)]	[O(3), O(4)]	[O(5), O(6)]	[O(5'), O(6)]	[O(7), O(8)]
O(1)–C(1)	1.307 (9)	1.27 (1)	1.33 (2)	1.31 (2)	1.29 (1)
O(2)–C(7)	1.310 (9)	1.29 (1)	1.36 (3)	1.25 (2)	1.29 (1)
C(1)–C(7)	1.46 (1)	1.47 (1)	1.43 (3)	1.41 (3)	1.44 (1)
C(1)–C(2)	1.38 (1)	1.38 (1)	1.38 (3)	1.38 (3)	1.39 (1)
C(2)–C(3)	1.37 (1)	1.37 (1)	1.38 (3)	1.39 (3)	1.37 (2)
C(3)–C(4)	1.39 (1)	1.38 (1)	1.40 (3)	1.35 (3)	1.34 (3)
C(4)–C(5)	1.40 (1)	1.35 (1)	1.33 (3)	1.35 (3)	1.41 (3)
C(5)–C(6)	1.35 (1)	1.36 (1)	1.32 (3)	1.39 (3)	1.38 (2)
C(6)–C(7)	1.38 (1)	1.42 (1)	1.45 (3)	1.41 (3)	1.39 (2)
C(7)C(1)C(2)	128 (1)	124 (1)	127 (2)	126 (2)	129 (1)
C(1)C(2)C(3)	129 (1)	133 (1)	129 (2)	131 (2)	128 (2)
C(2)C(3)C(4)	129 (1)	126 (1)	128 (2)	127 (2)	122 (2)
C(3)C(4)C(5)	127 (1)	128 (1)	129 (3)	128 (2)	125 (3)
C(4)C(5)C(6)	129 (1)	130 (1)	129 (3)	131 (2)	129 (2)
C(5)C(6)C(7)	131 (1)	131 (1)	130 (2)	126 (2)	132 (2)
C(6)C(7)C(1)	126 (1)	125 (1)	125 (2)	128 (2)	124 (1)
O(1)C(1)C(7)	113 (1)	113 (1)	110 (2)	114 (2)	113 (1)
O(2)C(7)C(1)	113 (1)	113 (1)	120 (2)	112 (2)	114 (1)
O(1)C(1)C(2)	120 (1)	123 (1)	123 (2)	119 (2)	118 (1)
O(2)C(7)C(6)	121 (1)	122 (1)	114 (2)	120 (2)	121 (1)

choice of two possible geometries exists: $b = 1.13$ – 1.17 (D_{2d} dodecahedron and D_2 square antiprism), and $b = 1.17 \rightarrow 1.22$ (D_2 square antiprism and D_4 square antiprism). The angular parameters for the tetrakis-tropolonates ($b = 1.13 \rightarrow 1.16$) are given in Table 3 together with the parameters produced for the D_{2d} dodecahedron and D_2 square antiprism by the calculations described above. The angular parameters θ_A and θ_B serve as the most useful coordinates with which to separate different stereochemistries. At $b = 1.15$, a projection onto the θ_A – θ_B plane shows the minima corresponding to the D_{2d} dodecahedron and D_2 square antiprism lying in a shallow trough; the values of θ_A and θ_B for the tetrakis-tropolonates place them at different points in the bottom of the same trough between the two idealized geometries. The extent to which the tropolonates are distorted from D_{2d} dodecahedral geometry towards a D_2 square antiprism increases in the series ZrT_4 ($b = 1.145$), NbT_4^+ ($b = 1.16$) and ScT_4^- ($b = 1.13$). [It should be noted that the C_{2v} bicapped trigonal prism used by Porai-Koshits & Aslanov (1972) in their analysis of eight-coordinate geometry would also lie in the same trough, midway between the D_{2d} dodecahedron and the D_2 square antiprism.]

The values of φ_A and φ_B (the angles that metal-donor-atom bonds make with the approximate fourfold inversion axis) for the MT_4 species are consistently lower than the values predicted by the calculations, and reflect the close contacts between atoms O(1) and O(6), and O(4) and O(7) (Fig. 1). It has been noted previously (Davis & Einstein, 1975) that such non-

imposed short contacts always occur between donor atoms of approximately coplanar adjacent ligands where the possibility exists for overlap of lone pairs of electrons on each donor atom, and interaction with empty *d* orbitals on the metal. The lower values of φ_A and φ_B have been attributed to lengthening of $M-(A$ donor atom) bonds relative to $M-(B$ donor atom) bonds as a result of the more highly repulsive bonds exerted on each *A* donor atom. The ratio of $M-A/M-B$ for the tetrakis-tropolonates is 1.01, but it is not clear why the $M-A$ bonds should increase in length to relieve repulsive forces only to then adjust to give close contacts (and subsequent high repulsive energy). This would be explained, however, by invoking the attractive force resulting from lone-pair interaction which would 'cushion' the high repulsive forces caused by close contact.

Tropolonate ligands and chloroform molecules

Bond lengths and angles within the tropolonate ligands are given in Table 5 and include values for both positions of ligand 3. The dimensions do not differ significantly from those obtained in previous structural studies on metal tropolonates (Guggenberger & Muetterties, 1972; Davis & Einstein, 1974, 1975). The seven-membered rings are very nearly planar in each ligand, with slight twisting of the C skeleton relative to the plane formed by the metal and O donor atoms, the angle of twist ranging from 1.05° (ligand 3) to 9.33° (ligand 1).

C—Cl bond lengths within the chloroform molecules of crystallization average 1.71 Å, and the Cl—C—Cl angles average 111°.

We would like to thank the National Research Council of Canada for support, and for a postgraduate scholarship (to ARD). We would also like to thank Professor D. L. Kepert (University of Western Australia, Nedlands) for a preprint of a forthcoming review.

References

- BLIGHT, D. G. & KEPERT, D. L. (1972). *Inorg. Chem.* **11**, 1556–1561.
 CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.
 DAVIS, A. R. & EINSTEIN, F. W. B. (1974). *Inorg. Chem.* **13**, 1880–1884.
 DAVIS, A. R. & EINSTEIN, F. W. B. (1975). *Inorg. Chem.* **14**, 3030–3036.
 EINSTEIN, F. W. B. & JONES, R. D. G. (1972). *Inorg. Chem.* **11**, 395–400.
 GUGGENBERGER, L. J. & MUETTERTIES, E. L. (1972). *J. Am. Chem. Soc.* **94**, 8046–8055.
 HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**, 235–243.
 KEPERT, D. L. (1978). *Prog. Inorg. Chem.* In the press.
 MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Q. Rev. Chem. Soc.* **21**, 109–194.
 PORAI-KOSHITS, M. A. & ASLANOV, L. (1972). *Zh. Strukt. Khim.* **13**, 266–277.

Acta Cryst. (1978). **B34**, 2115–2118

Structure Cristalline du Bis(malonato)béryllate de Potassium Hémihydraté: $K_2[Be(CO_2CH_2CO_2)_2] \cdot \frac{1}{2}H_2O$

PAR GÉRARD DUC, RENÉ FAURE ET HENRI LOISELEUR

Laboratoire de Chimie Analytique 2, Université Claude Bernard, 43 boulevard du 11 Novembre 1918,
 69621 Villeurbanne, France

(Reçu le 6 janvier 1978, accepté le 8 février 1978)

Crystals of potassium bis(malonato)beryllate hemihydrate, $K_2[Be(CO_2CH_2CO_2)_2] \cdot \frac{1}{2}H_2O$, are monoclinic, space group $C2/c$, with $a = 22.082$ (3), $b = 9.486$ (2), $c = 15.183$ (4) Å, $\beta = 140.41$ (3)° and $Z = 8$. Mo $K\alpha$ intensities were collected on an automatic four-circle diffractometer and the structure was determined by means of the Patterson function and Fourier syntheses. An anisotropic full-matrix least-squares refinement was performed yielding a final R of 0.035 for the 1958 actually measured reflexions. The Be atom and two malonato groups make up the complex $[Be(CO_2CH_2CO_2)_2]^{2-}$ anion in which each ligand contributes, by means of two chelating O atoms, to a tetrahedral coordination of the Be atom with Be—O bond lengths between 1.609 (3) and 1.623 (3) Å. Dihedral angles between the COO and CCC planes in some malonic acid compounds are compared.