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Structure of Di-μ-(+)-tartrato-bis[aquazinc(II)] Trihydrate, $[Zn_2(C_4H_4O_6)_2(H_2O)_2].3H_2O$ and Anomalous Scattering by Zinc

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(*Received* 16 *July* 1984; *accepted* 1 *November* 1984)

Abstract. $M_r = 517\cdot0$, orthorhombic, $P2_12_12_1$, $a = 11\cdot256\,(3)$, $b = 18\cdot021\,(7)$, $c = 7\cdot960\,(3)$ Å, $V = 1615$ Å^3, $Z = 4$, $D_x = 2\cdot126\,(2)$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0\cdot70930$ Å, $\mu = 31\cdot3$ cm^{-1}, $F(000) = 1048$, $T = 296$ K, $R = 0\cdot047$ for 3728 reflections. The structure consists of cyclic double chelates which are linked by additional strong coordination of each Zn to a carboxyl O atom of an adjacent group and further by hydrogen bonds. Ave. Zn—O distances are 2·040 (14) (carboxyl), 2·158 (24) (hydroxyl), and 2·059 (4) Å (water). A determination of the anomalous scattering term f'' for Zn and Mo $K\alpha$ radiation gives 1·47 (3) e/atom.

Introduction. In search of crystals for study of anomalous X-ray scattering with synchrotron radiation (*e.g.* Templeton, Templeton, Phizackerley & Hodgson, 1982) we prepared crystals of this Zn salt and determined its structure. Its properties of composition, symmetry, chemical stability, and crystalline quality are suitable for this purpose, and it has been used to measure the X-ray scattering by the Zn^{2+} ion at wavelengths near its K absorption edge (Templeton & Templeton, 1984). Here we report the crystal structure parameters which we needed for analysis of the K-edge experiments, and also a determination of f'' of Zn for Mo $K\alpha$ radiation.

Experimental. Crystals of the title compound were grown by diffusion-controlled precipitation from silica gel using the technique described by Hopwood & Nicol (1972). Crystal 0·09 × 0·20 × 0·33 mm with 15 faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 23 reflections, $20° < 2\theta < 32°$; analytical absorption correction, range 1·26 to 1·41; max. $(\sin\theta)/\lambda = 0\cdot651$ Å^{-1}, h 0 to 14, k 0 to 23, l −10 to 10; three standard reflections, $\sigma = 1\cdot6$, 1·3, 1·4%, no correction for decay; 4093 data, 3730 unique (including 546, $I < \sigma$), 2 low-angle reflections deleted because of poor agreement, $R_{\rm int} = 0\cdot017$; structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier methods, 14 H atoms located in ΔF maps; refinement on F, 301 parameters including f'' for Zn, H atoms with isotropic thermal parameters, anisotropic thermal parameters for other atoms, all O—H bond distances restrained to 0·90 (5) Å, water H—H to 1·50 (10) Å; $R = 0\cdot047$ for 3728 reflections (0·029 for 3182 for which $I > \sigma$), $wR = 0\cdot030$, $S = 0\cdot94$; $w = [\sigma(F)]^{-2}$, derived from $\sigma^2(F^2) = \{[\sigma(F^2)$, counting statistics only$] + (0\cdot03\,F^2)^2\}$; max. $\Delta/\sigma = 0\cdot16$; max. empirical isotropic correction for extinction 7% of F; max. and min. of ΔF synthesis 0·6 and −0·9 e Å^{-3}; atomic f for Zn^{2+}, $O^{1/2-}$ (carboxyl, interpolated), neutral O and C, and spherical bonded H from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965).

Discussion. Atomic parameters are listed in Table 1.† The basic structural unit of this salt is a cyclic double chelate, Fig. 1. Similar groups occur in various tartrate

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39878 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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complexes of Cu, Sb and V (*e.g.* Kiosse, Golovastikov & Belov, 1964; Forrest & Prout, 1967; Tapscott, Belford & Paul, 1968; Prout, Carruthers & Rossotti, 1971; Missavage, Belford & Paul, 1972; Zalkin, Templeton & Ueki, 1973). Each Zn atom is bonded to a carboxyl O atom and a more distant hydroxyl one of each tartrate ion in this chelate (Table 2). Sixfold coordination of each Zn atom is completed by a water molecule and an additional carboxyl O of a neighboring group. The additional O atom, which is nearly as close as any other neighbor, links the groups into a sheet which extends indefinitely in the x and z directions. Bond angles at Zn, listed in Table 2, deviate considerably from 90 or 180° because of the constraints of the chelation bite.

Table 1. *Atomic parameters*

$B_{\rm eq} = \sum(B_{ii})/3.$

	x	y	z	$B_{\rm eq}$(Å^2)
Zn(1)	0·28317 (3)	0·14944 (2)	0·61860 (4)	1·535 (8)
Zn(2)	0·71936 (3)	0·14113 (2)	0·90016 (4)	1·517 (8)
O(1)	0·3385 (2)	0·33168 (11)	0·9147 (3)	2·15 (5)
O(2)	0·2609 (2)	0·23328 (11)	0·7857 (3)	2·36 (6)
O(3)	0·4498 (2)	0·20952 (11)	0·6004 (3)	2·01 (5)
O(4)	0·5681 (2)	0·21391 (12)	0·9257 (3)	1·73 (5)
O(5)	0·6846 (2)	0·31988 (12)	0·5881 (3)	2·19 (5)
O(6)	−0·2450 (2)	0·22214 (11)	0·7282 (3)	2·00 (5)
O(7)	0·4269 (2)	−0·05161 (12)	0·4902 (3)	2·31 (6)
O(8)	0·3372 (2)	0·05895 (12)	0·4878 (3)	2·02 (6)
O(9)	0·3700 (2)	0·08035 (12)	0·8075 (3)	1·92 (6)
O(10)	0·6094 (2)	0·08380 (11)	0·7090 (3)	1·87 (6)
O(11)	0·5620 (2)	−0·05446 (12)	1·0161 (3)	2·14 (6)
O(12)	0·6390 (2)	0·05895 (12)	1·0320 (3)	1·88 (5)
W(1)	0·6475 (2)	−0·0702 (2)	0·3263 (3)	2·47 (6)
W(2)	1·0020 (3)	0·2504 (2)	0·7515 (4)	3·19 (7)
W(3)	0·3799 (2)	−0·11088 (14)	0·1979 (3)	2·19 (6)
W(4)	0·6311 (4)	0·1073 (2)	0·3801 (4)	5·4 (1)
W(5)	0·3716 (3)	0·0927 (2)	1·1406 (4)	5·0 (1)
C(1)	0·3423 (3)	0·2794 (2)	0·8102 (4)	1·47 (7)
C(2)	0·4552 (3)	0·2747 (2)	0·7033 (4)	1·50 (7)
C(3)	0·5668 (3)	0·2754 (2)	0·8118 (4)	1·28 (6)
C(4)	0·6779 (3)	0·2719 (2)	0·6999 (4)	1·50 (7)
C(5)	0·3931 (3)	0·0066 (2)	0·5591 (4)	1·51 (7)
C(6)	0·4237 (3)	0·0144 (2)	0·7461 (4)	1·41 (7)
C(7)	0·5605 (3)	0·0159 (2)	0·7680 (4)	1·48 (7)
C(8)	0·5893 (3)	0·0062 (2)	0·9525 (4)	1·61 (7)

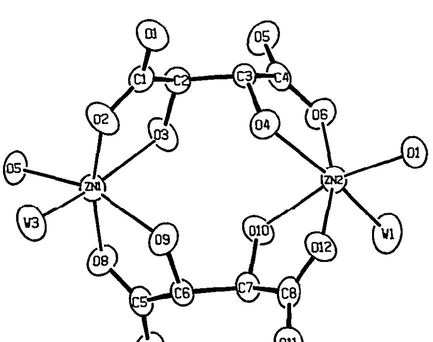

Fig. 1. Cyclic double chelate in the title compound.

Table 2. *Interatomic distances* (Å), *and bond angles* (°) *at* Zn

Zn(1)–O(2)	2·029 (2)	Zn(2)–O(1$^{\rm ii}$)	2·052 (2)
Zn(1)–O(5$^{\rm i}$)	2·060 (2)	Zn(2)–O(6)	2·041 (2)
Zn(1)–O(8)	2·028 (2)	Zn(2)–O(12)	2·028 (2)
Zn(1)–O(3)	2·171 (2)	Zn(2)–O(4)	2·159 (2)
Zn(1)–O(9)	2·183 (2)	Zn(2)–O(10)	2·217 (2)
Zn(1)–W(3$^{\rm iii}$)	2·062 (2)	Zn(2)–W(1$^{\rm iv}$)	2·056 (3)
C(1)–O(1)	1·258 (4)	C(5)–O(7)	1·244 (4)
C(1)–O(2)	1·252 (3)	C(5)–O(8)	1·268 (4)
C(1)–C(2)	1·532 (4)	C(5)–C(6)	1·534 (4)
C(2)–O(3)	1·434 (4)	C(6)–O(9)	1·420 (4)
C(2)–C(3)	1·524 (4)	C(6)–C(7)	1·550 (4)
C(3)–O(4)	1·432 (4)	C(7)–O(10)	1·422 (4)
C(3)–C(4)	1·537 (4)	C(7)–C(8)	1·514 (4)
C(4)–O(5)	1·244 (4)	C(8)–O(11)	1·243 (4)
C(4)–O(6)	1·267 (3)	C(8)–O(12)	1·272 (4)

O–O distances in hydrogen bonds

O(4)–H(7)···W(2$^{\rm v}$)	2·751 (4)	W(2)–H(8)···O(6)	2·834 (4)
O(9)–H(13)···W(5)	2·661 (4)	W(3)–H(9)···O(7)	2·614 (3)
O(10)–H(5)···W(4)	2·664 (4)	W(3)–H(10)···O(11$^{\rm vi}$)	2·707 (3)
W(1)–H(11)···O(7)	2·825 (4)	W(5)–H(14)···O(8$^{\rm vii}$)	2·856 (4)
W(1)–H(12)···O(11)	2·665 (3)		

Symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (iii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iv) $\frac{3}{2}-x, -y, \frac{1}{2}+z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (vi) $x, y, -1+z$; (vii) $x, y, 1+z$.

Bond angles at Zn

O–Zn(1)–O angles

	O(3)	O(5)	O(8)	O(9)	W(3)
O(2)	77·24 (8)	104·90 (10)	166·55 (10)	91·63 (10)	86·56 (10)
O(3)		106·16 (09)	96·18 (9)	86·76 (9)	163·31 (9)
O(5)			88·14 (9)	160·78 (9)	81·68 (9)
O(8)				76·16 (9)	98·81 (11)
O(9)					89·74 (9)

O–Zn(2)–O angles

	O(4)	O(6)	O(10)	O(12)	W(1)
O(1)	107·61 (9)	100·52 (9)	165·74 (9)	95·41 (9)	82·96 (10)
O(4)		77·51 (8)	84·68 (9)	92·46 (9)	168·45 (10)
O(6)			89·01 (9)	163·13 (9)	96·29 (10)
O(10)				76·44 (9)	85·48 (10)
O(12)					91·11 (11)

The structure is further connected by a network of hydrogen bonds (Table 2). Three hydroxyl H atoms and six water ones are found at H-bond sites. Another H atom [on W(4)] appears not to form such a bond. Four other H atoms [one each on O(3), W(2), W(4), and W(5)] could not be located. We conclude that they are not in hydrogen bonds, or else are disordered between alternative bonds.

The bond geometry within the tartrate molecules is normal. Bond distances, averaged for the two to eight examples which are independent in the crystal but equivalent chemically, are C–O (carboxyl) = 1·256 (12), C–O (hydroxyl) = 1·427 (7), C–C (end) = 1·529 (10), and C–C (middle) = 1·537 (18) Å (e.s.d.'s from scatter).

The inclusion of both members of each Bijvoet pair in the data set permits a good determination of f'' for Zn; the result is 1·47 (3) e/atom in good agreement with 1·431 calculated by Cromer & Liberman (1970) for Mo $K\alpha_1$. The positive sign of this result confirms that the absolute configuration, set to give the accepted configuration of the (+)-tartrate ions, is correct.

This work was supported by the National Science Foundation under grant No. CHE-8217443 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76F00098. One of the authors (DZ) gratefully acknowledges financial support from the Ministry of Education of the People's Republic of China.

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Crystallographic Analysis of Two Rhodium(III) Hydride Complexes, Bis{1,1′-bis[*tert*-butyl(phenyl)phosphino]ferrocene-*P*,*P*′}-tri-μ-hydrido-dihydridodirhodium(III) Chlorate Methanol Solvate, $[\mathrm{Rh_2H_5\{Fe[P(C_4H_9)(C_5H_4)(C_6H_5)]_2\}_2]ClO_4.CH_3OH}$ (1), and Bis[1,1′-bis(di-*tert*-butylphosphino)ferrocene-*P*,*P*′]-tri-μ-hydrido-dihydridodirhodium(III) Chlorate, $[\mathrm{Rh_2H_5\{Fe[P(C_4H_9)_2(C_5H_4)]_2\}_2]ClO_4}$ (2)

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(*Received* 13 *June* 1984; *accepted* 3 *October* 1984)

Abstract. $[(L\,L)\mathrm{HRh}(\mu\text{-H})_3\mathrm{RhH}(L\,L)]\mathrm{ClO_4}$ $\{(L\,L) = rac\text{-Fe}[\eta^5\text{-C}_5\text{H}_4\text{P(Ph)(CMe}_3)]_2\}$ (1): $M_r = 1371{\cdot}2$, monoclinic, $P2_1/n$, $a = 18{\cdot}708$ (4), $b = 14{\cdot}857$ (2), $c = 21{\cdot}853$ (4) Å, $\beta = 92{\cdot}95$ (2)°, $V = 6065{\cdot}88$ Å^3, $Z = 4$, $D_x = 1{\cdot}501$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 11{\cdot}89$ cm^{-1}, $F(000) = 2824$, $T = 293$ K, final $R = 0{\cdot}045$ for 5732 observed reflections. $[(L'\,L')\mathrm{HRh}(\mu\text{-H})_3\mathrm{RhH}(L'\,L')]\mathrm{ClO_4}$ $\{(L'\,L') = \text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{P(CMe}_3)_2]_2\}$ (2): $M_r = 1259{\cdot}2$, monoclinic, $P2_1/c$, $a = 15{\cdot}276$ (3), $b = 14{\cdot}751$ (2), $c = 25{\cdot}950$ (3) Å, $\beta = 90{\cdot}85$ (1)°, $V = 5846{\cdot}83$ Å^3, $Z = 4$, $D_x = 1{\cdot}430$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 12{\cdot}26$ cm^{-1}, $F(000) = 2624$, $T = 293$ K, final $R = 0{\cdot}059$ for 4180 observed reflections. The structure of (1) contains an unusual RhPH skeletal structure in which each Rh atom (in the 3+ oxidation state) has three Rh—H bridging bonds [average 1·77 (8) Å], a single Rh—H terminal bond [average 1·56 (12) Å] and two Rh—P bonds. It is tentatively proposed that (2) contains a similar arrangement.

Introduction. In a recent communication (Butler, Cullen, Kim, Einstein & Jones, 1984), we reported the synthesis and crystallographic characterization of rhodium hydrides formed from cationic rhodium complexes $[(L\,L)\mathrm{RhNBD}]^+$ [where $L\,L$ is a bidentate ferrocenylphosphine ligand $\mathrm{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}R_1R_2)$; $R_1 = \mathrm{Bu}^t$, $R_2 = \mathrm{Ph}$ or $R_1 = R_2 = \mathrm{Bu}^t$ and NBD = norbornadiene]. The present report describes, in more detail, the crystallographic aspects of this work.

Experimental. Crystal data for (1) and (2) are given in Table 1. Precession and Weissenberg photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) used to determine approximate cell dimensions and space group. Cell dimensions determined by least-squares refinement of diffractometer angles of 25 reflections, for both (1) ($25 < \theta < 34°$) and (2) ($20 < 2\theta < 29°$), Mo $K\alpha_1$ radiation. Data collected on Enraf–Nonius CAD-4F diffractometer. Background measurements made by extending scan range by 25% at each side of scan. 2 standard

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