Title

STRUCTURE OF ZINC (+)-TARTRATE 2.5-HYDRATE, Zn(C4H4O6) (H2O)2.5, AND ANOMALOUS SCATTERING BY ZINC

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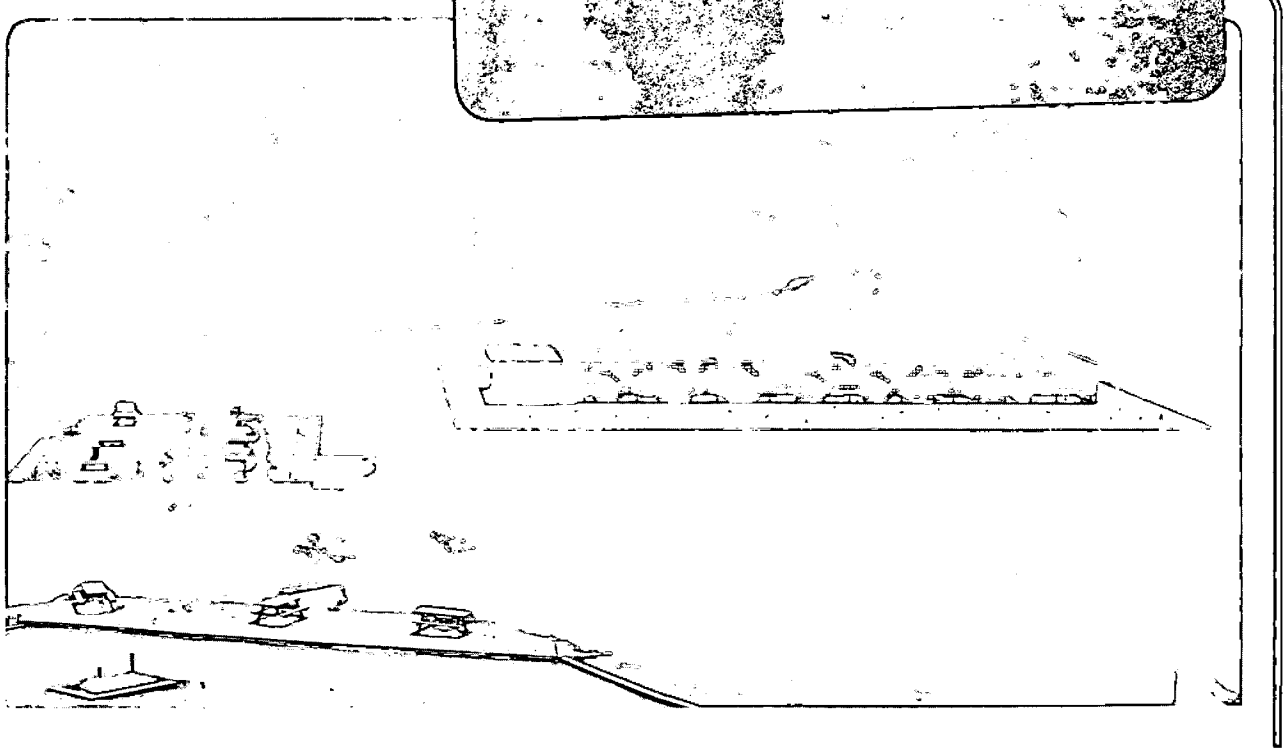

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STRUCTURE OF ZINC (+)-TARTRATE 2.5-HYDRATE, $Zn(C_4H_4O_6)(H_2O)_{2.5}$, AND ANOMALOUS SCATTERING BY ZINC

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Abstract. M_r = 258.5, orthorhombic, $P2_12_12_1$, a = 11.256(3), b = 18.021(7), c = 7.960(3) Å, V = 1615(1) $Å^3$, Z = 8, D_x = 2.126(2) g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1)$ = 0.70930 Å, μ = 31.3 cm^{-1}, F(000) = 1034.5, T = 296 K, R = 0.047 for 3728 reflections. The structure consists of cyclic double chelates which are linked by additional strong coordination of each zinc to a carboxyl oxygen 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 zinc and Mo $K\alpha$ radiation gives 1.47(3) e/atom.

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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 zinc 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 zinc 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 zinc for Mo $K\alpha$ radiation.

Experimental. Zinc tartrate 2.5-hydrate crystals were grown by diffusion-controlled precipitation from silica gel using the technique described by Hopwood & Nicol (1972). A crystal 0.09 x 0.20 x 0.33 mm with 15 faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 23 reflections, $20^0 < 2\theta < 32^0$; analytical absorption correction, range 1.26 to 1.41; max. $(\sin\theta)/\lambda$ = 0.651, h -14 to 14, k 0 to 23, l 0 to 10; three standard reflections, σ = 1.6, 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_{int} = 0.017; structure solved by MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier methods, 14 hydrogen atoms located in ΔF maps; refined on F, 301 parameters including f'' for Zn, hydrogen 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 = 0.047 for 3728 reflections (0.029 for 3182 for which $I>\sigma$), wR = 0.030, S = 0.94; $w = [\sigma(F)]^{-2}$, p = 0.03 in calc. of $\sigma(F^2)$; max. (shift/σ) = 0.16, max. 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 (1974); local unpublished programs and ORTEP (Johnson, 1965). Atomic parameters are listed in Table 1.*

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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. (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The basic structural unit of this salt is a cyclic double chelate, Fig. 1. Similar groups occur in various tartrate complexes of copper, antimony and vanadium (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 zinc atom is bonded to a carboxyl oxygen atom and a more distant hydroxyl one of each tartrate ion in this chelate (Table 2). Six-fold coordination of each zinc atom is completed by a water molecule and an additional carboxyl oxygen of a neighboring group. The additional oxygen 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 zinc range from 76^{0} to 108^{0} (or 161^{0} to 168^{0} for trans neighbors); the smallest angles are those constrained by the chelation bite.

The structure is further connected by a network of hydrogen bonds (Table 2). Three hydroxyl hydrogen atoms and six water ones are found at

H-bond sites. Another hydrogen atom (on W4) appears not to form such a bond. Four other hydrogen 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 2 to 8 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 zinc; the result is 1.47(3) e/atom in good agreement with 1.431 calculated by Cromer & Liberman (1970) for MoKα_1. The positive sign of this result confirms that the absolute configuration, set to give the accepted configuration of the (+)-tartrate ions, is correct.

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Table 1. Atomic parameters for zinc (+)-tartrate 2.5-hydrate

$B_{eq} = \Sigma(B_{ii})/3$, $Å^2$.

	x	y	z	B_{eq}
Zn(1)	.28317(3)	.14944(2)	.61860(4)	1.535(8)
Zn(2)	.71936(3)	.14113(2)	.90016(4)	1.517(8)
O(1)	.3385(2)	.33168(11)	.9147(3)	2.15(5)
O(2)	.2609(2)	.23328(11)	.7857(3)	2.36(6)
O(3)	.4498(2)	.20952(11)	.6004(3)	2.01(5)
O(4)	.5681(2)	.21391(12)	.9257(3)	1.73(5)
O(5)	.6846(2)	.31938(12)	.5881(3)	2.19(5)
O(6)	.7550(2)	.22214(11)	.7282(3)	2.00(5)
O(7)	.4269(2)	-.05161(12)	.4902(3)	2.31(6)
O(8)	.3372(2)	.05895(12)	.4878(3)	2.02(6)
O(9)	.3700(2)	.08035(12)	.8075(3)	1.92(6)
O(10)	.6094(2)	.08380(11)	.7090(3)	1.87(6)
O(11)	.5620(2)	-.05446(12)	1.0161(3)	2.14(6)
O(12)	.6390(2)	.05895(12)	1.0320(3)	1.88(5)
W1	.6475(2)	-.0702(2)	.3263(3)	2.47(6)
W2	1.0020(3)	.2504(2)	.7515(4)	3.19(7)
W3	.3799(2)	-.11088(14)	.1979(3)	2.19(6)
W4	.6311(4)	.1073(2)	.3801(4)	5.4(1)
W5	.3716(3)	.0927(2)	1.1406(4)	5.0(1)
C(1)	.3423(3)	.2794(2)	.8102(4)	1.47(7)
C(2)	.4552(3)	.2747(2)	.7033(4)	1.50(7)
C(3)	.5668(3)	.2754(2)	.8118(4)	1.28(6)
C(4)	.6779(3)	.2719(2)	.6999(4)	1.50(7)
C(5)	.3931(3)	.0066(2)	.5591(4)	1.51(7)
C(6)	.4237(3)	.0144(2)	.7461(4)	1.41(7)
C(7)	.5605(3)	.0159(2)	.7680(4)	1.48(7)
C(8)	.5893(3)	.0062(2)	.9525(4)	1.61(7)

Table 2. Interatomic distances, Å

Zn(1)-O(2)	2.029(2)	Zn(2)-O(1^{ii})	2.052(2)
Zn(1)-O(5^{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^{iii})	2.062(2)	Zn(2)-W(1^{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)

Hydrogen bonds:

O(4)-H(7)...W(2^{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^{vi})	2.707(3)
W(1)-H(11)...O(7)	2.825(4)	W(5)-H(14)...O(8^{vii})	2.856(4)
W(1)-H(12)...O(11)	2.665(3)		

Symmetry code: (i) -1/2 + x, 1/2 - y, 1 - z; (ii) 1/2 + x, 1/2 - y, 2 - z; (iii) 1/2 - x, -y, 1/2 + z; (iv) 3/2 - x, -y, 1/2 + z; (v) -1/2 + x, 1/2 - y, 2 - z; (vi) x, y, -1 + z; (vii) x, y, 1 + z.

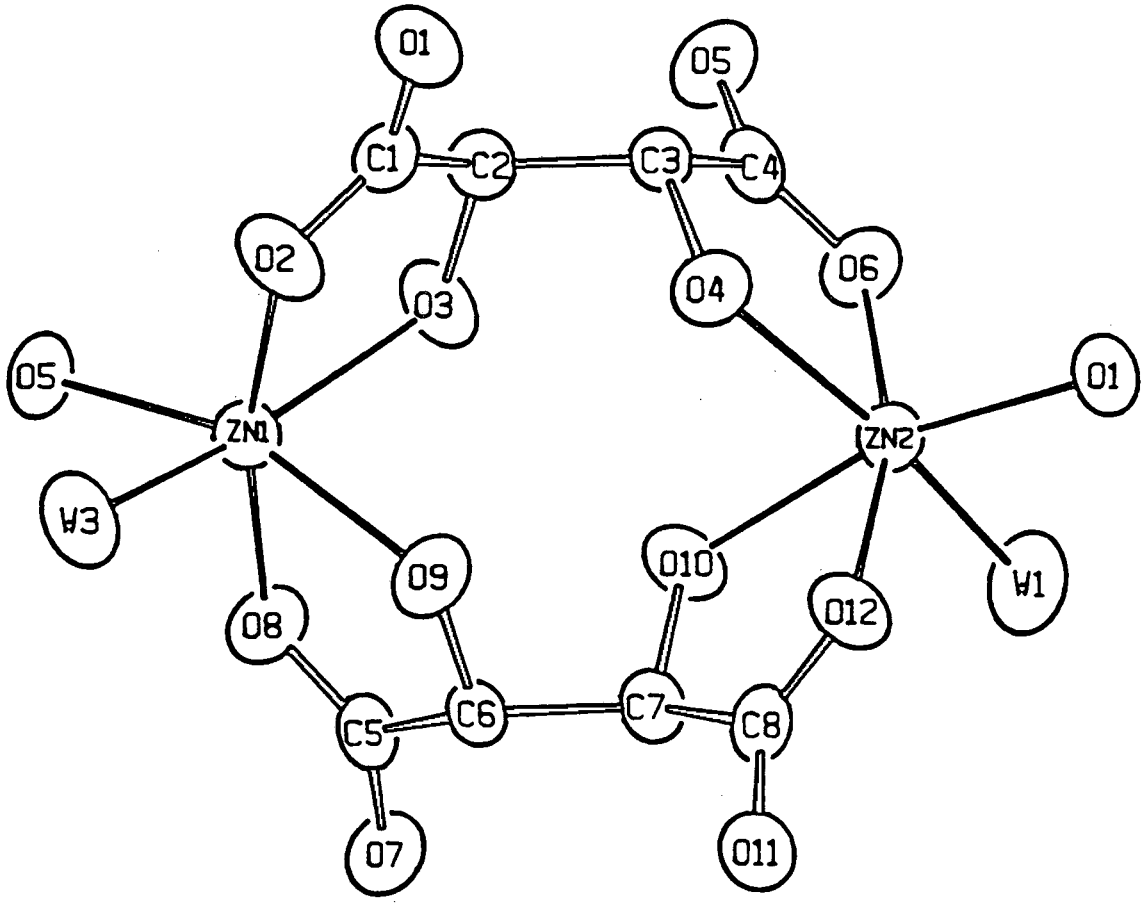

Fig. 1. Cyclic double chelate in zinc (+)-tartrate; thermal ellipsoids at 75% probability level.

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