

Discussion. Atomic parameters are in Table 1 and bond distances in Table 2.*

The crystal structure consists of discrete ions linked by water molecules (Table 2, Fig. 1), producing chains of anions and chains of cations parallel to **b**. Different chains are linked by water molecules. These chains are located so that parallel to (100) the crystal structure

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38721 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

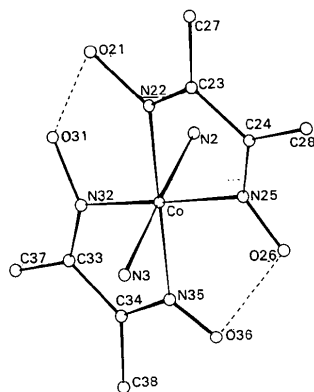


Fig. 2. View of the diamminebis(dimethylglyoximate)cobalt(III) cation.

consists of alternate layers of anions and cations, while parallel to (010) are alternate layers of ions and water molecules.

The bond distances and angles of each ion are very close to those reported in the literature. The Ni—CN bond distances are shorter than the C(*sp*²)—Ni distance of 2.16 (1) Å (Seiler & Dunitz, 1980) due to *sp* hybridization of the C atom. The intramolecular hydrogen bonds between the oxime groups (Fig. 2) are in agreement with the study of Chakravorty (1974).

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Bis[1,3-bis(2-hydroxyphenyl)-1,3-propanedionato]bis(ethanol)zinc(II), $\text{C}_{34}\text{H}_{34}\text{O}_{10}\text{Zn}$

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Abstract. $M_r = 668.0$, triclinic, $P\bar{1}$, $a = 13.028$ (2), $b = 11.872$ (2), $c = 10.971$ (2) Å, $\alpha = 102.28$ (1), $\beta = 87.14$ (1), $\gamma = 112.53$ (2)°, $V = 1530.6$ (7) Å³, $Z = 2$, $D_x = 1.45$ Mg m⁻³, λ (Mo *K*α) = 0.71069 Å, $\mu = 0.889$ mm⁻¹, $F(000) = 696$, $T = 295$ K. Final $R = 0.06$ for 3025 observed reflections. The structure

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consists of chains of molecules parallel to [011] linked by hydrogen bonds. The Zn²⁺ ion is surrounded by six O atoms in a distorted octahedral shape. The 1,3-bis(2-hydroxyphenyl)-1,3-propanedionato anions act as bidentate ligands. The six-membered Zn–propanedione rings have half-chair form.

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Introduction. The title compound was synthesized by Llobet, Teixidor & Casabó (1983). In order to determine the geometry of the compound, an X-ray analysis was carried out.

Experimental. Yellow elongated prisms, 0.3 × 0.1 × 0.1 mm. Philips PW-1100 diffractometer, Mo K α , graphite monochromator, ω -scan technique. Cell parameters from 25 reflections. 3136 independent reflections with $\theta \leq 25^\circ$, range of hkl : -12 to 12, -12 to 12, 0 to 11, 3025 with $I \geq 2.5\sigma(I)$. No significant variation of intensity in three standard reflections Lp correction, absorption ignored. Zn and four coordinated O atoms from a Patterson synthesis, remaining non-H atoms from ΔF synthesis. Anisotropic full-matrix least-squares refinement on F , phenyl rings refined as rigid groups. 29 (of 34) H from ΔF synthesis, refined with overall isotropic temperature factor. $w = [\sigma^2(F_o) + 0.00029|F_o|^2]^{-1}$; final $R = 0.060$, $R_w = 0.058$, $S = 0.294$. $\Delta/\sigma_{\max} = 2.4$. $\Delta\rho = 0.6$ and -1.2 e \AA^{-3} . Anomalous-scattering factors for all atoms from *International Tables for X-ray Crystallography* (1974). Calculations carried out with *SHELX76* (Sheldrick, 1976) on an IBM 4341 computer.

Discussion. Atomic parameters are in Table 1* and selected bond lengths and angles in Table 2. A perspective view of the molecule is shown in Fig. 1.

The structure consists of chains, parallel to [011], of molecules linked by hydrogen bonds [O(6)-H...O(32)] 2.813 (7) and O(5)-H...O(42ⁱⁱ) 2.804 (7) \AA , symmetry code: (i) = $x, 1-y, 1-z$; (ii) = x, y, z . Each Zn²⁺ ion is surrounded by six O atoms in a distorted octahedral geometry. The 1,3-bis(2-hydroxyphenyl)-1,3-propanedionato ligands act in a bidentate fashion. The O atoms of the ethanol ligands occupy the axial sites, while the O atoms of the bidentate ligands form the equatorial plane [deviations of O atoms from mean plane ca 0.035 (7) \AA].

The Zn-propanedione rings adopt a half-chair form, with Zn deviating from the mean plane defined by the propanedione. The C-O and C-C bond distances of this ring [mean values 1.300 (9) and 1.39 (1) \AA respectively] have values intermediate between single and double bonds. This electron delocalization could explain the shortening of the Zn-O(propanedionato) distance [mean 2.020 (7) \AA] with respect to the Zn-O(ethanol) distance [mean 2.177 (3) \AA], or those observed in the literature for octahedral Zn-O geometry (2.17 \AA) (van Niekerk, Schoening & Talbot, 1953; Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates (apart from five belonging to the ethanol molecules) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38720 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature coefficients for the non-H atoms with e.s.d.'s in parentheses

$$B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Zn	143 (1)	2630 (1)	2338 (1)	3.37 (4)
O(1)	1474 (4)	2385 (4)	1459 (5)	3.8 (3)
C(1)	2478 (6)	3226 (7)	1476 (7)	3.1 (4)
O(2)	949 (4)	4476 (4)	2469 (5)	4.1 (3)
C(2)	2014 (6)	5077 (7)	2426 (7)	3.3 (4)
O(3)	-1183 (4)	2898 (4)	3177 (5)	4.0 (3)
C(3)	-2180 (6)	2077 (7)	3138 (7)	3.2 (4)
O(4)	-657 (4)	788 (4)	2303 (5)	3.9 (3)
C(4)	-1710 (6)	188 (7)	2491 (7)	3.3 (4)
C(5)	-2738 (6)	4489 (7)	1956 (7)	3.6 (4)
C(6)	-2438 (6)	802 (7)	2847 (7)	3.5 (4)
O(5)	-588 (5)	2375 (6)	512 (5)	5.6 (3)
O(6)	937 (5)	2937 (5)	4148 (5)	5.1 (3)
O(12)	2071 (5)	590 (5)	701 (6)	5.5 (3)
C(11)	3349 (4)	2739 (4)	910 (5)	3.1 (3)
C(12)	3097 (4)	1458 (4)	583 (5)	3.8 (3)
C(13)	3906 (4)	1014 (4)	73 (5)	4.9 (4)
C(14)	4968 (4)	1851 (4)	-111 (5)	4.8 (4)
C(15)	5220 (4)	3132 (4)	215 (5)	5.1 (5)
C(16)	4411 (4)	3576 (4)	725 (5)	4.1 (4)
O(22)	548 (5)	6401 (5)	3169 (7)	7.6 (4)
C(21)	2424 (4)	6463 (3)	2904 (5)	3.3 (4)
C(22)	1659 (4)	7028 (3)	3230 (5)	4.4 (4)
C(23)	2032 (4)	8314 (3)	3683 (5)	5.8 (5)
C(24)	3169 (4)	9034 (3)	3811 (5)	5.8 (5)
C(25)	3934 (4)	8469 (3)	3486 (5)	5.9 (5)
C(26)	3562 (4)	7183 (3)	3032 (5)	5.0 (4)
O(32)	-1730 (4)	4621 (5)	4400 (6)	5.0 (3)
C(31)	-3079 (3)	2578 (4)	3455 (5)	3.2 (4)
C(32)	-2791 (3)	3814 (4)	4088 (5)	3.7 (4)
C(33)	-3614 (3)	4298 (4)	4393 (5)	5.0 (5)
C(34)	-4725 (3)	3546 (4)	4066 (5)	5.5 (5)
C(35)	-5013 (3)	2310 (4)	3434 (5)	5.2 (5)
C(36)	-4190 (3)	1826 (4)	3128 (5)	4.1 (4)
O(42)	-319 (4)	-1167 (5)	1460 (6)	4.7 (3)
C(41)	-2072 (4)	-1198 (3)	2333 (5)	3.0 (3)
C(42)	-1362 (4)	-1787 (3)	1810 (5)	3.4 (3)
C(43)	-1700 (4)	-3075 (3)	1663 (5)	4.4 (4)
C(44)	-2748 (4)	-3776 (3)	2039 (5)	4.3 (4)
C(45)	-3459 (4)	-3187 (3)	2562 (5)	4.8 (4)
C(46)	-3121 (4)	-1899 (3)	2709 (5)	4.1 (4)
C(51)	-1468 (10)	2558 (11)	16 (11)	8.1 (8)
C(52)	-1534 (9)	3709 (10)	364 (11)	7.5 (7)
C(61)	985 (9)	2123 (9)	4830 (10)	6.6 (6)
C(62)	1643 (11)	1401 (12)	4314 (11)	9.4 (8)

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

Zn-O(1)	2.029 (5)	C(4)-C(6)	1.40 (1)
Zn-O(2)	2.011 (5)	C(1)-C(11)	1.512 (10)
Zn-O(3)	2.018 (5)	C(2)-C(21)	1.502 (8)
Zn-O(4)	2.022 (5)	C(3)-C(31)	1.500 (11)
Zn-O(5)	2.174 (6)	C(4)-C(41)	1.501 (9)
Zn-O(6)	2.180 (6)	O(1)...O(12)	2.508 (7)
C(1)-O(1)	1.305 (7)	O(2)...O(22)	2.493 (7)
C(2)-O(2)	1.298 (8)	O(3)...O(32)	2.519 (7)
C(3)-O(3)	1.286 (8)	O(4)...O(42)	2.502 (7)
C(4)-O(4)	1.310 (8)	O(1)...H(O12)	1.55 (6)
C(1)-C(5)	1.39 (1)	O(2)...H(O22)	1.69 (6)
C(2)-C(5)	1.39 (1)	O(3)...H(O32)	1.62 (6)
C(3)-C(6)	1.39 (1)	O(4)...H(O42)	1.61 (6)
O(2)-Zn-O(1)	88.2 (2)	Zn-O(4)-C(4)	127.9 (5)
O(4)-Zn-O(3)	88.1 (2)	C(5)-C(1)-O(11)	122.9 (7)
O(3)-Zn-O(2)	90.9 (2)	C(5)-C(2)-O(2)	122.8 (6)
O(4)-Zn-O(1)	92.8 (2)	C(6)-C(3)-O(3)	123.6 (8)
O(5)-Zn-O(1)	88.1 (2)	C(6)-C(4)-O(4)	122.3 (7)
O(5)-Zn-O(2)	92.6 (2)	C(11)-C(1)-O(1)	115.4 (6)
O(5)-Zn-O(3)	90.7 (2)	C(21)-C(2)-O(2)	115.6 (7)
O(5)-Zn-O(4)	90.2 (2)	C(31)-C(3)-O(3)	115.9 (6)
O(6)-Zn-O(1)	90.5 (2)	C(41)-C(4)-O(4)	115.4 (7)
O(6)-Zn-O(2)	85.7 (2)	C(11)-C(1)-C(5)	121.7 (6)
O(6)-Zn-O(3)	90.8 (2)	C(21)-C(2)-C(5)	121.6 (6)
O(6)-Zn-O(4)	91.6 (2)	C(31)-C(3)-C(6)	120.5 (6)
Zn-O(1)-C(1)	126.8 (5)	C(41)-C(4)-C(6)	122.3 (6)
Zn-O(2)-C(2)	126.9 (6)	C(1)-C(5)-C(2)	127.9 (6)
Zn-O(3)-C(3)	126.5 (5)	C(3)-C(6)-C(4)	127.5 (6)

The phenyl rings linked to C(1) and C(2) are each twisted by 7.1 (7)° with respect to the propanedione plane. This value is modified in the rings at C(3) and C(4) [twist angles 18.0 (7) and 9.8 (7)° respectively] by the intermolecular hydrogen bonds. These twists and the C(sp²)-C(phenyl) bond distances indicate that the

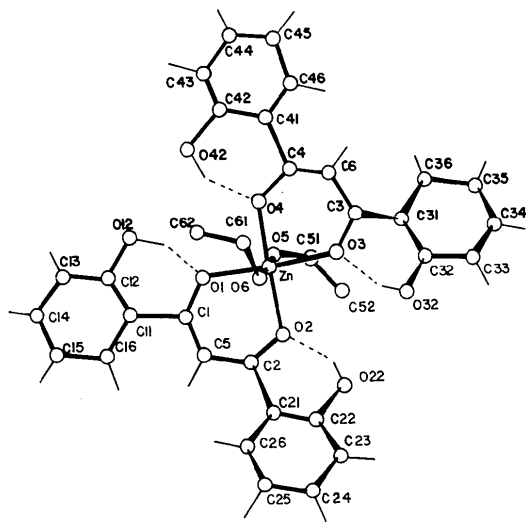


Fig. 1. View of the molecule showing the numbering of the atoms.

electron resonance of propanedione does not extend to the phenyl rings. The hydroxy groups are hydrogen-bonded to adjacent coordinated O atoms. The mean distance is 2.505 (9) Å, similar to that observed in other inorganic compounds with intramolecular hydrogen bonds such as the bis(glyoximato)metal complexes (Solans, Font-Altaba & Briansó, 1983; Nuvas, Briansó, Solans, Font-Altaba & de Matheus, 1983; Solans, Font-Altaba, Bermejo & Alvarez, 1983).

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One-Dimensional *versus* Three-Dimensional Order in Bis(trimethylenediamine)platinum(II) Dichlorobis(trimethylenediamine)platinum(IV) Tetrafluoroborate, [Pt(C₃H₁₀N₂)₂][Pt(C₃H₁₀N₂)₂Cl₂](BF₄)₄, Bis(trimethylenediamine)platinum(II) Dibromobis(trimethylenediamine)platinum(IV) Perchlorate, [Pt(C₃H₁₀N₂)₂][PtBr₂(C₃H₁₀N₂)₂](ClO₄)₄ and Bis(trimethylenediamine)platinum(II) Dibromobis(trimethylenediamine)platinum(IV) Tetrafluoroborate, [Pt(C₃H₁₀N₂)₂][PtBr₂(C₃H₁₀N₂)₂](BF₄)₄. A Re-Refinement of Their Crystal Structures

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Abstract. The structures of the title compounds, described as three-dimensionally ordered in orthorhombic space group *A222* [Matsumoto, Yamashita & Kida (1978). *Bull. Chem. Soc. Jpn.*, **51**, 3514–3518], have been re-refined in space groups *Amm2* and *A2₁22* using the original reflection data; better agreement between observed and calculated structure factors was obtained. Re-refinement leads to one-dimensionally ordered structures where no distinction can be made between the two oxidation states of platinum atoms.

Moreover, significant differences are obtained for Pt–Br distances, conformation of the chelate rings and anion packing.

Introduction. The title compounds belong to the family of mixed-valence platinum compounds analogous to Wolfram's red salt [Pt(NH₂CH₂CH₃)₄][Pt(NH₂CH₂CH₃)₄Cl₂Cl₄·4H₂O] (Wolfram, 1900), and consist of linear chains of roughly planar [Pt(ligands)] units bridged by halide ions.