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Structure of Diaquabis(4-chlorobenzoato)zinc(II)

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Abstract

The crystal structure of the complex [Zn(4-$ClC_6H_4COO)_2(H_2O)_2$] is reported here. Molecules of the complex are bridged by hydrogen bonds forming infinite planes parallel to the *bc* plane. The coordination geometry of the Zn atom is very deformed tetrahedral with four normal Zn—O bonds [1.973 (5) (2 ×) and 1.991 (5) Å (2 ×)]. There are two additional weak interactions at longer Zn···O distances [2.456 (5) Å (2 ×)].

Comment

As part of our study on the synthesis, crystal chemistry, properties and biological activity of zinc carboxylates with and without additional ligands the title complex was isolated and its crystal structure determined. Details of preparation, identification and properties will be published elsewhere (Černák, 1993).

The Zn atom sits on a twofold axis and the coordination polyhedron around it is a very deformed tetrahedron with four normal Zn—O bonds [1.973 (5) (2 ×) and 1.991 (5) Å (2 ×)]. An interesting feature of this structure is the presence of two additional weak Zn···O interactions [2.456 (5) Å (2 ×)] involving the non-coordinated O atoms from adjacent carboxylic groups. These additional interactions may determine the orientation of the carboxylic groups. The same type of very deformed tetrahedral coordination, as well as similar additional weak interactions, was found in both the salicylato complex [Zn(2-$HOC_6H_4COO)_2$-$(H_2O)_2$] (Rissanen, Valkonen, Kokkonen & Leskelä, 1987) and the nitrobenzoato complex [Zn(4-$NO_2C_6H_4COO)_2(H_2O)_2$] (Gusejnov, Musaev, Amiraslanov, Usubaliev & Mamedov, 1983), the

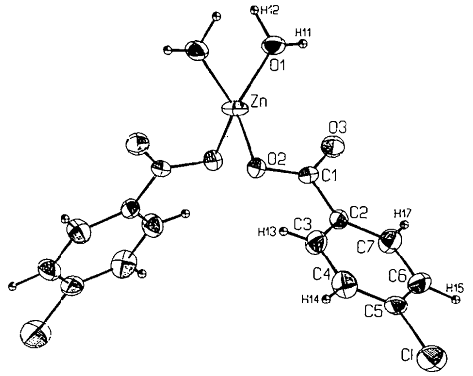

Fig. 1. *ORTEP* drawing of the title compound showing the atomic labeling scheme. Thermal ellipsoids are drawn at the 40% probability level.

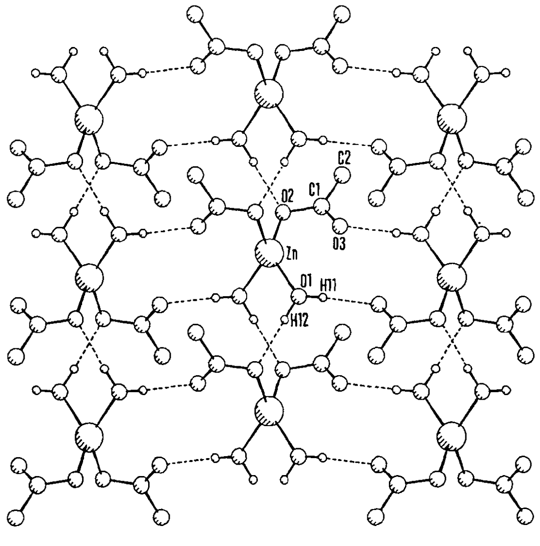

Fig. 2. Schematic drawing of the hydrogen bonding. Benzene rings are omitted for clarity.

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weak interactions exhibiting values of 2.523 (4) Å (2×) for the salicyclato and 2.522 and 2.511 Å for the nitrobenzoato complex. Tetrahedral coordination of the Zn atom was also observed in the aminobenzoato complex $[Zn(4\text{-}NH_2C_6H_4COO)_2(H_2O)_{1.5}]$, but the chromophore was ZnO_2N_2 with two N atoms from bridging amino groups (Amiraslanov, Nadžafov, Usubaliev, Musaev, Movsumov & Mamedov, 1980). Only one weak Zn—O interaction was found for this complex with a distance of 2.494 (8) Å, the second distance of 3.395 (8) Å being too long for effective interaction.

As with the other chlorobenzoato zinc complexes, three different structures were described for zinc complexes with 2-chlorobenzoic acid, these being:

(1) $Zn(2\text{-}ClC_6H_4COO)_2$ ($P2_1/n$) built up of infinite 3,1 chains in which the carboxylic groups bridge the Zn atoms (Clegg, Harbron, Hunt, Little & Straughan, 1990);

(2) $Zn(2\text{-}ClC_6H_4COO)_2$ ($P2_1/c$) built up of infinite 2,2 chains (Nakacho, Misawa, Fujuwara, Wakahara & Tomita, 1976*a*) and

(3) $Zn_2(OH)(H_2O)_2(2\text{-}ClC_6H_4COO)_3$ built up of complicated infinite chains in which two different Zn atoms are present exhibiting coordination numbers of 5 and 6 (Nakacho, Misawa, Fujuwara, Wakahara & Tomita, 1976*b*).

The structure of zinc benzoate is comprised of 3,1 chains (Gusejnov, Musajev, Usubaliev, Amiraslanov & Mamedov, 1984), and is similar to that found in the first modification of 2-chlorobenzoate.

Experimental

Crystal data

$[Zn(C_7H_4ClO_2)_2(H_2O)_2]$
$M_r = 412.5$
Monoclinic
$C2/c$
$a = 26.119\ (9)$ Å
$b = 4.989\ (2)$ Å
$c = 11.910\ (7)$ Å
$\beta = 106.29\ (4)°$
$V = 1490\ (7)$ Å^3
$Z = 4$
$D_x = 1.839$ Mg m^{-3}
$D_m = 1.792\ (1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 4.6\text{-}6.7°$
$\mu = 2.018$ mm^{-1}
$T = 293$ K
Needles
0.5 × 0.1 × 0.05 mm
White
Crystal source: crystallization from aqueous solution

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.193$, $T_{max} = 1.001$
3675 measured reflections
1730 independent reflections
745 observed reflections $[I_o > 3\sigma(I_o)]$

$R_{int} = 0.022$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 33$
$k = 0 \rightarrow 6$
$l = -15 \rightarrow 14$
2 standard reflections monitored every 100 reflections
intensity variation: <6%

Refinement

Refinement on F
Final $R = 0.0400$
$wR = 0.0409$
$S = 0.363$
745 reflections
123 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F) + 0.011101F^2]$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn	0.0	0.57945 (20)	0.2500	0.334 (4)
Cl	−0.2236 (1)	1.6824 (4)	−0.1457 (2)	0.594 (8)
O1	0.0297 (2)	0.3006 (9)	0.1688 (4)	0.402 (19)
O2	−0.0602 (2)	0.8394 (8)	0.2088 (4)	0.331 (15)
O3	−0.0381 (2)	0.7520 (8)	0.0509 (4)	0.376 (17)
C1	−0.0665 (3)	0.8759 (10)	0.1013 (5)	0.285 (22)
C2	−0.1058 (2)	1.0735 (12)	0.0407 (5)	0.264 (20)
C3	−0.1447 (3)	1.1652 (13)	0.0891 (6)	0.364 (24)
C4	−0.1807 (3)	1.3495 (15)	0.0326 (7)	0.460 (31)
C5	−0.1784 (3)	1.4471 (12)	−0.0725 (6)	0.377 (26)
C6	−0.1403 (3)	1.3596 (13)	−0.1228 (6)	0.391 (25)
C7	−0.1042 (3)	1.1744 (13)	−0.0640 (6)	0.390 (27)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *and hydrogen-bonding geometry* (Å, °)

Zn—O1	1.973 (5)	O3—C1	1.242 (9)
Zn—O2	1.991 (5)	C1—C2	1.460 (8)
O2—C1	1.258 (8)	Cl—C5	1.719 (7)
O1—Zn—O2	136.9 (2)	O2—C1—C2	118.3 (5)
Zn—O2—C1	102.4 (4)	O2—C1—O3	119.7 (6)
O3—C1—C2	122.0 (6)		

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O3^{i}	0.81 (8)	1.89 (8)	2.699 (7)	177 (6)
O1—H12···O2^{ii}	0.89 (7)	1.84 (7)	2.721 (7)	170 (6)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, y-1, \frac{1}{2}-z$.

Intensities were corrected for Lorentz and polarization factors using *XP*21 (Pavelčík, 1986). The structure was solved by direct methods with *XFPS* (Pavelčík, Rizzoli & Andreeti, 1990), which provided positions for all non-H atoms, and completed using *SHELX*76 (Sheldrick, 1976). Anisotropic thermal parameters were refined for all non-H atoms. All H atoms were located from a difference Fourier map and refined with isotropic temperature factors fixed to (U_{iso}+0.01) Å^2 for bonded C and O atoms. Geometrical analysis was performed using *PARST* (Nardelli, 1983). *ORTEP* (Johnson, 1965) was employed for drawing the molecular structure and *MOLDRAW* (Ugliengo, Borzani & Viterbo, 1988) was used for the schematic drawing of hydrogen bonds.

The authors thank Mrs Heinrichová for help in the synthetic work.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and full bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71064 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1020]

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Structure of (*OC*-6-14)-Chlorodiiodooxobis(triphenylphosphine)rhenium(V)

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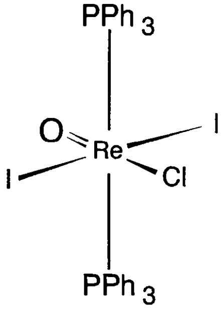
Abstract

The title compound is isostructural with the monoclinic polymorph of $[ReOCl_3\{P(C_6H_5)_3\}_2]$. It consists of octahedral $[ReOClI_2\{P(C_6H_5)_3\}_2]$ molecules of the *trans-trans* isomer, with the O═Re—Cl unit lying on a twofold axis. The bond lengths are Re═O 1.671 (8), Re—P 2.517 (2), Re—Cl 2.383 (4) and Re—I 2.734 (2) Å.

Comment

The triiodo complex $[ReOI_3\{P(C_2H_5)_3\}_2]$ was prepared by Fergusson & Heveldt (1976) by reacting KI with $[ReOCl_3\{P(C_2H_5)_3\}_2]$ in acetone. As a route to the corresponding $P(C_6H_5)_3$ complex, the same reaction was carried out on $[ReOCl_3\{P(C_6H_5)_3\}_2]$. Crystals of the mixed halide compound of the title were obtained when the product was recrystallized from CH_2Cl_2. Attempts are currently being made to determine whether this mixed chloro–iodo molecule was present in the reaction product or was generated by recrystallization.



The compound is isostructural with the monoclinic form of $[ReOCl_3\{P(C_6H_5)_3\}_2]$ (Lebuis & Beauchamp, 1993). The perfectly linear Cl—Re═O unit occupies a crystallographic twofold axis. The octahedron is remarkably regular, all *cis* angles being within 90.0 ± 2.3°. The largest distortion, found for the P—Re—P angle [175.46 (8)°], results from a small displacement of the Re—P bonds away from Re═O. The Re—P distance is the same as in $[ReOCl_3\{P(C_6H_5)_3\}_2]$ and on the short side of the range (2.519–2.553 Å) observed for the ethoxo–halide compounds $[ReO(OC_2H_5)X_2\{P(C_6H_5)_3\}_2]$ (Lebuis, Roux & Beauchamp, 1993). The Re—Cl and Re═O distances are also similar to those of the trichloro complex. On the other hand, the Re—I bonds [2.734 (2) Å] are shorter than in the iodo–alkoxo molecules $[ReO(OR)I_2\{P(C_6H_5)_3\}_2]$ ($R = CH_3$, C_2H_5) (2.764–2.806 Å) (Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983). The Re═O distances in these alkoxo compounds (mean 1.707 Å) are also greater than in the present case [1.671 (8) Å]. The difference of ~0.04 Å, also found between $[ReOCl_3\{P(C_6H_5)_3\}_2]$ and $[ReO(OC_2H_5)Cl_2\{P(C_6H_5)_3\}_2]$ (Graziani, Casellato, Rossi & Marchi, 1985), most likely reflects the variation in *trans* influence between the ethoxo and chloro ligands.

The P—C bonds (mean 1.822 Å) are normal. The phenyl rings are planar, but the P atom is displaced by 0.150 (15) Å from the plane of ring 3. Unequal Re—P—C angles [116.0 (3), 121.4 (3) and 104.4 (3)°] show that coordination does not take place exactly along the lone-pair direction. The phosphines adopt the same conformation as in the monoclinic form of $[ReOCl_3\{P(C_6H_5)_3\}_2]$ (Lebuis & Beauchamp, 1993). The P—C31 bond is nearly eclipsed with the Re═O bond [O—Re—P—C31, −7.1 (3)°], whereas one of