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Diaquabis(4-nitrobenzoato)zinc(II): a redetermination

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Key indicators

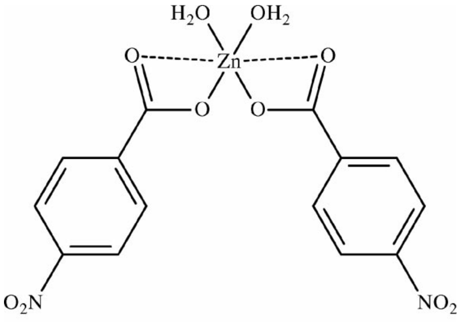
Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.004 Å
R factor = 0.028
wR factor = 0.074
Data-to-parameter ratio = 9.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Zn(O_2CC_6H_4NO_2)_2(H_2O)_2]$, has zinc in a coordination geometry intermediate between tetrahedral and octahedral, with each carboxylate ligand forming a primary and a secondary Zn—O bond; the lengths of these differ by more than 0.5 Å. The molecule has crystallographic twofold rotation symmetry. Intermolecular hydrogen bonds are formed between the aqua ligands as donors and carboxylate O atoms as acceptors, linking the molecules together into sheets, the closest contacts between which involve the nitro groups.

Comment

As part of a study of zinc complexes of carboxylic acids, we have attempted to prepare anhydrous zinc 4-nitrobenzoate and have obtained the title compound, (I), which incorporates two molecules of water as ligands to the Zn atom in addition to the two 4-nitrobenzoate groups.



(I)

The crystal structure of this complex has been reported previously by Guseinov *et al.* (1983), from data collected at room temperature. Although the space group was given as $P\overline{1}$, with a complete molecule as the asymmetric unit, use of the *ADSYM* procedure of *PLATON* (Spek, 2000) shows that this should be $C2/c$, with molecules lying on twofold rotation axes and an asymmetric unit containing only one ligand of each kind as well as the Zn atom. The transformed structure is essentially the same as that reported here, which has been determined from low-temperature data and is of higher precision.

The monomeric molecule (Fig. 1) has a highly distorted coordination geometry for zinc, intermediate between tetrahedral and octahedral. Each of the two symmetry-equivalent 4-nitrobenzoate ligands coordinates to Zn through a primary Zn—O bond and a considerably weaker secondary Zn—O bond, the difference in the bond lengths being >0.5 Å. The

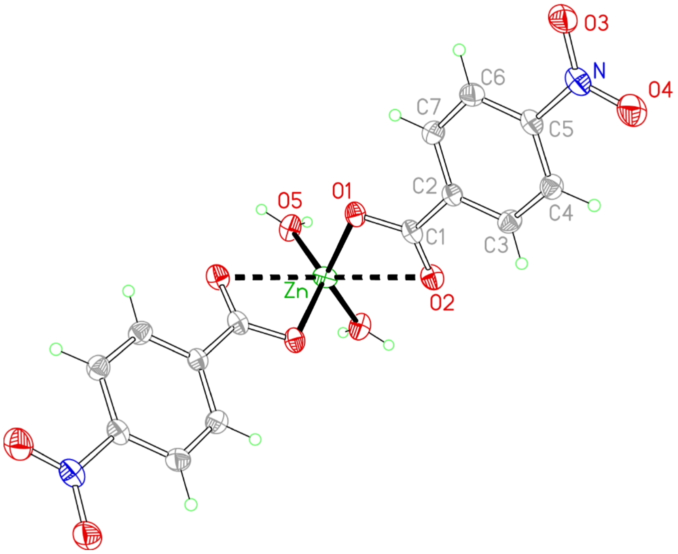


Figure 1
The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms. The view is down the *b* axis and the secondary Zn—O bonds are shown broken.

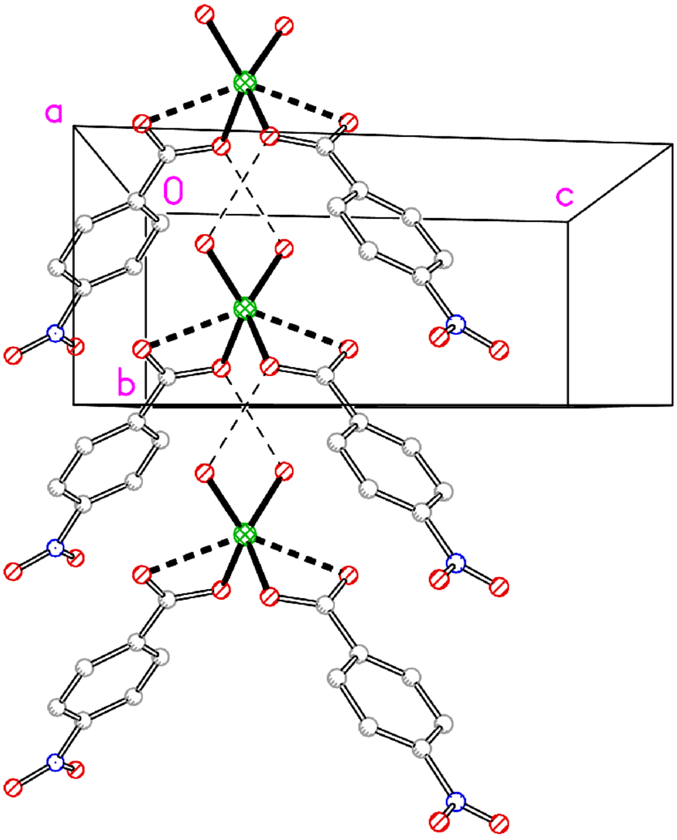


Figure 2
Chains of molecules linked along the *b* axis by O—H···O hydrogen bonds (shown dashed).

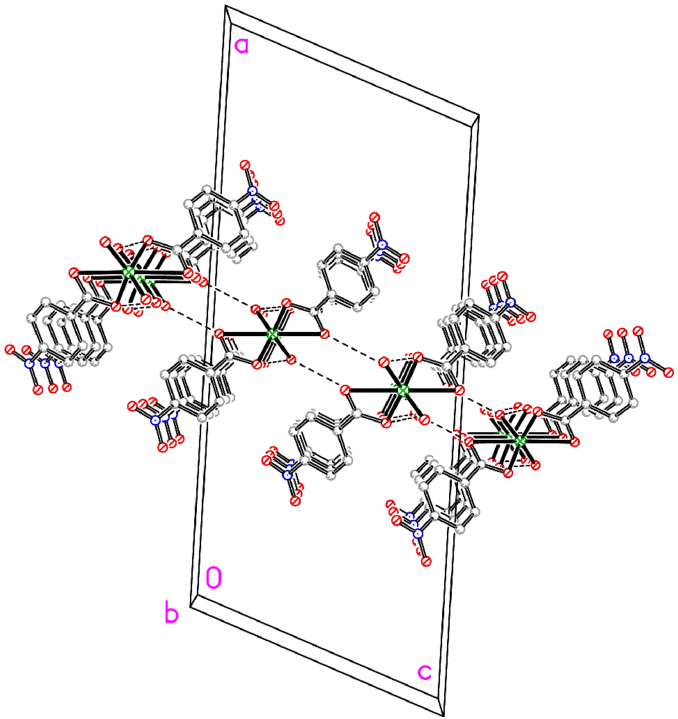


Figure 3
The crosslinking of chains of molecules by further O—H···O hydrogen bonds. The view direction is as for Fig. 1.

asymmetry of bonding by the two O atoms of the carboxylate function is also reflected in the C—O bond lengths, which differ by 0.04 Å, the shorter C—O bond being the one more weakly coordinated to zinc and having greater double-bond character.

The coordinated water molecules are involved in hydrogen bonding, acting as donors but not acceptors. One H atom of each aqua ligand hydrogen bonds to a carboxylate O atom in the next molecule along the short *b* axis, generating chains of molecules in this direction (Fig. 2). The other forms a hydrogen bond to a carboxylate O atom in an adjacent molecule, such that the chains of molecules are further crosslinked into sheets (Fig. 3). These sheets are stacked with shortest contacts involving their nitro groups.

Diaqua complexes of bis(carboxylato)zinc(II) are known for many different carboyxlates, and there are about 20 examples in the Cambridge Structural Database (Allen & Kennard, 1993). The structure of the title compound is typical, but the second Zn—O bond for each carboxylato ligand varies considerably in length, from a situation in which the two Zn—O bonds are equivalent in a symmetrically chelating carboxylate to over 2.8 Å for ligands which are essentially monodentate. The degree of asymmetry in the title compound lies towards the higher end of this observed range.

Experimental

The title compound was prepared from the reaction of $ZnSO_4 \cdot 7H_2O$ (0.01 mol) and sodium 4-nitrobenzoate (0.02 mol) solutions; sodium 4-nitrobenzoate was first obtained by adding 0.02 mol of 4-nitrobenzoic acid to an aqueous solution of 0.02 mol $NaHCO_3$. The mixture was set aside to crystallize at ambient temperature for several days, giving suitable colourless single crystals.

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Crystal data

$[Zn(C_7H_4NO_4)_2(H_2O)_2]$
$M_r = 433.63$
Monoclinic, $C2/c$
$a = 26.519\ (4)$ Å
$b = 5.1011\ (9)$ Å
$c = 12.143\ (2)$ Å
$\beta = 110.019\ (4)^\circ$
$V = 1543.4\ (5)$ Å^3
$Z = 4$
$D_x = 1.866$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3034 reflections
$\theta = 2.2$–25.3°
$\mu = 1.66$ mm^{-1}
$T = 160\ (2)$ K
Block, colourless
$0.52 \times 0.32 \times 0.24$ mm

Data collection

Siemens SMART 1K CCD diffractometer
ω rotation with narrow frames
Absorption correction: multi-scan (*XPREP*; Sheldrick, 1997)
$T_{\min} = 0.538$, $T_{\max} = 0.624$
3124 measured reflections
1278 independent reflections
1262 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 25.4^\circ$
$h = -30 \rightarrow 25$
$k = -5 \rightarrow 4$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.09$
1278 reflections
130 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 3.1320P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0018 (4)

Table 1
Selected geometric parameters (Å, °).

Zn—O5	1.9888 (18)	O1—C1	1.286 (3)
Zn—O1	2.0062 (16)	O2—C1	1.246 (3)
Zn—O2	2.5141 (17)		
O5—Zn—O5$^{\rm i}$	89.83 (11)	O5—Zn—O2$^{\rm i}$	82.99 (6)
O5—Zn—O1	102.13 (7)	O1—Zn—O2$^{\rm i}$	93.74 (6)
O5—Zn—O1$^{\rm i}$	136.40 (7)	O2—Zn—O2$^{\rm i}$	137.39 (8)
O1—Zn—O1$^{\rm i}$	97.44 (9)	C1—O1—Zn	102.22 (14)
O5—Zn—O2	129.54 (6)	C1—O2—Zn	79.85 (13)
O1—Zn—O2	57.01 (6)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$A\cdots$O2$^{\rm i}$	0.80 (2)	1.95 (2)	2.737 (2)	172 (3)
O5—H5$B\cdots$O1$^{\rm ii}$	0.79 (2)	2.01 (3)	2.794 (2)	169 (3)

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

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with $U_{\rm iso}$ constrained to be $1.2U_{\rm eq}$ of the carrier atom, in the organic ligands. For the coordinated water molecules, H atoms were refined with the restraint of similar O—H distances, and with $U_{\rm iso} = 1.5U_{\rm eq}({\rm O})$.

Data collection: *SMART* (Siemens, 1995); cell refinement: local programs; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Guseinov, G. A., Musaev, F. N., Amiraslanov, I. R., Usubaliev, B. T. & Mamedov, Kh. S. (1983). *Koord. Khim.* **9**, 1687–1694.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2000). *PLATON*. University of Utrecht, The Netherlands.

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