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Diaquabis(dimethyl sulfoxide)bis(2,4-dinitrobenzoato)cobalt(II)

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The title compound, [Co($C_7H_3N_2O_6$)$_2$(C_2H_6OS)$_2$(H_2O)$_2$], has been prepared and its structure established by an X-ray structure determination in order to assist the modelling of processes of chemisorption of organic salts formed by dinitrobenzoic acids (DNBH) and secondary amines (R_2NH) by metal surfaces. The 2,4-DNB ions and dimethyl sulfoxide (DMSO) molecules behave as monodentate ligands coordinated to the Co atom through their O atoms. These ligands, together with two molecules of water, form a slightly distorted octahedral coordination environment for the Co atom which is disposed at a centre of symmetry.

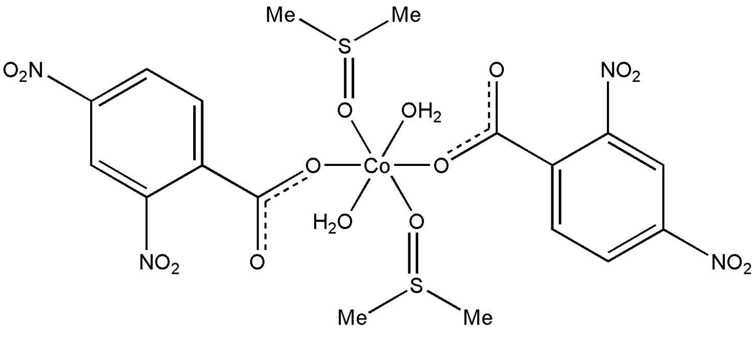
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.001 Å
Disorder in main residue
R factor = 0.026
wR factor = 0.075
Data-to-parameter ratio = 30.2

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

Comment

Both the dinitrobenzoate (DNB) ion and the dimethyl sulfoxide (DMSO) ligand have found application as 'volatile corrosion inhibitors'. They are known to be versatile reagents that, in complexes of such ligands with metals, can interact with the metal cation or remain as counter-anions. When involved in coordination processes, benzoates exhibit a wide range of coordination modes, where coordination to the metal atom is achieved *via* the O atoms of the carboxylate, and/or the nitro groups. The coordination mode adopted by the ligand is determined by the nature of the metal. The carboxylate group can coordinate the metal ions in a monodentate, bidentate or bridging fashion. In the previously reported model complexes [Cu($OCOCH_3$)(2,4-DNB)(OH_2)$_2$]·H_2O (Shvelashvili *et al.*, 2001), [Zn(DMSO)$_2$(3,5-DNB)$_2$(H_2O)$_2$] (Miminoshvili *et al.*, 2003) and (PipH)$_2$[$ZnCl_2$(3,5-DNB)$_2$] (where PipH$^+$ is protonated piperidine) (Miminoshvili *et al.*, 2004), the dinitrobenzoate ions act as monodentate ligands coordinated to the metal atom through an O atom of the carboxylate group.



(I)

The nature of the title compound, (I), was established by an X-ray structure determination and is shown in Fig. 1. The Co atom lies on a crystallographic centre of symmetry with the

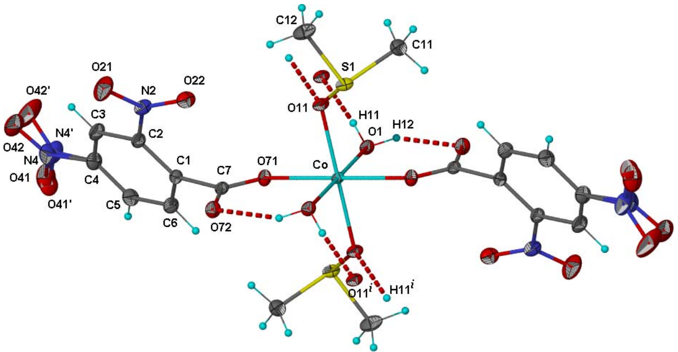


Figure 1
The complex molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Dashed lines represent hydrogen bonds. Both disorder components are shown. [Symmetry code: (i) $x - 1, y, z$.]

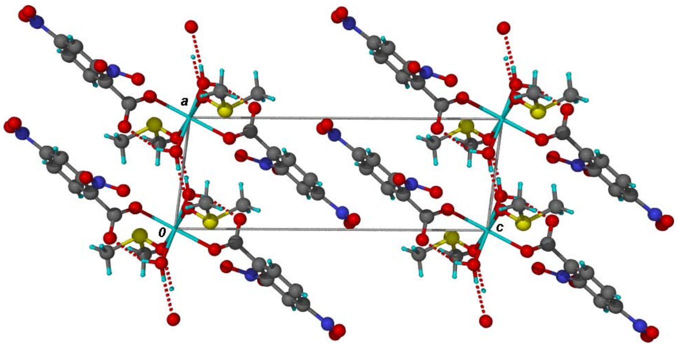


Figure 2
Packing diagram of (I), in a [101] projection, showing intermolecular hydrogen bonds (dashed lines).

ligands bonded to cobalt in an all-*trans* fashion. The configuration of the complex molecule is similar to that found in $[Zn(DMSO)_2(3,5\text{-}DNB)_2(H_2O)_2]$ (Miminoshvili *et al.*, 2003) with the 2,4-DNB anions acting as monodentate ligands. The coordination polyhedron around the Co atom is a slightly distorted octahedron (Table 1), with the O atoms of the DMSO groups in axial positions. The $Co-O_{DMSO}$ and $Co-O_{water}$ distances are in agreement with literature values [2.052 (2)–2.116 (2) Å (Okabe *et al.*, 2004), 2.055 (2)–2.167 (2) Å (Okabe & Muranishi, 2002) and 2.050 (2)–2.148 (2) Å (Tahir *et al.*, 1996)]. The *para* nitro group is disordered over two positions with occupancy factors of 0.5. The dihedral angles between the benzene ring and the planes O71/C7/O71, O21/N2/O22, O41/N4/O42 and O41′/N4′/O42′ are 67.08 (4), 25.98 (5), 5.8 (3) and 14.1 (2)°, respectively. The orientation of the DMSO molecule can be described by the torsion angles O1—Co—O11—S1 [−120.07 (4)°] and O71—Co—O11—S1 [151.48 (4)°]. The coordinated water molecule interacts with the uncoordinated carboxylate O atom through an intramolecular hydrogen bond [$O1\cdots O72^{ii}$ = 2.6979 (8) Å] and with the O atom of the DMSO through an intermolecular hydrogen bond [$O1\cdots O11^{iii}$ = 2.7397 (7) Å], forming polymeric chains along the [100] direction [symmetry codes: (ii) $-x, -y, -z$, (iii) $1 - x, -y, -z$] (Table 2 and Fig. 2). The structure of (I) presented here is thus consistent with our assumption regarding the character of the interactions of DMSO and 2,4-DNB ions with a metal as monodentate ligands that coordinate through their O atoms, reflecting the chemisorption processes which may be relevant to the action of dinitrobenzoates as corrosion inhibitors.

Experimental

A solution of $CoSO_4\cdot 7H_2O$ (1.40 g, 0.005 mol) in DMSO (15 ml) and piperidinium 2,4-dinitrobenzoate (2,86 g, 0.010 mol) were mixed and filtered. The filtrate was allowed to stand at room temperature for 24 h, over which time pale pink crystals deposited slowly. The crystals (m.p. 578 K) were collected, washed with diethyl ether and dried at room temperature. The scheme of the chemical reaction could be expressed as follows:

$$CoSO_4 + 2(PipDNB) + DMSO \rightarrow Co(DNB)_4(DMSO)_4 + (Pip)_2SO_4.$$

Analysis found: Co 9.09, C 31.35, H 3.97, N 8.93%; calculated for $C_{18}H_{22}CoN_4O_{16}S_2$: Co 8.75, C 32.10, H 3.29, N 8.32%.

Crystal data

$[Co(C_7H_3N_2O_6)_2(C_2H_6OS)_2(H_2O)_2]$
M_r = 673.45
Triclinic, $P\overline{1}$
a = 5.3620 (1) Å
b = 8.5764 (2) Å
c = 15.0992 (4) Å
α = 75.564 (1)°
β = 80.400 (1)°
γ = 79.137 (1)°
V = 655.13 (3) Å^3
Z = 1
D_x = 1.707 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7974 reflections
θ = 16.4–37.5°
μ = 0.90 mm^{-1}
T = 153 (2) K
Prism, pale pink
0.32 × 0.24 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.762, T_{max} = 0.877
12953 measured reflections
6696 independent reflections
5851 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 37.5°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.075
S = 1.07
6696 reflections
222 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.0384P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—O1	2.0735 (5)	S1—O11	1.5269 (6)
Co—O11	2.0949 (5)	S1—C11	1.7868 (10)
Co—O71	2.1139 (5)	S1—C12	1.7854 (9)
O1—Co—O11	90.83 (2)	O11—S1—C11	104.50 (4)
O1—Co—O11^{ii}	89.17 (2)	O11—S1—C12	104.12 (4)
O11—Co—O71	87.36 (2)	C11—S1—C12	97.07 (5)
O11—Co—O71^{ii}	92.64 (2)	S1—O11—Co	121.19 (3)
O71—Co—O1	88.50 (2)	C7—O71—Co	128.47 (5)
O71—Co—O1^{ii}	91.50 (2)		

Symmetry code: (ii) $-x, -y, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H11$\cdots$O11^{iii}	0.829 (9)	1.924 (9)	2.7397 (7)	167.9 (13)
O1—H12$\cdots$O72^{ii}	0.829 (9)	1.932 (10)	2.6979 (8)	153.3 (13)
C12—H123$\cdots$O72^{iv}	0.98	2.42	3.3268 (11)	154
C3—H3$\cdots$O42^{v}	0.95	2.44	3.344 (3)	158
C3—H3$\cdots$O42$'^{v}$	0.95	2.43	3.377 (3)	174

Symmetry codes: (ii) $-x, -y, -z$; (iii) $1 - x, -y, -z$; (iv) $-x, 1 - y, -z$; (v) $2 - x, 1 - y, -1 - z$.

Water H atoms were refined isotropically with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). All other H atoms were refined as riding, with C—H distances of 0.95–0.98 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for the aryl H atoms and 1.5$U_{\rm eq}$(C) for the methyl H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXTL*.

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