metal-organic compounds

Diaquabis(dimethyl sulfoxide)bis(3,5-dinitrobenzoato)zinc(II) and the synthesis of the Cu, Ni and Co analogs

Elguja B. Miminoshvili,[a] Alexandre N. Sobolev,[b]* Tamara N. Sakvarelidze,[a] Ketevan E. Miminoshvili[a] and Elguja R. Kutelia[a]

[a]Republican Centre of Structural Studies, Georgia Technical University, 77 Kostava Avenue, Tbilisi 380075, Georgia, and [b]Chemistry Section, School of Biomedical and Chemical Sciences, University of Western Australia, 35 Stirling Highway, Crawley, 6009 WA, Australia
Correspondence e-mail: ans@crystal.uwa.edu.au

In order to model processes of chemisorption in organic salts formed between dinitrobenzoic acids (DNBH) and secondary amines (R_2NH), a series of compounds of composition [M^{II}(3,5-DNB)$_2$(DMSO)$_2$(H$_2$O)$_2$] (where M^{II} is Zn, Cu, Ni or Co, 3,5-DNB is the 3,5-dinitrobenzoate ion, and DMSO is dimethyl sulfoxide) have been prepared. In diaquabis-(dimethyl sulfoxide)bis(3,5-DNB)zinc(II), [Zn(C$_7$H$_3$N$_2$O$_6$)$_2$-(C$_2$H$_6$OS)$_2$(H$_2$O)$_2$], the 3,5-DNB ions and molecules of DMSO are monodentate ligands that are coordinated to the Zn atom through their O atoms. These ligands, together with two molecules of water, form a slightly distorted octahedral coordination environment for the Zn atom, which lies on a center of symmetry.

Comment

The complexes of Co, Ni, Cu and Zn obtained by the reaction of dialkylammonium 3,5-dinitrobenzoates with hydrated metal sulfates in dimethyl sulfoxide (DMSO) have the same stoichiometry, with two molecules each of water and DMSO accompanying each metal bis(3,5-dinitrobenzoate) moiety. Both the 3,5-dinitrobenzoate ion (3,5-DNB) and the DMSO ligands 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 (Hundal *et al.*, 1996) or lattice 'solvents', and thus play significant roles in the hydrogen bonding in the crystal structures. When involved in coordination processes, benzoates exhibit a wide range of coordination modes. The carboxylate group can coordinate the metal ions in a monodentate, bidentate or bridging fashion. A typical example of monodentate coordination of 3,5-DNB is in the structure of tetraaquabis(3,5-DNB)cobalt(II) tetrahydrate

(Tahir *et al.*, 1996), where 3,5-DNB ions are involved in the coordination sphere of the Co atom in *trans* positions. The benzoate ions act as bidentate ligands in complexes such as bipyridinebis(*p*-nitrobenzoato)copper(II) (Usubaliev *et al.*, 1981) and tetrakis(benzoato)bis(pyridine)dicopper(II) (Speier & Fülöp, 1989), where Cu atoms are octahedrally coordinated by four O atoms from two carboxyl groups and two N atoms from the two pyridines in a *trans* configuration. The [Cu$_3$-(3,5-DNB)$_6$(CH$_3$OH)$_2$]$_n$ complex is a linear polymeric chain, in which the 3,5-DNB ions form all of the bridges (Hökelek *et al.*, 1998). The DMSO molecule can have different modes of coordination or can pack in the crystals as crystalline solvent molecules. The reaction of benzylamine with palladium chloride in the presence of DMSO gives [PdCl$_2$(C$_7$H$_9$N)$_2$]·2Me$_2$SO (Decken *et al.*, 2000). In the crystal structure, these molecules are packed in such way that each DMSO molecule bridges two palladium complex molecules through long-range intermolecular interactions (H···Cl and H···O), thus forming infinite chains. In complexes of platinum with 2-methoxy-pyridine, of composition [PtCl$_2$(C$_6$H$_7$NO)(C$_2$H$_6$OS)] (Arvanitis *et al.*, 2000), and in [RuCl$_2$(C$_7$H$_7$NO)(C$_2$H$_6$OS)$_2$] (Pal & Pal, 2002), DMSO is coordinated to the metal atoms through

(I)
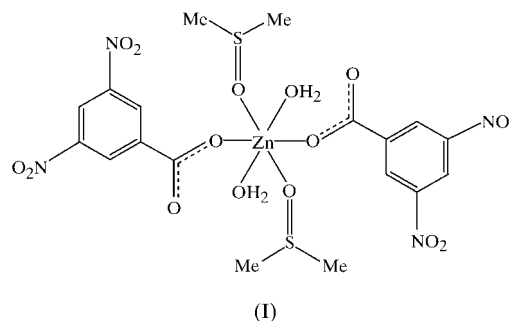
the S atom. The same type of coordination is observed in heteroligand complexes of ruthenium(II) (Coe *et al.*, 1993) and vanadium(III) (Magill *et al.*, 1993). In the trinuclear [Ni$_3$-(C$_{17}$H$_{16}$N$_2$O$_2$)$_2$(C$_2$H$_3$O$_2$)$_2$(C$_2$H$_6$OS)$_2$] complex with salicyl-idene-1,3-propanediaminate ligands (Ülkü *et al.*, 1997), the coordination octahedron of the terminal Ni atoms comprises
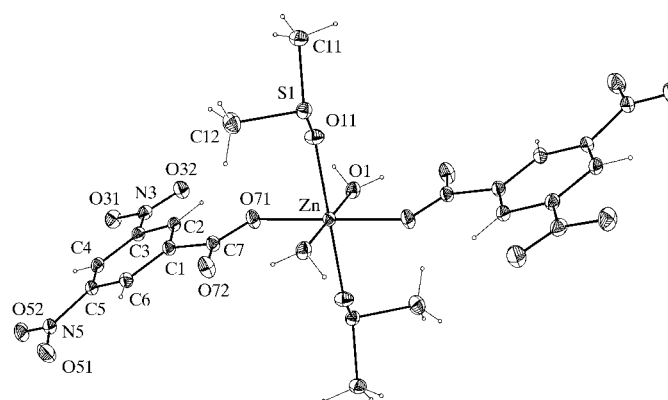

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

two O and two N atoms of the aromatic ligand in the equatorial plane and O atoms of acetate and DMSO molecules in axial positions. It has been reported that [Ru(tpy)(bpy)(DMSO)](CF$_3$SO$_3$)$_2$ (tpy is terpyridine and bpy is bipyridine) demonstrates intermolecular phototriggered linkage isomerism in the solid state (Rack *et al.*, 2001).

In the title compound, (I), Zn is shown to lie on a crystallographic center of symmetry, with the ligands bonded to Zn in an all-*trans* fashion (Fig. 1). The coordination polyhedron around the Zn atom is a slightly distorted octahedron (Table 1) that involves the O atoms of the DMSO groups in axial positions. The O—Zn—O angles around the Zn atom are in the range 86.53 (3)–93.47 (3)° (Table 1). The Zn—O11 bond is slightly longer than other examples in the literature [*e.g.* Zn—O$_{DMSO}$ = 2.122 Å (Lalioti *et al.*, 1998) or 2.10 (1) and 2.12 (1) Å (Persson, 1982)]. The Zn—O71 distance falls within the range for typical Zn—O$_{carboxylate}$ bonds [2.047 (1)– 2.180 (2) Å], and the Zn—O1 distance is also comparable to literature values [Zn—O$_{water}$ = 2.052 (1)–2.195 (3) Å; Arranz-Mascaros *et al.*, 2000; Lalioti *et al.*, 1998; Nefedov *et al.*, 1991; Persson, 1982; Sequeira *et al.*, 1992; Tahir *et al.*, 1997]. The other ligand geometries correspond to normal values and are in good agreement with literature data (Shvelashvili *et al.*, 2001). The conformation of the molecule is described by the dihedral and torsion angles. The angle between the plane of the carboxylate groups and the equatorial plane formed by water atom O1, the Zn atom and carboxyl atom O71 is 13.7 (1)°; the angle between the equatorial plane and the plane of the benzene ring is 23.2 (1)°. The nitro and carboxylate groups of the 3,5-DNB molecules are planar and are approximately coplanar with the benzene ring; the angles between the benzene ring and planes O71/C7/O72, O31/N3/ O32 and O51/N5/O52 are 10.1 (1), 5.1 (2) and 8.2 (1)°, respectively. The coordinated water molecules are bonded to the uncoordinated carboxylate O atoms with particularly strong intramolecular hydrogen bonds [O1···O72^i = 2.6292 (11) Å; symmetry code: (i) 1 − x, −y, 1 − z]. The
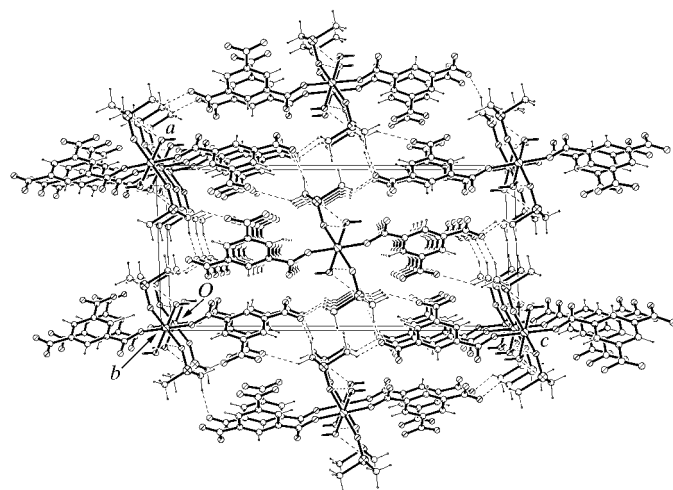
orientation of the DMSO fragment in the molecule can be described by the angle between planes O1/Zn/O11 and Zn/ O11/S1 [14.7 (1)°], where one of the methyl groups (atom C11) lies almost in the Zn/O11/S1 plane. The C11—S1— O11—Zn torsion angle is 176.49 (5)° and C12—S1—O11—Zn is −80.86 (6)°. The crystal packing of (I) consists of columns parallel to the *b* axis (Fig. 2), where molecules in neighboring columns are linked by weak hydrogen bonds (Table 2) that comprise the shortest intermolecular interaction.

The 3,5-DNB ion and DMSO are monodentate ligands that are coordinated to the metal through their O atoms. This conformation reflects the chemisorption processes and confirms that dinitrobenzoates may act as corrosion inhibitors. The monodentate carboxylate O-atom binding implies that the rest of the ligand should project from the metal surface, thus inhibiting the approach of further molecules to the metal.

Experimental

Solutions of ZnSO$_4$·7H$_2$O (1.43 g, 0.005 mol) in DMSO (15 ml) and piperidinium 3,5-dinitrobenzoate (2.86 g, 0.010 mol) in DMSO (15 ml) were mixed and filtered. The filtrate was allowed to stand at room temperature for 24 h over which time colorless crystals deposited slowly. The crystals were collected, washed with diethyl ether and dried at room temperature (Table 3). The same technique was used for the synthesis of analogous compounds with Cu, Ni and Co. All the complexes obtained in this way showed low solubility in water. 2,4-Dinitrobenzoates could be obtained with similar ease.

Crystal data

[Zn(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_2$H$_6$OS)$_2$(H$_2$O)$_2$]	D_x = 1.795 Mg m^{-3}
M_r = 679.89	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8192
a = 10.479 (2) Å	reflections
b = 5.296 (1) Å	θ = 16.4–37.5°
c = 22.686 (5) Å	μ = 1.23 mm^{-1}
β = 91.96 (3)°	T = 153 (2) K
V = 1258.3 (4) Å^3	Prism, colorless
Z = 2	0.20 × 0.20 × 0.14 mm

Data collection

Bruker SMART CCD diffractometer	6588 independent reflections
	5319 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.031
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 37.6°
	h = −17 → 17
T_{min} = 0.791, T_{max} = 0.847	k = −9 → 8
24 698 measured reflections	l = −38 → 38

Table 1
Selected geometric parameters (Å, °).

Zn—O1	2.0857 (7)	S1—O11	1.5245 (8)
Zn—O11	2.1475 (8)	S1—C11	1.7875 (10)
Zn—O71	2.0747 (7)	S1—C12	1.7846 (11)
O1—Zn—O11	86.53 (3)	O11—S1—C11	103.63 (5)
O1^i—Zn—O11	93.47 (3)	O11—S1—C12	105.92 (5)
O11—Zn—O71	85.81 (3)	C12—S1—C11	98.05 (5)
O11—Zn—O71^i	94.19 (3)	S1—O11—Zn	128.21 (4)
O71—Zn—O1	88.61 (3)	C7—O71—Zn	127.75 (6)
O71—Zn—O1^i	91.39 (3)		

Symmetry code: (i) 1 − x, −y, 1 − z.

Figure 2
Perspective packing diagram in the [101] projection, showing the intermolecular hydrogen bonds (dashed lines).

metal-organic compounds

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.01$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
6588 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}
195 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1—H11···O11[ii]	0.844 (10)	2.128 (11)	2.8851 (11)	149.1 (13)
O1—H12···O72[i]	0.840 (10)	1.835 (11)	2.6292 (11)	156.2 (14)
C11—H111···O31[iii]	0.98	2.49	3.2968 (14)	140
C11—H112···O52[iv]	0.98	2.51	3.2376 (14)	131
C11—H113···O1[ii]	0.98	2.50	3.3214 (15)	141
C12—H121···O52[v]	0.98	2.42	3.2389 (14)	141

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Table 3
Analytical data for the title complex and the Cu, Ni and Co analogs (calculated values in parentheses).

	Complex	Metal (%)	C (%)	H (%)	N (%)
(I)	[Zn(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$] (Colorless)	10.01 (9.61)	32.48 (31.80)	3.00 (3.26)	8.75 (8.24)
(II)	[Cu(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$] (Light green)	8.48 (9.37)	32.25 (31.88)	3.43 (3.27)	9.17 (8.26)
(III)	[Ni(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$] (Green)	8.41 (8.72)	32.78 (32.11)	3.19 (3.29)	8.88 (8.32)
(IV)	[Co(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$] (Pale pink)	9.21 (8.75)	32.75 (32.10)	3.05 (3.29)	8.43 (8.32)

Water H atoms were refined isotropically. All other H atoms were refined as riding, with a C—H distance of 0.98 Å for methyl and 0.95 Å for aromatic H atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

References

Arranz-Mascaros, P., Lopez-Garzon, R., Gutierrez-Valero, M. D., Godino-Salido, M. L. & Moreno, J. M. (2000). *Inorg. Chim. Acta*, **304**, 137–143.
Arvanitis, G. M., Holmes, C. E., Johnson, D. G. & Berardini, M. (2000). *Acta Cryst.* C**56**, 1332–1333.
Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Coe, B. J., Meyer, T. J. & White, P. S. (1993). *Inorg. Chem.* **32**, 4012–4020.
Decken, A., Pisegna, G. L., Vogels, C. M. & Westcott, S. A. (2000). *Acta Cryst.* C**56**, 1071–1072.
Hundal, G., Martinez-Ripoll, M., Hundal, M. S. & Poonia, N. S. (1996). *Acta Cryst.* C**52**, 789–792.
Hökelek, T., Mert, Y. & Ünaleročlu, C. (1998). *Acta Cryst.* C**54**, 310–313.
Lalioti, N., Raptopoulou, C. P., Terzis, A., Panagiotopoulos, A., Perlepes, S. P. & Manessi-Zoupa, E. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1327–1333.
Magill, C. P., Floriani, C., Chiesi-Villa, A. & Rizzoli, C. (1993). *Inorg. Chem.* **32**, 2729–2735.
Nefedov, S. E., Struchkov, Yu. T., Konnik, O. V. & Shul'gin, V. F. (1991). *Ukr. Khim. Zh.* (*Russ. Ed.*), **57**, 685–688.
Pal, S. & Pal, S. (2002). *Acta Cryst.* C**58**, m273–m274.
Persson, I. (1982). *Acta Chem. Scand. Ser. A*, **36**, 7–13.
Rack, J. J., Winkler, J. R. & Gray, H. B. (2001). *J. Am. Chem. Soc.* **123**, 2432–2433.
Sequeira, A., Rajagopal, H., Gupta, M. P., Vanhouteghem, F., Lenstra, A. T. H. & Geise, H. J. (1992). *Acta Cryst.* C**48**, 1192–1197.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Shvelashvili, A. E., Miminoshvili, E. B., Bel'skii, V. K., Amirkhanashvili, K. D., Adeishvili, G. P. & Sakvarelidze, T. N. (2001). *Georgian Eng. News*, **1**, 105–109.
Speier, G. & Fülöp, V. (1989). *J. Chem. Soc. Dalton Trans.* **11**, 2331–2332.
Tahir, M. N., Ülkü, D. & Movsumov, E. M. (1996). *Acta Cryst.* C**52**, 1392–1394.
Tahir, M. N., Ülkü, D., Movsumov, E. M. & Hökelek, T. (1997). *Acta Cryst.* C**53**, 176–179.
Ülkü, D., Ercan, F., Atakol, O. & Dinçer, F. N. (1997). *Acta Cryst.* C**53**, 1056–1057.
Usubaliev, B. T., Amiraslanov, I. R., Nadzhafov, G. N., Movsumov, E. M., Musaev, F. N. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 440–444.