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

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

*Republican Centre of Structural Studies, Georgia Technical University, 77 Kostava Avenue, Tbilisi 380075, Georgia, and
bChemistry Section, School of Biomedical and Chemical Sciences, University of Western Australia, 35 Stirling Highway, Crawley, 6009 WA, Australia

Correspondence e-mail: ane@crystal.uwa.edu.au

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In order to model processes of chemisorption in organic salts formed between dinitrobenzoic acids (DNBH) and secondary amines (R2NH), a series of compounds of composition [MII(3,5-DNB)2(DMSO)2(H2O)2] (where MII 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(C7H3N2O6)2(C2H6OS)2(H2O)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 bipyrindinebis(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 [Cu₆(3,5-DNB)₆(CH₃OH)₁₂]₄ complex is a linear polymeric chain, in which the 3,5-DNB ions form all of the bridges (Hökellek 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 [PdCl₂(C₆H₅N)₂]·2Me₂SO (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 [PtCl₂(C₆H₇NO)(C₂H₆OS)] (Arvanitis et al., 2000), and in [RuCl₂(C₇H₇NO)(C₂H₆OS)₂] (Pal & Pal, 2002), DMSO is coordinated to the metal atoms through 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 [Ni₃(C₁₇H₁₆N₂O₂)₂(C₂H₃O₂)₂(C₂H₆OS)₂] complex with salicylidene-1,3-propanediaminate ligands (Ulku 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 \([\text{Ru}(tpy)(bpy)(\text{DMSO})](\text{CF}_3\text{SO}_3)_2\) (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–Ocarboxylate bonds [2.047 (1)–2.180 (2) Å], and the Zn–O1 distance is also comparable to literature values [Zn–Owater = 2.052 (1)–2.195 (3) Å; Arranz-Mascarós 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 benzene ring and planes O71/C7/O72, O31/N3/O72i = 23.2 (1)°, and the Zn–O11 bond is approximately coplanar with the benzene ring; the angles between the benzene ring and planes O71/C7/O72, O31/N3/O72i = 86.53 (3)±93.47 (3)° (Table 1). The Zn–O1 bond is 176.49 (5)° and 88.61 (3)°, respectively. The coordinated water molecules are bonded to the carboxylate groups and the equatorial plane formed by the metal atom. The conformation of the molecule is described by the angle between planes O1/Zn/O11 and Zn/O71/S1 [14.7 (1)°].

### Experimental

Solutions of ZnSO4.7H2O (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.

### Table 1

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Selected geometric parameters (Å, °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn–O1</td>
<td>2.0857 (7)</td>
</tr>
<tr>
<td>Zn–O11</td>
<td>2.1475 (8)</td>
</tr>
<tr>
<td>Zn–O71</td>
<td>2.0747 (7)</td>
</tr>
<tr>
<td>O1–Zn–O11</td>
<td>86.53 (3)</td>
</tr>
<tr>
<td>O1′–Zn–O11</td>
<td>94.37 (3)</td>
</tr>
<tr>
<td>O1′–Zn–O71</td>
<td>94.19 (3)</td>
</tr>
<tr>
<td>O1–Zn–O71</td>
<td>176.49 (5)</td>
</tr>
<tr>
<td>O71–Zn–O1</td>
<td>2.0747 (7)</td>
</tr>
<tr>
<td>O71–Zn–O1′</td>
<td>91.39 (3)</td>
</tr>
</tbody>
</table>

### Figure 2

Perspective packing diagram in the [011] projection, showing the intermolecular hydrogen bonds (dashed lines).
metal-organic compounds

Refinement

Refinement on $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.071$

$S = 1.01$

6588 reflections

195 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F^2) + (0.04P)^2]$

where $P = (F^2 + 2F^2)/3$

$\Delta/\sigma_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.61 e \AA^{-3}$

$\Delta\rho_{\text{min}} = -0.31 e \AA^{-3}$

Hydrogen-bonding geometry ($\AA$, °).

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>D–H</th>
<th>H···A</th>
<th>D···A</th>
<th>D–H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1−H11−O11w</td>
<td>0.844 (10)</td>
<td>2.128 (11)</td>
<td>2.8851 (11)</td>
<td>149.1 (13)</td>
</tr>
<tr>
<td>O1−H12−O72w</td>
<td>0.840 (10)</td>
<td>1.835 (11)</td>
<td>2.6292 (11)</td>
<td>156.2 (14)</td>
</tr>
<tr>
<td>C11–H111−O31ii</td>
<td>0.98</td>
<td>2.49</td>
<td>3.2686 (14)</td>
<td>140</td>
</tr>
<tr>
<td>C11−H112−O52iv</td>
<td>0.98</td>
<td>2.51</td>
<td>3.2376 (14)</td>
<td>131</td>
</tr>
<tr>
<td>C11−H113−O11w</td>
<td>0.98</td>
<td>2.50</td>
<td>3.3214 (15)</td>
<td>141</td>
</tr>
<tr>
<td>C12−H121−O52v</td>
<td>0.98</td>
<td>2.42</td>
<td>3.3289 (14)</td>
<td>141</td>
</tr>
</tbody>
</table>

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

Table 3

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) [Zn(C$_2$H$_5$N$_2$O$_5$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$]</td>
<td>10.01</td>
<td>32.48</td>
<td>3.00</td>
<td>8.75</td>
</tr>
<tr>
<td>(Colorless)</td>
<td>(9.61)</td>
<td>(31.80)</td>
<td>(3.26)</td>
<td>(8.24)</td>
</tr>
<tr>
<td>(II) [Cu(C$_2$H$_5$N$_2$O$_5$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$]</td>
<td>8.48</td>
<td>32.25</td>
<td>3.43</td>
<td>9.17</td>
</tr>
<tr>
<td>(Light green)</td>
<td>(9.37)</td>
<td>(31.88)</td>
<td>(3.27)</td>
<td>(8.26)</td>
</tr>
<tr>
<td>(III) [Ni(C$_2$H$_5$N$_2$O$_5$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$]</td>
<td>8.41</td>
<td>32.78</td>
<td>3.19</td>
<td>8.88</td>
</tr>
<tr>
<td>(Green)</td>
<td>(8.72)</td>
<td>(32.11)</td>
<td>(3.29)</td>
<td>(8.32)</td>
</tr>
<tr>
<td>(IV) [Co(C$_2$H$_5$N$_2$O$_5$)$_2$(C$_2$H$_6$SO)$_2$(H$_2$O)$_2$]</td>
<td>9.21</td>
<td>32.75</td>
<td>3.05</td>
<td>8.43</td>
</tr>
<tr>
<td>(Pale pink)</td>
<td>(8.75)</td>
<td>(32.10)</td>
<td>(3.29)</td>
<td>(8.32)</td>
</tr>
</tbody>
</table>

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: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXL (Bruker, 1998); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1404). Services for accessing these data are described at the back of the journal.

References


m120 Elguja B. Miminoshvili et al. [Zn(C2H5N2O5)2(C2H6OS2)2(H2O)]2 Acta Cryst. (2003). C59, m118–m120