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Bis(1,10-phenanthroline-*N*,*N*′)(thiosulfato-*O*,*S*)nickel(II)–water–methanol (1/0.92/1.4) and bis(2,2′-bipyridyl-*N*,*N*′)(thiosulfato-*O*,*S*)-nickel(II)–water–methanol (1/2/0.55)

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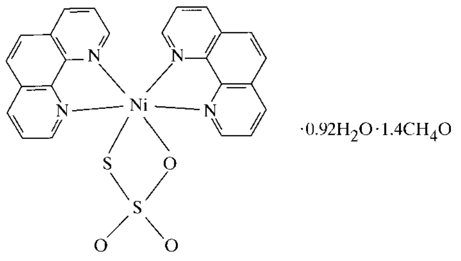
The title compounds, $[Ni(S_2O_3)(C_{12}H_8N_2)_2]\cdot0.92H_2O\cdot1.4CH_4O$ and $[Ni(S_2O_3)(C_{10}H_8N_2)_2]\cdot2H_2O\cdot0.55CH_4O$, are monomeric, containing nickel(II) in a distorted octahedral coordination environment provided by the four N atoms of two bidentate bipy or phen groups and one S and one O atom from a chelating thiosulfate anion. The crystals are highly unstable outside their mother liquors and are stabilized in solution by a not fully determined number of water and methanol solvate molecules. The phenanthroline structure includes two independent moieties related by a non-crystallographic inversion center. The thiosulfate anions display the usual S—O lengthening found when the anion acts in a bidentate mode.

Comment

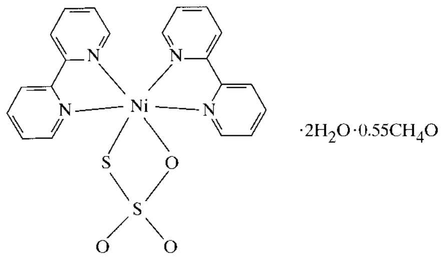
A search for thiosulfate complexes in the latest version (Version 5.18) of the Cambridge Structural Database (Allen & Kennard, 1993) reveals some 32 structures in which the anion behaves as a coordinating ligand, displaying a variety of binding modes. Nickel is the cation in only one of these structures, *i.e.* tetrakis(thiourea-*S*)(thiosulfato-*O*,*S*)nickel(II) monohydrate (Gasparri *et al.*, 1969), in which the ligand is bidentate, a rather unusual mode of coordination found only in three other complexes with two different metals, *viz*: bis(η_5-cyclopentadienyl)(thiosulfato-*O*,*S*)molybdenum (Kubas & Ryan, 1984), tetraethylammonium (η_5-cyclopentadienyl)bis(μ_2-thio)(thiosulfato-*S*,*O*)bis(oxomolybdenum) (Kim & Coucouvanis, 1993) and *cis*-bis(ethylenediamine)(thiosulfato)cobalt(II) perchlorate (Murdock *et al.*, 1985). This type of binding to the cation usually results in a lengthening of the S—O bond involving the O atom which is coordinated to the metal.

Recently, two crystal structures of nickel thiosulfate complexes have been reported, namely triaqua(2,2′-bipyridyl-*N*,*N*′)(thiosulfato-*S*)nickel(II) dihydrate and triaqua(1,10-phenanthroline-*N*,*N*′)(thiosulfato-*S*)nickel(II) monohydrate (Freire *et al.*, 1999), in which the anion binds to the cation in a monodentate mode through sulfur. In this case, only slight distortions are observed in the anion geometry. Nickel(II), a borderline acid ion in the Pearson (1973) classification, may be expected to bind either to the hard (O) or soft (S) end of the thiosulfate group, thus resulting in different modes of coordination, depending on other concurring factors, such as crystal-field stabilization, shapes of accompanying ligands, intermolecular forces such as van der Waals and hydrogen bonding, *etc.*

The coordination chemistry of nickel(II) is important in some bacterial systems, and complexes in which N, O and/or S atoms are bonded to the metal might provide valuable information about these type of bonds, some of which are present in biological systems (Sigel & Sigel, 1994). In this line of thought, we report herein the synthesis, characterization and structure of two novel nickel thiosulfate complexes, namely $[Ni(S_2O_3)(phen)_2]\cdot0.92H_2O\cdot1.40CH_3OH$, (I), and $[Ni(S_2O_3)(bpy)_2]\cdot2H_2O\cdot0.55CH_3OH$, (II), where bpy is bipyridine and phen = 1,10-phenanthroline.



(I)



(II)

The compounds are not isostructural, but the two structures have some common features: they are monomeric and all the ligands are bidentate, the organic groups binding through the two N atoms and the thiosulfate through oxygen and sulfur (Figs. 1 and 2). This leads to very similar nickel environments of a distorted octahedral NiN_4OS type. The steric hindrance imposed by the rigid character of the organic ligands and the chelate (S,O) thiosulfate are largely responsible for the distortions.

Crystals of (I) contain two molecules in the asymmetric unit, occupying general positions in space group $P\overline{1}$. There is, however, a striking non-crystallographic center of symmetry at $x = 0.252$ (4), $y = 0.487$ (2) and $z = 0.255$ (2) which relates the two moieties. The degree of this pseudosymmetry can be assessed by a least-squares fit of the atoms of one of the two molecules to the inverted positions of the atoms of the other. When this is performed, the r.m.s. deviation of the matching pairs is 0.24 Å, with larger deviations for the thiosulfates and an almost perfect match for the planar phen groups. This fitting worsens dramatically when the solvent molecules are also considered, and this reveals why the structure does not really crystallize in a more symmetric space group (monoclinic with a single molecule per asymmetric unit); the included solvent molecules do not exist in pairs related by the pseudocenter of symmetry. As a result of the pseudosymmetry, both Ni ions have almost identical environments, with the four Ni—N distances [2.060 (5)–2.095 (6) Å] being normal for a hexacoordinated nickel cation, and only slightly longer than those observed in S-bonded nickel thiosulfates (2.041–2.070 Å; Freire *et al.*, 1999). The S,O-chelating thiosulfate completes the coordination sphere, in a similar way to that of the thiourea complex of Gasparri *et al.* (1969). The mean Ni—S distance, 2.462 (1) Å, compares fairly well with the values reported for Ni—S bonded complexes. A relevant feature in the anion is the considerable lengthening observed in the S—O bonds involving the O atom which coordinates to nickel (O_{coord}) compared with the non-coordinated ones (O_{non}) [S—O_{coord} 1.495 (3) and 1.489 (3) Å *versus* S—O_{non} 1.448 (3) and 1.450 (3) Å, for molecules *A* and *B*, respectively]. As expected, concomitantly smaller S—S—O angles appear [S—S—O_{coord} 102.6 (1) and 102.7 (1)° *versus* S—S—O_{non} 110.1 (1) and 109.7 (2)°, for molecules *A* and *B*, respectively]. Similar effects have already been reported in the literature (Kubas & Ryan, 1984; Murdock *et al.*, 1985; Kim & Coucouvanis, 1993; Gasparri *et al.*, 1969).

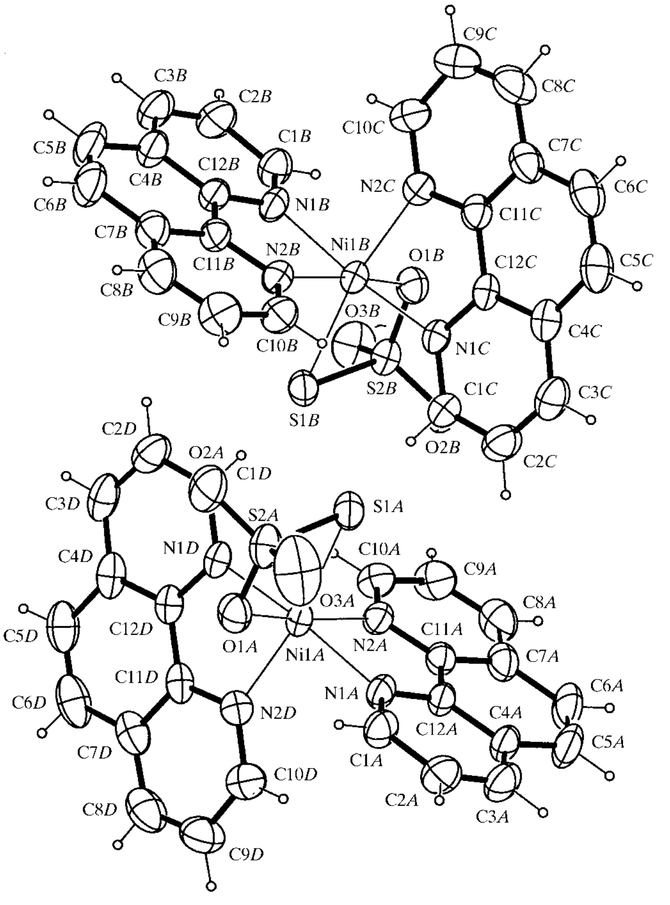


Figure 1

The molecular diagram for (I). Note the pseudosymmetry center across the two independent moieties. Displacement ellipsoids are drawn at the 50% probability level.

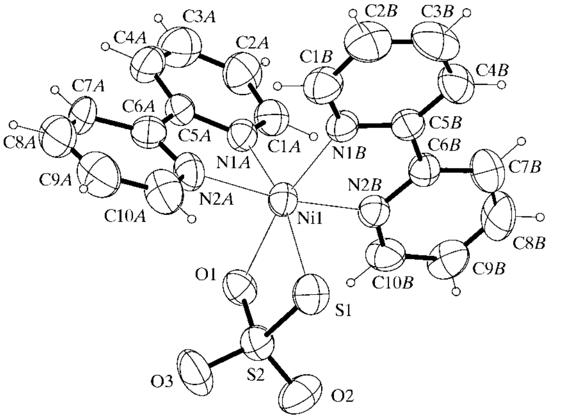


Figure 2

The molecular diagram for (II). Displacement ellipsoids are drawn at the 50% probability level.

The phenanthroline ligands are basically planar (r.m.s. deviations from the best planes of 0.022, 0.026, 0.029 and 0.020 Å for phen groups *A*, *B*, *C* and *D*). In each octahedron, the groups are very nearly perpendicular to each other and to the closed coordination loop subtended by the chelate thiosulfate (maximum departures from 90° of 4.9 and 6.5° for molecules *A* and *B*, respectively).

As already mentioned, in complex (II), the four N atoms in the Ni coordination core are provided by two bidentate bipyridine groups, with Ni—N distances in the range 2.060 (5)–2.095 (6) Å. The same trend as in (I), regarding bonds and angles, is observed in the coordinated thiosulfate as shown by the following (mean) values: S—O_{coord} 1.484, S—O_{non} 1.457 Å; S—S—O_{coord} 103.2, S—S—O_{non} 111.1°.

The bipy ligands present a noticeable twisting of the individual pyridinic groups along the C5—C6 bonds [5.1 (3) and 6.2 (3)° in groups *A* and *B*, respectively], and subtend an angle of 99.7 (1)° to each other. The thiosulfate loop, instead, is almost perfectly perpendicular to both (91.0 and 89.3°).

The quality of the results obtained in both structures precludes a detailed analysis of the hydrogen-bonding schemes. However, the large number of protons known to be available for the interactions, as well as the evidence of many short (<3.00 Å) O···O contacts, allows us to speak of a rather complex hydrogen-bonding network interconnecting the monomers, even though the intervening H atoms could not be found directly. Further evidence of the stabilizing role of these interactions is provided by the fact that the solvent loss which takes place at atmospheric conditions practically destroys the crystal lattices in only a few minutes.

Experimental

The synthesis of (I) was performed by direct mixing of the reactants (in the form of aqueous solutions of nickel nitrate and sodium thiosulfate, and a methanolic solution of 1,10-phenanthroline, in a 1:3:2 molar ratio). On standing, well shaped pale grey prisms were obtained, which were quite stable in solution but which proved totally unstable outside their mother liquors, to the extent that they collapsed in a few minutes in a dry atmosphere. This required the mounting of the specimens intended for data collection in sealed capillaries with a drop of stabilizing mother liquors. In this way, the crystals survived for months without any evidence of decay. The IR spectra contain the characteristic peaks of the coordinated ligands: 1143 cm^{-1} for thiosulfate, and 727, 854 and 1516 cm^{-1} for phenanthroline. Crystals of (II) were slightly harder to obtain. Direct mixing of solutions as in (I) (with bipyridine replacing phenanthroline, and in the same 1:3:2 molar ratio), resulted in the growth of specimens too small for X-ray analysis. Relatively few, but reasonably good, crystals were then obtained by first allowing the methanolic solution of bipyridine to diffuse into an aqueous solution of the inorganic compounds, followed by several days in which a fraction of the solvent was allowed to evaporate. Though more stable than crystals of compound (I), they also decayed appreciably when left under atmospheric conditions, and were therefore accordingly encapsulated.

Compound (I)

Crystal data

$[\text{Ni}(\text{S}_2\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)_2]\cdot0.92\text{H}_2\text{O}\cdot$-$1.4\text{CH}_4\text{O}$
$M_r = 592.66$
Triclinic, $P\overline{1}$
$a = 12.613$ (2) Å
$b = 18.855$ (3) Å
$c = 11.3048$ (19) Å
$\alpha = 90.467$ (18)°
$\beta = 100.365$ (15)°
$\gamma = 87.202$ (13)°
$V = 2641.4$ (7) Å^3
$Z = 4$
$D_x = 1.49$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–15.0°
$\mu = 0.94$ mm^{-1}
$T = 293$ (2) K
Polyhedral, pale grey
0.30 × 0.28 × 0.22 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\text{min}} = 0.76$, $T_{\text{max}} = 0.80$
12 469 measured reflections
11 915 independent reflections
7271 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.018$
$\theta_{\text{max}} = 27.51°$
$h = 0 \rightarrow 15$
$k = -24 \rightarrow 24$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.164$
$S = 0.954$
11915 reflections
737 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.089P)^2 + 2.571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.01$
$\Delta\rho_{\text{max}} = 0.88$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.63$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Ni1*A*—N2*A*	2.071 (3)	Ni1*B*—N2*B*	2.076 (3)
Ni1*A*—N1*A*	2.086 (3)	Ni1*B*—N1*B*	2.082 (3)
Ni1*A*—N1*D*	2.092 (3)	Ni1*B*—N1*C*	2.087 (3)
Ni1*A*—O1*A*	2.093 (3)	Ni1*B*—N2*C*	2.092 (3)
Ni1*A*—N2*D*	2.094 (3)	Ni1*B*—O1*B*	2.110 (3)
Ni1*A*—S1*A*	2.4613 (11)	Ni1*B*—S1*B*	2.4624 (11)
S1*A*—S2*A*	2.0249 (14)	S1*B*—S2*B*	2.0260 (13)
S2*A*—O3*A*	1.449 (3)	S2*B*—O2*B*	1.450 (3)
S2*A*—O2*A*	1.445 (3)	S2*B*—O3*B*	1.452 (3)
S2*A*—O1*A*	1.494 (3)	S2*B*—O1*B*	1.492 (3)

Compound (II)

Crystal data

$[\text{Ni}(\text{S}_2\text{O}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2]\cdot2\text{H}_2\text{O}\cdot$-$0.55\text{CH}_4\text{O}$
$M_r = 536.84$
Monoclinic, $C2/c$
$a = 20.754$ (4) Å
$b = 20.895$ (4) Å
$c = 14.402$ (3) Å
$\beta = 132.919$ (12)°
$V = 4573.7$ (17) Å^3
$Z = 8$
$D_x = 1.56$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–15.0°
$\mu = 1.074$ mm^{-1}
$T = 293$ (2) K
Polyhedra, pale grey
0.33 × 0.30 × 0.28 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\text{min}} = 0.71$, $T_{\text{max}} = 0.74$
4123 measured reflections
3914 independent reflections
2159 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.075$
$\theta_{\text{max}} = 25°$
$h = -24 \rightarrow 18$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.183$
$S = 0.971$
3914 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.085P)^2 + 8.029P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.01$
$\Delta\rho_{\text{max}} = 0.67$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.40$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

Ni1—N2*B*	2.060 (5)	Ni1—S1	2.465 (2)
Ni1—N1*B*	2.076 (5)	S1—S2	2.024 (3)
Ni1—N1*A*	2.078 (6)	S2—O3	1.456 (5)
Ni1—N2*A*	2.095 (6)	S2—O2	1.457 (5)
Ni1—O1	2.125 (5)	S2—O1	1.485 (5)

The very elusive solvent molecules in both structures (water and methanol) were very difficult to find and refine, a fact which is reflected in the final *R* factors. Due to the instability of the compounds outside their mother liquors, no chemical or thermogravimetric analyses were feasible. Thus, single-crystal X-ray diffraction remained the ultimate analytical tool, and the results obtained with this technique for the overall solvate contents were those with which the compounds have been formulated in the present work. These results must, however, be looked on with caution and taken only as a lower bound for the actual values for the compounds in solution. This idea is fully supported by the extreme instability of the solvates and corroborated by the fact that most of the solvent sites appeared disordered or only partially occupied. H atoms in the organic ligands were included at their expected positions. Those in the solvates were obviously not found.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1130). Services for accessing these data are described at the back of the journal.

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