

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1046). Services for accessing these data are described at the back of the journal.

## References

- Bruker (1997). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Byers, P., Drew, M. G. B., Hudson, M. J., Isaacs, N. S. & Madic, C. (1994). *Polyhedron*, **13**, 349–352.
- Castellano, E. E. & Becker, R. W. (1981). *Acta Cryst.* B37, 61–67, 1998–2001.
- Chan, G. Y. S., Drew, M. G. B., Hudson, M. J., Iveson, P. B., Liljenzin, J. O., Skålberg, M., Spjuth, L. & Madic, C. (1997). *J. Chem. Soc. Dalton Trans.* pp. 649–660.
- Cuillerdier, C., Musikas, C., Hoel, P., Nigond, L. & Vitard, X. (1991). *Sep. Sci. Technol.* **26**, 1229–1244.
- Den Auwer, C., Charbonnel, M. C., Drew, M. G. B., Grigoriev, M., Hudson, M. J., Iveson, P. B., Madic, C., Nierlich, M., Presson, M. T., Revel, R., Russel, M. L. & Thuéry, P. (1999). *Inorg. Chem.* Submitted.
- Drew, M. G. B. (1977). *Coord. Chem. Rev.* **24**, 179–275.
- Madic, C. & Hudson, M. J. (1998). Final Report of the European Communities EUR-18038 (Contract F12W-CT91-0112). Luxembourg: Office for Official Publications of the European Communities.
- Nigond, L. (1992). Thesis, Université de Clermont-Ferrand II, France.
- Nigond, L., Musikas, C. & Cuillerdier, C. (1994). *Solvent Extr. Ion Exch.* **12**, 261–296, 297–323.
- Nonius (1997). *Kappa-CCD Software*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). In *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. London and New York: Academic Press.
- Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1998). *PLATON*. University of Utrecht, The Netherlands.

*Acta Cryst.* (1999). **C55**, 1436–1438

## Bis[ $\mu$ -2,2',2''-nitrilotriethanethiolato(2-)-N,S,S':S']dinickel(II)

SIÂN C. DAVIES, DAVID J. EVANS, DAVID L. HUGHES AND STEVEN LONGHURST

Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Colney, Norwich NR4 7UH, England.  
E-mail: dave.evans@bbsrc.ac.uk

(Received 5 March 1999; accepted 3 June 1999)

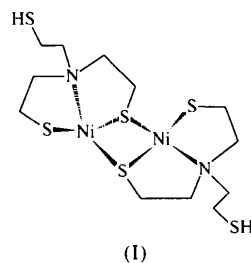
## Abstract

The neutral dimeric title complex, [Ni<sub>2</sub>(C<sub>6</sub>H<sub>13</sub>NS<sub>3</sub>)<sub>2</sub>], has crystallographic twofold symmetry and two square-planar NiS<sub>3</sub>N planes hinged through a pair of bridging thiolate S atoms, with a folding angle of 110.84(6)°. The thiol group of each ligand is pendant and links

molecules in chains through weak S—H···S hydrogen bonds.

## Comment

The title compound, (I), a neutral dimeric complex, has been prepared previously (Colpas *et al.*, 1990) and by analogy was assumed to have a structure similar to that of the dimeric complex of nickel with the ligand bis(2-mercaptoethyl)[2-(methylthio)ethyl]amine. We confirm here this assumption and show the presence of two pendant thiol groups.



The X-ray analysis of (I) shows the dimeric complex to consist of two square-planar NiS<sub>3</sub>N units hinged together through a pair of bridging thiolate S atoms (Fig. 1). The two halves are related by a crystallographic twofold axis. Therefore, the N and one thiolate S atom of each ligand are bonded to a single Ni atom, the second thiolate S atom bridges the two Ni atoms, and the thiol arm is pendant and forms rather weak S—H···S hydrogen bonds to link the molecules in sheets parallel to the *bc* plane.

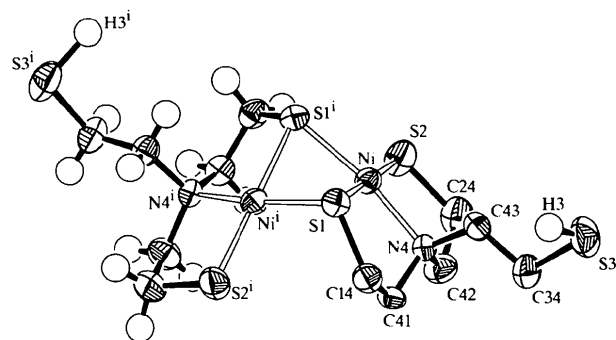


Fig. 1. A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms are shown with an arbitrary radius and H atoms in one half of the molecule have been omitted for clarity. The molecule lies across a crystallographic twofold axis. [Symmetry code: (i)  $\frac{1}{2} - x, y, -z$ .]

The angle between the normals to the two NS<sub>3</sub> mean planes is 107.47(6)°. The folding angle, defined by Colpas *et al.* (1990) as the angle between the normals to the intersecting NiS<sub>2</sub> planes, is 110.84(6)°. These

dimensions and those in the Ni<sub>2</sub>S<sub>2</sub> core are very similar to those collated by Colpas *et al.* (1990).

In several complexes of the [N(CH<sub>2</sub>CH<sub>2</sub>S)<sub>3</sub>]<sup>3-</sup> ligand with vanadium, iron, molybdenum and tungsten (Davies *et al.*, 1997, 1998), the ligand is tetradentate and forms a trigonal-pyramidal pattern around the metal centre; the fifth, apical, site of the trigonal bipyramid is occupied by a neutral or anionic monodentate ligand. The trithiolate-amine ligand shows pseudo-threefold symmetry about the M—N axis, and the N—C—C—S torsion angles are all *ca* +50° or all *ca* -50°. In the present nickel complex, the tridentate ligand shows approximate mirror symmetry, with N—C—C—S torsion angles in the thiolate arms of 41.6 (6) and -49.3 (7)°, and a *trans* arrangement in the pendant thiol arm [N—C—C—S angle -177.7 (4)°].

## Experimental

To a solution of nickel(II) acetylacetonate (0.49 g, 1.91 mmol) in benzene (50 ml) was added tris(2-mercaptoethyl)amine (0.40 g, 2.03 mmol). An immediate colour change from green to dark red occurred. After stirring for 30 min, a small amount of insoluble brown material was removed by filtration and the filtrate then allowed to stand for 5 d at room temperature. The dark-red crystalline product was collected, washed with diethyl ether and dried *in vacuo* (0.31 g, 65%). IR (KBr disc):  $\nu_{\text{SH}}$  2479 cm<sup>-1</sup>.

### Crystal data

[Ni<sub>2</sub>(C<sub>6</sub>H<sub>13</sub>NS<sub>3</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 508.13  
 Monoclinic  
*A*2/*a*  
*a* = 23.727 (3) Å  
*b* = 5.8370 (5) Å  
*c* = 14.377 (2) Å  
 $\beta$  = 98.337 (10)°  
*V* = 1970.1 (4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.713 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega/\theta$  scans  
 Absorption correction:  
 $\psi$  scan (EMPABS;  
 Sheldrick *et al.*, 1977)  
*T<sub>min</sub>* = 0.780, *T<sub>max</sub>* = 0.975  
 2185 measured reflections  
 1726 independent reflections

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.044  
 $wR(F^2)$  = 0.097

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25  
 reflections  
 $\theta$  = 9–10°  
 $\mu$  = 2.543 mm<sup>-1</sup>  
*T* = 293 (1) K  
 Thin plate  
 0.14 × 0.12 × 0.01 mm  
 Dark red-brown

907 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.039  
 $\theta_{\text{max}}$  = 24.97°  
 $h$  = -28 → 28  
 $k$  = -1 → 6  
 $l$  = -1 → 17  
 3 standard reflections  
 frequency: 167 min  
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$

*S* = 0.963  
 1726 reflections  
 104 parameters  
 H atoms treated by a  
 mixture of independent  
 and constrained refinement

$\Delta\rho_{\text{max}} = 0.511 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni—S1	2.208 (2)	Ni—Ni <sup>i</sup>	2.726 (2)
Ni—S1 <sup>i</sup>	2.168 (2)	S1—C14	1.822 (6)
Ni—S2	2.158 (2)	S2—C24	1.826 (7)
Ni—N4	1.953 (5)	S3—C34	1.803 (6)
S1—Ni—S2	179.29 (9)	Ni <sup>i</sup> —S1—C14	111.9 (2)
S1 <sup>i</sup> —Ni—S1	81.71 (8)	Ni—S2—C24	98.0 (2)
S2—Ni—S1 <sup>i</sup>	98.16 (7)	Ni—N4—C41	106.4 (3)
S2—Ni—N4	91.4 (2)	Ni—N4—C42	109.0 (4)
N4—Ni—S1 <sup>i</sup>	168.63 (15)	Ni—N4—C43	107.6 (4)
S1—Ni—N4	88.8 (2)	C41—N4—C42	108.4 (5)
Ni—S1—Ni <sup>i</sup>	77.04 (6)	C41—N4—C43	112.9 (5)
Ni—S1—C14	98.1 (2)	C42—N4—C43	112.3 (5)
S1—C14—C41—N4	41.6 (6)	C14—C41—N4—C42	-173.0 (5)
S2—C24—C42—N4	-49.3 (7)	C42—N4—C43—C34	-62.3 (7)
C24—C42—N4—C43	-70.5 (7)	C41—N4—C43—C34	60.7 (7)
C24—C42—N4—C41	164.1 (5)	N4—C43—C34—S3	-177.7 (4)
C14—C41—N4—C43	61.9 (7)		

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
S3—H3...S2 <sup>ii</sup>	1.44 (7)	2.65 (7)	3.913 (3)	144 (4)

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

Methylene H atoms were included in idealized positions, with all parameters riding on those of the parent C atoms. The thiol H atom was identified as a difference peak and was refined freely.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1992). Cell refinement: CAD-4 EXPRESS. Data reduction: CAD4 (Hursthouse, 1976). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1971). Software used to prepare material for publication: SHELXL93.

The Biotechnology and Biological Sciences Research Council is thanked for funding and the John Innes Foundation is thanked for a studentship (SL).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1327). Services for accessing these data are described at the back of the journal.

## References

- Colpas, G. J., Kumar, M., Day, R. O. & Maroney, M. J. (1990). *Inorg. Chem.* **29**, 4779–4788.  
 Davies, S. C., Hughes, D. L., Janas, Z., Jerzykiewicz, L., Richards, R. L., Sanders, J. R. & Sobota, P. (1997). *Chem. Commun.* pp. 1261–1262.  
 Davies, S. C., Hughes, D. L., Richards, R. L. & Sanders, J. R. (1998). *Chem. Commun.* pp. 2699–2700.  
 Enraf-Nonius (1992). CAD-4 EXPRESS. Enraf-Nonius, Delft, The Netherlands.  
 Hursthouse, M. B. (1976). CAD4. Program for Data Reduction. Queen Mary College, London.

Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Sheldrick, G. M., Orpen, A. G., Reichert, B. E. & Raithby P. R. (1977). *EMPABS. Program to Apply Semi-empirical Absorption Corrections*. 4th Eur. Crystallogr. Meet., Oxford. Abstracts, p. 147.

*Acta Cryst.* (1999). **C55**, 1438–1440

### *trans*-Diaquabis(3-hydroxybenzoato-*O*)bis(nicotinamide-*N*<sup>1</sup>)cobalt(II)

TUNCER HÖKELEK<sup>a\*</sup> AND HACALI NECEFOĞLU<sup>b</sup>

<sup>a</sup>Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and <sup>b</sup>Kafkas University, Department of Chemistry, 63100 Kars, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr

(Received 10 March 1999; accepted 12 May 1999)

#### Abstract

The title compound, [Co(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], is a monomeric and centrosymmetric cobalt complex. It contains two 3-hydroxybenzoate anions, two nicotinamide (NA) molecules and two water molecules as ligands. Each ligand is monodentate. The two nearest carboxylate O atoms and the two water O atoms form a slightly distorted square-planar arrangement around the Co atom [with distances of 2.099 (3) and 2.132 (3) Å, respectively], while the distorted octahedral coordination is completed by the pyridine N atoms of the NA ligands at a distance of 2.139 (4) Å. There is an intramolecular hydrogen bond between the nicotinamide N and O atoms [N⋯O 2.228 (6) Å], and the hydroxybenzoate and water O atoms form inter- [2.662 (5) Å] and intramolecular [2.586 (5) Å] hydrogen bonds, respectively, with the non-coordinated O atom of the carboxylate group.

#### Comment

Nicotinamide (NA) is a form of niacin. A deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. The nicotinic acid derivative *N,N*-diethylnicotinamide (DNA) is an important respiratory stimulant. There are only a few examples of structure determinations of Co<sup>II</sup> complexes with nicotinic and/or benzoic acid derivatives as ligands, e.g. [Co(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>(NA)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [(II), where NA is nicotinamide, C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O; Hökelek & Necefoğlu, 1999], [Co(C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub>)<sub>2</sub>(NA)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [(III); Hökelek & Necefoğlu, 1998], [Co(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(DNA)<sub>2</sub>(H<sub>2</sub>O)] [(IV), where DNA is diethylnicotinamide, C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O;

Hökelek & Necefoğlu, 1997], [M(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] [(V), where M = Zn<sup>II</sup> and Co<sup>II</sup>; Tahir *et al.*, 1997], [Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(DNA)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [(VI); Mikelashvili, 1982] [Co(*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] [(VII); Nadzhafov *et al.*, 1981] and [Co(*p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] [(VIII); Amiraslanov *et al.*, 1979].

The structure–function–coordination relationships of the arylcarboxylate ion in Co<sup>II</sup> complexes of benzoic acid derivatives depend on the nature and position of the substituted groups in the phenyl ring, the nature of the additional ligand molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981; Adiwidjaja *et al.*, 1978; Amiraslanov *et al.*, 1979; Nadzhafov *et al.*, 1981; Antsyshkina *et al.*, 1980). When pyridine and its derivatives are used instead of water molecules, the structure is completely different (Catterick *et al.*, 1974). The crystal structure of complex (VI) is isostructural with the analogous Ni, Mn, Zn and Cd complexes (Sergienko *et al.*, 1980). In complexes (VII) and (VIII), the Co atoms are situated at centres of symmetry and are surrounded by six O atoms, forming slightly distorted octahedra. Four positions are occupied by water molecules and the other two by O atoms of the carboxyl groups of *p*-nitrobenzoate and *p*-amino-benzoate anions. In complexes (II) and (III), the Co atoms are also situated at centres of symmetry and are surrounded by four O atoms, forming slightly distorted square-planar arrangements, the distorted octahedral coordinations being completed by the pyridine N atoms of NA.

The structure determination of the title compound, (I), was undertaken to determine the ligand properties of NA and benzoate moieties and to compare the coordination geometries when the NA ligands are substituted by water, *i.e.* complexes (VII) and (VIII). The monomeric [Co(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(NA)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] molecules have the typical structure of NA complexes in which the metal atom has a *trans*-octahedral coordination. The complex has a centre of symmetry with the monodentate benzoate ions and NA ligand acting as monodentate ligands (Fig. 1). The four nearest symmetry-related carboxylate and water O atoms, with distances of 2.099 (3) and 2.132 (3) Å, respectively, form a slightly distorted square plane around the Co atom, while the slightly distorted octahedral arrangement is completed by the pyridine N atoms of NA ligands at distances of 2.139 (4) Å.

