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On the reaction of nickel(II) ions with thiolacetic acid

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Key indicators

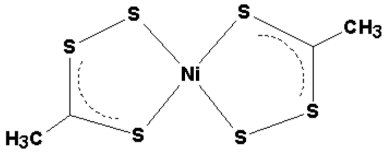
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.087
Data-to-parameter ratio = 18.7

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

An unexpected mononuclear nickel thiolate, bis(perthioacetato-*S*,*S*′)nickel(II), [Ni($C_2H_3S_3$)$_2$], has been obtained by the reaction of Ni^{II} ions with thiolacetic acid. It consists of a planar rectangular NiS$_4$ unit. Weak hydrogen bonds of the type C—H$\cdots$Ni form molecular ribbons along the *a* axis. Among the products, γ-sulfur is also detected.

Comment

Metal thiolates, including nickel thiolates, are a rich class of compounds and they are relevant to the coordination of metal ions by sulfur-containing amino acids in biological systems. They are also of interest as synthetic models related to metal sulfide catalysis (Krebs & Henkel, 1991). The reaction of Ni^{II} ions with thiolate ligands provides a large variety of structural possibilities ranging from mononuclear to polynuclear complexes including cyclic clusters and chain fragments. So far, several cyclic nickel thiolates have been synthesized and characterized by diffraction techniques; nevertheless, the governing factors of the degree of oligomerization of cyclic or chain nickel thiolates are still unknown. We believe that the study of structural systematics and relationships may lead to an understanding of the architecture of these compounds in order to design new cyclic clusters. Recently, we have reported the synthesis and structures of a pentanuclear and a hexanuclear cyclic nickel thiolate where the thiolate ligands differed only by the substituents on the β-C atom (Mahmoudkhani & Langer, 1999*a*,*b*). In order to understand the effect of electronic modulations on the α-C atom of the thiolate ligand, we have undertaken the reaction of Ni^{II} ions with thiolacetic acid. To our surprise, instead of a cyclic cluster, we obtained a mononuclear nickel thiolate, (I), in which the primary thiolcarboxylate ligand was transformed to a perthiocarboxylate ligand. This is, to the best of our knowledge, the first example of an alkylperthiocarboxylato–metal complex, although there are some reports on the structure of arylperthiocarboxylate-metal complexes (Coucouvanis *et al.*, 1985; Coucouvanis & Fackler, 1967; Fackler *et al.*, 1968; Lanferdi *et al.*, 1988).



(I)

These complexes are in general prepared by an oxidative addition of sulfur to the corresponding dithiocarboxylate–

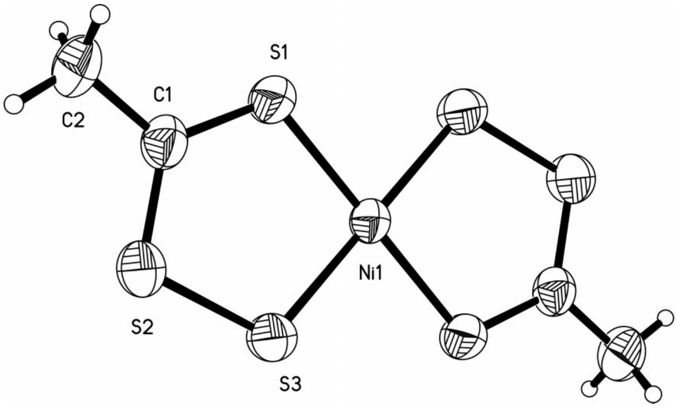


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

metal complex. But formation of this mononuclear nickel thiolate from the reaction of Ni^{II} ions with thiolacetic acid seems to be unique. Furthermore, we have also detected the formation of γ-sulfur by this reaction which makes the interpretation much more complicated. Complex (I) crystallizes in the monoclinic system with space group $P2_1/n$. The structure is centrosymmetric and the asymmetric unit contains only a half of the molecule. The complex consists of a planar rectangular NiS_4 unit with no trace of bridging by thiolate–S atom. The atomic numbering for the complex (I) is presented in Fig. 1. The bond distances and angles are about the same order as for other sulfur-rich nickel thiolates with a similar skeleton. The structure exhibits a hydrogen mediated interaction in the form of weak hydrogen bonds of the type C—H···M forming molecular ribbons along the *a* axis (see Fig. 2). The ability of metal centers to be involved in hydrogen bonds and hydrogen mediated interactions has been recently reviewed by Desiraju & Steiner (1999). For complex (I), the interaction C—H···Ni with an H···Ni distance of 3.15 Å and an angle of 134.3°, lies just in the range 2.5–3.2 Å to be regarded as a weak C—H···*M* hydrogen bond, and is shorter than the sum of van der Waals radii of 3.5 Å.

Experimental

Complex (I) was obtained by a microscale reaction of $NiCl_2{\cdot}H_2O$ (Aldrich) and thiolacetic acid (Aldrich) in the presence of KOH in ethanol according to the method of Mahmoudkhani & Langer (1999*a*,*b*). Solvents were removed by vacuum distillation and the products isolated by microextraction with benzene and subsequent crystallization from benzene–acetone solution. Crystals of (I) were obtained after a few days by slow evaporation of the solution in acetone when allowed to stand over silica gel in a desiccator.

Crystal data

$[Ni(C_2H_3S_3)_2]$
$M_r = 305.16$
Monoclinic, $P2_1/n$
$a = 5.3169$ (3) Å
$b = 6.1524$ (3) Å
$c = 15.9722$ (8) Å
$\beta = 92.50$ (1)°
$V = 521.98$ (5) Å^3
$Z = 2$
$D_x = 1.942$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3360 reflections
$\theta = 1$–25°
$\mu = 2.99$ mm^{-1}
$T = 297$ (2) K
Parallelepiped, dark red
0.30 × 0.25 × 0.04 mm

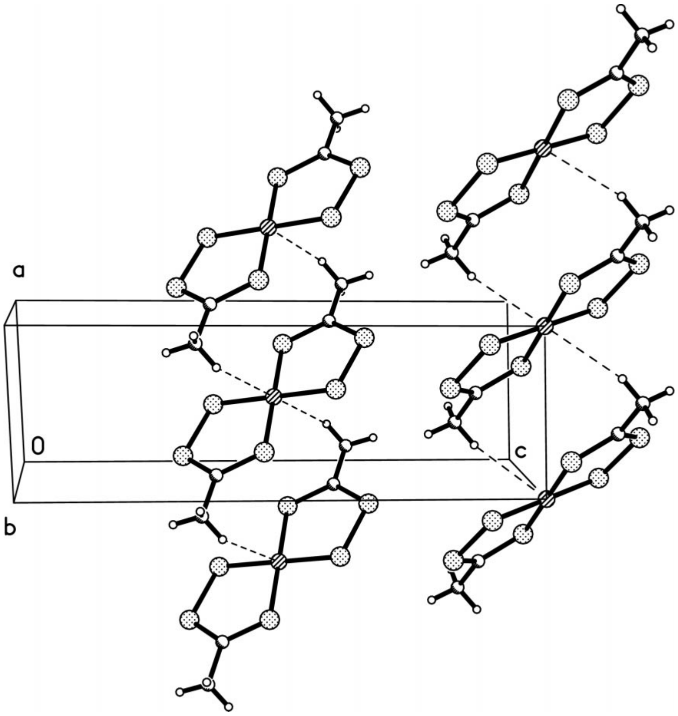


Figure 2
The molecular ribbons formed by weak hydrogen bonds in the crystal structure of (I).

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing; 1995)
$T_{min} = 0.467$, $T_{max} = 0.890$
4984 measured reflections
992 independent reflections
848 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 25.7°$
$h = -6 \rightarrow 6$
$k = -7 \rightarrow 7$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.02$
992 reflections
53 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S1	2.1579 (8)	S2—C1	1.668 (3)
Ni1—S3	2.1623 (8)	S1—C1	1.667 (3)
S3—S2	2.0322 (12)	C2—C1	1.496 (4)
S1—Ni1—S3^{i}	85.75 (3)	C1—S1—Ni1	110.05 (11)
S1—Ni1—S3	94.25 (3)	C2—C1—S1	120.0 (2)
S2—S3—Ni1	107.26 (4)	C2—C1—S2	116.8 (2)
C1—S2—S3	105.29 (11)	S1—C1—S2	123.14 (18)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2C···Ni1^{i}	0.96	3.15	3.880 (4)	134

Symmetry codes: (i) $1+x, y, z$.

H atoms were constrained to the ideal geometry using an appropriate riding model. The C—H distances (0.96 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on threefold averaged circular Fourier synthesis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (1997). *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Coucouvanis, D. & Fackler, J. P. Jr (1967). *J. Am. Chem. Soc.* **89**, 1346–1351.
Coucouvanis, D., Patil, P. R., Kanatzidis, M. G., Deterring, B. & Baenziger, N. C. (1985). *Inorg. Chem.* **24**, 24–31.
Desiraju, G. R. & Steiner, T. (1999). In *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press.
Fackler, J. P. Jr, Coucouvanis, D., Fetchin, J. A. & Seidel, W. C. (1968). *J. Am. Chem. Soc.* **90**, 2784–2788.
Krebs, B. & Henkel, G. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 769–788.
Lanferdi, A. M. M., Tiripicchio, A., Marsich, N. & Camus, A. (1988). *Inorg. Chim. Acta*, **142**, 269–275.
Mahmoudkhani, A. H. & Langer, V. (1999*a*). *Inorg. Chim. Acta*, **294**, 83–86.
Mahmoudkhani, A. H. & Langer, V. (1999*b*). *Polyhedron*, **18**, 3407–3410.
Sheldrick, G. M. (2001). *SADABS* (Version 2.02). University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.