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trans-Bis(*O*-ethyl dithiocarbonato-*S*,*S*′)bis(isoquinoline)nickel(II)

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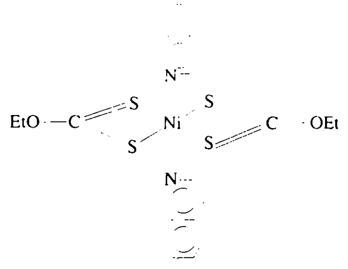
Abstract

The Ni atom in the title compound, $[Ni(C_2H_5OCS_2)_2(C_9H_7N)_2]$, has distorted octahedral coordination. It lies on a twofold axis and in the plane formed by the four S atoms of the two chelating ethyl xanthates. The two isoquinoline ligands occupy apical sites. The Ni—S and Ni—N bond lengths are 2.440 (2)–2.464 (2) and 2.091 (4) Å, respectively.

Comment

Comprehensive studies of the reactions of planar transition metal complexes with a wide variety of neutral N-atom donor ligands of different donor capacity have been carried out in recent years and the crystal structures of the products determined (Harrison, Begley & Kikabhai, 1986; Xiong, Zuo, You, Wu & Huang, 1995; Huang, Xiong & You, 1995). Despite this, alkyl xanthate metal complexes, and in particular their crystal structures, have received relatively little attention (Gable, Hoskins & Winter, 1985; Pang, Lucken & Bernardinelli, 1990). Tiekink & Winter (1986) reported the crystal structure of the 1:1 adduct formed between bis(*O*-ethyl xanthato)nickel(II) and triphenylphosphine. The structure of $[Ni(S_2COC_6H_{11})(PMePh_2)]$, which exhibits distorted square-pyramidal geometry, has also been described (Ballester, Gutierrez-Alonso, Perpinan, Gutierrez-Puebla & Ruiz-Valero, 1990). In a continuation of our investigation into the reactions of planar transition metal complexes with neutral nitrogen bases, we determined the crystal structure of *trans*-$[Ni(C_2H_5OCS_2)_2(C_9H_7N)_2]$, (I).



(I)

The Ni atom in (I) is coordinated to four S atoms and two *trans* N atoms to give slightly distorted octahedral geometry. The structure is very similar to those of $[Ni\{(C_2H_5O)_2PS_2\}_2(C_9H_7N)_2]$ (Huang, Xiong, Dong & You, 1995), $[Ni\{(C_4H_9O)_2PS_2\}_2(C_9H_7N)_2]$ (Xiong, You & Huang, 1995*b*), $[Ni\{(C_4H_9O)_2PS_2\}_2(4\text{-}APy)_2]$ (4-APy = 4-aminopyridine) (You, Xiong, Dong & Huang, 1994) and $[Ni\{(C_2H_5O)_2PS_2\}_2(C_7H_7N)_2]$ (Song, Xiong, You & Huang, 1995), which display Ni—S bond distances in good agreement with those in (I). These distances are much shorter than the apical Ni—S(4) bond lengths in $[Ni(C_2H_5OCS_2)_2PPh_3]$ [2.654 (2) Å] and $[Ni(C_6H_{11}OCS_2)_2PMePh_2]$ [2.722 (4) Å], in each of which the Ni atom adopts distorted square-pyramidal geometry with S(1), S(2), S(3) and P in the basal plane and S(4) apical (Tiekink & Winter, 1986; Ballester *et al.*, 1990). The Ni—N bond lengths in (I) are in agreement with those found in $[Ni(TTA)_2(3\text{-mpy})_2]$ [2.090 (6)–2.104 (6) Å] and $[Ni(TTA)_2(4\text{-mpy})_2]$[2.097 (4)–2.096 (4) Å] (TTA = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato, 3-mpy = 3-methylpyridine, 4-mpy = 4-methylpyridine) (Xiong, You, Dong, & Huang, 1995; Xiong, You & Huang, 1995*a*).

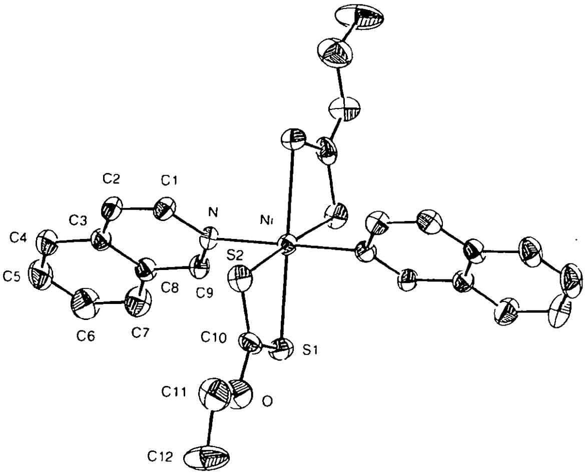


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Bis(*O*-ethyl dithiocarbonato-*S*,*S*′)nickel(II) was dissolved in ethanol, and excess isoquinoline was added until the colour of the solution changed from brown to green. Crystals of the title complex, (I), were obtained after the solution evaporated at room temperature.

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Crystal data

[$Ni(C_3H_5OS_2)_2(C_9H_7N)_2$]	Mo $K\alpha$ radiation
$M_r = 559.41$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25 reflections
Ccca	$\theta = 10.43–12.53°$
$a = 14.644$ (6) Å	$\mu = 1.062$ mm^{-1}
$b = 15.644$ (4) Å	$T = 296$ K
$c = 23.085$ (4) Å	Column
$V = 5288$ (4) Å^3	0.50 × 0.50 × 0.20 mm
$Z = 8$	Green
$D_x = 1.40$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	1550 observed reflections [$I > 3\sigma(I)$]
ω scans	$\theta_{\max} = 25°$
Absorption correction: ψ scans (Molecular Structure Corporation, 1985)	$h = 0 \rightarrow 17$
	$k = -18 \rightarrow 0$
	$l = 0 \rightarrow 27$
$T_{\min} = 0.955$, $T_{\max} = 1.000$	3 standard reflections monitored every 300 reflections
2586 measured reflections	intensity decay: 3.5%
2586 independent reflections	

Refinement

Refinement on F	$w = 1/\sigma^2(F)$
$R = 0.056$	$(\Delta/\sigma)_{\max} = 0.07$
$wR = 0.068$	$\Delta\rho_{\max} = 0.89$ e Å^{-3}
$S = 1.69$	$\Delta\rho_{\min} = -0.50$ e Å^{-3}
1550 reflections	Extinction correction: none
150 parameters	Atomic scattering factors from Cromer & Waber (1974)
H-atom parameters not refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	0	1/4	0.11481 (4)	3.09 (4)
S(1)	−0.1158 (1)	0.1924 (1)	0.18001 (7)	4.26 (8)
S(2)	−0.1223 (1)	0.1929 (1)	0.05257 (7)	4.55 (8)
O	−0.2525 (4)	0.1345 (3)	0.1262 (2)	6.3 (3)
N	0.0649 (3)	0.1308 (3)	0.1153 (2)	3.4 (2)
C(1)	0.0847 (4)	0.0877 (4)	0.0652 (2)	4.0 (3)
C(2)	0.1185 (4)	0.0071 (4)	0.0644 (3)	4.3 (3)
C(3)	0.1355 (4)	−0.0362 (3)	0.1166 (3)	3.9 (3)
C(4)	0.1693 (5)	−0.1212 (4)	0.1202 (3)	5.3 (3)
C(5)	0.1820 (5)	−0.1579 (4)	0.1726 (4)	6.7 (4)
C(6)	0.1646 (6)	−0.1143 (4)	0.2234 (3)	6.7 (4)
C(7)	0.1325 (5)	−0.0327 (4)	0.2219 (3)	5.6 (4)
C(8)	0.1170 (4)	0.0069 (3)	0.1681 (3)	3.7 (3)
C(9)	0.0819 (4)	0.0914 (3)	0.1643 (2)	3.6 (3)
C(10)	−0.1686 (4)	0.1697 (3)	0.1189 (3)	4.7 (3)
C(11)	−0.3053 (7)	0.1180 (5)	0.0777 (3)	8.0 (5)
C(12)	−0.3956 (6)	0.0816 (9)	0.1022 (3)	9.8 (6)

Table 2. *Selected geometric parameters (Å, °)*

Ni—N	2.091 (4)	Ni—N^{i}	2.091 (4)
Ni—S(1)	2.440 (2)	Ni—S(2)	2.464 (2)
Ni—S(1^{i})	2.440 (2)	Ni—S(2^{i})	2.466 (2)
S(1)—C(10)	1.648 (7)	S(2)—C(10)	1.713 (7)
O—C(10)	1.358 (7)	O—C(11)	1.384 (8)
N—C(9)	1.313 (6)	N—C(1)	1.370 (7)
N^{i}—Ni—N	179.4 (3)	S(1)—Ni—S(2)	73.74 (6)
S(1^{i})—Ni—S(2^{i})	73.74 (6)	N—Ni—S(2)	90.6 (1)
N—Ni—S(1^{i})	89.0 (1)	S(1^{i})—Ni—S(2)	177.32 (8)
S(2^{i})—Ni—S(2)	108.7 (1)	N^{i}—Ni—S(1)	90.6 (1)
S(2^{i})—Ni—S(1)	177.32 (7)	S(2^{i})—Ni—N^{i}	90.5 (1)
S(1)—Ni—S(1^{i})	103.9 (1)	S(1^{i})—Ni—N^{i}	89.0 (1)
Ni—S(1)—C(10)	83.0 (2)	Ni—S(2)—C(10)	81.0 (2)
S(1)—C(10)—S(2)	122.3 (4)		

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

Data collection was performed using *CONTROL* (Molecular Structure Corporation, 1986). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983). The heavy Ni atom was located in an E map and the remaining non-H atoms were located using the *DIRDIF* (Beurskens, 1984) program. H atoms were fixed geometrically with C—H = 0.95 Å, but were included in the refinement. The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all non-H atoms. All calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1212). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[bis(4-methylthiazolin-2-ylidene)gold(I)] Tetrachlorozincate Dichloromethane

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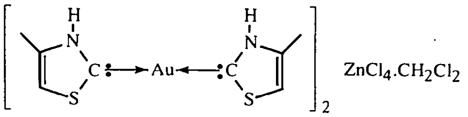
Abstract

The Au centres in the crystal structure of [Au(C_4H_5NS)$_2$][$ZnCl_4$]$_{0.5}$.0.5CH_2Cl_2 approach linear coordination [C—Au—C bond angle 179 (1)°]. Monomeric cations connecting through Au···Au interactions [3.330 (2) Å] form dimeric units that link through hydrogen bonds to the tetrachlorozincate anions. Dichloromethane is present as non-bonded and disordered solvent of crystallization.

Comment

The tendency of gold to form aurate complexes upon reaction with 2-lithiothiazolyl reagents has recently been investigated by Raubenheimer *et al.* (1994). The above-mentioned aurate complexes were shown to form mono- and biscarbene complexes after electrophilic attack with H$^+$ or CH$_3^+$. Structural information on this type of complex is important to the understanding of contributing resonance structures, as few gold(I) complexes of this type are known. An interesting feature of these, mostly linear, complexes is the Au···Au interaction to form dimeric units in the solid state.

The Au—C$_{carbene}$ bonds [Au—C1 1.92 (2), Au—C5 1.92 (2) Å] of the title compound, (I), are not significantly shorter than equivalent bonds found for *trans,trans*-bis[bis(*p*-tolylamino)carbene]gold(I) tetrafluoroborate (2.02 Å; Banditelli, Bonati, Calogero & Valle, 1984) and bis(4,5-dimethylimidazolinylidene)gold(I) chloromonohydrate (2.01 Å; Britten, Lock & Wang, 1992). Moreover, relaxation of the bond-length restraints placed on the ring atoms has the effect of lengthening these bonds slightly.



(I)

The crystal structure of the title compound consists of discrete dimeric bis(4-methylthiazolinylidene)gold(I) cations and tetrachlorozincate anions, bridged through hydrogen bonds (involving N and Cl atoms; Fig. 1) Each Au atom is linearly coordinated by two coplanar 4-methylthiazolin-2-ylidene ligands [C1—Au—C5 179 (1)°]. The ligands are oriented in such a way that the N atoms are on the same side of the cation and are directed towards two of the Cl atoms of the $ZnCl_4$ anion, forming hydrogen bonds [N1···Cl1 3.15 (3), N2···Cl2 3.06 (3) Å; Fig. 2]. The remaining two Cl atoms of the counterion bond to the next cationic Au unit (related by a twofold axis).

Pairs of Au atoms connect through short interactions [3.330 (2) Å] to form dimeric units in a staggered conformation [C1—Au···Au^i—C1^i torsion angle of 104.0 (10)°] with the S atoms slightly turned towards each other (Fig. 1). This intermolecular bonding pattern results in infinite columns of connected ions parallel to the *c* axis, surrounded by non-bonded disordered dichloromethane.

Pathaneni & Desiraju (1993) reported that in *X*Au*Y* (*X*, *Y* = any element) systems with Au···Au interactions,

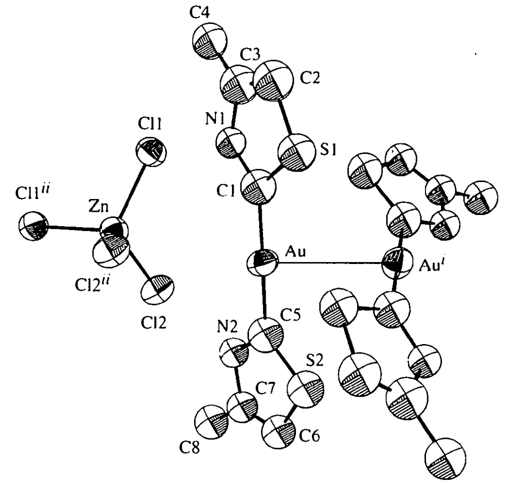


Fig. 1. An *ORTEP* (Hall & Stewart, 1990) drawing of the title compound showing the atomic labelling scheme with displacement ellipsoids drawn at 50% probability.

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