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(2-Thioxo-1,3-dithiole-4,5-dithiolato)-(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)nickel(II)

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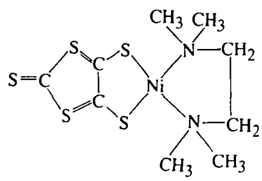
Abstract

The title compound, [Ni(C_3S_5)($C_6H_{16}N_2$)], contains a four-coordinate Ni atom which is bonded to two S atoms from the 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligand and to the two N atoms of the *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ligand. The mean Ni—S and Ni—N bond lengths are 2.169 (4) and 2.003 (9) Å, respectively.

Comment

Compounds containing the [Ni(dmit)$_2$] residue, where dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate, have aroused great interest because of their conductive and even superconductive properties (Valade, Legros, Tejel, Pomarede, Garreau, Bruniquel & Cassoux, 1991; Cornelissen, Haasnoot, Leloux & Reedijk, 1991), and several reports on their structures and electrical properties have appeared (Olk, Olk, Dietzsch, Kirmse & Hoyer, 1992; Cornelissen *et al.*, 1992). Herein, a new compound, [Ni(dmit){$(CH_3)_2NCH_2CH_2N(CH_3)_2$}], (I), is reported.



(I)

The title complex is a neutral molecule and its structure is essentially planar (Fig. 1). The central Ni atom is fourfold coordinated to two S atoms of the dmit ligand and to the two N atoms of the *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ligand. The Ni atom lies 0.038 (1) Å above the least-squares plane defined by atoms S1, S2, N1 and N2. The mean Ni—S bond distance is 2.169 (4) Å, which is slightly greater than corresponding values found in (smdt)[Ni(dmit)$_2$]$_2$ [average 2.162 (2) Å], (dmp)[Ni(dmit)$_2$]$_2$ [average 2.163 (6) Å] and (dmm)[Ni(dmit)$_2$]$_2$ [average 2.158 (8) Å], where smdt is *S*-methyl-1,3-dithianium, dmp is *N*,*N*-dimethylpyrolidinium and dmm is *N*,*N*-dimethylmorpholinium (Cornelissen *et al.*, 1992). The mean Ni—N bond distance [2.003 (9) Å] in the title compound is shorter than the mean Ni—N distance [2.130 (2) Å] found in [Ni(en)$_3$](NO$_3$), where en is ethylenediamine (Korp, Bernal, Palmer & Robinson, 1980).

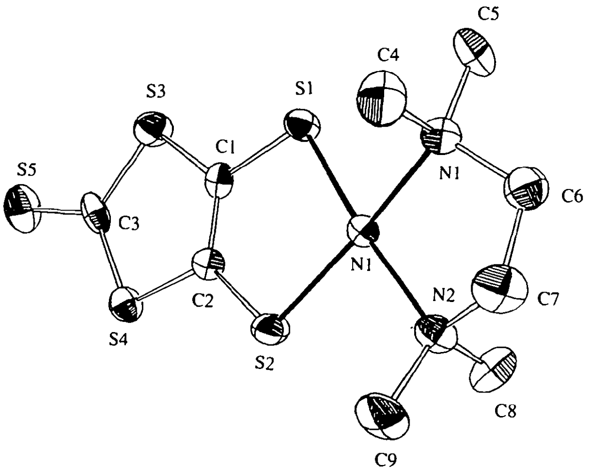


Fig. 1. *ORTEP*II view (Johnson, 1976) of the title compound. Displacement ellipsoids are shown at the 30% probability level.

Experimental

The title compound was obtained from the reaction of $(Me_4N)_2Ni(C_3S_5)_2$, $Cu(NO_3)_2$, $NaBH_4$ and $(CH_3)_2NCH_2CH_2N(CH_3)_2$, and was recrystallized from CH_3CN, CH_3COCH_3 and Et_2O.

Crystal data

[Ni(C_3S_5)($C_6H_{16}N_2$)]
$M_r = 371.23$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Monoclinic
$P2_1/n$
$a = 9.334\,(8)$ Å
$b = 11.112\,(5)$ Å
$c = 14.526\,(9)$ Å
$\beta = 98.14\,(7)^\circ$
$V = 1491\,(2)$ Å^3
$Z = 4$
$D_x = 1.653$ Mg m^{-3}

Cell parameters from 20 reflections
$\theta = 10\text{–}22.5^\circ$
$\mu = 1.96$ mm^{-1}
$T = 298$ K
Prism
0.5 × 0.2 × 0.2 mm
Black

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.38$, $T_{\max} = 0.68$
2963 measured reflections
2780 independent reflections

1356 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.041$
$\theta_{\max} = 25^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 250 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.054$
$wR = 0.063$
$S = 1.14$
1356 reflections
154 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + (0.020F_o)^2 + 1]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

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

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Ni	0.4415 (1)	0.1819 (1)	0.17681 (9)	1.64 (2)
S1	0.5289 (3)	0.0034 (3)	0.1637 (2)	2.20 (6)
S2	0.2521 (3)	0.1431 (3)	0.0758 (2)	2.70 (6)
S3	0.4023 (3)	−0.2185 (3)	0.0583 (2)	2.92 (7)
S4	0.1507 (3)	−0.0899 (3)	−0.0253 (2)	2.40 (6)
S5	0.1749 (3)	−0.3507 (3)	−0.0685 (2)	3.74 (7)
N1	0.5902 (9)	0.2173 (8)	0.2863 (6)	2.1 (2)
N2	0.3787 (9)	0.3543 (8)	0.1834 (6)	2.5 (2)
C1	0.394 (1)	−0.0667 (9)	0.0876 (7)	1.8 (2)
C2	0.279 (1)	−0.0060 (9)	0.0492 (7)	1.9 (2)
C3	0.240 (1)	−0.227 (1)	−0.0146 (7)	2.4 (2)
C4	0.533 (1)	0.169 (1)	0.3676 (8)	3.9 (3)
C5	0.741 (1)	0.168 (1)	0.2893 (8)	3.5 (3)
C6	0.604 (1)	0.349 (1)	0.2906 (8)	3.2 (3)
C7	0.459 (1)	0.406 (1)	0.2710 (9)	3.8 (3)
C8	0.426 (1)	0.416 (1)	0.1037 (9)	3.6 (3)
C9	0.223 (1)	0.379 (1)	0.185 (1)	4.3 (3)

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

Ni—S1	2.163 (4)	S5—C3	1.65 (1)
Ni—S2	2.175 (3)	N1—C4	1.46 (2)
Ni—N1	1.997 (8)	N1—C5	1.51 (1)
Ni—N2	2.009 (9)	N1—C6	1.47 (1)
S1—C1	1.74 (1)	N2—C7	1.50 (1)
S2—C2	1.73 (2)	N2—C8	1.47 (2)
S3—C1	1.74 (2)	N2—C9	1.49 (1)
S3—C3	1.72 (1)	C1—C2	1.33 (1)
S4—C2	1.76 (1)	C6—C7	1.49 (2)
S4—C3	1.74 (1)		
S1—Ni—S2	92.3 (2)	Ni—N2—C8	106.7 (7)
S1—Ni—N1	91.3 (3)	Ni—N2—C9	117.9 (7)
S1—Ni—N2	173.9 (3)	C7—N2—C8	108.8 (9)
S2—Ni—N1	169.6 (3)	C7—N2—C9	107 (1)
S2—Ni—N2	90.4 (2)	C8—N2—C9	109.2 (9)
N1—Ni—N2	87.1 (3)	S1—C1—S3	122.4 (5)
Ni—S1—C1	102.6 (3)	S1—C1—C2	120.8 (8)
Ni—S2—C2	102.1 (3)	S3—C1—C2	116.9 (7)
C1—S3—C3	97.9 (6)	S2—C2—S4	122.3 (6)
C2—S4—C3	97.6 (5)	S2—C2—C1	122.1 (8)
Ni—N1—C4	106.2 (6)	S4—C2—C1	115.4 (8)
Ni—N1—C5	119.6 (7)	S3—C3—S4	112.1 (7)
Ni—N1—C6	106.1 (6)	S3—C3—S5	124.8 (7)
C4—N1—C5	106.9 (8)	S4—C3—S5	123.2 (6)
C4—N1—C6	111.6 (9)	N1—C6—C7	111 (1)
C5—N1—C6	106.5 (8)	N2—C7—C6	109 (1)
Ni—N2—C7	107.1 (6)		

The Ni atom was located by direct methods (Main, 1983) and the remaining non-H atoms were located by Fourier syntheses. H atoms were placed in geometrically calculated positions, with C—H distances of 0.95 Å, but their parameters were not included in the refinement. The structure was refined by a full-matrix least-squares technique, with anisotropic displacement parameters for all non-H atoms. All calculations were performed on a Compaq PL4/50 computer.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN* (Main, 1983), *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 541–543

[*N*,*N*′-Bis(2-aminoethyl-κ*N*)-*N*,*N*′-bis(2-ammonioethyl)ethylenediamine-κ^2*N*,*N*′]-platinum(II) Bis(tetrachloroplatinate) Trihydrate

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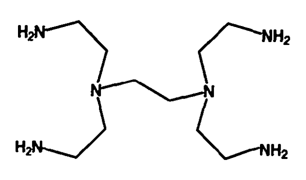
Abstract

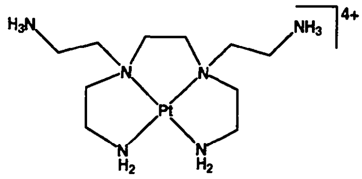
The reaction between K_2PtCl_4 and penten [*N*,*N*,*N*′,*N*′-tetrakis(2-aminoethyl)ethylenediamine] gave a Magnus-type double salt, $[Pt(C_{10}H_{30}N_6)][PtCl_4]_2.3H_2O$, in which the diprotonated penten ligand (pentenH_2) serves as a tetradentate chelating ligand. The complex involves an ion pair, $\{[Pt(pentenH_2)][PtCl_4]\}^{2+}$. These two mononuclear units have an attractive interaction for each other, with several hydrogen bonds formed between the amine groups and Cl atoms. The two Pt atoms are shifted out of their ideal coordination planes towards each other and the Pt···Pt distance within this unit is 3.414 (3) Å.

Comment

Our initial interest in penten, (1), lay in its use in the syntheses of binuclear complexes. The reaction between K_2PtCl_4 and penten, conducted at pH 0–5, gave the title complex as the sole product. The complex is a 1:2 salt of a tetravalent $[Pt(pentenH_2)]^{4+}$ cation, (2), and a divalent $PtCl_4^{2-}$ anion, and can be regarded as a Magnus-type double salt. It appears that penten prefers to behave as a tetradentate chelate, implying that the complexation of the two tertiary amines predominantly occurs prior to that of the primary amines.



(1) penten



(2) $[Pt(pentenH_2)]^{4+}$

Fig. 1 shows the structure of the complex salt. A stereodiagram of the crystal packing is shown in Fig. 2. All the C—N distances [1.42 (6)–1.65 (6) Å] indicate single-bond character. The $[Pt(pentenH_2)]^{4+}$ cation shows a large distortion from ideal square-planar geometry due to the strain caused by the three chelate rings, as shown in Table 2. All three coordination planes, however, are judged to be planar in the best-plane calculations performed with the four coordinated atoms, where the four-atom r.m.s. deviations are 0.041, 0.034 and 0.089 Å for the Pt(1), Pt(2) and Pt(3) planes, respectively. One interesting feature is that the Pt(1) and Pt(2) atoms are shifted out of their coordination planes towards each other by 0.14 (2) and 0.026 (8) Å, respectively. The Pt(1)···Pt(2) distance of 3.414 (3) Å is not as short as the distance of 3.25 Å reported for the Magnus green salt $[Pt(NH_3)_4][PtCl_4]$ (Atoji, Richardson & Rundle, 1957), but is comparable to the distance of 3.39 Å reported for $Pt(en)Cl_2$ (en = ethylenediamine) (Martin, Hunter, Kroening & Coley, 1971). These two planes are also attracted to each other, with four hydrogen bonds formed between the amine groups and the Cl atoms (Table 2). Although similar hydrogen-bonding interactions are achieved between the Pt(1) and Pt(3) planes, the Pt(1)···Pt(3) distance of 3.957 (3) Å is too long to be considered as a metal–metal interaction. The dihedral angle between the Pt(1) and Pt(2) planes is 27.6 (8)°, while that between the Pt(1) and Pt(3) planes is 30.6 (8)°. Moreover, this complex ion pair further interacts with neighbouring ion pairs through similar hydrogen bonds, resulting in the formation of a three-dimensional network. In addition, the water molecules also participate in this hydrogen-bonding network. Most of these interactions, however, appear to be insignificant due to the absence of metal–metal interactions. The ion pair formed between the Pt(1) and Pt(2) units in the asymmetric unit is, therefore, the only one which is expected to possess a meaningful metal–metal interaction. In conclusion, this compound can be regarded as a rare example of a double salt which does not have infinite Pt···Pt interactions, but rather has a dimeric Pt···Pt interaction. It is well known that the *d–d* transition of $PtCl_4^{2-}$ in the Magnus green salt is largely red-shifted due to exceptional crystal effects (Martin, Rush, Kroening & Fanwick, 1973). Such a shift in the *d–d* transition is, however, not promoted in the title compound, for both the colour and the UV–visible spectra of the compound resemble those of K_2PtCl_4 in the solid state.

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