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Bis(*N*,*N*-*cyclo*-heptamethylenedithiocarbamato-*S*,*S*′)platinum(II),† a Platinum Dithiocarbamate Containing a Large Carbocyclic Ring

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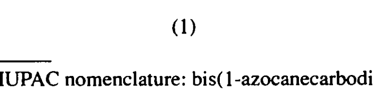
Abstract

The title compound, [Pt($C_8H_{14}NS_2$)$_2$], contains the largest carbocyclic dithiocarbamate ligand yet characterized. Typical Pt—S distances and S—Pt—S angles are observed, but there is a pronounced twist between the plane defined by Pt, S(1), S(2) and C(1) and that of N(1), C(2) and C(8), relative to open-chain analogues.

Comment

Metal complexes containing the α-dioximato ligand become more soluble in organic solvents by incorporation of a large carbocyclic ring in the ligand (Baxter, Heath, Raptis & Willis, 1992). Such a modification of a platinum bis(α-dioximato) complex, with incorporation of a C_8 backbone, led to the discovery of a novel unbridged platinum(III) dimer (Baxter, Heath, Raptis & Willis, 1992). We report here a similar modification of a dithiocarbamate ligand, resulting in an eight-membered ring, and present the crystal structure of the platinum(II) complex, (1). This is the first report of the structure of a platinum complex containing an *N*,*N*-*cyclo*-polymethylenedithiocarbamate ligand.



(1)

Structural characterizations of simple platinum(II) bisdithiocarbamates are scarce. We know of only one other study (Baker & Emett, 1992), where [Pt(S_2CNEt_2)$_2$] and [Pt($S_2CN(EtOH)_2$)$_2$] were reliably characterized. Early reports of the structure of bis(diethyldithiocarbamato)platinum(II) (Amanov, Kukina & Porai-Koshits, 1967, 1977) gave an *R* value of 0.14. Other studies (Ebihara *et al.*, 1990, 1992) involve structures where the S atoms form platinum-to-silver bridges. The Pt—S bond lengths and S—Pt—S angles found in this study are very similar to those reported by Baker & Emett (1992).

There is a significant twist of 12° between the plane defined by Pt, S(1), S(2) and C(1) and that of N(1), C(2) and C(8). This is larger than those discovered in [Pt(S_2CNEt_2)$_2$] (4°) and [Pt($S_2CN(EtOH)_2$)$_2$] (2°) (Baker & Emett, 1992). The larger twist in (1) may be attributed to crystal-packing effects since an examination of a molecular model reveals that there are no apparent steric barriers to a smaller dihedral angle.

The large carbocyclic ring does not impart any appreciable improvement in organosolubility over the diethyl analogue in conventional solvents such as dichloromethane, toluene, hexane and carbon tetrachloride. The packing diagram, showing the *bc* plane, indicates that there is a degree of interlocking of the

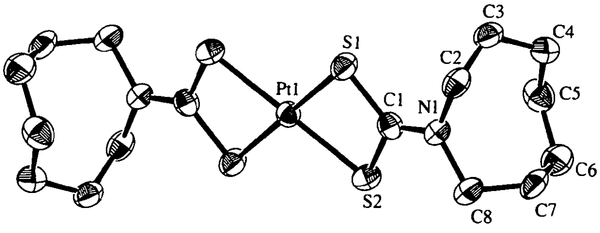


Fig. 1. The molecular structure of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

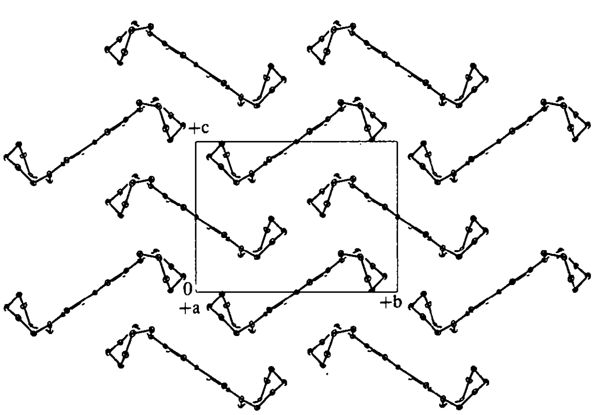


Fig. 2. Packing diagram viewed along the *bc* plane, with H atoms omitted, revealing an interlocking molecular network.

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† Alternative IUPAC nomenclature: bis(1-azocanecarbodithioato-*S*,*S*′)-platinum(II).

individual molecules (also evident in the *ac* plane, not shown) which perhaps limits solubility. Both compound (1) and $[Pt(S_2CNEt_2)_2]$ melt without decomposition at 538 (2) K (sealed *in vacuo*) to form clear liquids, reflecting the comparable stabilities of the crystal lattices, despite their rather different internal organizations.

Experimental

Sodium *N*,*N*-cycloheptamethylenedithiocarbamate was prepared from heptamethylene imine (Aldrich) and CS_2 according to the method of Klöpping & van der Kerk (1951). The platinum(II) complex was prepared by a standard literature procedure (Alison & Stephenson, 1973). Crystals of the title compound were obtained by slow cooling of a $CHCl_3$ solution.

Crystal data

$[Pt(C_8H_{14}NS_2)_2]$
$M_r = 571.74$
Monoclinic
$P2_1/n$
$a = 7.089\,(3)$ Å
$b = 13.781\,(1)$ Å
$c = 10.141\,(3)$ Å
$\beta = 91.39\,(3)^\circ$
$V = 990.4\,(4)$ Å^3
$Z = 2$
$D_x = 1.917$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 18.8$–21.1°
$\mu = 7.478$ mm^{-1}
$T = 295\,(1)$ K
Prism
$0.360 \times 0.200 \times 0.180$ mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical using azimuthal (ψ) scan data (North, Phillips & Mathews, 1968)
$T_{\min} = 0.716$, $T_{\max} = 1.000$
1998 measured reflections
1845 independent reflections

1291 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.01$
$\theta_{\max} = 25.05^\circ$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 150 reflections intensity decay: none

Refinement

Refinement on *F*
$R = 0.035$
$wR = 0.047$
$S = 2.82$
1291 reflections
107 parameters
H-atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 1.04$ e Å^{-3}
$\Delta\rho_{\min} = -1.23$ e Å^{-3}

Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: $1.2\,(5) \times 10^{-7}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Pt(1)	0	0	1/2	0.0340 (2)
S(1)	0.0674 (4)	0.1381 (2)	0.3792 (3)	0.0422 (8)
S(2)	−0.2919 (4)	0.0634 (2)	0.4362 (3)	0.0440 (9)
N(1)	−0.251 (1)	0.2235 (8)	0.287 (1)	0.048 (3)
C(1)	−0.171 (2)	0.1533 (9)	0.358 (1)	0.040 (3)
C(2)	−0.133 (2)	0.3024 (10)	0.229 (1)	0.042 (4)
C(3)	−0.073 (2)	0.3771 (10)	0.333 (1)	0.046 (4)
C(4)	−0.224 (2)	0.4343 (10)	0.399 (1)	0.050 (4)
C(5)	−0.361 (2)	0.373 (1)	0.485 (1)	0.054 (4)
C(6)	−0.555 (2)	0.351 (1)	0.415 (1)	0.058 (4)
C(7)	−0.552 (2)	0.316 (1)	0.272 (1)	0.049 (4)
C(8)	−0.458 (2)	0.2206 (10)	0.248 (1)	0.048 (4)

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

Pt(1)—S(1)	2.320 (3)	N(1)—C(1)	1.33 (2)
Pt(1)—S(2)	2.324 (3)	N(1)—C(2)	1.50 (2)
S(1)—C(1)	1.71 (1)	N(1)—C(8)	1.51 (2)
S(2)—C(1)	1.71 (1)	C(2)—C(3)	1.53 (2)
S(1)—Pt(1)—S(1)	180.0	C(2)—N(1)—C(8)	117.7 (10)
S(1)—Pt(1)—S(2)	74.8 (1)	S(1)—C(1)—S(2)	111.0 (7)
Pt(1)—S(1)—C(1)	87.2 (4)	S(1)—C(1)—N(1)	124.4 (10)
Pt(1)—S(2)—C(1)	87.0 (4)	S(2)—C(1)—N(1)	124.5 (9)
C(1)—N(1)—C(2)	120.5 (10)	N(1)—C(2)—C(3)	111.5 (10)
C(1)—N(1)—C(8)	121 (1)	N(1)—C(8)—C(7)	111 (1)

The θ-scan width used was $(1.30 + 0.3\tan\theta)^\circ$ at a speed of 4.0° min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were located from a difference map and fixed at ideal positions, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

The structure was solved by Patterson methods and expanded using Fourier techniques (*PATTY* in *DIRDIF*; Beurskens *et al.*, 1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993). Data collection and cell refinement were carried out using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1052). 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**, 539–541

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

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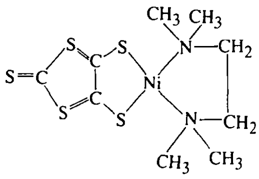
Abstract

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).

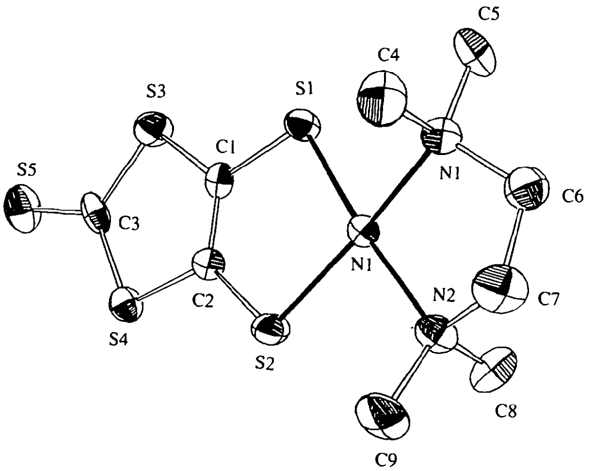


Fig. 1. *ORTEP*II view (Johnson, 1976) of the title compound. Displacement ellipsoids are shown at the 30% probability level.

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

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