Hall, 1972) on the CDC 7600 computer at the University of London Computer Centre, which supplemented local facilities.

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The Structures of Methyl 3-Phenyldithiocarbazate and Its Derivative, Square-Planar Bis(methyl *N'*-phenyldiazenecarbodithioato-*N'*,*S*)platinum

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Abstract

The crystal structures of the title compounds, $C_8H_{10}N_2S_2$, (I), monoclinic, $a = 10{\cdot}262\,(2)$, $b = 5{\cdot}939\,(1)$, $c = 17{\cdot}363\,(4)$ Å, $\beta = 108{\cdot}48\,(2)°$, $Z = 4$, space group $P2_1/c$, 934 reflections, $R = 0{\cdot}030$, and its neutral platinum complex $[Pt(C_8H_8N_2S_2)_2]$, (II), triclinic, $a = 5{\cdot}883\,(2)$, $b = 8{\cdot}426\,(4)$, $c = 9{\cdot}767\,(3)$ Å, $\alpha = 72{\cdot}43\,(3)$, $\beta = 91{\cdot}42\,(2)$, $\gamma = 92{\cdot}96\,(2)°$, $Z = 1$, space group $P\bar{1}$, 3492 reflections, $R = 0{\cdot}036$, have been determined from diffractometer data. The molecules of (I) have a *trans–cis* conformation and are coupled in dimers. The complex unit of (II) is monomeric: Pt occupies a centre of symmetry within a square-planar S_2N_2 environment of two ligands in a *cis–cis* conformation.

Introduction

As part of an investigation on the methyl esters of the *N*-substituted dithiocarbazic acid $R_1R_2N{-}NR_3{-}$

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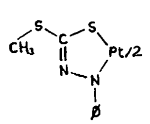
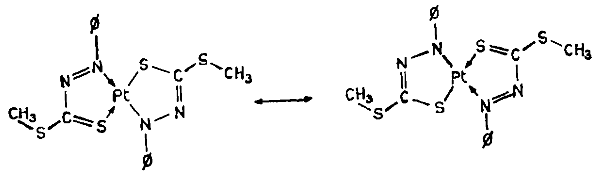
C(S)SCH$_3$, the behaviour of C$_6$H$_5$NHNHC(S)SCH$_3$ (= LH$_2$) as a ligand has been studied. Its neutral platinum complex [Pt{C$_6$H$_5$NNC(S)SCH$_3$}$_2$] (=PtL_2), obtained by oxidizing the complex [Pt{C$_6$H$_5$NNHC(S)SCH$_3$}$_2$] [= Pt(LH)$_2$], has been isolated (Tarli, 1979).

PtL_2 belongs to a series of electron-transfer complexes of the type PtN$_2$S$_2$ as studied by Forbes, Gold & Holm (1971) and Jenson, Bechgaard & Pedersen (1972). It is distinctive because of its intense blue colour in solution, with an absorption band in the visible region (λ = 720 cm^{-1}; ε = 10 500).

Its molecular and electronic structure can be formulated as a Pt^{IV} complex, with a localized C=N double bond:



or as a Pt^{II} complex, in terms of a valence-bond structure (Forbes *et al.*, 1971):



with extensive delocalization within the ligand plane.

In an attempt to clarify the problem by means of a structural determination, the X-ray analysis of the PtL_2 complex has been undertaken, together with an analysis of the free ligand, LH$_2$, for comparison.

Experimental

Samples of both compounds [(I), pale yellow; (II), blue prisms] were provided by Dr F. Tarli. They are stable in air and the X-ray beam. Accurate cell dimensions and the orientation matrix were obtained by a least-squares fit to the setting angles of 15 reflections on a Syntex $P2_1$ four-circle diffractometer.

Crystal data

(I): C$_8$H$_{10}$N$_2$S$_2$, M_r = 198.31, monoclinic, a = 10·262 (2), b = 5·939 (1), c = 17·363 (4) Å, β = 108·48 (2)°, U = 1003·7 Å^3. Systematic extinctions: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Space group $P2_1/c$. D_c = 1·31 for Z = 4, D_m = 1·30 (1) Mg m^{-3} (by flotation). Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 0·46 mm^{-1}.

(II): C$_{16}$H$_{16}$N$_4$PtS$_4$, M_r = 587·68, triclinic, a = 5·883 (2), b = 8·426 (4), c = 9·767 (3) Å, α = 72·43 (3), β = 91·42 (2), γ = 92·96 (2)°, U = 460·9 Å^3. Space group $P\bar{1}$ from the structure determination. D_c = 2·12 for Z = 1, D_m = 2·09 (1) Mg m^{-3} (by flotation). Mo $K\alpha$ radiation, μ = 8·46 mm^{-1}.

Data were collected on a Syntex $P2_1$ automated diffractometer by the θ–2θ scan technique with graphite-monochromated Mo $K\alpha$ radiation. Only the intensities of the reflections having $I \geq 3\sigma(I)$ were used in the refinement. The data were corrected for background and for Lorentz and polarization effects. A semi-empirical absorption correction, based on a 360° ψ scan around the scattering vector of the $4\bar{2}\bar{1}$ reflection, was also applied only to the PtL_2 data.

Calculation

Data reduction, Patterson and Fourier syntheses, structure factors and geometrical calculations were carried out on an HP-21MX computer of the CNR Research Area of Rome (Montelibretti), while least-squares refinements were performed on the Univac 1108 computer of Rome University. Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Structure solution and refinement

Both structures were solved by Patterson and Fourier techniques and refined by a full-matrix least-squares method. All non-hydrogen atoms had anisotropic temperature factors.

For (I), the H atoms were located from difference syntheses and were included in the refinement with isotropic temperature factors.

Each reflection was assigned a weight $w = (a + bF_o + cF_o^2)^{-1}$ with a = 5·0, b = 1·0 and c = 0·01. The final R was 0·030 for 934 reflections.

For (II), the H atoms of the phenyl group were included at the calculated positions with an isotropic temperature factor of 4·5 Å^2.

Each reflection was assigned a weight $w = \sin\theta/\lambda$. The final R was 0·036 for 3492 reflections.

Results and discussion

Atomic parameters for (I) are given in Table 1.* The compound has a *trans–cis* conformation. The molecules are coupled in dimers through hydrogen bonds S(1)···H–N(1) between the thione S atom and the imino group (S–H = 2·73 Å).

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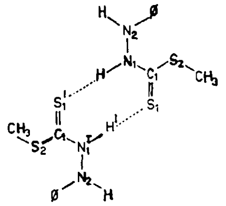
* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35318 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



The dimers are connected by a net of hydrogen bonds between S(1) and H(N2) of a symmetry-related amino group (S—H = 2·57 Å).

Table 1. *Final atomic coordinates, with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters, for* (I)

	x	y	z	B^*_{eq} (Å^2)
S(1)	0·35966 (9)	0·30110 (15)	0·47583 (5)	3·69
S(2)	0·09798 (9)	0·08934 (17)	0·36361 (7)	4·67
N(1)	0·3407 (3)	−0·0773 (5)	0·3973 (2)	3·47
N(2)	0·2731 (3)	−0·2530 (5)	0·3472 (2)	3·50
C(1)	0·2748 (3)	0·0988 (5)	0·4134 (2)	3·12
C(2)	0·0400 (6)	0·3439 (12)	0·3987 (6)	6·37
C(3)	0·2983 (3)	−0·2750 (5)	0·2720 (2)	2·99
C(4)	0·2580 (4)	−0·4741 (6)	0·2287 (2)	3·68
C(5)	0·2730 (4)	−0·4974 (8)	0·1533 (2)	4·39
C(6)	0·3275 (4)	−0·3248 (8)	0·1201 (2)	4·43
C(7)	0·3677 (4)	−0·1327 (7)	0·1628 (2)	4·16
C(8)	0·3540 (3)	−0·1034 (6)	0·2391 (2)	3·49
H(N1)	0·419 (4)	−0·091 (7)	0·419 (2)	
H(N2)	0·275 (4)	−0·376 (7)	0·374 (2)	
H(C2)	0·061 (6)	0·332 (11)	0·450 (4)	
H'(C2)	−0·044 (5)	0·341 (8)	0·387 (3)	
H"(C2)	0·066 (6)	0·476 (12)	0·376 (4)	
H(C4)	0·224 (3)	−0·587 (6)	0·252 (2)	
H(C5)	0·245 (4)	−0·637 (9)	0·127 (2)	
H(C6)	0·337 (4)	−0·337 (7)	0·073 (2)	
H(C7)	0·407 (4)	−0·011 (7)	0·144 (2)	
H(C8)	0·381 (3)	0·033 (7)	0·268 (2)	

* As defined by Willis & Pryor (1975).

Table 2. *Main interatomic distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses, for* (I)

S(1)—C(1)	1·667 (3)	C(2)—H"(C2)	0·95 (7)
S(1)—H(N1)^{I}	2·73 (4)	C(3)—C(4)	1·392 (5)
S(1)—H(N2)^{II}	2·57 (5)	C(3)—C(8)	1·378 (5)
S(2)—C(1)	1·747 (3)	C(4)—C(5)	1·373 (6)
S(2)—C(2)	1·800 (8)	C(4)—H(C4)	0·91 (4)
N(1)—N(2)	1·396 (4)	C(5)—C(6)	1·378 (6)
N(1)—C(1)	1·323 (5)	C(5)—H(C5)	0·95 (5)
N(1)—H(N1)	0·76 (7)	C(6)—C(7)	1·353 (6)
N(2)—C(3)	1·415 (5)	C(6)—H(C6)	0·86 (5)
N(2)—H(N2)	0·86 (4)	C(7)—C(8)	1·386 (6)
C(2)—H(C2)	0·85 (6)	C(7)—H(C7)	0·94 (4)
C(2)—H'(C2)	0·82 (5)		

C(1)—S(2)—C(2)	102·0 (2)	C(4)—C(3)—C(8)	119·8 (3)
C(1)—N(1)—N(2)	122·4 (3)	C(3)—C(4)—C(5)	119·8 (4)
N(1)—N(2)—C(3)	116·4 (3)	C(4)—C(5)—C(6)	120·4 (4)
S(1)—C(1)—S(2)	126·3 (2)	C(5)—C(6)—C(7)	119·5 (4)
S(1)—C(1)—N(1)	120·7 (2)	C(6)—C(7)—C(8)	121·6 (4)
S(2)—C(1)—N(1)	113·0 (2)	C(7)—C(8)—C(3)	119·0 (3)

Symmetry code: (I) $1 - x, -y, 1 - z$; (II) $x, 1 + y, z$.

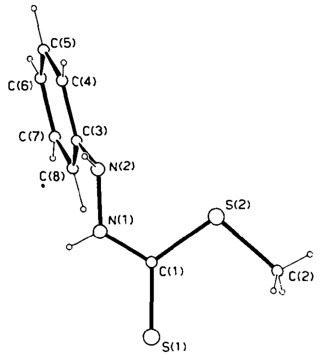


Fig. 1. Perspective view of the molecular structure of methyl 3-phenyldithiocarbazate (LH_2), showing its *trans–cis* conformation.

In Table 2 interatomic distances are reported, and Fig. 1 shows the molecular structure of the chemical unit.

The C(1)—S(1) and C(1)—N(1) distances are in agreement with extensive conjugation in the ligand plane. The N(1)—N(2) distance of 1·396 (4) Å is not significantly different from that found in the non-substituted methyl ester of 1·415 (3) Å (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977).

The angles around C(1) are identical to those in the analogous *trans–cis* 3,3-dimethyl compound (Manotti Lanfredi *et al.*, 1977), and are essentially determined by the steric hindrance of the *cis*-methyl group.

The H atoms of the methyl group are again *gauche* to the C=S bond.

The N(2)N(1)C(1)S(1)S(2)C(2) system is planar; the N(2)—C(3) bond does not lie in the plane because of a rotation around N(1)—N(2) of 68°. The rotation angle around N(2)—C(3) with respect to the N(1)N(2)C(3) plane is 15°.

Atomic parameters for (II) are given in Table 3.* Fig. 2 shows the molecular structure of (II): the Pt atom occupies a centre of symmetry within a square-planar S_2N_2 environment. The ligand has a *cis–cis* conformation, the only steric arrangement possible to complex the Pt with the formation of a five-membered ring.

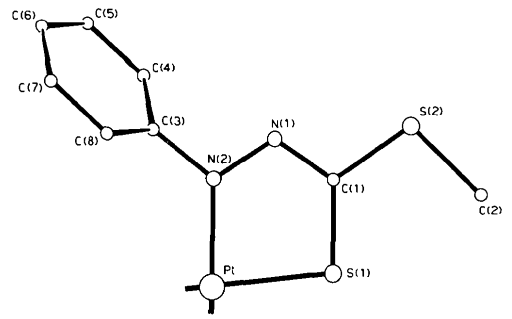


Fig. 2. Perspective view of the molecular structure of PtL_2. Since Pt is on a centre of symmetry, only one ligand molecule in a *cis–cis* conformation, is shown.

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* See previous footnote.

Table 3. *Final atomic coordinates, with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters, for* (II)

	x	y	z	B^*_{eq} (Å^2)
Pt	0·0	0·0	0·0	1·65
S(1)	0·2731 (3)	0·2066 (2)	−0·0132 (1)	2·39
S(2)	0·6379 (3)	0·3171 (2)	−0·2435 (2)	2·79
N(1)	0·3351 (8)	0·0843 (6)	−0·2308 (5)	1·98
N(2)	0·1448 (8)	−0·0077 (5)	−0·1770 (4)	2·28
C(1)	0·4048 (10)	0·1906 (6)	−0·1618 (5)	2·19
C(2)	0·7111 (13)	0·4326 (8)	−0·1199 (7)	3·09
C(3)	0·0727 (9)	−0·1126 (6)	−0·2622 (5)	2·00
C(4)	0·2248 (11)	−0·2161 (7)	−0·2925 (6)	2·64
C(5)	0·1607 (13)	−0·3102 (8)	−0·3841 (7)	2·95
C(6)	−0·0539 (13)	−0·2949 (8)	−0·4477 (6)	2·89
C(7)	−0·2052 (11)	−0·1905 (8)	−0·4177 (6)	2·73
C(8)	−0·1440 (10)	−0·0991 (7)	−0·3228 (5)	2·41

* As defined by Willis & Pryor (1975).

Table 4. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses, for* (II)

Pt–S(1)	2·284 (1)	N(2)–C(3)	1·429 (7)
Pt–N(2)	1·966 (4)	C(3)–C(4)	1·378 (9)
S(1)–C(1)	1·705 (6)	C(3)–C(8)	1·388 (8)
S(2)–C(1)	1·745 (5)	C(4)–C(5)	1·397 (10)
S(2)–C(2)	1·798 (8)	C(5)–C(6)	1·387 (10)
N(1)–N(2)	1·353 (4)	C(6)–C(7)	1·379 (10)
N(1)–C(1)	1·318 (8)	C(7)–C(8)	1·403 (9)
S(1)–Pt–N(2)	82·6 (1)	S(1)–C(1)–N(1)	123·2 (4)
Pt–S(1)–C(1)	96·5 (2)	S(2)–C(1)–N(1)	112·5 (4)
C(1)–S(2)–C(2)	102·8 (3)	C(4)–C(3)–C(8)	120·8 (5)
N(2)–N(1)–C(1)	114·0 (5)	C(3)–C(4)–C(5)	120·0 (6)
Pt–N(2)–N(1)	123·5 (4)	C(4)–C(5)–C(6)	119·7 (7)
Pt–N(2)–C(3)	126·1 (3)	C(5)–C(6)–C(7)	120·1 (7)
N(1)–N(2)–C(3)	110·4 (5)	C(6)–C(7)–C(8)	120·4 (6)
S(1)–C(1)–S(2)	124·2 (3)	C(3)–C(8)–C(7)	119·0 (6)

The complex unit is monomeric, and no interaction <3·4 Å is present. The bond distances and angles (see Table 4), compared with the analogous ones of (I) (LH_2), show no evidence of localized double bonds. Although there is a significant shortening of the N–N distance from 1·396 (4) Å in LH_2 to 1·353 (4) Å in PtL_2, due to the absence of H atoms on the N atoms (which become sp^2 hybridized), the N(1)–N(2) bond is not a pure double bond (N=N: 1·25 Å). The distances within the ligand confirm that there is extensive conjugation over the whole molecule: in fact C(1)–N(1), C(1)–S(2), and S(2)–C(2) are identical in LH_2 and PtL_2. The lengthening of the C(1)–S(1) distance is due to the donor function of S to Pt.

The Pt–S and Pt–N distances, compared with the analogous ones of 2·336 (7) and 2·06 (1) Å in the thiosemicarbazide–platinum complex (Gastaldi & Porta, 1972) in which Pt is again on a centre of symmetry in a *trans* PtS_2N_2 environment, show a statistically significant shortening [2·284 (1) and 1·957 (4) Å].

The evidence of extensive conjugation, and the values of the Pt–S and Pt–N distances attributable to the presence of a charge-transfer effect from the S and N atoms to Pt, leads us to exclude the formulation of PtL_2 in terms of Pt^{IV}. However, there are strong indications in favour of a Pt^{II} complex.

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