conflict between the ends of the chain is nevertheless well avoided by deviations from the ideal torsion angles 60 and 180° in every unit. In the complex described here, the four central O atoms [O(3), O(4), O(5), O(6)] are coplanar within 0·06 Å, the Ba cation lying only 0·10 Å out of the same plane. The two O atoms at one end of the chain [O(1) and O(2)] are above this plane by 1·97 and 1·53 Å; those at the other end [O(7) and O(8)] are below the plane by 1·26 and 1·71 Å. In this arrangement the distance between O(1) and O(7) is 3·29 Å, and between O(8) and O(2) 3·33 Å. As a consequence of this wrapping mode for both ends of the chain, the thiocyanate anions are no longer perfectly *trans* in apical positions.

The approximate twofold symmetry axis of the heptaglyme ligand, the *trans* arrangement of the anions, and the absence of coordinated water molecules, is reminiscent of the pentaglyme–Ca(SCN)₂ complex (Wei *et al.*, 1987c). Also in the pentaglyme complex the four O atoms that are coplanar with the cation are symmetrically located, implying an $ag^{\pm}a$ conformation with sign alternation in the three central units. Because of the need to fold more sharply onto the smaller Ca cation, both outer units deviate from this scheme both in torsion-angle sign and their numerical values.

There are no obvious linkages between the complex units.

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Platinum(II) Halide Complexes with Thiocarbamic Esters. Structure of *trans*-Bis[*O*-ethyl (*N*-ethyl)thiocarbamate]diiodoplatinum(II), [Pt(ETC)₂I₂]

BY R. BARDI* AND A. M. PIAZZESI

Biopolymer Research Centre, CNR, University of Padua, Via Marzolo 1, 35100 Padua, Italy

A. DEL PRA

Istituto Chimico Farmaceutico, University of Milan, Viale Abruzzi 42, 20131 Milan, Italy

AND L. TRINCIA†

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, University of Padua, Via Loredan 4, 35100 Padua, Italy

Abstract. [PtI₂(C₅H₁₁NOS)₂], $M_r = 715·3$, monoclinic, $C2/c$, $a = 11·232$ (3), $b = 14·987$ (3), $c = 11·306$ (3) Å, $\beta = 93·3$ (1)°, $V = 1900$ (8) Å³, $Z = 4$, $D_m = 2·50$, $D_x = 2·501$ g cm⁻³, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 108·9$ cm⁻¹, $F(000) = 1312$, $T = 297$ K, final $R = 0·0346$ ($wR = 0·0341$), 1593 unique reflections. The complex exhibits square-planar geometry about the metal atom. The thiocarbamic group is planar and is tilted 80·3 (3)° to the coordination plane. The Pt—S distance [2·314 (4) Å] is significantly shorter than the sum

* To whom correspondence should be addressed.

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of the covalent radii but is close to the distances found in similar compounds. The C=S, C—O and C—N bonds around the central C atom have partial double-bond character, as has been observed in other thiocarbamic ester complexes.

Introduction. Previous studies in coordination chemistry of platinum(II) and palladium(II) halide complexes with thiocarbamic esters R_1R_2N—C(S)OR', DMTC ($R_1 = R_2 = $ CH$_3$; $R' = $ C$_2$H$_5$), MTC ($R_1 = $ Me, R_2 = H; $R' = $ Et) and TC ($R_1 = R_2 = $ H; $R' = $ Et) (Sindellari, Faraglia, Zarli, Cavoli, Furlani & Scarcia, 1980; Faraglia, Sindellari & Zarli, 1981; Faraglia, Sindellari, Zarli & Agnoletti, 1982; Faraglia, Sindellari, Chiavegato & Sitran, 1983), have enabled us to isolate a series of complexes of stoichiometry higher than two only with primary and secondary thiocarbamates, because of stabilization of the halide ions by N···H···X bonding, as confirmed by X-ray analysis of [Pt-(PTC)$_3$Cl]Cl, where PTC is (n-C$_3$H$_7$)NH—C(S)OC$_2$H$_5$ (Bardi, Piazzesi, Del Pra, Celeste, Faraglia & Trincia, 1985).

Complexes with a metal:ligand ratio of 1:2 have been isolated with the above-mentioned ligands independently of the nature of the thiocarbamate. X-ray diffractometric studies have been carried out on some chloride, bromide and thiocyanate complexes (Bardi, Piazzesi & Sindellari, 1981; Bardi, Del Pra, Piazzesi & Berto, 1981; Bardi, Del Pra, Piazzesi, Sindellari & Zarli, 1981). Iodide complexes of formula PtL_2I$_2$ have been isolated also with DMTC, MTC and TC, but they have never been obtained as crystalline compounds, thus preventing their characterization unambiguously. Moreover, iodide complexes of higher stoichiometry have not been isolated up to now.

The present paper reports the synthesis and the characterization by IR spectroscopy of the complexes [Pt(ETC)$_4$]I$_2$ and trans-[Pt(ETC)$_2$I$_2$], where ETC is (C$_2$H$_5$)NH—C(S)OC$_2$H$_5$, and the crystal and molecular structure of trans-[Pt(ETC)$_2$I$_2$].

Experimental. The starting materials were commercial PtI$_2$ (Ega Products) and ETC, prepared as in the literature (Bardi, Piazzesi, Del Pra, Celeste, Faraglia & Trincia, 1985).

PtI$_2$ (0·2 g) was dissolved in a solution of ETC (ca 1 ml) in 2 ml of benzene. The yellow solution was filtered carefully. Addition of n-hexane (20 ml) yielded pale-yellow needles of the compound [Pt(ETC)$_4$]I$_2$. It is soluble in benzene, acetone and dichloromethane, slightly soluble in methanol and diethyl ether and insoluble in H$_2$O and n-hexane. M.p. 355–357 K. Found: C, 24·21; H, 4·38; N, 5·72%. Calc. for C$_{20}$H$_{44}$I$_2$N$_4$O$_4$PtS$_4$: C, 24·45; H, 4·51; N, 5·70%. IR: 3155 m br, 3108 m br; 1573 s cm^{-1}.

The compound trans-[Pt(ETC)$_2$I$_2$] crystallized slowly as orange-red needles by addition of n-hexane to

a benzene solution of [Pt(ETC)$_4$]I$_2$. It is soluble in acetone, benzene, dichloromethane, methanol and diethyl ether. It is insoluble in H$_2$O and n-hexane. M.p. 376–378 K. Found: C, 16·83; H, 3·10; N, 3·90%. Calc. for C$_{10}$H$_{22}$I$_2$N$_2$O$_2$PtS$_2$ C, 16·77; H, 3·10; N, 3·91%. IR: 3258 m br, 3095 vw; 1553 s; 20 w cm^{-1}.

Infrared spectra were obtained with a Perkin Elmer 580B spectrophotometer (Nujol mulls between KBr and polyethylene discs).

Single crystals of trans-bis[O-ethyl (N-ethyl)thiocarbamate]diiodoplatinum(II) [Pt(ETC)$_2$I$_2$], suitable for an X-ray structural analysis, were grown as orange-red plates by adding n-hexane to a dilute solution of [Pt(ETC)$_4$]I$_2$ in benzene, D_m measured by flotation; approximate unit-cell parameters estimated from preliminary Weissenberg and precession photographs.

Intensity data were collected from a crystal of approximate dimensions 0·3 × 0·2 × 0·15 mm on a Philips PW 1100 four-circle diffractometer; accurate unit-cell parameters and crystal-orientation matrices (together with their e.s.d.'s) were obtained from least-squares refinement of the 2θ, ω, χ and φ values of 20 carefully centered reflections with $10 < \theta < 17°$, operating in the $\theta/2\theta$ scan mode (scan width = 1·20°, scan speed = 0·030° s^{-1}, total background time = 20 s) using Mo $K\alpha$ radiation, monochromatized by a graphite crystal. 1593 independent reflections (2θ scan limit = 4–50° for $h = -13$ to 13, $k = 0$ to 17, $l = 0$ to 13) were measured, of which 1437 had $I \geq 3\sigma(I)$. During the data collection two standard reflections (242 and $\overline{2}4\overline{2}$) were measured every 180 min to check the stability of the crystal and the electronics: no variation in intensity. Intensities were corrected for Lorentz and polarization effects and were put on an absolute scale by Wilson's method. An experimental absorption correction was applied (North, Phillips & Mathews, 1968); min., max. transmission coefficients 0·83, 1·63.

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of the I atom. The positions of the remaining non-H atoms were derived from subsequent difference Fourier maps. The structure was refined by a full-matrix least-squares procedure. The function $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$) was minimized with $w = [\sigma^2(F_o) + 0·0002F_o^2]^{-1}$. Weighting-scheme analysis showed no serious dependence of the mean $w\Delta^2$ as a function of either $|F_o|$ or $\lambda^{-1}\sin\theta$. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). Allowance was made for the anomalous scattering of Pt, I and S atoms using values of f', f'' from International Tables for X-ray Crystallography (1974). The refinement was carried out allowing all non-H atoms to vibrate anisotropically. H atoms were placed in calculated idealized positions (X—H = 1·0 Å, where X is C, N) but not varied. The final conventional R value was 0·0346, $wR = 0·0341$ and $S = 4·50$; 105 parameters refined using 1437

Table 1. *Final atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å^2 ×10³) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt	0	0	0	38 (1)
I(1)	1682 (1)	340 (1)	−1434 (1)	56 (1)
S(1)	−654 (4)	1462 (3)	−146 (5)	46 (2)
O(1)	170 (11)	2900 (8)	1001 (12)	44 (4)
N(1)	1181 (11)	1669 (9)	1408 (14)	44 (5)
C(1)	285 (16)	2035 (11)	817 (16)	35 (5)
C(2)	−782 (17)	3408 (14)	362 (20)	53 (7)
C(3)	−856 (20)	4276 (13)	1010 (22)	66 (8)
C(4)	2088 (15)	2122 (11)	2162 (19)	46 (7)
C(5)	3267 (18)	1872 (21)	1781 (23)	74 (12)
HN(1)	1244	1004	1363	30

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pt–I(1)	2·610 (2)	I(1)–Pt–S(1)	90·5 (1)
Pt–S(1)	2·314 (4)	Pt–S(1)–C(1)	104·4 (6)
S(1)–C(1)	1·70 (2)	S(1)–C(1)–O(1)	122 (1)
O(1)–C(1)	1·32 (2)	S(1)–C(1)–N(1)	123 (1)
O(1)–C(2)	1·47 (2)	N(1)–C(1)–O(1)	114 (1)
N(1)–C(1)	1·30 (2)	C(1)–O(1)–C(2)	120 (1)
N(1)–C(4)	1·46 (2)	O(1)–C(2)–C(3)	106 (2)
C(2)–C(3)	1·50 (3)	C(1)–N(1)–C(4)	127 (1)
C(4)–C(5)	1·46 (3)	N(1)–C(4)–C(5)	109 (2)

observed reflections with $I \geq 3\sigma(I)$. For positional parameters $(\Delta/\sigma)_{max} = 0.50$. The residual electron density in the final difference map was within ± 0.7 e Å⁻³.

The calculations were carried out on the IBM 370/158 computer of the University of Padua with *SHELX76* (Sheldrick, 1976).

Final positional and thermal parameters of non-H atoms are in Table 1.* Bond distances and angles are listed in Table 2.

Discussion. The crystal structure (Fig. 1) described by the cell constants, the symmetry operations of the space group and the atomic parameters consists of discrete neutral molecules of *trans*-[Pt(ETC)₂I₂] separated by van der Waals contacts. The closest Pt···Pt approach is 5·65 (2) Å and all remaining intermolecular contacts agree with those predicted from radii sum rules. The crystal packing is shown in Fig. 2.

The coordination geometry about the Pt atom is square planar. I, S and Pt atoms lie strictly on the same plane owing to crystallographic symmetry requirements. The exact square-planar configuration is

* Lists of structure factors, H-atom coordinates, torsional angles, mean-plane data and short intramolecular non-bonding distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43854 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

indicated by the values of the two I—Pt—S angles [90·5 (1) and 89·5 (1)°, respectively]. Some steric crowding in the vicinity of the Pt atom is verified by some short intramolecular non-bonding distances.

The thiocarbamic moiety does not deviate significantly from planarity and it is tilted by 80·3 (3)° with respect to the coordination plane.

The Pt—I distance of 2·610 (2) Å in the present complex is slightly shorter than that predicted from covalent radii, 2·67 Å (Pauling, 1960), but it is very close to those found in the similar complexes *trans*-[PtI₂(PMe₃)₂], 2·599 (2) Å (Hitchcock, Jacobson & Pidcock, 1977), and *trans*-[PtI₂{(C₆H₁₁)₃P}₂], 2·612 (1) Å (Alcock & Leviston, 1974).

The Pt—S distance of 2·314 (4) Å, which is significantly shorter than the sum of the covalent radii, 2·35 Å (Pauling, 1960) for a σ-bonded S atom and a square-planar Pt atom, is close to the metal–sulfur distances observed in other Pd^{II} and Pt^{II} complexes of thiocarbamic esters, *e.g.* 2·285 (4) and 2·291 (4) Å in *cis*-dichlorobis[O-ethyl (N,N-dimethyl)thiocarbamate]-platinum(II) (Bardi, Piazzesi & Sindellari, 1981), 2·310 (1) in *trans*-dichlorobis[O-ethyl (N,N-dimethyl)-
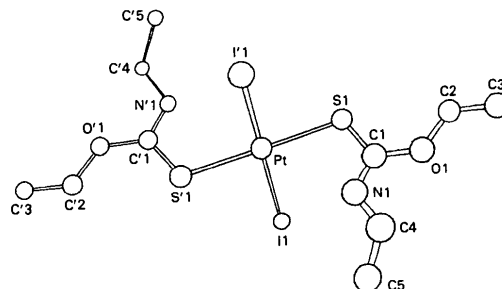

Fig. 1. The structure of *trans*-bis[O-ethyl (N-ethyl)thiocarbamate]-diiodoplatinum(II), [Pt(ETC)₂I₂], with the atomic numbering scheme.
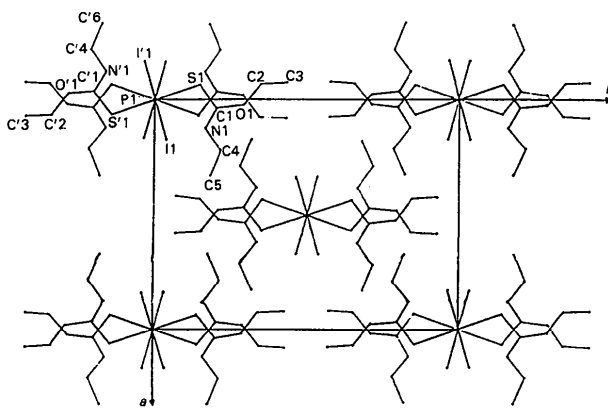

Fig. 2. The crystal packing of [Pt(ETC)₂I₂], as viewed down c.

thiocarbamate]platinum(II) (Bardi, Del Pra, Piazzesi & Berto, 1981), 2·303(5) Å in chlorotris[O-ethyl (N-propyl)thiocarbamate]platinum(II) chloride (Bardi, Piazzesi, Del Pra, Celeste, Faraglia & Trincia, 1985), 2·296 (6) Å in dichloro[O-methyl(N-allyl)thio-carbamate]palladium(II) (Porta, 1971), 2·288 (1) and 2·301 (1) Å in bis(thiobiuretato)M^{II} ($M = Pd$, Pt) (Girling & Amma, 1976).

Within the thiocarbamic ligand, the C=S, C—O and C—N bonds around the trigonal carbon C(1) have partial double-bond character and the observed C=S, C—O and C—N distances agree with those found for other complexes of thiocarbamic esters (Bardi, Piazzesi, Del Pra, Celeste, Faraglia & Trincia, 1985; Bardi, Del Pra, Piazzesi & Berto, 1981).

The preparation of $[Pt(ETC)_4]I_2$ from PtI_2 and ETC in benzene requires a large excess of ligand, otherwise mixtures of 1:2 and 1:4 species are obtained. When the pale yellow 1:4 complex is dissolved in benzene, the solution turns immediately to orange red, owing to formation of the *trans* species.

The IR spectrum of *trans*-$[Pt(ETC)_2I_2]$ shows, in the $\nu(NH)$ region, a medium intensity band at 3258 cm⁻¹, whereas $[Pt(ETC)_4]I_2$ presents two equally intense absorptions at 3155 and 3108 cm⁻¹. The $\nu(NH)$ absorptions of coordinated ligand are at lower energy with respect to free ETC (3380 sh, 3270 s br cm⁻¹) following the general trend observed in the MTC and TC adducts. The ETC absorption at 1530 cm⁻¹ (1550 sh cm⁻¹), assigned as mainly $\nu(CN)$ with a small $\delta(NH)$ contribution, shifts in the complexes at higher frequen-

cies, as expected for ligand coordination through the S atom.

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Insertion of Pt(PPh₃)₂ into the Coordinated Thiadiphosphirene Ring: Structure of [LCo{P₂SPt(PPh₃)₂}]BPh₄, L = 1,1,1-Tris(diphenylphosphinomethyl)ethane

BY MASSIMO DI VAIRA AND PIERO STOPPIONI

Dipartimento di Chimica, Università di Firenze, Via Maragliano, 77, 50144 Firenze, Italy

AND MAURIZIO PERUZZINI

Istituto ISSECC, CNR, Via J. Nardi, 39, 50132 Firenze, Italy

Abstract. [1,2,3-η^3-4,4-di(triphenylphosphine)-1,2,-3,4-thiadiphosphaplatinetel][1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(I) tetraphenylborate, [Co(C₃₆H₃₀P₄PtS)(C₄₁H₃₉P₃)][B(C₆H₅)₄], $M_r = 1816·5$, monoclinic, $P2_1$, $a = 19·379$ (11), $b = 21·819$ (12), $c = 10·201$ (8) Å, $\beta = 98·66$ (8)°, $V = 4264$ (5) Å³, $Z = 2$, $D_x = 1·414$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 20·5$ cm⁻¹, $F(000) = 1852$, room temperature, final $R = 0·051$ for 3508 observed reflections. Insertion of the Pt(PPh₃)₂ moiety into a bond of the P₂S ring coordinated to the cobalt atom in the [LCo(P₂S)]⁺ cation essentially involves cleavage of that bond, which lengthens to 2·810 (8) Å. The tetraatomic metallacycle which is formed is highly puckered.