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Protonation mediated interchange between *mono-* and *bi*dentate coordination of *N*-benzoyl-*N'*, *N'*-dialkylthioureas: crystal structure of *trans*-bis(*N*-benzoyl-*N'*, *N'*-di(n-butyl)thiourea-*S*)-diiodoplatinum(II)¹

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Abstract

Treatment of a chloroform/ethanol solution of *cis*-bis(*N*-benzoyl-*N'*, *N'*-di(*n*-butyl)thioureato-*S*,*O*)platinum(II) with an excess HI quantitatively converts the former *cis* complex into *trans*-bis(*N*-benzoyl-*N'*, *N'*-di(*n*-butyl)thioureau-*S*)diiodo-platinum(II). The crystal structure of the latter complex is reported and represents the first example of a Pt(II) complex in which the amidic *O*-donor atom of the usually bidentate *N*-benzoyl-*N'*, *N'*-di(butyl)thiourea ligand (HL) is pendant. In chloroform-*d*₃ solution, the *trans*-[Pt(HL-*S*)₂I₂] complex rapidly isomerizes to give a 1:4 mixture of the *cis* and *trans* isomers, as can be seen in the ¹H and ¹⁹⁵Pt NMR spectra. © 1998 Elsevier Science B.V.

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1. Introduction

N-benzoyl-*N'*, *N'*-dialkylthioureas (HL) are selective ligands for the platinum group metals (PGMs), and tend to coordinate predominantly in a bidentate (*S*,*O*) fashion to these soft metals ions, as has been well illustrated by several crystal structures of Pd(II) [1], Pt(II) [2] and Rh(III) [3,4]. The notable exceptions to this mode of coordination can be seen in the complexes of Ag(I) [5], Hg(II) [6] and Au(I) [7], in which the *N*,'*N'*-dialkyl substituted ligand binds to the metal ion through the S-atom only, this mode of coordination being presumably primarily determined by the linear coordination preferences of the metal ions in question. On the other hand, we have shown recently that in the case of *N*-acyl-*N'*-alkylthioureas, such as *N*-benzoyl-*N'*-propyl thiourea (H_2L^1), an intramolecular hydrogen-bond in-locks the amidic *O*-donor atom of the ligand into a stable sixmembered ring, with the consequence that the ligand coordinates to Pt(II) via the S-atom only, to yield a mixture of *cis*- and *trans*-[Pt(H_2L^1 -S)₂Cl₂] complexes; the *cis*-[Pt(H_2L^1 -S)₂Cl₂] complexes by X-ray crystallography [8].

As part of our interest in furthering our understanding of the coordination of these ligands specifically to the PGMs, we have studied the protonation of

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¹ This paper is dedicated to Professor Dr Lothar Bayer, on the occasion of his 60th birthday.

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cis-[Pt(L²-S,O)₂] with HX (X = Cl⁻, Br⁻ and HL² = N-benzoyl-N', N'-di(n-butyl)-thiourea) by means of ¹⁹⁵Pt NMR in chloroform solution [9], finding that protonation of the bound (S,O-chelated) ligand results in the reversible formation of at least two protonated species in solution, which could be formulated to be either cationic $[Pt(HL^2-S,O)(L^2-S,O)]X$ and $[Pt(HL^2-S,O)_2]X_2$ complexes, or more likely, the cis- and trans-[Pt(HL²-S)₂X₂] complexes, in which the X anion displaces amidic O-donor atom of the ligand from the coordination sphere of the metal ion. We here provide confirmation of the latter assignments in solution, by means of the crystal structure of the first example of an trans-[Pt(HL²- $S_{2}I_{2}$] complex, (1), in which a N-benzoyl-N', N'dialkylthiourea is coordinated to Pt(II) via the S-donor atom only, the O-donor atom of the ligand being pendant.

Table 1

Crystal data and structure refinement for 1

2. Experimental

2.1. Preparative methods

Cis-bis(*N*-benzoyl-*N*, *N'*-di(*n*-butyl)thioureato-*S*,*O*)platinum(II), was prepared as previously described [2]. 48.5 mg (0.0624 mmol) of this complex, dissolved in 20 cm³ of a 1:1 v/v mixture of chloroform and ethanol at room temperature, was treated with a freshly made solution of HI in ethanol (0.5 cm³ solution containing 0.374 mmol HI corresponding to a six-fold molar excess w.r.t. Pt(II)). The mixture was allowed to stir for 2 h at room temperature, followed by cooling to 4°C overnight. The orange precipitate was collected by centrifugation and dried at 60°C, yielding 55 mg of dry precipitate (85% yield w.r.t. Pt(II)) formulated to be [Pt(HL)₂I₂] based on elemental analysis. Recrystallization from mixtures

Identification code	ptila		
Empirical formula	$C_{32} H_{50} I_2 N_4 O_2 Pt S_2$		
Formula weight	1035.77		
Temperature	173(2)K		
Wavelength	0.70930 Å		
Crystal system	Triclinic		
Space group	ΡĪ		
Unit cell dimensions	a = 8.829(5) Å	$\alpha = 68.08(4)^{\circ}$	
	b = 10.905(6) Å	$\beta = 83.08(4)^{\circ}$	
	c = 10.992(4) Å	$\gamma = 74.81(5)^{\circ}$	
Volume	947.2(8) Å ³		
Z	1		
Density (calculated)	1.816 mg m ⁻³		
Absorption coefficient	5.476 mm ⁻¹		
F(000)	502		
Crystal size	$0.19 \times 0.19 \times 0.22$ mm		
Theta range for data collection	1.99–24.98°		
Index ranges	-10 < = h < = 10, 0 < = k < = 12, -11 < = l < = 13		
Reflections collected	3333		
Independent reflections	3333 [R(int) = 0.0000]		
Absorption correction: minimum, maximum	37.48, 99.75, 61.51%		
and average correction factor			
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	3333/0/201		
Goodness-of-fit on F^2	0.991		
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0718, wR2 = 0.1773		
R indices (all data)	R1 = 0.0960, wR2 = 0.1880		
Largest diff. peak and hole	4.806 and -5.935 e A^{-3}		

of ethanol/chloroform yielded deep orange crystals containing 37.8% C, 4.6% H and 5.5% N, while $C_3H_5I_2N_4O_2PtS_2$ requires 37.11% C, 4.87% H and 5.87% N.

2.2. NMR spectroscopy

¹H and ¹⁹⁵Pt NMR spectra were recorded in 5 mm tubes in CDCl₃ solution using a Varian Unity-400 spectrometer operating at 400 and 85.85 MHz, respectively. ¹H spectra were recorded at 25°C, while ¹⁹⁵Pt chemical shifts were measured at 30°C relative to the usual reference of external H₂PtCl₆ (500 mg in 1 cm³ 30% (v/v) D₂O/1 M HCl).

2.3. Crystal structure determination and refinement

Crystals of dimensions $0.19 \times 0.19 \times 0.22$ mm, crystallizing in the triclinic system were chosen for analysis. Data were collected at 173(2)K on an Enraf Nonius CAD4 diffractometer using graphitemonochromated Mo K α radiation ($\lambda = 0.7107$ Å) and corrected for Lorenz-polarization, as well as absorption effects. The structure was solved by direct methods [10] and refined using full-matrix leastsquares on F^2 [11]. Non-hydrogen atoms were treated anisotropically while hydrogen atoms were placed in geometrically calculated positions and linked to common temperature factors. Pertinent crystal and structure refinement data for C₃₂H₅₀I₂N₄O₂PtS₂ are given in Table 1.

3. Results and discussion

The addition of freshly prepared solution of HI in ethanol, to a brightly yellow solution of cis-[Pt(L²- $S,O)_2$] in chloroform (HI:Pt mol ratio ca. 4:1), results in the slow precipitation of a deep orange-brown crystalline material with composition C₃₂H₅₀I₂N₄O₂PtS₂. As is evident from the crystal structure below, this material is the *trans*-[Pt(HL²-S)₂I₂] complex, which is obtained in virtually quantitative yield. The ¹H NMR spectrum of the analytically pure crystals in CDCl₃ initially shows the presence of one species in solution only. The *trans*- $[Pt(HL^2-S)_2I_2]$ complex is conveniently characterized in solution by an amido N-H resonance at $\delta({}^{1}H) = 10.067$ ppm (the other ${}^{1}H$ resonances being unimportant and will not be considered further here); such N-H peaks are absent for the deprotonated ligands in the parent cis-[Pt(L²- S,O_{2} complex. After a short while in solution however, an additional set of ¹H resonances become evident in the spectrum, notably an N-H resonance at $\delta(^{1}H) = 10.223$ ppm. At steady state, two N-H resonances at 10.223 and 10.067 ppm reach a relative intensity ratio of 0.19:0.81, respectively. Evidently the *trans*-[Pt(HL²-S)₂I₂] complex isomerizes to yield a mixture of ca 81% trans- and 19% cis-[Pt(HL²- $S_{2}I_{2}$] species. The corresponding ¹⁹⁵Pt NMR spectrum of this solution confirms the presence of only two platinum complexes in solution, showing resonances at $\delta(^{195}\text{Pt}) = -4587$ and -4778 ppm, with relative intensities of 0.20:0.80, respectively. The higher field resonance (more negative ppm value) thus arises from the trans isomer, an assignment which is consistent with the generally observed order of the ¹⁹⁵Pt chemical shift for related complexes. In general, it has been observed that for complexes of general structure $[PtA_2X_2]$ (X = Cl⁻, Br⁻, I⁻), that the *cis diiodo* complexes show ¹⁹⁵Pt resonances downfield relative to the corresponding trans diiodo isomer, while for the analogous dichloro complexes isomers the shielding order is reversed; these shielding trends can usually be taken to distinguish the cis- and trans-isomers, although chemical shift trends alone do not prove the respective configuration of these square-planar d⁸ complexes [12].

In any event it is clear from the ¹H and ¹⁹⁵Pt NMR spectra that in CDCl₃ solution a mixture of *cis* and *trans* isomers exist in equilibrium, with the *trans* complex clearly being favoured for the *diiodo* compounds (K_e (CDCl₃, 298 K) = {*trans*-[Pt(HL²-S)₂I₂]/ *cis*-[Pt(HL²-S)₂I₂]} \approx 4). This distribution of isomers may be compared with that of the related but different dichloro complexes derived from the *N*-benzoyl-*N'*propylthiourea, for which the *cis* isomer is favoured in solution (K_e (CDCl₃, 298K) = 0.46) [8]. The overall solution chemistry of the formation of *trans*-[Pt(HL²-*S*)₂I₂] can thus be summarized as follows:



Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for 1. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	у	z	U(eq)	
Pt(1)	0	0	0	27(1)	
I(1)	1438(1)	-2447(1)	1443(1)	43(1)	
S (1)	2335(4)	622(3)	-698(3)	35(1)	
C(2)	3259(14)	-158(11)	-1773(10)	32(3)	
N(21)	4553(12)	129(10)	-2399(9)	33(2)	
C(21)	5086(14)	1292(12)	-2354(12)	37(3)	
C(22)	4198(19)	2659(14)	-3247(14)	53(4)	
C(23)	4325(22)	2877(16)	-4649(15)	59(4)	
C(24)	3476(24)	4283(18)	-5548(20)	78(5)	
C(25)	5634(15)	-744(12)	-3057(11)	38(3)	
C(26)	7093(15)	-1559(13)	-2250(14)	44(3)	
C(27)	6792(22)	-2603(13)	-903(15)	60(4)	
C(28)	6315(24)	-3752(16)	-967(18)	74(5)	
N(3)	2652(11)	-1114(9)	-1962(9)	30(2)	
C(4)	2216(13)	-997(12)	-3185(12)	34(3)	
O(1)	2443(10)	-84(8)	-4171(8)	40(2)	
C(41)	1580(14)	-2126(11)	-3179(12)	34(3)	
C(42)	994(15)	-1993(13)	-4367(13)	40(3)	
C(43)	408(17)	-3000(14)	-4460(14)	48(3)	
C(44)	387(17)	-4122(14)	-3380(17)	54(4)	
C(45)	968(18)	-4282(14)	-2204(17)	56(4)	
C(46)	1545(18)	-3286(12)	-2093(14)	46(3)	

Table 3 Bond lengths (Å) and angles (°) for 1

Pt(1)-S(1)#1	2.294(3)
Pt(1)-S(1)	2.294(3)
Pt(1) - I(1)	2.608(2)
Pt(1)-I(1)#1	2.608(2)
S(1)-C(2)	1.715(10)
C(2)-N(21)	1.31(2)
C(2)-N(3)	1.38(2)
N(21)-C(21)	1.48(2)
N(21)-C(25)	1.488(14)
C(21)-C(22)	1.51(2)
C(22)-C(23)	1.46(2)
C(23)-C(24)	1.53(3)
C(25)-C(26)	1.52(2)
C(26)-C(27)	1.54(2)
C(27)-C(28)	1.45(2)
N(3)-C(4)	1.39(2)
C(4)-O(1)	1.205(14)
C(4) - C(41)	1.48(2)
C(41) - C(46)	1.38(2)
C(41) - C(42)	1.41(2)
C(42) - C(43)	1.36(2)
C(43) - C(44)	1.34(2)
C(44) - C(45)	1.38(2)
C(45) - C(46)	1.36(2)
C(1)#1 Dr(1) C(1)	180.0
S(1)#1 = PI(1) = S(1)	180.0
S(1) = P(1) - I(1)	88.24(10) 01.76(10)
S(1) = P((1) = I(1)	91.76(10)
S(1) = P(1) =	91.70(10)
S(1) - P((1) - 1(1) # 1 V(1) = P((1) - 1 # 1	180.0
I(1) - PI(1) - I#I	180.0
V(2) - S(1) - FI(1)	108.9(4)
N(21) = C(2) = N(3) N(21) = C(2) = S(1)	120.6(9)
N(2) = C(2) = S(1)	110.8(8)
$\Gamma(3) = C(2) = S(1)$ C(2) = N(21) = C(21)	119.8(9)
C(2) = N(21) = C(25)	123 2(10)
C(21) = N(21) = C(25)	116 7(10)
N(21) = C(21) = C(22)	113 6(11)
C(23)-C(22)-C(21)	115.8(12)
C(22) - C(23) - C(24)	115.3(14)
N(21)-C(25)-C(26)	110.7(10)
C(25)-C(26)-C(27)	115.1(12)
C(28) - C(27) - C(26)	114.2(13)
C(2)-N(3)-C(4)	123.1(9)
O(1) - C(4) - N(3)	121.6(11)
O(1) - C(4) - C(41)	123.4(11)
N(3)-C(4)-C(41)	114.8(10)
C(46)-C(41)-C(42)	119.1(11)
C(46)-C(41)-C(4)	124.1(12)
C(42)-C(41)-C(4)	116.8(10)
C(43)-C(42)-C(41)	120.1(12)
C(44)-C(43)-C(42)	120.3(14)
C(43)-C(44)-C(45)	120.8(13)
C(46)-C(45)-C(44)	120.5(14)
C(45)-C(46)-C(41)	119.3(14)

Symmetry transformation used to generate equivalent atoms: #1 -x, -y, -z.



Fig. 1. The molecular structure of *trans*-bis(*N*-benzoyl-*N*,'*N*'-di(*n*-butyl)thiourea-S)diiodoplatinum(II), (1). The pendant *O*-donor atom of the ligand is twisted away from the metal centre to above and below the square plane of coordination. The intramolecular N3–H3…II contact is shown by (\dots) .

3.1. Crystal structure of trans-bis(N-benzoyl-N,'N'di(n-butyl)thiourea-S)diiodoplatinum(II), (1)

Triclinic crystals, suitable for X-ray diffraction, were grown from a mixture of ethanol and chloroform at room temperature. The structure was determined at 173K and corrected for absorption, in an attempt to locate the H-atom of the N–H moiety. The relevant crystallographic data, as well as the fractional atomic coordinates of all non-hydrogen atoms and the most important bond lengths and angles for the molecular structure of (1) are shown in Tables 1, 2 and 3, respectively.

The molecular structure of (1) is shown in Fig. 1, from which it is clear that the complex geometry about the Pt(II) atom is essentially square planar, while the N', N'-di(n-butyl)- and the N-benzoyl groups of the ligand are twisted to above and below the square plane, presumably held in place by a weak intramolecular N-H…I hydrogen-bond, as suggested by the only two significant non-covalent intramolecular N3-H3…I contacts [N3-H3…II 3.615(9) Å, H3…II 2.912(9) Å, and N3-H3…II 138.0°]; the sum of the van der Waals radii for the N-I contact is 3.65 Å, which is slightly longer than the observed N3–H3···I distance. Although the diffraction data was collected at 173K, it was unfortunately not possible to locate directly the H3 atom of the N3–H3 group in the presence of the large, polarizable iodide ion in this complex. There are no other significant intermolecular contacts between the individual complexes.

As might be expected, the Pt-S bond lengths (2.294(3) Å, Table 2) of (1), with the S-atoms in the trans configuration, are significantly longer compared to those of the related cis-bis(N-benzoyl-N'propylthioureato-S)dichloroplatinum(II) complex at 2.232(2) Å [8]. Moreover, it is interesting to note that the Pt-S bond lengths in (1) are also substantially longer than those for the trans-bis(N', N'-di(n-butyl)-N-naphthoylthioureato-S,O)platinum(II), (2), complex at 2.250(4) Å [13]. Nevertheless, speculation as to the possible reasons for these differences is inappropriate in view of (i) the bidentate (S,O) mode of coordination of the ligand in (2) compared to (1) and, (ii) the large differences in the size of the iodo ion, compared to the O-donor atom in (2), and the Cl⁻ ion in (1).

A comparison of the corresponding C=O, (O)C-N, N-C(S), C=S and (S)C-N(R) bond lengths of (1) (Table 2) with those of the unbound N', N'-di(nbutyl)-N-naphthoylthiourea ligand (1.215(3), 1.376(4), 1.420(6), 1.662(2) and 1.320(3) Å [14], shows these to be remarkable similar, suggesting that very little 'electronic rearrangement' takes place in the (protonated) ligand on coordination to Pt(II) through the S-atom. This is in contrast to the fairly extensive electron delocalization which occurs when the N', N'-dialkyl substituted ligands bind to Pt(II) through the S,O-donor atoms with a concomitant loss of a proton, as is observed in cis-[Pt(L²-S,O)₂] [2], and trans-bis(N'N'di(n-butyl)-N-naphthoylthioureato-S,O)platinum(II) [13].

In conclusion, we have shown that the coordination of *N*-benzoyl-*N*, *N'*-dialkylthioureas to Pt(II) can be controlled to be either a monodentate (*S*-) or bidentate (*S*,*O*-) mode, depending simply on whether the coordinated ligand is protonated or not. The coordination of these ligands to Pt(II) may thus be thought of being controlled by a 'protonation switch' in which the amidic O-donor atom can readily and reversibly be displaced from the metal centre by a coordinating halide ion. In view of the potential applications of N-acyl-N', N'-dialkylthioureas for the selective extraction and chromatographic separation of PGM complexes, the facile protonation mediated intrechange between mono- and bidentate coordination can have interesting and important consequences in understanding of the speciation of these metal complexes in solution, a subject we are exploring further at present.

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