

Platinum(II) complexes of *N,N'*-di-ⁿbutyldithiooxamide showing a peculiar ⁺N–H···Cl[−] interaction. The crystal and molecular structure of bis-di-ⁿbutyldithiooxamidato-platinum(II)

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(Received November 25, 1992; revised February 8, 1993)

Abstract

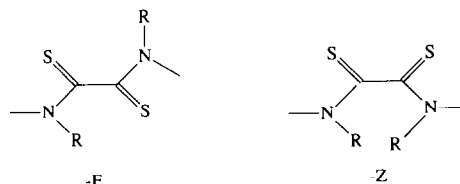
N,N'-di-ⁿbutyldithiooxamide, ⁿbu₂-DTO, reacts in chloroform with neutral complexes of the type *cis*-PtL₂Cl₂. When L = bz₂S or $\frac{1}{2}$ COD the tight contact ion pair {Pt(H₂-ⁿbu₂-DTO)₂²⁺, (Cl[−])₂} (1) is obtained for any metal to ligand ratio. When L is Me₂SO the ion pair {(Me₂SO)ClPt(H₂-ⁿbu₂-DTO⁺, (Cl[−]))} (2) separates in the solid state on adding the ligand to platinum in a 1:1 ratio. This monochelate complex, however, is unstable in chloroformic solution where a symmetrization equilibrium with the corresponding bis-chelate ion pair 1 and the dichloroplatinum starting material can be found. Compound 1 by reaction with pyridine, dipyridine, phenanthroline or similar nitrogen Lewis bases loses one or both HCl molecules so giving {Pt(H-ⁿbu₂-DTO)(H₂-ⁿbu₂-DTO)⁺, (Cl[−])} (3) or [Pt(H-ⁿbu₂-DTO)₂] (4), depending on the base concentration. Dissolution of 1 in a basic solvent (DMF, alcohols) leads to the formation of the neutral species 4, which is also formed when a chloroformic solution of 1 undergoes a double phase reaction with the −OH group of H−OH, =Al−OH or ≡Si−OH. Compound 4 crystallizes in the monoclinic space group *P*2₁/*c*, with *a* = 10.572(2), *b* = 10.748(1), *c* = 12.165(2) Å, β = 93.37(2)°, *V* = 1379.9(4) Å³, *Z* = 2 and *D*_{calc} = 1.58 g cm^{−3}; the structure was refined to *R* = 0.033 and *R*_w = 0.038. The [Pt(H-ⁿbu₂-DTO)₂] complex has imposed square-planar geometry about the Pt atom, two thioamide S atoms of the ⁿbu₂-DTO molecule acting as a chelating ligand. The two crystallographically independent values for the Pt–S bond distance are: Pt–S(1) = 2.297(3) Å and Pt–S(2) = 2.284(2) Å, the bond angles are very close to 90°. The deprotonated complex [Pt(H-ⁿbu₂-DTO)₂] (4) restores the ion pair by a double phase reaction with aqueous HCl, while none of the oxoacids is able to give {Pt(H₂-ⁿbu₂-DTO)₂²⁺, (Ox[−])₂} (Ox[−] = oxoanion). As a consequence, the ⁺N–H···Cl[−] hydrogen interaction in {Pt(H₂-ⁿbu₂-DTO)₂²⁺, (Cl[−])₂} is thought to be crucial in stabilizing the tight ion pair.

Introduction

Dithiooxamides are polyfunctional molecules which in principle can bind to a given metal ion in a variety of different fashions. They constitute a class of ligands possessing low-lying π* orbitals, and form intensely coloured metal complexes, long since known [1], which has a number of applications, including an important imaging process [2].

In the free form dithiooxamides exist as *E*-conformers with the two planes of the S–C–N moiety forming a dihedral angle. Steric interactions makes the existence of the conformer *Z* unlikely, and therefore DTO should behave toward coordination as a poor *S,S*-chelating ligand. However, *S,S*-coordination has been observed in most of the metal complexes of DTO, whereas *N,S*-coordination takes place in copper complexes [3] and

in certain polymeric complexes of nickel [4].



N,S-Coordination produces five-membered, planar, chelate rings, while the *S,S*-mode exhibits more complex structural arrangements. In fact, S–C–N planes are generally tilted towards each other, but when the metal group possesses an electron releasing ability, a planar S–C–C–S skeleton is preferred and a 'dithiolene' type complex is formed [5].

The *S,S*-coordination mode is also achieved when DTO chelates as rubeanate. In such a case however the S–C–C–S skeleton forms a plane, while the residual

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amidic hydrogens are involved in an N-H...N intramolecular hydrogen interaction.

Many papers have appeared on transition metal dithiooxamide complexes; however only in a few cases is DTO reported to act as a neutral bidentate donor ligand and without hydrogen bonds to others, i.e., halide, ligands.

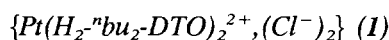
As for the periodic Group 10 metals, the synthesis of neutral and cationic Pd(II) and Pt(II) DTO complexes, and polymeric and cationic complexes of nickel has already been reported [6]. A very recent report deals with nickel(II) DTO neutral complexes [4]. Most of these complexes were prepared by adding an excess of ligands to M^{2+} solutions and the acidity of the medium directed the synthesis toward a cationic or a neutral product.

We now report the reactions of n -butyl substituted DTO with the neutral *cis*-[PtCl₂(Me₂SO)₂], *cis*-[PtCl₂(bz₂S)₂] and Pt(COD)Cl₂, in the low polar non-coordinating solvents CHCl₃. The bis sulfide and the olefinic substrates lead to the compound {Pt(H₂- n bu₂-DTO)₂}²⁺, (Cl⁻)₂ (1) either in a 1:1 or 1:2 metal to ligand ratio, while *cis*-Pt(Me₂SO)₂Cl₂, when reacted with the equimolar amount of the ligand, leads to {(Me₂SO)ClPt(H₂- n bu₂-DTO)⁺, (Cl⁻)} (2) which is the first example of a neutral DTO monochelate platinum(II) complex.

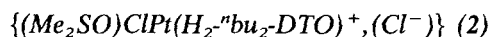
Experimental

Preparations

The ligand n bu₂-DTO [7], and the starting platinum(II) complexes, *cis*-Pt(Me₂SO)₂Cl₂ [8], Pt(COD)Cl₂ [9] and *cis*-Pt(bz₂S)₂Cl₂ [10] were synthesized according to literature procedures. The other reagents were commercially available and used without purification. Solvents were distilled over 4 Å molecular sieves.

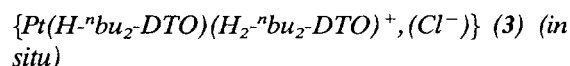


1 mmol of *cis*-[PtL₂Cl₂] was reacted in chloroform with 460.8 mg (2 mmol) of n bu₂-DTO. The purple solution was allowed to stand for 20 min and then hexane was added. 1 precipitated as a purple powder in almost quantitative yield. *Anal.* Calc. for C₁₀H₄₀Cl₂N₄PtS₄: H, 5.52; C, 32.87; N, 7.67; S, 17.55; Cl, 9.7. Found: C, 33.14; H, 5.59; N, 7.74; S, 17.37; Cl, 10.03%.

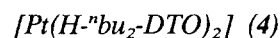


418 mg (1 mmol) of *cis*-Pt(Me₂SO)₂Cl₂ were reacted in chloroform with the stoichiometric quantity of n bu₂-DTO. After 20 min, hexane was added and 2 precipitated as a red-brown powder. *Anal.* Calc. for C₁₂H₂₆Cl₂N₂OPtS₃: H, 4.55; C, 25; N, 4.86; S, 16.68;

Cl, 12.3. Found: H, 4.43; C, 24.58; N, 4.98; S, 13.7; Cl, 12.3%.



16 mg of 1 (0.021 mmol) were dissolved in 1 ml of CDCl₃. Adding of the stoichiometric amount of 2,2'-bipyridine to the resulting solution leads to the complete removal of one mole of HCl per mole of 1 as revealed by the ¹H NMR spectrum (see Table 1).



100 mg of 1 were placed at the head of a preparative column of Al₂O₃ equilibrated with chloroform and eluted with a hexane/chloroform mixture (10/90). A red-orange solution was collected which, upon concentration, gave red crystals of 4 in 50% yield. *Anal.* Calc. for C₂₀H₃₈N₄PtS₄: H, 5.83; C, 36.52; N, 8.52; S, 19.46. Found: C, 35.98; H, 5.70; N, 8.87; S, 18.79%.

Instrumentation

A PE LAMDA 5 UV-Vis instrument, a PE FT-IR 1720 X spectrophotometer and a Bruker AMX R 300 spectrometer were employed to obtain UV-Vis, IR and ¹H NMR spectra, respectively. Conductivity measurements were made by means of a CDM 3 Radiometer instrument.

X-ray data collection and structure refinement

Suitable red crystals of 4 were obtained by slow evaporation of solvent from dichloromethane-hexane.

Diffraction measurements were made on a Siemens-P4/m four-circle diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ and Ψ values of 30 strong reflections in the range 15 < 2θ < 32°. The compound 4 crystallizes in the monoclinic space group P2₁/c, with a = 10.572(2), b = 10.748(1), c = 12.165(2) Å, β = 93.37(2)°, V = 1379.9(4) Å³, Z = 2 and D_{calc} = 1.58 g cm⁻³. Lorentz and polarization corrections were applied to the intensity data; γ-scan absorption (max. and min. transmission = 0.914/0.845) apportioned. During the course of the intensity data collection the crystals showed no loss in intensity. The structures were solved by using standard Patterson methods, successive least-squares refinements and difference Fourier maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter (U = 0.06 Å²).

The weighting scheme used in the last refinement cycles was w = 1.000/(σ²(F_o) + 0.004865F_o²), which

showed reasonable consistency in a test of $\omega\Delta^2$ for data sectioned with respect to both F_0 and $(\sin\theta)/\lambda$.

Scattering factors for non-hydrogen atoms were taken from ref. 11 and for hydrogen atoms from ref. 12. Anomalous dispersion corrections for Pt atoms were taken from ref. 13.

All calculations were performed with SHELX76 [14] and PARST [15] sets of programs on the VAX 3400 computer at the 'Centro Interdipartimentale di servizi per la Diffrazione a Raggi-X' dell'Università di Messina. See also 'Supplementary material'.

Results and discussion

The reactions of all *cis*-[PtL₂Cl₂] starting materials, when reacted with a two-fold quantity of ⁿbu₂-DTO, lead to the formation of compound **1**.

The ¹H NMR spectrum of **1** shows the simple butylic pattern of the DTO ligand (Table 1) but some significant differences are found in the N-H resonances and in the multiplicity of the butylic α hydrogen signals. In fact, the N-H protons upon complexation undergo a large downfield shift from 8 to 13.5 ppm, and this indicates that in complex **1** there are strong hydrogen interactions [16]. On the other hand, N-CH₂- signals, which appear as a quartet in the free ligand, become a triplet in complex **1**. We have not yet a definite explanation for this lowering in the multiplicity of the butylic α protons upon coordination.

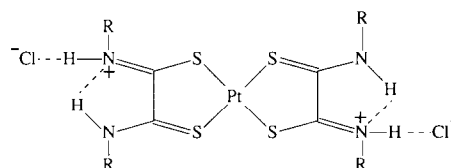
However, it is evident that the four butylic groups are magnetically equivalent. Thus, we can conclude that the two molecules of ⁿbu₂-DTO are linked to platinum through sulfur atoms; in fact, dithiooxamide derivatives with N₄ coordination are unknown. The two chlorine atoms per formula, shown by elemental analysis, are thought to be involved in strong ⁺N-H...Cl⁻ interactions. As a matter of fact, the solutions of **1** in solvents of low polarity (CH₂Cl₂, CHCl₃, C₆H₆), at

any concentration, do not conduct electric current, and we can formulate the compound **1** as a tight, extensively associated, ion pair {Pt(H₂-ⁿbu₂-DTO S,S')Pt}²⁺,(Cl⁻)₂.

The synthesis of a similar compound of platinum(II) containing neutral isobutyldithiooxamide has already been reported in the literature together with parent complexes of nickel and palladium [6b, c]; these species were presented as dications [M(H₂-R₂-DTO)₂]₂X₂ (M = Ni, Pd and Pt; X = halogen), stable in acidic media and behaving as 1:2 electrolytes, at least in dilute solutions of CDCl₃ [17].

This conflicts with our conductivity experiments, which showed, as stated above, the absolute lack of any measurable conductance in solvents of low polarity at any concentration of the complex.

The whole series of Group 10 metal complexes of neutral disubstituted dithiooxamides have also been represented with the following molecular geometry



which involves an electrostatic interaction between an amidic hydrogen and a positively charged iminic nitrogen. This is at least unusual, even when a resonance form is conceived.

On the other hand, steric hindrance does not allow both amidic hydrogens to be coplanar, as shown by the crystal structures of zinc and copper complexes with neutral dithiooxamides [17]; in the latter it has also been shown that the second amide function does not give rise to any hydrogen-bond interaction. On the basis of the above, the intramolecular N-H...N hydrogen bond seems highly unlikely.

TABLE 1. ¹H NMR data for *N,N'*-di-ⁿbutyldithiooxamide and its platinum(II) complexes in CDCl₃^a

	H _α ^b	H _β ^b	H _γ ^b	H _δ ^b	N-H	Pt-S-CH ₃
	3.69	1.75	1.45	0.98	8.40	
{Pt(H ₂ - ⁿ bu ₂ -DTO) ₂ } ²⁺ ,(Cl ⁻) ₂ }	3.76	1.96	1.49	1.00	13.5	
[Pt(H- ⁿ bu ₂ -DTO) ₂]	3.64	1.75	1.43	0.97	^d	
{Pt(H- ⁿ bu ₂ -DTO)(H ₂ - ⁿ bu ₂ -DTO) ⁺ ,(Cl ⁻)}	3.72	1.90	1.47	0.99	13.0	
{(Me ₂ SO)ClPt(H ₂ - ⁿ bu ₂ -DTO) ⁺ ,(Cl ⁻)}	^c	^c	^c	^c		3.50 ^e

^aChemical shifts are reported in ppm downfield from TMS. ^bH_α=quartet in the free ligand, triplet in the complexes; H_β=quintuplet; H_γ=sextuplet; H_δ=triplet. ^cThe signals of the coordinated ligands are not detectable. ^dN-H signals undetectable. ^eCoupling constants undetectable.

An additional factor which favours the twisting around the C-C axis of the chelate ligand in **1** is a more favourable charge delocalization on cyanine distortion [18], DTO ligands being made of two coupled monomethine merocyanine type fragments [19].

$\{\text{Pt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})_2\}^{2+}, (\text{Cl}^-)_2\}$ loses one or both molecules of HCl (Scheme 1) by means of pyridine, bipyridyl, alkylamines and other Lewis bases, giving **3** or **4**, respectively, depending on the amount of added base. The process can be monitored by UV-Vis spectroscopy and the resulting spectra clearly show two different processes, each of them characterized by well defined isosbestic points. Figure 1 shows the electronic spectra of the species **1**, **3** and **4**, obtained by adding to a chloroform solution of **1** (spectrum a), a proper amount of bipyridine corresponding to the complete removal of one molecule of HCl (b); spectrum (c) corresponds to the addition of a large excess of bipyridine and is identical to that of an authentic sample of **4** prepared independently.

The ^1H NMR spectrum of **3**, generated *in situ* by adding the proper amount of bases in a deuteriochloroform solution of **1**, shows the butylic pattern of the ligand as in **1** and **4**, but with different chemical shifts (see Table 1). The single pattern found for the substituent group in such an unsymmetrical complex could well be due to a rapid intermolecular exchange of HCl between different nitrogen sites.

The removal of hydrochloric acid from **1** can be obtained in different ways: (i) by solubilization of the compound in solvents which may be considered Brønsted bases such as DMF, alcohols, Me_2SO , acetone, etc.; (ii) by elution of a chloroform solution of complex **1** through an alumina or silica-gel column; (iii) by shaking a chloroform solution of the complex with water. The use of method (ii) gave massive quantities of $[\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})_2]$ (**4**) from which X-ray quality crystals were obtained.

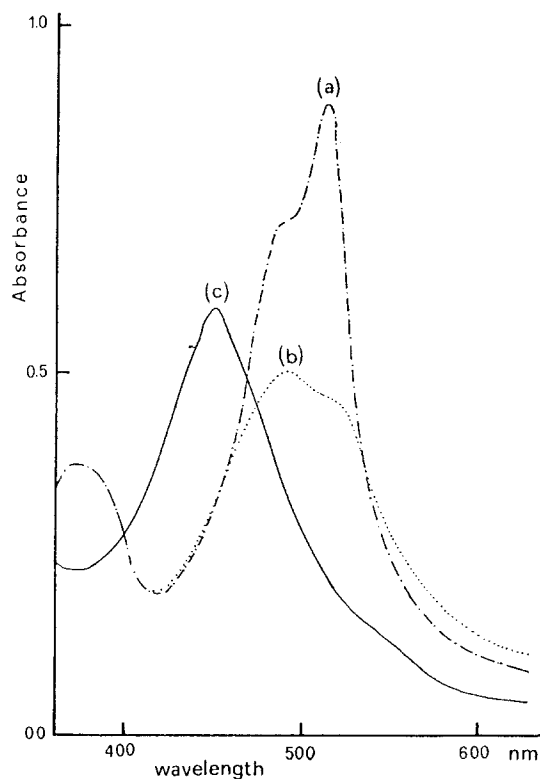
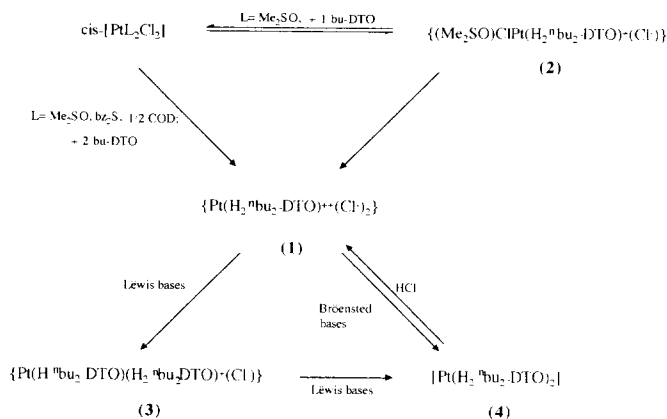


Fig. 1. Electronic spectra of: (a) $\{\text{Pt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})_2\}^{2+}, (\text{Cl}^-)_2\}$; (b) $\{\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})^+, (\text{Cl}^-)\}$; (c) $[\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})_2]$ in CHCl_3 .

^1H NMR of **4** in the butylic chain hydrogen region does not differ significantly from that of **1** and **3**; however, N-H signals were not detected over a wide spectral window.

We also observed the removal of HCl from **1** by shaking a chloroform solution of this complex with an aqueous solution of various oxoacids. At the same time, the double phase reaction of **4** with aqueous HCl restores **1** in the chloroform phase while none of the oxoacids is able to generate a species of the type $\{\text{Pt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})_2\}^{2+}, (\text{Ox}^-)_2\}$ (Ox^- = oxoanion). These facts clearly demonstrate that oxoanions, which can form hydrogen bonds too, are not able to stabilize platinum complexes of neutral dithiooxamides. Such a stabilization seems to be a specific property of chloride, and a major role is played by a specific and peculiar $^+N\text{-H}\cdots\text{Cl}^-$ interaction.

In connection with this, it is worth mentioning some recent reports dealing with the stabilization effect by chloride ion on certain organic protonated bases. It has been reported [20] that the 'naked' Cl^- constrains the diprotonated tetrapyrrolypyrazine in a distorted structure, while, on changing Cl^- with the hydrocarbon surrounded BPh_4^- ion, the distorted structure collapses to a quite planar dication showing intramolecular hydrogen bonds $\text{N-H}\cdots\text{N}$ as in 'proton sponges' [21].

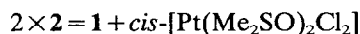


Scheme 1.

It has also been shown that Cl^- as a counterion stabilizes the diprotonated form of 5,10,15,20 tetraphenylporphine with respect to other anions in which the negative charge is delocalized (ClO_4^- , CH_3COO^- , etc.) [22] as a consequence of the fact that a small, densely charged anion such as Cl^- , in solvents of low polarity such as chloroform, is extensively associated into strong tight contact ion pairs $\text{H}_4\text{TPP}^{2+}(\text{Cl}^-)_2$.

A similar explanation can be invoked to explain the chemical behavior of $\{\text{Pt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})^{2+}, (\text{Cl}^-)_2\}$. In fact, the species $\{\text{Pt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})^{2+}, (\text{X}^-)_2\}$ exists only when X^- is a halide ion, which has the ability to create a strong tight contact ion pair with the dication $[\text{Pt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})^{2+}]$. All the factors which produce destabilization of the $^+\text{N-H}\cdots\text{Cl}^-$ interaction invariably lead to the deprotonated species $[\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})_2]$.

The reaction of *cis*- $[\text{PtCl}_2\text{L}_2]$ with an equimolar amount of $^n\text{bu}_2\text{-DTO}$ depends on the nature of the starting material. When $\text{L}=\text{bz}_2\text{S}$ or $\frac{1}{2}\text{COD}$, a mixture of **1** and unreacted starting material is obtained. When $\text{L}=\text{Me}_2\text{SO}$, forcing the precipitation with hexane, a red-brown compound is obtained which, on the basis of elemental analysis, can be formulated as the monochelate species $\{(\text{Me}_2\text{SO})\text{ClPt}(\text{H}_2\text{-}^n\text{bu}_2\text{-DTO})^+, (\text{Cl}^-)\}$ (**2**). The IR spectrum of **2** shows intense bands in the region $3400\text{--}2700\text{ cm}^{-1}$ indicating strong $^+\text{N-H}\cdots\text{Cl}^-$ interactions; furthermore, this spectrum is completely different from that of an equimolar mixture of **1** and starting *cis*- $[\text{PtCl}_2(\text{Me}_2\text{SO})_2]$. When **2** is dissolved in deuterated chloroform the ^1H NMR spectrum shows two groups of signals for Pt-S- CH_3 resonances. On of them, which is the most intense, is found at 3.54 ppm and is coincident with that of the starting complex *cis*- $[\text{Pt}(\text{Me}_2\text{SO})_2\text{Cl}_2]$; the other 1:4:1 signal (about 10% of the total intensities of Pt-S- CH_3 resonances) is at 3.5 ppm. The position of the butyl resonances also indicates the presence of **1**. Clearly, the monochelate complex **2** is unstable in chloroform solution, where it undergoes the following symmetrization equilibrium



The low solubility of **2** in a $\text{CHCl}_3/\text{hexane}$ mixture allows **2** to be obtained in an almost pure form.

The instability of **2** in solution makes the study of its chemical behaviour difficult. In particular, the symmetrization equilibrium prevents the use of **2** as starting material for the synthesis of a new class of compounds of type $\{(\text{L})\text{ClPt}(\text{H}_2\text{-R}_2\text{-DTO})^+, (\text{Cl}^-)\}$ (L =neutral ligand), profiting from the ease with which the molecule of Me_2SO can be removed.

Thus, future investigations will be devoted to obtaining other $\text{R}_2\text{-DTO}$ monochelate platinum complexes more stable in solution.

Molecular structure of $[\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})_2]$

As shown in Fig. 2, the crystal consists of discrete $[\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})_2]$ molecules separated by normal van der Waals distances. Final atomic coordinates and equivalent isotropic temperature factors are listed in Table 2, bond lengths and angles are listed in Table 3. The molecule has crystallographically-imposed *Ci* symmetry, with the platinum atom lying at the inversion centre, which requires the PtS_4 moiety to be planar.

The two crystallographically independent values for the Pt-S bond distance, which are 2.284(2) and 2.297(3) Å, respectively, are equal within three standard deviations and are equal to the values reported for the similar palladium complex $[\text{Pd}(\text{HdcDTO})_2]$ [17]. The S-Pt-S bond angles of 89.8(1) and 90.2(1)°, the $\text{S1}\cdots\text{S2}'$ and $\text{S1}\cdots\text{S2}$ separation of 3.232(4) and 3.246(4) Å, respectively, indicate a nearly idealized D_{4h} symmetry on the PtS_4 moiety. The mean C-S and C-N bond

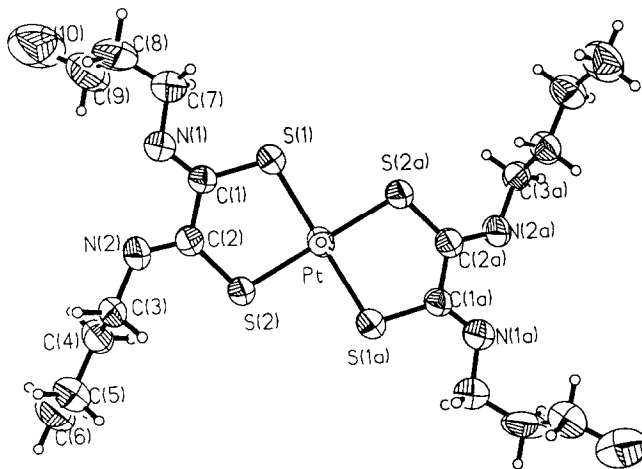


Fig. 2. Molecular structure of $[\text{Pt}(\text{H-}^n\text{bu}_2\text{-DTO})_2]$.

TABLE 2. Fractional atomic coordinates with equivalent isotropic thermal parameters ($\text{\AA}^2$)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}} \times 10^4$ ($\text{\AA}^2$)
Pt	0.0000	0.0000	0.0000	512(2)
S2	0.0966(2)	0.0703(3)	0.1610(2)	617(8)
S1	-0.1706(3)	0.1263(3)	0.0273(2)	672(8)
N1	-0.2015(8)	0.2775(9)	0.1992(7)	730(35)
C4	0.121(1)	0.128(1)	0.4592(8)	704(4)
C1	-0.1326(9)	0.196(1)	0.1529(7)	555(31)
N2	0.0203(9)	0.2369(9)	0.2993(8)	699(34)
C3	0.1356(9)	0.224(1)	0.3728(8)	720(43)
C2	-0.0068(9)	0.1730(9)	0.2107(7)	555(33)
C5	0.237(1)	0.114(1)	0.5375(9)	806(47)
C7	-0.325(1)	0.307(1)	0.148(1)	900(53)
C6	0.219(1)	0.021(1)	0.628(1)	1058(62)
C8	-0.404(1)	0.382(2)	0.219(1)	1301(83)
C9	-0.449(2)	0.309(2)	0.316(1)	1689(119)
C10	-0.523(2)	0.376(5)	0.388(2)	3187(259)

TABLE 3. Bond distances (Å) and angles (°)

Pt-S2	2.284(2)	C1-C2	1.488(13)
Pt-S1	2.297(3)	N2-C3	1.475(13)
S2-C2	1.690(10)	N2-C2	1.296(13)
S1-C1	1.730(9)	C5-C6	1.508(19)
N1-C1	1.286(14)	C7-C8	1.483(21)
N1-C7	1.452(14)	C8-C9	1.513(26)
C4-C3	1.485(16)	C9-C10	1.401(41)
C4-C5	1.520(14)		
S2-Pt-S1	89.8(1)	C4-C3-N2	112.2(9)
Pt-S2-C2	104.8(3)	C1-C2-N2	116.8(9)
Pt-S1-C1	104.0(3)	S2-C2-N2	121.8(8)
C1-N1-C7	118.4(9)	S2-C2-C1	121.4(7)
C3-C4-C5	113.6(9)	C4-C5-C6	113.0(9)
S1-C1-N1	125.0(7)	N1-C7-C8	112.6(10)
N1-C1-C2	114.9(8)	C7-C8-C9	112.9(10)
S1-C1-C2	119.8(7)	C8-C9-C10	115.9(20)
C3-N2-C2	126.0(9)		

distances of 1.700(10) and 1.290(10) Å fall in the range reported for other dithiooxamide derivatives [23].

The central C1-C2 bond of 1.488(13) Å shows the expected shortening and the sum of the bond angle 360.0(8)° around them confirms their sp^2 hybridization. This bond value, together with the value for the C-S and N-C distances, suggests a large degree of multiple bond delocalization over the S-C-N system.

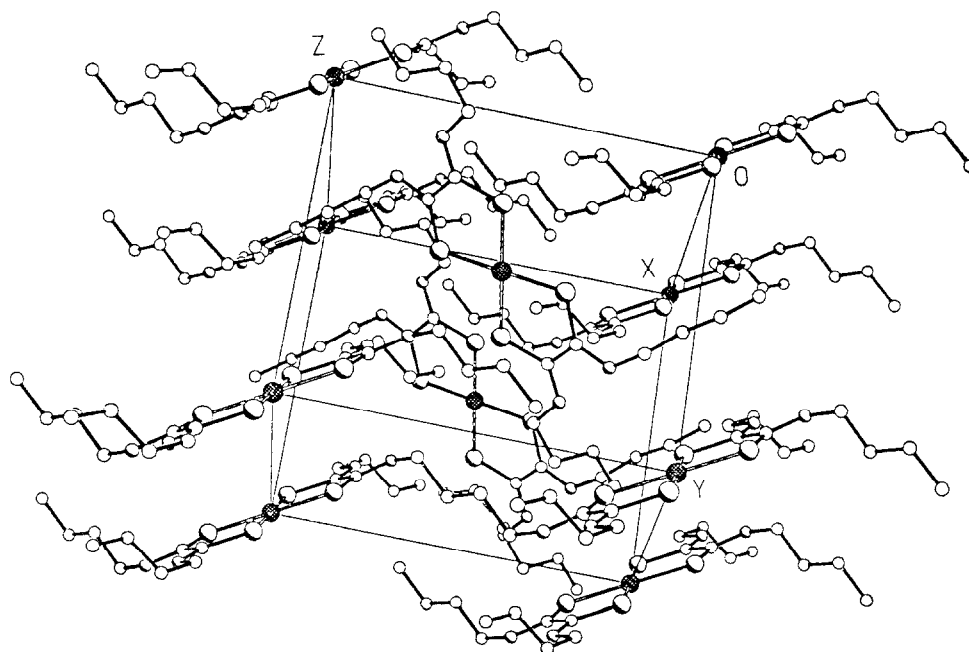
The location of the H atoms connected to either N1 or N2 was unsuccessful; as there is a residue of electronic density of about 0.55 e Å³ near N1 (at 1.12 Å) we are

inclined to a statistical disorder of the H atom between N1 and N2, and by the C1-N1-C7 and C2-N2-C3 bond angles which are 118.4(9) and 125.4(9)°, respectively. Such a difference arises from the molecular packing rather than from a different hybridization of the two nitrogen atoms which is sp^2 for both. Molecular packing, reported in Fig. 3, is also responsible for the large thermal parameters of the butylic chain C7...C10 and then for the short bond distances.

The thioamidic group is nearly planar with a small torsion angle about the central C-C bond; $-4(1)^\circ$ for SCCS and $-1(1)^\circ$ for NCCN. The planarity of the ligand clearly indicates the existence of intramolecular hydrogen-bonding interactions between the amide nitrogen atoms {N1...N2}, the separation of which (2.61(1) Å) is comparable to the value of 2.57 Å reported for a neutral palladium complex [17]. In other (H₂-DTO) cationic complexes or in *N,N'*-disubstituted dithiooxamides the dihedral angle θ between the amidic groups is far from planarity, the minimum value reported being 35.0° in [Cu(H₂dbzDTO)₂][ClO₄]₂ [17]. The mean value for the N-C(sp^3) bond distances of 1.465(1) Å is in agreement with the generally accepted values for such bonds.

Supplementary material

Hydrogen coordinates, anisotropic temperature factors and calculated and observed structure factors are available from the authors on request.

Fig. 3. Molecular packing of [Pt(H-ⁿbu₂-DTO)₂].

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