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Platinum assisted cyclization of *S*-methyl 3-acyl-2-methyldithiocarbazates under mild conditions. Crystal structure of $[Pt_2(\mu\text{-SMe})(terpy)_2][ClO_4]_3$ †

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Received 18th June 1999, Accepted 15th September 1999

The reaction of the newly synthesized aqua complex $[Pt(terpy)(OH_2)][BF_4]_2$ with *S*-methyl 3-acyl-2-methyldithiocarbazates under a variety of experimental conditions has been studied. Using a 2 : 1 metal to ligand ratio in methanol, a platinum assisted cyclization was observed. The reaction products were Δ^2-1,3,4-oxadiazoline-5-thione derivatives and the binuclear tricationic complex $[Pt_2(\mu\text{-SMe})(terpy)_2]^{3+}$ whose molecular structure has been determined by X-ray crystallography. This platinum assisted transformation is proposed as a new synthetic route to Δ^2-1,3,4-oxadiazoline-5-thiones under mild conditions. In the presence of an excess of a non-co-ordinating acid ($HClO_4$, CH_3SO_3H or CF_3SO_3H) the cyclization is completely quenched and complexes with co-ordinated *S*-methyl 3-acyl-2-methyldithiocarbazates have been isolated. A general mechanism which accounts for the observed transformations is proposed on the basis of ^{1}H NMR and UV/Vis evidence.

Introduction

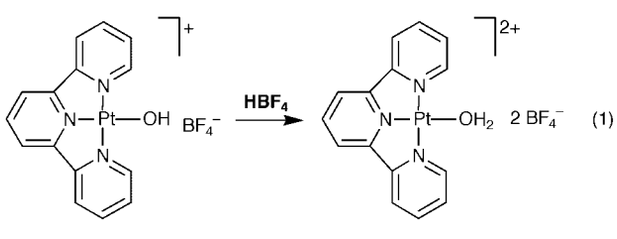
Largely available biomolecules such as amino acids, peptides, carbohydrates and steroids present structural characteristics that could be advantageously introduced in components of co-ordination compounds designed for various applications. For example biocompatibility and organotropism are relevant properties for metal complexes of pharmaceutical significance while the presence of chiral centres can be exploited in the preparation of transition metal catalysts for asymmetric reactions.[1]

In this context we focused our attention on new ligands based on chemical modifications of natural amino acids. In particular we recently reported the preparation of N-protected amino acids conjugated with *S*-methyl 2-methyldithiocarbazate[2] in an attempt to associate the natural characteristics of amino acids with the well known co-ordinating properties of dithiocarbazic acid derivatives.[3] In principle, dithiocarbazate derivatives **Ia**–**Ic** should behave as versatile ligands acting as monodentate neutral sulfur or nitrogen (*via* N2) donors, as anionic monodentate ligands (after N3 deprotonation) and finally as neutral S–S or anionic N3–S (also after N3 deprotonation) chelating ligands. However, to our knowledge, only the last co-ordination mode has been reported for various dithiocarbazates.[3]

We are currently interested in studying the co-ordinating ability of this series of ligands toward transition metals of recognized pharmaceutical value. We reported[2] the preparation of complexes of Tc^V and Re^V and planned to explore the interactions of functionalized amino acids with Pt^{II}, whose value in medicine has been consolidated during many years of research and clinical application since the discovery of the antitumour activity of cisplatin $[Pt(NH_3)_2Cl_2]$.[4] With this aim we examined the behaviour of **Ia**–**Ic** as monodentate neutral ligands by treating them with the aqua complex $[Pt(terpy)(OH_2)][BF_4]_2$ (terpy = 2,2′ : 6′,2″-terpyridine), where a single co-ordination position is available through substitution of the water ligand. Platinum complexes containing the terdentate aromatic ligand terpyridine have attracted great attention both for their chemical properties[5] and for their activity as DNA intercalators.[6]

Results and discussion

Although the aqua species **2** is known in solution[7] it has never been isolated in the solid state. We succeeded in isolating it as its tetrafluoroborate salt by treating the known hydroxo species **1**[8] with tetrafluoroboric acid, eqn. (1). The analytical and spectroscopic data for **2** are reported in the Experimental section. Using complex **2** as a substrate for nucleophilic substitution at platinum with the functionalized amino acids **Ia**–**Ic** we observed that the process course and products depend on the acidity of the reaction medium.



1 **2**

The reaction of complex 2 with the ligands Ia–Ie at natural pH

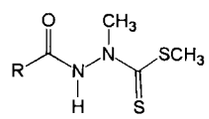
The interaction of **2** with the ligand **Ia** was first investigated. After the addition of **Ia** to a red-orange solution of **2** in a 1 : 1 ratio in MeOH, eqn. (2), a prompt change of colour was observed, followed by the formation of a green precipitate. On

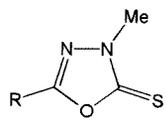
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3877/

Table 1 Selected ^{1}H NMR data of ligands **Ia**–**Ie** and heterocyclic derivatives **IIa**–**IIe**[a]

Compound	SCH_3	NCH_3	$C_\alpha H_n$	NHC_α	NHN	Others
Ia[b]	2.45 (s)	3.60 (s)	3.90 (d, 5.5)	5.50 (t, 5.5)	8.90 (br s)	5.10 (s, CH_2Ph)
IIa		3.67 (s)	4.43 (d, 6.2)	5.27 (t, 6.2)		5.15 (s, CH_2Ph)
Ib[b]	2.50 (s)	3.60 (s)	4.35 (q d, 7.3)	5.40 (d, 7.3)	9.00 (br s)	1.46 (CH_3C_α, d, 7.3), 5.10 (CH_2Ph, s)
IIb		3.61 (s)	4.95 (q d, 7.7)	5.32 (d, 7.7)		1.54 (CH_3C_α, d, 7.7) 5.11, 5.05 (CH_2Ph, d, 4.5)
Ic[b]	2.45 (s)	3.48 (s)	4.58 (t d, 8.0)	5.46 (d, 8.0)	8.90 (br s)	3.20 (CH_2C_α, m), 5.20 (CH_2Ph, s)
IIc		3.60 (s)	5.15[c]	5.15[c]		3.18 (CH_2C_α, m), 5.09 (CH_2Ph, s)
Id[d]	2.60 (s)	3.85 (s)			8.50 (br s)	7.5–8.0 (Ph, m)
IId[d]		3.82 (s)				7.5–8.0 (Ph, m)
Ie[d]	2.55 (s)	3.65 (s)			8.36 (s)	2.8 (CH_3CO, s)
IIe[d]		3.83 (s)				2.38 (CH_3CO, s)

[a] All spectra were recorded in $CDCl_3$; δ, J in Hz in parentheses. [b] *cf.* ref. 2. [c] Overlapped signals for $C_\alpha H$ and NHC_α. [d] *cf.* ref. 11.





Ia R = CH_2-NH-CO-O-CH_2-Ph

Ib R = CH(CH$_3$)-NH-CO-O-CH_2-Ph

Ic R = CH(CH_2Ph)-NH-CO-O-CH_2-Ph

Id R = Ph

Ie R = CH_3

IIa R = CH_2-NH-CO-O-CH_2-Ph

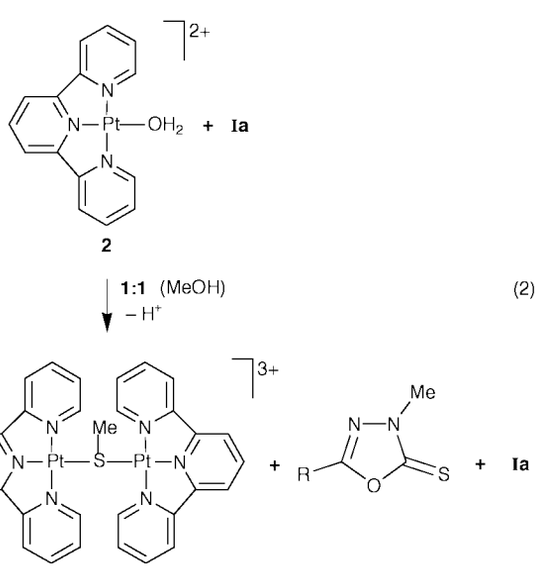
IIb R = CH(CH$_3$)-NH-CO-O-CH_2-Ph

IIc R = CH(CH_2Ph)-NH-CO-O-CH_2-Ph

IId R = Ph

IIe R = CH_3

(a) *S*-methyl 3-acyl-2-methyldithiocarbazates (b) Δ^2-1,3,4-oxadiazoline-5-thiones



the basis of elemental analysis, IR, ^{1}H NMR, and conductivity measurements (see Experimental section), the green solid was identified as the binuclear tricationic complex **3**: the presence of a SMe bridging group was unequivocally proved by the observation of a signal in the ^{1}H NMR, presenting a 1:8:18:18:8:1 pattern typical of a proton equally coupled to two platinum nuclei.[9] The same cationic complex isolated as its perchlorate salt (**3′**, see Experimental section) was recrystallized from CH_3NO_2 affording crystals suitable for structure determination (Fig. 1), below described in detail.

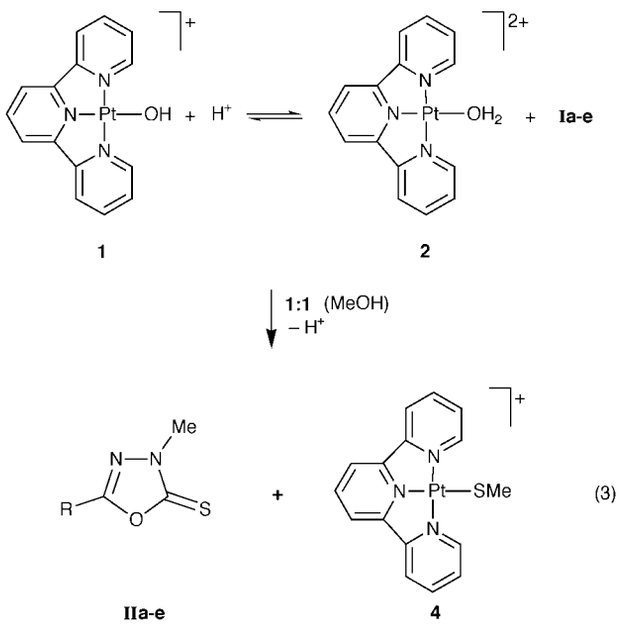
After the separation of the platinum containing product **3** the remaining solution was evaporated to dryness and the residue analysed by ^{1}H NMR; it was identified as a 1:1 mixture of unchanged **Ia** and a second species with a similar pattern but lacking both the SMe group and the hydrazidic proton of CON*H*NCH_3. These observations suggest that half the amount of **Ia** had undergone a fragmentation (with transfer of the SMe group to the Pt–terpy moiety) and a cyclization process to give the 1,3,4-oxadiazoline derivative **IIa**, eqn. (2). This experiment indicates that two equivalents of aqua complex **2** are required for complete conversion of **Ia** into **IIa** and in fact when the same reaction was performed using a 2:1 platinum:ligand ratio **Ia** was completely consumed and **IIa** was the only product recovered from the solution.

The heterocycle **IIa** was isolated and characterized by ^{1}H NMR, infrared, mass spectrometry and elemental analysis (see Experimental section and Table 1). Its infrared spectrum shows single bands for the stretchings of C=O and N–H, at 1692 and 3293 cm^{-1} respectively, while in the spectrum of the precursor **Ia** there are two bands for each functional group [1686 and 1707 cm^{-1} for ν(C=O); 3322 and 3391 cm^{-1} for ν(N–H)]. Another new band, observed at 1624 cm^{-1}, can be assigned to the endocyclic C=N bond[10] and finally the wavenumber for ν(C=S) of **IIa** (1179 cm^{-1}) is consistent with literature data for analogous compounds.[11]

The same cyclization process occurs when two equivalents of **2** are treated with the alanine and phenylalanine derivatives **Ib** and **Ic**, giving the Δ^2-1,3,4-oxadiazoline-5-thiones **IIb** and **IIc** respectively. Compounds **IIa**–**IIc** belong to a class of heterocycles which has been reported to show a wide range of biological and pharmaceutical activities and a remarkable variety of uses.[10]

The platinum assisted cyclization described here can be proposed as a new synthetic route to 1,3,4-oxadiazolinethiones, alternative to the reported reaction of acylhydrazine with thiophosgene $CSCl_2$.[12] A variety of substituents can be introduced in the ring position 2, including chiral carbon directly bonded to the ring as in **IIb** and **IIc**.

With the aim to check the generality of the reaction and to prove that the amino acidic residue of **Ia**–**Ic** has no role in the process, we carried out a series of experiments and found that the simple acyldithiocarbazate derivatives **Id** and **Ie** are completely transformed in the presence of two equivalents of the aqua complex **2**, giving the corresponding 1,3,4-oxadiazolinethiones **IId** and **IIe** which have been previously prepared and characterized.[11] We then observed that **Ia**–**Ie** can be quantitatively transformed into **IIa**–**IIe** also using a single equivalent of the hydroxo species **1**: in this case the platinum is recovered as the monothiolate complex **4**, eqn. (3). The complete characterization of the newly synthesized heterocycles **IIa**–**IIc** and of the model compounds **IId** and **IIe** is reported in the Experimental section and in Table 1.



Compounds **Ia**–**Ie** do not undergo cyclization in the presence of a base (NEt_3) or an acid (*p*-toluenesulfonic acid or HCl) under mild conditions, but it has been reported before that simple 3-acyl-2-methyldithiocarbazates like **Id** and **Ie** do undergo cyclization when refluxed for four hours in EtOH in the presence of NEt_3.[11] It is worth noticing that, although our method is based on the use of expensive platinum compounds, it requires milder conditions (no acid or base added, room temperature) and shorter time and therefore can be particularly convenient when perishable substrates are used on a small scale.

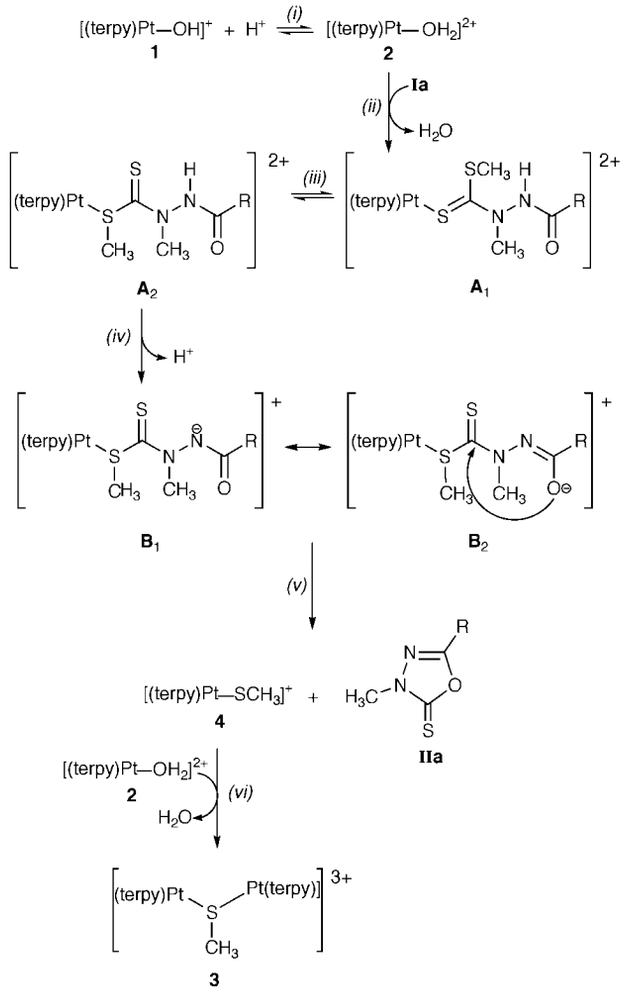
The reaction between complex 2 and Ia in the presence of an added acid

During a series of experiments aimed to clarify the mechanism of the above reaction we noticed that the acidity of a solution containing 3×10^{-3} mol dm^{-3} of both complex **2** and **Ia** increases from pH 3.5 to 1.4. Consequently we considered that the addition of an acid could inhibit the cyclization process thus allowing us to identify the primary product of the interaction of **2** with **Ia**.

In two distinct experiments the reagents were mixed at a concentration of 5×10^{-5} mol dm^{-3} in the presence of different amounts of the non-co-ordinating acid CH_3SO_3H (10^{-3} and 10^{-2} mol dm^{-3}) and the reaction was followed by UV/Vis spectrophotometry. In both cases the observed spectral changes in the region 310–400 nm (where **Ia** and **IIa** do not absorb) indicated a three stage process. The first stage was completed in the time required for mixing of the reagents and it was followed by two slower processes. The last involves only two species as indicated by the presence of several isosbestic points (at 312, 322, 330, 335 and 347 nm). The final spectrum corresponds exactly to that of the platinum monothiolate complex **4**, as shown by comparison with an authentic sample (see Experimental section).

We observed that both the second and third steps are slower at higher acid concentrations and therefore it should be possible to accumulate the product of the first step using an excess of acid.

With this aim we followed the reaction of complex **2** with **Ia**, 3×10^{-2} mol dm^{-3} each, by ^1H NMR spectrometry, in CD_3OD, with added CF_3SO_3H (10^{-1} mol dm^{-3}). Under these conditions the cyclization process does not occur at an appreciable rate and the spectrum shows the formation of a single species where no signal shows platinum coupling. This species was isolated as a solid under preparative conditions and characterized by elemental analysis and IR spectroscopy as complex $\mathbf{A_1}$ (see Experimental section) where unaltered **Ia** is co-ordinated to platinum (see Scheme 1). The substantial invariance of the stretching of



Scheme 1

the C=O group (1709 cm^{-1}) and the lack of platinum coupling in the ^1H NMR signal of SMe induces us to exclude the involvement of these groups in the co-ordination of the ligand.

If complex $\mathbf{A_1}$ is redissolved in acid-free methanol it rapidly evolves to **4** and heterocycle **IIa**.

We also succeeded in isolating the product of the second step $\mathbf{A_2}$ by carrying out the reaction under the UV/Vis experimental conditions but using perchloric acid instead of CH_3SO_3H. In this way $\mathbf{A_2}$ precipitated as its perchlorate salt, was collected and analysed by ^1H NMR in CD_3NO_2 solution. The spectrum shows the presence of co-ordinated **Ia** and in particular a platinum coupled S*Me* signal [^3J(Pt–H) = 34.2 Hz] indicating

that in this case the co-ordination occurs through the S atom of that group (Scheme 1).

Mechanistic considerations

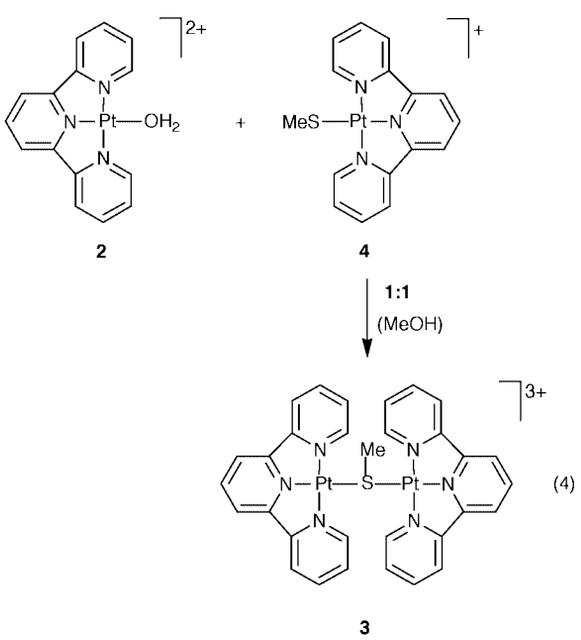
All the above described experimental observations can be rationalized in a general picture of the reaction mechanism, shown in Scheme 1. First of all, in an aqueous medium or in MeOH, the aqua complex **2** is related to the hydroxo species **1** *via* the pH dependent equilibrium *(i)*. However, it is well known that hydroxo species of Pt^{II} are completely inert towards OH^- substitution [13] and therefore **2** is the only reacting species.

In step *(ii)* compound **Ia** promptly replaces the co-ordinated water of the aqua complex **2**, giving an intermediate $\mathbf{A_1}$ which we formulate as a thionic sulfur bonded platinum complex, on the basis of the above discussed spectroscopic data. The species $\mathbf{A_1}$ undergoes isomerization to $\mathbf{A_2}$ where **Ia** is co-ordinated *via* SMe [step *(iii)*].

The following step *(iv)* is the spontaneous deprotonation of the hydrazidic NH resulting in the monocationic intermediate **B** described by two canonical forms $\mathbf{B_1}$ and $\mathbf{B_2}$. This step accounts for the observed increase of acidity during the reaction and is inhibited in the presence of an added acid.

The subsequent step *(v)* is ring closure occurring through intramolecular nucleophilic attack of the carbonyl oxygen of $\mathbf{B_2}$ on the thionic carbon with simultaneous cleavage of the C–S bond and outgoing of **4** as a stabilized leaving group.

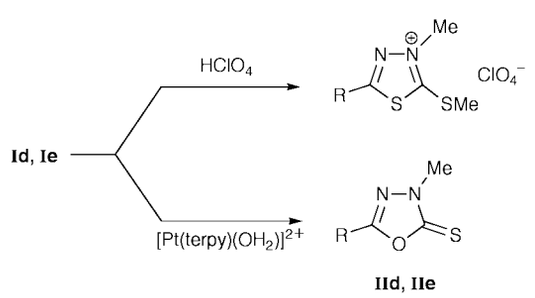
As soon as complex **4** is formed it reacts with the residual aqua complex **2** producing the binuclear species **3** [step *(vi)*]: this side reaction is faster than the overall cyclization process and therefore the observed Pt:ligand 2:1 stoichiometry is required for the complete transformation of **Ia**. To prove this hypothesis we prepared complex **3** by mixing **2** and **4**, eqn. (4) and Experimental section.‡



2 **4** **3**

In Scheme 1 it is assumed that the cyclization process is the driving force for cleavage of the C–S bond in the co-ordinated ligand. This hypothesis is supported by the observation that when we carried out a comparison reaction between **2** and the uncyclizable *S*-methyl 2-methyldithiocarbazate no subsequent C–S breaking occurred after the substrate co-ordination.

It is interesting that, according to ref. 11, compounds **Id** and **Ie** undergo cyclization to 2-alkylthio-1,3,4-thiadiazolium cations in the presence of a stoichiometric amount of $HClO_4$, while in the presence of **2** we found that they give 1,3,4-oxadiazolidine-5-thiones (Scheme 2). We suggest that this behaviour might be ascribed to the presence of Pt–terpy acting as a protecting group for the C=S function.



Scheme 2

‡ Step (*vi*) requires the presence of complex **2** in an appreciable concentration and therefore is not observed when the reaction is carried out in a very diluted solution or when the platinum containing reagent is the hydroxo complex **1**, eqn. (3). Under this last condition equilibrium (*i*) is well shifted towards the non-reactive species **1**, but even in this case the reaction proceeds since the released proton shifts the equilibrium towards the reactive species **2**. As a consequence, the reaction is self-maintained and **2** never reaches a concentration high enough to make step (*vi*) faster than the formation of **4**.

Table 2 Selected bond distances (Å) and angles (°) for complex **3′**

Pt1–S1	2.307(2)	Pt2–S1	2.313(3)
Pt1–N1	2.034(8)	Pt2–N4	2.033(8)
Pt1–N2	1.945(6)	Pt2–N5	1.971(10)
Pt1–N3	2.027(10)	Pt2–N6	2.024(9)
S1–C1	1.822(10)		
S1–Pt1–N1	103.4(2)	S1–Pt2–N4	104.2(3)
S1–Pt1–N2	176.4(1)	S1–Pt2–N5	172.5(3)
S1–Pt1–N3	95.5(2)	S1–Pt2–N6	94.7(2)
N1–Pt1–N2	80.1(3)	N4–Pt2–N5	79.4(4)
N1–Pt1–N3	161.0(3)	N2–Pt2–N6	161.1(4)
N2–Pt1–N3	80.9(3)	N5–Pt2–N6	82.0(3)
Pt1–S1–C1	100.8(3)	Pt2–S1–C1	104.0(3)
Pt1–S1–Pt2	121.7(2)		

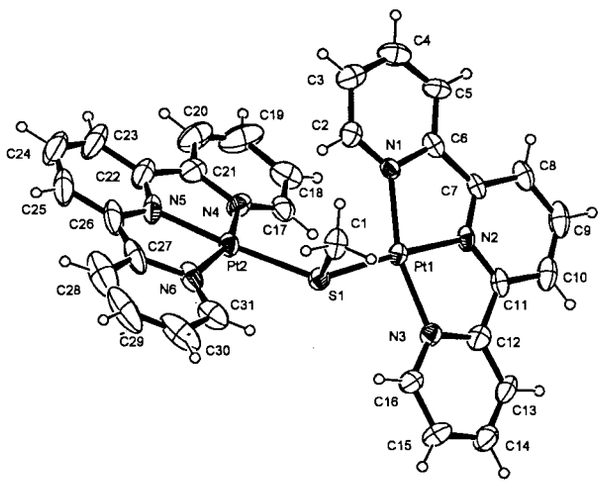


Fig. 1 An ORTEP [14] view of the $[Pt_2(\mu\text{-SMe})(terpy)_2]^{3+}$ cation showing thermal ellipsoids at 30% probability and the atom numbering scheme.

Crystal structure of $[Pt_2(\mu\text{-SMe})(terpy)_2][ClO_4]_3$ 3′

Selected bond distances and angles are reported in Table 2 and Fig. 1 shows the ORTEP [14] drawing of the complex cation. The asymmetric unit is built up by the $[Pt_2(\mu\text{-SMe})(terpy)_2]^{3+}$ cation and three perchlorate anions. The cation consists of two platinum(II) atoms co-ordinated to a terdentate terpyridine ligand and sharing, as fourth ligand, the sulfur of the methanethiolate anion. The co-ordination geometry of both platinum atoms is considerably distorted from perfect square planar

owing to the constraints of the terpyridine ligand which give rise to a narrowing of N–Pt–N(*cis*) angles to 79.4°. These distortions are associated with a significant shortening of Pt–N (middle) distances to 1.945 and 1.971 Å with respect to the other Pt–N distances ranging from 2.024 to 2.033 Å. This is in agreement with the structural data of similar complexes of Pt^{II} with ter- or tetra-dentate ligands[7,15–18] and with data derived from a sample of 31 structures of platinum(II) complexes, containing at least two pyridine ligands, which show that the shortening of the Pt–N distance is always associated with a strained or very strained environment characterized by N(py)–Pt–X(*cis*) angles ≈ 80°, independently of the nature of the X atom.[15]

The Pt–S^- distances of 2.31 Å, on average, are in perfect agreement with those observed in the structures of similar (2,2′:6′,2″-terpyridine)thiolatoplatinum(II) compounds[7] and other square planar platinum(II) complexes.[19–21] The planes defined by the Pt and the four co-ordinated atoms, Pt1, N1, N2, N3, S1 and Pt2, N4, N5, N6 and S1, form an angle of 50.7(2)°. No intermolecular interactions shorter than the sum of van der Waals radii are observed.

Binuclear platinum(II) complexes with a bridging thiolate have been reported before,[9a,b,22] but **3′** represents the first reported species with two Pt(terpy) units bridged by that group. Moreover only a few compounds containing a single thiolate bridge between two transition metal centres have been structurally characterized.[23]

Experimental

The complexes [Pt(terpy)(OH)][BF_4],[8a] [Pt(terpy)(OH)][ClO_4][8b] and [Pt(terpy)Cl]Cl·2H_2O[24] were prepared by literature methods. The amino acid derivatives **Ia**, **Ib** and **Ic** were prepared as we reported before.[2] For the synthesis of **Id** and **Ie** a literature procedure was followed.[11]

All chemicals and solvents were reagent grade used without further purification. Elemental analyses were performed using a Carlo Erba model EA1110 instrument. The FT-IR spectra were recorded on a Nicolet 510P FT-IR instrument in KBr, proton NMR spectra on a Bruker AM 200 spectrometer with $SiMe_4$ as internal standard, MS-FAB (fast atom bombardment) spectra by a Hewlett Packard MS engine HP5989 A mass spectrometer using a *p*-nitrobenzyl alcohol matrix, the MS-Maldi spectrum by a Hewlett Packard Maldi-Toff G2025A spectrometer and electronic spectra on a Perkin-Elmer Lambda 15 spectrophotometer. Conductivity measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and a CDC 334 immersion cell. pH Measurements were made with a Hanna HI-8417 Digital pH-meter.

Preparations

[Pt(terpy)(OH_2)][BF_4]$_2$ 2. To a bright orange solution of [Pt(terpy)(OH)][BF_4] (0.2 g, 0.37 mmol) in water (10 mL), 2.5 mL of 0.15 mol dm^{-3} HBF_4 were added dropwise. The solution promptly turned pale yellow: after 10 min of stirring it was taken to dryness to give product **2** as an orange powder that was dried *in vacuo* over P_2O_5 (0.205 g, 90%) (Found: C, 29.65; H, 2.2; N, 7.3. $C_{15}H_{13}B_2F_8N_3OPt$ requires C, 29.75; H, 2.2; N, 7.4%). IR: *ν*(co-ordinated H_2O) 1653 cm^{-1}. FAB$^+$MS: *m*/*z* 446, [Pt(terpy)(OH_2)]$^{+\bullet}$; and 428, [Pt(terpy)]$^+$. UV/Vis: λ_{max}/nm (MeOH) 339 (*ε*/dm^3 mol^{-1} cm^{-1} 6200), 326 (5600), 308 (6400) and 280 (12600); ^{1}H NMR (CD_3NO_2): *δ* 7.9, 8.2–8.8 (2m, 9 H) and 9.3 (d, H^6 + $H^{6''}$, $^3J_{PtH}$ = 32 Hz).

Reaction between [Pt(terpy)(OH_2)][BF_4]$_2$ 2 and Ia in 1:1 ratio. To an orange solution of the aqua species **2** (50 mg, 0.08 mmol) in 15 mL of MeOH, 27 mg (0.08 mmol) of **Ia** were added. Under stirring at room temperature, the precipitation of a green solid was completed in 1 h. The precipitate was filtered off, washed with water and dried *in vacuo* over P_2O_5, to obtain complex **3** as a green-yellow powder (yield: 75 mg, 80%). The remaining solution was completely evaporated under reduced pressure and the residue recrystallized from EtOH–water to form a white powder, which was analysed as a 1:1 mixture of unchanged **Ia** and the corresponding heterocyclic derivative **IIa**, on the basis of ^{1}H NMR (see Table 1).

Compounds IIa–IIe. *Method (a).* When the reagents **2** and **Ia** were mixed in a 2:1 molar ratio under the same conditions as the previous reaction, the only Pt containing product was complex **3**, while **Ia** was converted into **IIa** (yield: 70%). Under the same conditions, **Ib** was converted into **IIb** (70%), **Ic** into **IIc** (68%), **Id** into **IId** (74%) and **Ie** into **IIe** (72%).

Method (b). To an orange solution of [Pt(terpy)(OH)][BF_4] **1** (50 mg, 0.095 mmol) in 15 mL of MeOH an equimolar amount of **Ia** was added: the solution immediately turned purple. It was stirred at 0 °C until the precipitation of complex **4** as a purple solid was completed (*ca.* 30 min). A second aliquot of product **4** was precipitated on reducing the volume of the remaining purple solution and adding diethyl ether. It was washed with water and dried *in vacuo* over P_2O_5 (yield: 40 mg, 75%). The remaining colourless solution was taken to dryness under reduced pressure and the oily residue recrystallized with EtOH and water to give a white solid of pure product **IIa** (yield: 85%). Following the same method, **Ib** was converted into **IIb** (75%), **Ic** into **IIc** (74%), **Id** into **IId** (90%) and **Ie** into **IIe** (85%). Compound **IIa** (Found: C, 51.1; H, 4.6; N, 15.05; S, 11.5. $C_{12}H_{13}N_3O_3S$ requires C, 51.3; H, 4.7; N, 15.0; S, 11.5%): IR *ν*(N–H) 3293, *ν*(C=O) 1692, *ν*(C=N) 1624 and *ν*(C=S) 1179 cm^{-1}; FAB$^+$MS: *m*/*z* 280, [MH]$^+$; Maldi *M* 279; for ^{1}H NMR in each case see Table 1. Compound **IIb** (Found: C, 52.9; H, 5.4; N, 14.1; S, 10.0. $C_{13}H_{15}N_3O_3S$ requires C, 53.2; H, 5.15; N, 14.3; S, 10.9%): IR *ν*(N-H) 3316, *ν*(C=O) 1690, *ν*(C=N) 1614 and *ν*(C=S) 1179 cm^{-1}. Compound **IIc** (Found: C, 61.8; H, 5.2; N, 11.1; S, 8.3. $C_{19}H_{19}N_3O_3S$ requires C, 61.8; H, 5.2; N, 11.4; S, 8.7%): IR *ν*(N–H) 3310, *ν*(C=O) 1697, *ν*(C=N) 1624 and *ν*(C=S) 1182 cm^{-1}. Compound **IId** (Found: C, 55.9; H, 4.3; N, 14.3; S, 16.5. $C_9H_8N_2OS$ requires C, 56.2; H, 4.2; N, 14.6; S, 16.7%): IR *ν*(C=N) 1609 and *ν*(C=S) 1184 cm^{-1}. Compound **IIe** (Found: C, 36.5; H, 4.3; N, 21.3; S, 24.0. $C_4H_6N_2OS$ requires C, 36.9; H, 4.65; N, 21.5; S, 24.6%): IR *ν*(C=N) 1630 and *ν*(C=S) 1180 cm^{-1}.

[Pt(terpy)(SMe)][BF_4] 4. The complex [Pt(terpy)Cl]Cl·2H_2O (50 mg, 0.09 mmol) was dissolved in 15 ml of MeOH and solid NaSMe (6.5 mg, 0.09 mmol) added. The solution immediately turned deep purple and NaCl started to precipitate. The solid was filtered off and the solution concentrated to dryness under reduced pressure. The purple solid was washed with water and diethyl ether and then redissolved in MeOH (10 mL); 2.7 mL of a 0.05 mol dm^{-3} solution of $NaBF_4$ were added to precipitate [Pt(terpy)(SMe)][BF_4] **4**. The purple solid was finally separated by centrifugation, washed with MeOH and dried *in vacuo* over P_2O_5 (yield: 35 mg, 70%) (Found: C, 33.95; H, 2.3; N, 7.5; S, 5.6. $C_{16}H_{14}BF_4N_3PtS$ requires C, 34.2; H, 2.5; N, 7.5; S, 5.7%). $\Lambda_{eq}(CH_3NO_2)$ = 77 Ω^{-1} cm^2 mol^{-1}. FAB$^+$MS: *m*/*z* 475, [Pt(terpy)(SMe)]$^+$; and 428, [Pt(terpy)]$^+$. UV/Vis: λ_{max}/nm (MeOH) 346 (*ε*/dm^3 mol^{-1} cm^{-1} 6000), 330 (6400) and 315 (6600). ^{1}H NMR (CD_3OD): *δ* 7.9, 8.3–8.5 (2m, 9 H), 9.5 (d, H^6 + $H^{6''}$, $^3J_{PtH}$ = 45) and 2.15 (s, SMe, $^3J_{PtH}$ = 41 Hz, 1:4:1). NMR Experiments showed that **4** is also formed in the reaction between the aqua complex **2** and an excess of NaSMe in CD_3OD.

[Pt_2(μ-SMe)(terpy)$_2$][BF_4]$_3$ 3. The complex [Pt(terpy)(SMe)][BF_4] **4** (45 mg, 0.8 mmol) was dissolved in 20 ml of MeOH to give a purple solution. An equimolar amount of solid [Pt(terpy)(OH_2)][BF_4]$_2$ **2** (50 mg) was added. In 30 min the mixture clarified and [Pt_2(μ-SMe)(terpy)$_2$][BF_4]$_3$ **3** precipitated as a green-yellow solid that was collected, washed with water and dried *in vacuo* over P_2O_5 (yield: 65 mg, 70%) (Found: C, 31.75;

H, 2.15; N, 7.5; S, 2.55. $C_{31}H_{25}B_3F_{12}N_6Pt_2S$ requires C, 31.9; H, 2.2; N, 7.2; S, 2.75%). $\Lambda_{eq}(CH_3NO_2) = 271\ \Omega^{-1}\ cm^2\ mol^{-1}$. FAB$^+$MS: *m*/*z* 475, [Pt(terpy)(SMe)]$^+$; and 428, [Pt(terpy)]$^+$. UV/Vis: λ_{max}/nm (MeOH) 345 (ε/dm^3 mol^{-1} cm^{-1} 7400), 329 (9600), 315 (8800) and 279 (17000). ^{1}H NMR (CD_3NO_2): δ 7.8, 8.3–8.7 (2m, 9 H); 9.7 (d, H^6 + H$^{6''}$, $^3J_{PtH} = 37$) and 2.9 (s, μ-SMe, $^3J_{PtH} = 36$ Hz, 1 : 8 : 18 : 8 : 1).

$[Pt_2(\mu\text{-SMe})(terpy)_2][ClO_4]_3$ 3′. 25.4 mL of an orange aqueous solution of 7×10^{-3} mol dm^{-3} $[Pt(terpy)(OH_2)][ClO_4]_2$, generated *in situ* from [Pt(terpy)(OH)][ClO_4] and $HClO_4$ in equimolar amounts, were added to a solution of the ligand **Ia** (60 mg, 0.18 mmol) in 10 mL of MeOH. After a few minutes the solution clarified and the green product **3′** precipitated. The reaction was complete in *ca.* 2 h. The solid was filtered off and washed with water (yield: 100 mg, 95%) (Found: C, 30.95; H, 2.15; N, 7.05; S, 2.75. $C_{31}H_{25}Cl_3N_6O_{12}Pt_2S$ requires C, 30.95; H, 2.1; N, 7.0; S, 2.7%). The ^{1}H NMR signals are identical with those of complex **3**.

[Pt(terpy){S=C(SMe)NMeNHC(O)CH_2NHC(O)OCH_2Ph}]-$[CF_3SO_3]_2$ A_1. The complex [Pt(terpy)(OH)][BF_4] **1** (24 mg, 0.045 mmol) was dissolved in 2 ml of MeOH and the pH was adjusted to 1 using CF_3SO_3H. When an equimolar amount of **Ia** was added the solution turned bright yellow. After stirring for a few minutes $\mathbf{A_1}$ was precipitated as a yellow solid by adding diethyl ether (yield: 30 mg, 70%) (Found: C, 34.0; H, 2.7; N, 8.1; S, 11.9. $C_{30}H_{28}F_6N_6O_9S_4Pt$ requires C, 34.2; H, 2.7; N, 8.0; S, 12.2%). δ_H (CD_3NO_2) 3.15 (SCH_3, s), 3.71 (NCH_3, s), 4.04 [$C_\alpha H_2$, d, $^3J(CH_2–NH) = 5.8$], 5.12 (CH_2Ph, s), 5.55 (NHC$_\alpha$, br s), 7.2–8.6 (aromatic protons), 8.80 [H^6, d, J(Pt–H) = 40.0 Hz] and 9.94 (NHN, s).

Crystal structure determination of complex 3′

Crystal data. $C_{31}H_{25}Cl_3N_6O_{12}Pt_2S$, $M = 1202.16$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.538(1)$, $b = 21.802(2)$, $c = 13.969(1)$ Å, $\beta = 106.38°$, $U = 3663.5(5)$ Å^3, $T = 295$ K, $Z = 4$, $D_c = 2.180$ g cm^{-3}, μ(Mo-Kα) = 79.78 cm^{-1}, $F(000) = 2288$, 8473 reflections measured ($2 \leq \theta \leq 30°$), 7935 unique ($R_{int} = 0.026$), corrected for Lorentz-polarization and absorption effects (ψ-scan method, minimum transmission factor = 0.820), and used in all calculations. Final $R\ [F^2 \geq 2\sigma(F^2)] = 0.051$ and $wR(F^2) = 0.14$. Programs used DIRDIF,[25] SHELXL 97[26] and PARST.[27]

CCDC reference number 186/1648.

See http://www.rsc.org/suppdata/dt/1999/3877/ for crystallographic files in .cif format.

Acknowledgements

This work was supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica in the framework of the Project "Pharmacological and Diagnostic Properties of Metal Complexes" (co-ordinator Professor G. Natile). We thank Mr M. Fratta for the elemental analyses and technical assistance and Mr E. Angeli for recording FAB$^+$MS spectra.

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Paper 9/04859F