ELSEVIER

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 315 (2001) 196–204

Inorganica Chimica Acta

Studies on Pt–S bonds. Methylsulfanyl-acetato, -benzoato and -phenolato complexes of the $Pt^{(II)}(PPh_3)_2$ and $Pt^{(II)}$(dppe) moieties and the crystal structure of bis-triphenylphosphine(methylsulfanylacetato)platinum(II) nitrate

Alessandro Pasini [a,*1], Silvia Rizzato [b,*2], Daniele De Cillis [a]

[a] *Dipartimento di Chimica Inorganica Metallorganica e Analitica and CNR Centre, via Venezian 21, 20133 Milan, Italy*
[b] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via Venezian 21, 20133 Milan, Italy*

Received 15 July 2000; accepted 24 January 2001

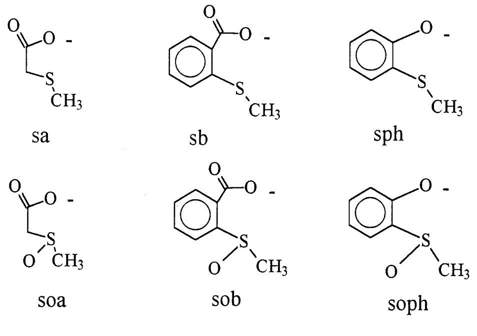
Abstract

Bis-triphenylphosphine and bis(diphenylphosphine)ethane platinum(II) complexes with the chelating anionic ligands methylsulfanyl-acetato (sa), -benzoato (sb) and -phenolato (sph) have been synthesised and characterised. Infrared and multinuclear NMR spectra are in accordance with chelation of these ligands through the sulfur and the anionic oxygen atoms. The structure of $[Pt(PPh_3)_2(sa)]NO_3$ has been determined through X-ray diffraction and confirms chelation of sa. ^1H NMR spectra suggest that the chelate ring in this compound is rigid, with the same conformation found in the solid state, while in the analogous dppe complex both chelate rings undergo inversion of conformation at room temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Platinum complexes; Sulphur ligand complexes

1. Introduction

In the past years we have been studying some amine platinum(II) complexes with the chelating ligands L of Scheme 1, in which the donor sites are sulfur and anionic oxygen atoms [1–4].



Scheme 1.

These studies were performed in order to obtain insight into some properties of Pt–S bonds, because of their relevance to the chemistry, biochemistry and pharmacodynamics of *cis*-platin and its analogues [5]. However, there are other reasons of interest in the chemistry of the interaction of S-containing substrates with transition metal ions, such as catalysis, catalysts poisoning, hydrodesulfurisation and Clauss chemistry (conversion of H_2S to elemental sulfur). We therefore decided to expand the scope of the coordination chemistry of the ligands of Scheme 1. This paper reports some of the studies on the Pt–phosphine system, i.e. the synthesis and characterisation of compounds **1**–**6** of Scheme 2, as well as the X-ray structure of **1**.

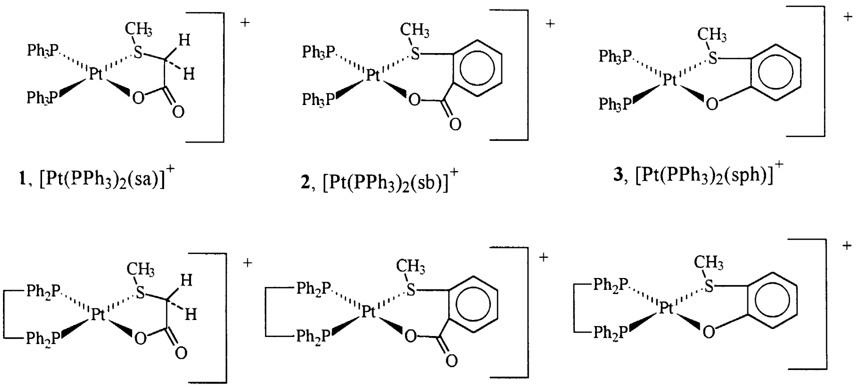
2. Experimental

Analyses (C, H, N) were done at the Microanalytical Laboratory, the Milan University, and are reported in Table 1. IR spectra were recorded with a JASCO FTIR

---

[1] *Corresponding author. Tel.: +39-02-266 80676; fax: +39-02-236 2748; e-mail: alessandro.pasini@unimi.it
[2] *Corresponding author. E-mail: silvia@csmtbo.mi.cnr.it

PII: S0020-1693(01)00353-X



1, $[Pt(PPh_3)_2(sa)]^+$
2, $[Pt(PPh_3)_2(sb)]^+$
3, $[Pt(PPh_3)_2(sph)]^+$
4, $[Pt(dppe)(sa)]^+$
5, $[Pt(dppe)(sb)]^+$
6, $[Pt(dppe)(sph)]^+$

Scheme 2.

5300, while ^1H, proton decoupled ^{31}P and ^{195}Pt NMR spectra were obtained with a Bruker Avance DRX 300 instruments with Me_4Si, H_3PO_4 and Na_2PtCl_6, respectively, as external references.

All chemicals were of reagent grade. *cis*-$[PtCl_2(PPh_3)_2]$ [6], $[PtCl_2(dppe)]$ [7] and *cis*-$[Pt(NH_3)_2(NO_3)_2]$ [8] were obtained by literature methods. 2-(Methylsulfanyl)phenol (Aldrich) and methylsulfanyl acetic acid (Fluka) were used as received, the other ligands were prepared as described elsewhere [2].

2.1. Preparation of the complexes

cis-Dinitratobis(triphenylphosphine)platinum(II), *cis*-$[Pt(NO_3)_2(PPh_3)_2]$. A twofold excess of $AgNO_3$ (1.213 g, 6.6 mmol) was added to a solution of 1.361 g (1.64 mmol) of $[PtCl_2(PPh_3)_2]$ in 50 ml of CH_2Cl_2. The slurry was refluxed in the dark for 6 h, filtered and the filtrate concentrated to 5 ml. Addition of diisopropyl ether gave 1.029 g (75%) of a white precipitate.

Bis(diphenylphoshine)ethanedinitratoplatinum(II), $[Pt(dppe)(NO_3)_2]$. It was prepared by the same procedure, starting from 0.625 g (0.94 mmol) of $[PtCl_2(dppe)]$ and 0.644 g (3.8 mmol) of $AgNO_3$ in 50 ml of CH_2Cl_2. Yield 87%, 0.590 g.

Methylsulfanylacetatobis(triphenylphosphine) platinum(II) nitrate, $[Pt(PPh_3)_2(sa)]NO_3$ (**1**).

1. Hsa (0.017 g, 0.155 mmol) was treated with 1.55 ml of 0.1 M KOH, evaporated to dryness under reduced pressure, and mixed with 0.136 g (0.161 mmol) of *cis*-$[Pt(NO_3)_2(PPh_3)_2]$ in 20 ml of CH_2Cl_2. The solution was refluxed for 8 h in the dark, hot filtered and concentrated to drops under reduced pressure. The product was obtained by addition of diisopropyl ether. Yield 67%, 0.090 g.
2. One-pot reaction. 0.025 g of Ag_2CO_3 (0.091 mmol) and 0.031 g (0.182 mmol) of $AgNO_3$ were added to a solution of *cis*-$[PtCl_2(PPh_3)_2]$ (0.138 g, 0.174 mmol) and Hsa (0.018 g, 0.174 mmol) in 25 ml of CH_2Cl_2. This slurry was stirred in the dark at room temperature for 8 h, filtered and concentrated in vacuo to 5 ml. 0.115 g (74%) of a white solid was obtained by addition of diisopropyl ether.

The other complexes were prepared by similar methods, in 60–80% yields, $[Pt(PPh_3)_2(sb)]NO_3$ (**2**), could not obtained by the one-pot procedure.

Diamminemethylsulfanylacetatoplatinum(II) nitrate, $[Pt(NH_3)_2(sa)]NO_3$. Lithium hydroxide (0.013 g, 0.543 mmol) and *cis*-$[Pt(NH_3)_2(NO_3)_2]$ [8] (0.202 g, 0.569 mmol) were added to 0.060 g of Hsa (0.569 mmol) in 10 ml of water. The solution was heated at 50°C for 5 h, filtered and evaporated to dryness under reduced pressure. The residue was washed twice with methanol to remove $LiNO_3$ and dried in vacuo. Yield 70%, 0.143 g.

2.2. Crystal structure of $[Pt(PPh_3)_2(sa)]NO_3\cdot 1/2H_2O\cdot 1/4CH_2Cl_2$

Colourless crystals of compound **1**, suitable for X-ray diffraction studies, were obtained by slow diffusion of diisopropyl ether into a concentrated CH_2Cl_2 solution. A crystal was mounted at room temperature (293 K) on an Enraf–Nonius CAD-4 diffractometer, and 25 reflec-

Table 1
Elemental analyses, % (required values in parentheses)

Compound	C	H	N
$[Pt(NO_3)_2(PPh_3)_2]$	50.0 (51.3)	3.7 (3.6)	3.2 (3.3)
$[Pt(dppe)(NO_3)_2]$	43.3 (43.5)	3.4 (3.4)	3.8 (3.8)
$[Pt(PPh_3)_2(sa)]NO_3\cdot H_2O$	51.7 (51.8)	4.3 (4.1)	1.6 (1.6)
$[Pt(PPh_3)_2(sb)]NO_3\cdot H_2O$	54.4 (54.6)	3.9 (4.1)	1.4 (1.5)
$[Pt(PPh_3)_2(sph)]NO_3\cdot H_2O$	55.3 (55.0)	4.4 (4.2)	1.3 (1.5)
$[Pt(dppe)(sa)]NO_3\cdot H_2O$	44.9 (44.7)	4.2 (4.0)	1.6 (1.8)
$[Pt(dppe)(sb)]NO_3\cdot 2H_2O$	47.4 (47.6)	4.0 (4.1)	1.8 (1.6)
$[Pt(dppe)(sph)]NO_3\cdot H_2O$	49.0 (48.8)	4.1 (4.1)	1.5 (1.7)
$[Pt(NH_3)_2(sa)]NO_3$	9.1 (9.1)	2.6 (2.8)	10.4 (10.6)

Table 2
Crystallographic data and structure refinement for compound **1**

Compound	**1**
Empirical formula	$[C_{39}H_{35}O_2P_2PtS](NO_3)\cdot 1/4CH_2Cl_2\cdot 1/2H_2O$
Formula weight	917.01
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	
a (Å)	10.599(4)
b (Å)	36.749(3)
c (Å)	19.389(3)
β (°)	91.95(2)
V (Å^3)	7548(3)
Z	8
$D_{calc.}$ (g cm^{-3})	1.613
Absorption coefficient (mm^{-1})	3.939
θ range for data collection (°)	3–25
Index ranges	$-12 \leq h \leq 12$, $0 \leq k \leq 43$, $0 \leq l \leq 22$
Reflections collected	13 797
Independent reflections	7220 [$R_{int} = 0.0455$]
Data/restraints/parameters	7220/775/884
Goodness-of-fit on F^2	1.087
Observed reflections criterion	$I > 1\sigma(I)$
Final R indices [a,b] (observed data)	$R_1 = 0.0683$, $wR_2 = 0.1453$
Weighting parameters, a,b [c]	0.0729, 87.1083
Largest difference peak and hole (e Å^3)	1.344 and −1.076

[a] $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma\, wF_o^4]^{1/2}$.

[c] Weighting: $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 3
^{31}P NMR spectral data [a]

Compound	δ ($J_{Pt–P}$)	δ ($J_{Pt–P}$)	$J_{P–P}$
$[PtCl_2(PPh_3)_2]$	14.88 (3672)		
$[Pt(NO_3)_2(PPh_3)_2]$	3.62 (4010)		
1	5.51 (3561) [b]	17.35 (3326) [c]	22.4
2	4.97 (3581) [b]	18.64 (3332) [c]	22.2
3	5.52 (3311) [b]	19.22 (3390) [c]	22.8
$[PtCl_2(dppe)]$	41.73 (3619)		
$[Pt(dppe)(NO_3)_2]$	32.94 (3942)		
4	34.64 (3307) [b]	45.97 (3273) [c]	7.9
5	35.99 (3377) [b]	44.32 (3300) [c]	6.4
6	34.41 (3087) [b]	43.54 (3311) [c]	9.2

[a] $CHCl_3$-d solutions; δ values in ppm from H_3PO_4; $J_{Pt–P}$ (in parentheses) and $J_{P–P}$ in Hz.

[b] *trans* to O.

[c] *trans* to S. For these assignments see text.

tions within $8.0 \leq \theta \leq 11.0°$ were centred using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 2. Crystal data and details associated with data collection and structure refinement are also given in Table 2. An ω-scan mode was used with a scan interval of 1.4°, with a θ range of 3–25°. Intensities were checked by monitoring three standard reflections every 3 h; a decay of 7% was observed. The diffracted intensities were corrected for Lorentz, polarisation, decay and background effects. An empirical absorption correction was applied, based on ψ-scans of three suitable reflections having χ values close to 90° (ψ 0–360°, every 10°). The structure was solved by a combination of direct methods (SIR-97) [9] and difference Fourier method and refined by full-matrix least-squares on F^2 (SHELX-97) [10]. Anisotropic thermal displacement parameters were assigned to all non-hydrogen atoms but the CH_2Cl_2 molecule with half-occupancy. All hydrogen atoms were located on calculated positions and introduced in the final stages of the refinement as fixed atom contributions riding on their parent atoms. Molecular drawings were produced with SCHAKAL-99 program [11].

3. Results and discussion

3.1. Preparation and characterisation of the complexes

The nitrato complexes *cis*-$[Pt(NO_3)_2(PPh_3)_3]$ and $[Pt(dppe)(NO_3)_2]$ were easily obtained by reaction of the dichloro derivatives with an excess of $AgNO_3$. The monodentate O-coordinate nature of the nitrato group is confirmed by the absence, in their IR spectra, of a band around 1380 cm^{-1}, characteristic of ionic nitrate, and the presence of three bands at about 1500, 1270 and 980 cm^{-1} attributable to monodentate NO_3 group [12]. ^{31}P NMR spectral data are given in Table 3. The increase of about 300 Hz of the ^{31}P–^{195}Pt coupling constants, on passing from the dichloro to the dinitrato complexes, is in accordance with the literature data [13] and it is due to the lower *trans* influence of the NO_3 ligand.

Two routes were employed to synthesise complexes **1–6**: reaction of the nitrato complexes with the potassium salt of L and a 'one-pot' method, mixing in CH_2Cl_2 *cis*-$[PtCl_2(PPh_3)_2]$, or $[PtCl_2(dppe)]$, $AgCO_3$, $AgNO_3$ and HL, according to (Phos = PPh_3 or $\frac{1}{2}$ dppe):

$$[PtCl_2(Phos)_2] + 1/2Ag_2CO_3 + AgNO_3 + HL$$
$$\rightarrow [PtL_2(Phos)_2] + 2AgCl + CO_2$$

This latter method, however, failed for the preparation of **2**.

The white to pale yellow complexes are air stable and slightly hygroscopic and were obtained with some water of crystallisation, as suggested by analytical data (Table 1), and by a broad IR band in the 3500 cm^{-1} region. They are soluble in organic solvents.

When the above reactions were carried out with the sulfoxide ligands of Scheme 1, we obtained intractable mixtures in which the starting dichloro or dinitrato complexes were the predominant species (^{31}P NMR evidence). We have previously found that the sulfoxide moiety of these ligands are bound to the Pt$^{(II)}$(en) species less strongly than the thioether groups [2–4], and it may be that the presence of a *trans* phosphine further destabilises the Pt–sulfoxide bond. Only in the case of L = soph, ^{31}P NMR spectra of these mixtures showed the presence of minor amounts of species whose spectral parameters can be attributed to $[Pt(PPh_3)_2(soph)]^+$ ($\delta = 4.3$, $J_{Pt–P} = 3405$ Hz and 15.8 ppm, $J_{Pt–P} = 3248$, $J_{P–P} = 23$ Hz) and $[Pt(dppe)(soph)]^+$ ($\delta = 31.6$, $J_{Pt–P} = 3136$ Hz and 40.55 ppm, $J_{Pt–P} = 3097$, $J_{P–P} = 7.5$ Hz). This is in accordance with our previous finding that the soph chelate ring is the most stable between those of the sulfoxides of Scheme 1 [3]. Attempts to isolate these complexes, however, failed.

Table 4
^{1}H NMR data [a]

	SCH_3 $J_{Pt–H}/J_{P–H}$	SCH_2	
1	2.21	3.35 (d, $J_{H–H}$, 17)	4.69 (d, $J_{H–H}$, 17)
	39/3.5	36.5/4.1	
2	2.79		
	30/4.5		
3	2.24		
	30/4.5		
4	1.96	3.6 (br)	4.0 (br)
	33/3.2	see text	
5	2.74		
	29/3.7		
6	1.89		
	34/3.5		
$[Pt(NH_3)_2(sa)]NO_3$ [b]	2.52	3.50 (d, $J_{H–H}$, 17)	3.86 (d)
	48	47	
$[Pt(en)(sa)]NO_3$ [b,c]	2.80	3.5	3.85
	48	47	
Hsa	2.21	3.21	
Hsb	2.48		
Hsph	2.35		

[a] $CHCl_3$-d solutions; δ values in ppm versus Me_4Si, coupling constants in Hz; the doublets due to H–H coupling are indicated as d, with *J* values in parentheses.

[b] H_2O-d_2 solutions.

[c] See Refs. [2,3].

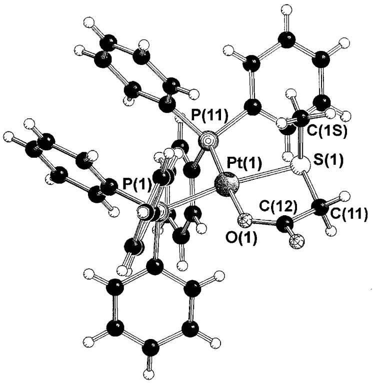


Fig. 1. A SCHAKAL view of one of the two independent cations in **1**.

For comparison purposes we have synthesised $[Pt(NH_3)_2(sa)]NO_3$. Characterisation data are given in Tables 1 and 4. Interestingly, this complex is less stable than the analogous compound with chelating ethylenediamine, $[Pt(en)(sa)]^+$ [2,3], if an excess of sa^- is used in the synthesis, ammonia is released and a white product, insoluble in all solvents, is obtained, whose elemental analysis is consistent with the formula $[Pt(sa)_2]$. This confirms the weakening of the Pt–NH_3 bonds *trans* to thioethers: for instance also methionine releases ammonia from cisplatin yielding [Pt(methionine)$_2$], a stable metabolite of cisplatin [14].

The IR spectra of complexes **1**–**6** show a sharp band around 1380 cm^{-1}, assigned to the ionic nitrate group. For **1**, **2**, **4** and **5** coordination of the carboxylato moiety is suggested by a band in the range 1650 and 1630 cm^{-1} for the sa and sb derivatives respectively, assigned to ν_{asym} of coordinated COO [1–3]. These facts, together with the non-equivalence of the phosphorus atoms and the appearance of Pt–H coupling of the SCH_3 protons in the ^{31}P and ^{1}H NMR spectra (Tables 3 and 4), are in accordance with chelation of sa, sb and sph.

For **1** chelation of sa was confirmed by an X-ray structure determination.

3.2. Structure of $[Pt(PPh_3)_2(sa)](NO)_3$ (1)

The crystal structure of **1** consists of the packing of $[Pt(PPh_3)_2(sa)]^+$ cations and NO_3^- anions in a 1:1 ratio with normal non-bonding interactions. Molecules of CH_2Cl_2 and water are also included in the crystal.

A SCHAKAL view of one of the two independent cations is shown in Fig. 1, relevant bond distances and angles are reported in Table 5. The two independent cationic complexes are very similar. The platinum ion is coordinated to two P atoms and to the S and O (carboxylato) atoms of chelating sa. The coordination geometry is quasi-planar, the Pt, P(1), P(11), S(1) and O(1) atoms lie within 0.02–0.04 Å out of the best plane defined by these atoms. The deviation from the idealised square coordination arises from the obliged bite angle of sa, 84°, a value in the range of that of other Pt(II) complexes with similar chelating ligands [15,16]. The presence of *cis*-bulky phosphines may also contribute to such a deviation, as suggested for other *cis*-Pt$^{(II)}$(PPh$_3$)$_2$ complexes [15,17,18]. The P–Pt–P angle (97°) is similar to that observed in other *cis*-Pt(PPh$_3$)$_2$ complexes which present stacking of two phenyl rings [16], as found in **1**.

Table 5
Selected bond distances (Å) and angles (°) in compound **1**

Pt(1)–O(1)	2.058(11)	O(1)–Pt(1)–P(1)	84.8(3)
Pt(1)–P(11)	2.244(4)	P(11)–Pt(1)–P(1)	97.17(15)
Pt(1)–P(1)	2.310(4)	O(1)–Pt(1)–S(1)	84.0(3)
Pt(1)–S(1)	2.334(4)	P(11)–Pt(1)–S(1)	94.08(15)
S(1)–C(1S)	1.81(2)	C(1S)–S(1)–Pt(1)	101.1(7)
S(1)–C(11)	1.814(17)	C(11)–S(1)–Pt(1)	96.5(6)
C(11)–C(12)	1.52(2)	O(1)–C(12)–C(11)	116.9(14)
C(12)–O(12A)	1.205(17)	C(12)–O(1)–Pt(1)	122.8(10)
C(12)–O(1)	1.274(18)	C(12)–C(11)–S(1)	113.8(11)
Pt(2)–O(2)	2.069(12)	O(2)–Pt(2)–P(2)	84.2(4)
Pt(2)–P(22)	2.237(4)	P(22)–Pt(2)–P(2)	99.25(15)
Pt(2)–P(2)	2.308(4)	O(2)–Pt(2)–S(2)	83.4(4)
Pt(2)–S(2)	2.335(4)	P(22)–Pt(2)–S(2)	93.17(15)
S(2)–C(2S)	1.780(17)	C(2S)–S(2)–Pt(2)	103.0(6)
S(2)–C(21)	1.785(17)	C(21)–S(2)–Pt(2)	95.4(6)
C(21)–C(22)	1.48(2)	O(2)–C(22)–C(21)	119.8(16)
C(22)–O(22A)	1.24(2)	C(22)–O(2)–Pt(2)	117.7(11)
C(22)–O(2)	1.321(19)	C(22)–C(21)–S(2)	112.6(12)

Table 6
^{195}Pt NMR of compounds $[Pt(PPh_3)_2L]^+$ and $[Pt(dppe)L]^+$ [a]

L	$Pt(PPh_3)_2$	Pt(dppe)
sa	−4446 (3554, 3324)	−4556 (3305, 3275)
sb	−4312 (3576, 3335)	−4548 (3374, 3294)
sph	−4451 (3317, 3309)	−4569 (3309, 3090)

[a] $CHCl_3$-d solutions; δ values from Na_2PtCl_6; all spectra are doublets of doublets, see text; J_{Pt-P} in Hz, are given in parentheses.

The Pt–O bond is longer than that of the analogous cationic complex $[Pt(en)(soa)]^+$ [1], an effect of the *trans* influence of the PPh_3 group, higher than that of ethylenediamine. Interestingly also the Pt–S bond in **1** is longer than that of the en–soa derivative [1], again this must be a reflection of the *trans* influence of phosphine since our previous reactivity studies on the amine complexes with these ligands [2–4] and the instability of the mixed phosphine sulfoxide derivatives reported above, suggest that the Pt–sulfoxide bonds are weaker than those between Pt and thioethers. Finally the Pt–P bond *trans* to S is longer than that *trans* to O.

The chelate ring of sa is twisted and the methyl group is axial, a feature not uncommon in five-member chelate rings with a methyl group bound to an S [1,15] or a N (of *N*-methyl amino acids [19,20]) donor atom.

3.3. NMR studies

^{31}P NMR data are collected in Table 3. The different chemical shift values shown by the PPh_3 and the dppe complexes are related to the presence of the five-membered chelate ring of dppe [21,22]. The spectra of compounds **1–6** show, as expected, two doublets (due to P–P coupling) of the two inequivalent P atoms, both with Pt–P satellites. The resonances at higher field are assigned to the P atom *trans* to the carboxylato moieties, by comparison with literature data of other mixed phosphine carboxylato or alcolato Pt(II) complexes [23–25]. In the carboxylato derivatives, **1**, **2**, **4** and **5**, these resonances display the larger Pt–P coupling constants. In Pt(II) complexes, where back donation is negligible, the magnitude of the Pt–P coupling constant is related to the strength of the P → Pt donor bond [26], which is higher for P *trans* to the carboxylato group, because of the low *trans* influence expected for oxygen donor ligands [27]. Interestingly in the sph derivatives, **3** and **6**, the resonances at higher fields, assigned to the phosphorus atom *trans* to O, show a low J_{Pt-P}, the phenolato ligand must therefore have a *trans* influence stronger than that of other oxygen donor atoms. This fact can be related with the high stability and/or inertness of the Pt–O(phenolato) bond in $[Pt(en)(sph)]^+$ reported in our previous studies [2,3].

The non-equivalence of the phoshine ligands is confirmed by the ^{195}Pt NMR spectra, which are doublets of doublets. The chemical shift values in Table 6 are the mean values of the four lines, of equal intensities, of these spectra. The PPh_3 derivatives display $-\delta$ values only slightly lower than those of the dppe complexes, in accordance with the fact that the donor atoms set is the predominant influence on δ(Pt), with only minor influence of the ligands backbones [28,29]. These spectra also confirm the values of the Pt–P coupling constants (with discrepancies < 8 Hz, see Table 6).

There are certain features of the ^{1}H NMR spectra (Table 4) that are worthy of discussion:

1. The methyl groups of the sa and sph derivatives resonate at fields similar or slightly higher than those of the free ligands, in contrast to what usually observed upon coordination of these moiety to Pt(II) [1–4,30]. At least in the case of **1**, it could be that the low field shift, expected upon coordination, is almost cancelled by the fact that the SCH_3 group is placed in the shielding region of one phenyl ring of the phosphine (see C(1S) in Fig. 1), a behaviour reported for a similar case [15]. Incidentally this fact supports the hypothesis that the conformation of the sa chelate ring of **1** in solution is the same as that found in the solid state as discussed below. Only for the sb complexes we observed the expected low field shift, we have no explanation for this in the absence of structural data.
2. The resonances of the CH_3S groups of all compounds are doublets with satellites due to the coupling with ^{195}Pt (^{3}J between 29 and 36 Hz, see an example in Fig. 2). The doublets are due to ^{4}J coupling with ^{31}P, as the resonances become singlets in the $\{^{31}P\}$ spectra. The P–H coupling was confirmed by HMQC experiments which showed cross peaks between the ^{31}P resonances at lower fields and those of the CH_3 protons. Incidentally these experi-

ments confirm the assignments of the ^{31}P signals discussed above.

3. The Pt–H coupling constants of the SCH_3 group are lower than those of $[Pt(en)L]^+$ [1–3] and $[Pt(NH_3)_2(sa)]^+$ (see Table 4), which are all around 48–50 Hz, again an effect of the *trans* influence of phosphine, since, for instance in *cis*-$[PtCl_2(methionine)]$, where the SCH_3 is *trans* to a chloride, $J_{Pt-H} = 56$ Hz [31].
4. In Fig. 2 the spectrum of **1** is reported and compared to those of $[Pt(NH_3)_2(sa)]^+$ and $[Pt(en)(sa)]^+$. In all these spectra the diastereotopic protons of CH_2 of chelated sa appear as two doublets, those at higher field showing Pt–H couplings. Moreover in the case of **1** such high field doublet is further split presumably because of the four bonds coupling with ^{31}P (Fig. 2(b)), although this was not confirmed in the HMQC experiment. The separation of the two doublets is larger for **1** (about 1.3 ppm) than for the amine derivatives (0.3–0.4 ppm). This behaviour suggests that the conformation of the chelate rings of sa in these compounds must be rigid, in particular in the case of **1** such conformation is probably similar to that found in the solid state, in which the two CH_2 protons are fixed in the pseudo-axial and pseudo-equatorial positions and must experience different magnetic environments. The Pt–S–C(11)–H torsion angles are 96.9 and − 146.0° and only for the latter (pseudo-equatorial) proton can relevant Pt–H and P–H couplings be operative. These show up only in the 3.35 ppm signal, which, therefore, must be attributed to such a proton.
5. The room temperature spectrum of **4** is different from that of the other sa complex, as it consists of broad resonances in the CH_2 region. Upon lowering the temperature these resonances, as well as those of the phenyl protons, become sharper (Fig. 3) and at 173 K the CH_2 protons of sa appear as two doublets ($J_{H-H} = 17.0$ Hz) centred at 3.52 and 3.98 ppm, with the high field doublet showing little resolved Pt–H satellites. Clearly the chelate rings of both sa and dppe in **4** are not rigid at room temperature, but undergo an inversion of conformation, whose rate must be below the fast exchange limit at 300 K, since we observe four broad resonances. The rate of inversion of both chelate rings is decreased at 173

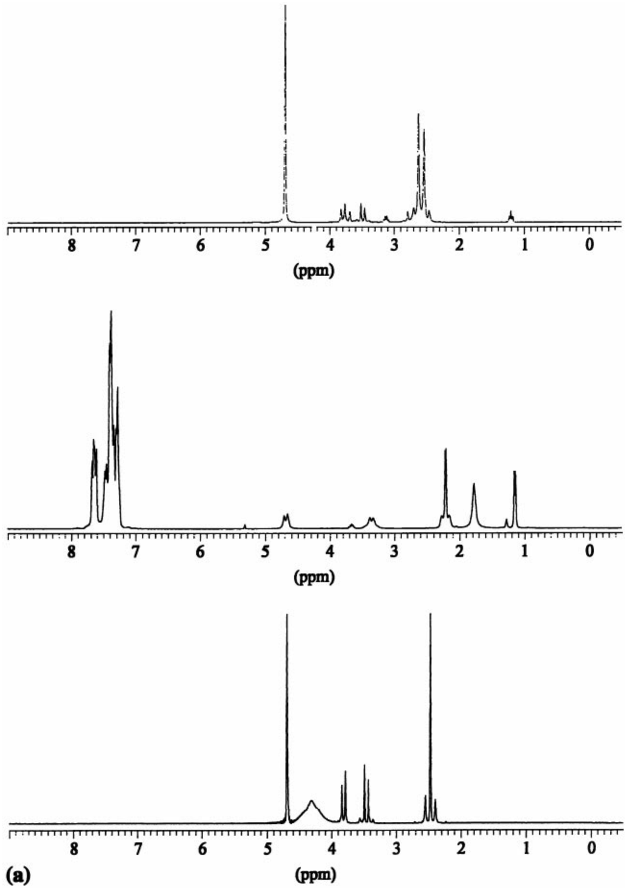


Fig. 2. (a) ^1H NMR spectra (300 MHz, room temperature) of: (top to bottom) $[Pt(en)(sa)]NO_3$ (H_2O-d_2 solution) [2,3]; $[Pt(PPh_3)_2(sa)]NO_3$, **1**, ($CHCl_3$-d solution) and $[Pt(NH_3)_2(sa)]NO_3$ (H_2O-d_2 solution); (b) expansion of the ^1H NMR spectrum of **1** ($CHCl_3$-d solution) in the CH_3S and CH_2S regions. The resonances at about 1.2 and 3.7 ppm in the spectrum of **1** are due to diisopropylether.

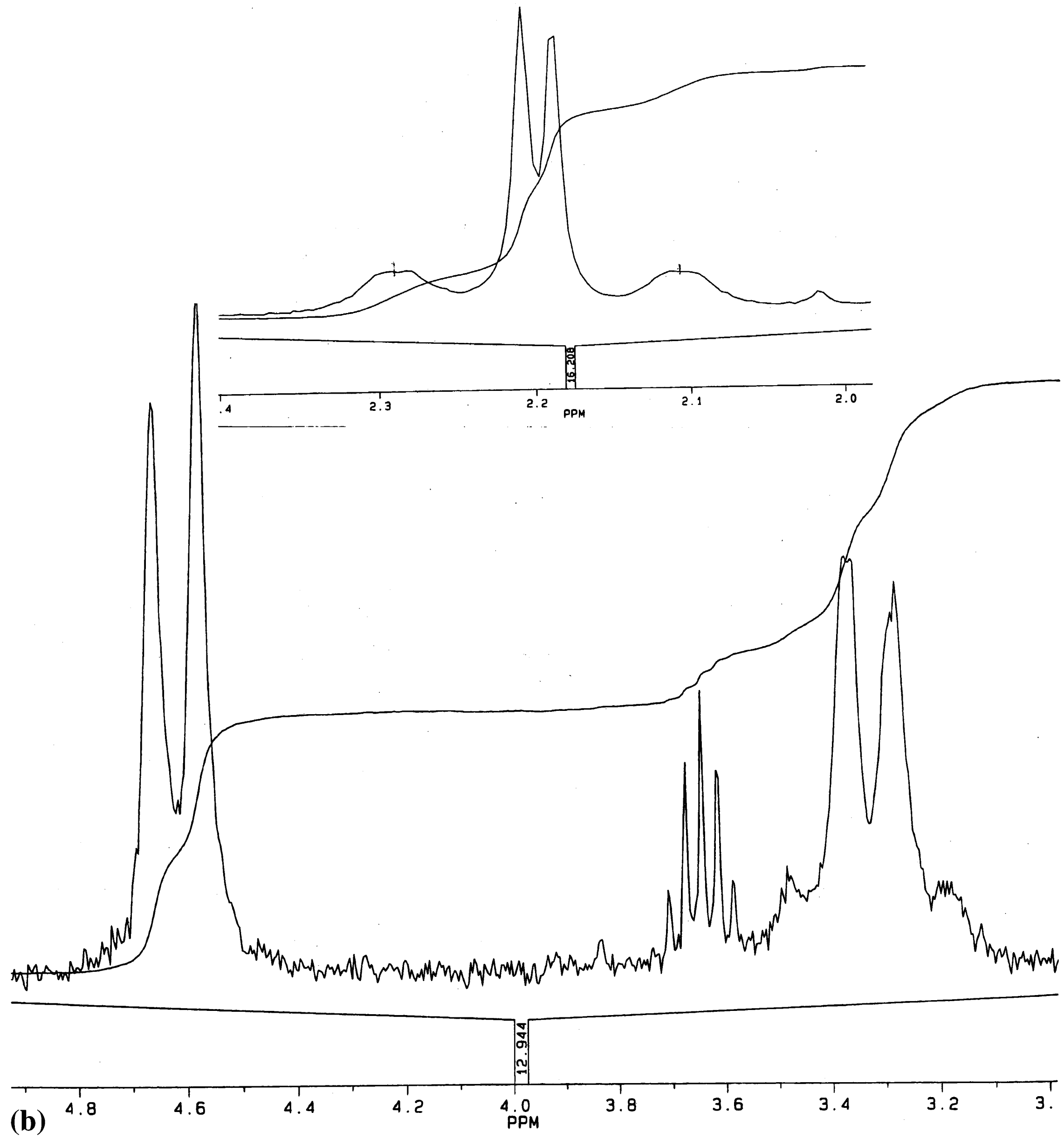


Fig. 2. (*Continued*)

K. Note that at this temperature the separation of the two doublets is smaller that that found for **1**, either because we have not yet reached the slow exchange limit, or as a consequence of the different conformations of the sa chelate rings of **1** and **4**. As to the origin of the different conformational freedoms of the sa chelate rings in the two compounds, we think that the stacking of the phenyl rings observed in **1** may render the whole molecule rigid. Such a stacking may not be present in **4**, but in the absence of an X-ray structure this remains a hypothesis.

4. Conclusions

The compounds presented here are representative of a class of platinum(II) complexes in which the donor sets are P, S and an anionic oxygen donor atoms. The relative *trans* influences and *trans* effects of these atoms play important roles on bond lengths, strengths and stability, as suggested by comparison with the analogous $[Pt(en)L]^+$ complexes described elsewhere [1–4]. Thus we observe a difference of the two Pt–P bond lengths, as well as a lengthening of the Pt–O and Pt–S bonds, the latter not only in comparison with the

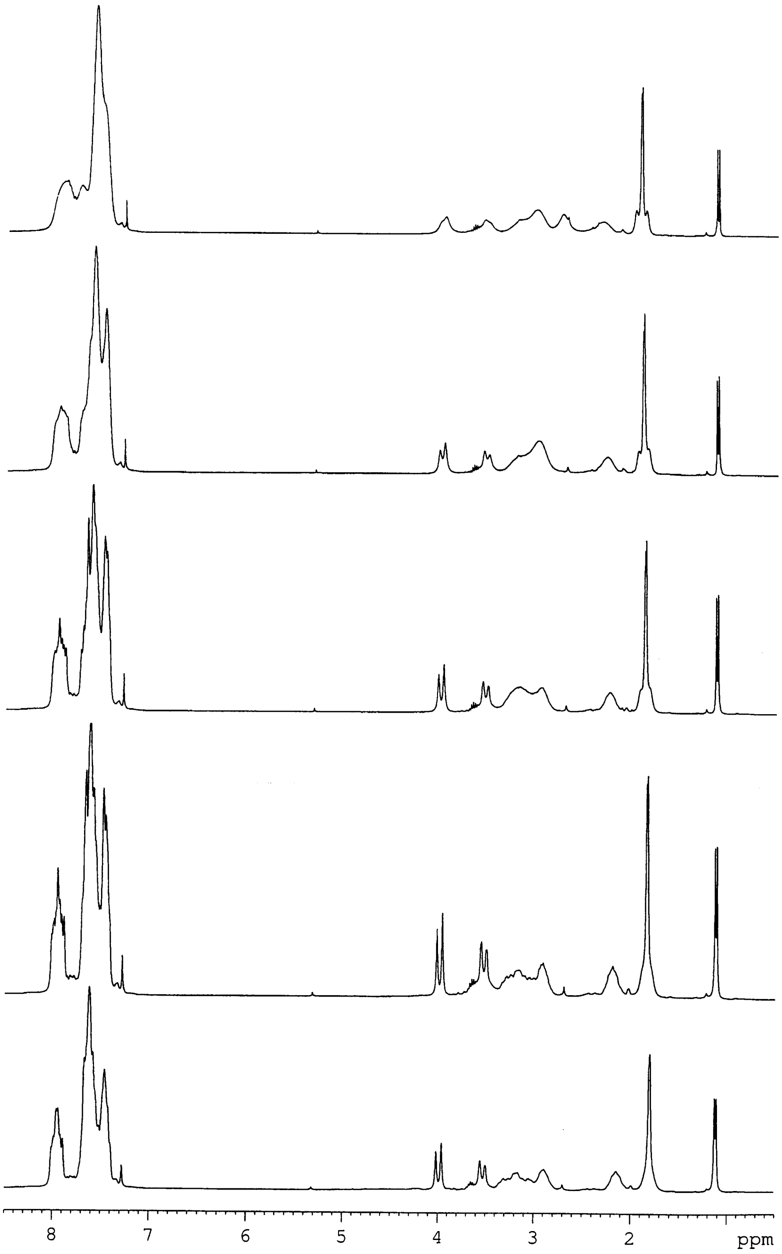


Fig. 3. ^{1}H NMR spectra (300 MHz) of a CH_2Cl_2-d_2 solution of [Pt(dppe)(sa)]NO_3 (**4**), at various temperatures: (top to bottom) 300, 273, 223, 200 and 173 K. The signals at about 1 and 3.7 ppm are due to diisopropyl ether.

relatively weaker Pt–S (sulfoxide) bond [1], but also with various Pt–S (thioether) bonds *trans* to ligands such as Cl or amine [32]. Note also the relatively low value of the Pt–H coupling constants of the SCH_3 group and the lower J_{Pt-P} of the phosphorus atom *trans* to S. The fact that we failed to obtain the sulfoxide derivatives must also be due to the low strength of the Pt–S bonds *trans* to P, since Pt$^{(II)}$ amine sulfoxide complexes are isolable [1–3].

Another interesting point, related to the presence of phenylphosphine, is the different conformational freedoms of the sa chelate rings in **1** and **4**, which may arise from some intramolecular interactions as proposed above.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 151938. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-

336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Crystal data, best coordination plane and samples of the ^{1}H, ^{31}P and ^{195}Pt NMR spectra can be obtained from the authors.

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial help.

References

[1] A. Pasini, G. D'Alfonso, C. Manzotti, M. Moret, S. Spinelli, M. Valsecchi, Inorg. Chem. 33 (1994) 4140.

[2] A. Pasini, P. Perego, M. Balconi, M. Lupatini, J. Chem. Soc., Dalton. Trans. (1995) 579.

[3] A. Pasini, M. Moroni, J. Chem. Soc., Dalton. Trans. (1997) 1093.

[4] A. Pasini, C. Fiore, Inorg. Chim. Acta 285 (1999) 249.

[5] E.L.M. Lempers, J. Reedjik, Adv. Inorg. Chem. 37 (1991) 175.

[6] L. Malatesta, C. Cariello, J. Chem. Soc. (1958) 2323.

[7] G.K. Anderson, H.C. Clark, J.A. Davies, Inorg. Chem. 20 (1981) 3607.

[8] A. Pasini, C. Caldirola, S. Spinelli, M. Valsecchi, Synth. React. Inorg. Met.-Org. Chem. 23 (1993) 1021.

[9] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidorri, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.

[10] G.M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1977.

[11] E. Keller, SCHAKAL-99, University of Freiburg, Germany, 1999.

[12] B.M. Gatehouse, S.E. Livingstone, R.S. Nyholm, J. Chem. Soc. (1957) 4222.

[13] G.G. Mather, G.J.N. Rapsey, A. Pidcock, Inorg. Nucl. Chem. Lett. 9 (1973) 567.

[14] P.D.S. Murdoch, J.D. Ranford, P.J. Sadler, S.J. Berners-Price, Inorg. Chem. 32 (1993) 2249 (and references therein).

[15] R.T. Boeré, N.C. Payne, C.J. Willis, Can. J. Chem. 64 (1986) 1474.

[16] F. Demartin, M. Pizzotti, F. Porta, S. Cenini, J. Chem. Soc., Dalton Trans. (1987) 605.

[17] S.A. Bryan, D.M. Roundhill, Acta Crystallogr., Sect. C 39 (1983) 184.

[18] U. Belluco, R. Bertani, R.A. Michelin, M. Mozzon, G. Bombieri, F. Benetollo, Gazz. Chim. Ital. 124 (1994) 487.

[19] J.F. Blount, H.C. Freeman, A.M. Sargeson, K.R. Turnbull, Chem. Commun. (1967) 324.

[20] S. Larsen, K.J. Watson, A.M. Sargeson, K.R. Turnbull, Chem. Commun. (1968) 847.

[21] P.S. Pregosin, R.W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer, Berlin, 1979 (and references therein).

[22] P.E. Garrou, Chem. Rev. 81 (1981) 229.

[23] G.K. Anderson, G.J. Lumetta, Inorg. Chim. Acta 118 (1986) L9.

[24] G.K. Anderson, G.J. Lumetta, Inorg. Chem. 26 (1987) 1291.

[25] R.S. Paonessa, A.L. Pignano, W.C. Trogler, Organometallics 4 (1985) 647.

[26] C.J. Cobley, P.C. Pringle, Inorg. Chim. Acta 265 (1997) 107.

[27] T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335.

[28] E.G. Hope, W. Levason, N.A. Powell, Inorg. Chim. Acta 115 (1986) 187.

[29] P.S. Pregosin, in: P.S. Pregosin (Ed.), Transition Metal Nuclear Magnetic Resonance. In: Studies in Inorganic Chemistry, vol. 13, Elsevier, Amsterdam, 1991, p. 217.

[30] Z. Guo, G. Faraglia, S. Sitran, Polyhedron 13 (1994) 659.

[31] R.E. Norman, J.D. Ranford, P.J. Sadler, Inorg. Chem. 31 (1992) 877.

[32] S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365.