Platinum Complexes of the Methyl Esters of Dithiocarbazic Acid and 3-Phenyldithiocarbazic Acid †

Claudio Battistoni, Anna Maria Giuliani, Ernesto Paparazzo, and Franco Tarli *
Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del C.N.R., Area della Ricerca di Roma del C.N.R., Italy

---

The ligand behaviour of the methyl esters of dithiocarbazic acids $NH_2NHC(=S)SMe$ (L) and $NHPhNHC(=S)SMe$ (PhL) in the diamagnetic complexes $[PtL_2Cl_2]$, $[Pt(L - H)_2]$, $[Pt(L - 2H)_2]$, $[Pt(PhL)_2Cl_2]$, $[Pt(PhL - H)(PhL)Cl]$, $[Pt(PhL - H)_2]$, and $[Pt(PhL - 2H)_2]$ have been investigated. The electronic, i.r., and *X*-ray photoelectron spectra of the solids have been studied; electrochemical and n.m.r. studies in solution have been performed. The ligands are co-ordinated in neutral and/or anionic deprotonated form. In the deep coloured complexes containing the doubly deprotonated ligands the metal remains essentially in the +2 oxidation state whereas the ligands have become oxidized. Moreover these complexes show electron-transfer properties. Isomerism has been observed for many complexes.

Derivatives of dithiocarbazic acid $NH_2NHC(=S)SH$ are the subject of a growing number of reports, which confirms the interest in the properties of these molecules, whose behaviour can be considerably modified by *N*- and *S*-substitution. We are interested in the co-ordinating properties of these potentially multidentate ligands towards transition metals.[1] Here we report a study on the ligating behaviour of the methyl ester of dithiocarbazic acid $NH_2NHC(=S)SMe$ (L) and its N^3-phenyl substituted derivative $NHPhNHC(=S)SMe$ (PhL) towards platinum. Preliminary results on this topic have been presented at a conference.‡ Previous literature reports on platinum co-ordination compounds of esters of dithiocarbazic acid are limited to $[Pt\{NH_2N=C(S)SMe\}_2]$[2] and complexes with Schiff bases of dithiocarbazic esters, as potential carcinostatic agents.[2-5]

Experimental

Materials.—The chemicals were commercial analytical grade reagents and were used without further purification, except the solvents used for electrochemical measurements which were purified as described in ref. 6. Nitrogen gas and helium gas were ultra-high-purity commercial products. All the compounds were dried *in vacuo* (1 Torr) over P_2O_5, unless stated otherwise.

Preparation of the Ligands.—L, PhL, and L·HCl were prepared following reported methods.[1,7]

Preparation of the Complexes.—$[PtL_2Cl_2]$. A boiling solution of $K_2[PtCl_4]$ (0.7 mmol) in HCl (30 cm^3, 2 mol dm^{-3}) was added to a boiling solution of L (1.4 mmol) in HCl (30 cm^3, 2 mol dm^{-3}). The compound separated immediately and after 10 min stirring and boiling it was filtered off, washed with hot 2 mol dm^{-3} HCl, and dried over pellets of KOH (yield 50%).

trans-$[Pt(L - H)_2]$ $[L - H = NH_2N=C(S)SMe]$. A boiling solution of $K_2[PtCl_4]$ (0.8 mmol) in water (20 cm^3) was added to a boiling solution of L (1.6 mmol) in water (20 cm^3). After immediate separation of the solid product, the mixture was boiled and stirred for 10 min; the precipitate was filtered off, washed with hot water and then hot ethanol, and dried (yield 50%). When the reaction is carried out at 0 °C the *cis* isomer is obtained as the major product (yield 10%).

$[Pt(L - 2H)_2]$ $[L - 2H = NHNC(S)SMe]$. $[Pt(L - H)_2]$ (1.82 mmol) was dissolved in pyridine (200 cm^3). After 30 min, 30% aqueous H_2O_2 (50 cm^3) was added and after 4.5 h stirring water (400 cm^3) was added. After 24 h the compound was filtered off, washed with water until the smell of pyridine had disappeared, and dried (yield 50%).

$[Pt(PhL)_2Cl_2]$. A solution of PhL (2.4 mmol) in ethanol (50 cm^3) was added to a solution of $K_2[PtCl_4]$ (1.2 mmol) in water (40 cm^3), with addition of HCl (2 cm^3, 1 mol dm^{-3}). After 2 h stirring, the product was filtered off and dried (yield 70%).

$[Pt(PhL - H)(PhL)Cl]$ $[PhL - H = NHPhN=C(S)SMe]$. A solution of $K_2[PtCl_4]$ (1.5 mmol) in water (20 cm^3) was added to a solution of PhL (3.0 mmol) in water–ethanol (1 : 2, 120 cm^3). After 2 h stirring the product was filtered off, washed with water and ethanol, and dried (yield 50%). The same compound is obtained by reacting $K_2[PtCl_4]$ with PhL in molar ratio 1 : 1.

$[Pt(PhL - H)_2]$. A boiling solution of $K_2[PtCl_4]$ (1.2 mmol) in water (25 cm^3) was added to a solution of PhL (2.8 mmol) in ethanol (40 cm^3). After 10 min boiling the product was filtered off, washed with hot water–ethanol (1 : 2), and dried (yield 50%). The same compound is obtained when working in an N_2 atmosphere in basic medium.

$[Pt(PhL - 2H)_2]$ $[PhL - 2H = NPhNC(S)SMe]$. $K_2[PtCl_4]$ (1.4 mmol) in water (20 cm^3) was added to a solution of PhL (2.8 mmol) in ethanol (40 cm^3). After 5 min stirring, NH_4OH (1 mol dm^{-3}) was added until pH 9 was reached; air was bubbled through for 20 h. The product was filtered off, washed with water–ethanol (1 : 2), dried and crystallized from CS_2 (yield 90%).

Analytical data are in Table 1. Microanalyses were performed by the Microanalytical Service of the Area della Ricerca di Roma del C.N.R.

Physical Measurements.—The visible solution spectra were recorded with a Perkin-Elmer 330 spectrophotometer. Visible reflectance spectra, i.r. spectra, and magnetic moments were measured as in ref. 1. All the compounds are diamagnetic.

Electrochemical measurements. Diffuse current polarography, alternating current polarography, cyclovoltammetry, and coulometry were performed with the apparatus and under the conditions reported in ref. 6.

X-Ray photoelectron spectra. The spectra were recorded on the VG ESCA 3 Mk. II of the ESCA Service of the Area della Ricerca di Roma del C.N.R. The exciting source was provided by the unmonochromatised Al-K_α radiation (1 486.6 eV). The

---

† *Non-S.I. units employed*: Torr ≈ 133 Pa, eV = 1.60×10^{-19} J.

‡ F. Tarli, C. Battistoni, and E. Paparazzo, presented in part at the International Conference of the Platinum Group Metals, Bristol, July, 1981.

Table 1. Analytical data of platinum complexes

Compound	Colour	Analysis (%) *			
		C	H	N	Cl
[PtL_2Cl_2]	Pale yellow	9.6(9.6)	2.3(2.4)	10.95(11.0)	13.8(13.9)
[Pt(L − H)$_2$]	Pale yellow	11.1(11.0)	2.3(2.3)	12.7(12.8)	
[Pt(L − 2H)$_2$]	Blue-green dichroic crystals	11.0(11.0)	1.85(1.9)	12.5(12.8)	
[Pt(PhL)$_2$Cl$_2$]	Pale yellow	29.15(29.0)	3.0(3.0)	8.25(8.45)	10.4(10.3)
[Pt(PhL − H)(PhL)Cl]	Pale yellow	30.7(30.7)	3.0(3.0)	8.9(8.95)	5.8(5.9)
[Pt(PhL − H)$_2$]	Pale yellow	32.5(32.6)	3.1(3.0)	9.5(9.5)	
[Pt(PhL − 2H)$_2$]	Dark green crystals	32.7(32.7)	2.7(2.7)	9.5(9.5)	

* Calculated values are in parentheses.

vacuum in the analyser was 10^{-9} Torr. The samples were dusted on a double-sided Scotch tape: except for Pt metal, the C 1*s* peak (at 285.0 eV) from the contamination layer was used as a reference for the correction of charging effects. A constant voltage of 20 eV was set through the hemispheres of the analyser operated in the fixed analyser transmission mode. The experiments were performed at *ca.* 300 K and replicated at the temperature of liquid nitrogen in order to check if, under *X*-ray irradiation, any change occurred in both the peak positions and shapes: no appreciable difference was revealed between the two conditions. The binding energy (b.e.) values result from the average of three independent sample depositions. The reproducibility was within ± 0.2 eV. The Pt^0 spectrum was obtained from a platinum plate subjected to several minutes Ar^+ ion etching in order to remove surface contamination. The binding energy value for Pt^0 4*f* doublet was referred to the spectrometer Fermi level calibrated against the Au $4f_{\frac{7}{2}}$ peak at 83.7 ± 0.1 eV. Curve peak-fitting was carried out by means of a Du Pont 310 curve resolver using a Gaussian shape fit.

Nuclear magnetic resonance spectroscopy. The ^1H n.m.r. spectra were recorded with the Bruker WP 200 instrument (operating at 200 MHz) of the n.m.r. service of the Area della Ricerca di Roma del C.N.R. $(CD_3)_2SO$ was used as the solvent and for field-frequency lock. All experiments were performed at 25 ± 1 °C.

Results and Discussion

Preparation and Properties of Platinum Complexes.—The ligands L and PhL react readily with $K_2[PtCl_4]$ in water or aqueous ethanol, respectively, giving diamagnetic Pt^{II} co-ordination compounds. The result of the preparation depends critically on the reaction conditions. The temperature exerts a deep influence on the preparation of *cis–trans* isomers of [Pt(L − H)$_2$]: the *trans* isomer is prepared in boiling water, whereas the *cis* isomer is obtained at 0 °C. The reaction of PhL with $K_2[PtCl_4]$ in aqueous ethanol is also temperature dependent: [Pt(PhL − H)$_2$] is prepared at boiling temperature while [Pt(PhL − H)(PhL)Cl] is obtained at room temperature. When the reaction media are strongly acidified (HCl), [PtL_2Cl_2] and [Pt(PhL)$_2$Cl$_2$] are obtained whereas in basic media (NH_4OH) the deep coloured complexes, [Pt(L − 2H)$_2$] and [Pt(PhL − 2H)$_2$], containing the doubly deprotonated ligands, can be prepared. When the reactions in basic media are performed in an N_2 atmosphere, [Pt(L − H)$_2$] and [Pt(PhL − H)$_2$] are formed, thus showing the essential role of oxygen in the deprotonation of both N atoms of the ligands. Oxidations can be carried out also by reacting [Pt(L − H)$_2$] or [Pt(PhL − H)$_2$] in basic solvents [Me_2SO, *NN*-dimethylformamide (dmf), or pyridine] with oxidants such as H_2O_2 and quinone or electrochemically in dmf (see below). All the compounds containing neutral and/or anionic monodeprotonated ligands dissolve in dipolar aprotic solvents such as Me_2SO and dmf, except [PtL_2Cl_2] which is decomposed by solvents. The solutions become deeply coloured in air indicating the formation of [Pt(L − 2H)$_2$] or [Pt(PhL − 2H)$_2$], which is confirmed by changes of the electronic spectra. All the platinum compounds examined tend to give in air the stable most oxidized compounds; this is also the case in the solid state. [Pt(L − 2H)$_2$] and [Pt(PhL − 2H)$_2$] dissolve in most organic solvents, markedly differing in this respect from the other complexes prepared.

Infrared Spectra.—Data are given in Tables 2 and 3. In the spectrum of [PtL_2Cl_2] several bands between 2 920 and 2 420 cm^{-1}, attributable to quaternary ammonium groups,[8,10] suggest that the ligand is co-ordinated in the form of an ammonium salt. Its formation is explained by the high concentration of HCl in the reaction medium, which allows the reaction of the ligand in the form of L·HCl. A band at 1 530 cm^{-1}, which is not shifted on deuteriation, is assigned to a $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{N})$ partial double bond, suggesting N^2-deprotonation of the ligand. Bands attributable to ν(Pt−N) and to ν(Pt−S), which are not shifted on deuteriation, suggest chelation of the ligand deprotonated at N^2 through N^2 and non-methylated S: [Pt{NH_3N=C(S)SMe}$_2$Cl$_2$]. The tentative assignments of the bands attributable to ν(Pt−N) and to ν(Pt−S) have been made following those already reported [11] and considering the shifts observed after deuteriation. The co-ordination of ligands through N^3 in the complexes [Pt(L − H)$_2$], [Pt(L − 2H)$_2$], [Pt(PhL − H)$_2$], and [Pt(PhL − H)(PhL)Cl] is suggested by the shifts of bands attributable to ν(N − H) to lower frequencies with respect to the bands of the free ligands. *trans*-[Pt(L − H)$_2$] exhibits a spectrum very similar to that already known for *trans*-[Ni(L − H)$_2$] [1,11] whereas the spectrum of the *cis* isomer shows broadened unresolved bands, according to lowered symmetry. In the spectrum of [Pt(L − 2H)$_2$] a strong band at 3 220 cm^{-1} is assigned to ν(N − H) of the doubly deprotonated ligand. The bands attributable to a $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{N})$ partial double bond are found in the spectra of both complexes [Pt(L − 2H)$_2$] and [Pt(PhL − 2H)$_2$] at 1 450 cm^{-1}, at a lower frequency than is observed for the complexes containing monodeprotonated ligands, suggesting higher delocalization of electron density over the whole molecules. Moreover the identical spectral position indicates a lack of conjugation of the phenyl ring, which has indeed been found by *X*-ray determination [12] to be out of the plane of the chelate ring.

Electronic Spectra.—[PtL_2Cl_2], [Pt(L − H)$_2$], [Pt(PhL)$_2$Cl$_2$], [Pt(PhL − H)(PhL)Cl], and [Pt(PhL − H)$_2$] show ill resolved electronic reflectance spectra (Table 4) characteristic of square-planar Pt^{II} complexes. The spectra of the deep coloured [Pt(L − 2H)$_2$] and [Pt(PhL − 2H)$_2$] are typical of platinum electron-transfer complexes,[13] with prominent charge transfer (c.t.) bands at 15.4×10^3 and 13.7×10^3 cm^{-1}, respectively. The red shift of the c.t. band of [Pt(PhL −

Table 2. I.r. spectra (cm^{-1}) of platinum complexes of L

L	L·HCl	[PtL$_2$Cl$_2$]	[Pt(L − H)$_2$]	[Pt(L − 2H)$_2$]	Tentative assignment (prevalent contribution)
3 280m	3 110br	2 920br	3 220m	3 220s	ν(N–H)
3 210m	3 070br	2 840br	3 180m		
3 170m	2 920br	2 540br	3 040m		
	2 820br	2 500br			
	2 780br	2 420br			
	2 640br				
	2 560br				
1 600m	1 580s	1 590s	1 620m		δ(NH$_2$) or δ(NH$_3^+$)
1 580m		1 550 (sh)	1 580s		
1 520s	1 530s				δ(N–H) + ν(C–N)
	1 510				
		1 530m	1 500s	1 450s	ν(C $\underline{\cdots}$ N)
1 380s					ν(C $\underline{\cdots}$ N) + δ(N–H)
1 155s			1 260w	1 250s	ν(NCSS) + ν(C=S)
				1 135s	
1 010s	1 070s	1 080s	1 000s	1 040s	ν(C $\underline{\cdots}$ S)
		1 000s			
975 (sh)	980s	990m	980s	960 (sh)	ν(N–N) + ν(C–S)
945s	950m	970 (sh)	965s	955m	
			900w		ν(Pt–N)
		565s	530w	520w	
			475w		
		325w	330m	330w	ν(Pt–S)

Table 3. I.r. spectra (cm^{-1}) of platinum complexes of PhL

PhL	[Pt(PhL)$_2$Cl$_2$]	[Pt(PhL − H)$_2$]	[Pt(PhL − 2H)$_2$]	Tentative assignment (prevalent contribution)
3 190s	3 240m	3 060s		ν(N–H)
3 180 (sh)	3 140m			
3 120m	3 060m			
3 040m	3 040 (sh)	3 040s	3 040w	benzene ring modes
1 620s	1 610s	1 610w	1 580w	benzene ring modes
1 610(sh)		1 590w		
1 545s	1 540s			δ(N–H) + ν(C $\underline{\cdots}$ N)
		1 535s	1 450s	ν(C $\underline{\cdots}$ N)
1 340s				ν(C $\underline{\cdots}$ N) + δ(N–H)
1 045vs	1 025s	1 025w	1 050s	ν(C $\underline{\cdots}$ S) + ν(N–N)
1 030 (sh)				
965s	970 (sh)	990s	1 020w	
955s	955s	970s	995w	
		552w		ν(Pt–N)
	320m	315w	350m	ν(Pt–S)
	305			ν(Pt–Cl)

2H)$_2$] relative to that of [Pt(L − 2H)$_2$], due to a distinct electron-withdrawing effect of the phenyl group on the highly delocalized electronic system of the ligand, suggests prevalent ligand→metal character of the c.t. band.[14]

Electrochemical Measurements.—The electrochemical behaviour of [Pt(L − 2H)$_2$] and [Pt(PhL − 2H)$_2$] in dmf solution gives evidence of electron-transfer properties. They have been investigated through d.c., a.c., and cyclic voltammetry and coulometry; data are reported in Tables 5 and 6 and in Figures 1 and 2, respectively. The range +0.1000 to −2.000 V was investigated in reduction. Both compounds show well defined polarographic waves corresponding to the reduction in two steps: equations (1) and (2).

Reversibility is suggested by cyclovoltammetric and a.c. voltammetric data and confirmed for the first step by coulometry. The agreement between experimental and calculated charge is within 10% for both compounds. The shift of $E_{\frac{1}{2}}{}^1$ and $E_{\frac{1}{2}}{}^2$ to less negative values by replacing the hydrogen by the phenyl group {$E_{\frac{1}{2}}{}^1 = -0.445$, $E_{\frac{1}{2}}{}^2 = -1.230$ V for [Pt(L − 2H)$_2$]; $E_{\frac{1}{2}}{}^1 = -0.215$, $E_{\frac{1}{2}}{}^2 = -0.912$ V for [Pt(PhL − 2H)$_2$]} is consistent with the electron-withdrawing effect of the phenyl group. Investigations on oxidation in the range 0.000 to +1.500 V show polarographic waves corresponding to non-reversible processes. The effect of the phenyl group is, however, confirmed by the shift to more positive values of $E_{\frac{1}{2}}$ in oxidation {$E_{\frac{1}{2}} = +0.935$ V for [Pt(L − 2H)$_2$]; $E_{\frac{1}{2}} = +1.150$ V for [Pt(PhL − 2H)$_2$]}.

$$[\mathrm{Pt(L-2H)_2}]^0 \underset{-1e}{\overset{+1e}{\rightleftharpoons}} [\mathrm{Pt(L-2H)_2}]^- \underset{-1e}{\overset{+1e}{\rightleftharpoons}} [\mathrm{Pt(L-2H)_2}]^{2-} \quad (1)$$

$$[\mathrm{Pt(PhL-2H)_2}]^0 \underset{-1e}{\overset{+1e}{\rightleftharpoons}} [\mathrm{Pt(PhL-2H)_2}]^- \underset{-1e}{\overset{+1e}{\rightleftharpoons}} [\mathrm{Pt(PhL-2H)_2}]^{2-} \quad (2)$$

The electrochemical oxidation of [Pt(L − H)$_2$] and [Pt-

Table 4. Electronic (reflectance) spectra of platinum complexes

Compound	Chromophore	10^{-3} ν ^{a}/cm^{-1}
$[PtL_2Cl_2]$		29.9, 35.7
$[Pt(L - H)_2]$		[27.8], 34.8, [37.3]
$[Pt(L - 2H)_2]$	*trans*-PtN_2S_2 ^{b}	[14.6], 15.8, [20.0], 26.7, 37.0
		15.4(4.38),^{c} 23.6(3.20),^{c} 39.5(4.34),^{c} 47.6(4.37) ^{c}
$[Pt(PhL)_2Cl_2]$		21.3, 31.8
$[Pt(PhL - H)(PhL)Cl]$		[22.0], [26.7], 21.8
$[Pt(PhL - H)_2]$		[22.2], 22.5
$[Pt(PhL - 2H)_2]$	*trans*-PtN_2S_2 ^{d}	13.7, 21.5, [22.7], 30.5, 38.5
		13.6(4.43),^{c} [22.0](3.73),^{c} 24.0(3.82),^{c} 31.5(4.18),^{c} [40.0](4.23),^{c} 45.7(4.43) ^{c}
$[Pt\{NPhNC(S)NHPh\}_2]$ ^{e}		13.3(4.51), 23.8(3.73), [25.0](3.71), 29.7(4.31), 36.9(4.48), [43.5](4.38)

^{a} log (ε/dm^3 mol^{-1} cm^{-1}) in parentheses; shoulders are given in square brackets. ^{b} From *X*-ray data; see ref. 16. ^{c} In tetrahydrofuran. ^{d} See ref. 12. ^{e} In 95% aqueous ethanol, see ref. 13.

Table 5. D.c. and a.c. voltammetric data for the reduction at a pulsing platinum electrode of $[Pt(L - 2H)_2]$ and $[Pt(PhL - 2H)_2]$ in dmf solution ^{a}

		D.c.					
Compound	Concentration (mol dm^{-3})	$E_{\frac{1}{2}}^{1}$/V	$E_{\frac{1}{2}}^{2}$/V	i^1/μA	i^2/μA	slope$^{1\,b}$/V	slope$^{2\,b}$/V
$[Pt(L - 2H)_2]$	5×10^{-4}	−0.445	−1.230	3.04	3.04	0.070	0.070
$[Pt(PhL - 2H)_2]$	5×10^{-4}	−0.215	−0.912	3.53	3.52	0.052	0.070
		A.c.					
Compound	Concentration (mol dm^{-3})	E_p^{1}/V	E_p^{2}/V	i_p^{1}/μA	i_p^{2}/μA	$E_{\frac{p}{2}}^{1c}$/V	$E_{\frac{p}{2}}^{2c}$/V
$[Pt(L - 2H)_2]$	5×10^{-4}	−0.460	−1.260	1.80	0.36	0.100	0.140
$[Pt(PhL - 2H)_2]$	5×10^{-4}	−0.200	−0.920	0.65	0.45	0.096	0.092

^{a} Solution containing 0.1 mol dm^{-3} $[NEt_4][ClO_4]$; pulsing time, $t_p = 2$ s; $\theta_c = 20$ °C; a.c. voltammetric curves were recorded using $\omega = 75$ Hz and $\Delta E = 10$ mV; all potentials *vs.* saturated calomel electrode. ^{b} Slope was calculated using $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ values. ^{c} Width at half peak height.

Table 6. Cyclic voltammetric data for $[Pt(L - 2H)_2]$ and $[Pt(PhL - 2H)_2]$ in dmf solution

Compound	Concentration (mol dm^{-3})	E_p^1(cat)/V	E_p^2(cat)/V	ΔE_p^1 */V	ΔE_p^2 */V	i^1(cat)/i^1(an)	i^2(cat)/i^2(an)
$[Pt(L - 2H)_2]$	5×10^{-4}	−0.460	−1.260	0.080	0.060	1.0	1.1
$[Pt(PhL - 2H)_2]$	5×10^{-4}	−0.210	−0.940	0.060	0.080	1.0	1.3

* Cathodic to anodic peak potential separation.

$(PhL - 2H)_2]$ in dmf solution was investigated in the range 0.000 to +1.500 V. Both compounds show polarographic waves corresponding to non-reversible processes. Coulometry of $[Pt(PhL - H)_2]$ at +1.000 V shows that two electrons are transferred in the process $[Pt(PhL - H)_2] \longrightarrow [Pt(PhL - 2H)_2]$ (the oxidized compound is recovered in 90% yield).

N.M.R. Data.—The ^{1}H n.m.r. parameters for the compounds under investigation are reported in Table 7. $[Pt(L - H)_2]$ exists in solution as a mixture of the *cis* and *trans* isomers of the PtN_2S_2 chromophore. Equilibrium between the two forms is slow on the n.m.r. time-scale and is shifted towards the formation of the *trans* isomer at increasing temperature. The N^3–H resonances are shifted to low field upon complexation and exhibit ^{195}Pt satellites [^2J(Pt–N–H) = 45.9 and 43.9 Hz for the *trans* and *cis* isomers respectively], thus supporting chelation through the terminal N atom. The same behaviour has already been observed for the corresponding chelate of Ni^{II}.[15] In the case of $[Pt(L - 2H)_2]$ only one resonance is observed for each type of proton, suggesting that in this case only one isomer is present in solution, which, according to *X*-ray evidence has a *trans* chromophore.[16] The spectral position of the N^3–H resonance suggests the formation of a pseudo-aromatic penta-atomic ring, similar to pyrazole,* indicating chelation through the terminal nitrogen. Coupling to ^{195}Pt and the large downfield shift of the S–Me group support this finding.

$[Pt(PhL)_2Cl_2]$. This complex exhibits n.m.r. behaviour different from the others of the series. The N^3–H resonance is not shifted to low field relative to the free ligand and no ^{195}Pt satellites are observed in the ^{1}H spectrum; on the other hand the spectral position of the S–Me group is the same as for the other compounds examined. These findings suggest that the ligand behaves as unidentate and co-ordination occurs through its thiono-sulphur. Not only *cis–trans* isomerism can be expected for this complex, but the ligand itself can exist in the *Z*- and *E*-conformation because of the partial double bond character of the N^2–C bond. Four signals are observed both for the N^2–H and for the S–Me protons, suggesting that all four possible isomers are present in solution. Several resonances are observed also for N^3–H, partly overlapping the phenyl multiplets. No attempt has been made to assign the resonances.

$[Pt(PhL - H)_2]$. The n.m.r. spectra support chelation through the terminal nitrogen atom and the thiono-sulphur. The N^3–H resonance appears as four singlets, with ^{195}Pt satellites, markedly shifted to low field as compared to the

---

* For substituted pyrazoles the chemical shift of N^1–H varies between 10.3 and 13.5 p.p.m.[17,18]

Table 7. Hydrogen-1 n.m.r. data (δ/p.p.m.)[a] for platinum complexes (θ_c = 25 °C, ν_0 = 200 MHz)

Compound	N^3–H	N^3–Ph	N^2–H	S–Me
L	5.2, 7.8		10.74	2.39, 2.32
cis-$[Pt(L - H)_2]$	8.61(43.9 ± 0.5)			2.50
trans-$[Pt(L - H)_2]$	8.82(45.9 ± 0.5)			2.47
$[Pt(L - 2H)_2]$	11.43(90.6 ± 0.5)			2.88
PhL	8.31	6.6[b]	11.16	2.20
$[Pt(PhL)_2Cl_2]$	7.0—7.1[c]	7.0[b]	11.49[d] 11.60 11.63 11.75	2.53[d] 2.59 2.49 2.51
cis-$[Pt(PhL - H)_2]$	10.31(51 ± 1) 10.94(53 ± 1)	7.1[b]		2.51 2.52
trans-$[Pt(PhL - H)_2]$	11.59(60 ± 2) 11.63(64 ± 2)	7.1[b]		2.50 2.49
$[Pt(PhL - 2H)_2]$[e]		7.34[b]		2.63

[a] Values relative to $SiMe_4$ = 0 p.p.m.; values of ^2J(Pt–N–H)/Hz are in parentheses. [b] Centre of multiplet. [c] Overlapping the phenyl multiplet. [d] Most abundant, *ca.* 45—50%. [e] In CS_2.

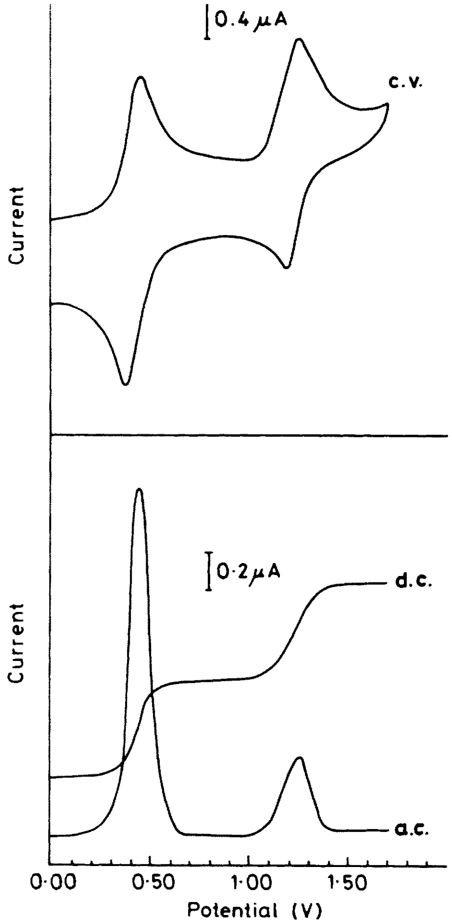

Figure 1. D.c., a.c., and cyclic voltammetry (c.v.) at a platinum electrode of $[Pt(L - 2H)_2]$ in dmf. Supporting electrolyte-$[NBu_4][ClO_4]$ (0.1 mol dm^{-3})

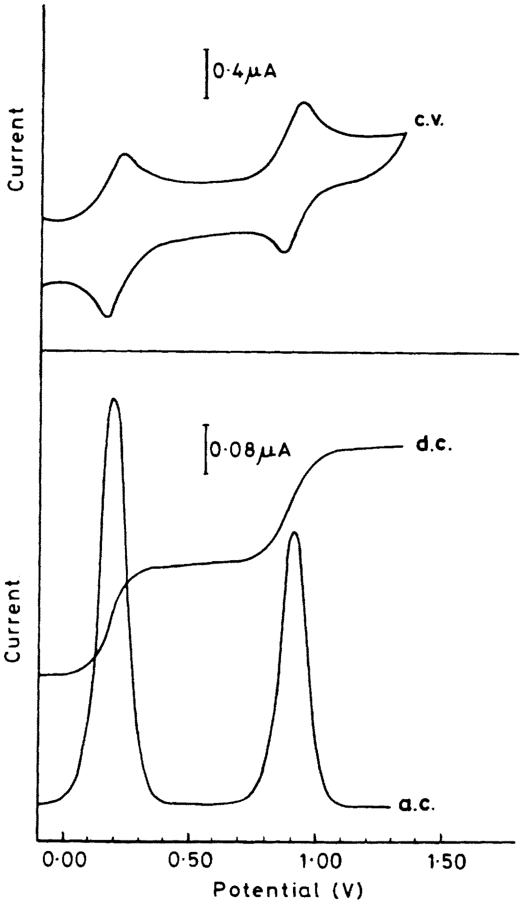

Figure 2. D.c., a.c., and cyclic voltammetry at a platinum electrode of $[Pt(PhL - 2H)_2]$ in dmf. Supporting electrolyte $[NBu_4][ClO_4]$ (0.1 mol dm^{-3})

free ligand. This large downfield shift is related both to co-ordination itself which decreases the electronic density on the nitrogen atom and to the formation of the chelate ring with some delocalization of the electrons giving rise to a ring current. The complex may exhibit *cis–trans* isomerism and in addition the phenyl ring of the ligand may be coplanar with the N^2–N^3–H moiety or perpendicular to it. Therefore several environments may exist for each type of proton. By analogy with the other terms of the series we may assign the two high-field N^3–H resonances and the two low-field S–Me peaks to the *cis* isomers: this is supported by variable-temperature measurements. At higher than room temperature (80 °C)

Table 8. Core orbital binding energies (eV) for the complexes and reference compounds *

Compound	Pt $4f_{\frac{7}{2}}$	Pt $4f_{\frac{5}{2}}$	N 1*s*	N^2	N^3	Δ*N*	S 2*p*	S^A	S^B	ΔS	Cl 2*p*
$[PtL_2Cl_2]$	73.5 (2.0)	76.9 (2.0)	400.8 (2.8)	400.1 (1.8)	401.4 (1.8)	1.3	164.4 (2.8)	163.4 (2.3)	164.9 (2.3)	1.5	198.6 (2.8)
$[Pt(L - H)_2]$	73.1 (1.8)	76.4 (1.8)	400.3 (3.5)	399.4 (1.8)	401.2 (1.8)	1.8	163.9 (2.9)	163.1 (2.3)	164.7 (2.3)	1.6	
$[Pt(L - 2H)_2]$	73.2 (1.9)	76.5 (1.9)	400.4 (3.0)	399.7 (1.8)	401.1 (1.8)	1.4	164.1 (3.0)	163.4 (2.3)	164.9 (2.3)	1.5	
$[Pt(PhL)_2Cl_2]$	73.3 (1.8)	76.6 (1.8)	400.6 (2.7)	399.9 (1.8)	401.3 (1.8)	1.4	164.2 (2.8)	163.4 (2.3)	165.0 (2.3)	1.6	199.1 (2.9)
$[Pt(PhL - H)(PhL)Cl]$	73.2 (1.9)	76.5 (1.9)	400.7 (3.0)	400.0 (1.9)	401.5 (1.8)	1.5	164.3 (3.0)	163.6 (2.3)	165.0 (2.3)	1.4	199.3 (3.0)
$[Pt(PhL - H)_2]$	73.2 (1.8)	76.5 (1.8)	400.0 (3.5)	399.1 (1.8)	400.9 (1.8)	1.8	164.0 (2.8)	163.2 (2.3)	164.8 (2.3)	1.6	
$[Pt(PhL - 2H)_2]$	73.5 (1.8)	76.8 (1.8)	400.4 (2.7)	399.8 (1.8)	401.0 (1.8)	1.2	164.1 (2.8)	163.3 (2.3)	164.9 (2.3)	1.6	
L·HCl			400.3 (3.0)	399.5 (1.8)	401.0 (1.8)	1.5	164.4 (3.0)	163.4 (2.3)	164.9 (2.3)	1.5	198.6 (2.8)
L			400.2 (3.0)	399.5 (1.8)	400.9 (1.8)	1.3	164.0 (3.0)	163.4 (2.3)	164.7 (2.3)	1.3	
PhL			400.5 (2.7)	399.6 (1.8)	400.8 (1.8)	1.2	163.8 (3.0)	163.1 (2.3)	164.5 (2.3)	1.4	
$[Pt\{Et_2NC(=S)S\}_2]$	72.5 (1.7)	75.8 (1.7)	400.0 (1.8)				163.3 (2.3)				
$K_2[PtCl_6]$	75.8 (1.7)	79.1 (1.7)									199.7 (2.7)
$K_2[PtCl_4]$	73.4 (1.7)	76.7 (1.7)									199.8 (2.7)
Pt^0 (metal foil)	71.0 (1.6)	74.3 (1.6)									

* F.w.h.m. values are in parentheses. S^A and S^B represent the non-methylated and methylated sulphur binding energies, respectively, obtained after the curve-fitting procedure.

only one N^3–H is observed, corresponding to the coalesced two low-field resonances; when the sample is taken again to room temperature the two peaks at 11.59 and 11.63 are again observed. A parallel trend is observed for the S–Me resonances. This finding is in agreement with the greater ease shown by the dithiocarbazic ester ligands to form *trans* complexes.

$[Pt(PhL - 2H)_2]$. This is insoluble in Me_2SO and the spectrum was obtained in CS_2 solution. As in the case of $[Pt(L - 2H)_2]$, only one isomer, which by *X*-ray structural analysis has been determined to be *trans*-$[PtN_2S_2]$,[12] is observed by n.m.r. spectroscopy. No spectrum has been obtained for $[PtL_2Cl_2]$ because of its insolubility in Me_2SO and in other suitable solvents.

X-Ray Photoelectron Spectra.—The Pt $4f_{\frac{7}{2},\frac{5}{2}}$ doublet binding energy measurements can serve as a probe for establishing the extent to which the electron density over the metal is influenced by the progressive deprotonation of the ligands, both in the phenyl derivative and in the unsubstituted forms. Data on $K_2[PtCl_4]$, $K_2[PtCl_6]$, $[Pt\{Et_2NC(S)S\}_2]$, and Pt metal are also included as a reference for the assignment of the Pt oxidation state in the complexes considered here.

Table 8 collects the elemental b.e.s. and the full width at half-maximum (f.w.h.m.) values of the various compounds (including L, L·HCl, and PhL) and of reference samples. The Pt $4f_{\frac{7}{2}}$ orbital exhibits b.e. values ranging from 73.1 to 73.5 eV in all the compounds examined. Comparison with literature data [19] and the close similarity of the values for $[Pt\{Et_2NC(S)S\}_2]$, $K_2[PtCl_4]$ and the title complexes suggest the presence of Pt^{II} in all these compounds. Furthermore, the two components of the Pt 4*f* doublet exhibit a nearly constant f.w.h.m. (1.8—2.0 eV) and are well resolved without any additional contributing component throughout the series (Figure 3). This leads to the conclusion that no mixed oxidation state occurs for the metal.[20] The constancy of the b.e.s. in the complexes seems to indicate that the platinum experiences a similar electron density independently of the ligand to which it is co-ordinated; this conclusion is based on the assumption that the relaxation energy contribution to the Pt 4*f* photoemission process is similar for all the complexes.

A peak-fitting procedure in the N 1*s* region was attempted assuming the contribution of two Gaussian peaks, each with a f.w.h.m. value around that found for the N 1*s* peak (1.8 eV) of $[Pt\{Et_2NC(S)S\}_2]$, in which each ligand has a single N atom. Similarly, the f.w.h.m. of the asymmetric sulphur band of the same compound (made up of the unresolved $2p_{\frac{3}{2},\frac{1}{2}}$ spin–orbit components), 2.3 eV, was assumed as the contribution of a unique S species [21] to be considered in the S 2*p* broadened bands of the examined complexes.

Treating the N 1*s* region first, we note that the lower b.e. component lies around 400 eV for the non-deprotonated compounds {namely $[PtL_2Cl_2]$, $[Pt(PhL)_2Cl_2]$, and $[Pt(PhL - H)(PhL)Cl]$} and the higher component around 401.4 eV. By comparison of these results with those related to $[Pt\{Et_2NC(S)S\}_2]$, in which the nitrogen is not co-ordinated to the metal, it is easy to note the close similarity between the low b.e. components of the title compounds and the N 1*s* value in $[Pt\{Et_2NC(S)S\}_2]$. This leads us to the assignment of the low b.e. component to the N^2 atom whilst the higher b.e. component should be considered as deriving from the N^3 atom. This indicates that the N^3 atom, which is known to be co-ordinated to Pt,[12] is involved in an electron back-donation mechanism toward the metal and, therefore, it experiences an appreciable negative charge release. As far as $[Pt(PhL - H)_2]$ and $[Pt(L - H)_2]$ are concerned, it is easily realised from Table 8 that, in both cases, there is a net decrease of the low b.e. component relative to the three compounds cited above. Referring to the scheme $\frac{1}{2}[Pt\{NHR{-}N{=}C(\bar{S})SMe\}]$ (I) $\longleftrightarrow$ $\frac{1}{2}[Pt\{NHR{-}\bar{N}{-}$

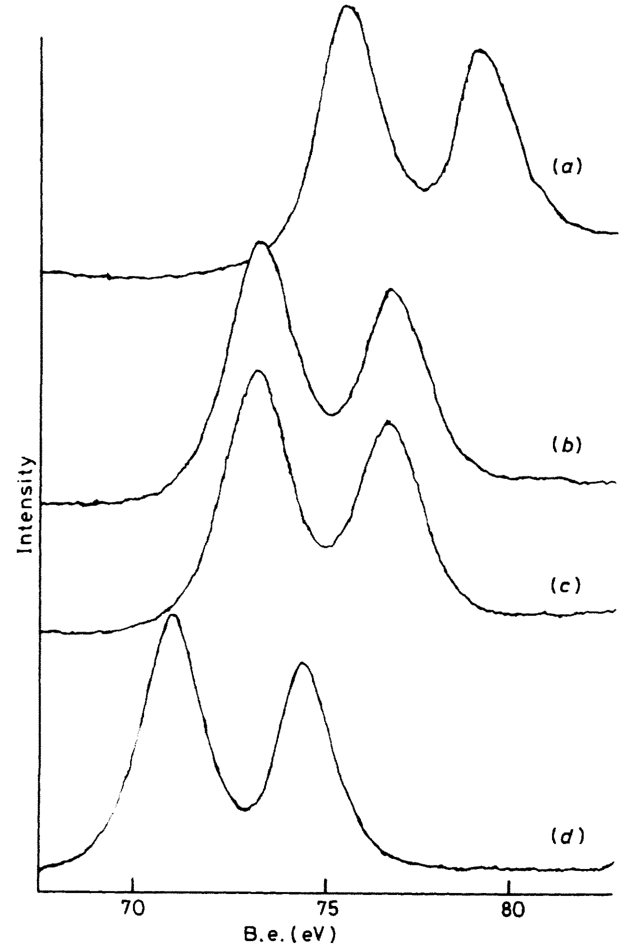

Figure 3. *X*-Ray photoelectron spectra of the $4f_{\frac{7}{2},\frac{5}{2}}$ doublet: (*a*) $K_2[PtCl_6]$, (*b*) $[PtL_2Cl_2]$, (*c*) $K_2[PtCl_4]$, (*d*) Pt metal

C(=S)SMe}] (II) (R = H or Ph), the relatively large shift toward low b.e.s of N^2 could be explained in terms of a major contribution of (II) in which a formal negative charge lies over this atom. Table 8 also shows for $[Pt(PhL - 2H)_2]$ and $[Pt(L - 2H)_2]$ a slight increase in b.e. for N^2 and a value of N^3 which is similar to that of the ' parent ' complexes $[Pt(PhL - H)_2]$ and $[Pt(L - H)_2]$. The resulting decrease in energy separation ΔN in both $[Pt(PhL - 2H)_2]$ and $[Pt(L - 2H)_2]$ can be ascribed to a larger electron delocalization over the N^2–N^3 bond according to *X*-ray data,[12,16] which show an extensive conjugation over the whole molecule. Indeed, the b.e.s in the latter complexes clearly resemble those of $[Pt(PhL)_2Cl_2]$ and $[Pt(PhL - H)(PhL)Cl]$. This can be interpreted in view of the fact that the second deprotonation of the complexes does not result in an increase of the negative charge but in a purely formal increase of the oxidation state of the nitrogens.

Considering now the S 2*p* region and again referring to the b.e. values in $[Pt\{Et_2NC(S)S\}_2]$ in which two equivalent sulphur atoms are present, we assigned the lower b.e. component to the Pt-co-ordinated sulphur and the higher component to the ester sulphur. The ΔS values (*i.e.* the b.e. separation between the two components obtained after peak-fitting) are more or less constant for all the complexes, a trend presumably due to the different chemical environment of S^A (co-ordinated to Pt) and S^B (bonded to the $^-CH_3$ group) which plays a major role in determining the electron density over the two sulphur atoms, regardless of the deprotonation state.

For the Cl 2*p* region, the results indicate the following. First, no appreciable difference is apparent between $[PtL_2Cl_2]$ and L·HCl. This fact, coupled with the constancy in the f.w.h.m. value, indicating the chemical equivalence of the two Cl atoms, suggests that both the Cl atoms lie outside the chromophore sphere [22] in the above complex. Secondly, $[Pt(PhL)_2Cl_2]$ and $[Pt(PhL - H)(PhL)Cl]$ exhibit b.e.s which are intermediate between the values given by ' pure ' anionic Cl (*e.g.* L·HCl) and platinum-co-ordinated Cl (*e.g.* $K_2[PtCl_4]$ and $K_2[PtCl_6]$). Consequently, the *X*-ray photoelectron spectra cannot give, in our opinion, any definite assignment on the chemical nature of the Cl atoms in these two complexes. We can only infer that, on the basis of the f.w.h.m. values, indicating a unique Cl species [22] in both cases, two equivalent Cl atoms are present in $[Pt(PhL)_2Cl_2]$.

Acknowledgements

We thank Dr. R. Andruzzi for assistance in the electrochemical measurements, and Mr. G. Chiozzini and Mr. M. Zugarini for help in experimental work.

References

1 A. Monaci and F. Tarli, *J. Chem. Soc., Dalton Trans.*, 1980, 499 and refs. therein.
2 M. Akbar Ali, S. E. Livingstone, and D. J. Phillips, *Inorg. Chim. Acta*, 1971, **5**, 119, 493; 1973, **7**, 179.
3 M. Das and S. E. Livingstone, *Inorg. Chim. Acta*, 1976, **19**, 5.
4 M. Das and S. E. Livingstone, *Br. J. Cancer*, 1978, **37**, 466.
5 S. K. Sengupta, S. K. Shani, and R. N. Kapoor, *Indian J. Chem., Part A*, 1980, **19**, 810.
6 R. Andruzzi and A. Trazza, *J. Electroanal. Chem.*, 1978, **86**, 201.
7 J. Sandstrom, *Ark. Kemi*, 1951, **4**, 297.
8 N. E. Colthup, L. H. Daly, and S. E. Wiberly, ' Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964.
9 K. Nakamoto, ' Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley, New York, 1978.
10 U. A. Jayasooriya and D. B. Powell, *Inorg. Chem.*, 1982, **21**, 1054.
11 D. Fac-Michalska and B. B. Kedzia, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 1976, **24**, 403.
12 G. Dessy and V. Fares, *Acta Crystallogr., Sect. B*, 1980, **36**, 2266.
13 C. E. Forbes, A. Gold, and R. H. Holm, *Inorg. Chem.*, 1971, **10**, 2479.
14 A. B. P. Lever, ' Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.
15 D. Gattegno and A. M. Giuliani, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1553.
16 G. Dessy and V. Fares, personal communication.
17 L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, 1966, **31**, 1878.
18 C. L. Habraken, M. T. Munter, and J. C. P. Westgeest, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 56.
19 W. M. Riggs, *Anal. Chem.*, 1972, **44**, 830.
20 J. K. Barton, S. A. Best, S. J. Lippard, and R. A. Walton, *J. Am. Chem. Soc.*, 1978, **100**, 3785.
21 C. Battistoni, M. Bossa, C. Furlani, and G. Mattogno, *J. Electron Spectrosc. Relat. Phenom.*, 1973, **2**, 355.
22 V. I. Nefedov, *J. Electron Spectrosc. Relat. Phenom.*, 1977, **12**, 459.

Received 13*th June* 1983; *Paper* 3/993