Electron-transfer Platinum Complexes of Esters of Dithiocarbazic Acid. The Crystal and Molecular Structure of $[Pt\{N(CH_2Ph)NC(S)SMe\}_2]$†

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The ligand behaviour of the esters of dithiocarbazic acid NHRNHC(=S)SR′ in intensely coloured complexes containing the doubly deprotonated ligands $[Pt\{NRNC(S)SR'\}_2]$ (R = H, R′ = CH_2Ph; R = CH_2Ph, R′ = Me or CH_2Ph; R = Pr^i, R′ = Me; R = hexyl, R′ = Me or CH_2Ph) has been investigated by electronic, i.r., and ^1H n.m.r. spectroscopy and electrochemistry. The crystal and molecular structure of $[Pt\{N(CH_2Ph)NC(S)SMe\}_2]$ has also been determined. All the complexes have a square-planar *trans*-PtN_2S_2 chromophore; they are dithiolene-like and show electron-transfer properties.

We have recently[1] investigated the co-ordination properties of $NH_2NHC(=S)SMe$ (L^1) and NHPhNHC(=S)SMe (PhL^1) in platinum complexes prepared under different chemical conditions. The ligands are co-ordinated in neutral and/or anionic deprotonated form, and the intensely coloured complexes containing the doubly deprotonated ligands are dithiolene-like and show electron-transfer properties.

Here we report an extension of that investigation to the co-ordinating properties of the benzyl ester of dithiocarbazic acid $NH_2NHC(=S)SCH_2Ph$ (L^2) and of the methyl and benzyl esters of N^3-substituted dithiocarbazic acids. This work deals in particular with platinum complexes containing the doubly deprotonated ligands. The esters considered are: L^2, $NH(CH_2Ph)NHC(=S)SMe$ ($PhCH_2L^1$), $NH(CH_2Ph)NHC(=S)SCH_2Ph$ ($PhCH_2L^2$), $NH(C_6H_{13})NHC(=S)SMe$ ($C_6H_{13}L^1$), $NH(C_6H_{13})NHC(=S)SCH_2Ph$ ($C_6H_{13}L^2$), and $NH(Pr^i)NHC(=S)SMe$ (Pr^iL^1).

Experimental

Materials.—The chemicals were commercial analytical grade reagents and used without further purification, except for the solvents employed for electrochemical measurements which were purified as described in ref. 2. Nitrogen gas was a ultra-high-purity commercial product. All the compounds were dried *in vacuo* (1 Torr) over P_2O_5, unless otherwise stated. Deuteriated solvents were Merck UVASOL or Wilmad products (minimum isotopic purity 99.9%).

Preparation of the Ligands.—The compound $NH_2NHC(=S)SCH_2Ph$ (L^2) was prepared as reported.[3a] The N^3-substituted esters, NHRNHC(=S)SR′ (R = Pr^i, hexyl, or CH_2Ph; R′ = Me or CH_2Ph), were prepared by hydrogenation of the appropriate Schiff bases.

Preparation of the Schiff Bases.—$CH_3(CH_2)_4CH=NNHC(=S)SMe$. The compound $CH_3(CH_2)_5CHO$ (33 mmol) was added to a solution of L^1 (33 mmol) in absolute ethanol (150 cm^3) and stirred for 2 h. The volume of the solution was reduced at low pressure (10 Torr), and the white product was filtered off, washed with absolute ethanol, and dried; yield 76%, m.p. 46 °C (from light petroleum, b.p. 40—60 °C).

The compound $CH_3(CH_2)_4CH=NNHC(=S)SCH_2Ph$ was prepared similarly from L^2; yield 80%, m.p. 41 °C (from n-hexane). The compounds $Me_2C=NNHC(=S)SMe$ and $PhCH=NNHC(=S)SR'$ (R′ = Me or CH_2Ph) were prepared as described in ref. 3(*b*)—(*d*).

Table 1. Analytical data for the ligands and platinum complexes

		Analysis (%)[a]			
Compound	Colour	C	H	N	S
L^2	White	48.5 (48.45)	5.1 (5.1)	14.0 (14.1)	32.3 (32.35)
$PhCH_2L^1$	White	50.9 (50.9)	5.5 (5.7)	13.3 (13.2)	30.1 (30.1)
$PhCH_2L^2$	White	62.4 (62.5)	5.6 (5.6)	9.7 (9.7)	22.25 (22.2)
$C_6H_{13}L^1$	Colourless liquid	46.4 (46.6)	8.7 (8.8)	13.3 (13.6)	30.9 (31.1)
$C_6H_{13}L^2$	White	59.4 (59.5)	7.8 (7.85)	9.9 (9.9)	22.6 (22.7)
Pr^iL^1	White	36.7 (36.8)	6.7 (6.8)	17.1 (17.2)	39.1 (39.3)
$[Pt(L^2 - H)_2]$	Yellow	32.4 (32.6)	3.0 (3.1)	9.4 (9.5)	21.55 (21.8)
$[Pt(L^2 - 2H)_2]$	*b*	32.8 (32.7)	2.8 (2.7)	9.4 (9.5)	21.6 (21.8)
$[Pt(PhCH_2L^1 - 2H)_2]$	*b*	35.0 (35.1)	3.3 (3.3)	9.0 (9.1)	20.9 (20.8)
$[Pt(PhCH_2L^2 - 2H)_2]$	*b*	47.0 (46.9)	3.7 (3.7)	7.1 (7.3)	16.6 (16.7)
$[Pt(C_6H_{13}L^1 - 2H)_2]$	*b*	31.8 (31.8)	5.3 (5.3)	9.1 (9.3)	21.2 (21.2)
$[Pt(C_6H_{13}L^2 - 2H)_2]$	*b*	44.3 (44.5)	5.5 (5.3)	7.1 (7.4)	16.7 (17.0)
$[Pt(Pr^iL^1 - 2H)_2]$	*b*	23.2 (23.1)	3.9 (3.9)	10.5 (10.8)	24.8 (24.7)

[a] Calculated values in parentheses. [b] Red-green dichroic crystals.

Hydrogenation of the Schiff Bases.—The hydrogenation was performed with $NaBH_4$ according to a reported method:[4] Pr^iL^1, yield 46%, m.p. 78 °C (from hot n-hexane); $C_6H_{13}L^1$: yield 67%, m.p. 18 °C (from hot n-hexane); $C_6H_{13}L^2$, yield 73%, m.p. 41 °C (from hot n-hexane); $PhCH_2L^1$, yield 68%, m.p. 51 °C (from cyclohexane); $PhCH_2L^2$, yield 51%, m.p. 101 °C (from n-hexane and benzene).

Preparation of the Complexes.—$[Pt(L^2 - H)_2]$ [$L^2 - H$ = $NH_2N=C(S)SCH_2Ph$]. A boiling solution of $K_2[PtCl_4]$ (1.26 mmol) in water (20 cm^3) was added to a boiling solution of L^2

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† Bis[methyl 3-benzyldithiocarbazato(2 –)-N^3S]platinum(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: Torr ≈ 133 Pa.

(2.52 mmol) in ethanol (60 cm^3). After boiling for 15 min, the product was filtered off, washed with hot water–ethanol (1:2), and dried; yield 81%, m.p. 245 °C (decomp.).

$[Pt(L^2 - 2H)_2][L^2 - 2H = NHNC(S)SCH_2Ph]$. The complex $[Pt(L^2 - H)_2]$ (1.19 mmol) was dissolved in pyridine (100 cm^3). After 5 min, 30% aqueous H_2O_2 (50 cm^3) was added and after stirring for 4.5 h water (400 cm^3) was added. After 2 h the blue compound was filtered off, washed with water until the smell of pyridine had disappeared, dried (yield 72%), and crystallised from diethyl ether; yield 23%.

$[Pt(PhCH_2L^1 - 2H)_2][PhCH_2L^1 - 2H = N(CH_2Ph)NC(S)SMe]$. A solution of $K_2[PtCl_4]$ (0.7 mmol) in water (20 cm^3) was added to a solution of $PhCH_2L^1$ (1.4 mmol) in ethanol (30 cm^3). After a few minutes the solution became yellow and a yellow precipitate formed. Then NH_4OH (1 mol dm^{-3}) was added until pH 9 was reached. The dark green product was filtered off, washed with water–ethanol (1:2), dried (yield 88%), and crystallised from boiling CS_2; yield 26%, m.p. 209 °C (decomp.).

The complexes $[Pt(PhCH_2L^2 - 2H)_2]$ $[PhCH_2L^2 - 2H = N(CH_2Ph)NC(S)SCH_2Ph]$, yield 92%, m.p. 201 °C (decomp.) (from boiling benzene, yield 20%), $[Pt(C_6H_{13}L^1 - 2H)_2]$ $[C_6H_{13}L^1 - 2H = N(C_6H_{13})NC(S)SMe]$, yield 81%, m.p. 77—78 °C (decomp.) (from boiling n-hexane, yield 23%), $[Pt(C_6H_{13}L^2 - 2H)_2]$ $[C_6H_{13}L^2 - 2H = N(C_6H_{13})NC(S)SCH_2Ph]$, yield 45%, m.p. 104 °C (decomp.) (from hot benzene), and $[Pt(Pr^iL^1 - 2H)_2]$ $[Pr^iL^1 - 2H = NPr^iNC(S)SMe]$, yield 82%, m.p. 193 °C (from boiling CS_2), were prepared following the procedure reported for $[Pt(PhCH_2L^1 - 2H)_2]$.

The analytical data are collected 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, i.r. spectra of Nujol or poly(chlorotrifluoroethylene) mulls with a Perkin-Elmer 983 spectrophotometer. Visible reflectance spectra and magnetic moments were measured as described in ref. 5. All the compounds were diamagnetic. Melting points were taken on a Buchi MSP-20 apparatus and are uncorrected.

Electrochemical Measurements.—D.c. and a.c. polarography and cyclovoltammetry were performed, as reported in ref. 2, with an Amel model 471 three-electrode multifunctional assembly. The working electrode was a standard Amel pulsing or stationary electrode and the counter electrode was a platinum wire. A $Hg|Hg_2Cl_2$, NaCl (saturated, aq)|agar–NaCl(aq)|agar (1.5%, w/v)–dmf–water (40%, v/v)–NEt_4ClO_4 (saturated) | methyl cellulose (5%, w/v)–dmf–NEt_4ClO_4 (saturated) sintered-glass disc (dmf = dimethylformamide) served as reference electrode. Its potential was 40 mV *vs.* an aqueous saturated calomel electrode (s.c.e.), the liquid junction potential being included. All potentials reported in Tables 6 and 7 are quoted with respect to the reference electrode with an accuracy of ±5 mV.

N.M.R. Spectra.—The ^1H n.m.r. spectra were recorded with a 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. The deuteriated solvent was used for field-frequency lock. All experiments were performed at 25 ± 1 °C.

Table 2. Final atomic co-ordinates, with estimated standard deviations (e.s.d.s) in parentheses for $[Pt(PhCH_2L^1 - 2H)_2]$

Atom	*x*	*y*	*z*
Pt	0.0	0.0	0.0
S(1)	0.048 8(1)	0.120 3(1)	−0.192 7(2)
S(2)	0.164 8(1)	−0.007 4(2)	−0.417 2(2)
N(1)	0.106 2(4)	−0.149 6(5)	−0.206 5(5)
N(2)	0.059 4(3)	−0.158 6(4)	−0.087 1(5)
C(1)	0.105 1(4)	−0.019 9(6)	−0.262 0(6)
C(2)	0.140 7(5)	0.174 3(7)	−0.478 8(8)
C(3)	0.056 9(4)	−0.308 5(5)	−0.043 0(6)
C(4)	−0.030 3(4)	−0.387 5(5)	−0.155 8(6)
C(5)	−0.135 4(5)	−0.371 7(6)	−0.150 4(6)
C(6)	−0.216 1(5)	−0.438 6(8)	−0.251 0(8)
C(7)	−0.190 0(6)	−0.528 5(6)	−0.365 0(8)
C(8)	−0.087 4(6)	−0.546 5(7)	−0.371 2(8)
C(9)	−0.007 1(5)	−0.474 3(5)	−0.265 6(7)

Table 3. Bond distances (Å) and angles (°), with e.s.d.s in parentheses for $[Pt(PhCH_2L^1 - 2H)_2]$

Pt–S(1)	2.280(1)	C(3)–C(4)	1.522(9)
Pt–N(2)	1.937(4)	C(4)–C(5)	1.396(8)
S(1)–C(1)	1.704(5)	C(4)–C(9)	1.369(8)
S(2)–C(1)	1.753(5)	C(5)–C(6)	1.365(10)
S(2)–C(2)	1.808(7)	C(6)–C(7)	1.429(9)
N(1)–N(2)	1.356(6)	C(7)–C(8)	1.370(11)
N(1)–C(1)	1.322(7)	C(8)–C(9)	1.407(11)
N(2)–C(3)	1.474(7)		
S(1)–Pt–N(2)	82.5(1)	S(2)–C(1)–N(1)	113.1(4)
Pt–S(1)–C(1)	96.4(2)	N(2)–C(3)–C(4)	111.0(5)
C(1)–S(2)–C(2)	103.1(3)	C(5)–C(4)–C(9)	118.8(6)
N(2)–N(1)–C(1)	112.8(4)	C(4)–C(5)–C(6)	122.6(5)
Pt–N(2)–N(1)	124.7(3)	C(5)–C(6)–C(7)	117.6(6)
Pt–N(2)–C(3)	126.9(3)	C(6)–C(7)–C(8)	120.7(7)
N(1)–N(2)–C(3)	108.3(4)	C(7)–C(8)–C(9)	119.6(6)
S(1)–C(1)–S(2)	123.3(3)	C(8)–C(9)–C(4)	120.7(6)
S(1)–C(1)–N(1)	123.6(4)		

Crystal Structure Determination for $[Pt\{N(CH_2Ph)NC(S)SMe\}_2]$.—*Crystal data.* $C_{18}H_{20}N_4PtS_4$, $M = 615.73$, monoclinic, $a = 13.103(3)$, $b = 9.455(2)$, $c = 8.924(2)$ Å, $\beta = 104.10(2)°$, $U = 1\,072.2(4)$ A^3, systematic extinctions: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$, space group $P2_1/n$, $D_m = 1.88$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1.89$ g cm^{-3}, $F(000) = 596$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 72.05$ cm^{-1}.

A selected crystal (0.2 × 0.3 × 0.8 mm) suitable for *X*-ray investigation was mounted on a glass capillary for data collection, at room temperature, on a Nicolet $P2_1$ four-circle autodiffractometer. The cell dimensions were obtained by least-squares refinement of the setting angles of 15 automatically centred reflections ($2\theta > 30°$).

Data collection. The intensities of 1 951 independent reflections having $I \geqslant 3\sigma(I)$ were collected by the θ—2θ scan technique with graphite-monochromated Mo-K_α radiation and corrected for Lorentz and polarization effects. A semiempirical absorption correction, based on a 360° ψ scan around the scattering vector of selected reflections was applied.

Structure solution and refinement. The structure was determined by Patterson and Fourier methods and 125 parameters were refined by least-squares (16 observations per parameter) to a final conventional $R = (\Sigma|\Delta F|/\Sigma|F_o|) = 0.0303$, $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0318$. The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme $w = 1/[\sigma(F_o)]^2$. Anisotropic thermal parameters were used for all non-hydrogen atoms, and a fixed isotropic thermal parameter of 4.0 A^2 for hydrogen atoms located by a difference Fourier and then included at calculated positions. Final atomic co-ordinates for non-hydrogen atoms are given in Table 2, interatomic distances and angles in Table 3.

Calculations were performed on a Data General MV 8000

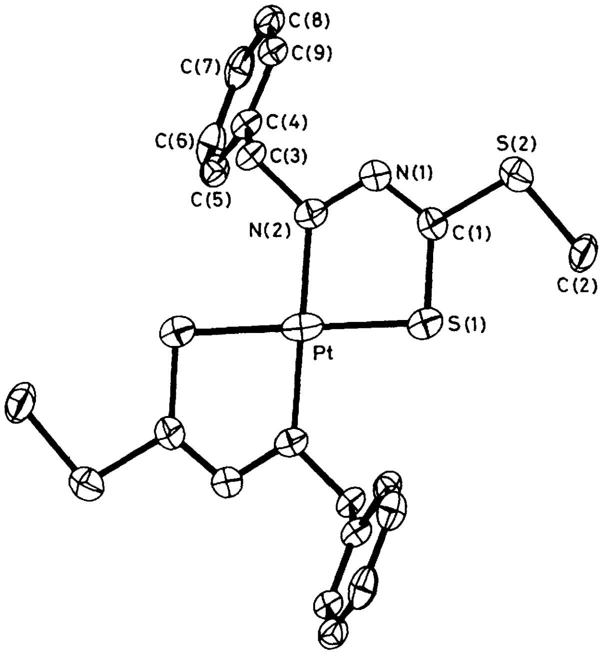

Figure 1. A perspective view of the molecular structure of [Pt($PhCH_2L^1-2H)_2$], projected on to the PtN_2S_2 co-ordination plane. Thermal ellipsoids are drawn at the 30% probability level (see D. Capitani, S. Cerrini, and R. Spagna, Abstracts of the 15th Meeting of the Italian Crystallographic Association, Roma, 1985, p. 85)

computer using the SIR-CAOS program system.[6] Neutral-atom scattering factors (f' and f'' values) were taken from ref. 7.

Results and Discussion

Preparation and Properties of the Platinum Complexes.—All the ligands react readily with $K_2[PtCl_4]$ in aqueous ethanol. If the medium is made strongly basic, crystalline intensely coloured compounds which contain doubly deprotonated ligands are formed. We assume that there is progressive deprotonation of the ligands, in accord with the reactions of L^1 and PhL^1 with $K_2[PtCl_4]$.[1] The complexes are soluble in most organic solvents, showing differences dependent on the N^3 substituents, *e.g.* substitution of an alkyl group for the proton markedly enhances the solubility. None of the complexes is very stable in donor solvents, *e.g.* the deep green solution of [Pt($PhCH_2L^1$ − 2H)$_2$] in Me_2SO turns orange after a few days due to the formation of the corresponding Schiff-base complex [Pt(PhCH=NN=C(S)SMe)$_2$]. This behaviour is strictly dependent on the N^3 substituent; further investigation on the reactivity of such complexes is in progress and will be the object of a future report.[8b]

I.r. Spectra.—The i.r. spectrum of [Pt(L^2 − H)$_2$] shows absorption bands at 3 186, 3 146, and 3 111 cm^{-1}, which can be assigned to ν(N–H), at 1 586 and 1 576 cm^{-1} attributable to $\delta(NH_2)$, and a strong band at 1 500 cm^{-1} assigned to $\nu(\mathrm{C}\overset{...}{-}\mathrm{N})$ of the partial double bond of the ligand deprotonated at N^2. The spectrum of [Pt($C_6H_{13}L^2$ − H)$_2$][8b] exhibits bands attributable to ν(N–H) at 3 080 and 3 090 cm^{-1} and a strong band at 1 544 cm^{-1} attributable to $\nu(\mathrm{C}\overset{...}{-}\mathrm{N})$. In the spectra of both compounds the ν(N–H) bands are shifted to lower frequencies relative to the free ligands, which is diagnostic of N^3-co-ordination. In the spectrum of [Pt(L^2 − 2H)$_2$] a strong band at 3 112 cm^{-1} is assigned to ν(N–H) of the twice deprotonated ligand. Its shift to lower wavenumbers relative to [Pt(L^1 − 2H)$_2$] (3 220 cm^{-1}) is in agreement with the electron-attracting effect of the benzyl group. The spectra of [Pt(RL − 2H)$_2$] (L = L^1 or L^2) lack the bands attributable to ν(N–H), thus confirming that both N atoms of the ligands are deprotonated. The bands attributable to $\nu(\mathrm{C}\overset{...}{-}\mathrm{N})$ of the doubly deprotonated ligands are not found above 1 470 cm^{-1}, in agreement with a higher electronic delocalisation over the whole molecule, higher than for the complexes with the monodeprotonated ligands whose spectra exhibit these bands in the range 1 550—1 500 cm^{-1}. All the complexes reported in the present work show bands attributable to ν(Pt–N) and to ν(Pt–S) in the ranges 541—527 and 406—373 cm^{-1} respectively, supporting NS-chelation of the ligands.

Description of the Structure.—Figure 1 shows the molecular structure of [Pt{N(CH_2Ph)NC(S)SMe}$_2$] which consists of monomeric complex units, with no interaction between symmetry-related units below 3.5 Å. The platinum atom lies on a centre of symmetry within a distorted square-planar geometry. The C(3)N(2)N(1)C(1)S(1)S(2)C(2) system is highly planar, the maximum out-of-plane displacement being 0.095 Å. The ligand has a *cis–cis* conformation, strictly resembling the [Pt(PhL^1 − 2H)$_2$] analogue.[9] The bond distances and angles are also not very different from those found in that complex, the only significant difference being the Pt–N(2) bond length of 1.937(4) Å, shorter than the corresponding one of 1.966(4) Å, and related to the different σ influence of the benzyl group compared with the phenyl group on the substituted nitrogen atom: N(2)–C(3)(benzyl) 1.474(7); N(2)–C(3)(phenyl) 1.429(7) Å.

N.M.R. Spectra.—The ^1H n.m.r. parameters for the compounds are collected in Table 4. They afford clear evidence that co-ordination to the platinum atom occurs through the terminal nitrogen atom: ^{195}Pt satellites are observed in every case for the substituent on N^3, be it a proton or an alkyl group.

The complex [Pt(L^2 − H)$_2$] exists in solution as a mixture of the *cis* and *trans* isomers of the N_2S_2 chromophore. By analogy with [Pt(L^1 − H)$_2$],[1] we assign the low-field N^3–H resonance (δ 9.03 p.p.m.) to the *trans* isomer (70% abundant); the ^2J(Pt–N–H) value is smaller for this isomer than for the other, as found for [Pt(L^1 − H)$_2$].[1] The N^3–H resonances exhibit a large downfield shift compared to the free ligand, indicating a decreased electron density on the co-ordinated nitrogen. The very low-field (δ 14.11 p.p.m.) spectral position of the N^3–H resonance of [Pt(L^2 − 2H)$_2$] suggests that, upon complexation, a pseudo-aromatic penta-atomic ring, similar to pyrazole is formed, as had been found for the corresponding L^1 complex.[1] Electron delocalisation and the ring current explain the downfield shift, not only of the N^3–H signal but also that of the S–CH_3 resonance. We propose a *trans*-N_2S_2 chromophore for this complex, by analogy with the corresponding, certainly *trans*, L^1 chelate, since the two have almost identical ^2J(Pt–N–H) values (90 and 90.6 Hz for the L^2 and L^1 complexes, respectively).

In [Pt($PhCH_2L^1$ − 2H)$_2$] chelation through the terminal N atom and the thione sulphur is indicated both by the presence of the ^{195}Pt satellites on the N^3–CH_2 signal (^3J = 15.3 Hz) and by the large downfield shift of this signal and that of the N^3–CH_2 and S–CH_3 resonances relative to the free ligand. This deshielding is related both to a decrease in the electron density at the co-ordinated atoms and to the ring current arising from some electron delocalisation in the chelate ring. The low-field shift of the N^3–CH_2 resonance of [Pt($PhCH_2L^2$ − 2H)$_2$] is also related to co-ordination through the terminal nitrogen, as indicated by the ^{195}Pt satellites on this signal. The ^3J(Pt–N–C–H) value is the same as that found for the corresponding $PhCH_2L^1$ complex, suggesting that the same

Table 4. Proton n.m.r. parameters (δ/p.p.m.)[a] for the ligands and platinum complexes (298 ± 1 K; B_o = 4.7 T)

			N^3–R					S–R′	
Compound	Solvent	N^3–H	α	β	Others	N^2–H	S–CH_3	CH_2	C_6H_5
L^2	$(CD_3)_2SO$	5.23				8.58		4.49[b] 4.51	7.44[c]
$[Pt(L^2 - H)_2]$	$(CD_3)_2SO$	8.82 (42.6 ± 0.5)						4.39	7.44[c]
	$(CD_3)_2SO$	9.03[d] (42.0 ± 0.5)							
$[Pt(L^2 - 2H)_2]$	$(CD_3)_2SO$	14.11 (90 ± 1)						4.70	7.6[c]
$PhCH_2L^1$	$(CD_3)_2SO$	5.99	3.94	7.34[c]		11.00	2.38		
$[Pt(PhCH_2L^1 - 2H)_2]$	CS_2		5.91 (15.3 ± 0.3)	7.55[c]			2.98		
$PhCH_2L^2$	$(CD_3)_2SO$	6.12	4.05	7.43[c]		11.15		4.48	7.43[c]
$[Pt(PhCH_2L^2 - 2H)_2]$	CD_2Cl_2		5.73 (15.0 ± 0.3)	7.35[c]				4.46	7.35[c]
Pr^iL^1	$CDCl_3$	3.87	3.17[d] 3.33	1.11		8.89	2.54[d] 2.64		
$[Pt(Pr^iL^1 - 2H)_2]$	$CDCl_3$		5.16 (9.4 ± 0.3)	1.50			2.71		
$C_6H_{13}L^1$	$CDCl_3$	4.10	2.86[c,d] 2.90	1.46[c]	1.25[c] (γ,δ,ε-CH_2) 0.83 (CH_3)	9.57	2.49[d] 2.57		
$[Pt(C_6H_{13}L^1 - 2H)_2]$	$CDCl_3$		4.58 (14.3 ± 0.3)	1.95[c]	1.33[c] (γ,δ,ε-CH_2) 0.88 (CH_3)		2.70		
$C_6H_{13}L^2$	$CDCl_3$	4.90	2.88[e] 2.96	1.49[c]	1.28[c] (γ,δ,ε-CH_2) 0.87 (CH_3)	8.66		4.46[e] 4.52	7.96[c]
$[Pt(C_6H_{13}L^2 - 2H)_2]$	$CDCl_3$		4.57 (14.7 ± 0.3)	1.94[c]	1.32[c] (γ,δ,ε-CH_2) 0.89 (CH_3)			4.44	7.34

[a] Values relative to $SiMe_4$ (0 p.p.m.), ^2J(Pt–N–H) or ^3J(Pt–N–C–H)/Hz in parentheses. [b] Most abundant, *ca.* 56%. [c] Centre of multiplet; other multiplicities and related *J* values not reported. [d] Most abundant, *ca.* 70%. [e] Most abundant, *ca.* 65%.

trans geometry found in the crystal structure of the latter is present also in this compound.

The complex $[Pt(Pr^iL^1 - 2H)_2]$ is formed by chelation through the thione sulphur and the terminal nitrogen, as evidenced by the downfield shift of the N^3–CH_2 resonance and by the presence of ^{195}Pt satellites; electron delocalisation over the whole molecule is indicated by the deshielding of the SCH_3 group which is not directly involved in the bonding. The ^3J(Pt–N–C–H) value, however, is considerably lower than those observed for the other complexes, but we have not yet investigated this question.

The complexes $[Pt(C_6H_{13}L^1 - 2H)_2]$ and $[Pt(C_6H_{13}L^2 - 2H)_2]$ show ^{195}Pt satellites and a considerable downfield shift for the N^3–CH_2 resonance, suggesting chelation through the terminal N atom. The ^3J(Pt–N–C–H) values (14.3 and 14.7 Hz, respectively) are practically identical and differ very little from those found for complexes containing the doubly deprotonated $PhCH_2L^1$ and $PhCH_2L^2$ ligands: this finding suggests the same *trans* geometry for all the four N_2S_2 chelates.

Electronic Spectra.—The electronic spectra of the NRNC(S)SR′ complexes (R = H, Pr^i, hexyl, or CH_2Ph; R′ = Me or CH_2Ph) are very similar and show features common to dithiolene platinum complexes with electron-transfer properties (see Figure 2).[10]

The prominent strong bands in the range 14 000—15 000 cm^{-1} (log ε = 4.5), absent in the case of $[Pt(L^2 - H)_2]$, are assigned to ligand-to-metal charge-transfer (l.m.c.t.) absorption bands in accord with our previous report on the complexes $[Pt(L^1 - 2H)_2]$ and $[Pt(PhL^1 - 2H)_2]$.[1] From Table 5 it appears that the energies of these bands follow the trend: $[Pt(L - 2H)_2]$ (*ca.* 15 400 cm^{-1}) > $[Pt(RL - 2H)_2]$ (*ca.* 14 500

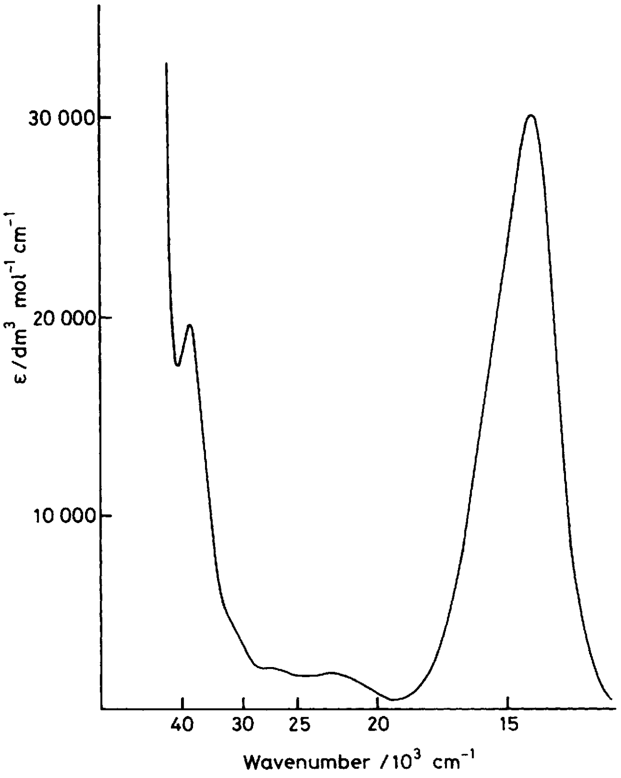

Figure 2. Electronic spectra of $[Pt(C_6H_{13}L^2 - 2H)_2]$ in thf

cm^{-1}) > [Pt(PhL^1 − 2H)$_2$] (13 600 cm^{-1}, L = L^1 and L^2). From *X*-ray diffraction data it is known that [Pt(L^1 − 2H)$_2$], [Pt(PhL^1 − 2H)$_2$], and [Pt(PhCH$_2$L^1 − 2H)$_2$] (see text) have a square-planar *trans*-PtN$_2$S$_2$ chromophore. The close similarity of all the electronic spectra of the platinum complexes containing the doubly deprotonated ligands suggests the same conformation of the chromophore, and is confirmed by the lack of any lowering of symmetry in their i.r. spectra. For a given metal ion, the l.m.c.t. band energies decrease as the ligand becomes more readily oxidisable.[11] Hence the shift in these bands to lower energies depends on the substituent on N^3 which lies on a five-membered highly delocalised chelate ring. The electron-withdrawing ability of the N^3 substituents follows the order: H > CH$_2$Ph = C$_6$H$_{13}$ = Pr^i > Ph. The behaviour of the alkyl groups relative to the hydrogen atom is in accord with what has been observed for the basicity constants of alkyl-substituted hydrazines which are lower than for unsubstituted hydrazine.[12]

Table 5. Electronic solution and reflectance spectra (10^3 cm^{-1}) of the platinum complexes[a]

Compound	Chromophore	
[Pt(L^1 − H)$_2$][b]		27.8 (sh), 34.8, 37.3 (sh)
[Pt(L^1 − 2H)$_2$][b]	*trans*-PtN$_2$S$_2$[c]	15.4 (4.38), 23.6 (3.20), 39.5 (4.34), 47.6 (4.37)
		14.6 (sh), 15.8, 20.0 (sh), 26.7, 37.0
[Pt(L^2 − H)$_2$]		28.6 (sh), 32.1
[Pt(L^2 − 2H)$_2$]		15.2 (4.46), 23.0 (3.28), 28.09 (sh) (3.37), 32.5 (sh)
		15.5, 17.4, 21.5, 26.0 (3.66), 38.8 (4.23)
[Pt(Pr^{i}L^1 − 2H)$_2$]		14.5 (4.45), 21.0 (sh) (3.10), 22.9 (3.24), 23.8 (sh), (3.2), 27.8 (sh) (3.32), 31.2 (sh), 35.5 (sh) (4.05), 38.6 (4.20)
		14.6, 16.0, 21.2 (sh), 23.8, 26.3
[Pt(C$_6$H$_{13}$L^1 − 2H)$_2$]		14.5 (4.10), 20.8 (sh) (2.87), 24.6 (3.45), 28.0 (3.57), 36.1 (sh) (4.23), 38.2 (4.30)
		14.5, 20.8
[Pt(C$_6$H$_{13}$L^2 − 2H)$_2$]		14.4 (4.48), 22.7 (3.25), 26.9 (3.34), 31.2 (sh) (2.57), 38.0 (4.29)
		13.1, 16.1 (sh), 20.1, 24.7
[Pt(PhCH$_2$L^1 − 2H)$_2$]	*trans*-PtN$_2$S$_2$[d]	14.4 (4.46), 20.5 (sh) (2.05), 22.6 (2.22), 27.0 (sh) (2.42), 31.2 (sh) (2.69), 38.0 (4.43)
		14.5, 23.3, 27.0, 31.2
[Pt(PhCH$_2$L^2 − 2H)$_2$]		14.4 (4.52), 20.5 (sh), 22.3 (2.29), 27.1 (3.50), 31.2 (sh) (3.75), 37.9 (4.34)
		14.6, 21.0, 27.2
[Pt(PhL^1 − 2H)$_2$][b]	*trans*-PtN$_2$S$_2$[e]	13.6 (4.43), 22.0 (sh) (3.73), 24.0 (3.82), 31.5 (4.18), 40.0 (sh) (4.23), 45.7 (4.43)
		13.7, 21.5, 22.7 (sh), 30.5, 38.5

[a] Log (ε/dm^3 mol^{-1} cm^{-1}) in parentheses. In tetrahydrofuran. [b] See ref. 1. [c] See ref. 8*a*. [d] From *X*-ray data (see text). [e] See ref. 9.

Finally, the presence of low-lying high-intensity c.t. absorptions (metal–ligand or ligand–ligand) in the transition range of square-planar platinum complexes (22 000—28 000 cm^{-1}) prevents an attribution of the *d–d* bands. This is also evident from the values of the absorption coefficient: for *d–d* transitions of square-planar platinum complexes log ε values of about 2 are expected, whereas here values in the range 2.7—3.4 were found.

Electrochemical Measurements.—Polarographic (d.c. and a.c.) and cyclovoltammetric data for the platinum complexes are reported in Tables 6 and 7, respectively. As for dithiolene and dithiolene-like complexes with a five-membered delocalised chelate ring,[13] the electrochemical data indicate that the present complexes belong to an electron-transfer series (Scheme).

$$\underset{(\mathbf{1})}{[\mathrm{Pt(N_2S_2)}]^+} \underset{-1e}{\overset{+1e}{\rightleftarrows}} \underset{(\mathbf{2})}{[\mathrm{Pt(N_2S_2)}]} \underset{-1e}{\overset{+1e}{\rightleftarrows}} \underset{(\mathbf{3})}{[\mathrm{Pt(N_2S_2)}]^-} \underset{-1e}{\overset{+1e}{\rightleftarrows}} \underset{(\mathbf{4})}{[\mathrm{Pt(N_2S_2)}]^{2-}}$$

Scheme.

Complex (**2**) shows in the range 0 to −2.0 V *vs.* s.c.e. well defined polarographic and cyclovoltammetric processes (see Figure 3) corresponding to the formation of the reduced forms (**3**) and (**4**). Both processes are monoelectronic and electrochemically quasi-reversible as inferred from the values of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ in d.c. polarography (slopes 1 and 2 in Table 6), from the width of the a.c. waves at half-height ($\Delta E^1_{p/2}$ and $\Delta E^2_{p/2}$ in Table 6), and from the cyclovoltammetric cathodic/anodic current ratios which are close to the theoretical values for monoelectronic reversible processes. Due to the very negative reduction potentials complexes (**3**) and (**4**) are oxidatively very unstable and their isolation has not been possible.

Cyclovoltammetric oxidation of [Pt(PhL^1 − 2H)$_2$] in the range 0—1.5 V *vs.* s.c.e. in CH$_2$Cl$_2$ reveals a monoelectronic reversible process at E_p = +1.230 V attributable to the

Table 6. D.c. and a.c. voltammetric data for the reduction at a pulsing platinum electrode in dmf solution[a]

		D.c.					A.c.			
Compound	Concentration (mmol dm^{-3})	$E^1_{\frac{1}{2}}$/V	$E^2_{\frac{1}{2}}$/V	Slope 1[b]/ V	Slope 2[b]/ V	Concentration (mmol dm^{-3})	E^1_p/V	E^2_p/V	$E^1_{p/2}$[c]/V	$E^2_{p/2}$[c]/V
[Pt(L^1 − 2H)$_2$][d]	0.5	−0.445	−1.230	0.070	0.070	0.5	−0.460	−1.260	0.100	0.140
[Pt(L^2 − 2H)$_2$]	1.0	−0.340	−1.125	0.070	0.090	1.0	−0.330	−1.145	0.115	0.115
[Pt(PhL^1 − 2H)$_2$][d]	0.5	−0.215	−0.912	0.052	0.070	0.5	−0.200	−0.920	0.096	0.092
[Pt(PhCH$_2$L^1 − 2H)$_2$]	0.5	−0.340	−1.250	0.050	0.090	1.0	−0.330	−1.270	0.120	0.140
[Pt(PhCH$_2$L^2 − 2H)$_2$]	0.5	−0.305	−1.200	0.070	0.070	1.0	−0.290	−1.225	0.125	0.125
[Pt(Pr^{i}L^1 − 2H)$_2$]	1.0	−0.425	−1.370	0.070	0.070	1.0	−0.440	−1.390	0.125	0.140
[Pt(C$_6$H$_{13}$L^1 − 2H)$_2$]	1.0	−0.410	−1.265	0.070	0.070	1.0	−0.360	−1.300	0.120	0.125
[Pt(C$_6$H$_{13}$L^2 − 2H)$_2$]	1.0	−0.360	−1.290	0.070	0.060	1.0	−0.385	−1.320	0.125	0.128

[a] Containing 0.1 mol dm^{-3} NEt$_4$ClO$_4$, pulsing time, t_p = 2 s; 20 °C; a.c. voltammetric curves were recorded using ω = 75 Hz and ΔE = 10 mV. [b] Calculated using $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ values. [c] Width at half peak height. [d] See ref. 1.

Table 7. Cyclic voltammetric data for platinum complexes in dmf solution

Compound	Concentration (mmol dm^{-3})	E^1_{pc}/V	E^2_{pc}/V	$\Delta E^1_{pc}{}^a$/V	$\Delta E^2_{pc}{}^a$/V	i^1_c/i^1_a	i^2_c/i^2_a
$[Pt(L^1 - 2H)_2]^b$	0.5	−0.460	−1.260	0.080	0.060	1.0	1.1
$[Pt(L^2 - 2H)_2]$	1.0	−0.360	−1.150	0.075	0.080	1.0	1.3
$[Pt(PhL^1 - 2H)_2]^b$	0.5	−0.210	−0.940	0.060	0.080	1.0	1.3
$[Pt(PhCH_2L^1 - 2H)_2]$	1.0	−0.365	−1.265	0.080	0.045	1.1	1.1
$[Pt(PhCH_2L^2 - 2H)_2]$	1.0	−0.320	−1.210	0.080	0.050	1.1	1.0
$[Pt(Pr^iL^1 - 2H)_2]$	1.0	−0.440	−1.380	0.070	0.060	1.0	1.0
$[Pt(C_6H_{13}L^1 - 2H)_2]$	1.0	−0.400	−1.255	0.075	*c*	1.0	*c*
$[Pt(C_6H_{13}L^2 - 2H)_2]$	1.0	−0.385	−1.315	0.080	0.090	1.0	1.0

[a] Cathodic to anodic peak potential separation. [b] See ref. 1. [c] Poorly resolved oxidation wave.

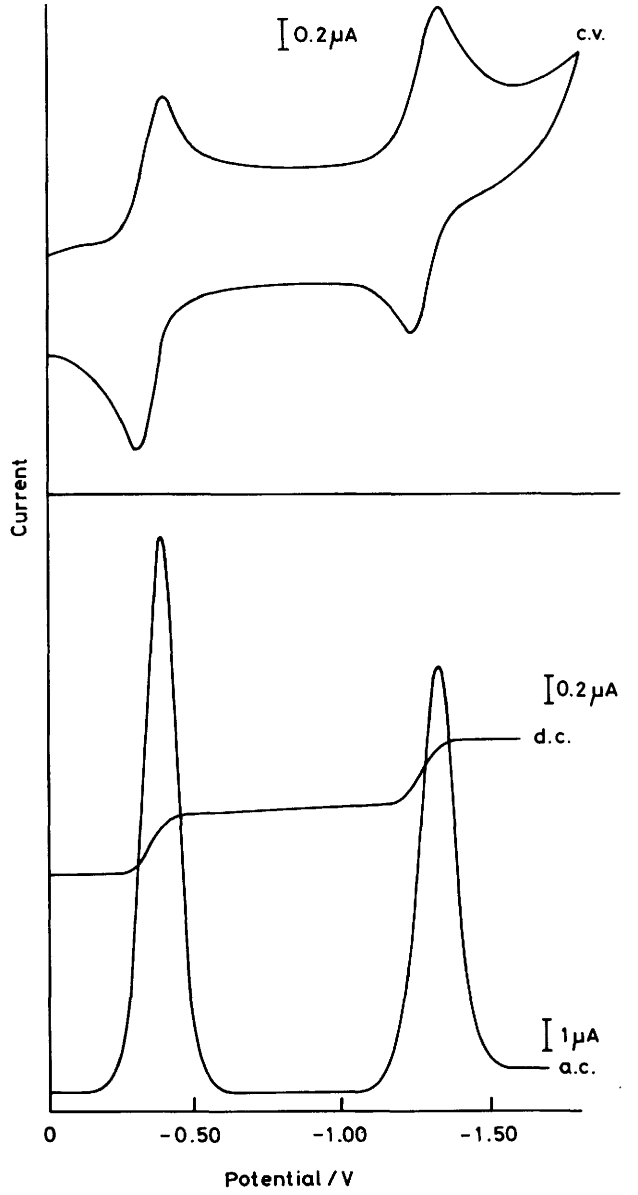

Figure 3. D.c., a.c., and cyclic voltammetry (c.v.) at a platinum electrode of $[Pt(C_6H_{13}L^2-2H)_2]$ in dmf–0.1 mol dm^{-3} NBu_4ClO_4

formation of complex (**1**), whereas for the remaining platinum complexes, E_p values of *ca.* 1.1 V corresponding to an incompletely reversible process have been found.

As for the N^3-substituent (R) effects in the complexes $[Pt(RL - 2H)_2]$ ($L = L^1$ or L^2) (see Tables 6 and 7), a remarkable influence of the phenyl group is observed when the E^1_p and E^2_p values are compared with those of unsubstituted $[Pt(L - 2H)_2]$, whereas alkyl substituents show intermediate effects on E^1_p and shift E^2_p. An enhanced delocalisation of the negative charge due to the N^3-phenyl group is probably the reason for the increase in E^1_p relative to the corresponding unsubstituted complexes, in accord with the changes in electronic spectra (see text).

Finally, it should be noted that substitution of the benzyl for the methyl group on sulphur influences the $E_{\frac{1}{2}}$ and E_p values and this is of interest since the substitution occurs on an atom not co-ordinated to the metal. This behaviour is in accord with electron spectroscopy for chemical analysis and *X*-ray results which show a highly delocalised electronic system over the whole molecule.[1]

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