Mixed Chloro-, *NN*-Dialkyldithiocarbamato-, and *S*-Alkyl *NN*-dialkyldithiocarbamate Complexes of Platinum(II). Crystal Structure of $[PtCl(S_2CNEt_2)(MeS_2CNEt_2)]$†

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The platinum(II) complexes $[PtCl(S_2CNMe_2)(EtS_2CNEt_2)]$ (**1**), $[PtCl(S_2CNEt_2)(MeS_2CNMe_2)]$ (**2**), and $[PtCl(S_2CNEt_2)(MeS_2CNEt_2)]$ (**3**) have been prepared and characterized by i.r. and ^1H n.m.r. spectroscopy. The crystal and molecular structure of compound (**3**) has been solved by *X*-ray diffraction methods and refined by least squares to a final *R* value of 0.037. The platinum atom is bonded, in the usual square-planar arrangement, to the sulphur atoms of the bidentate $^-S_2CNEt_2$ group, to the thiocarbonyl sulphur of the dithioester molecule, and to the chlorine atom. In solution the complexes release the weakly bonded dithioester molecule.

Recently we reported various *S*-alkyl *NN*-dialkyldithiocarbamate complexes of platinum(II) and palladium(II) halides which were tested for *in vitro* cytostatic activity against KB cells,[1,2] a line derived from a human epidermoid carcinoma of the mouth. In the complexes of general formula $[PtX_2L_2]$ ($L = R^1S_2CNR^2{}_2$; R^1, R^2 = Me or Et), the ligand was bound in a unidentate manner through the thiocarbonyl sulphur, whereas in the series $[PtX_2L]$ it was found to coordinate through both sulphur atoms. In synthesizing the 1:2 complexes, the formation of the side products containing the $^-S_2CNR_2$ group was occasionally observed. In particular, when platinum halides were dissolved in acetone solutions containing a large excess of MeS_2CNEt_2, small amounts of the species $[PtX(S_2CNEt_2)(MeS_2CNEt_2)]$ (X = Cl, Br, or I) separated in a few days, suggesting a slow *S*-demethylation process in the dithioester molecule.[2] In this new class of mixed platinum(II) complexes both ligands can potentially behave as uni- or bi-dentate. The versatile $^-S_2CNR_2$ ion can act either as a chelating species or, in the presence of strong donors, as unidentate.[3–5] Moreover in a binuclear platinum(II) compound the group $^-S_2CNMe_2$ was found simultaneously to chelate one platinum atom and bridge (through one of the chelating sulphur atoms) a second platinum atom.[6]

Therefore it was worthwhile to determine the bonding around platinum and to develop a general preparative procedure to be used also with *S*-ethyl dithioesters, which do not undergo *S*-de-ethylation in the presence of platinum halides, at least at room temperature. Our interest in such platinum(II) complexes is due also to the detoxicant and immunopharmacological properties of $Na(S_2CNEt_2)$ and MeS_2CNEt_2,[7] and to the protective effect of thiocarbonyl donors on platinum-induced nephrotoxicity.[8] Moreover *S*-methyl transfer is of importance in biological systems.[9] This paper reports the preparation and characterization of the compounds $[PtCl(S_2CNMe_2)(EtS_2CNEt_2)]$ (**1**), $[PtCl(S_2CNEt_2)(MeS_2CNMe_2)]$ (**2**), and $[PtCl(S_2CNEt_2)(MeS_2CNEt_2)]$ (**3**) and the crystal and molecular structure of (**3**).

Experimental

All reactions were carried out at room temperature. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer (Nujol mulls between KBr and polyethylene discs) and ^1H n.m.r. spectra on a JEOL FX 90Q spectrometer. The reagents were platinum(II) chloride (Johnson Matthey), hydrated $Na(S_2CNEt_2)$ (C. Erba), and $Na(S_2CNMe_2)$ (Fluka). The ligands and the reaction intermediate $[Pt_2(\mu\text{-}Cl)_2(S_2CNMe_2)_2]$ were prepared according to literature procedures.[1,2] The compound $[Pt_2(\mu\text{-}Cl)_2(S_2CNEt_2)_2]$ was prepared by gradually adding an acetone solution of $Na(S_2CNEt_2)$ (0.82 mmol, 4 cm^3) to a suspension of $PtCl_2$ in the same solvent (0.78 mmol, 2 cm^3) with stirring. The reaction proceeded in the heterogeneous phase yielding (24 h) a yellow product, which was filtered off, washed with water and acetone, and dried *in vacuo*. The analytical and i.r. data indicated that the compound was impure, containing *ca.* 8% $[Pt(S_2CNEt_2)_2]$. I.r.: $\nu_{max.}$(CN) 1 532, $\nu_{max.}$(PtCl) 310 cm^{-1}.

Preparation of $[PtCl(S_2CNEt_2)(MeS_2CNEt_2)]$ (**3**).—This compound was prepared by stirring a suspension of $[Pt_2(\mu\text{-}Cl)_2(S_2CNEt_2)_2]$ (0.3 mmol) in an acetone solution of MeS_2CNEt_2 (1.2 mmol, 12 cm^3) for 24 h. The red-orange solution was filtered from a yellow residue. After addition of n-hexane (3 cm^3) the solution was kept at *ca.* −20 °C. Orange crystals of the compound used in the *X*-ray structure determination separated slowly (2—3 d, yield 75%), m.p. 82 °C (decomp.) (Found: C, 24.4; H, 4.3; N, 5.1. Calc. for $C_{11}H_{23}ClN_2PtS_4$: C, 24.4; H, 4.3; N, 5.2%).

Complexes (**1**) and (**2**) were prepared similarly by using the appropriate reagents: $[PtCl(S_2CNMe_2)(EtS_2CNEt_2)]$, m.p. 90 °C (decomp.) (Found: C, 21.3; H, 3.9; N, 5.2. $C_{10}H_{21}ClN_2PtS_4$ requires C, 21.7; H, 4.0; N, 5.3%); $[PtCl(S_2CNEt_2)(MeS_2CNMe_2)]$, m.p. 119—121 °C (decomp.) (Found: C, 21.4; H, 3.9; N, 5.3. $C_9H_{19}ClN_2PtS_4$ requires C, 21.0; H, 3.7; N, 5.3%).

X-*Ray Crystal Structure of* $[PtCl(S_2CNEt_2)(MeS_2CNEt_2)]$.—*Crystal data.* $C_{11}H_{23}ClN_2PtS_4$, $M = 542.1$, monoclinic, $a = 10.410(3)$, $b = 10.757(3)$, $c = 8.307(2)$ Å, $\beta = 100.39(2)°$, $U = 915(0.43)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group *Pn* (no. 7), $Z = 2$, $D_c = 1.97$ g

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† Chloro(diethyldithiocarbamato-*SS'*)(*S*-methyl diethyldithiocarbamate-*S'*)platinum(II).

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

cm^{-3}, orange, air-stable parallelepipeds, $\mu(\text{Mo-}K_\alpha) = 78.38$ cm^{-1}.

Data collection and processing. Philips diffractometer, ω—2θ mode, profile scanning method,[10] graphite-monochromated Mo-K_α radiation; 1 728 reflections measured ($1.5 \leqslant \theta \leqslant 25°$, $+h$, $+k$, $\pm l$), 1 612 unique [merging $R = 0.032$ after absorption correction (minimum transmission factor = 0.72, absorption corrections performed by North's method[11])], giving 1 599 with $I > 3\sigma(I)$. Linear and isotropic crystal decay, *ca.* 4%, corrected during data processing with the local program RIFLUP.[12] The Ibers instability factor p, determined from the dispersion of equivalent reflections, was 0.045. Statistical treatment of reflections was performed with a local version of the program SORT originating from the Brookhaven National Laboratory and from the State University of New York at Buffalo.

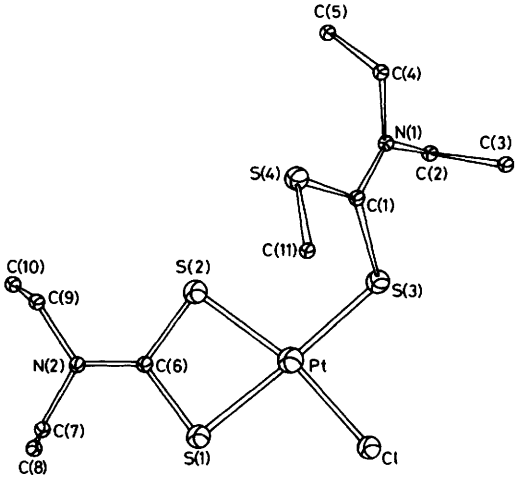


Figure. Structure of $[\text{PtCl(S}_2\text{CNEt}_2\text{)(MeS}_2\text{CNEt}_2\text{)}]$. Projection on the equatorial plane of the platinum atom

Table 1. Relative atomic co-ordinates (× 10^5 for Pt, 10^4 for others) for $[\text{PtCl(S}_2\text{CNEt}_2\text{)(MeS}_2\text{CNEt}_2\text{)}]$

Atom	*X/a*	*Y/b*	*Z/c*
Pt	25 000	22 098(3)	25 000
Cl	632(2)	3 416(2)	1 794(2)
S(1)	2 022(2)	954(2)	189(2)
S(2)	4 242(1)	827(2)	2 663(2)
S(3)	3 061(1)	3 369(2)	4 849(2)
S(4)	5 958(2)	3 216(2)	4 712(3)
C(1)	4 653(5)	3 295(5)	5 756(8)
N(1)	4 993(6)	3 303(5)	7 410(6)
C(2)	3 983(7)	3 221(7)	8 445(8)
C(3)	3 519(8)	4 523(7)	8 821(9)
C(4)	6 361(7)	3 502(7)	8 302(9)
C(5)	6 935(12)	2 249(11)	8 874(16)
C(6)	3 509(6)	215(6)	798(8)
N(2)	4 001(5)	−645(5)	18(8)
C(7)	3 367(8)	−1 011(7)	−1 677(9)
C(8)	3 873(10)	−247(9)	−2 935(11)
C(9)	5 245(7)	−1 287(7)	665(11)
C(10)	4 999(11)	−2 474(11)	1 574(18)
C(11)	5 398(7)	4 079(8)	2 884(8)

Structure analysis and refinement. A three-dimensional Patterson map showed the position of Pt and clearly indicated a non-centrosymmetric space group. Repeated Fourier syntheses were performed until the molecular model was completed, then several cycles of least squares with $w = 1$ for all reflections were performed, using the SHELX package of programs,[13] leading to $R = 0.0376$. At this point, with weights $w = \sigma^{-2}(F_o^{\,2})$, secondary isotropic extinction, dominated by mosaic spread with a Lorentzian distribution function, was assumed. The R factor was reduced insignificantly 0.0372; in fact, no extinction-affected reflections were found (only one reflection is slightly affected: $10\bar{1}$, $y = 0.96$). The final agreement factors were $R = 0.0372$, $R' = 0.0487$, and the goodness of fit was 2.34. The positional parameters obtained from the final LINEX (same source as SORT) refinement are given in Table 1.

Results and Discussion

The complexes have been prepared in acetone by treating $[\text{Pt}_2(\mu\text{-Cl})_2(\text{S}_2\text{CNR}_2)_2]$ with an excess of the appropriate dithioester. Crystalline samples were obtained in a few days by adding small amounts of n-hexane. The compounds could not be recrystallized, owing to partial dithioester release in most solvents.

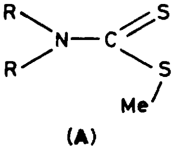
The $[\text{PtCl(S}_2\text{CNEt}_2\text{)(MeS}_2\text{CNEt}_2\text{)}]$ crystal consists of mononuclear complexes in which the platinum atom has the usual square-planar co-ordination (Figure). Bond lengths and angles are reported in Table 2, while some least-squares planes of chemical interest are in Table 3. The chelated $^-\text{S}_2\text{CNEt}_2$ anion resembles that observed in the complexes $[\text{Pt(S}_2\text{CNEt}_2)_2(\text{PR}_3)]$ (R = Ph[3] or cyclohexyl[14]), where either uni- or bi-dentate dithiocarbamato groups are present. The molecular geometry of the whole complex is very similar to that of $[\text{PtCl(S}_2\text{CNEt}_2\text{)(PPh}_3\text{)}]$,[15] notwithstanding slight differences in bond lengths. The principal plane (2 in Table 3) of the $^-\text{S}_2\text{CNEt}_2$ is slightly bent (4.6°) with respect to the co-ordination plane and the two Pt–S bond distances are equal (mean 2.329 Å), whereas in the phosphine adduct the Pt–S bond *trans* to phosphorus (2.349 Å) is longer than that *trans* to chlorine (2.294 Å), due to the static *trans* effect of phosphine. The mean C–S bond distance in the symmetrical bidentate ligand is 1.731

Table 2. Bond distances (Å) and angles (°) in $[\text{PtCl(S}_2\text{CNEt}_2\text{)(MeS}_2\text{CNEt}_2\text{)}]$

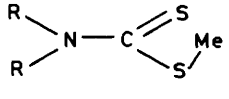
Platinum core			
Pt–Cl	2.323(2)	Pt–S(2)	2.330(2)
Pt–S(1)	2.327(2)	Pt–S(3)	2.300(2)
Bidentate ligand		Unidentate ligand	
S(1)–C(6)	1.732(7)	S(3)–C(1)	1.694(5)
S(2)–C(6)	1.729(7)	S(4)–C(1)	1.741(7)
C(6)–N(2)	1.305(9)	C(1)–N(1)	1.356(8)
N(2)–C(7)	1.470(9)	N(1)–C(2)	1.476(9)
N(2)–C(9)	1.487(9)	N(1)–C(4)	1.497(9)
C(7)–C(8)	1.498(13)	C(2)–C(3)	1.532(11)
C(9)–C(10)	1.528(15)	C(4)–C(5)	1.516(14)
		S(4)–C(11)	1.786(7)

Bidentate ligand		Unidentate ligand	
S(1)–Pt–S(2)	74.1(0.1)	S(2)–Pt–S(3)	102.8(0.1)
S(1)–Pt–Cl	94.1(0.1)	S(3)–Pt–Cl	89.1(0.1)
S(1)–C(6)–S(2)	108.3(0.4)	S(3)–C(1)–S(4)	124.7(0.4)
S(1)–C(6)–N(2)	125.8(0.5)	S(3)–C(1)–N(1)	120.4(0.4)
S(2)–C(6)–N(2)	125.7(0.5)	S(4)–C(1)–N(1)	114.9(0.4)
C(7)–N(2)–C(9)	116.5(0.6)	C(4)–N(1)–C(2)	115.7(0.5)
C(6)–N(2)–C(9)	121.8(0.6)	C(1)–N(1)–C(2)	120.5(0.5)
C(6)–N(2)–C(7)	121.7(0.6)	C(1)–N(1)–C(4)	123.6(0.5)
N(2)–C(7)–C(8)	110.6(0.7)	N(1)–C(4)–C(5)	108.3(0.7)
N(2)–C(9)–C(10)	111.4(0.7)	N(1)–C(2)–C(3)	110.4(0.6)
C(6)–S(2)–Pt	88.7(0.2)	C(1)–S(3)–Pt	115.5(0.2)
C(6)–S(1)–Pt	88.8(0.2)	C(1)–S(4)–C(11)	103.5(0.3)

Å, slightly longer than the corresponding value in the phosphine complex (1.71 Å), and the S···S 'bite' distance is 2.805(2) Å (2.82 Å in the phosphine complex). The dithioester molecule, whose principal plane (4 in Table 3) is bent by 47.5° with respect to the co-ordination plane, binds the platinum atom through the thiocarbonyl sulphur, the Pt–S bond [2.300(2) Å] being considerably shorter than the corresponding bonds to the bidentate anion. The situation in the dithioester moiety resembles that of the analogous ligand in the complex [{$HgCl_2$-[$MeS_2CN(CH_2)_4$]}$_2$].[16] The thiocarbonyl and thioester C–S bond distances are respectively 1.694(5) and 1.741(7) Å in our complex and 1.68 and 1.77 Å in the mercury complex, the related S···S 'bite' distances being equal [3.043(3) Å]. The C–N bond distance in the bidentate anion [1.305(9) Å] is shorter than the corresponding distance in the unidentate dithioester [1.356(8) Å], indicating a higher C–N double-bond character in the former. The dithioester C–N bond distance is significantly longer than that observed in the mercury complex (1.31 Å) suggesting a lower stability of the platinum complex. In free dithiocarbamic esters the SMe group can assume two configurations with respect to the thiocarbonyl group. On the basis of i.r. and proton n.m.r. data the MeS_2CNH_2 molecule has been found to prefer the configuration (**A**).[17] In our case, as in the mercury complex, the methyl group is bent inside and the α angle at the sulphur atom is 103.5°. No interaction between platinum and the SMe sulphur is observed [Pt···S(4) 3.888(2) Å], while there is possibly weak interaction between platinum and the methyl group [Pt···C(11) 3.592(8) Å].



(A)



(B)

Table 3. Equations of weighted least-squares planes, in the form $Ax + By + Cz = D$, where x, y, and z are co-ordinates in Å referred to orthogonal axes and obtained from fractional co-ordinates by applying the matrix: $\|a, 0, c\cos\beta|0, b, 0|0, 0, c\sin\beta\|$. Deviations (Å × 10^3) of relevant atoms from the planes are in square brackets

	A	*B*	*C*	*D*
Plane 1: Pt, S(1), S(2), S(3), Cl	0.587 4(6)	0.641 3(5)	−0.493 7(6)	1.828 5(24)
[Pt −4(1), S(1) −27(2), S(2) 27(2), S(3) −15(2), Cl 33(2), S(4) 1 718(2), C(6) 73(7), N(2) 182(6)]				
Plane 2: S(1), S(2), C(6), N(2)	0.538 4(13)	0.699 8(16)	−0.469 5(14)	1.763 5(37)
[S(1) 0(2), S(2) 0(2), C(6) −5(6), N(2) 2(6), C(7) 141(8), C(8) 1 584(10), C(9) −101(8), C(10) −1 555(13), Pt 140(1)]				
Plane 3: N(2), C(6), C(7), C(9)	0.596 6(33)	0.700 6(28)	−0.391 5(41)	2.011 8(154)
[N(2) −6(6), C(6) 3(6), C(7) 4(8), C(9) 4(8)]				
Plane 4: S(3), S(4), C(1), N(1)	0.053 8(11)	0.998 5(1)	−0.007 6(3)	3.721 1(120)
[S(3) 0(2), S(4) 0(2), C(1) −3(5), N(1) 1(5), C(2) −158(8), C(3) 1 209(8), C(4) 279(8), C(5) −1 043(12), C(11) 922(9), Pt −1 243(1)]				
Plane 5: N(1), C(1), C(2), C(4)	−0.121 0(41)	0.992 4(5)	−0.022 0(35)	2.923 2(272)
[N(1) −25(5), C(1) 9(5), C(2) 15(8), C(4) 15(8)]				

Dihedral angles (°)

1 2 4.6(1), 2 3 5.6(2), 1–4 47.5(1), 4–5 10.1(2)

Attempts to determine the position of the methyl hydrogens failed, probably owing to the high thermal motion of this group. Such an interaction could account for the appreciable torsion angle around the C–N bond in the dithioester molecule (10.1°), whereas the torsion angle is smaller in the bidentate moiety (5.6°). The Pt–Cl distance [2.323(2) Å] is shorter than in the phosphine complex (2.331 Å) and comparable with corresponding distances in the thiocarbamic ester derivatives [PtCl-$(EtOSCNHPr)_3$]Cl[18] and *cis*-[$PtCl_2(EtOSCNMe_2)_2$].[19] The shortest contacts between non-hydrogen atoms are Cl···C(4^I) 3.577(8) (I $-\frac{1}{2} + x$, $1 - y$, $-\frac{1}{2} + z$) and C(3)···C(11^{II}) 3.537(11) Å (II $-\frac{1}{2} + x$, $1 - y$, $\frac{1}{2} + z$), thus the crystal packing is normal.

The significant i.r. bands of the ligand and complexes are reported in Table 4. The free ligands exhibit a broad absorption about 1 500 cm^{-1} assigned to C–N bond stretching, which shifts to higher energy on co-ordination. When the ligands are unidentate through the thiocarbonyl sulphur atom, the Δν values are of the order of 20—30 cm^{-1}, as observed for [MX_2L_2] and [HgX_2L] (M = Pt or Pd; L = EtS_2CNMe_2, MeS_2CNMe_2, or EtS_2CNEt_2).[1,2,20] The complexes reported in this paper show, in the ν(CN) region, two absorptions of medium intensity, the one at higher wavenumber belonging to the chelated dithiocarbamate and the second (around 1 500 cm^{-1}) to the unidentate dithioester. The small ν(CN) shift with respect to the corresponding free-ligand value (Δν 8—15 cm^{-1}) is in accord with the structural data, where a relatively long C–N distance suggested a low double-bond character for the C–N bond. When unidentate through the thiocarbonyl sulphur, dithiocarbamic esters behave as weak donors, probably owing to steric hindrance of the thioester alkyl group. The complexes tend to release the neutral ligand molecule in most solvents to give the starting products [$Pt_2(\mu\text{-}Cl)_2(S_2CNR_2)_2$]. Similarly the 1:2 adducts [PtX_2L_2] (L = EtS_2CNEt_2, EtS_2CNMe_2, MeS_2CNEt_2, or MeS_2CNMe_2) readily yielded the sparingly

Table 4. Proton n.m.r. spectra[a] ($CDCl_3$ solutions at 25 °C, δ/p.p.m.) and i.r. wavenumbers (cm^{-1}, Nujol mulls)

	Position in dithioester				Position in dithiocarbamate ion			
Compound[b]	α-N[c]	β-N	α-S	β-S	α-N	β-N	ν(CN)	ν(PtCl)
MeS_2CNEt_2	4.0—3.8	1.30	2.67				1 485s	
[$PtCl(S_2CNEt_2)(MeS_2CNEt_2)$]	4.4—3.9	1.41	3.14		3.57—3.54	1.29	1 530m, 1 493m	305s
MeS_2CNMe_2	3.6—3.4		2.69				1 502s	
[$PtCl(S_2CNEt_2)(MeS_2CNMe_2)$]	4.0—3.6[d]		3.02		3.6[d]	1.28	1 530m, 1 515 (sh)	308s
EtS_2CNEt_2	4.0—3.8	1.27	3.32	1.35			1 488s	
[$PtCl(S_2CNMe_2)(EtS_2CNEt_2)$]	4.4—3.9	1.39	3.7[c]	1.28	3.22—3.17		1 562m, 1 502m	308s

[a] Recorded immediately after dissolution; on standing decomposition processes are observed. [b] For the free esters, the data are in accord with those obtained in previous studies (J. L. Richards, D. S. Tarbell, and E. H. Hoffmeister, *Tetrahedron*, 1968, **24**, 6485; M. Honda, M. Komura, J. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, 1968, **30**, 3231; J. R. Grunwell, *J. Org. Chem.*, 1970, **35**, 1500). [c] Broad signals. [d] The α-N signals of both moieties are partially superimposed.

soluble [PtX_2L], in which the ligand is bidentate through the two sulphur atoms.[1,2] In this case a noticeable ν(CN) shift was observed ($\Delta\nu \approx 95$ cm^{-1}), suggesting for this class of ligand a strong tendency to give stable complexes by chelation.

Given the energy of the barriers to rotation about the C–N bond, of the order of 63 kJ mol^{-1},[21–23] it is not surprising that the dithioester molecule is planar. Consequently the nitrogen substituents are magnetically non-equivalent.[24,25] The proton n.m.r. spectra of the free ligands (Table 4) show two broad signals in the range 3.3—4.0 p.p.m., due to protons belonging to groups α with respect to nitrogen, whereas the β-N protons give one signal at 1.3 p.p.m. On co-ordination, sharpening and downfield shift of the α-N proton resonances are expected, owing to electron withdrawal which enhances the barrier to rotation about the C–N bond. For example, the spectrum of [$HgI_2(MeSCNEt_2)$] in bromobenzene[20] contains two sharp quartets at 3.6 and 4.0 p.p.m. and two triplets at 2.1 and 2.2 p.p.m., due to the methylene and methyl-nitrogen substituents respectively, whereas the SMe singlet is at 2.6 p.p.m. (2.5 p.p.m. for the free ligand). On the contrary the spectra of our complexes present broad α-N signals, shifted downfield with respect to the corresponding free-ligand resonances, and unresolved β-N proton signals, indicating rapid ligand exchange in solution. A significant downfield shift (*ca.* 0.5 p.p.m.) of the α-S resonances is also observed, suggesting some interaction between the metal and thioester group in solution. The chelated dithiocarbamates are characterized by two sharp very close α-N proton signals, as in the analogous phoshine complexes, whereas one β-N proton triplet is observed. The behaviour of the complexes in solution is in accord with the structural data, showing the dithioester molecule to be sterically strained by the sulphur substituent owing to the square-planar arrangement around platinum. Moreover halide exchange by interaction with the SR group cannot be excluded. On standing the n.m.r. solutions undergo partial decomposition leading possibly to formation of the species [$Pt(S_2CNR_2)_2$].

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References

1 G. Faraglia, L. Sindellari, L. Trincia, A. Furlani, and V. Scarcia, *Inorg. Chim. Acta*, 1985, **106**, 31.
2 A. Furlani, V. Scarcia, G. Faraglia, L. Sindellari, L. Trincia, and M. Nicolini, *Eur. J. Med. Chem.*, 1986, **21**, 261.
3 J. P. Fackler, L. D. Thompson, I. J. B. Lin, T. A. Stephenson, R. O. Gould, J. M. C. Alison, and A. J. F. Fraser, *Inorg. Chem.*, 1982, **21**, 2397.
4 J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1973, 254.
5 M. C. Cornock and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1977, 501.
6 A. B. Goel, S. Goel, D. Van Derweer, and C. G. Brinkley, *Inorg. Chim. Acta*, 1982, **64**, L173.
7 G. Renoux, M. Renoux, K. Biziere, J. M. Guillaumin, P. Bardos, and D. Degenne, *Immunopharmacol.*, 1984, **7**, 89.
8 R. F. Borch, D. L. Bodenner, and J. C. Katz, *Dev. Oncol.*, 1984, **17**, 154.
9 L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Nature* (*London*), 1966, **211**, 519.
10 M. S. Lehman and F. K. Larsen, *Acta Crystallogr., Sect A*, 1974, **30**, 580.
11 A. C. T. North, D. C. Philips, and F. S. Mathews, *Acta Crystallogr., Sect A*, 1968, **24**, 351.
12 M. Biagini Cingi, G. Bandoli, D. A. Clemente, and A. Tiripicchio, *J. Appl. Crystallogr.*, 1980, **13**, 197.
13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.
14 P. C. Christidis and P. J. Reutzeperis, *Acta Crystallogr., Sect. B*, 1979, **35**, 2543.
15 L. T. Chan, H-W. Chen, J. P. Facker, A. F. Masters, and W-H. Pan, *Inorg. Chem.*, 1982, **21**, 4291.
16 P. D. Brotherton, J. M. Epstein, A. H. White, and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1974, 2341.
17 K. R. Gayathri Devi, D. N. Sathyanarayana, and S. Monogaron, *Spectrochim. Acta, Part A*, 1981, **37**, 31.
18 R. Bardi, A. M. Piazzesi, A. del Pra, M. Celeste, G. Faraglia, and L. Trincia, *Inorg. Chim. Acta*, 1985, **102**, 45.
19 R. Bardi, A. M. Piazzesi, and L. Sindellari, *Inorg. Chim. Acta*, 1981, **47**, 225.
20 H. C. Brinkhoff and J. M. A. Dautzenberg, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 117.
21 A. E. Lemire and J. C. Thompson, *Can. J. Chem.*, 1970, **48**, 824.
22 A. E. Lemire and J. C. Thompson, *J. Am. Chem. Soc.*, 1971, **93**, 1163.
23 C. H. Yoder, A. Komoriya, J. E. Kochanowski, and F. H. Suydam, *J. Am. Chem. Soc.*, 1971, **93**, 6515.
24 B. L. Edgar, D. J. Duffy, M. C. Palazzotto, and L. H. Pignolet, *J. Am. Chem. Soc.*, 1973, **95**, 1125.
25 B. M. Dahl and P. H. Nielsen, *Acta Chem. Scand., Ser. B*, 1974, **28**, 1091.

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