Thermochimica Acta, 161 (1990) 63–73
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL *S*-DEMETHYLATION IN PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH *S*-METHYL *N*,*N*-DIALKYLDITHIOCARBAMATES

G. FARAGLIA * and L. SINDELLARI

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Loredan 4, 35100-Padova (Italy)

S. SITRAN

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020-Padova (Italy)

(Received 22 August 1989)

ABSTRACT

The thermal behaviour of the dithiocarbamic ester complexes $[M(MeS_2CNMe_2)X_2]$ (M = Pd or Pt; X = Cl or Br) and $[Pd(MeS_2CNEt_2)Cl_2]$ has been examined up to 1100 °C. The first decomposition step involves MeX release to form the corresponding species $[M(S_2CNMe_2)X]_n$ and $[Pd(S_2CNEt_2)Cl]_n$. The degradation intermediates have been isolated and characterized by elemental analyses and IR and NMR (^1H and ^{13}C) spectra. Their possible structure is discussed and correlated with the properties of the starting dithiocarbamic ester adducts. On heating, the mixed complexes $[Pt(S_2CNEt_2)(MeS_2CNR_2)Cl]$ (R = Me or Et) undergo an analogous *S*-demethylation process, MeCl being evolved at temperatures lower than those of the same process for the $[Pt(MeS_2CNMe_2)X_2]$ species.

INTRODUCTION

We have previously studied various palladium(II) and platinum(II) halide complexes with dithiocarbamic esters, of general formulae $[M(RS_2CNR_2)X_2]$ and $[M(RS_2CNR_2)_2X_2]$ (M = Pd or Pt; R = Me or Et; X = Cl, Br or I) [1,2]. On the evidence of IR spectra, the 1 : 2 adducts have a *trans* geometry and contain monodentate dithioester bound through thiocarbonyl sulphur, whereas in the 1 : 1 complexes the ligand acts as bidentate through both sulphur atoms. The M–X IR absorptions favour a *cis* geometry for the species $[Pt(RS_2CNR_2)X_2]$ (X = Cl or Br), whereas they suggest the presence of halide bridges in the analogous palladium derivatives. All complexes have been tested for in vitro cytostatic activity against KB cells, a line derived

---

* Author to whom correspondence should be addressed.

0040-6031/90/$03.50

from a human epidermoid carcinoma, and some of them have shown significant activity values [1,2]. Meanwhile, it has been observed that the adducts can undergo S-dealkylation in solution, yielding species containing the N,N-dialkyldithiocarbamato moiety. The effect was particularly evident for the platinum 1 : 2 adducts; in either dichloromethane or acetone solution, there separated on standing small fractions of the mixed complexes $[Pt(S_2CNR_2)(RS_2CNR_2)X]$. From X-ray structural data the $[Pt(S_2CNEt_2)(MeS_2CNEt_2)Cl]$ species was found to contain chelate diethyldithiocarbamato ion and monodentate dithioester, the latter weakly bonded to platinum through thiocarbonyl sulphur [3].

It was thus considered worthwhile to examine the adduct degradation modes, either in the solid state or in solution. Interest in the interaction of sulphur donors with palladium(II) and platinum(II) halides stems from the detoxicant properties of sulphur derivatives against metal poisoning and, in particular, from the use of $Na(S_2CNEt_2)$ to overcome the nephrotoxicity of the drug *cis*-$[Pt(NH_3)_2Cl_2]$ [4,5].

EXPERIMENTAL

The ligands S-methyl N,N-dimethyldithiocarbamate (MeS_2CNMe_2) and S-methyl N,N-diethyldithiocarbamate (MeS_2CNEt_2) were prepared by reaction of the appropriate salt, $Na(S_2CNR_2)$, with MeI in $EtOH/H_2O$ [6]. The oily products were dissolved in diethyl ether, washed with water and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. MeS_2CNMe_2 was recrystallized from *n*-pentane. MeS_2CNEt_2 was a pale yellow oil, which was washed with *n*-hexane. Traces of *n*-hexane were removed in vacuo and the product was used without further purification. Platinum and palladium halides were Johnson Matthey products.

Preparation of the complexes

The complexes $[M(MeS_2CNMe_2)X_2]$ (M = Pd or Pt; X = Cl or Br) and $[Pd(MeS_2CNEt_2)Cl_2]$ were prepared by reaction of the appropriate metal halide with the ligand in molar ratio 1 : 1.1 (solvent CH_2Cl_2; reaction time 2–3 h). The 1 : 1 adducts, which were quite insoluble in dichloromethane, were filtered off and washed thoroughly with CH_2Cl_2 in order to remove traces of the related 1 : 2 species, which are soluble in this solvent in the presence of excess ligand. They were then washed with *n*-pentane and dried in vacuo. Yields were 60–70%.

The species $[M(S_2CNMe_2)X]_n$ (M = Pd or Pt; X = Cl or Br) and $[Pd(S_2CNEt_2)Cl]_n$ were prepared by thermal degradation (in N_2) of the corresponding 1 : 1 adducts of the appropriate dithiocarbamic ester. The experimental conditions will be discussed in the following section.

The complexes $[Pt(S_2CNEt_2)(L)Cl]$, in which L is MeS_2CNMe_2 or MeS_2CNEt_2, were prepared by reaction of $[Pt(S_2CNEt_2)Cl]_n$ and dithiocarbamic ester in acetone, following the method reported in ref. 3.

Measurements

The IR spectra were recorded by using Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers, using Nujol mulls between KBr and polyethylene discs. The NMR (^1H and ^{13}C) spectra were obtained with a JEOL FX 90Q spectrometer. The TG, DTG and DTA curves, either in N_2 or air (flow rate 250 cm^3 min^{-1}; heating rate 5 °C min^{-1}) were recorded on a Netzsch STA 429 thermoanalytical instrument (reference material Al_2O_3).

RESULTS AND DISCUSSION

Thermogravimetric tests of selected palladium(II) and platinum(II) complexes with dithiocarbamic esters were carried out either in air or in N_2 (Table 1). As shown in Fig. 1, degradation of $[Pd(MeS_2CNMe_2)Cl_2]$ in air starts at 118 °C, the first step in the TG curve representing evolution of MeCl (endotherm at 160 °C) to give $[Pd(S_2CNMe_2)Cl]_n$ as an intermediate. This species is stable over a wide temperature range (170–280 °C); subsequently the sample melts with decomposition (endotherm at 327 °C), the final pyrolysis product being palladium (550 °C). The weight increase observed at higher temperatures is probably due to reaction of metal with oxygen to form PdO (exotherm at 552 °C). The oxygen uptake is less than expected for a stoichiometric process and probably involves only the surface layer of the residue in the crucible. In fact, the palladium-to-oxygen ratio approaches unity in tests performed by using decreasing amounts of starting material. Oxygen is completely released at higher temperatures, as shown by the endotherm at 812 °C (Fig. 1). When $[Pd(MeS_2CNMe_2)Cl_2]$ is heated in N_2, the thermogravimetric curves coincide up to the second endothermic process (ca. 350 °C), but the following exotherms are broader than in air. Pyrolysis ends at 550 °C, the final product being palladium. No further process is observed up to 1100 °C. Degradation of $[Pd(MeS_2CNEt_2)Cl_2]$ in N_2 follows an analogous trend, MeCl being evolved at about the same temperature as for the previous complex (Fig. 2). Intermediate melting is clearly indicated by the endotherm at 235 °C and is followed by sample pyrolysis to palladium. Also, in this case, the sample weight is unchanged up to 1100 °C, no peak being observed in the DTA curve. Parallel tests for $[Pd(MeS_2CNMe_2)Br_2]$ show that the first decomposition process concerns MeBr release (endotherm at 164 °C). The MeX evolution temperatures are very close for the three palladium complexes, suggesting that the demethylation process is independent of the halide and of the alkyl substituent at the

TABLE 1

Thermal data for the complexes

Compound	Decomposition interval (°C)	TG weight loss (%)		DTA peak temperature (°C) [a]
		Experimental	Calculated	
$[Pt(MeS_2CNMe_2)Cl_2]$ [b]	129–200	12.72	12.58 (MeCl)	182 (endo)
	215–415	39.55	38.80 (to Pt)	354 (exo), 372 (exo)
$[Pt(MeS_2CNMe_2)Br_2]$ [b]	132–210	18.58	19.37 (MeBr)	194 (endo)
	232–500	40.23	40.83 (to Pt)	367 (exo), 490 (exo)
$[Pd(MeS_2CNMe_2)Cl_2]$ [b]	118–170	15.91	16.15 (MeCl)	160 (endo)
	285–550	50.48	49.80 (to Pd)	327 (md), (351, 358) (exo), 445 (exo)
	550–620 [c]	–	–	552 (exo)
	790–820 [c]	–	–	812 (endo)
$[Pd(MeS_2CNMe_2)Br_2]$ [b]	100–180	23.71	23.65 (MeBr)	164 (endo)
	310–570	50.24	49.84 (to Pd)	332 (md), 340 (exo), 510 (exo)
	570–620 [c]	–	–	575 (exo)
	790–830 [c]	–	–	810 (endo)
$[Pd(MeS_2CNEt_2)Cl_2]$ [d]	125–175	14.52	14.82 (MeCl)	163 (endo)
	175–250	0	0	235 (m)
	250–470	52.66	53.94 (to Pd)	295 (endo), 357 (exo), 460 (exo)
$[Pt(S_2CNEt_2)(MeS_2CNEt_2)Cl]$ [d]	80–125	9.18	9.31 (MeCl)	92 (endo)
	125–280	0	0	270 (m)
	280–580	48.45	48.79 (to PtS) [e]	304 (endo), 356 (exo), 385 (exo)
$[Pt(S_2CNEt_2)(MeS_2CNMe_2)Cl]$ [b]	115–150	9.81	9.82 (MeCl)	125 (endo)
	150–268	0	0	248 (m)
	268–500	52.26	52.23 (to Pt)	310 (endo), 362 (exo), 413 (exo)

[a] Endo, decomposition endotherm; exo, decomposition exotherm; m, melting endotherm; md, melting with decomposition. [b] In air. [c] See text. [d] In nitrogen. [e] Calculated value for platinum as pyrolysis residue 54.70%.

nitrogen atom. The thermograms of the analogous 1 : 1 platinum adducts indicate that the decomposition intermediate exists in a narrow temperature range. As is shown in Fig. 3 for $[Pt(MeS_2CNMe_2)Cl_2]$, MeCl release occurs at 182°C, ca. 20°C higher than for the corresponding process in the palladium parent complex. The species $[Pt(S_2CNMe_2)Cl]_n$ is stable up to

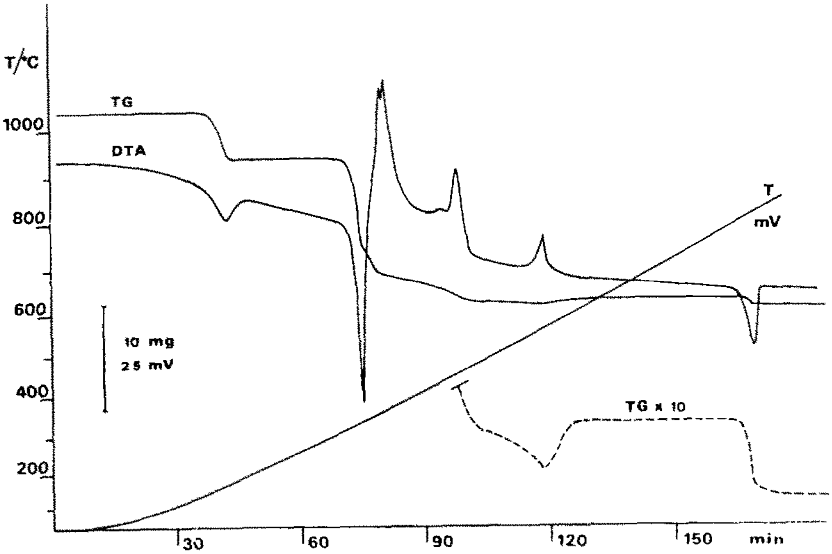

Fig. 1. Thermograms of [Pd(MeS_2CNMe_2)Cl_2] (27.99 mg) in air.

215 ° C, as shown by the expanded TG curve, and then undergoes a gradual degradation process which ends at 415 ° C. The total weight loss in air agrees with formation of platinum as the pyrolysis residue. In N_2 the thermograms are identical up to 200 ° C. The subsequent degradation process is slower than in air, the corresponding DTA peaks being less intense. The sample weight is constant above 600 ° C and agrees well with PtS as final product.

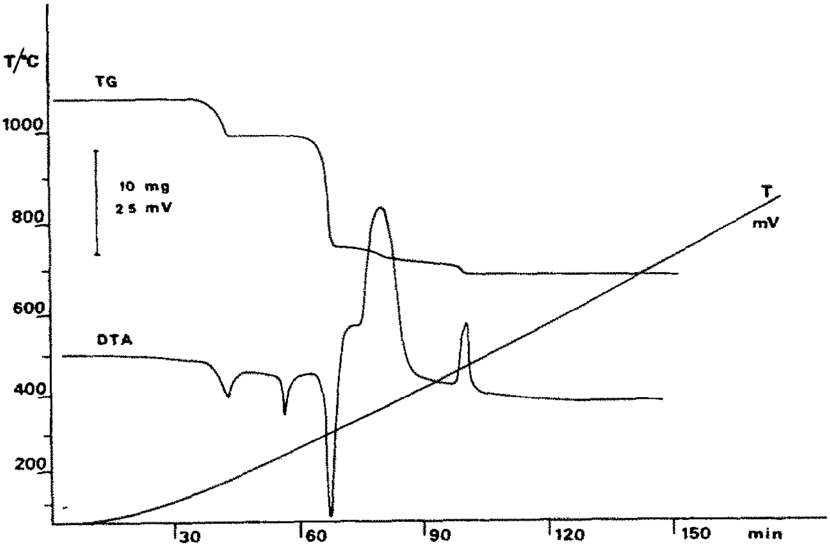

Fig. 2. Thermograms of [Pd(MeS_2CNEt_2)Cl_2] (25.31 mg) in nitrogen.

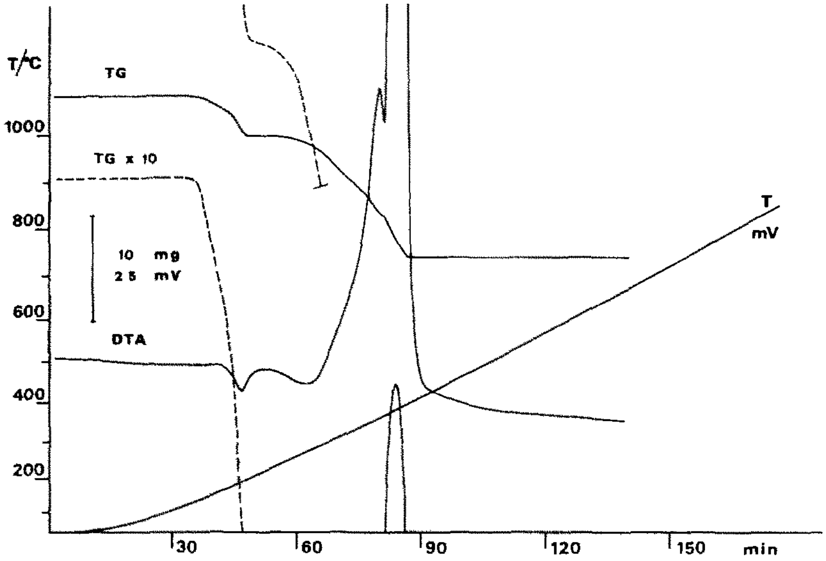

Fig. 3. Thermograms of [Pt(MeS$_2$CNMe$_2$)Cl$_2$] (29.08 mg) in air.

Methyl chloride release is also the first process in thermal degradation of the platinum mixed complexes and is observed at 125 °C for [Pt(S$_2$CNEt$_2$)(MeS$_2$CNMe$_2$)Cl] (Fig. 4). The intermediate species [Pt(S$_2$CNEt$_2$)(S$_2$CNMe$_2$)] melts at 248 °C and begins to decompose at 268 °C, the final

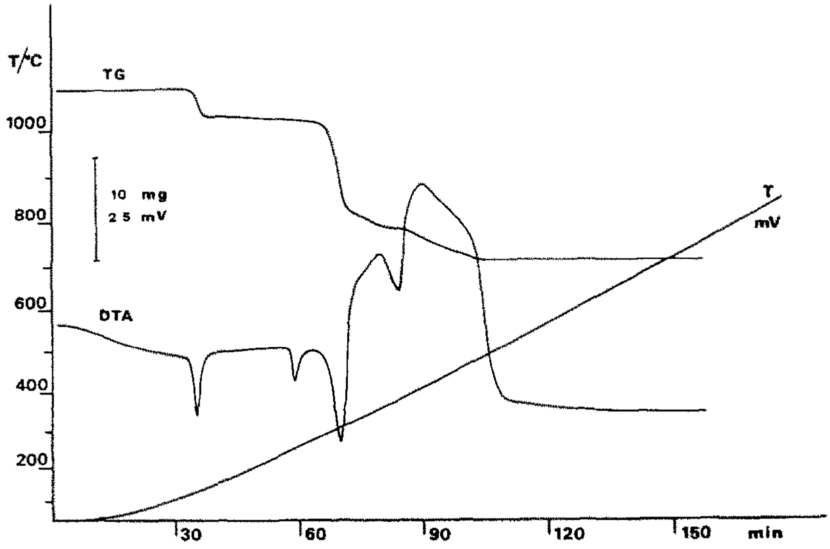

Fig. 4. Thermograms of [Pt(S$_2$CNEt$_2$)(MeS$_2$CNMe$_2$)Cl] (26.51 mg) in air.

TABLE 2

Analytical data [a] and IR wavenumbers (cm^{-1})

Compound	Empirical formula	Colour	C (%)	H (%)	N (%)	ν(CN) [b]
$[Pd(S_2CNMe_2)Cl]_n$	$C_3H_6ClNPdS_2$	Pink–red	13.58 (13.75)	2.23 (2.31)	5.21 (5.34)	1564
$[Pd(S_2CNMe_2)Br]_n$	$C_3H_6BrNPdS_2$	Pink	11.53 (11.75)	1.87 (1.97)	4.45 (4.57)	1566
$[Pd(S_2CNEt_2)Cl]_n$	$C_5H_{10}ClNPdS_2$	Pink–red	20.54 (20.70)	3.63 (3.47)	4.65 (4.83)	1543
$[Pt(S_2CNMe_2)Cl]_n$	$C_3H_6ClNPtS_2$	Brown–yellow	10.58 (10.27)	1.66 (1.72)	3.89 (3.99)	1580
$[Pt(S_2CNMe_2)Br]_n$	$C_3H_6BrNPtS_2$	Orange	9.39 (9.12)	1.42 (1.53)	3.36 (3.54)	1576

[a] Calculated values in parentheses. [b] Strong absorptions.

product in air (at 500 ° C) being platinum. The thermogram trend suggests that thermal decomposition of similar mixed species could be of help in the synthesis of platinum complexes containing two dithiocarbamato ions with different nitrogen substituents. Evolution of MeCl occurs at a lower temperature in $[Pt(S_2CNEt_2)(MeS_2CNEt_2)Cl]$, the corresponding endotherm being observed at 92° C (Table 1). Because the thermogravimetric analysis of this compound has been carried out in N_2, the pyrolysis residue at 580 ° C is probably PtS.

In order to correlate the 1 : 1 adduct decomposition in solution with the corresponding decomposition on heating, a detailed study on the thermal degradation intermediates has been carried out. The species listed in Table 2 were prepared by heating the appropriate complex $[M(MeS_2CNR_2)X_2]$ directly on the thermobalance crucible under a N_2 flux. Heating was stopped immediately after the appearance of the first endotherm in the related DTA curve, with particular attention to the easily decomposable platinum derivatives. The colour of the palladium complexes tends to be pink, whereas the platinum complexes are yellow (X = Cl) or orange (X = Br).

The CN stretch absorption (Table 2) in $[Pt(S_2CNMe_2)X]_n$ is observed at higher frequencies than for the corresponding palladium complexes. As an example, it occurs at 1580 cm^{-1} for $[Pt(S_2CNMe_2)Cl]_n$ as against a value of 1564 cm^{-1} in $[Pd(S_2CNMe_2)Cl]_n$. Previously we synthesized $[Pt(S_2CNMe_2)Cl]_n$ samples by reaction of $PtCl_2$ and $Na(S_2CNMe_2) \cdot 2H_2O$ in acetone (molar ratio 1 : 1) [1]. The yellow solid was essentially the chloro-dimethyldithiocarbamato complex, impure for $PtCl_2$ and $[Pt(S_2CNMe_2)_2]$, and exhibited the ν(CN) absorption at 1560 cm^{-1}, close to that of the palladium complexes listed in Table 2. Similarly, the significant absorptions for the complex $[Pd(S_2CNEt_2)Cl]_n$ in this paper (ν(CN), 1543 cm^{-1}; ν(Pd–Cl), 289 cm^{-1} (Table 3)) differ from those of samples obtained by reacting $K_2[PdCl_4]$

TABLE 3

IR wavenumbers in the 600–150 cm^{-1} region (ν(M–hal) in italics)

Compound	Wavenumbers (cm^{-1}) [a]										
[Pd(S_2CNMe$_2$)Cl]$_n$	567 vvw	534 vvw	439 w		385 w	358 vw	*298* ms	265 mw	215 m		
[Pd(S_2CNMe$_2$)Br]$_n$	571 vvw	533 vvw	440 w	407 vvw	381 m	349 vvw		262 mw		*167* m	
[Pt(S_2CNMe$_2$)Cl]$_n$	567 w	546 w	434 w		388 w	355 w	*315* s	267 vw	234 vw		
[Pt(S_2CNMe$_2$)Br]$_n$	565 w	547 w	434 mw		385 w	354 w	314 vw	264 vw	241 vw	206 sh	*202* ms
[Pd(S_2CNEt$_2$)Cl)$_n$	571 vw	551 vw	476 vvw	401 w	381 m	353 vw	*289* ms	253 vvw		207 m	

[a] w, weak; m, medium; s, strong; v, very.

and $[Pd(S_2CNEt_2)_2]$ in chloroform (ν(CN), 1536 cm^{-1}; ν(Pd–Cl), 310 cm^{-1}), which probably have a dimeric structure [7]. The generally different shapes of the IR spectra of the platinum and palladium complexes reported in this paper might depend on the different configuration of the starting 1 : 1 adducts which are used in the thermogravimetric tests. In fact, all the $[M(MeS_2CNMe_2)X_2]$ (M = Pd or Pt) complexes contain a bidentate ligand, as suggested by the C–N band position (1590–1600 cm^{-1}) at noticeably higher energy than that of the free ligand (1502 cm^{-1}) [1,2]. Two Pt–X absorptions (X = Cl, 325 cm^{-1} and 317 cm^{-1}; X = Br, 224 cm^{-1} and 210 cm^{-1}) supported the *cis* geometry of platinum complexes. The ν(Pd–Cl) absorptions in $[Pd(MeS_2CNMe_2)Cl_2]$, at 318 cm^{-1} and 296 cm^{-1}, were close to those of phosphine or amine *cis* adducts [8,9], but the Pd–Br bands in the analogous bromo derivative were at an energy so low (186 and 176 cm^{-1}) as to support the presence of halide bridges. Because IR spectra cannot exclude the formation of ligand bridges also, the nature of the 1 : 1 palladium adducts with dithiocarbamic esters is uncertain.

The thermal degradation intermediate $[Pt(S_2CNMe_2)Cl]_n$, which stems from a *cis* 1 : 1 adduct, does not contain chloride bridges, which would lead to a band at ca. 260 cm^{-1}, as in the dimers $[Pt_2(L)_2Cl_4]$ (L = sulphoxide or phosphine) [10–13]. Along with the strong Pt–Cl absorption at 315 cm^{-1} (Table 3), the complex spectrum contains a weak band at 265 cm^{-1}, common to the other complexes and due probably to M–S bond vibrations. Moreover, the ν(CN) absorption is identical to that observed for the binuclear complex $[PtCl_3(PEt_3)_2(S_2CNMe_2)]$, in which the dithiocarbamato ion acts as bidentate in the $PtCl(S_2CNMe_2)(PEt_3)$ moiety and at the same time bonds, via one of the sulphur atoms, to the second platinum atom bearing two chlorine atoms and one PEt_3 molecule [14]. In our case thermal degradation could cause intermolecular MeCl evolution, each platinum atom in the $[Pt(S_2CNMe_2)Cl]$ unit attaining the usual tetracoordination by a polymeric arrangement of S–Pt bonds between two adjacent units. Except for the Pt–Br absorption at 202 cm^{-1}, the $[Pt(S_2CNMe_2)Br]_n$ spectrum matches that of the chloro analogue over the whole 4000–200 cm^{-1} range, suggesting a similar configuration. Conversely the palladium intermediates $[Pd(S_2CNMe_2)X]_n$ should retain the bridge framework present in the parent 1 : 1 adducts. Notwithstanding that the IR spectra do not exclude the presence of bridging dithiocarbamato ion, these complexes should contain chelate-S_2CNMe_2 and halide bridges, as suggested by the Pd–X bands (X = Cl, 298 cm^{-1}; X = Br, 167 cm^{-1}), very close to the lower energy Pd–X absorption in the starting complexes. Whereas the Pd–Cl stretching frequencies are in the range observed for other μ-Cl palladium complexes [15,16], the low energy of the Pd–Br band in $[Pd(S_2CNMe_2)Br]_n$ is unusual.

When mother solutions of the $[M(MeS_2CNR_2)X_2]$ species preparation are left standing at room temperature for a few days, small amounts of solids separate, analytical data for which are in accordance with the formula

[M(S_2CNR_2)X], whereas the colour and IR spectra often do not coincide with those of the corresponding thermal degradation intermediates. The fact is not surprising, because apparently similar products derive from different precursors. Thermal intermediates come from 1 : 1 adducts containing a bidentate dithiocarbamic ester, whereas in the mother solutions the more soluble [M(MeS_2CNR_2)$_2$$X_2$] species are present, in which the ligand is monodentate. *S*-Demethylation is probably easier in species containing monodentate dithioester, as suggested by the MeCl release temperature in [Pt(S_2CNMe_2)(MeS_2CNMe_2)Cl], which is noticeably lower than for [Pt(MeS_2CNMe_2)Cl_2] (125 °C vs. 185 °C, Table 1).

The compounds listed in Table 2 are insoluble in common solvents, as for the parent 1 : 1 precursors. They dissolve in dimethyl sulphoxide (DMSO) giving yellow solutions, except for [Pd(S_2CNMe_2)Cl]$_n$; this forms a greenish solution from which a dark green unidentified product separates slowly. This strongly coordinating solvent should break down the polymer to form mixed species of the type [M(S_2CNR_2)(DMSO)X]. The proton NMR spectra of the [M(S_2CNMe_2)X]$_n$ species in deuterated DMSO contain the NMe_2 singlet signal at 3.26 ppm, whereas the ethyl proton signals in [Pd(S_2CNEt_2)Cl]$_n$ are observed at 3.69 and 1.19 ppm. In the same solvent, the [Pd(S_2CNEt_2)Cl]$_n$ ^{13}C carbon resonances are at 201.85 ppm (CS_2) and 12.20 ppm (CH_3). The ethyl CH_2 signal is obscured by the solvent multiplet, as for the methyl carbon signal in [M(S_2CNMe_2)X]$_n$. The [Pd(S_2CNMe_2)Cl]$_n$ CS_2 carbon signal is observed at 202.20 ppm. The corresponding [Pt(S_2CNMe_2)Cl]$_n$ resonance (201.85 ppm) displays satellites due to coupling with ^{195}Pt ($J = 125$ Hz).

ACKNOWLEDGEMENT

The authors thank Mr. Stefano Sitran for technical assistance.

REFERENCES

1 G. Faraglia, L. Sindellari, L. Trincia, A. Furlani and V. Scarcia, Inorg. Chim. Acta, 106 (1985) 31.
2 A. Furlani, V. Scarcia, G. Faraglia, L. Sindellari, L. Trincia and M. Nicolini, Eur. J. Med. Chem., 21 (1986) 261.
3 D.A. Clemente, G. Faraglia, L. Sindellari and L. Trincia, J. Chem. Soc., Dalton Trans., (1987) 1823.
4 R.F. Borch, D.L. Bodenner and J.C. Katz, Dev. Oncol., 17 (1984) 154.
5 M.A. Basinger, M.M. Jones, S.G. Gilbreath IV, E.M. Walker, Jr., E.P. Fody and M.A. Mayhue, Toxicol. Appl. Pharmacol., 97 (1989) 279.
6 C.E. Holloway and M.H. Gitliz, Can. J. Chem., 45 (1967) 2659.
7 J.G.M. Van der Linden, W. Blommerde, A.H. Dix and F.W. Pijpers, Inorg. Chim. Acta, 24 (1977) 261.

8 J.H. Nelson, J.A. Rahn and W.H. Bearden, Inorg. Chem., 26 (1987) 2192.
9 R.J.H. Clark, V.B. Croud and M. Kurmoo, J. Chem. Soc., Dalton Trans., (1985) 815.
10 I.V. Pakhomova, Yu.N. Kukushkin, L.V. Konovalov and V.V. Strukov, Russ. J. Inorg. Chem., 29 (1984) 575 (Engl. Transl.).
11 I.V. Pakhomova, L.V. Konovalov, N.T. Komyagin, A.I. Yanovskii, Yu.T. Struchkov and Yu. N. Lukin, J. Gen. Chem. USSR, 58 (1988) 647 (Engl. Transl.).
12 G. Annibale, M. Bonivento, L. Canovese, L. Cattalini, G. Michelon and M.L. Tobe, Inorg. Chem., 24 (1985) 797.
13 M.L. Tobe, A.T. Treadgold and L. Cattalini, J. Chem. Soc., Dalton Trans., (1988) 2347.
14 A.B. Goel, S. Goel, D. Van Derveer and C.B. Brinkley, Inorg. Chim. Acta, 64 (1982) L173.
15 G. Tresoldi, G. Bruno, P. Piraino, F. Faraone and G. Bombieri, Inorg. Chim. Acta, 51 (1981) 263.
16 G. Pneumatikakis, A. Yannopoulos, J. Markopoulos and C. Angelopoulos, Inorg. Chim. Acta, 152 (1988) 101.