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The behaviour of dithiocarbamic ester palladium(II) and platinum(II) complexes in dimethyl sulfoxide

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Abstract

The complexes $[M(MeS_2CNMe_2)X_2]$ (M = Pd or Pt; X = Cl or Br) decompose in dimethyl sulfoxide, yielding species which contain the dimethyldithiocarbamato moiety. In order to clarify the degradation pathway, the mixed species $[M(S_2CNMe_2)(Me_2SO)X]$ have been prepared and characterized by infrared and ^1H NMR spectroscopy and by thermal analysis (TG, DTG and DTA). Although all square planar mixed complexes contain S-bound dimethyl sulfoxide, the platinum derivatives are stabler than the palladium analogues, which release easily the Me_2SO molecule either on heating or in solution to form the $[Pd(S_2CNMe_2)X]_n$ species. Accordingly Me_2SO interaction with the $[M(MeS_2CNMe_2)X_2]$ complexes depends on the different solvent to metal donor ability. The nature of the interaction products is discussed on the basis of proton NMR spectra in deuterated dimethyl sulfoxide.

Introduction

Palladium and platinum(II) halides form with dithiocarbamic esters (RS_2CNR_2, R = Me or Et) either 1:2 adducts, in which the ligand acts as monodentate through thiocarbonyl sulfur, or 1:1 complexes, in which the ester molecule coordinates through both sulfur atoms [1, 2]. A number of these compounds showed significant *in vitro* cytostatic activity against KB tumor cells, a line derived from a human epidermoid carcinoma. Because the complexes are generally insoluble in water, the activity tests were performed by using drug suspensions in saline [2]. All dithiocarbamic ester adducts are easily soluble in dimethyl sulfoxide, which is widely used as a solvent in activity tests of water insoluble species. The ability of dimethyl sulfoxide to coordinate metal ions is well known [3]. In particular palladium(II) and platinum(II) halide complexes with *O*-ethylthiocarbamic esters decompose in dimethyl sulfoxide, the nature of the reaction products depending on the nitrogen substituents in the ligand molecule [4]. In fact the solvent removes all ligand molecules in the complexes $[Pt(EtOSCNR_2)_2X_2]$ (R = Me or Et; X = halide), whereas the N-monosubstituted thiocarbamic ester analogues, like $[Pt(EtOSCNHMe)_2X_2]$, release one ligand molecule and retain a noticeable cytostatic activity, possibly due to formation of active mixed complexes in solution. Consequently we prepared and characterized mixed platinum(II) complexes, of general formula $[Pt(L)(Me_2SO)X_2]$ (L = $EtOSCNR_2$, EtOSCNHR, $EtOSCNH_2$ or thioamide; X = halide), whose *cis* geometry was in favour of activity [5–7].

It was then worthwhile to examine the behaviour of dithiocarbamic ester complexes in dimethyl sulfoxide, on remembering that the species $[M(RS_2CNR_2)X_2]$ and $[M(RS_2CNR_2)_2X_2]$ (M = Pd or Pt) can undergo slow S-dealkylation in solution, yielding products which contain the *N,N*-dialkyldithiocarbamato moiety [1, 2, 8]. A recent thermogravimetric study has shown that the complexes $[M(MeS_2CNMe_2)X_2]$ (M = Pd or Pt; X = Cl or Br) release MeX on heating yielding the corresponding $[M(S_2CNMe_2)X]_n$ species as stable intermediates [9].

This paper reports the synthesis and characterization of the mixed complexes $[M(S_2CNMe_2)(Me_2SO)X]$ (M = Pd or Pt; X = Cl or Br) along with a study on the behaviour of the parent dithiocarbamic ester derivatives $[M(MeS_2CNMe_2)X_2]$ in dimethyl sulfoxide.

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Experimental

The ligand *S*-methyl *N,N*-dimethyldithiocarbamate (MeS_2CNMe_2) was prepared by reaction of $Na(S_2CNMe_2)$ with MeI in $EtOH/H_2O$ [10]. The oily product was dissolved in diethylether, washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was recrystallized from n-pentane. Platinum and palladium halides were Johnson Matthey products. The species $[M(S_2CNMe_2)X]_n$ (M = Pd or Pt; X = Cl or Br) were obtained by thermal degradation of the complexes $[M(MeS_2CNMe_2)X_2]$, which were prepared by reaction of the appropriate metal salt with MeS_2CNMe_2 (molar ratio, 1:1.1; solvent, CH_2Cl_2; reaction time, 2–3 h). The first decomposition step in $[M(MeS_2CNMe_2)X_2]$ concerns MeX release to form the corresponding $[M(S_2CNMe_2)X]_n$ intermediate. Experimental conditions and intermediate properties have been reported in ref. 9.

Preparation of $[Pt(S_2CNMe_2)(Me_2SO)X]$

These were prepared by reaction of $[Pt(S_2CNMe_2)X]_n$ and Me_2SO in dichloromethane (molar ratio 1:1.5). As an example, $[Pt(S_2CNMe_2)(Me_2SO)Br]$ was obtained by stirring overnight a suspension of the pink intermediate $[Pt(S_2CNMe_2)Br]_n$ (0.15 mmol) in a CH_2Cl_2 solution of Me_2SO (0.23 mmol in 1.5 cm^3). The orange–yellow solid was filtered and dissolved in CH_2Cl_2. A small amount of an unidentified orange residue was discarded and the solution was treated with n-pentane until turbidity. The complex was filtered and washed with n-pentane. Yield 65%. Further fractions of the crystalline product were obtained by adding n-pentane to the mother solution.

Preparation of $[Pd(S_2CNMe_2)(Me_2SO)X]$

The complexes were obtained by reaction of $[Pd(S_2CNMe_2)X]_n$ and Me_2SO (molar ratio, *c*. 1:6) in a mixture of CH_2Cl_2 and n-pentane (1:1 in volume). $[Pd(S_2CNMe_2)(Me_2SO)Cl]$ was obtained by stirring a suspension of $[Pd(S_2CNMe_2)Cl]_n$ (0.3 mmol) in a Me_2SO solution in CH_2Cl_2/n-pentane (2 mmol in 3 cm^3; reaction time, 3 h). The pink intermediate changed gradually into the orange product, which was filtered, washed with 1 cm^3 of CH_2Cl_2/n-pentane (1:2 in volume) and finally with n-pentane. Yield 80%. The product obtained by adding n-pentane to the mother solution was generally a mixture of $[Pd(S_2CNMe_2)(Me_2SO)Cl]$ and $[Pd(S_2CNMe_2)Cl]_n$. In fact the complexes $[Pd(S_2CNMe_2)(Me_2SO)X]$ dissolve in acetone, benzene and CH_2Cl_2 with immediate release of Me_2SO and consequent precipitation of the insoluble $[Pd(S_2CNMe_2)X]_n$ species.

Measurements

Infrared spectra were registered on Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers as nujol mulls between KBr and polyethylene discs. ^1H NMR spectra were obtained with a Jeol FX 90Q spectrometer. The TG, DTG and DTA curves were obtained by the Netzsch STA 429 thermoanalytical equipment either in air or in dinitrogen (flux rate, 250 cm^3 min^{-1}; heating rate, 5 °C min^{-1}; reference material, neutral Al_2O_3).

Results and discussion

The mixed complexes (Table 1) were prepared by reaction of dimethyl sulfoxide with the polymeric species $[M(S_2CNMe_2)X]_n$ (M = Pd or Pt; X = Cl or Br), which were prepared by thermal degradation of the parent $[M(MeS_2CNMe_2)X_2]$ complexes [9]. Samples were heated directly on the thermobalance crucible under dinitrogen flux. The process was stopped immediately after the appearance of the DTA peak due to MeX evolution, in order to avoid overheating of the intermediate. Otherwise reaction of $[Pd(S_2CNMe_2)X]_n$ intermediates with Me_2SO leads to product mixtures in which green unidentified species are present. Whereas the platinum mixed adducts are easily obtained by reaction of $[Pt(S_2CNMe_2)X]_n$ with a slight excess of Me_2SO in dichloromethane, the preparation of the palladium analogues requires a large Me_2SO excess in a medium (dichloromethane/n-pentane 1:1 in volume) which depresses the adduct solubility. Unlike the platinum complexes, the palladium analogues are unstable in the common solvents (alcohols, acetone, benzene or dichloromethane), in which they release Me_2SO with immediate precipitation of the pink $[Pd(S_2CNMe_2)X]_n$ species.

The lower stability of the palladium mixed complexes with respect to the platinum analogues is confirmed by the thermal analysis data (Table 2). As shown in Fig. 1, degradation of $[Pt(S_2CNMe_2)(Me_2SO)Cl]$ in air starts at 150 °C, the first step in the TG curve concerning evolution of Me_2SO (endotherm at 197 °C) to give $[Pt(S_2CNMe_2)Cl]_n$. The intermediate is stable in the 210–275 °C temperature interval and successively decomposes to platinum. The thermograms of $[Pt(S_2CNMe_2)(Me_2SO)Br]$ show a similar trend but in this case the decomposition intermediate $[Pt(S_2CNMe_2)Br]_n$ is stable in a narrow temperature range near 220 °C. In fact sample pyrolysis occurs in two close steps, Me_2SO evolution (endotherm at 203 °C) being immediately followed by $[Pt(S_2CNMe_2)Br]_n$ degradation. Dimethyl sulfoxide release is also the first process in thermal degradation

TABLE 1. Analyses[a] and selected infrared absorptions

Compound[b]	Colour	C%	H%	N%	ν(CN)	Me_2SO[c]
$[Pt(S_2CNMe_2)(Me_2SO)Cl]$[d]	yellow	13.78 (14.00)	2.71 (2.82)	3.19 (3.26)	1577	1128 1029
$[Pt(S_2CNMe_2)(Me_2SO)Br]$	dark yellow	12.75 (12.69)	2.51 (2.56)	2.87 (2.96)	1575	1124 1021
$[Pd(S_2CNMe_2)(Me_2SO)Cl]$[e]	pale orange	17.43 (17.65)	3.43 (3.56)	4.04 (4.12)	1573	1118 1022
$[Pd(S_2CNMe_2)(Me_2SO)Br]$	orange	15.62 (15.61)	3.02 (3.14)	3.56 (3.64)	1572	1118 1022

[a] Calculated values in parentheses. [b] General formula $C_5H_{12}XNOMS_3$ (X = Cl or Br; M = Pd or Pt). [c] Dimethyl sulfoxide absorptions in the ν(SO) region (see text). [d] Cl: found, 8.45%; calc., 8.27%. [e] Cl: found, 10.78%; calc., 10.42%.

TABLE 2. Thermal data of the complexes (in air)

Compound	Decomposition interval (°C)	TG weight loss (%)		DTA peak temperature (°C)[a]
		Found	Calculated	
$[Pt(S_2CNMe_2)(Me_2SO)Cl]$	150–210	17.54	18.22 (Me_2SO)	197 (endo), 200 (sh)
	275–430	36.86	36.29 (to Pt)	350 (exo), 364 (exo)
$[Pt(S_2CNMe_2)(Me_2SO)Br]$	160–220	16.40	16.51 (Me_2SO)	203 (endo)
	220–555	42.52	42.27 (to Pt)	290(endo), 360 (exo), 515 (exo), 540 (exo)
$[Pd(S_2CNMe_2)(Me_2SO)Cl]$	82–145	22.38	22.96 (Me_2SO)	123 (endo), 140 (sh)
	290–535	46.48	45.76 (to Pd)	324 (md), 354 (exo), 437 (exo)
	535–810[b]			537 (exo), 808 (endo)
$[Pd(S_2CNMe_2)(Me_2SO)Br]$	80–135	19.72	20.31 (Me_2SO)	116 (endo), 129 (sh)
	300–560	52.22	52.02 (to Pd)	327 (md), 485 (exo)
	560–820[b]			570 (exo), 805 (endo)

[a] (endo), decomposition endotherm; (exo), decomposition exotherm; (md), melting with decomposition. [b] See text.

of the palladium mixed complexes, but it is observed at noticeably lower temperatures. Degradation of the species $[Pd(S_2CNMe_2)(Me_2SO)X]$ starts at 80 °C, the first step endotherms being at 123 (X = Cl) and 116 (X = Br) °C, well below those of the platinum complexes. Consequently the species $[Pd(S_2CNMe_2)X]_n$ are stable in a wide temperature range (*c.* 140–290 °C). The sharp endotherm at 327 °C in the DTA curve of $[Pd(S_2CNMe_2)(Me_2SO)Cl]$ (Fig. 1(a)) originates from intermediate melting with contemporaneous decomposition. Sample combustion ends at 535 °C, the residue being palladium. The weight increase observed above this temperature (expanded TG curve in Fig. 1(a)) is due to non-stoichiometric uptake of oxygen in the residue surface to form PdO. Oxygen is then released at a higher temperature, as shown by the endotherm at 808 °C. Thermograms of parallel tests in dinitrogen coincide with those in air up to the beginning of the intermediate degradation, which ends generally at *c.* 550 °C. The pyrolysis residues are Pd or PtS and no further process is observed up to 1100 °C [9].

The infrared spectra of the $[M(S_2CNMe_2)X]_n$ intermediates supported a different nature of the polymer framework for M = Pd or Pt [9]. The ν(CN) and ν(Pt–X) absorptions suggested the presence of sulfur bridges and terminal halides in the species $[Pt(S_2CNMe_2)X]_n$ (X = Cl: ν(CN), 1580 cm^{-1}; ν(Pt–Cl), 315 cm^{-1}. X = Br: ν(CN), 1576 cm^{-1}; ν(Pt–Br), 202 cm^{-1}) whereas the species $[Pd(S_2CNMe_2)X]_n$ should contain halide bridges (X = Cl: ν(CN), 1566 cm^{-1}; ν(Pd–Cl), 298 cm^{-1}. X = Br: ν(CN), 1564 cm^{-1}; ν(Pd–Br), 167 cm^{-1}). Dimethyl sulfoxide coordination causes the breaking off of the polymeric arrangement to form structurally similar square planar complexes. In fact the mixed complexes (Table 1) show close ν(CN) absorptions (1572–1577 cm^{-1}), the metal–halide stretching frequencies being as expected for terminal halides (Table 3). Accordingly the Pt–X absorptions are observed

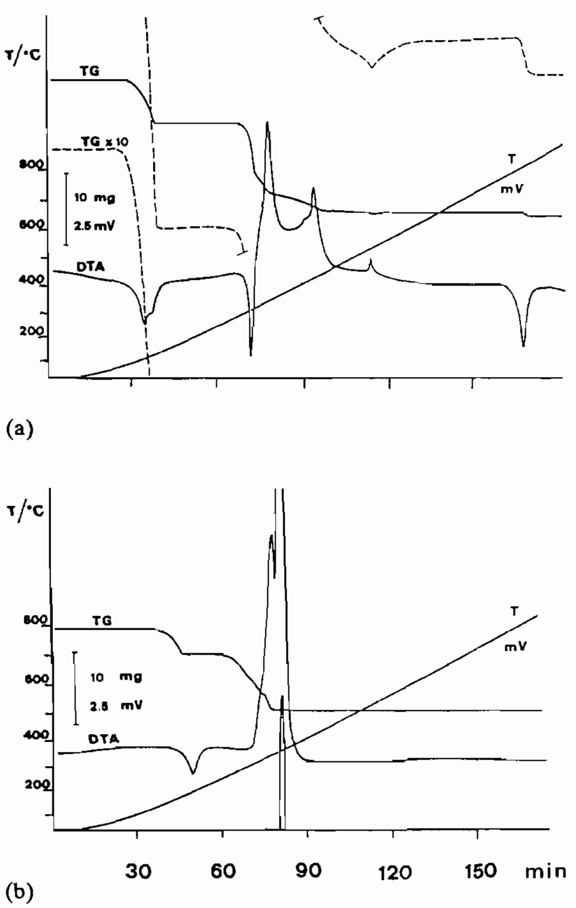

Fig. 1. Thermograms in air: (a) [Pd(S_2CNMe_2)(Me_2SO)Cl] (27.26 mg); (b) [Pt(S_2CNMe_2)(Me_2SO)Cl] (21.16 mg).

at 315 (Cl) and 204 (Br) cm^{-1}, as for the starting [Pt(S_2CNMe_2)X]$_n$ complexes, whereas the Pd–X absorptions (Cl, 306; Br, 192 cm^{-1}) undergo a noticeable shift to high energy with respect to those of the halide bridged [Pd(S_2CNMe_2)X]$_n$ complexes. Owing to the ambidentate nature of sulfoxides, the different metal to ligand bond strength in the palladium and platinum mixed complexes could depend on a different Me_2SO coordination site (either oxygen or sulfur). The ν(S=O) infrared absorptions in the 900–1200 cm^{-1} region are diagnostic of the binding atom [3]. As a general criterion, the S=O absorption, at 1055 cm^{-1} in free Me_2SO, shifts to higher energy (up to 1200 cm^{-1}) in S-bound and to lower energy (down to 890 cm^{-1}) in O-bound complexes. Along with weak absorptions of the dimethyldithiocarbamato moiety, the mixed species show two strong bands in the 900–1200 cm^{-1} region (Table 1), at *c.* 1025 and 1120 cm^{-1}, common to the already reported [Pt(L)(Me_2SO)X_2] complexes (L = thiocarbamic ester or thioamide), in which the presence of S-bound Me_2SO was confirmed by NMR (^{1}H and ^{13}C) spectra [5–7]. In particular the absorption at *c.* 1120 cm^{-1}

TABLE 3. Infrared absorptions (450–150 cm^{-1})^a

Compound	Frequencies (cm^{-1})											
[Pt(S_2CNMe_2)(Me_2SO)Cl]	442ms	437sh	419w	393vw		358m	*315*ms	304sh	270wbr	242vw		209vw
[Pt(S_2CNMe_2)(Me_2SO)Br]	435ms	432sh	418w	390vw		358m			262wbr	235vw	220vw	*204*m
[Pt(S_2CNMe_2)Br]$_n$^{b}		434mw		385w	354w		314w		264vw	241vw	206sh	202ms
[Pd(S_2CNMe_2)(Me_2SO)Cl]		442mw	419ms	389mw	375w	347ms	*306*ms	303sh	268vw	242vw	226mw	
[Pd(S_2CNMe_2)(Me_2SO)Br]		441mw	420ms	386mw		348ms			264vw	236vw		*192*m
[Pd(S_2CNMe_2)Br]$_n$^{b}		440w	407vvw	381m	349vvw				262mw			*167*m

^{a}Metal–halide frequencies in italics. ^{b}From ref. 9.

should be assigned as ν(S=O), whereas the one at lower energy should originate from CH_3 rock [11]. The $[Pt(L)(Me_2SO)X_2]$ spectra contained two intense absorptions at *c.* 440 and 380 cm^{-1}, assigned to symmetric and asymmetric stretching of the CSO group in coordinated Me_2SO, respectively. In $[Pt(S_2CNMe_2)(Me_2SO)X]$ (Table 3) the high energy band is almost unchanged, whereas the latter is observed at 358 cm^{-1}. The low energy shift could indicate that Me_2SO is a weaker S-donor in $[Pt(S_2CNMe_2)(Me_2SO)X]$, in which it is *trans* to chelated dimethyldithiocarbamato sulfur, than in $[Pt(L)(Me_2SO)X_2]$, in which it is *trans* to the halide owing to the complex *cis* geometry. The *trans* effect is of great importance in the reactivity of platinum square planar complexes [12]. An analogous *trans* influence was observed in the mixed complexes $[Pt(S_2CNR_2)(RS_2CNR_2)X]$ (R = Me or Et), which release easily in solution the dithioester molecule, weakly bonded through the thiocarbonyl sulfur atom [8]. As regards the $[Pd(S_2CNMe_2)(Me_2SO)X]$ complexes, the low energy shift of both CSO group vibrations (420 and 348 cm^{-1}) supports a correlation with bond weakening. The weak band at *c.* 265 cm^{-1} (Table 3), observed either in the mixed species or in the starting products, is due to the sulfur–metal bond in the dithiocarbamato moiety.

The $[Pt(S_2CNMe_2)(Me_2SO)X]$ complexes dissolve in deuterated chloroform yielding yellow solutions. The proton NMR spectra contain two close singlets (at 3.27 and 3.30 ppm) for the non-equivalent methyl groups of the chelated dithiocarbamato moiety along with the coordinated dimethyl sulfoxide resonance, which shows the satellites due to proton coupling with ^{195}Pt (X = Cl: 3.37 ppm; *J*, 20.6 Hz. X = Br: 3.45 ppm; *J*, 20.9 Hz). The palladium analogues dissolve in deuterated chloroform with immediate decomposition. The solutions, initially orange, turn to colourless in a few minutes with parallel precipitation of the pink $[Pd(S_2CNMe_2)X]_n$ species. Consequently the NMR spectra show the free Me_2SO resonance at 2.62 ppm, along with a broad NMe_2 resonance at *c.* 3.3 ppm, whose intensity decreases quickly. All complexes dissolve in deuterated dimethyl sulfoxide. Owing to solvent exchange, the related spectra display the free Me_2SO resonance at 2.51 ppm along with the NMe_2 proton singlet at 3.26 ppm. The spectra of aged solutions (up to 1 month) are unchanged.

Fig. 2. Proton NMR spectrum of MeS_2CNMe_2 in d_6-Me_2SO.

The knowledge of the interaction of the $[M(S_2CNMe_2)X]_n$ species with dimethyl sulfoxide is of help in explaining the behaviour of the parent dithiocarbamic ester adducts in the solvent. As shown in Fig. 2, the proton NMR spectrum of MeS_2CNMe_2 contains two broad NMe_2 signals (3.33 and 3.44 ppm) along with the SMe singlet at 2.53 ppm. Due to the energy of the barrier to rotation about the C–N bond, in the order of 63 kJ mol^{-1} [13–15], the dithioester molecule is planar and the nitrogen methyl substituents are non-equivalent. Proton NMR spectra of the thiocarbamic ester adducts $[M(MeS_2CNMe_2)X_2]$ (M = Pd or Pt; X = halide) in deuterated dimethyl sulfoxide suggest complex decomposition in solution, the related trend depending on the metal. On principle, solvent interaction could produce either ligand release or ligand S-demethylation, already observed in various media [1, 2]. The spectrum of $[Pt(MeS_2CNMe_2)Cl_2]$, registered immediately after dissolution (Fig. 3(a)) contains strong signals of free dithioester (ppm: 2.53, 3.34, 3.44). The weak signals at 2.93 and 3.82 ppm should be due to coordinated dithioester. Moreover partial S-demethylation to form $[Pt(S_2CNMe_2)(d_6\text{-}Me_2SO)Cl]$ should occur, proved by the weak resonance at 3.26 ppm, whose intensity increases with time (Fig. 3(b)). After one week such a signal is the most intense of the spectrum, free ligand being already present for ~20%. Except for a higher intensity of the coordinated ligand resonances, the spectrum of $[Pt(MeS_2CNMe_2)Br_2]$ looks initially like that of the chloroanalogue. In this case the S-demethylation process is faster, the main signal after three days being the one at 3.24 ppm. The weak signals observed at 2.83 and 3.82 ppm belong to coordinated ligand, whereas the free MeS_2CNMe_2 resonances are almost absent. Dimethyl sulfoxide being a strong S-donor towards platinum, its interaction with $[Pt(MeS_2CNMe_2)X_2]$ causes initially dithioester release. Along with the starting adduct the solution should contain MeS_2CNMe_2 and solvated [Pt(d_6-

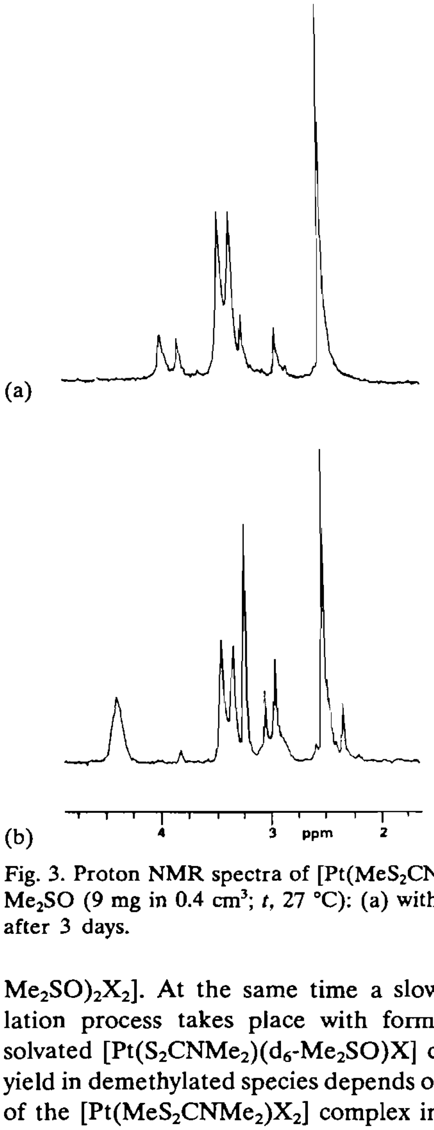

Fig. 3. Proton NMR spectra of [Pt(MeS$_2$CNMe$_2$Cl$_2$] in d$_6$-Me$_2$SO (9 mg in 0.4 cm^3; *t*, 27 °C): (a) within 10 min; (b) after 3 days.

Me$_2$SO)$_2$X$_2$]. At the same time a slow S-demethylation process takes place with formation of the solvated [Pt(S$_2$CNMe$_2$)(d$_6$-Me$_2$SO)X] complex. The yield in demethylated species depends on the amount of the [Pt(MeS$_2$CNMe$_2$)X$_2$] complex in solution. In fact the rate of formation of the mixed complex is greater for the bromo derivative, whose initial solution contains a lower amount of free dithioester. After two weeks the spectra of the chloro and bromo solutions are identical. Along with the main signal at 3.26 ppm, they contain weak unassigned signals which do not coincide with those of either free or coordinated dithioester. The initial spectrum of [Pd(MeS$_2$CNMe$_2$)Br$_2$] (Fig. 4(a)) displays broad resonances (ppm: 2.73, 3.41, 3.64) of coordinated ligand. The NMe$_2$ resonance separation, larger than in free dithioester, is caused by electron withdrawal on coordination with a parallel increase of the C–N double bond. The spectrum does not contain free ligand resonances, whereas a growing signal is observed at 3.26 ppm. The coordinated ligand resonances weaken with time and after 1 day (Fig. 4(b)) the main signal of the spectrum is the one at 3.26 ppm. Solutions of [Pd(MeS$_2$CNMe$_2$)Cl$_2$] show an identical behaviour, the decomposition process being complete within 3 days. Because dimethyl sulfoxide is a weak donor towards palladium, the [Pd(MeS$_2$CNMe$_2$)X$_2$] adducts do not release an appreciable amount of dithioester, solvent interaction playing probably a role in the monodentate or bidentate nature of the coordinated dithioester. Recently we suggested [9] that S-dealkylation should be favoured for dithiocarbamic ester complexes in which the ligand acts as monodentate through thiocarbonyl sulfur.

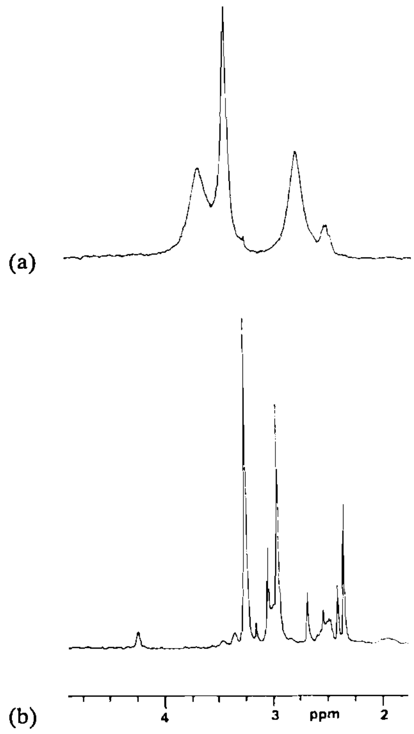

Fig. 4. Proton NMR spectra of [Pd(MeS$_2$CNMe$_2$)Br$_2$] in d$_6$-Me$_2$SO (8 mg in 0.4 cm^3; *t*, 27 °C): (a) within 5 min; (b) after 1 day.

Conclusions

The complexes [M(MeS$_2$CNMe$_2$)X$_2$] (M = Pd or Pt; X = halide) decompose in dimethyl sulfoxide, the final decomposition product being mainly the solvated [M(S$_2$CNMe$_2$)X] moiety. The degradation pathway depends on the dimethyl sulfoxide to metal bond strength. Because MeX evolution occurs in coordinated dithioester, the process rate is higher for the palladium adducts, which do not release ligand in solution. The solids obtained by treating aged solutions with successive dichloromethane/n-pentane fractions consisted essentially of

$[M(S_2CNMe_2)(Me_2SO)X]$ and $[M(S_2CNMe_2)X]_n$ mixtures, along with small amounts of unidentified products containing metal halides.

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