Pergamon

Polyhedron Vol. 14, No. 13–14, pp. 1905–1914, 1995
Elsevier Science Ltd
Printed in Great Britain
0277–5387/95 $9.50+0.00

0277–5387(94)00459–5

DECOMPOSITION INTERMEDIATES IN PALLADIUM–DITHIOESTER SYSTEMS

GIUSEPPINA FARAGLIA,* DANIELA LONGO and VALERIA CHERCHI

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Loredan, 4, 35131, Padova, Italy

and

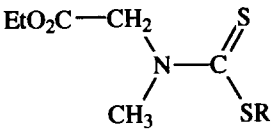
SERGIO SITRAN

Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, C.N.R., Padova, Italy

(*Received* 5 *August* 1994; *accepted* 26 *October* 1994)

Abstract—Palladium dihalides react with the ligands $EtO_2CCH_2(CH_3)NCS_2R$ (R = Me, ESDTM; R = Et, ESDTE) in non-polar solvents yielding the *trans*-$[Pd(ESDTR)_2X_2]$ (X = Cl, Br or I) complexes in which the dithioester molecule coordinates through thiocarbonyl sulphur. Thermal degradation of these complexes has been investigated up to 1000°C. The first decomposition step involves evolution of one alkyl halide molecule to form the [Pd(ESDT)(ESDTR)X] (X = Cl or Br) intermediates. At higher temperature S-dealkylation of the neutral ligand takes place with consequent formation of $[Pd(ESDT)_2]$ as a second intermediate. The mixed species [Pd(ESDT) (ESDTR)X] have been also prepared by reaction of $[Pd(ESDT)X]_n$ with the appropriate dithioester, as for the [Pd(ESDT)(DMDTM)X] (X = Cl or Br; DMDTM = MeS_2CNMe_2) analogues. The complexes have been characterized by elemental analyses and IR and ^1H NMR spectroscopy. The behaviour of the 1 : 2 adducts and of the related mixed species in solution is described on the basis of proton NMR spectra.

Owing to the detoxicant properties of sulphur donors against heavy metal intoxication[1,2] we have studied platinum(II) and palladium(II) complexes with sulphur containing amino acids (i.e. methionine and analogues).[3–5] Moreover, in continuation of our studies on platinum and palladium complexes with dithiocarbamic esters (RS_2CNR_2; R = alkyl),[6,10] recently we reported the palladium complexes $[Pd(ESDTR)X_2]\cdot nC_6H_6$ (X = Cl or Br; $n < 1$) in which the sarcosine ethyl ester derivatives acted as bidentate ligand



R = Me, ESDTM

R = Et, ESDTE

through both sulphur atoms.[11] These complexes were found to undergo slow S-dealkylation in various media to form the dithiocarbamato derivatives $[Pd(ESDT)X]_n$ (X = Cl or Br; ESDT = $EtO_2CCH_2(CH_3)NCS_2^-$). In the course of the 1 : 1 adduct synthesis we observed the presence of side products which should originate from decomposition of unstable 1 : 2 adducts formed casually in minor amounts. It was thus considered worthwhile

* Author to whom correspondence should be addressed.

to investigate the conditions in which the 1:2 adducts are formed along with their stability in either the solid state or in solution, in order to extend the study to dithioesters containing the sarcosine moiety, whose acidic proton could cause a more complicated reaction pattern in the presence of metal halides.

EXPERIMENTAL

Materials

The dithioesters ESDTM ($C_7H_{13}NO_2S_2$) and ESDTE ($C_8H_{15}NO_2S_2$) were prepared by reaction of sarcosine ethyl ester with CS_2 and then with the appropriate alkyl halide in $EtOH/H_2O$,[11] DMDTM ($MeS_2CN(Me)_2$, $C_4H_9NS_2$) was prepared by reaction of $Na(S_2CNMe_2)$ with MeI in $EtOH/H_2O$.[12] Palladium halides were Johnson Matthey products. The complexes $[Pd(ESDT)X]_n$ (X = Cl or Br) have been obtained by heating the parent $[Pd(ESDTM)X_2]$ species on an oil bath (120°C) under reduced pressure.[11]

Preparation of the complexes

The complexes $[Pd(ESDTM)_2X_2]$ (X = Cl or Br) have been prepared in benzene by reaction of metal salt and ligand in molar ratio 1:3. As an example, $[Pd(ESDTM)_2Br_2]$ was prepared by adding ESDTM (3.1 mmol) to a $PdBr_2$ suspension in anhydrous benzene (1.0 mmol in 3 cm^3) with vigorous stirring (18 h). The heterogeneous reactions yielded a greenish–beige solid which was filtered, washed with n-hexane and dried under reduced pressure. The complexes $[Pd(ESDTM)_2I_2]$ and $[Pd(ESDTE)_2X_2]$ (X = Cl, Br or I) could be prepared only by using either n-pentane or n-hexane as solvents. As an example, $[Pd(ESDTE)_2Cl_2]$ was obtained in quantitative yield by reacting $PdCl_2$ (0.9 mmol) with ESDTE (3.2 mmol in 4 cm^3 of n-hexane) with stirring (48 h) at room temperature. The reaction course was followed by successive IR spectra of the suspension in order to determine the absence of either 1:1 complexes or decomposition products. The nutmeg complex was filtered, washed with n-hexane and dried *in vacuo* (5 min). All 1:2 adducts should be stored in a freezer, since they decompose gradually when kept at room temperature, the degradation process being evident after 2 days on the basis of proton NMR spectra. When washed with C_6H_6, MeOH, CH_2Cl_2 and other common solvents the 1:2 adducts release one of the ligand molecules to form the corresponding 1:1 complexes.

The $[Pd(ESDT)_2]$ complex was obtained by thermal degradation of freshly prepared $[Pd(ESDTM)_2X_2]$ (X = Cl or Br) samples. The solid 1:2 adduct was heated in an oil bath (140°C) under reduced pressure. After 1 h the solid residue was removed and finely ground in a mortar, then it was heated again (140°C) for a further 2 h. By this method, a yellow solid (m.p. 192°C) was obtained, which was scarcely soluble in CH_2Cl_2. When aged samples of 1:2 adducts were used as starting products orange solids were obtained in analogous conditions, which dissolved partly in CH_2Cl_2. The insoluble fraction was a yellow solid identical to the previous one (m.p. 192°C). By addition of n-pentane to the orange solution an orange solid separated, whose IR and NMR spectra were like those of the yellow product. Conversely the two fractions showed a different thermal behaviour, which will be discussed below. Melting points of orange samples from different preparations varied in the 180–187°C range and the elemental analyses were slightly lower than expected for $[Pd(ESDT)_2]$ (Table 1; found for orange product (mean): C, 28.8; H, 4.0; N, 5.5%). This fact should not be due to partial formation of the corresponding $[Pd(ESDT)X]_n$ species, which are insoluble in CH_2Cl_2.

The complex [Pd(ESDT)(ESDTM)Cl] was obtained as a red oil by gradual heating of $[Pd(ESDTM)_2Cl_2]$ samples up to 83°C in an oil bath under reduced pressure (10 min), whereas the complex [Pd(ESDT)(ESDTM)Br] was prepared analogously by using $[Pd(ESDTM)_2Br_2]$ as starting product (t_{max} = 90°C; red oil). The oil purity was tested by elemental analysis and IR and NMR spectroscopy. The difficulty in obtaining pure products by this method depends on the incipient degradation of those intermediates to form $[Pd(ESDT)_2]$ below 100°C. Pure samples of the [Pd(ESDT)(L)X] species (X = Cl, Br, L = ESDTM or ESDTE) were prepared by adding the appropriate ligand to a $[Pd(ESDT)X]_n$ suspension in deuterated chloroform ($CDCl_3$; molar ratio 1:1; 1.5 mmol in 4 cm^3). The reddish–orange solution, evaporated to dryness in a rotavapor, yielded the red oily product. The mixed complexes [Pd(ESDT)(DMDTM)X] (X = Cl or Br) were prepared analogously. In this case particular attention should be paid to removing the last traces of $CDCl_3$ under reduced pressure. In fact the oils form a foam which tends to release DMDTM by prolonged pumping *in vacuo*. It is preferable to stop $CDCl_3$ evolution at the first hint of foaming. The solvent amount left in different samples can be estimated by thermogravimetry.

The $[Pd(ESDT)(L)_{0.5}X]$ (X = Cl or Br; L = ESDTM, ESDTE or DMDTM) species pre-

Table 1. Analytical data and selected IR wavenumbers

Compound	Formula	Colour	Found (Calc.)(%) C	H	N	Wavenumbers (cm^{-1})		
$[Pd(ESDTM)_2Cl_2]$	$C_{14}H_{26}Cl_2N_2O_4PdS_4$	nutmeg	28.3 (28.4)	4.4 (4.4)	4.7 (4.7)	1737		1501
$[Pd(ESDTM)_2Br_2]$	$C_{14}H_{26}Br_2N_2O_4PdS_4$	greenish beige	24.8 (24.7)	3.8 (3.8)	4.1 (4.1)	1737		1501
$[Pd(ESDTM)_2I_2]$	$C_{14}H_{26}I_2N_2O_4PdS_4$	brown	20.3 (21.6)	3.1 (3.4)	3.3 (3.6)	1739		1500
$[Pd(ESDTE)_2Cl_2]$	$C_{16}H_{30}Cl_2N_2O_4PdS_4$	pinkish nutmeg	29.5 (30.9)	4.7 (4.8)	4.3 (4.5)	1742		1505
$[Pd(ESDTE)_2Br_2]$	$C_{16}H_{30}Br_2N_2O_4PdS_4$	pinkish nutmeg	25.6 (27.1)	4.2 (4.2)	3.7 (3.9)	1743		1507
$[Pd(ESTE)_2I_2]$	$C_{16}H_{30}I_2N_2O_4PdS_4$	brown	22.9 (23.9)	3.5 (3.7)	3.3 (3.5)	1746		1503
$[Pd(ESDT)_2]$	$C_{12}H_{20}N_2O_4PdS_4$	pale yellow	29.1 (29.4)	4.1 (4.1)	5.7 (5.7)	1742	1519	
[Pd(ESDT)(ESDTM)Cl]	$C_{13}H_{23}ClN_2O_4PdS_4$	red oil	30.3 (28.8)	4.6 (4.2)	5.2 (5.2)	1742	1528	1500 sh
[Pd(ESDT)(ESDTM)Br]	$C_{13}H_{23}BrN_2O_4PdS_4$	red oil	26.9 (26.6)	4.1 (3.9)	4.8 (4.8)	1740	1525	1500 sh
[Pd(ESDT)(ESDTE)Cl]	$C_{14}H_{25}ClN_2O_4PdS_4$	red oil	30.1 (30.2)	4.8 (4.5)	5.0 (5.0)	1742	1528	1501 sh
[Pd(ESDT)(ESDTE)Br]	$C_{14}H_{25}BrN_2O_4PdS_4$	red oil	28.5 (28.0)	4.3 (4.2)	4.6 (4.7)	1744	1528	1505 sh
[Pd(ESDT)(DMDTM)Cl]	$C_{10}H_{19}ClN_2O_4PdS_4$	red oil	24.7 (25.5)	4.1 (4.0)	5.6 (6.0)	1743	1524	
[Pd(ESDT)(DMDTM)Br]	$C_{10}H_{19}BrN_2O_4PdS_4$	red oil	21.6 (23.3)	3.3 (3.7)	4.8 (5.4)	1742	1523	
$[Pd(ESDT)(ESDTM)_{0.5}Cl]$	$C_{9.5}H_{16.5}ClN_{1.5}O_3PdS_3$	pale orange	25.9 (26.0)	3.9 (3.8)	4.7 (4.8)	1741	1533	1500 sh
$[Pd(ESDT)(ESDTM)_{0.5}Br]$	$C_{9.5}H_{16.5}BrN_{1.5}O_3PdS_3$	pale orange	24.3 (23.6)	3.6 (3.4)	4.5 (4.3)	1744	1532	1500 sh
$[Pd(ESDT)(ESDTE)_{0.5}Cl]$	$C_{10}H_{17.5}ClN_{1.5}O_3PdS_3$	pale orange	26.9 (27.0)	3.8 (3.9)	4.7 (4.7)	1740	1530	1500 sh
$[Pd(ESDT)(ESDTE)_{0.5}Br]$	$C_{10}H_{17.5}BrN_{1.5}O_3PdS_3$	pale orange	23.8 (24.5)	3.3 (3.6)	4.2 (4.3)	1742	1530	1500 sh
$[Pd(ESDT(DMDTM)_{0.5}Cl]$	$C_8H_{14.5}ClN_{1.5}O_2PdS_3$	pale orange	23.7 (23.9)	3.8 (3.6)	5.2 (5.2)	1743	1525	
$[Pd(ESDT)(DMDTM)_{0.5}Br]$	$C_8H_{14.5}BrN_{1.5}O_2PdS_3$	pale orange	21.0 (21.5)	3.1 (3.2)	4.5 (4.7)	1743	1525	

cipitated as pale orange solids by addition of n-pentane to CH_2Cl_2 or $CDCl_3$ solutions containing $[Pd(ESDT)X]_n$ and L in molar ratio 1 : 1. Products were filtered, washed with n-pentane and dried *in vacuo*.

Measurements

The IR spectra were recorded using Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers, in Nujol mulls between KBr and polyethylene discs or in KBr pellets. Far IR spectra of oily complexes were of Nujol mulls containing a drop of $CDCl_3$ to improve the sample homogeneity. The proton NMR spectra were obtained with JEOL FX 90Q spectrometer (ppm from TMS). The TG, DTG and DTA curves in 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

The main condition for synthesizing the 1 : 2 palladium adducts with ESDTE (or ESDTM) is to employ a solvent in which those species are insoluble in the presence of ligand excess. Accordingly the $[Pd(ESDTM)_2X_2]$ (X = Cl or Br) complexes have been prepared by reaction of palladium halide and ESDTM in benzene at molar ratio 1 : 3 (Table 1). In this case the palladium dihalide suspension turns directly into the nutmeg 1 : 2 complex without formation of the yellow $[Pd(ESDTM)X_2]$ species as reaction intermediate. The synthesis of either $[Pd(ESDTM)I_2]$ or $[Pd(ESDTE)_2X_2]$ (X = Cl, Br or I) must be carried out in n-pentane (or n-hexane), otherwise mixtures containing 1 : 1 adduct along with S-dealkylated species are obtained. Solid 1 : 2 adducts cannot be washed with the usual solvents (benzene too) because they extract the ligand to form the corresponding 1 : 1 complexes when X = Cl or Br. The iodo derivatives, which have no tendency to form the 1 : 1 species, decompose directly into PdI_2. The thermal behaviour of the 1 : 2 adducts (Table 2) resembles that of $[Pd(ESDTM)_2Cl_2]$. As shown in Fig. 1, degradation in air starts at 75°C, the first step in the TG curve representing evolution of one MeCl molecule (sharp endotherm at 90°C) to form [Pd(ESDT)(ESDTM)Cl] as a first intermediate. The successive release of the second MeCl molecule occurs gradually over the range 100–180°C the related endotherm being broad with a maximum at *ca* 140°C. Pyrolysis of the $[Pd(ESDT)_2]$ intermediate to palladium takes place over the range 210–450°C. The weight increase in the 450–820°C range, common to all complexes, depends on non-stoichiometric oxygen uptake on the metal surface to form PdO which successively decomposes to Pd (endotherm at 808°C). The TG curves of the other 1 : 2 complexes do not show any evident inflection after evolution of the first alkyl halide molecule, an unique broad step to form $[Pd(ESDT)_2]$ being observed in the 65–200°C range. The corresponding DTA curves present one endotherm below 100°C followed by a nearly flat trend correlated to evolution of the second alkyl halide molecule.

The $[Pd(ESDT_2)]$ complex was obtained by heating freshly prepared samples of $[Pd(ESDTM)_2X_2]$ (X = Cl or Br) in an oil bath (*ca* 140°C) for several hours. This yellow complex melts at 195°C (Fig. 2), sample degradation being observed in the range 238–400°C. Massive weight loss corresponds to the endotherm at 304°C, followed by the combustion exotherm at 383°C. Orange samples of the same species (see Experimental) melt at lower temperatures (184–190°C range) and present a weak endotherm at *ca* 250°C. The main difference in the DTA curve consists of an evident exothermic process at 340°C in addition to the final one at 390°C. The different thermal behaviour of yellow or orange samples depends probably on a different network of intermolecular sulphur bonds, owing to the versatility of the dithiocarbamato ligands. As an example, the dithiocarbamato ligand is bidentate in the $PtCl(S_2CNMe_2)(PEt_3)$ moiety of the binuclear complex $[Pt_2Cl_3(PEt_3)_2(S_2CNMe_2)]$ and at the same time bonds the second platinum atom through one of the sulphur atoms.[13]

In accordance with the degradation trend of the 1 : 2 complexes, the synthesis of the [Pd(ESDT)(ESDTR)X] (X = Cl or Br) mixed species was attempted by gradually heating $[Pd(ESDTR)_2X_2]$ samples up to a temperature slightly lower than that of the first degradation endotherm. Such a method was successful for the oily [Pd(ESDT)(ESDTM)X] species only, whose analytical and spectral data supported the formulation. In the other cases the oils were impure due to a more or less amount of $[Pd(ESDT)_2]$. As a general method, the mixed complexes were prepared by dissolving $[Pd(ESDT)X]_n$ (X = Cl or Br) samples in a $CDCl_3$ (or CH_2Cl_2) solution containing equimolar ESDTR. After solvent evolution under reduced pressure red sticky oils were obtained, which did not solidify in different solvents at low temperatures. As shown in Fig. 3, the fist step in the [Pd(ESDT)(ESDTM)Br] thermograms concerns MeBr release (60–160°C), the related broad endotherm (max. 140°C) being similar to that of the second step in the $[Pd(ESDTM)_2Br_2]$ degradation. The sharp endotherm at 190°C corresponds to melt-

Table 2. Thermal data for the complexes

Compound	Decomposition interval (°C)	Tg weight loss %		DTA peak temperature (°C)
		Experimental	Calculated	
$[Pd(ESDTM)_2Cl_2]$	75–100	8.1	8.5 (MeCl)	90 endo
	100–208	8.9	8.5 (MeCl)	broad endo, max *ca* 140
	210–450	64.6	65.0 (to Pd)	300 endo, 340–380 exo
	450–810[a]			808 endo
$[Pd(ESDTM)_2Br_2]$	80–185	28.4	27.9 (2 MeBr)	99 endo[b]
	185–410	58.0	56.5 (to Pd)	300 endo, 340 exo, 386 exo
	410–830[a]			819 endo
$[Pd(ESDTM)_2I_2]$	75–210	31.9	36.6 (2 MeI)	82 endo[b]
	210–590	54.6	49.7 (to Pd)	278 endo
	590–830[a]			817 endo
$[Pd(ESDTE)_2Cl_2]$	65–170	19.9	20.8 (2 EtCl)	78 endo[b]
	170–410	61.9	62.0 (to Pd)	290 endo, 260 exo, 402 exo
	410–830[a]			815 endo
$[Pd(ESDTE)_2Br_2]$	65–187	29.9	30.7 (2 EtBr)	70 endo[b]
	187–390	54.5	54.3 (to Pd)	260 endo, 326 exo, 383 exo
	390–830[a]			813 endo
$[Pd(ESDTE)_2I_2]$	75–200	35.8	38.8 (2 EtI)	82 endo[b]
	200–590	51.8	47.9 (to Pd)	283 endo
	590–830[a]			817 endo
$[Pd(ESDT)_2]$	190–238	0.0	0.0	195 m
	238–400	78.4	78.3 (to Pd)	304 endo, 325 exo, 383 exo
	400–830[a]			819 endo
[Pd(ESDT)(ESDTM)Cl]	70–200	13.8	9.3 (MeCl)	192 vw endo[c]
	200–400	67.3	71.1 (to Pd)	302 endo, 348 exo, 378 exo
	400–830[a]			817 endo
[Pd(ESDT)(ESDTM)Br]	60–175	17.0	16.2 (MeBr)	broad endo max 140
	175–215	0.0	0.0	190 m
	215–400	63.9	65.6 (to Pd)	301 endo, 340–380 exo br
	400–830[a]			818 endo
[Pd(ESDT)ESDTE)Cl]	60–170	12.7	11.6 (EtCl)	broad endo max *ca* 140
	170–220	0.0	0.0	192 m
	220–380	68.4	69.3 (to Pd)	306 endo, 343, 359 exo
	400–830[a]			817 endo
$[Pd(ESDT)(ESDTM)_{0.5}Br]$	90–190	10.6	9.8 (0.5 MeBr)	[c]
	190–400	68.9	68.1 (to Pd)	268 endo, 335 exo, 388 exo
	400–840[a]			817 endo

[a] See text.
[b] Followed by a very broad endotherm before decomposition. See text.
[c] The DTA curve before 190°C is meaningless.

ing of the $[Pd(ESDT)_2]$ intermediate whose degradation follows the usual trend.

The complexes [Pd(ESDT)(DMDTM)X] (X = Cl or Br) were prepared by slow evaporation of $CDCl_3$ solutions containing equimolar $[Pd(ESDT)X]_n$ and DMDTM. Their thermograms have not been reported because the oily samples retain traces of solvent (see Experimental) which is released at about the same temperature of alkyl halide evolution. Attempts to prepare the related asymmetric dithiocarbamate [Pd(ESDT)(DMDT)] by heating the mixed complexes (140°C) under reduced pressure yielded a product impure for $[Pd(ESDT)X]_n$, white crystals of sublimed DMDTM being observed on the walls of the test tubes.

By adding n-hexane to $CDCl_3$ (or CH_2Cl_2) solutions containing the [Pd(ESDT)(L)X] (L = ESDTM, ESDTE or DMDTM) complexes orange solids separated having the formula $[Pd(ESDT)(L)_{0.5}X]$. Their thermograms were similar to those of the corresponding 1 : 1 mixed species,

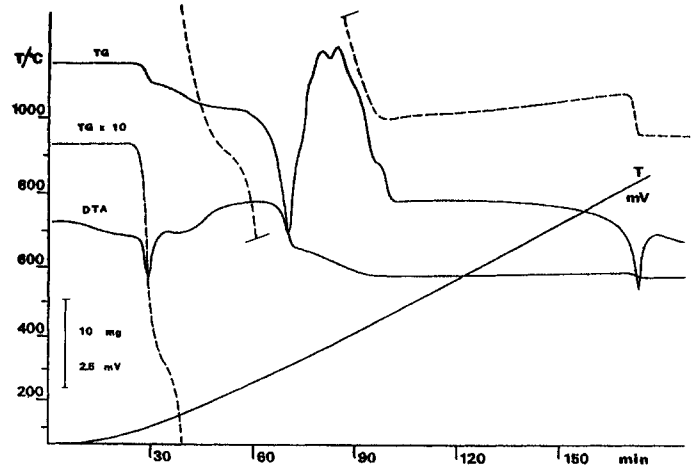


Fig. 1. Thermograms of $[Pd(ESDTM)_2Cl_2]$ (30.59 mg).

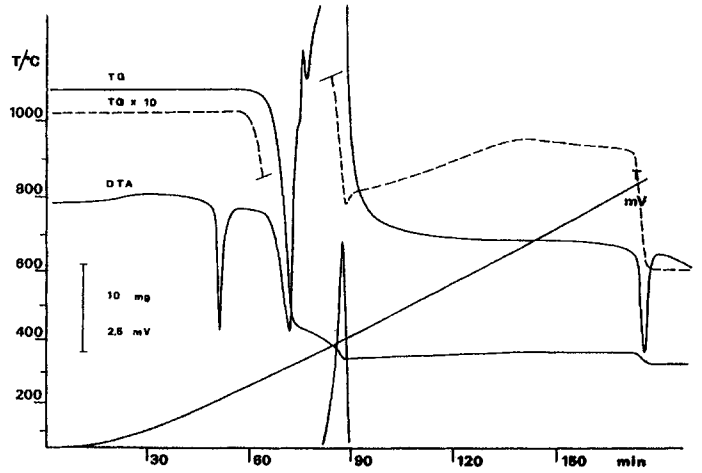


Fig. 2. Thermograms of $[Pd(ESDT)_2]$ (39.90 mg).

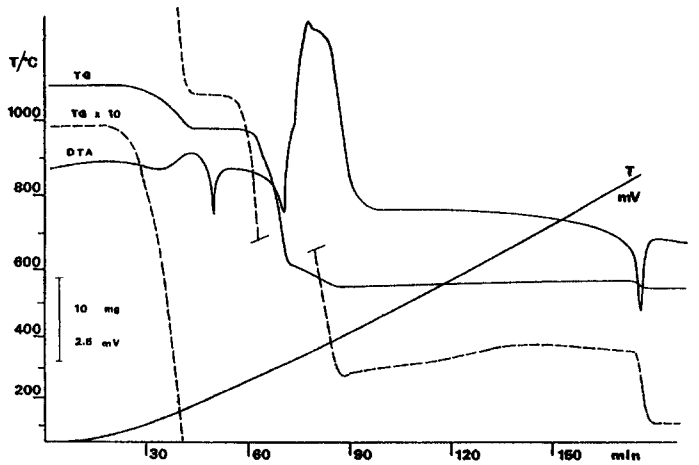


Fig. 3. Thermograms of [Pd(ESDT)ESDTM)Br] (29.03 mg).

apart from evolution of 50% of an alkyl halide molecule.

The infrared spectrum of ESDTR contains a sharp absorption at 1744 cm^{-1} due to vibration of the esterified carboxyl in the sarcosine moiety, which is little changed in the complexes (Table 1). The ν(CN) band position depends on the coordination mode (monodentate or bidentate) in dithioester complexes, owing to the different shifts (*ca* 90 or 20 cm^{-1} respectively[6,7]) to high energy with respect to the free ligand. The corresponding absorption is observed at *ca* 1505 cm^{-1} in the 1 : 2 complexes compared with 1474 and 1485 cm^{-1} in free ESDTM and ESDTE respectively, supporting ligand coordination through the thiocarbonyl sulphur. The corresponding band in $[Pd(ESDT)_2]$ is observed at 1519 cm^{-1} compared with a value of *ca* 1530 cm^{-1} in $[Pd(ESDT)X]_n$. Two ν(CN) bands are present in the [Pd(ESDT)(L)X] (L = ESDTM or ESDTE) spectra, the one at *ca* 1525 cm^{-1} belonging to the dithiocarbamato ion, whereas the ν(CN) of monodentate neutral ligand gives the shoulder at *ca* 1500 cm^{-1}. Because the ν(CN) absorption falls at *ca* 1525 cm^{-1} in the complexes containing monodentate DMDTM (1502 cm^{-1} in free DMDTM[6]), both dithiocarbamato and neutral ligand absorptions fall at nearly the same frequency in the [Pd(ESDT)(DMDTM)X] species, whose spectra contain a strong band at *ca* 1524 cm^{-1}. Far IR spectra (Table 3) are consistent with a *trans* geometry of the 1 : 2 complexes, owing to the presence of one ν(Pd-halide) absorption (Cl, *ca* 335 cm^{-1}; Br, *ca* 265 cm^{-1}; I, *ca* 220 cm^{-1}). The insertion of monodentate ligand does not influence the ν(Pd—Cl) value in $[Pd(ESDT)Cl]_n$. The related band is present at 299 cm^{-1} in this complex and it is observed at *ca* 301 cm^{-1} in the mixed complexes. This fact suggests that the polymeric nature of $[Pd(ESDT)X]_n$ does not involve halide bridges but is probably attained through bridging sulphur atoms. Accordingly the Pd—Br absorption is at *ca* 163 cm^{-1} in the bromo-mixed species against 168 cm^{-1} for $[Pd(ESDT)Br]_n$.

Owing to the barrier to rotation about the CN bond (*ca* 63 kJ mol^{-1}), the dialkyl dithioester molecule is planar and the nitrogen substituents are magnetically non-equivalent.[14–18] For this reason the proton NMR spectrum of DMDTM in $CDCl_3$ (Table 4) contains two distinct singlets for the methyl groups bound to nitrogen (3.38 and 3.55 ppm), along with the SCH_3 signal at 2.64 ppm. Because sarcosine dithioesters contain two different substituents at the nitrogen atom, the planar molecules can be present in the isomeric forms

Table 3. IR wavenumbers in the 500–200 cm^{-1} region [ν (Pd–hal) underlined]

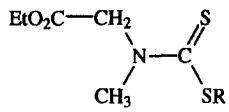
Compound	Wavenumbers (cm^{-1})[a]											
$[Pd(ESDTM)_2Cl_2]$	492w	436w			352	328s	324sh	303vw		255w		190w
$[Pd(ESDTM)_2Br_2]$	491w	434w	400vvw		354vw		324w	302vw	261m	253sh		
$[Pd(ESDTM)_2I_2]$	490m	432m			357vvw		328m	302vvw	257vw	228sh	219w	
$[Pd(ESDTE)_2Cl_2]$	481w	433w	402vvw	388vw		339s	332sh	320sh	268vvw	234vvw		200vvw
$[Pd(ESDTE)_2Br_2]$	493w	433w	400vvw	388vw	355w		332w	307vw	265m	247sh		190vvw
$[Pd(ESDTE)_2I_2]$	492m	433m			355vvw		331w	306vvw	246vvw		220w	
$[Pd(ESDT)_2]$	493w	437w			353vw		328m	305sh	256w			192vvw
$[Pd(ESDT)(ESDTM)Cl]^b$	489wbr	432w	400vvw	376ms	347m		325sh	301m		227vvw		
$[Pd(ESDT)(ESDTM)Br]^b$	486wbr	431w	401vvw	376m	356ms		329sh		363vwbr			194w
$[Pd(ESDT)(ESDTE)Cl]^b$	496wbr	432w	402vw	377m	347m		324sh	301m		224vw		
$[Pd(ESDT)(ESDTE)Br]^b$	486wbr	430w	403vvw	374m	341w		329sh		263vwbr			185w
$[Pd(ESDT)(DMDTM)Cl]^b$	480wbr	442sh	428m	374ms	344w		320sh	299ms		224wbr		
$[Pd(ESDT)(DMDTM)Br]^b$		442sh	429m	375ms	349w		324vw		260w			185m

[a] w, weak; m, medium; s, strong; v, very.
[b] In $CDCl_3$; the band at *ca* 375 cm^{-1} is of solvent.

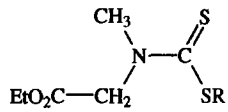
Table 4. Proton NMR data (ppm, $CDCl_3$, $T = 25°C$)

Compound	O-CH_2-CH_3	O-CH_2-CH_3	SR	NCH_2	NCH_3
ESDTM	4.22	1.29	2.64	4.80, 4.50wbr	3.43, 3.50wbr
ESDTE	4.22	1.28	3.24	4.80, 4.48wbr	3.43, 3.50wbr
			1.33		
DMDTM			2.64		3.38, 3.55
[Pd(ESDTM)Cl_2][a]	4.29, 4.31w	1.32, 1.35w	3.12, 3.00w	(5.09, 4.89, 4.80, 4.55)	3.63, 3.59w
[Pd(ESDTM)$_2Cl_2$][b]	4.23	1.29	3.09br	5.25br	3.46
[Pd(ESDTM)$_2Br_2$][b]	4.25	1.31	3.07br	5.27br	3.49
[Pd(ESDT)$_2$]	4.18	1.25		4.48	3.35
[Pd(ESDT)$_2$][c]	4.21	1.26		4.62	3.40
[Pd(ESDT)Cl]$_n$[a,d]	4.17	1.23		4.62	3.31
[Pd(ESDT)(DMDTM)Cl]	4.25	1.31		1.41	3.33
			2.94[e]		3.52, 3.96[e]
[Pd(ESDT)(DMDTM)$_{0.5}$Br]	4.24	1.31		4.38	3.32
			2.95[e]		3.53, 3.96[e]
[Pd(ESDT)(ESDTM)Cl]	4.21	1.28		4.41	3.32
	4.21[e]	1.28[e]	2.89br[e]	5.10, 4.60w[e]	3.50[e]
[Pd(ESDT)(ESDTM)Br]	4.22	1.29		4.42	3.33
	4.22[e]	1.29[e]	2.90br[e]	5.10, 4.62w[e]	3.52[e]
[Pd(ESDT)(ESDTE)Cl]	4.24	1.30		4.45	3.31
	4.24[e]	1.30[e]	3.60[e,f]	5.19, 4.65w[e]	3.52[e]
			1.35, 1.45[e]		
[Pd(ESDT)(ESDTE)$_{0.5}$Br]	4.24	1.31		4.38	3.33
	4.24[e]	1.31[e]	[g]	5.28, 4.62[e]	3.53[e]

[a] From ref. 11.
[b] Depending on concentration, weak signals of [Pd(ESDTM)X] (X = Cl or Br) and free ligand are always present.
[c] In d_6-acetone.
[d] In d_6-dimethyl sulphoxide.
[e] Neutral ligand.
[f] Multiplet.
[g] Obscured by the nearby signals.



Anti



Syn

bearing the NCH_3 group in *anti* or *syn* position with respect to the thiocarbonyl group. The presence of both isomers gives rise to two NCH_3 and two NCH_2 proton signals in the ligand spectra, whose relative amount cannot be estimated from integrated areas. The isomer resonances are in fact very close (i.e. NCH_3 3.43, 3.50 wbr) and superimposed in part, only one signal being observed for the OEt and SR proton groups. Conversely the [Pd(ESDTR)X_2] adducts, in which bidentate dithioester is present, clearly contained both ligand isomers, as for [Pd(ESDTM)Cl_2] (Table 4) which shows two signals for each proton group except for NCH_2 (four signals in the 4.50–5.10 ppm range). The NMR spectrum of [Pd(ESDT)$_2$] (Fig. 4a) is very simple, one signal for each proton group being present. In particular the NCH_2 and NCH_3 protons produce the singlets at 4.48 and 3.35 ppm respectively. In the [Pd(ESDT)(DMDTM)Cl] spectrum (Fig. 4b) the neutral ligand resonances are shifted well downfield with respect to free DMDTM, as expected on coordination. In this case the SCH_3 resonance is at 2.94 ppm, whereas the signals of the non-equivalent N-methyl groups are at 3.52 and 3.96 ppm, the pattern for the ESDT moiety being unchanged. The [Pd(ESDT)(DMDTM)$_{0.5}$X] spectra show an analogous trend except for the presence of an half neutral ligand easily detected by integrated areas. As shown in Fig. 5, the [Pd(ESDT)(ESDTM)Cl] spectrum contains the SCH_3 resonance of the neutral ligand at 2.89 ppm and the NCH_3 singlet at 3.50 ppm, well separated from the corresponding singlet in the ESDT ion (3.32 ppm). The OEt proton resonances coincide for both coordinated moieties, whereas the ESDTM NCH_2 protons produce two

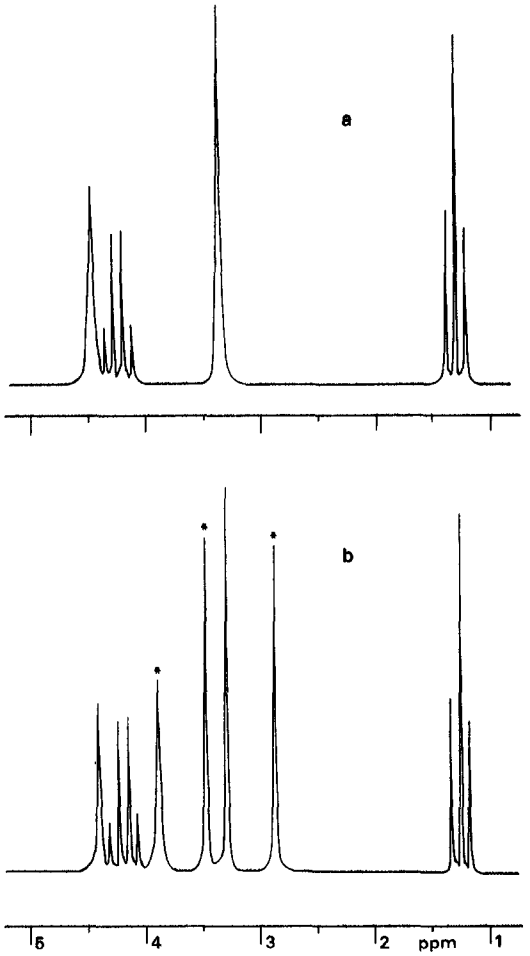


Fig. 4. Proton NMR spectra in $CDCl_3$: (a) $[Pd(ESDT)_2]$; (b) [Pd(ESDT)(DMDTM)Cl] (the DMDTM signals are labelled with an asterisk).

signals of different intensity (5.10 and 4.60 ppm) downfield with respect to the corresponding signal in ESDT (4.41 ppm). The other mixed species show an analogous behaviour, the spectra being unchanged over several days.

The $[Pd(ESDTM)_2Cl_2]$ spectrum, registered immediately after sample dissolution in $CDCl_3$, consists essentially of one signal for each proton group, the SCH_3 and NCH_2 resonances being at 3.09 and 5.25 ppm respectively. Moreover weak signals assigned to free ligand (SCH_3, 2.65 ppm) and $[Pd(ESDTM)Cl_2]$ (SCH_3, 3.15 ppm) suggest a dissociation equilibrium (*ca* 10% in a *ca* 0.13 M solution). The solution spectrum changes in time and after one week it coincides with that of [Pd(ESDT)(ESDTM)Cl] (Fig. 5), free ligand signals being absent. An analogous behaviour is observed in deuterated acetone notwithstanding a larger initial dissociation (*ca* 60%). The spectral trend, which is similar for $[Pd(ESDTM)_2Br_2]$, supports S-demethylation of the 1 : 1 intermediate to form the mixed complex

$$[Pd(ESDTM)_2X_2] \rightleftharpoons [Pd(ESDTM)X_2]$$

$$+ ESDTM \xrightarrow{-MeX} [Pd(ESDT)(ESDTM)X]$$

which is stable. The $[Pd(ESDTE)_2X_2]$ (X = Cl or Br) species dissociate in $CDCl_3$ to a larger extent than for the ESDTM analogues. The dealkylation process occurs in part owing to slow precipitation of the $[Pd(ESDTE)X_2]$ complex in the NMR tube. The $[Pd(ESDTR)_2I_2]$ complexes decompose to PdI_2 $CDCl_3$ within a few minutes, the solution NMR spectra being essentially those of the corresponding free ligands.

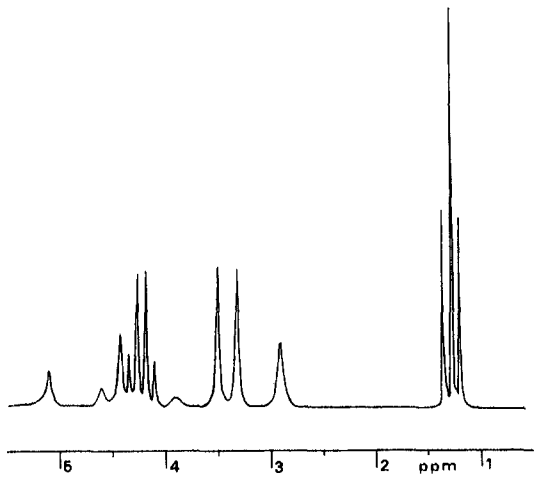


Fig. 5. Proton NMR spectrum of [Pd(ESDT)(ESDTM)Cl] in $CDCl_3$.

REFERENCES

1. M. Bruley-Rosset, I. Vergnon and G. Renoux, *Int. J. Immunopharmacol.* 1986, **8**, 287.
2. R. F. Borch, P. C. Dedon, A. Gringeri and T. J. Montine, in *Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy* (Edited by M. Nicolini), p. 216. Martinus Nijhoff, Boston (1988).
3. Z. J. Guo, D. Fregona, G. Faraglia and S. Sitran, *J. Coord. Chem.* 1993, **28**, 209.
4. Z. J. Guo, U. Casellato, G. Faraglia, R. Graziani and S. Sitran, *J. Chem. Soc., Dalton Trans.* 1993, 2509.
5. Z. J. Guo, G. Faraglia and S. Sitran, *Polyhedron* 1994, **13**, 659.
6. G. Faraglia, L. Sindellari, L. Trincia, A. Furlani and V. Scarcia, *Inorg. Chim. Acta* 1985, **106**, 31.
7. A. Furlani, V. Scarcia, G. Faraglia, L. Sindellari, L. Trincia and M. Nicolini, *Eur. J. Med. Chem.* 1986, **21**, 261.

8. D. A. Clemente, G. Faraglia, L. Sindellari and L. Trincia, *J. Chem. Soc., Dalton Trans.* 1987, 1823.
9. G. Faraglia, L. Sindellari and S. Sitran, *Thermochim. Acta* 1990, **161**, 63.
10. G. Faraglia and S. Sitran, *Inorg. Chim. Acta* 1990, **176**, 67.
11. G. Faraglia, L. Sindellari and S. Sitran, *Trans. Met. Chem.* 1994, **19**, 248.
12. C. E. Holloway and M. H. Gitliz, *Can. J. Chem.* 1967, **45**, 2659.
13. A. B. Goel, D. Van Derveer and C. B. Brinkley, *Inorg. Chim. Acta* 1982, **64**, L173.
14. A. E. Lemire and J. C. Thompson, *Can. J. Chem.* 1970, **48**, 824.
15. A. E. Lemire and J. C. Thompson, *J. Am. Chem. Soc.* 1971, **93**, 1163.
16. C. H. Yoder, A. Komoriya, J. E. Kochanowski and F. H. Suydam, *J. Am. Chem. Soc.* 1971, **93**, 6515.
17. B. L. Edgar, D. J. Duffy, M. C. Palazzotto and L. H. Pignolet, *J. Am. Chem. Soc.* 1973, **93**, 1125.
18. B. M. Dahl and P. H. Nielsen, *Acta Chem. Scand., Ser.* 13 1974, **28**, 1091.