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# Functionalized dithioester and dithiocarbamato complexes of platinum(II) halides

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**Abstract**—Platinum dihalides react with the dithioester $EtO_2CCH_2(CH_3)NCS_2Me$ (ESDTM) yielding the complexes $Pt(ESDTM)X_2$ and *trans*-$Pt(ESDTM)_2X_2$ (X = Cl or Br). In the 1 : 2 adducts the ligand acts as monodentate through the thiocarbonyl sulfur, whereas it is S,S chelated in the $Pt(ESDTM)X_2$ species. These complexes release easily methyl halide either in solid or in solution to form species containing the related dithiocarbamato moiety (ESDT, $EtO_2CCH_2(CH_3)NCS_2^-$). The first decomposition step in thermal degradation of the $Pt(ESDTM)X_2$ complexes involves evolution of one methyl halide molecule to form the related $[Pt(ESDT)X]_n$ intermediate and leading finally to platinum metal. In the same conditions the *trans*-$Pt(ESDTM)_2X_2$ complexes undergo demethylation of both ligand molecules, the $Pt(ESDT)_2$ intermediate being stable up to 250°C. The dithioester adducts and the related degradation intermediates have been characterized by elemental analyses and IR and $^1H$ NMR spectroscopy. The complex behaviour in various solvents has been described by proton NMR data. © 1997 Elsevier Science Ltd

*Keywords*: platinum; dithioester; dithiocarbamate; NMR; thermal decomposition.

Sulfur containing molecules are currently under study as chemoprotectants in platinum-based chemotherapy. In particular thiocarbonyl and thiol donors showed promising properties for chemical use in modulating cisplatinum nephrotoxicity [1]. In this line we have reported various palladium and platinum complexes with thio- and dithiocarbamic esters, which were tested for *in vitro* cytostatic activity against KB tumor cells [2,3]. In order to dispose of functionalized dithiocarbamic esters, the study has been extended to dithioesters derived from sarcosine, of general formula $EtO_2CCH_2(Me)NCS_2R$ (R = alkyl), with particular attention to their behaviour towards palladium and mercury halides [4,6]. As concern the $ESDTM/PdX_2$ (X = Cl or Br) system complexes of the type $Pd(ESDTM)X_2$ have been isolated in which dithioester acted as bidentate through both sulfur atoms. The behaviour of those species in solution and in solid state supported the formation of degradation intermediates containing the dithiocarbamato anion, such as $[Pd(ESDT)X]_n$ and Pd(ESDT)(DMSO)X. Moreover the 1 : 2 complexes *trans*-$Pd(ESDTM)_2X_2$ were prepared, whose decomposition yielded, along with the fully demethylated $Pd(ESDT)_2$ species, the mixed Pd(ESDT)(ESDTM)X complexes, which contain both dithiocarbamato and dithioester moieties. Owing to the versatility of this class of ligands, it was considered worthwhile to investigate the $ESDTM/PtX_2$ system, as a preliminary study on the interaction of dithioesters and dithiocarbamates with platinum-amine complexes of the type *cis*- and *trans*-$PtAm_2X_2$.

## EXPERIMENTAL

### *Materials*

The ligand ESDTM was prepared by reaction of sarcosine ethyl ester with $CS_2$ and then with MeI in $EtOH/H_2O$ [5]. Platinum halides were Johnson Matthey products.

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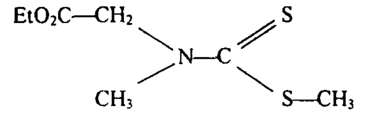
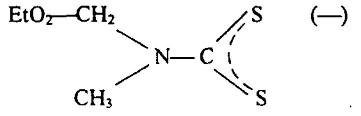


ESDTM



ESDT

*Preparation of the complexes*

The complexes Pt(ESDTM)$X_2$ (X = Cl or Br) have been prepared in anhydrous benzene by reaction of metal halide and ESDTM in molar ratio 1 : 1. As an example, Pt(ESDTM)$Cl_2$ was prepared by adding stoichiometric $PtCl_2$ to a benzene solution of ESDTM (1.5 mmol in 10 $cm^3$) with vigorous stirring (24 h). The reaction vessel was covered by aluminum foil, because light seems to favour the formation of demethylated side products. The red–orange solution was separated from a small brown residue (probably $PtCl_2$) by centrifugation and then evaporated to *ca.* 2 $cm^3$ in a rotavapor. By addition of *n*-pentane a red oil separated, which was decanted and treated with further *n*-pentane fractions. The resulting yellow powder was filtered, washed with *n*-pentane and dried under reduced pressure. (Yield, 75%.) The complexes can be recrystallized by quickly adding *n*-pentane to a freshly prepared $CH_2Cl_2$ solution, in order to avoid the presence of decomposition products. The same complexes were also obtained as acetonitrile solvates by performing the reaction in this solvent. The Pt(ESDTM)$Cl_2 \cdot 0.3CH_3CN$ species was prepared by reaction of $PtCl_2$ and ligand with vigorous stirring (1.8 mmol in 8 $cm^3$; molar ratio 1 : 1; 7 h). The reaction vessel was kept in an ice bath in order to minimize the amount of demethylated products. The deep orange solution was taken to dryness at room temperature in a rotavapor. The oily residue, treated with *n*-pentane fractions, changed into a yellow powder, which was dried *in vacuo*. (Yield, 90%.) The amount of acetonitrile, estimated by thermogravimetric and proton NMR data and confirmed by elemental analysis, was in accordance with 0.3 $CH_3CN$ moles for one Pt(ESDTM)$X_2$ unit in samples from different preparations.

The complexes *trans*-Pt$(ESDTM)_2X_2$ (X = Cl or Br) have been prepared in anhydrous benzene by reaction of $PtX_2$ and ligand in molar ratio 1 : 3. In particular, the reaction of $PtCl_2$ (1.2 mmol) and ESDTM (3.7 mmol in 7 $cm^3$ of benzene) with stirring at room temperature out of the light (24 h) yielded a nutmeg solid, which was filtered, washed with benzene (1 $cm^3$) and *n*-pentane, and dried *in vacuo*. (Yield, 70%.) Attempts to either recrystallize or prepare the complexes in different solvents gave products of lower purity. When $PtCl_2$ and ESDTM were reacted in acetonitrile (molar ratio 1 : 2; ice bath; 2 h) a red solution was obtained, which was taken to dryness in a rotavapor at room temperature. The oily residue, treated with benzene/*n*-pentane, yielded a solid which was a mixture of Pt(ESDTM)$Cl_2$ and Pt$(ESDT)_2$, clearly identified by the $\nu$(CN) absorptions. When the reaction was performed in *n*-hexane (molar ratio 1 : 2; room temperature; 4 days), following the method used for the palladium analogues, a dark-orange powder separated; when this was recrystallized from $CH_2Cl_2$/*n*-pentane, it was found to consist of a mixture of the demethylated species Pt(ESDT)(ESDTM)Cl and Pt$(ESDT)_2$.

The Pt$(ESDT)_2$ complex has been obtained by thermal degradation of *trans*-Pt$(ESDTM)_2X_2$ samples heated up to 214°C directly on the thermobalance crucible. The compound was also obtained by dissolving Pt$(ESDTM)_2X_2$ samples in acetonitrile. Under reflux (8 h) the solutions separated gradually the lemon-yellow solid, which was filtered, washed with *n*-pentane and dried under reduced pressure. (Yield, 70%). By evaporation to dryness, the mother solutions yielded orange oils, which on the basis of the analytical and spectral data, were identified as Pt(ESDT)(ESDTM)X species.

The $[Pt(ESDT)X]_n$ species (X = Cl or Br) were prepared by thermal degradation of Pt(ESDTM)$X_2$ or Pt(ESDTM)$X_2 \cdot 0.3CH_3CN$ in solid phase (150°C; oil bath) and subsequent recrystallization of the degradation intermediates from $CH_2Cl_2$/*n*-pentane. The same complexes are formed when acetonitrile solutions of the appropriate Pt(ESDTM)$X_2$ precursor were heated under reflux (2 h). By addition of *n*-pentane oily products separated, which turned into solid samples when kept under *n*-pentane.

The Pt(ESDT)(DMSO)X complexes have been prepared by mixing DMSO (1.0 mmol) and $[Pt(ESDT)X]_n$ (0.7 mmol) in dichloromethane (6 $cm^3$) with vigorous stirring (24 h). By addition of *n*-pentane the adducts precipitated as oils, which were decanted and treated with further *n*-pentane fractions until solidification. Owing to their hygroscopicity, the resulting powders were stored under dinitrogen.

The prepared complexes are listed in Table 1, along with the elemental analysis data.

*Measurements*

Elemental analyses were carried out on a Fisons EA1108 CHNS-O microanalyser. IR spectra were recorded on Nicolet 5SXC FT-IR and 20F Far-IR spec-

Table 1. Analytical[a] and physical data

| Compound | Formula | Colour | C | H | N | S |
|---|---|---|---|---|---|---|
| ESDTM | $C_7H_{13}NO_2S_2$ | white | 41.2(40.6) | 6.2(6.3) | 7.1(6.8) | 31.2(30.9) |
| $Pt(ESDTM)Cl_2 \cdot 0.3CH_3CN$ | $C_{7.6}H_{13.9}Cl_2N_{1.3}O_2PtS_2$ | yellow | 18.3(18.8) | 2.5(2.9) | 3.4(3.7) | 13.6(13.2) |
| $[Pt(ESDT)Cl]_n$[b,c] | $C_6H_{10}ClNO_2PtS_2$ | orange | 16.7(17.0) | 2.3(2.4) | 3.1(3.3) | 15.6(15.1) |
| *trans*-$Pt(ESDTM)_2Cl_2$ | $C_{14}H_{26}Cl_2N_2O_4PtS_4$ | nutmeg | 25.2(24.7) | 3.7(3.8) | 4.0(4.1) | 19.3(18.8) |
| $Pt(ESDTM)Br_2$ | $C_7H_{13}Br_2NO_2PtS_2$ | yellow | 15.5(15.0) | 2.2(2.3) | 2.4(2.5) | 12.0(11.4) |
| $Pt(ESDTM)Br_2 \cdot 0.3CH_3CN$ | $C_{7.6}H_{13.9}Br_2N_{1.3}O_2PtS_2$ | dark orange | 16.3(15.9) | 2.5(2.4) | 3.4(3.2) | 11.6(11.2) |
| $[Pt(ESDT)Br]_n$[b,c] | $C_6H_{10}BrNO_2PtS_2$ | brick-red | 15.6(15.4) | 2.1(2.1) | 2.9(3.0) | 14.4(13.7) |
| *trans*-$Pt(ESDTM)_2Br_2$ | $C_{14}H_{26}Br_2N_2O_4PtS_4$ | dark beige | 22.5(21.8) | 3.6(3.4) | 3.7(3.6) | 17.2(16.7) |
| $Pt(ESDT)_2$[d,e] | $C_{12}H_{20}N_2O_4PtS_4$ | lemon yellow | 25.0(24.9) | 3.5(3.5) | 4.8(4.8) | 22.8(22.1) |
| Pt(ESDT)(DMSO)Cl | $C_8H_{16}ClNO_3PtS_3$ | bright yellow | 19.4(19.2) | 3.2(3.2) | 2.6(2.9) | 19.0(19.2) |
| Pt(ESDT)(DMSO)Br | $C_8H_{16}BrNO_3PtS_3$ | orange | 18.3(17.6) | 3.0(3.0) | 2.6(2.6) | 17.6(17.6) |

[a] Calculated values (%) in parentheses.

[b] Sample obtained from $Pt(ESDTM)X_2$ in $CH_3CN$ under reflux.

[c] Sample prepared by thermal degradation of solid $Pt(ESDTM)X_2$ (150°C).

[d] Sample prepared by thermal degradation of $Pt(ESDTM)_2Cl_2$ (214°C).

[e] Sample obtained from $Pt(ESDTM)_2Br_2$ in $CH_3CN$ under reflux.

trometers as either Nujol mulls between KBr and polyethylene discs or KBr pellets. NMR ($^1H$, 89.55 MHz) spectra were measured using a Jeol FX 90Q spectrometer. Thermogravimetric data in air were obtained on Netzsch STA 429 thermoanalytical equipment (flux rate, 250 $cm^3$ $min^{-1}$; heating rate, 5°C $min^{-1}$; ref. material $Al_2O_3$).

## RESULTS AND DISCUSSION

The $Pt(ESDTM)X_2$ complexes have been prepared in benzene by reaction of platinum halide with ESDTM in stoichiometric ratio (Table 1). When the same reaction was performed in acetonitrile, the corresponding $[Pt(ESDTM)X_2] \cdot 0.3CH_3CN$ solvates were obtained, whereas samples from analogous syntheses in either dichloromethane or methanol contained variable amounts of the $[Pt(ESDT)X]_n$ species, suggesting appreciable evolution of methyl halide at room temperature. As for the palladium analogues, the synthesis of the *trans*-$Pt(ESDTM)_2X_2$ species requires a solvent in which the product is scarcely soluble in order to minimize the formation of dithiocarbamato derivatives. For this reason the 1 : 2 complexes have been prepared by reaction of $PtX_2$ and ESDTM at molar ratio 1 : 3 in benzene. The suspension changed gradually to form the *trans*-$Pt(ESDTM)_2X_2$ complexes in solid phase, which could not be recrystallized from the usual solvents owing to their easy decomposition. By operating in acetonitrile at molar ratio $PtX_2$ to ESDTM 1 : 2, product mixtures were obtained containing, along with the 1 : 1 adduct $Pt(ESDTM)X_2$ and the fully demethylated species $Pt(ESDT)_2$, the mixed intermediate Pt(ESDT)(ESDTM)X, the desired *trans*-$Pt(ESDTM)_2X_2$ species being present in traces. As a general remark, the $PtX_2$–ESDTM complexes are less stable than the palladium analogues in either solution or in solid phase, and should be stored in a freezer. The $Pt(ESDT)_2$ complex was obtained by thermal degradation of freshly prepared *trans*-$Pt(ESDTM)_2X_2$ samples, which were heated up to 214°C in the thermobalance crucible. The thermograms of *trans*-$Pt(ESDTM)_2Cl_2$ (Fig. 1) are consistent with evolution of two MeCl molecules in the 70–210°C interval (Table 2). The endotherm at 84°C corresponds essentially to release of the first MeCl molecule to form the Pt(ESDT)(ESDTM)Cl intermediate, whereas in the 110–210°C interval slow evolution of the latter MeCl takes place to form $Pt(ESDT)_2$, whose pyrolysis to platinum ends at 460°C. Attempts to synthesize the mixed species Pt(ESDT)(ESDTM)Cl by gentle heating of *trans*-$Pt(ESDTM)_2Cl_2$ in oil bath (65°C) were unsuccessful, the residue containing always variable amounts of $Pt(ESDT)_2$. Conversely pure samples of the corresponding Pd(ESDT)(ESDTM)X species were easily obtained by using such a method, which were stable in various media. The thermal behaviour of *trans*-$Pt(ESDTM)_2Br_2$ follows a trend similar to

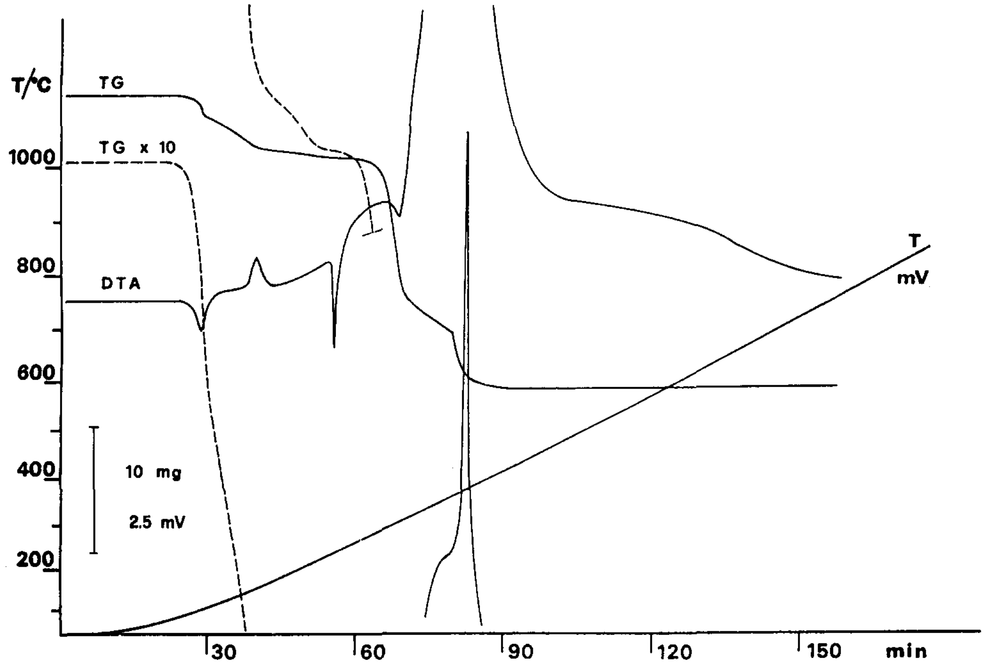


Fig. 1. Thermograms of *trans*-Pt(ESDTM)$_2$Cl$_2$ (32.71 mg).

that of the chloro-derivative, the formation of Pt(ESDT)$_2$ being evident from its melting endotherm. The Pt(ESDT)$_2$ complex can be also prepared by decomposition of *trans*-Pt(ESDTM)$_2$X$_2$ samples in acetonitrile under reflux. The solution separated gradually the lemon-yellow bis-dithiocarbamate, whereas small fractions identified as Pt(ESDT)(ESDTM)X were recovered by taking into dryness the residual mother solution. As shown in Fig. 2, the Pt(ESDT)$_2$ complex melts without decomposition at 223°, sample degradation to platinum occurring in the 250–450°C interval. The [Pt(ESDT)X]$_n$ species have been prepared by heating samples of the corresponding Pt(ESDTM)X$_2$ complexes in an oil bath up to 150°C. As shown in Fig. 3, degradation of Pt(ESDTM)Br$_2$ starts at 60°C, the first step cor-

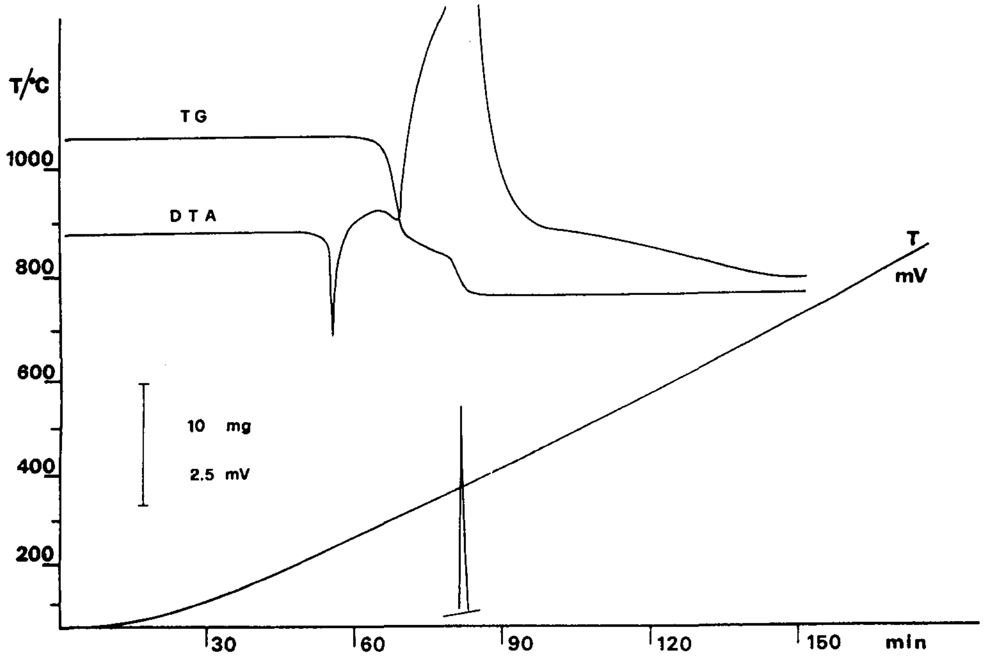


Fig. 2. Thermograms of Pt(ESDT)$_2$ (20.00 mg).

Table 2. Thermal data for the complexes

| Compound | Decomposition interval (°C) | Tg weight loss % Experimental | Calculated | DTA Peak temperature (°C)[a] |
|---|---|---|---|---|
| $Pt(ESDTM)Cl_2 \cdot 0.3CH_3CN$ | 40–175 | 13.5 | 12.9 ($CH_3Cl$, $0.3CH_3CN$) | *ca* 90 endo broad |
| | 175–420 | 47.3 | 46.9 (to Pt) | 364 exo, 396 exo |
| $Pt(ESDTM)Br_2$ | 55–150 | 17.4 | 16.9 ($CH_3Br$) | 110 endo |
| | 203–580 | 47.6 | 48.4 (to Pt) | [b]545 exo |
| $[Pt(ESDT)Cl]_n$[c] | 185–420 | 52.8 | 53.9 (to Pt) | *ca* 360 sh, 396 exo |
| $Pt(ESDT)Br]_n$[c] | 180–580 | 57.7 | 58.2 (to Pt) | [b]560 exo |
| *trans*-$Pt(ESDTM)_2Cl_2$ | 65–210 | 15.0 | 14.8 ($2CH_3Cl$) | 84 endo, 155 endo broad |
| | 210–460 | 56.5 | 56.5 (to Pt) | 221 m, 320 sh, 334 exo |
| *trans*-$Pt(ESDTM)_2Br_2$ | 70–210 | 26.6 | 24.7 ($2CH_3Br$) | 92 endo, 150 endo broad |
| | 210–465 | 48.2 | 49.9 (to Pt) | 221 m, 367 exo, 392 exo, 412 exo |
| $Pt(ESDT)_2$[d] | 20–250 | 0.0 | 0.0 | 223 m |
| | 250–450 | 64.6 | 66.4 (to Pt) | 337 sh, 364 exo |
| Pt(ESDT)(DMSO)Cl | 80–430 | 59.1 | 61.1 (to Pt) | 360 exo, 402 exo |
| Pt(ESDT)(DMSO)Br | 80–600 | 63.6 | 64.2 (to Pt) | 490 exo, 560 exo |

[a] exo, exotherm; endo, endotherm; m, melting endotherm; sh, shoulder.
[b] The DTA curve is nearly flat in the 210–500°C interval.
[c] Sample obtained from $Pt(ESDTM)X_2$ (X = Cl or Br) in $CH_3CN$ under reflux.
[d] Sample obtained from $Pt(ESDTM)_2Br_2$ in $CH_3CN$ under reflux.

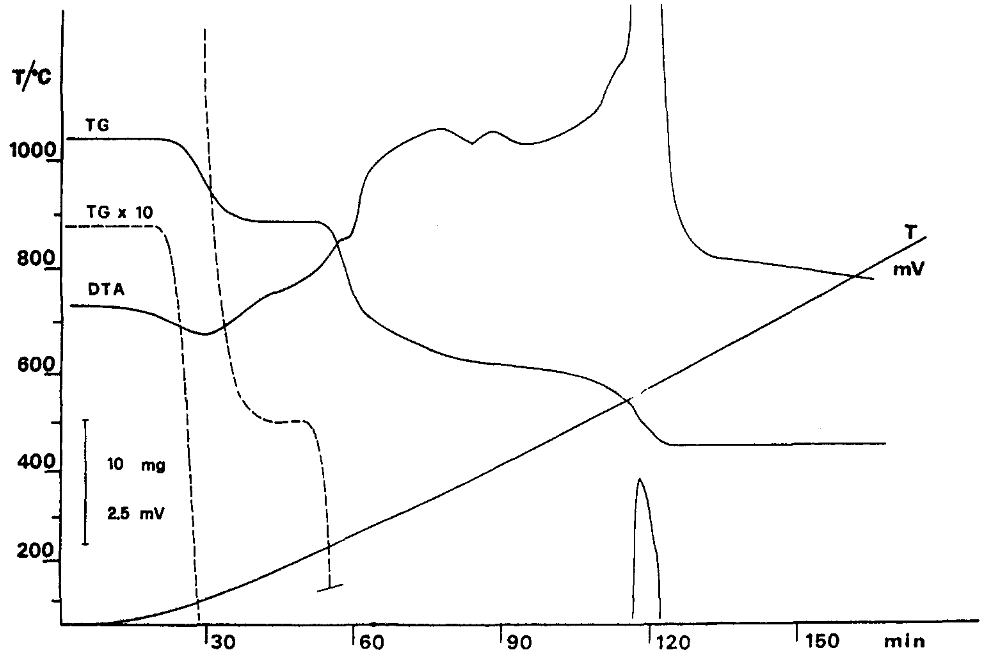


Fig. 3 Thermograms of Pt(ESDTM)$Br_2$ (37.73 mg).

responding to the release of one MeBr molecule (weight loss of 17.4% against a calculated value of 16.9%). The $[Pt(ESDT)Br]_n$ intermediate is stable in an appreciably wide temperature range (140–180°C) and decomposes gradually to platinum where heated up to 600°C. The $[Pt(ESDT)X]_n$ species can be also prepared by slow decomposition of the corresponding Pt(ESDTM)$X_2$ complexes in refluxing acetonitrile. The related thermograms (Table 2) confirm that the $[Pt(ESDT)X]_n$ species are stable up to 180°C. They decompose without melting at higher temperatures to form platinum, the pyrolysis process being complete at 420°C for X = Cl against 580°C for X = Br. The Pt(ESDT)(DMSO)X complexes have been prepared in dichloromethane from $[Pt(ESDT)X]_n$ in the presence of a slight excess of dimethyl sulphoxide. The thermograms of those species (Table 2) do not show any significant feature. As an example, the Pt(ESDT)(DMSO)Cl complex decomposes gradually to platinum in the 80–430°C range, no step correlable to dimethyl sulphoxide evolution being observed.

The infrared spectrum of ESDTM contains in the 1700–1450 $cm^{-1}$ region two strong absorptions, the one at 1744 $cm^{-1}$ being originated by the ester group of the sarcosine moiety, whereas the band at 1474 $cm^{-1}$ is assigned as $\nu$(CN). Whereas the $\nu$(CO) is unchanged in the complexes (Table 3), the position of the $\nu$(CN) band allows to deduce the ligand coordination modes toward platinum. As observed previously, when the dithioester molecule binds as monodentate through the thiocarbonyl sulfur, small high energy shift of the $\nu$(CN) absorption with respect to free ligand (*ca* 20 $cm^{-1}$) is observed, whereas the shift is more marked (*ca* 90 $cm^{-1}$) in complexes containing S,S bidentate moieties [3,7]. Accordingly, the strong $\nu$(CN) absorption is observed at 1504 $cm^{-1}$ for the *trans*-Pt$(ESDTM)_2X_2$ species and at *ca* 1570 $cm^{-1}$ in the Pt(ESDTM)$X_2$ adducts, containing the chelated ligand. In the Pt$(ESDT)_2$ spectrum the $\nu$(CN) band is at 1527 $cm^{-1}$, whereas it is observed at higher energy in complexes containing one dithiocarbamato group, as for $[Pt(ESDT)Cl]_n$ (1555 $cm^{-1}$) or Pt(ESDT)(DMSO)Cl (1543 $cm^{-1}$). Moreover the Pt(ESDT)(DMSO)X complexes show two strong absorptions in the 900–1200 $cm^{-1}$ region, which is diagnostic of the binding atom in coordinated dimethyl sulfoxide [8]. The $\nu$(SO) absorption, at 1128 $cm^{-1}$ in both complexes, is at high energy with respect to free DMSO (1055 $cm^{-1}$), as expected of an S-bound molecule, whereas the one at 1022 $cm^{-1}$ should originate from $CH_3$ rock [9,10]. The fact that the $\nu$(CN) absorptions of coordinated ESDTM (monodentate or bidentate) are easily distinguishable from those of the dithiocarbamato derivatives allows to appreciate the presence of dealkylated products in samples of either *trans*-Pt$(ESDTM)_2X_2$ or Pt(ESDTM)$X_2$ prepared by different methods. The complex geometry is confirmed by the platinum–halide absorptions in the far IR region (Table 3). The spectra of the Pt(ESDTM)$X_2$ species contain two bands due to Pt–X vibrations (Cl, 327 and 316 $cm^{-1}$; Br, 209 and 219 $cm^{-1}$), as expected for the *cis* square-planar geometry caused by the S,S chelate. The presence of one Pt-X absorption for the *trans*-Pt$(ESDTM)_2X_2$ species (Cl, 317 $cm^{-1}$; Br, 231 $cm^{-1}$) is in accordance with a *trans* geometry, common to similar complexes with variously substituted dithioesters. The Pt$(ESDT)_2$ spectrum contains below 400 $cm^{-1}$ weak ligand bands, whereas in the

Table 3. Selected IR frequencies ($cm^{-1}$)[a] [ν (Pt–hal) underlined]

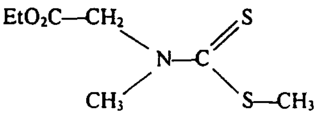
| Compound | ν(CO) | ν(CN) | Far infrared | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ESDTM | 1744s | 1474s | 431m | | | 355vw | | 336mw | | | 298m | | | |
| $Pt(ESDTM)Cl_2 \cdot 0.3CH_3CN$ | 1743s | 1571s | 435m | 396sh | | 382w | | 327s | 316sh | | 242vw | 210vw | | |
| $[Pt(ESDT)Cl]_n$[b] | 1742s | 1555s | 435w | 390vw | | 355vw | | | 317s | | 283sh | | | |
| *trans*-$Pt(ESDTM)_2Cl_2$ | 1739s | 1504s | 428m | | | 351w | | | 317s | | 252vbr | | | 183w |
| $Pt(ESDTM)Br_2$ | 1743s | 1570s | 437m | 396sh | 378m | 342vw | | 324w | 300vw | 279vw | 225sh | 219 | 209s | |
| $[Pt(ESDT)Br]_n$[b] | 1742s | 1554s | 435wbr | | | 389w | 365br | 329vw | | 227sh | 204ms | | | |
| *trans*-$Pt(ESDTM)_2Br_2$ | 1738s | 1503s | 428m | | | 355w | 322m | 303vw | | | 253m | 231m | | 187w |
| $Pt(ESDT)_2$[b] | 1743s | 1527s | 436w | 417vw | 401vw | 363m | 342w | 328w | | | | 196w | | |
| Pt(ESDT)(DMSO)Cl | 1743s | 1543s | 432m | 414w | 381w | 364m | 347w | 320sh | 312m | 301sh | 275w | 251w | 224w | 200w |
| Pt(ESDT)(DMSO)Br | 1743s | 1543s | 431m | 411w | 378w | 363m | 346w | 320w | | 297w | 274w | 250w | 222w | 201m |

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

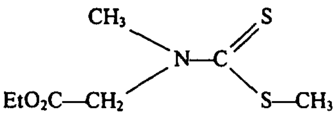
[b] Samples obtained by thermal degradation in either solid or solution have identical spectra.

$[Pt(ESDT)X]_n$ spectra the platinum halide absorptions are observed at 317 $cm^{-1}$ (X = Cl) and 204 $cm^{-1}$ (X = Br), the values being close to those for Pt(ESDT)(DMSO)X samples (Cl, 312 $cm^{-1}$ ; Br, 201 $cm^{-1}$). On taking into account a series of dimers of the type $[Pt(L)Cl_2]_2$ (L = phosphine, thioester or dimethyl sulfoxide), containing either bridging or terminal chlorine atoms, the Pt–Cl absorptions are observed in the 325–305 $cm^{-1}$ (terminal) and 300–260 $cm^{-1}$ (bridging) regions [11–13]. On this basis the polymeric $[Pt(ESDT)X]_n$ species should not contain halide bridges, which are instead present in the palladium $[Pd(ESDT)X]_n$ analogues, the related Pd-X absorptions being at 299 $cm^{-1}$ (X = Cl) and 168 $cm^{-1}$ (X = Br) [6]. It is possible that in the $[Pt(ESDT)X]_n$ complexes the platinum atom could attain the usual tetracoordination by a polymeric arrangement of Pt—S bonds between two adjacent units. In the binuclear complex $[Pt_2Cl_3(PEt_3)_2(S_2CNMe_2)]$ the dithiocarbamato ion acts as bidentate in the $Pt(S_2CNMe_2)(PEt_3)Cl$ moiety and at the same time binds, through one of the sulfur atoms, the second platinum atom bearing two chlorine atoms and one phosphine molecule [14]. Moreover in the binuclear complex $K[Pt_2Cl_5(CH_3SCH_2CH_2CH(NH_2)CH_2OH)]$ the methioninol molecule is S,N chelated to a $PtCl_2$ unit and also coordinated through the same sulphur atom to the other platinum atom of the $PtCl_3^-$ unit [15]. Moreover sulfur bridges are usual in aminothiolato complexes. As an example, in the exanuclear $[Pt_6(SCH_2CH_2NH_2)_8]Br_4$ complex all sulfur atoms of the S,N chelated anions bind two platinum atoms forming an extended network of bridges [16].

Because barrier to rotation about the CN bond is significant (*ca* 66 kJ $mol^{-1}$), the dialkyl dithioester molecule is planar and the nitrogen substituents are non equivalent [17–21]. Accordingly the proton NMR spectrum of $CH_3S_2CN(CH_3)_2$ in deuterated chloroform contains two singlets for the methyl groups bound to nitrogen (3.38 and 3.55 ppm) along with the $SCH_3$ signal at 2.64 ppm. When a dithioester molecule bears two different substituents at the nitrogen atom, it can exist in two isomeric forms which originate two series of signals of different intensity for equivalent proton groups. As shown in Table 4, the proton NMR spectrum of ESDTM in deuterated chloroform contains one signal for each OEt proton group ($CH_3$, 1.29 ppm ; $CH_2$, 4.22 ppm) and $SCH_3$ (2.64 ppm), whereas two resonances are observed for the nitrogen substituents ($NCH_2$, 4.80 and 4.50 ppm ; $NCH_3$, 3.50 and 3.43 ppm). This fact suggests that the planar dithioester molecule is present in the isomeric forms bearing the $NCH_3$ group in *syn* or *anti* position with respect to the thiocarbonyl group. The relative amount of the isomers cannot be estimated from integrated areas, because the related resonances are close and superimposed in part, the species present in low amount originating the weak signals at 3.50 ($NCH_3$) and 4.50 ($NCH_2$) ppm. The presence of both ligand isomers coordinated to platinum is evident in the



Anti



Syn

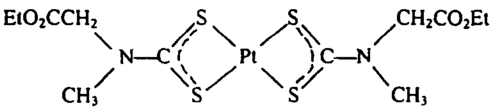
$Pt(ESDTM)X_2$ spectra. The spectrum of a freshly prepared solution of $Pt(ESDTM)Br_2$ in deuterated chloroform (Fig. 4) contains two signals for the $SCH_3$ group of the S,S chelated ligand, well downfield (3.27 and 3.14 ppm) with respect to the corresponding singlet in free ESDTM (2.64 ppm). Both resonances present the satellites caused by proton coupling with $^{195}Pt$, with a $J$ value of *ca* 46 Hz. A slight downfield shift is also observed for the $NCH_3$ proton signals (3.66 and 3.45 ppm) whereas the $NCH_2$ protons originate a complex pattern in the 5.30–4.30 ppm range, already observed in the palladium analogues, the number of the signals changing with the solvent. The $Pt(ESDTM)Br_2$ spectrum in deuterated acetone follows a similar trend, apart from a different multiplicity of the $NCH_2$ signals. On standing, aged solutions of the $Pt(ESDTM)X_2$ species show a progressive decrease of the $SCH_3$ signal intensities, with a parallel increasing of two new singlets in the $NCH_3$ region (at *ca* 3.4 and 3.8 ppm), which are characteristic of the demethylated $[Pt(ESDT)X]_n$ species.

The *trans*-$Pt(ESDTM)_2Cl_2$ spectrum, registered immediately after sample dissolution in deuterated chloroform, contains two broad signals for each $SCH_3$ (3.09 and 2.95 ppm), $NCH_3$ (4.09 and 3.47 ppm) and $NCH_2$ (5.48 and 4.50 ppm) proton group, caused also in this case by the presence of both ligand isomers, which bind to platinum through the thiocarbonyl sulfur atom. As expected, the uncoordinated $SCH_3$ signals do not present the satellites due to $^{195}Pt$ coupling, whereas the OEt signals are nearly unchanged with respect to free ESDTM. Within a few minutes, weak signals appear which are due to free ligand (4.78, 3.41 and 2.62 ppm) and $Pt(ESDT)_2$ (3.28 ppm). The spectrum registered after one day is indicative of massive decomposition of *trans*-$Pt(ESDTM)_2Cl_2$ to form $Pt(ESDT)_2$ which separates as a yellow powder. The $SCH_3$ signals fade, whereas the more intense signals are those at 3.28 and 4.30 ppm, due respectively to the $NCH_3$ and $NCH_2$ protons in $Pt(ESDT)_2$. The behaviour of the *trans*-$Pt(ESDTM)_2X_2$ species in chloroform is quite different from that of the palladium analogues. In fact the *trans*-$Pd(ESDTM)_2X_2$ species decomposed by evolution of only one MeX molecule to give the Pd(ESDT)(ESDTM)X mixed complexes quantitatively, which were stable in various solvents, no evidence of complete demethylation to form the *bis*-dithiocarbamate $Pd(ESDT)_2$ being observed. The *trans*-$Pt(ESDTM)_2X_2$ spectra in deuterated acetone support a large dissociation to $Pt(ESDTM)X_2$ and ligand, with consequent formation of both $[Pt(ESDT)X]_n$ and $Pt(ESDT)_2$ in aged solutions. As shown in Table 4, the $Pt(ESDT)_2$ spectrum in deuterated dimethyl sulfoxide is simple and contains one signal for each $OCH_2$ (4.18 ppm) and $NCH_2$ (4.44 ppm, broad) proton group, whereas the OEt methyl and $NCH_3$ protons originate two very close signals of equal intensity. This behaviour suggests that the chelated moieties can assume two non equivalent positions in the planar arrangement of the molecule.

The spectrum does not change with time, no appreciable interactions with solvent being present, which have been instead observed or the $[Pt(ESDT)X]_n$ complexes.

The spectra of the mixed Pt(ESDT)(DMSO)X complexes contain two very close signals for the $NCH_3$ (3.34 and 3.32 ppm) and $NCH_2$ (4.35 and 4.32 ppm) proton groups, as for the $S(CH_3)_2$ protons of dimethyl sulfoxide, whose S-coordination to platinum is confirmed by the presence of the satellites caused by proton coupling with $^{195}Pt$. The resonance splitting can be imputed to the position of the entering dimethyl sulfoxide molecule in the complex coordination plane. Because of the different substituents at the nitrogen atom of the planar dithiocarbamato anion, the DMSO molecule can be in either *cis* or *trans* position with respect of the $NCH_3$ group, giving rise to slightly different resonances. The spectrum of Pt(ESDT)(DMSO)Cl in deuterated dimethyl sulfoxide contains unsplitted singlets for the $NCH_3$ (3.28 ppm) and $NCH_2$ (4.55 ppm) protons, owing to fast solvent exchange.

The spectrum of $[Pt(ESDT)Br]_n$ in deuterated acetone (Fig. 5) shows two broad singlets for each $NCH_3$ (3.80 and 3.43 ppm) and $NCH_2$ (5.10 and 4.62 ppm) proton group, splitting of the ester $OCH_2$ resonance



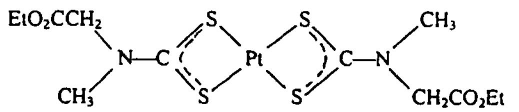


Table 4. $^{1}$H NMR data (ppm; T, *ca* 25°C)

| Compound | Solvent | O$CH_2$CH$_3$ | OCH$_2$$CH_3$ | SCH$_3$ | NCH$_3$ | NCH$_2$ | Other |
|---|---|---|---|---|---|---|---|
| ESDTM | $CDCl_3$ | 4.22 | 1.29 | 2.64 | 3.50wbr, 3.43 | 4.80, 4.50wbr | |
| | $(CD_3)_2CO$ | 4.18 | 1.23 | 2.59 | 3.56wbr, 3.46 | 4.86, 4.50wbr | |
| $Pt(ESDT)_2$ | $(CD_3)_2SO$ | 4.18 | 1.222, 1.219 | | 3.199, 3.202 | 4.44 | |
| | $CDCl_3$[a] | 4.26 | 1.31[b] | | 3.28[b] | 4.30 | |
| $[Pt(ESDT)Br]_n$ | $CDCl_3$ | 4.27br | 1.32 | | 3.75(32%),<br>3.35(68%) | (5.27, 5.08, 4.90, 4.82, 4.63, 4.25[c]) | |
| | $(CD_3)_2CO$[d] | 4.28, 4.24w | 1.30 | | 3.80(32%),<br>3.43(68%) | 5.10(65%), 4.62(35%) | |
| | $(CD_3)_2SO$[e] | 4.18 | 1.22 | | 3.65w, 3.37 | 5.03br, 4.58wbr | |
| | $(CD_3)_2SO$[f] | 4.18 | 1.22 | | 3.26 | 4.52 | |
| $[Pt(ESDT)Cl]_n$ | $CDCl_3$ | 4.24 | 1.31 | | 3.75w, 3.37 | (5.28, 5.10, 4.97, 4.88, 4.62, 4.35) | |
| | $(CD_3)_2SO$[e] | 4.19 | 1.22 | | 3.65w, 3.35 | 5.03br, 5.62wbr | |
| | $(CD_3)_2SO$[f] | 4.19 | 1.22 | | 3.27 | 4.53 | |
| *trans*-$Pt(ESDTM)_2Cl_2$[g] | $CDCl_3$ | 4.23 | 1.28 | 3.09, 2.95w | 4.09wbr, 3.47 | 5.48, 4.50wbr | |
| *trans*-$Pt(ESDTM)_2Br_2$[g] | $CDCl_3$ | 4.24 | 1.29 | 3.05, 2.84w | 4.06wbr, 3.48 | 5.50, 4.51wbr | |
| $Pt(ESDTM)Cl_2 \cdot 0.3CH_3CN$ | $CDCl_3$ | 4.30 | 1.33 | 3.28w, 3.19[h] | 3.68w, 3.46 | (5.47, 5.29, 5.09, 4.89, 4.69, 4.61, 4.52, 4.41) | 2.01($CH_3CN$) |
| $Pt(ESDTM)Br_2$ | $CDCl_3$ | 4.31w, 4.29 | 1.32 | 3.27w, 3.14[h] | 3.66w, 3.45 | (5.31, 5.11, 4.97, 4.78, 4.55, 4.44) | |
| | $(CD_3)_2CO$ | 4.31 | 1.30 | 3.29, 3.22[h] | 3.75w, 3.50 | (5.15, 5.12, 5.0, 4.88, 4.72, 4.62) | |
| Pt(ESDT)(DMSO)Cl | $CDCl_3$ | 4.24 | 1.29 | | 3.34, 3.32 | 4.35, 4.32 | 3.369, 3.358 (DMSO)[i] |
| | $(CD_3)_2CO$ | 4.24 | 1.27 | | 3.397, 3.391 | 4.552, 4.541 | 3.365, 3.350 (DMSO)[i] |
| | $(CD_3)_2SO$ | 4.19 | 1.23 | | 3.28 | 4.55 | 2.54 (DMSO)[j] |
| Pt(ESDTM)(DMSO)Br | $CDCl_3$ | 4.24 | 1.31 | | 3.33, 3.31 | 4.33, 4.30 | 3.45, 3.44 (DMSO)[i] |

[a] Very diluted saturated solution.

[b] Unresolved splitting.

[c] Obscured in part by the $OCH_2$ signal.

[d] The spectrum is unchanged after one day.

[e] The spectrum registered immediately after solubilization contains weak signals at 3.26 and 4.52 ppm. See Fig. 6.

[f] Registerd after one day.

[g] Immediately after solubilization. After *ca* 5 min the spectrum contains weak ESDTM (4.78, 3.41 and 2.62 ppm) and $Pt(ESDT)_2$ (3.28 ppm) signals.

[h] Both signals present the satellites due to $^{195}$Pt–$^{1}$H coupling (*J*, *ca* 46 Hz).

[i] $^{195}$Pt–$^{1}$H coupling (*J*, *ca* 21.4 Hz).

[j] Deuterated solvent exchange.

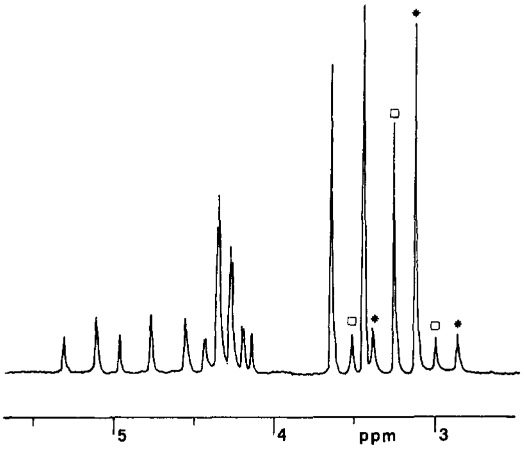


Fig. 4. Proton NMR spectrum of Pt(ESDTM)$Br_2$ in $CDCl_3$ (the $SCH_3$ signals and the related satellites are labelled).

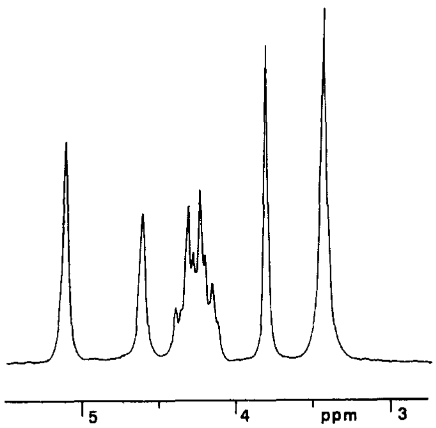


Fig. 5. Proton NMR spectrum of $[Pt(ESDT)Br]_n$ in deuterated acetone.

being also observed. The spectrum does not change with time, as for that in chloroform, no interaction with solvent being evident. At contrary the spectrum of a solution of $[Pt(ESDT)Br]_n$ in deuterated dimethyl sulphoxide is influenced by the solvent. As shown in Fig. 6a, the spectrum registered immediately after dissolution is similar to that of the acetone solution, the main signals for $NCH_3$ (3.65 and 3.37 ppm) and $NCH_2$ (5.03 and 4.58 ppm) having the same shape of those of Fig. 5. Moreover two new singlets arise, at 3.26 ($NCH_3$) and 4.52 ($NCH_2$) ppm, which increase with time while the original structure of the spectrum fades. After one day the spectrum is that of Fig. 6c, which coincides with the spectrum of Pt(ESDT)(DMSO)Br in the same solvent. When the $[Pd(ESDT)X]_n$ analogues were dissolved in dimethyl sulphoxide, the spectrum was immediately like that of Fig. 6c, the proton group resonances being at 3.33 ppm ($NCH_3$) and 4.41 ppm ($NCH_2$). The fact could confirm the different coordination modes in the platinum and palladium dithiocarbamato derivatives. The solvent could break quickly the halide bridges present in the $[Pd(ESDT)X]_n$ species, whereas could interact slowly with the $[Pt(ESDT)X]_n$ polymers, which probably contain sulfur bridges. This fact could be of some importance in further studies on the reaction of the $[M(ESDT)X]_n$ (M = Pd or Pt) complexes with primary amines and chelating diamines, the product nature depending on the time and solvent medium.

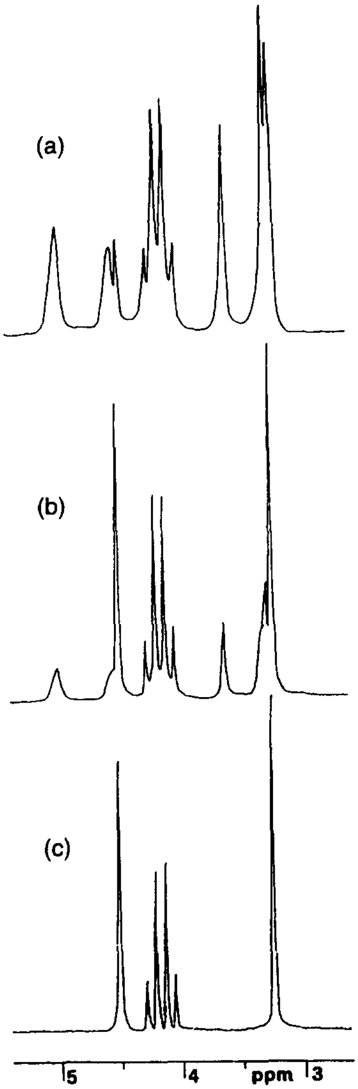


Fig. 6. Proton NMR spectrum of $[Pt(ESDT)Br]_n$ in deuterated dimethyl sulphoxide: (a) within 15 min; (b) after 1 h; (c) after 1 d.

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