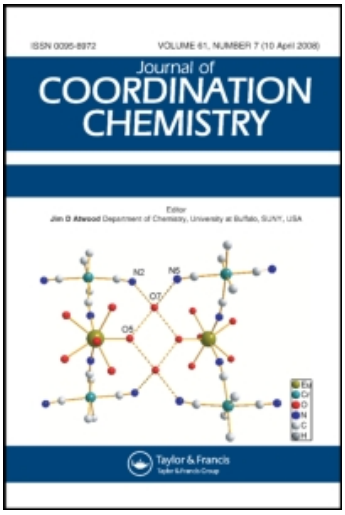


**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# PALLADIUM DIHALIDE COMPLEXES WITH D,L-ETHIONINE

Zijian Guo[ab]; Dolores Fregona[a]; Giuseppina Faraglia[a]; Sergio Sitran[bc]
[a] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padova, Italy [b] Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova, Italy [c] Department of Basic Courses, Agricultural University of Hebei, Baoding, P.R.C.

**To cite this Article** Guo, Zijian , Fregona, Dolores , Faraglia, Giuseppina and Sitran, Sergio(1993) 'PALLADIUM DIHALIDE COMPLEXES WITH D,L-ETHIONINE', Journal of Coordination Chemistry, 28: 3, 209 — 216
**To link to this Article: DOI:** 10.1080/00958979308037099
**URL:** http://dx.doi.org/10.1080/00958979308037099

J. Coord. Chem. 1993, Vol. 28, pp. 209–216
Reprints available directly from the publisher
Photocopying permitted by license only



# PALLADIUM DIHALIDE COMPLEXES WITH *D,L*-ETHIONINE

ZIJIAN GUO,* DOLORES FREGONA, GIUSEPPINA FARAGLIA

*Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, 35131 Padova, Italy*

and

SERGIO SITRAN§

*Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti, 35020 Padova, Italy*

*(Received August 11, 1992)*

By reaction of palladium halides with *D,L*-ethionine (*D,L*-EthH; molar ratio 1:1) in dichloromethane solutions containing an excess of 2,6-dimethyl-4H-pyran-4-one (DMP) [Pd(*D,L*-EthH)$X_2$] (X=Cl, Br or I) complexes have been isolated. When the solvent was benzene [Pd(*D,L*-EthH)$X_2$]·DMP adducts were obtained in which the DMP molecule does not bind to the metal. The complexes have been characterized by infrared and nmr ($^1$H and $^{13}$C) spectroscopy and by thermogravimetric measurements (TG, DTG and DTA). The importance of DMP in determining the reaction course is discussed.

KEY WORDS: *D,L*-Ethionine, dimethyl-4-pyrone, palladium complexes, synthesis, nmr.



## INTRODUCTION

Interest in transition metal complexes with S-containing amino acids depends on the possibility for metals to bind methionine residues (and in general sulphur sites) in proteins.[1] Moreover sulphur donors are currently under study for their detoxicant properties against heavy metal poisoning and in particular against nephrotoxicity of platinum drugs.[2,3] In this field we reported palladium(II) and platinum(II) complexes with thiocarbonyl donors, which were tested for *in vitro* cytostatic activity against a KB tumor cell line,[4,5] along with platinum-amine complexes of various stoichiometries.[6] Several recent papers concern the interaction of methionine (and derivatives) with platinum(II) halides or *cis*-diamineplatinum(II) in aqueous solution,[7–10] whereas analogous palladium complexes have rarely been reported.[11] In particular studies on the palladium(II)-ethionine (EthH) system concern essentially the [Pd(*D,L*-EthH)$Cl_2$] complex, in which the amino acid acts as an S,N donor forming a six membered chelate ring, the intramolecular arrangement involving NH hydrogen bonds with chlorine and oxygen atoms.[12,13] This compound and related mixed species

* On leave from the Department of Basic Courses, Agricultural University of Hebei, Baoding, P.R.C.
§ Author for correspondence.

containing purines, pyrimidines and nucleosides[14,15] have been prepared in water from $K_2[PdCl_4]$, following a general method used in the synthesis of S-amino acid complexes. Because palladium halides form with DMP (2,6-dimethyl-4H-pyran-4-one) the complexes $[Pd(DMP)_2X_2]$ (X=Cl or Br), in which the weakly bound O-donor can be easily replaced by chelating ligands,[16] we thought it worthwhile to use those species as intermediates in the preparation of the palladium halide-ethionine species in organic media.

## EXPERIMENTAL

### *Chemicals*

The ligand *D,L*-EthH ($C_6H_{13}NO_2S$, *D,L*-2amino-4-(ethylthio)-butanoic acid, Aldrich) and DMP ($C_7H_8O_2$, 2,6-dimethyl-4H-pyran-4-one, Ega Chemie) were used as supplied. Palladium halides were Johnson Matthey products. $[Pd(DMP)_2Cl_2]$ was prepared by the method reported in ref. 16.

### *Preparation of the Complexes*

The complexes $[Pd(D,L\text{-EthH})X_2]\cdot DMP$ (X=Cl, Br or I) were prepared in benzene by reacting equimolar amounts of $PdX_2$ and ethionine in the presence of DMP in excess. As an example, $[Pd(D,L\text{-EthH})Cl_2]\cdot DMP$ was obtained from a suspension of $PdCl_2$ (1 mmol) and *D,L*-EthH (1 mmol) in a benzene solution of DMP (4 mmol in 3 $cm^3$) with vigorous stirring. The reaction proceeded gradually (3d), yielding a pale yellow solid, which was filtered, washed with benzene and *n*-pentane and dried *in vacuo* (Yield, 95%). The complexes $[Pd(D,L\text{-EthH})X_2]\cdot DMP$ (X=Br or I) were prepared with an identical procedure in the presence of larger excess of DMP (molar ratio up to 1:8, yield, 85–95%). When washed with $CH_2Cl_2$ or acetone, solid samples of the $[Pd(D,L\text{-EthH})X_2]\cdot DMP$ complexes released DMP to form unsolvated ethionine adducts.

$[Pd(D,L\text{-EthH})X_2]$ (X=Cl, Br or I) complexes were also prepared by reaction of $PdX_2$ (1 mmol) and ethionine (1 mmol) in a $CH_2Cl_2$ solution of DMP (4 mmol in 3 $cm^3$). After 3d stirring at room temperature a suspension of the appropriate complex was obtained, and which contained small traces of unreacted palladium halide. Solid complex and solution was decanted from the dark residue. The suspension was centrifuged and the solid was washed with $CH_2Cl_2$ and dried *in vacuo* (Yield 85–95%). If DMP was absent, the reaction of palladium halide with ethionine (molar ratio 1:1) was slow and incomplete within one week in either $CH_2Cl_2$ or benzene. When an equimolar amount of ethionine was added to a $[Pd(DMP)_2Cl_2]$ solution in $CH_2Cl_2$, formation of $[Pd(D,L\text{-EthH})Cl_2]$ was slow and the final solid (3d) contained unreacted dimethyl-4-pyrone adduct.

In order to verify that the product obtained in organic media was like that from water, the complex $[Pd(D,L\text{-EthH})Cl_2]$ was prepared by gradually adding the ligand (2 mmol) to a $K_2[PdCl_4]$ solution in warm water (2 mmol in 5 $cm^3$).[12] A yellow solution formed within 5 minutes, and which was kept at 60°C for half an hour with vigorous stirring. A yellow solud separated on cooling was filtered, washed with small quantities of $H_2O$, EtOH and $Et_2O$ and dried *in vacuo* (Yield, 80%). Properties and spectra of such a solid were identical to those of samples prepared in $CH_2Cl_2$ or obtained by washing DMP from the $[Pd(D,L\text{-EthH})Cl_2]\cdot DMP$ complex.

*Measurements*

Infrared spectra were recorded using Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers, in nujol mulls between KBr and polyethylene discs. Nmr ($^1H$ and $^{13}C$) spectra were obtained with a JEOL FX 90Q spectrometer. 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 $Al_2O_3$). The melting points (uncorrected) were determined using a Buchi apparatus.

## RESULTS AND DISCUSSION

The [Pd(*D*,*L*-EthH)$X_2$] (X=Cl, Br or I) complexes have been prepared in dichloromethane by reaction of the appropriate palladium salt with ethionine in the presence of a large excess of dimethyl-4-pyrone (Table 1). The product formed at first in the reaction mixture was [Pd(DMP)$_2X_2$] which reacted with a stoichiometric amount of ethionine to form the 1:1 adduct. According to proton nmr spectra, the [Pd(DMP)$_2Cl_2$] complex has been found dissociate partially in dichloromethane to form free ligand and a 1:1 adduct.[16] Addition of dimethyl-4-pyrone forces the equilibrium towards formation of the 1:2 adduct favouring ethionine reaction. In fact, the direct reaction of [Pd(DMP)$_2Cl_2$] with ethionine in dichloromethane was slow, yielding a mixture of [Pd(*D*,*L*-EthH)$Cl_2$], [Pd(DMP)$_2Cl_2$] and [Pd(DMP)$Cl_2$]$_n$. Since palladium halides do not react appreciably with stoichiometric ethionine within one week, the importance of dimethyl-4-pyrone in determining the reaction trend in dichloromethane is evident. When palladium halides and ethionine were allowed to react in benzene in the presence of excess dimethyl pyrone, the species [Pd(*D*,*L*-EthH)$X_2$]·DMP were obtained, and which easily released the external ligand molecule when washed with dichloromethane or acetone to yield the corresponding unsolvated species. Since all reactions occur heterogeneously, the coordination framework could be in principle different from that of samples prepared in water, owing to the possibility of ethionine acting as bridging ligand in the presence of halide bridges. For this reason [Pd(*D*,*L*-EthH)$Cl_2$] samples were prepared in water from stoichiometric ethionine and $K_2[PdCl_4]$;[12] they possessed thermal and spectroscopic properties identical with those of samples prepared in organic media.

The thermal behaviour of the complexes has been measured up to 1100°C (Table 2). As shown in Fig. 1, [Pd(*D*,*L*-EthH)$Cl_2$] melts at 198°C with incipient decomposition. The weight loss up to 345°C (46.5%) compares well with formation of $PdCl_2$ as a degradation intermediate (47.9%), whose combustion in air gives the strong exotherm at 374°C. Under air flux powdered palladium absorbs oxygen on the surface with partial formation of palladium oxide, whose decomposition occurs at 815°C. The [Pd(*D*,*L*-EthH)$Cl_2$]·DMP complex (Fig. 2) melts at 166°C, the endotherm at 209°C belonging to evolution of both ethionine and dimethyl-4-pyrone. In fact the experimental weight loss up to 350°C (59.4%) is close to that expected for palladium halide formation (61.2%). Above 350°C the thermograms coincide with those of the unsolvated species. The bromo complex thermograms do not identify a common degradation intermediate. Owing to the general flatness of the DTA curve, no exothermic process is seen to 550°C. Conversely, the thermograms of [Pd(*D*,*L*-EthH)$I_2$] resemble those of the chloro analogue, ethionine being evolved below 330°C. The DTA curve shows the combustion exotherm of palladium iodide at 495°C, sample

**Table 1** Analytical data (calculated values in parentheses) and selected ir frequencies

| Compound | Colour | m.p.(°C)[a] | C% | H% | N% | Ir ($cm^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [Pd(*D,L*-EthH)$Cl_2$][b] | yellow | 194–196 | 21.08 (21.16) | 3.86 (3.85) | 4.08 (4.11) | 3260m | 3175m | 3105w | 1709s | | | 1570w | | |
| [Pd(*D,L*-ethH)$Br_2$][b] | yellow | 199–200 | 16.82 (16.78) | 3.06 )3.05) | 3.07 (3.26) | 3253m | 3183m | 3098w | 1709s | | | 15567w | | |
| [Pd(*D,L*-EthH)$I_2$][b] | reddish brown | 183–185 | 13.83 (13.77) | 2.56 (2.50) | 2.61 (2.68) | 3249m | 3198m | 3104w | 1706s | | | 1565w | | |
| [Pd(*D,L*-EthH)$Cl_2$]·DMP[c] | yellow | 166–168 | 33.07 (33.60) | 4.51 (4.55) | 2.93 (3.01) | 3274m | 3218m | 3133m | 1707m | 1649vs | 1603w | 1575, | 1564vw | 1524s |
| [Pd(*D,L*-EthH)$Br_2$]·DMP[c] | yellow | 165–167 | 28.02 (28.21) | 3.79 (3.82) | 2.46 (2.53) | 3274m | 3225w | 3119w | 1707m | 1655vs | 1589w | 1572, | 1562sh | 1539s |
| [Pd(*D,L*-EthH)$I_2$]·DMP[c] | brown | 137–138 | 24.07 (24.11) | 3.33 (3.27) | 2.12 (2.16) | 3277m | 3226w | 3120w | 1708m | 1654vs | 1588w | 1572, | 1561sh | 1543s |

[a]With decomposition.
[b]$C_6H_{13}XNO_2PdS$ (X=Cl, Br or I).
[c]$C_{13}H_{21}XNO_4PdS$ (X=Cl, Br or I).

**Table 2** Thermal data for the complexes

| Compound | Decomposition interval (°C) | TG weight loss % | | DTA peak temperature (°C)[a] |
|---|---|---|---|---|
| | | Experimental | Calculated | |
| [Pd(*D,L*-EthH)$Cl_2$] | 180–345 | 46.5 | 47.9 (EthH) | 198m[c] |
| | 345–395 | 22.1 | 20.8 (to Pd) | 374exo |
| | 395–860[b] | | | 815endo |
| [Pd(*D,L*-EthH)$Br_2$] | 200–565 | 75.6 | 75.2 (to Pd) | 209m, (216, 221sh)[d] |
| | 565–835[b] | | | 808endo |
| [Pd(*D,L*-EthH)$I_2$] | 173–332 | 33.8 | 31.2 (EthH) | 182m[e] |
| | 332–583 | 47.1 | 48.4 (to Pd) | 495exo br |
| | 583–831[b] | | | 810endo |
| [Pd(*D,L*-EthH)$Cl_2$]·DMP | 130–350 | 59.4 | 61.2 (EthH + DMP) | 166m, 209endo[c] |
| | 350–450 | 17.3 | 15.3 (to Pd) | 374exo |
| | 450–826[b] | | | 815endo |
| [Pd(*D,L*-EthH)$Br_2$]·DMP | 145–605 | 81.0 | 80.8 (to Pd) | 159m, 205endo br[d] |
| | 605–850[b] | | | 803endo |
| [Pd(*D,L*-EthH)$I_2$]·DMP | 92–623 | 88.3 | 83.6 (to Pd) | 136m, 215endo br[e] |
| | 623–831[b] | | | 812endo |

[a]m, melting endotherm; exo, exotherm; endo; endotherm.
[b]See text.
[c]Very broad exo, max at 313°C.
[d]Shapeless DTA curve in the 250–550°C temperature interval.
[e]Very broad exo at *ca* 320°C.

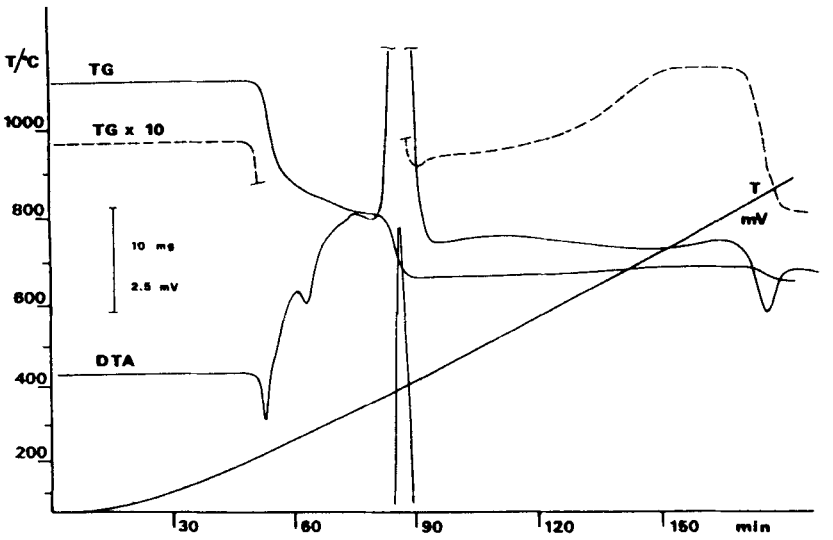


**Figure 1** Thermograms of [Pd(*D*,*L*-EthH)$Cl_2$] in air (28.25 mg).

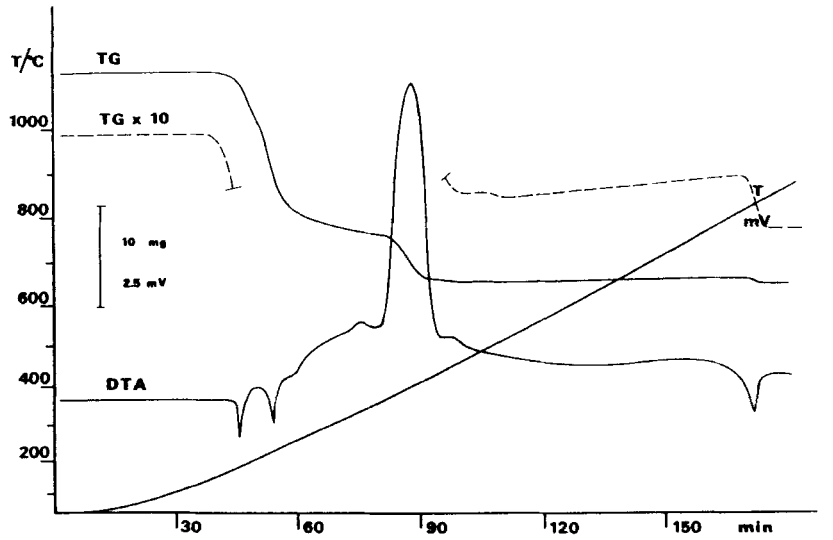


**Figure 2** Thermograms of [Pd(*D*,*L*-EthH)$Cl_2$]·DMP in air (26.88 mg).

pyrolysis ending at 583°C. The melting temperature of the DMP adducts decreases with increasing halide mass and is lower than that of the corresponding unsolvated species.

Infrared absorptions above 3000 $cm^{-1}$ (Table 1) originate from $\nu(NH_2)$ vibrations of the coordinated amino group. The presence of three bands in the 3100–3250 $cm^{-1}$ region was observed in either *cis* or *trans*-[$Pt(L)_2Cl_2$] (L = straight chain amine), the

related peaks being at *ca* 3240, 3210 and 3130 $cm^{-1}$.[17] As for amino complexes, the $NH_2$ bending mode gives rise to a weak band at *ca* 1570 $cm^{-1}$ whereas the strong absorption at *ca* 1710 $cm^{-1}$ is characteristic of the undissociated -COOH moiety. Complex spectra in the 1700–1500 $cm^{-1}$ range are quite different from that of unbound ethionine, which, as for *D,L*-methionine,[18] shows $\delta(NH_3)$ and $\nu$(C=O) absorptions at 1656, 1621 $cm^{-1}$ and 1603, 1581 $cm^{-1}$ respectively. As regards dimethylpyrone, the free ligand spectrum contains two strong absorptions at 1669 $cm^{-1}$ and 1611 $cm^{-1}$, which have been assigned to $\nu$(C=C) and $\nu$(C=O) respectively, the shoulder at 1559 $cm^{-1}$ belonging to ring vibrations.[19] On coordination the ring absorptions undergo a downfield shift of the order of 20 $cm^{-1}$ whereas the position of the carbonyl absorptions depends on the metal (1570–1520 $cm^{-1}$).[20,21] The trend observed for the [Pd(*D,L*-EthH)$X_2$]·DMP complexes (strong absorptions at *ca* 1650 and 1540 $cm^{-1}$) support the presence of coordinated dimethylpyrone, which could replace either $NH_2$ or halide bonds. Interaction with Pd—N could be excluded by analogies in the $\nu(NH_2)$ and $\delta(NH_2)$ regions with unsolvated complexes. Moreover only slight low energy shifts are observed in the Pd—X absorptions (Table 3), whereas halide removal from the coordination sphere should cause important changes. As expected for a *cis* geometry, [Pd(*D,L*-EthH)$Cl_2$] shows two strong absorptions at 330 and 302 $cm^{-1}$, which shift to 327 and 289 $cm^{-1}$ in the DMP adduct. These values compare well with those of *cis* complexes in which palladium chloride coordinates to P, N or S donors.[22–24] In particular the Pd—Cl absorptions in the thiocarbamic ester complex [Pd(EtOC(S)$NHCH_3)_2Cl_2$] were found at 343 and 318 $cm^{-1}$.[25] Insertion of a third ligand molecule yielded [Pd(EtOC(S)$NHCH_3)_3Cl]^-$, in which one Pd—Cl band (308 $cm^{-1}$) is present. Only one Pd—X absorption was observed for [Pd(EtOC-(S)$NHCH_3)_2X_2$] (Br, 261 $cm^{-1}$; I, 227 $cm^{-1}$) and [Pd(DMTP)$_2X_2$] (DMTP, 2,6-dimethyl-4H-pyran-4-thione; Br, 265 $cm^{-1}$; I, 218 $cm^{-1}$),[26] as for either ethionine adducts (Br, 254 $cm^{-1}$; I, 209 $cm^{-1}$) or related dimethylpyrone solvates (Br, 251 $cm^{-1}$; I, 195 $cm^{-1}$). Moreover the [Pd(*D,L*-EthH)$X_2$]·DMP complex spectra contain broad absorptions at *ca* 2000 $cm^{-1}$ (Cl, 1950 and 1880 $cm^{-1}$; Br or I, 1830 $cm^{-1}$).[27]

The fact that dimethylpyrone is weakly bound in the prepared complexes is confirmed by nmr ($^1H$ and $^{13}C$) spectroscopy in various solvents (Table 4).[28] Free DMP proton resonances are observed at *ca* 2.2 ($CH_3$) and 6.0 (CH) ppm, whereas the carbonyl and ring COC carbon signals fall at *ca* 180 and 166 ppm respectively. The stronger signals in the carbon nmr spectra belong to the pyrone CH (*ca* 113 ppm) and $CH_3$ (*ca* 19 ppm) groups. The [Pd(*D,L*-EthH)$X_2$] complexes are nearly insoluble in common solvents, except for the iodo-derivative, which is slightly soluble in acetone. The presence of DMP enhances the iodo complex solubility, allowing the $^{13}C$ nmr spectrum to be recorded in this solvent. As regards coordinated ethionine, the proton nmr spectra in either dimethylsulphoxide or *N,N*-dimethylformamide consist of broad signals except for the SEt proton resonance, at *ca* 3.0 ($CH_2$) and 1.4 ($CH_3$) ppm. The CH and $\gamma CH_2$ signals are observed upfield in dimethylsulphoxide (3.3 and 2.65 ppm respectively) with respect to dimethylformamide (3.6 and 2.9 ppm), the $\beta CH_2$ resonances being spread in the 1.6–2.7 ppm range, owing to the nearby chiral center. The broad signals at *ca* 4.6 ppm, whose integrals correspond to two protons, have been assigned to the $NH_2$ group whereas the COOH proton gives very broad signals below 11 ppm, and whose position depends on concentration. The [Pd(*D,L*-EthH)$I_2$]·DMP spectrum in deuterated acetone matches those in other solvents except for $\beta CH_2$, obscured by solvent absorption, and for the $NH_2$ signals, spread in the 2.5–3.5 ppm range. Owing to the presence of coordinated ligand isomers derived from

**Table 3** Infrared data in the 500–150 $cm^{-1}$ region ($\nu$(Pd—hal) in italics)

| Compound | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [Pd(*D,L*-EthH)$Cl_2$] | 492m | 451vw | 400w | 387m | | *330s* | *302s* | | 266m | | 223m | 209sh | 194w |
| [Pd(*D,L*-EthH)$Cl_2$]·DMP | 471m | 452m | 397w | 386vw | 359m | *327s* | *289m* | 281vw | | 255w | 226vw | 203m | |
| [Pd(*D,L*-EthH)$Br_2$] | 486m | 445vw | 395w | 381m | | | 319w | | 271w | *254m* | 223m | 195m | 165mbr |
| [Pd(*D,L*-EthH)$Br_2$]·DMP | 468w | 452vw | 391sh | 381m | 356mw | | 323w | 281vw | 267vw | *251m* | 227mw | 196m | 186m |
| | | | | | | | | | | | | 206m | |
| [Pd(*D,L*-EthH)$I_2$] | 481m | 445vw | 385w | 371m | | | 321w | | 252w | 249vw | 227m | *209m* | 170m |
| | | 439vw | | | | | | | | | | | |
| [Pd(*D,L*-EthH)$I_2$]·DMP | 462w | 447w | 392sh | 378m | 356mw | | 319vw | 280vw | 265vw | 254vw | 227w | *195m* | 164m |

**Table 4** Nmr data (solvent, $(CD_3)_2SO$; ppm; T = 25°C)

| | Compound | αCH | $\beta CH_2$[a] | $\gamma CH_2$[a] | $SCH_2CH_3$ | $SCH_2CH_3$ | $NH_2$ | COOH[b] |
|---|---|---|---|---|---|---|---|---|
| $^1$H nmr | | | | | | | | |
| | [Pd(*D,L*-EthH)$Cl_2$]·DMP[c] | 3.30 | 1.98, 2.21 | 2.65, 2.70 | 2.95 | 1.36 | 4.60 | 13.3 |
| | [Pd(*D,L*-EthH)$Cl_2$][d] | 3.59 | 2.17, 2.46 | 2.85 | 3.09 | 1.44 | 4.68 | 11.2 |
| | [Pd(*D,L*-EthH)$Br_2$] | 3.30 | 2.0, 2.2, 2.5 | 2.66 | 3.02 | 1.35 | 4.60 | 12.5 |
| | [Pd(*D,L*-EthH)$I_2$]·DMP[d,e] | 3.68 | 2.0–2.5 | 2.95 | 3.22 | 1.44 | 4.65 | 10.7 |
| | [Pd(*D,L*-EthH)$I_2$]·DMP[f] | 3.73 | | 2.94, 2.98w | 3.24 | 1.46, 1.40w | | |
| $^{13}$C nmr | | | | | | | | |
| | [Pd(*D,L*-EthH)$Cl_2$][d] | 52.5 | 31.7 | 28.7[g] | 28.3[g] | 13.3 | | 172.6 |
| | [Pd(*D,L*-EthH)$Cl_2$]·DMP[h] | 51.3 | 30.7 | 27.3[g] | 26.9[g] | 12.8 | | 171.7 |
| | [Pd(*D,L*-EthH)$Br_2$] | 51.0 | 31.3 | 27.0[g] | 26.9[g] | 13.1 | | 171.9 |
| | [Pd(*D,L*-EthH)$I_2$]·DMP[f,i] | 52.1 | 33.1 | 30.6[g] | 28.3[g] | 14.0 | | 172.6 |
| | [Pd(*D,L*-EthH)$I_2$]·DMP[d,l] | 52.2 | 32.6 | 28.2[g] | 27.6[g] | 13.9 | | 173.2 |

[a]Maxima of broad signals spread in a wide ppm range, especially for $\beta CH_2$.
[b]Very broad signals whose position varies with concentration.
[c]DMP signals at 2.20($CH_3$) and 6.03(CH) ppm.
[d]In deuterated DMF.
[e]DMP: 2.25($CH_3$) and 6.06(CH) pp.
[f]In deuterated acetone, see text.
[g]Tentative assignment.
[h]DMP signals (ppm): 178.6 (CO), 165.6 (COC), 113.0 (CH), 19.1 ($CH_3$).
[i]The signals at 30.6 and 28.3 overlap the solvent multiplets. DMP: 180.6 (CO), 166.3 (COC), 113.8 (CH), 19.4 ($CH_3$).
[l]DMP: 179.5 (CO), 166.5 (COC), 113.7 (CH), 19.5 ($CH_3$).

inversion at the sulphur atom,[7-10] the nmr spectra of platinum complexes with methionine or ethionine contain doubled signals for all proton groups. For example, the [Pt(*L*-EthH)$Cl_2$] spectrum in $D_2O$ contains two sets of SEt sgnals at 1.41 and 1.42 ppm ($CH_3$) and 2.8 and 3.2 ppm ($CH_2$),[10] the same trend being observed by us in the solvents used for palladium complexes. Conversely, the palladium adducts give a single set of signals for either proton or carbon nmr. The -COOH carbon resonance falls at *ca* 172 ppm, whereas the CH and $\beta CH_2$ signals are observed at *ca* 52 and 32 ppm, respectively. It is hard to assign the $CH_2$—S—$CH_2$ carbon resonance, which are very close in the 26–29 ppm range, whereas the SEt $CH_3$ signal appears at *ca* 13.5 ppm.

*Acknowledgements*

This work was partially supported by Progetto Finalizzato "Chimica Fine II" C.N.R., Roma. The Authors thank Miss Daniela Longo for technical assistance.

*References*

1. C.A. McAuliffe and S.G. Murray, *Inorg. Chim. Acta Rev.*, 103 (1972).
2. M. Bruley-Rosset, I. Vergnon and G. Renoux, *Int. J. Immunopharmacol.*, **8**, 287 (1986).
3. R.F. Borch, P.C. Dedon, A. Gringeri and T. Montine, in M. Nicolini (ed): "*Platinum and Other Metal Corodination Compounds in Cancer Chemotherapy*", (Martinus Nijhoff, Boston, 1988) p. 216.
4. G. Faraglia, L. Sindellari, V. Cherchi, A. Furlani, A. Papaioannou and V. Scarcia, *Transition Met. Chem.*, in press, and references therein.
5. G. Faraglia and S. Sitran, *Inorg. Chim. Acta*, **176**, 67 (1990), and references therein.
6. V. Cherchi, G. Faraglia, S. Sindellari, S. Sitran, A. Furlani and V. Scarcia, *Inorg. Chim. Acta*, **155**, 267 (1989), and references therein.
7. D.D. Gummin, E.M.A. Ratilla and N.M. Kostic, *Inorg. Chem.*, **25**, 2429 (1986).
8. T.G. Appleton, J.W. Connor and J.R. Hall, *Inorg. Chem.*, **27**, 130 (1988).
9. T. Grochowski and K. Samochocka, *J. Chem. Soc., Dalton Trans.*, 1145 (1992).
10. R.E. Norman, J.D. Ranford and P.J. Sadler, *Inorg. Chem.*, **31**, 877 (1992).
11. L.D. Pettit and M. Bezer, *Coord. Chem. Rev.*, **61**, 97 (1985).
12. S.E. Livingstone and J.D. Nolan, *Inorg. Chem.*, **7**, 144 (1968).
13. F. Bigoli, E. Leporati and M.A. Pellinghelli, *Acta Cryst., Sect. B*, **35**, 1465 (1979).
14. B.T. Khan, K. Najmuddin, S. Shamsuddin and S.M. Zakeeruddin, *Inorg. Chim. Acta*, **170**, 129 (1990).
15. B.T. Khan, J. Bhatt, K. Najmuddin, S. Shamsuddin and K. Annapoorna, *J. Inorg. Biochem.*, **44**, 55 (1991).
16. D. Fregona, Z.J. Guo, G. Faraglia and S. Sitran, *Transition Met. Chem.*, in press.
17. G. Faraglia, L. Sindellari and S. Sitran, *Thermochim. Acta*, **78**, 159 (1984).
18. A. Grunenberg and D. Bougeard, *Ber. Bunsenges. Phys. Chem.*, **90**, 485 (1986).
19. A.R. Katritzky and R.A. Jones, *Spectrochim. Acta*, **17**, 64 (1961).
20. G. Faraglia, Z.J. Guo and S. Sitran, *Polyhedron*, **10**, 351 (1991).
21. G. Faraglia, D. Fregona, Z.J. Guo and S. Sitran, *Thermochim. Acta*, **191**, 95 (1991).
22. J.H. Nelson, J.A. Rahn and W.H. Bearden, *Inorg. Chem.*, **26**, 2192 (1987).
23. R.J.H. Clark, V.B. Croud and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 815 (1985).
24. L. Sindellari, G. Faraglia, B. Zarli, P. Cavoli, A. Furlani and V. Scarcia, *Inorg. Chim. Acta*, **46**, 57 (1980).
25. G. Faraglia, L. Sindellari and B. Zarli, *Inorg. Chim. Acta*, **48**, 247 (1981).
26. G. Faraglia, F. Barbaro and S. Sitran, *Transition Met. Chem.*, **15**, 242 (1990).
27. C.A. McAuliffe, *J. Chem. Soc. (A)*, 641 (1967).
28. S. Sitran, D. Fregona and G. Faraglia, *J. Coord. Chem.*, **20**, 193 (1989).