A Study on the Palladium(II)–Methionine–2,6-Dimethyl-4*H*-pyran-4-one System†

Zijian Guo,[a] Umberto Casellato,[b] Giuseppina Faraglia,*,[a] Rodolfo Graziani[a] and Sergio Sitran[b]

[a] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, dell'Università, Padova, Italy*
[b] *Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, C.N.R., Padova, Italy*

The methionine (Met) complexes [PdX$_2$L]·dmp (X = Cl, Br or I; L = D-, L- or DL-Met; dmp = 2,6-dimethyl-4*H*-pyran-4-one) have been prepared in benzene by reaction of palladium dihalides with methionine in the presence of an excess of dmp, whereas in dichloromethane the corresponding [PdX$_2$L] adducts have been isolated. The crystal structure of [PdI$_2$(DL-Met)]·dmp was determined by X-ray crystallography and refined to a final *R* of 0.065, based on 1720 observed reflections. The crystal is monoclinic, *P*2$_1$/*c*, with *a* = 11.851(3), *b* = 14.953(3), *c* = 11.303(2) Å, β 109.94(4)°. The Pd is co-ordinated by two I and one chelate Met ligand in a distorted square-planar geometry. Relevant bond distances are: Pd–I 2.594(2) and 2.621(2) Å, Pd–S 2.318(4) Å and Pd–N 2.08(1) Å. The dmp molecule is bound to the methionine carboxyl by a hydrogen bond.

Literature reports on methionine (Met) complexes of palladium concern mainly chloro-derivatives, which are prepared by reaction of K$_2$[PdCl$_4$] and the ligand in water.[1–5] The crystal structure of [PdCl$_2$(DL-Met)] was consistent with an S,N chelated ligand with intermolecular hydrogen bonds occurring between carboxyl groups of adjacent molecules.[6] These contacts seem to be absent in the analogous [PdCl$_2$(L-Met)],[5] whereas both [PtCl$_2$(DL-Met)] and [PtCl$_2$(L-Met)] are dimers owing to hydrogen-bonding carboxyls.[7] Moreover recent papers have concerned mixed complexes of palladium and platinum containing methionine (or its derivatives) along with amines, pyrimidines or peptides in an attempt to explain the interaction of these metals with thiol groups of proteins.[8–14] Palladium dihalides were found to form 1:2 adducts with 4-pyrones such as 2,6-dimethyl-4*H*-pyran-4-one (dmp), in which the ligand is weakly bound to palladium through the carbonyl oxygen.[15]

This paper reports a study on the interaction of PdX$_2$ (X = Cl, Br or I) with methionine (L-, D-, DL-Met) and dmp in benzene or dichloromethane, along with the X-ray crystal structure of [PdI$_2$(DL-Met)]·dmp.

Experimental

Chemicals.—The reagents L-, D-, DL-methionine (Janssen) and dmp (C$_7$H$_8$O$_2$, 2,6-dimethyl-4*H*-pyran-4-one, Ega Chemie) were used as supplied. Palladium halides were Johnson Matthey products.

Preparation of Complexes.—The complexes [PdCl$_2$L]·dmp (L = L-, D-, DL-Met, X = Cl, Br or I) were prepared in benzene at room temperature by reaction of PdX$_2$ and methionine (molar ratio 1:1) in the presence of an excess of dmp (molar ratio from 1:4 to 1:8; reaction time, 3 d). For example, the complex [PdCl$_2$(L-Met)]·dmp was obtained by stirring a suspension of PdCl$_2$ (1.0 mmol) and L-Met (1.0 mmol) in a benzene solution of dmp (4.0 mmol in 3 cm^3), the heterogeneous reaction proceeding slowly (3 d). The first product was [PdCl$_2$(dmp)$_2$] which successively reacted with methionine to form a pale yellow solid which was filtered off, washed with *n*-pentane and dried *in vacuo* (yield, 90%). The other complexes were prepared analogously (yield 85–95%), complete reaction of PdI$_2$ requiring a larger dmp excess (molar ratio 1:8). When washed with dichloromethane, acetone or methanol the complexes released the external dmp molecule to form the related [PdX$_2$L] adducts.

The complexes [PdX$_2$L] (L = D-, L-, DL-Met; X = Cl, Br or I) have been prepared by the following procedures: (*i*) by reaction of PdX$_2$ with Met (molar ratio 1:1) in a dichloromethane solution of dmp (molar ratio 1:4; yields > 80%). For example, [PdBr$_2$(D-Met)] was prepared by treating PdBr$_2$ (1.0 mmol) and D-Met (1.0 mmol) in a CH$_2$Cl$_2$ solution of dmp (4.0 mmol). The reaction proceeded at room temperature upon vigorous stirring (2 d). The orange solid was separated by centrifugation, washed with CH$_2$Cl$_2$ and *n*-pentane, and dried *in vacuo* (yield, 82%). Samples of [PdX$_2$L] obtained by washing the parent [PdX$_2$L]·dmp complexes with dichloromethane showed infrared spectra identical to those of samples prepared by this method.

(*ii*) By addition of methionine to an aqueous solution of K$_2$[PdX$_4$] (X = Cl or Br, molar ratio 1:1) at room temperature with stirring (0.5 h). A yellow solid separated on standing (12 h, 5 °C), which was washed with water, ethanol and diethyl ether, and dried *in vacuo* (yield, 50%).

(*iii*) By reaction of K$_2$[PdX$_4$] (X = Cl or Br) and methionine (molar ratio 1:1) in a warm aqueous solution (60 °C).[1,5]

Samples of [PdX$_2$(DL-Met)] (X = Cl, Br or I) showed identical infrared spectra whatever the synthetic method employed, whereas the L- and D-Met chloro- or bromo-derivatives presented spectral differences especially above 3000 cm^{-1}, correlated probably to a different hydrogen-bonding bridge network. Preparation procedures and complex type were: [PdCl$_2$(L-Met)] (A) [(*i*) and (*ii*)], (B) (*iii*); [PdCl$_2$(D-Met)] (A) (*i*), (B) (*ii*); [PdBr$_2$(L-Met)] (A) (*i*), (B) (*ii*); [PdBr$_2$(D-Met)] [(*i*)–(*iii*)]; [PdX$_2$(DL-Met)] (X = Cl or Br) [(*i*)–(*iii*)]; [PdI$_2$(DL-Met)] (*i*). When the [PdI$_2$L]·dmp (L = D- or L-Met) complexes were washed with dichloromethane, brownish solids were formed the infrared spectra of which showed bands due to free methionine. Such a behaviour could suggest the instability of the [PdI$_2$L] (L = D- or L-Met) adducts in the absence of dmp.

Analytical and melting-point data for the complexes are given in Table 1.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and melting-point data for the complexes

Compound	M.p./°C	Analysis[a] (%) C	H	N
[PdCl$_2$(L-Met)]·dmp[b]	171–172	32.55	4.20	3.00
		(32.00)	(4.25)	(3.10)
[PdCl$_2$(D-Met)]·dmp[b]	170–171	31.95	4.45	3.25
[PdCl$_2$(DL-Met)]·dmp[b]	173–175	31.95	4.25	3.05
[PdBr$_2$(L-Met)]·dmp[b]	169–171	26.85	3.60	2.60
		(26.70)	(3.55)	(2.60)
[PdBr$_2$(D-Met)]·dmp[b]	172–173	27.05	3.70	2.60
[PdBr$_2$(DL-Met)]·dmp[b]	184–186	26.70	3.55	2.55
[PdI$_2$(L-Met)]·dmp[b]	135–137	23.35	3.15	2.25
		(22.75)	(3.00)	(2.20)
[PdI$_2$(D-Met)]·dmp[b]	136–137	23.10	3.10	2.15
[PdI$_2$(DL-Met)]·dmp[b]	168–170	22.60	3.05	2.15
[PdCl$_2$(L-Met)][c] (A)	189–190	18.45	3.45	4.10
		(18.40)	(3.40)	(4.30)
[PdCl$_2$(L-Met)][c] (B)	189–191	18.10	3.35	4.30
[PdCl$_2$(D-Met)][c] (A)	190–192	18.15	3.35	4.30
[PdCl$_2$(D-Met)][c] (B)	187–189	18.40	3.45	4.20
[PdCl$_2$(DL-Met)][c]	189–191	18.35	3.40	4.25
[PdBr$_2$(L-Met)][c] (A)	181–182	14.90	2.70	3.30
		(14.45)	(2.65)	(3.35)
[PdBr$_2$(L-Met)][c] (B)	191–192	14.25	2.60	3.40
[PdBr$_2$(D-Met)][c]	192–193	14.20	2.55	3.40
[PdBr$_2$(DL-Met)][c]	199–200	14.45	2.70	3.35
[PdI$_2$(DL-Met)][c]	174–175	12.00	2.20	2.65
		(11.80)	(2.20)	(2.75)

[a] Calculated values in parentheses. [b] $C_{12}H_{19}X_2NO_4PdS$ (X = Cl, Br or I). [c] $C_5H_{11}X_2NO_2PdS$ (X = Cl, Br or I).

Table 2 Crystal and intensity data for [PdI$_2$(DL-Met)]·dmp

Empirical formula	$C_{12}H_{19}I_2NO_4PdS$
M	633.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.851(3)
b/Å	14.953(3)
c/Å	11.303(2)
α/°	90.0
β/°	109.94(4)
γ/°	90.0
U/Å^3	1882.9(8)
D_c/g cm^{-3}	2.23
Z	4
F(000)	1192
μ(Mo-Kα)/cm^{-1}	43
Scan method	$\theta/2\theta$
θ_{max}/°	50
Scan speed/° min^{-1}	2
Unique reflections	3324
Observed reflections	1720
λ(Mo-Kα)/Å	0.7107
Corrections	Lorentz polarization, absorption
w	$1.00/[\sigma^2(F) + 0.011\,695F^2]$
Final R	0.065
Final R'	0.062

Table 3 Fractional coordinates for [PdI$_2$(DL-Met)]·dmp

Atom	x	y	z
Pd	0.143 6(1)	−0.036 79(7)	0.133 6(1)
I(1)	0.138 0(1)	0.135 25(7)	0.087 7(1)
I(2)	0.272 6(1)	−0.065 52(8)	−0.007 3(1)
N(1)	0.044(1)	−0.007 2(9)	0.249(1)
C(1)	−0.033(1)	−0.074(1)	0.280(1)
C(2)	−0.103(1)	−0.027(1)	0.356(1)
O(1)	−0.096(1)	0.048 4(8)	0.382(1)
O(2)	−0.176(1)	−0.084 8(9)	0.381(1)
C(3)	0.037(2)	−0.154(1)	0.345(1)
C(4)	0.065(1)	−0.223(1)	0.258(1)
S	0.170 7(4)	−0.187 2(3)	0.185 2(5)
C(5)	0.305(2)	−0.189(1)	0.317(2)
O(3)	0.286(1)	0.023 9(9)	0.473(1)
C(6)	0.343(1)	0.079(1)	0.433(2)
C(7)	0.427(1)	0.052(1)	0.368(1)
C(8)	0.483(1)	0.111(1)	0.322(1)
O(4)	0.468 4(9)	0.198 5(8)	0.332(1)
C(9)	0.396(1)	0.232(1)	0.391(2)
C(10)	0.335(1)	0.173(1)	0.443(1)
C(11)	0.563(2)	0.086(1)	0.250(2)
C(12)	0.388(2)	0.330(1)	0.393(2)

Measurements.—Elemental analyses were carried out on a C. Erba 1106 microanalyser at the Department of Inorganic Chemistry of the University of Padova. IR spectra were recorded on Nicolet 5SXC FT-IR and 20F far-IR spectrometers as either Nujol mulls between KBr and polyethylene discs or KBr pellets. NMR (^1H and ^{13}C) spectra were measured in deuteriated *N*,*N*-dimethylformamide (dmf) and dimethyl sulfoxide (dmso) using a JEOL FX 90Q spectrometer (in ppm from $SiMe_4$ as internal standard; proton-decoupled ^{13}C). 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}; reference Al_2O_3). Melting points were measured by a Büchi instrument.

X-Ray Crystal Structure Determination.—Crystals of [PdI$_2$(DL-Met)]·dmp were grown by slow evaporation of an acetone solution of the complex. A crystal of maximum dimension 0.2 mm was used for the analysis. Data collection was made with Mo-Kα radiation on a Philips PW 1100 diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data are reported in Table 2. The crystals are stable under irradiation. Solution of the structure was achieved by Patterson and Fourier methods, alternated with cycles of full-matrix least-squares refinement of the atomic parameters. Because of the difficulty in locating the H atoms on the electron density maps they were introduced in calculated positions with fixed C–H distances and thermal parameters (C–H 0.96, U_{iso} = 0.08 Å^2). Anisotropy was introduced for all non-hydrogen atoms. Refinement of scale factor, positional and thermal parameters minimized the function $\Sigma w(F)^2$. At convergence the highest shift on the refined parameters was 0.21 times the standard deviation and the highest map residual was 2.2 e Å^{-3}. Form factors for the atoms were supplied internally by the SHELX program system.[16] Final atomic parameters are listed in Table 3, bond distances and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

The [PdX$_2$(Met)]·dmp complexes (Table 1) have been prepared in benzene by reaction of a stoichiometric ratio of palladium dihalide and methionine in the presence of an excess of dmp. By operating in dichloromethane the [PdX$_2$(Met)] complexes were isolated.

X-Ray Diffraction Study.—As shown in Fig. 1, [PdI$_2$(DL-Met)]·dmp is a molecular complex in which the metal ion is four-co-ordinate in a rather distorted square-planar environment. Distortions from the idealized geometry are mainly due to the relatively large chelation angle of 96.9° subtended by the bidentate ligand. This, and possible steric hindrance of the ligand with the large halogen atoms, could be responsible for significant deviation of S and N from the I_2NS co-ordination

Table 4 Bond distances (Å) and angles (°) for [PdI$_2$(DL-Met)]·dmp

I(1)–Pd	2.621(2)	I(2)–Pd	2.594(2)
Pd–N	2.08(1)	Pd–S	2.318(4)
C(1)–N	1.48(2)	C(1)–C(2)	1.54(2)
C(1)–C(3)	1.50(2)	C(2)–O(1)	1.17(2)
C(2)–O(2)	1.32(2)	C(3)–C(4)	1.55(2)
C(4)–S	1.80(2)	C(5)–S	1.77(2)
O(3)–C(6)	1.24(2)	O(6)–C(7)	1.49(3)
C(6)–C(10)	1.41(2)	C(7)–C(8)	1.31(2)
C(8)–O(4)	1.33(2)	O(8)–C(11)	1.50(3)
O(4)–C(9)	1.35(2)	C(9)–C(10)	1.39(2)
C(9)–C(12)	1.47(2)		
I(1)–Pd–I(2)	91.22(6)	I(2)–Pd–S	86.2(1)
I(2)–Pd–N	177.1(4)	I(1)–Pd–S	173.8(2)
I(1)–Pd–N	86.2(4)	N–Pd–S	96.2(4)
Pd–N–C(1)	122.6(9)	N–C(1)–C(3)	112(1)
N–C(1)–C(2)	109(1)	C(2)–C(1)–C(3)	114(1)
C(1)–C(2)–O(2)	110(1)	C(1)–C(2)–O(1)	125(1)
O(1)–C(2)–O(2)	125(1)	C(1)–C(3)–C(4)	115(1)
C(3)–C(4)–S	115(1)	Pd–S(1)–C(4)	110.3(6)
C(4)–S–C(5)	100.4(1)	Pd–S–C(5)	103.5(6)
O(3)–C(6)–C(10)	125(1)	O(3)–C(6)–C(7)	122(1)
C(7)–C(6)–C(10)	113(1)	C(6)–C(7)–C(8)	121(1)
C(7)–C(8)–C(11)	123(1)	C(7)–C(8)–O(4)	122(1)
O(4)–C(8)–C(11)	114(1)	C(8)–O(4)–C(9)	122(1)
O(4)–C(9)–C(12)	116(1)	O(4)–C(9)–C(10)	119(1)
C(10)–C(9)–C(12)	126(1)	C(6)–C(10)–C(9)	123(1)

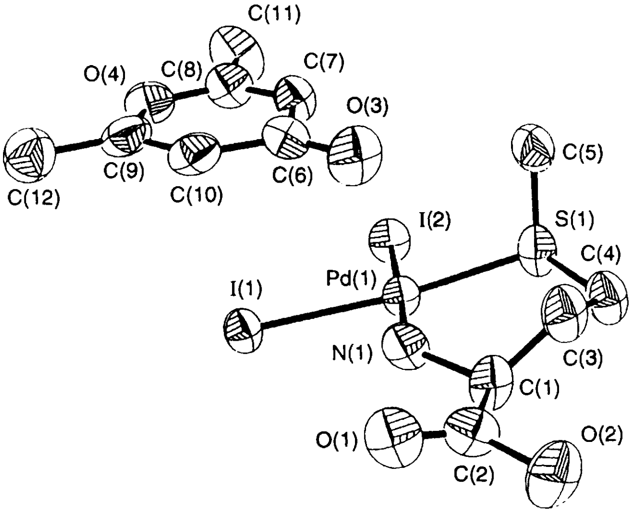

Fig. 1 The crystal structure of [PdI$_2$(DL-Met)]·dmp

plane [I(1) −0.001, I(2) +0.001, S(1) −0.025, N(1) +0.142, Pd +0.109 Å]. On the other hand two Pd ··· I contact distances of 3.724 Å, at the upper limit of the van der Waals radii sum (3.72 Å), are present between centrosymmetric molecules in the crystal, as shown in Fig. 2. On this basis the compound could be alternatively described as an incipient dimeric complex with the metal atom in a pseudo-square-pyramidal geometry, the fifth co-ordination site being filled, in a broad sense, by the bridging I(1) atom of the neighbouring molecule. The Pd–I bond distances (mean 2.608 Å) agree well with the sum of the covalent radii (2.61 Å), the small differences between the two observed values being probably due to the different nature of the *trans* donor atoms, or to the above mentioned bridging contact of I(1). The Pd–S bond length [2.318(4) Å] agrees with the covalent radii sum (2.30 Å) while the Pd–N bond distance is significantly longer [2.08(1) Å *vs.* 2.03 Å]. This, along with the fact that the Pd–N–C angle is 123° (N is bonded to four atoms and should be considered sp^3 hybridized), and that Pd–I(2) (which is *trans* to N) is slightly shorter than Pd–I(1) (which is *trans* to S) seems to suggest some weakness of the Pd–N bond. The methionine–Pd ring shows a flattened-chain conformation, the orientation of the methyl group bound to sulfur suggesting an *S* configuration. This ring has a puckered structure, atoms being alternately displaced from the calculated mean plane [Pd +0.002, N −0.196, C(2) +0.120, C(3) −0.309, C(4) +0.303, S −0.026 Å]. As a whole, the molecule resembles those of the analogous [PdCl$_2$(L-Met)],[5] [PdCl$_2$(DL-Met)][6] and [PdCl$_2$(DL-etn)] [etn = ethionine, EtSCH$_2$CH$_2$CH(NH$_2$)CO$_2$H][17] compounds. The NH$_2$ group makes an intramolecular NH ··· I(1) contact which falls within the values (< 3.2 Å) accepted for H ··· I hydrogen bonds. It is also involved in an NH ··· O(3) hydrogen bond [N ··· O 3.15(1), H ··· O 2.16(2) Å, NH ··· O 168(2)°] which links the complex to one clathrate dmp molecule. An additional O(2) ··· O(3) contact of 2.59 Å strongly suggests the presence of a hydrogen bond between the carboxyl group and another dmp molecule. Unfortunately, the position of the corresponding H atom could not be determined in this case. This extensive net of hydrogen bonds, together with the observed Pd ··· I interactions, seems to confer stability and compactness to the crystal packing.

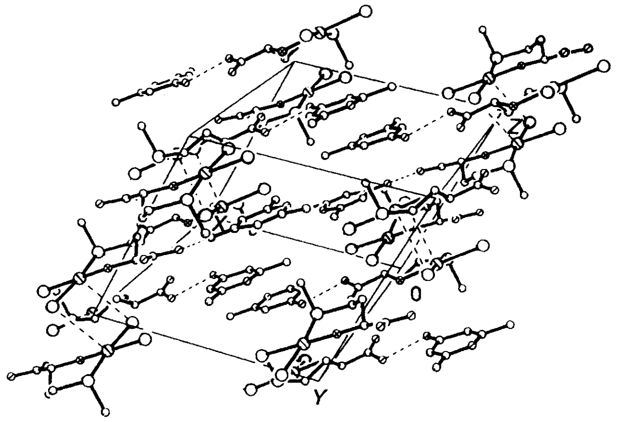

Fig. 2 View of the crystal packing

IR Spectra.—The ν(NH) absorptions of co-ordinated NH$_2$ in the [PdX$_2$(Met)]·dmp complexes are observed in the range 3100–3300 cm^{-1}. These bands, found at 3288, 3168 and 3105 cm^{-1} in [PdCl$_2$(L-Met)]·dmp, undergo slight shifts dependent on halide or ligand diastereoisomer. The asymmetric stretch of the unionized carboxyl group causes a strong absorption at *ca.* 1710 cm^{-1}, the δ(NH$_2$) band being at *ca.* 1560 cm^{-1}. The ring vibrations of free dmp (1669 and 1599 cm^{-1})[18] are nearly unchanged in the adduct series, whereas the ν(C=O) absorption is found at *ca.* 1540 cm^{-1} as opposed to 1611 cm^{-1} in free ligand. The lowering in energy (71 cm^{-1}) caused by hydrogen bonding (Fig. 2) is of the order expected for strong O-acceptors (50–80 cm^{-1}). As a general remark, the [PdX$_2$(Met)] spectra present more or less marked changes which depend mainly on the synthetic method employed. The effect is particularly evident for the [PdX$_2$(L-Met)] and [PdX$_2$(D-Met)] complexes, which have been isolated in two forms. The absorptions of the A forms (*ca.* 3320, 3275, 3200 and 3126 cm^{-1}; 1743 cm^{-1}) differ clearly from those of the B forms (*ca.* 3224, 3170, 3112 and 3100 cm^{-1}; 1710 cm^{-1}). The fact that dmp does not affect the palladium co-ordination environment is confirmed by the close similarity of the Pd–X absorptions in the [PdX$_2$(Met)] and [PdX$_2$(Met)]·dmp complex series. Two bands assignable to Pd–Cl bond stretches are observed in all the chloro derivatives (*ca.* 327 and 300 cm^{-1}) the high-energy one being split in the A species containing either D- or L-diastereoisomers. The bromo- and iodo-complex spectra contain only one absorption assignable to a Pd–X stretch (at *ca.* 250 and 200 cm^{-1} respectively). The spectra of the [PdX$_2$L]·dmp adducts, in which L is D- or L-Met,

Table 5 Proton and carbon-13 NMR data for the complexes (25 °C)

	$\delta(^1H)$						
Compound	Solvent[a]	α-CH	β-CH_2	γ-CH_2[b]	SCH_3	CO_2H[c]	NH_2[b]
[$PdCl_2$(L-Met)]	dmf	3.68	1.75–2.35	2.90	2.61	13.0	4.70
	dmso	3.30	1.75–2.20	2.66	2.51	13.2	4.60
[$PdCl_2$(D-Met)]	dmso	3.25	1.75–2.24	2.64	2.43	13.4	4.45
[$PdCl_2$(DL-Met)]	dmf	3.66	1.75–2.35	2.86	2.58	13.0	4.68
[$PdBr_2$(D-Met)]	dmf	3.68	1.80–2.50	2.88	2.65	13.6	4.70
	dmso	3.28	1.80–2.20	2.67	2.48	13.3	4.58
[$PdBr_2$(DL-Met)]·dmp[d]	dmso	3.30	1.75–2.10	2.66	2.51	13.2	4.59
[PdI_2(DL-Met)]	dmso	3.40	1.70–2.30	2.74	2.59	13.4	4.56
[PdI_2(D-Met)]·dmp[e]	$(CD_3)_2CO$	3.74	2.20–2.70	2.90	2.72	*f*	4.33
	$\delta(^{13}C)$						
[$PdCl_2$(DL-Met)]	dmf	52.4	31.5	28.5	21.3	172.6	
	dmso	51.4	30.2	27.1	20.7	171.8	
[$PdBr_2$(DL-Met)]·dmp[g]	dmso	51.0	30.1	26.6	21.4	172.0	
[$PdBr_2$(D-Met)]	dmf	52.3	31.1	27.8	21.9	172.8	

[a] Deuteriated solvents. [b] Maximum of broad signals. [c] Very broad signals whose position varies with concentration. [d] Signals for dmp at δ 2.25 (CH_3) and 6.05 (CH). [e] Signals for dmp at δ 2.23 (CH_3) and 6.01 (CH). [f] Not observed. [g] Signals for dmp at δ 178.6 (CO), 165.4 (COC), 113.0 (CH) and 19.1 (CH_3).

contain a very broad absorption at *ca.* 1930 cm^{-1}, whereas the DL-Met analogues present two broad absorptions at *ca.* 1890 and 2400 cm^{-1}, which are probably due to the hydrogen-bridge framework.[1]

NMR Spectra.—The NMR signals of the reported complexes do not depend on either ligand isomer or halide (Table 5). Owing to their low solubility in common solvents, dmf or dmso solutions were used, and were found to be stable with time. Proton NMR spectra of the methionine complexes support the fact that dmso does not remove the S,N-chelated methionine from the metal co-ordination sphere. In this solvent the SCH_3 singlet (δ *ca.* 2.50) is well downfield in respect to the free ligand (δ 2.20)[19] while the broad NH_2 signal (δ 4.6) compares well with values for [$PtX_2(amine)_2$] complexes.[20] The carboxyl proton gives rise to a very broad signal at δ *ca.* 13, which is sometimes difficult to observe. The β- and γ-CH_2 resonances appear as broad multiplets, the former especially so. Spectra in dmf, which is a weak O-donor towards palladium,[15] display an analogous trend, the CH and γ-CH_2 proton resonances being shifted downfield (*ca.* 0.3 ppm). The spectra of the dmp adducts are coincident with those of unsolvated species, apart from the presence of free dmp signals at δ *ca.* 2.2 (CH_3) and 6.0 (CH). Carbon-13 NMR spectra show the SCH_3 and CH carbon resonances at *ca.* δ 21 and 51 respectively, the carboxyl carbon being observed at δ *ca.* 172. Owing to the presence of two diastereoisomers of the chelated methionine, the [Pt(L-Met)X_2] (X = Cl or Br) spectra showed two signals for each proton (or carbon) group.[14] One set of signals for the palladium species could suggest the presence of one methionine isomer, although fast inversion at the SCH_3 sulfur cannot be excluded.

Thermogravimetric Data.—The thermal behaviour of the [PdX_2(Met)]·dmp (X = Cl or Br) adducts has been examined up to 1000 °C. The weight loss in the first degradation step (140–380 °C) supports evolution of both dmp and Met to form PdX_2 as a degradation intermediate, whose combustion to Pd occurs below 500 °C. The [PdI_2(DL-Met)]·dmp thermograms show a similar trend, whereas those of the L- or D-Met analogues contain one endothermic peak at 111 °C due to a phase transition before melting (137 °C). Phase-transition peaks have been observed in free L- and DL-Met which have been ascribed to structure modifications characterized by either conformation changes or slightly modified hydrogen bonding.[21] The [PdX_2(Met)] complexes melt at temperatures higher than those of the corresponding dmp adducts (Table 1). Gradual evolution of both methionine and halide occurs below 600 °C with no particularly significant features.

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