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Novel Chelates of Pd(II) Dithiocarbamates. Spectroscopic Studies and Thermal Behaviour

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Abstract

Complexes of Pd(II) with dithiocarbamate derived from α-amino acid (glycine, DL-alanine, DL-valine, L-valine and DL-leucine) have been synthesized. The complexes have been characterized by chemical analysis, infrared, electronic, ^{1}H and ^{13}C NMR and X-ray photoelectron spectroscopies, magnetic susceptibilities measurements, mass spectrometry and TG and DSC analysis.

The stoichiometry of these complexes is Pd:L = 1:2 and coordination around the metallic cation seems to be distorted square planar, close to D_{2h}. Coordination takes place through the sulphur atoms of the ligands and the carboxylic group is in a free, acidic form. Both sulphur atoms are chemically equivalent, according to the XPS results. ^{1}H and ^{13}C NMR spectra for the DL- and L-valine derivatives indicate that different complexes DD, DL and DL do not have any spectroscopic difference due to the large distance between the chiral centers. Thermal decomposition of the complexes takes place through a multi-step process, the first step being a decarboxylation, followed by a complex pyrolysis that leads to palladium oxide. The thermal stability of these complexes decreases in the order $Pd(dtc\text{-}DL\text{-}val)_2 > Pd(dtc\text{-}DL\text{-}ala)_2 > Pd(dtc\text{-}gly)_2 > Pd(dtc\text{-}DL\text{-}leu)_2$. The mass spectrometric data indicate that the $[S_2C{-}NH{-}CH_2{-}COO]^+$ ion is formed in all cases, with the final formation of $[S_2C]^+$ for the ligands. For the complexes, however, the species $[S\text{-}C\text{-}ala]^+$, $[S\text{-}C\text{-}val]^+$ and $[S\text{-}C\text{-}leu]^+$ are formed.

Introduction

Dithiocarbamates (dtc) are a large family of compounds which have been deeply investigated from several points of view, because of their great interest in different fields. In the most recent years, many studies have been developed in order to gain information on the role that the complexes formed by dtc and metal ions play in vulcanization reactions, high-pressure lubrifying agents, fungicides and pesticides, their range of applications covering fields as different as chemical industry, biology and biochemistry. The residual toxicity of dtc used as fungicides in agriculture is actually unknown in many cases, in spite of studies carried out with rats that have shown they are neurotoxic, affecting, for instance, the cholinergic inervation of the intestine [1–4].

These organo–sulphur compounds have a large ability as donors. One of the most intriguing features of the dtc complexes is their structures, as the existence of square-planar complexes with sulphur donor atoms is quite unusual; the delocalization of the electronic charge cancels the free rotation of the amino group [5]. We have previously studied several complexes formed by dtc derivatives of amino acids and Ni(II), Cu(II), Pt(II), and, taking into account the fast formation of these complexes and their similarities with the derivatives of Pt(II) with DDP and analogues, it is possible that this sort of complex plays an important role as detoxicants with immunopharmacological properties, and probably also in the treatment of gastro-intestinal tumors, where the Pt(II) derivatives have proved to be almost useless [6].

Experimental

Materials

Glycine, DL-alanine, DL-valine, L-valine and DL-leucine were purchased from FLUKA, A.G.; S_2C was from Carlo Erba, and $PdCl_2$ from Aldrich Chem. All other reactives were of high purity and were used as purchased, without any further purification.

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Methods

Chemical analyses for C, H and N, both for the ligands and the complexes, were carried out by conventional methods. Barium and palladium were determined by atomic absorption (Perkin-Elmer, model 2380).

Magnetic susceptibility measurements were performed at room temperature in a Stanton MC-5 Gouy type balance, using $Hg[Co(SCN)_4]$ for calibrating.

Electronic spectra were recorded in a Shimadzu UV-240 double beam spectrophotometer, using fresh methanol solutions of the samples.

Infrared spectra were recorded in the 4000–200 cm^{-1} range in a Perkin-Elmer FT-1730 instrument coupled to a Perkin-Elmer 3600 Data Station; KBr pellets were used to record spectra above 400 cm^{-1} and Nujol and polyethylene discs below 400 cm^{-1}.

X-ray photoelectron spectra were recorded using a Leybold-Heraeus LHS-10 apparatus, using Al Kα radiation, under a pressure of 10^{-9} Torr and using the C(1s) peak at 284.6 eV as reference.

Proton NMR (200.13 MHz) and ^{13}C NMR (50.3 MHz) were recorded on a Bruker WP 200SY spectrometer in CD_3OD solutions using TMS as internal standard. DEPT experiments were performed to assign C multiplicities.

Thermogravimetric (TG) and Differential scanning calorimeter (DSC) curves were recorded on a Mettler TA-3000 system with a Mettler TG-50 thermobalance and a Mettler DSC-20 differential scanning calorimeter. TG diagrams were recorded in a dynamic atmosphere of pure air (100 ml min^{-1}), at a heating rate of 10 °C min^{-1}. DSC curves were obtained in a static atmosphere of air at the same heating rate as for the TG curves.

The mass spectra were recorded in a HP-4988A apparatus, working in the injection direct probe mode with a heating ramp of 25–300 °C at a heating rate of 40 °C/min.

Preparation of the Compounds

All complexes were obtained following a similar method. An aqueous solution of barium dithiocarbamate was slowly added over an aqueous solution of $PdCl_2$ recently prepared by dissolving this salt in water previously heated at 80–90 °C and filtered once the dissolution was reached. The metal salt ligand molar ratio was Pd:Ba = 1:2. The barium dithiocarbamate used as ligands had been previously obtained following the method described by Musil and Irgolic [7] and described elsewhere [8]. Dithiocarbamates of glycine, DL-alanine, DL-valine, L-valine and DL-leucine were obtained.

The solution of $PdCl_2$, which originally is pale yellow, instantaneously changes to deep yellow or even to orange, thus suggesting that the complex is formed immediately, according to the following equation:

$$Pd^{2+} + 2Ba(S_2C\text{–}NH\text{–}CH(R)\text{–}COO) \xrightarrow[(2)\,H^+]{(1)\,Et_2O}$$

$$Pd(S_2C\text{–}NH\text{–}CH(R)\text{–}COOH)_2 + BaCl_2$$

$R = H, CH_2, CH(CH_3)_2, CH_2\text{–}CH(CH_3)_2$

In order to remove barium, the solution is placed in a separation funnel and diaethyl ether is added, followed by the stoichiometric amount of HCl 0.5 M to yield $BaCl_2$; barium remains in the aqueous solution, while the complex moves to the organic phase. The solvent is slowly removed by evaporation. The solid thus obtained, with a bright yellow colour, seemed to be crystalline, but no definite X-ray diffraction pattern could be obtained. Final yield was 80%. The solid was finally dried in a dessicator with P_4O_{10}. Results from the chemical analysis for the compounds obtained are summarized in Table 1.

TABLE 1. Analtyical data

Compounds	C		H		N		Ba		Pd	
	Exp.	Theoret.	Exp.	Theoret.	Exp.	Theoret.	Exp.	Theoret.	Exp.	Theoret.
Ba(gly dtc)·$3H_2O$	10.21	10.57	2.85	2.64	4.26	4.11	40.92	40.35		
Ba(DL-ala dtc)·$3H_2O$	14.02	14.54	3.26	3.10	3.82	3.95	38.55	38.75		
Ba(DL-val dct)·$3H_2O$	18.60	18.82	4.01	3.92	3.58	3.66	35.77	35.90		
Ba(L-val dtc)·$3H_2O$	18.72	18.82	3.98	3.92	3.70	3.66	35.43	35.90		
Ba(DL-leu dtc)·$3H_2O$	21.14	21.24	4.16	4.29	3.61	3.54	34.68	34.72		
Pd(gly dtc)$_2$	18.55	17.70	2.02	1.96	7.06	6.88			26.11	26.16
Pd(DL-ala dtc)$_2$	22.49	22.10	2.93	2.76	6.68	6.45			24.55	24.48
Pd(DL-val dtc)$_2$	29.47	29.36	4.06	4.08	6.10	5.71			21.93	21.68
Pd(L-val dtc)$_2$	29.49	29.36	4.10	4.08	5.98	5.71			22.07	21.68
Pd(DL-leu dtc)$_2$	33.02	32.41	4.91	4.63	5.80	5.40			20.49	20.51

TABLE 2. Main FT-IR bands of the ligands and the complexes

Compounds	ν(N–H)	ν(C_1–N)	ν(C_2–N)	ν(COO^-)		ν(COOH)	ν(C–S)		ν(Pd–S)
				asym.	sym.		asym.	sym.	
Ba(gly dtc)·$3H_2O$	3214	1516	1081	1569	1418		1004	596	
Ba(DL-ala dtc)·$3H_2O$	3318	1529	1164	1557	1417		964	637	
Ba(DL-val dtc)·$3H_2O$	3382	1489	1153	1562	1412		968	670	
Ba(L-val dtc)·$3H_2O$	3387	1490	1159	1568	1409		972	669	
Ba(DL-leu dtc)·$3H_2O$	3415	1471	1163	1571	1406		968	670	
Pd(gly dtc)$_2$	3341	1493	1121			1703	994	635	339
Pd(DL-ala dtc)$_2$	3297	1510	1103			1703	980	674	338
Pd(DL-val dtc)$_2$	3241	1510	1092			1709	990	656	331
Pd(L-val dtc)$_2$	3224	1505	1115			1719	987	651	332
Pd(DL-leu dtc)$_2$	3234	1510	1084			1718	970	658	327

Results and Discussion

FT-IR Spectroscopy

The positions of the main IR bands in the spectra of the ligands and of the complexes are summarized in Table 2.

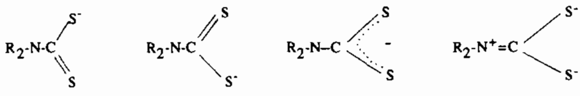
In previous papers, detailed analysis of the IR spectra of free amino acids, ligands derived from amino acids and coordination compounds, similar to those included in the present study, have been reported [8]. Our data on the IR spectra of the ligands show a broad band between 3500–3200 cm^{-1} due to the overlapping of the stretching modes of ν(N–H) and ν(O–H) groups due to the amino groups and the water molecules. For the complexes, this band is less broad and is recorded between 3500–3200 cm^{-1}. This indicates therefore the absence of water molecules in these samples. A band at 3300 cm^{-1} has been previously ascribed to the ν(N–H) stretching mode of dithiocarbamates.

There are two bands that can be ascribed to stretching modes of the C–N group, one belonging to the dithiocarbamate moiety ν(C_1–N) and the other to the amino acid group ν(C_2–N). These bands are recorded between 1510–1480 and 1160–1150 cm^{-1} for the free ligands and between 1520–1490 and 1120–1080 cm^{-1} for the complexes. From crystallographic data reported for the barium salt of the dithiocarbamate derivative from glycine, Ba(dtc gly)·$3H_2O$ [9], the C_1–N distance is 132.2 pm, lower than that corresponding to the C_2–N group (146.5 pm), this last being almost coincident with that corresponding to a single C–N bond (147.0 pm). So, it can be undoubtedly concluded that the band between 1510–1490 cm^{-1} corresponds to the stretching mode of the C–N group of the dithiocarbamate moiety, while that at 1120–1080 cm^{-1} is due to the $NCCO_2^-$ group, on the basis of the larger bond order predicted for the C–N bond from simple valence-bond theory.

The position of the band originated by the ν(C_1–N) has been widely used to discuss the multiplicity of this bond in dithiocarbamates [10, 11]. This behaviour could be originated by the ability of the amines to donate electron density, that could be addressed towards the sulphur bonds via the π system, so leading to a reinforcement of the C–N bond and a shift of its characteristic IR absorption band towards higher wavenumbers [11, 12]. McClaverty and Morrison [13] have attributed this shift of the C_1–N band as a consequence of a "mesomeric drift of electrons from the dithiocarbamate group towards the metal ion".

The slight shift towards lower wavenumbers of the band due to the ν(C_1–N) stretching mode in Pd(II) complexes with respect to Pt(II) is due to the higher acceptor ability of platinum.

The dithiocarbamate ligand can be easily drawn by means of the following resonant forms:



a b c d

From the physicochemical properties of these compounds here studied, the most stable form seems to be the form c, where both sulphur atoms are equivalent and support a delocalized negative charge, together with a multiple bond between the nitrogen and the carbon atoms.

The most informative bands due to the carboxylic group are recorded between 1700–1400 cm^{-1} both for the ligands and for the complexes. For the ligands, isolated as barium salts, two bands are recorded, one for the antisymmetric mode at 1570–1560 cm^{-1} and another between 1420–1400 cm^{-1} due to the symmetric mode. However, the spectra of the complexes show only one band, very intense, between 1720–1700 cm^{-1}, due to the stretching mode of the free carboxylic group. This behaviour undoubtedly demonstrates that the coordination of the ligand does not take place through the carboxylic group.

The ascription of the bands due to the $-CS_2$ has been a matter of controversy among many authors. These bands are usualiy coupled and are very sensitive to the environment of this group [14], but are very useful for distinguishing between monodentate and bidentate ligands. While several authors [15, 16] ascribe these two bands to the ν(C–S) modes of the C=S and C–S units, others [14, 17] ascribe them to the symmetric and antisymmetric modes of the C$\underline{\cdots}$S moiety. Taking into account our crystallographic data for the barium salt of the glycine dithiocarbamate, that indicate almost coincident C–S bond lengths, the second ascription should be valid, as we have confirmed by XP spectra, that (see below) show only a band due to the $S(2p_{3/2})$ level, this confirming the equivalency of both sulphur atoms.

Finally, the Pd–S stretching mode is recorded between 340–325 cm^{-1} as a sharp, intense band, its position being very close to that reported by other authors [18, 19].

Magnetic Properties and Electronic Spectra

All complexes here synthesized are diamagnetic. This result, together with the chemical analysis data and the infrared results, lead us to the conclusion that the local geometry around the Pd(II) cation is square planar, a geometry specially stable for cations with d^8 configuration. However, the symmetry is not usually D_{4h}, as the S–S distance along the edge of the 'square' between sulphur atoms belonging to different ligands is somewhat larger than that between two sulphur atoms belonging to the same ligand, thus giving rise to a D_{2h} symmetry.

Electronic spectra are essentially identical in all cases. Data including the number of bands and their positions, have been summarized in Table 3.

The weakest band, named band I, is due to a metal–ligand charge transfer process which, according to some authors, corresponds to $^1Ag \rightarrow {}^1Au$ [20], although some different authors ascribed it to a charge transfer from the d orbitals of the metal to the π^* system of the ligands [10, 14].

TABLE 3. Electronic spectra of the Pd(II) complexes

Electronic transitions	λ_{max} (nm)	log ϵ
Band I M(d) $\rightarrow$ L(π^*)	460	3.60
Band II L(n) $\rightarrow$ L(π^*)	350	4.76
Band III L(π) $\rightarrow$ L(π^*)	298	5.72
Band IV L(π) $\rightarrow$ L(π^*)	238	5.23
	205	5.09

Band II corresponds to an intraligand transition n–π^*, as described in the literature [8, 10] for transition between levels more or less originated by sulphur atoms.

Band III corresponds to an intraligand transition π–π^* and is the most intense band recorded here (log ϵ = 5.72). This band has been ascribed to a transition between levels originated by the S$\underline{\cdots}$C$\underline{\cdots}$S moiety and very often it shifts depending on the nature of the central atom, but not on the nature of the rest of the ligand [8, 18].

Band IV is here recorded as a split band. It shows a very large extinction coefficient and also corresponds to a π–π^* intraligand transition, although due to molecular orbitals originated in the N$\underline{\cdots}$C$\underline{\cdots}$S moiety [8, 10, 14]. This band shows an hypsochromic shift relative, depending on the other atoms bound to the nitrogen atom [18].

X-ray Photoelectron Spectra

The binding energy values for Ba(dtc-DL-leu)·$3H_2O$ and Pd(dtc-DL-leu)$_2$ are included in Table 4. It should be also stressed that the Pd/X (X = N, S, C) atomic ratios calculated from the chemical analysis study and from the XPS data show a very good agreement (0.5 and 0.4 for X = N, 0.25 and 0.25 for X = S, and 0.07 and 0.06 for X = C).

The average binding energy for O(1s) is 533.0 eV for the complex, and 531.2 eV for the ligand, thus confirming the larger negative charge in the ligand, where the moiety $-COO^-$ exists.

TABLE 4. Electron binding energies

Ligand	Ba		S	N	C			O
Ba(DL-leu dtc)·$3H_2O$	$3d_{3/2}$	$3d_{5/2}$	2p	1s	1s			1s
					ref.	CS_2^-	COO^-	
Binding (eV)	795.5	780.1	161.9	399.2	284.6	286.2	288.0	531.2
Complex	Pd		S	N	C			O
Pd(DL-leu dtc)$_2$	$3d_{3/2}$	$3d_{5/2}$	2p	1s	1s			1s
					ref.	CS_2^-	COOH	
Binding (eV)	342.5	337.3	162.6	400.0	284.6	286.5	289.0	533.0

For the N(1s) orbital, the binding energy in the complex is 400.0 eV and for the ligand 399.2 eV, very close, indicating that the nitrogen atom has no donor activity in this complex.

The signal due to C(1s) is used as reference (284.6 eV), but, in addition, small peaks can be recorded at 286.5 and 289.0 eV (complex) and 286.2 and 288.0 eV (ligand), that should be ascribed to carbon atoms from the dithiocarbamate and carboxylic groups, respectively (see Fig. 1).

The fact that the binding between the ligand and the metal atoms takes place through the sulphur atoms can be checked again from the binding energy for the S(2p) orbitals, 162.6 eV (complex) and 161.9 eV (ligand). This sort of information is used by several authors [21, 22] to argue about the existence of simple or double S–S bonds, according to the resonance forms above depicted; our results seem to be quite definitive, as only one signal is recorded (see Fig. 2), thus definitely confirming that both sulphur atoms within each ligand molecule should be equivalent.

The $3d_{3/2}$ and $3d_{5/2}$ values for the palladium orbitals (342.5 and 337.3 eV, respectively) agree very well with those reported in the literature for Pd(+2) species [23]. Those for barium occur at 795.5 and 780.1 eV, coincident with those for compounds formed by this same cation and similar anions, as previously reported by others [24]. A correlation between these values and the electronegativity difference between the palladium cation and the donor ligand atoms is meaningless, due to the probable π-acceptor ability of these ligands.

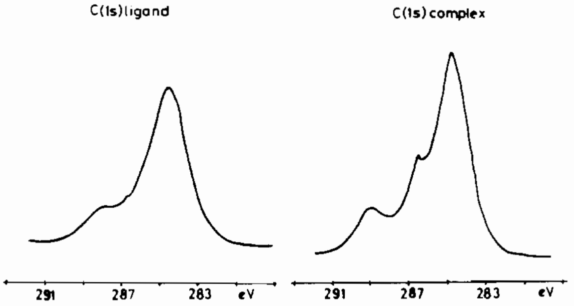


Fig. 1. Binding energy of carbon 1s X-ray photoelectron spectra.

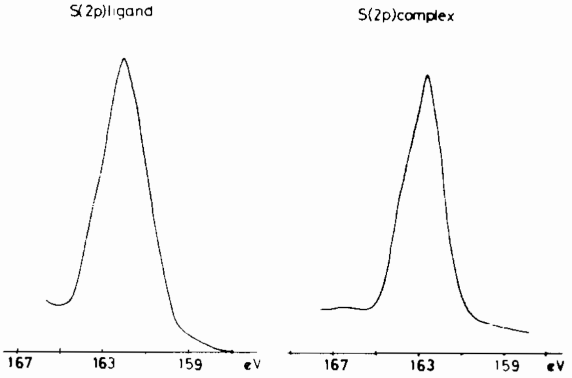
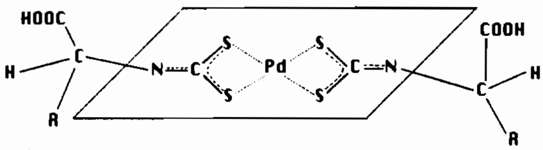


Fig. 2. Binding energy of sulphur 2p X-ray photoelectron spectra.

^{1}H and ^{13}C NMR Spectroscopy

The main features of these compounds recorded using these techniques have been summarized in Fig. 3 and Tables 5 and 6. The values for the ^{1}H signals are very close for the ligands and the corresponding complexes. A general shift towards larger δ values is observed from one ligand to the corresponding complex, probably due to the larger electron density existing on these protons in the former case. The results obtained for the dithiocarbamate derivates of DL- and L-valine indicate that there is no difference in the behaviour shown by these complexes derived for the different chiralities of the carbon atom.



Scheme 1.

The values for the ^{13}C signals are in agreement for the structure above suggested for these complexes. Again, no definitive conclusion can be reached about the existence of LL, DD, or DL diastereoisomers, from the results obtained for the derivatives of DL- and L-valine, because no difference was observed in their spectra.

It may be concluded that the distance between the chiral carbon atoms of the ligands lead to a complete equivalence between the protons and the carbon atoms, thus cancelling any duplication of the NMR signals.

Thermal Study

TG and DSC techniques have been used to follow the thermal behaviour of these complexes. According to the results obtained, the complexes are not volatile and their decomposition takes place in different steps; the main features have been summarized in Table 7.

The complexes obtained with the dithiocarbamate derivatives of glycine, DL-alanine, and DL-valine show a similar behaviour, with two main processes: first an endothermic one, probably corresponding to a multiple decarboxylation process, and a strong second one, also exothermic, probably corresponding to pyrolysis of the organic matter existing in these compounds. The decomposition enthalpy for Pd(dtc-DL-ala)$_2$ is $\Delta H = 113.4$ kJ mol^{-1}. However, the com-

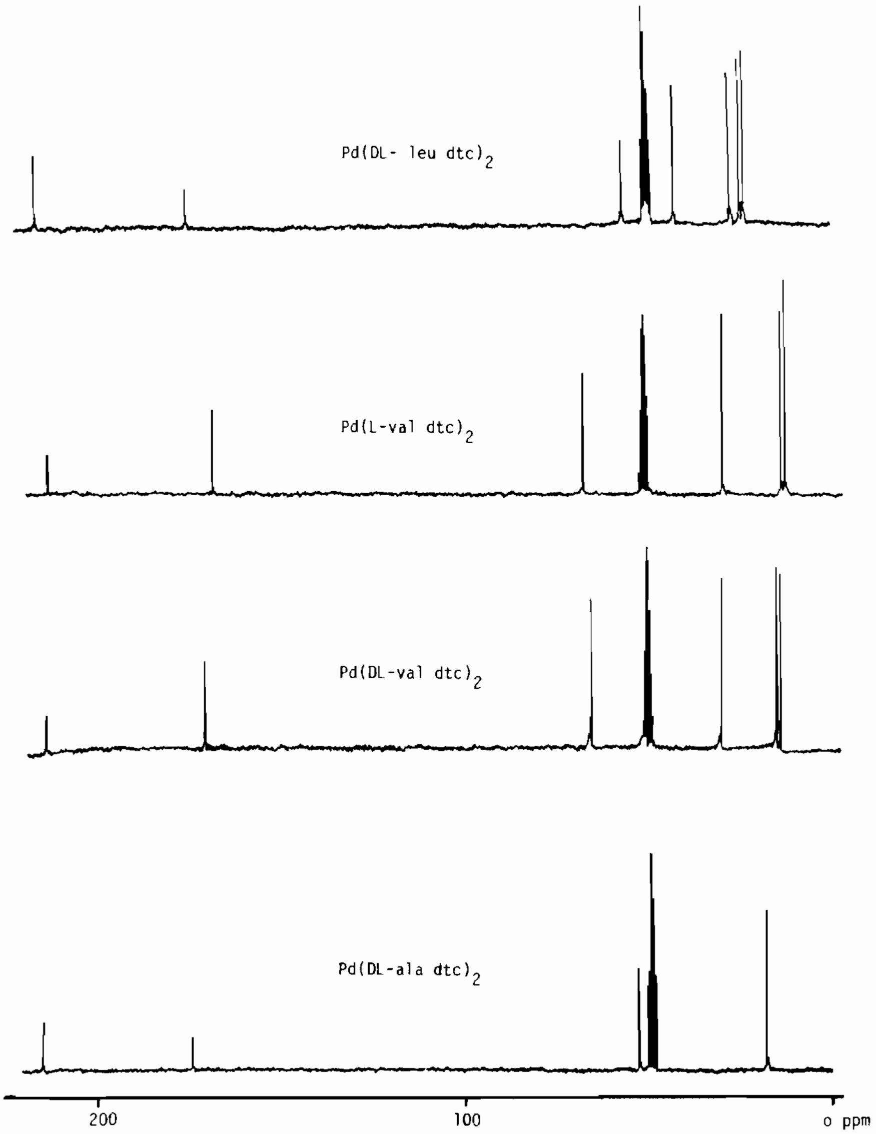


Fig. 3. ^{13}C NMR shifts of the complexes.

plex obtained with the dithiocarbamate derivative of DL-leucine exhibits a very different decomposition pattern; the decomposition temperature is lower than for the other complexes, the first endothermic peak is double, and several exothermic peaks, due to pyrolysis processes, are recorded.

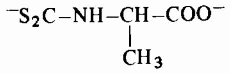
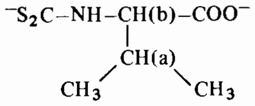
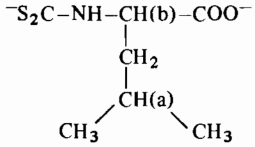
From the temperature corresponding to decomposition, the complexes can be listed in the following stability order: Pd(dtc-DL-val)$_2$ > Pd(dtc-DL-ala)$_2$ > Pd(dtc-gly)$_2$ > Pd(dtc-DL-leu)$_2$.

The final product of the decomposition is palladium oxide, as confirmed by X-ray diffraction and infrared spectroscopy, as well as from the experimental and expected weight loss.

Mass Spectra

The complexes and the ligands here studied have been submitted to analysis by mass spectrometry. All ligands show a common signal at *m*/*e* = 149 amu, corresponding to $[S_2C-NH-CH_2-COO]^+$, indicating a large stability for this group, where the lateral chain of the amino acid has been lost. As observed with other dithiocarbamates studied in the literature [25, 26], the molecular ion is not recorded. For the glycine-derivative ligand, peaks are recorded at *m*/*e* = 203 (loss of two water molecules, from the three existing in the parent ligand) and 167 (loss of the remaining water molecule). Similar conclusion for the other ligands would be ill-founded, as no crys-

TABLE 5. ^1H NMR data[a]

L	$BaL \cdot 3H_2O$				$Pd(HL)_2$		
	δ (ppm)		J (Hz)		δ (ppm)		J (Hz)
$^{-}S_2C{-}NH{-}CH_2{-}COO^{-}$	CH_2	4.03(s)			CH_2	4.29(s)	
 $^{-}S_2C{-}NH{-}CH(CH_3){-}COO^{-}$	CH_3	1.17(d)	$CH_3{-}CH$	6.80	CH_3	1.57(d)	7.2
	CH	4.38(q)			CH	4.83(q)	7.2
 $^{-}S_2C{-}NH{-}CH(b)(CH(a)(CH_3)_2){-}COO^{-}$	CH_3	0.78(d)	all	7.0	CH_3	1.07(d)	6.7
		0.77(d)				1.08(d)	6.7
	CH(a)	2.02(m)			CH(a)	2.35(m)	6.6
	CH(b)	4.47(d)			CH(b)	4.67(d)	5.8
 $^{-}S_2C{-}NH{-}CH(b)(CH_2{-}CH(a)(CH_3)_2){-}COO^{-}$	CH_3	0.8(d)	all	7.0	CH_3	1.04(d)	6.0
		0.8(d)				1.05(d)	6.0
	$CH_2 + CH(a)$	1.51(m)			$CH_2 + CH(a)$	1.80(m)	
	CH(b)	4.47(dd)			CH(b)	4.80(dd)	8.4

[a] Symbols for multiplicities of signals, s = singlet, d = doublet, q = quartet, m = multiplet.

TABLE 6. ^{13}C NMR data (δ, ppm)[a]

Complexes	S_2C	COOH	C(1)	C(2)	C(3)	C(4)
$Pd(DL\text{-}ala\ dtc)_2$	214.46	173.67	52.32	17.46		
$Pd(DL\text{-}val\ dtc)_2$	215.12	172.70	62.35	32.07	18.53 19.36	
$Pd(L\text{-}val\ dtc)_2$	214.93	172.37	62.14	32.09	18.55 19.37	
$Pd(DL\text{-}leu\ dtc)_2$	214.65	174.23	51.51	41.41	26.02	22.06 23.22

[a] Atom numbering:

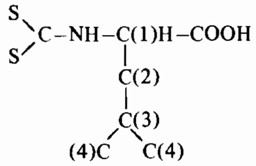

$S_2C{-}NH{-}C(1)H(C(2){-}C(3)(C(4))_2){-}COOH$

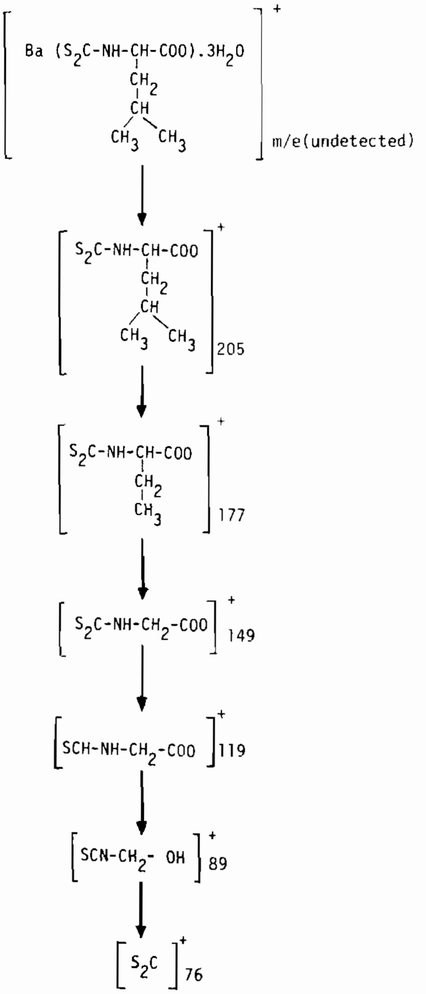
TABLE 7. Thermal data for the complexes

	TG(DTG)		% Weight loss (%)			DSC	
	T (°C)	Process		Exp.	Theoret.	T (°C)	Process
$Pd(gly\ dtc)_2$	200–390	decarboxylation				200 (endo + exo)	decarboxylation
	390–420	pyrolysis	PdO		30.04	420 (exo)	pyrolysis
$Pd(DL\text{-}ala\ dtc)_2$	175–200	decarboxylation				200 (endo)	decarboxylation
	200–430	pyrolysis	PdO	28.32	28.17	420 (exo)	pyrolysis
$Pd(DL\text{-}val\ dtc)_2$	180–210	decarboxylation				210 (endo)	decarboxylation
	210–300	pyrolysis	PdO	24.95	24.31	320 (exo)	pyrolysis
$Pd(DL\text{-}leu\ dtc)_2$	135–190	decarboxylation				188 (endo)	decarboxylation
	190–235	pyrolysis				330 (exo)	pyrolysis
	235–280	pyrolysis	PdO	23.59	23.61	350 (exo)	pyrolysis
	280–410	pyrolysis				390 (exo)	pyrolysis

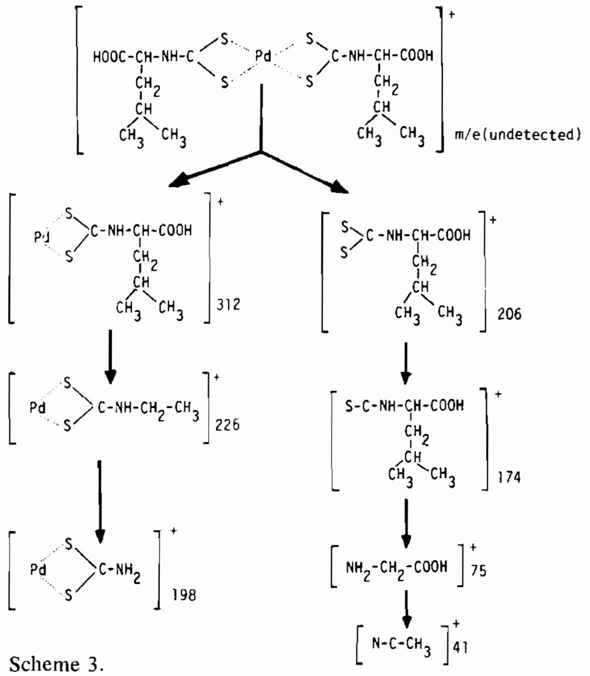
tallographic evidence exists on the number of water molecules existing in the barium salts (only the glycine derivative has been studied), although from the TG results, *c.* three water molecules should exist in all cases.

A step-by-step decomposition process is here proposed, based on the results obtained for the DL-leucine derivative (Scheme 2). From this Scheme, it can be concluded that after the loss of water, the dithiocarbamate ion is formed, and then breaks down, depending on the specific amino acid it has been obtained from. This is because the decomposition pattern seems to depend on the length of the lateral chain, finally producing the common ion with m/e = 149 amu. Finally, a sulphur atom seems to be lost and, after a series of identified peaks, the $[S_2C]^+$ species (m/e = 76 amu) is formed.

With respect to the complexes, the analysis is rather complicated and should depend on the nature of the metal–ligand bond. Ascription is done on the basis of the most common ions for all complexes and the behaviour reported in the literature [27, 28] for similar compounds. Again, the analysis is step-by-step depicted for Pd(dtc-DL-leu)$_2$ (see Scheme 3).



Scheme 2.



Scheme 3.

From this scheme we could conclude that a whole ligand is lost, as peaks are recorded at m/e = 164 (DL-alanine), 192 (DL-valine) and 206 (DL-leucine) (unfortunately, the mass spectrum for the glycine derivative could not be recorded). These ligands lose a sulphur atom and in all cases the peaks at m/e = 132 (S-C-ala), 160 (S-C-val) and 174 (S-C-leu) are recorded. Among all other peaks recorded, only three are common to all complexes studied, and that can be tentatively ascribed to $[PdS_2{-}C{-}NH{-}CH_2{-}CH_3]^+$ (m/e = 226), $[PdS_2{-}C{-}NH_2]^+$ (m/e = 198) and $[N{-}C{-}CH_3]^+$ (m/e = 41).

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