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New PtS_4 Chromophores of Dithiocarbamates Derived from α-Amino Acids: Synthesis, Characterization and Thermal Behaviour

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Abstract

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

The stoichiometry of these complexes is Pt:L = 1:2 and coordination around the metallic cation seems to be a 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. ^{13}C NMR spectra indicate that all complexes are optically inactive due to the close vicinity of 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 metallic platinum. The thermal stability of these complexes decreases in the order $Pt(gly\ dtc)_2 > Pt(DL\text{-}ala\ dtc)_2 > Pt(DL\text{-}val\ dtc)_2 > Pt(DL\text{-}leu\ dtc)_2$.

Introduction

Metallic dithiocarbamates have received much interest in the last few years because of their very diverse applications in such different fields as accelerators in vulcanization, high pressure lubricants and fungicides and pesticides in biological and biochemical fields [1].

Dithiocarbamates are organo-sulphur compounds with high donating properties. We have prepared compounds of the type $[PtS_4]$, through reaction between Pt(II) and dithiocarbamates derived from α-amino acids, previously synthesized by us as barium salts, $Ba(aa\ dtc)\cdot 3H_2O$, (aa = glycine, DL-alanine, DL-valine, DL-leucine). These sort of compounds show detoxicant and immunopharmacological properties [2] and react readily with Pt(II), so providing an interesting route to withdraw from the organism Pt(II) in excess, from antitumoral therapy with *cis*-DDP (*cis*-dichlorodiamminplatinum) and its derivatives. A study of their detoxicant properties is under way, as it is well known that these compounds have a marked nephrotoxicity [3]. Intravenous infusion of diethyl dithiocarbonate reduces nephrotoxicity when administered in conjunction with *cis*-platinum chemotherapy [4].

Experimental

Materials

Glycine, DL-alanine, DL-valine, and DL-leucine were purchased from Fluka, A.G.; S_2C was from Carlo Erba and $(NH_4)_2(PtCl_4)$ from Aldrich Chem. All other reactives were of high purity and were used as purchased, without any further purification.

Methods

Chemical analyses for C, H and N, both for the ligands and the complexes were carried out by conventional methods. Barium and platinum were determined by atomic absorption (Perkin-Elmer, mod. 2380), and TG analysis (Mettler TG-50) was used as well to confirm the platinum content.

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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 solutions of the samples in methanol.

Infrared spectra were recorded in the 4000–200 cm^{-1} range in a Perkin-Elmer FT-IR 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 200 SY spectrometer in CD_3OD solutions using TMS as internal standard. DEPT experiments were performed to assign C multiplicities.

Thermogravimetric (TG) and Differential Scanning Calorimetry (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 analysis.

Preparation of the Complexes

A similar method was used to obtain all complexes studied in this work. An aqueous solution of barium dithiocarbamate is slowly added to an aqueous solution of $(NH_4)_2(PtCl_4)$ (Pt:Ba molar ratio = 1:2). Previously, the barium salts of the dithiocarbamates derived from the α-amino acids (glycine, DL-alanine, DL-valine, and DL-leucine) were obtained following a method similar to that described by Musil and Irgolic [5] and described elsewhere [6, 7].

The brick red solution of $(NH_4)_2(PtCl_4)$ changes its colour immediately to pale yellow upon addition of the ligand, suggesting the fast formation of the new complex, according to a reaction that we assume to be

$$Pt^{2+} + 2Ba(S_2C\text{–}NH\text{–}CH(R)\text{–}COO) \xrightarrow[(2)\ HCl]{(1)\ Et_2O} Pt(S_2C\text{–}NH\text{–}CH(R)\text{–}COOH)_2$$

($R = H, CH_3, CH(CH_3)_2, CH_2CH(CH_3)_2$)

In order to remove Ba^{2+} cations, the solution is transferred to a separation funnel, where diethylether and then HCl 0.1 N are added, this last in the stoichiometric amount to form $BaCl_2$. The ether is left to evaporate, leaving a deep-orange solid that is purified with ether (yield 80%) in a desiccator over P_4O_{10}.

Chemical analyses data for the ligands and the complexes are shown in Table 1.

Results and Discussion

The most significant bands recorded in the IR spectra of the ligands and the complexes have been collected in Table 2.

TABLE 1. Analytical data[a]

Compounds	C (%)	H (%)	N (%)	Ba (%)	Pt (%)
Ba(gly dtc)·$3H_2O$	10.21	2.85	4.26	40.92	
	(10.57)	(2.64)	(4.11)	(40.35)	
Ba(DL-ala dtc)·$3H_2O$	14.02	3.26	3.82	38.55	
	(14.54)	(3.10)	(3.95)	(38.75)	
Ba(DL-val dtc)·$3H_2O$	18.60	4.01	3.58	35.77	
	(18.82)	(3.92)	(3.66)	(35.90)	
Ba(DL-leu dtc)·$3H_2O$	21.14	4.16	3.61	34.68	
	(21.24)	(4.29)	(3.54)	(34.72)	
Pt(gly dtc)$_2$	14.02	1.52	5.35		39.20
	(14.54)	(1.62)	(5.65)		(39.21)
Pt(DL-ala dtc)$_2$	18.32	2.27	5.34		37.12
	(18.35)	(2.29)	(5.35)		(37.28)
Pt(DL-val dtc)$_2$	24.68	3.43	4.87		33.26
	(24.87)	(3.45)	(4.84)		(33.69)
Pt(DL-leu dtc)$_2$	27.47	4.01	4.71		32.84
	(27.67)	(3.95)	(4.62)		(32.14)

[a] Calculated values are given in parentheses.

TABLE 2. Ascription of the main IR bands of the ligands and the complexes

Compounds	ν(N–H)	$\nu(C_1\cdots N)$	$\nu(C_2–N)$	$\nu(COO^-)$		ν(COOH)	$\nu(C\cdots S)$		ν(Pt–S)
				as	s		as	s	
Ba(gly dtc)·$3H_2O$	3214	1516	1082	1569	1418		1004	596	
Ba(DL-ala dtc)·$3H_2O$	3318	1529	1164	1557	1417		964	637	
Ba(DL-val dtc)·$3H_2O$	3387	1492	1159	1568	1409		972	669	
Ba(DL-leu dtc)·$3H_2O$	3415	1490	1163	1571	1406		968	670	
Pt(gly dtc)$_2$	3340	1505	1119			1704	995	669	338
Pt(DL-ala dtc)$_2$	3452	1516	1138			1704	967	663	338
Pt(DL-val dtc)$_2$	3458	1526	1097			1724	1029	669	318
Pt(DL-leu dtc)$_2$	3231	1516	1084			1718	1025	658	318

For both sets of compounds, a broad band at 3500–3300 cm^{-1}, due to the N–H stretching modes [1, 9] is recorded.

The carboxylic group bands in the 1600–1400 cm^{-1} region are different for the ligands and the complexes. While for the ligands (isolated in the form of barium salts) two bands are recorded at 1570–1560 (antisymmetric ν(COO) mode) and 1420–1400 (symmetric ν(COO) mode) cm^{-1}, the platinum complexes show only an intense band at 1725–1700 cm^{-1} corresponding to vibration of the free carboxylic group. This behaviour clearly states that coordination in the complexes does not take place through the carboxylic group, but through the sulphur atoms of the ligands [2, 8, 9].

With regard to the ν(C–N) stretching modes, two bands are recorded, one due to the stretching mode of the C–N unit corresponding to the bond between the dithiocarbamate carbon atom (C_1–N), see labelling of the carbon atoms in Table 4) and the amino acid nitrogen atom, and another corresponding to the $\nu(C_2–N)$ mode. These bands are recorded between 1510–1480 and 1160–1150 cm^{-1} for the ligands and 1530–1500 and 1140–1100 cm^{-1} for the complexes, respectively. Crystallographic data previously reported by us [6] for the barium salt of one of the ligands here used, Ba(dtc gly)·$3H_2O$, have shown that the C_1–N distance (132.2 pm) is shorter than that found in the C–N moiety of the amino acid fragment (146.5 pm), which coincides with that corresponding to a single C–N bond (147.0 pm); then, it can be safely assumed that the band at 1530–1510 cm^{-1} corresponds to the C–N stretching mode of the S_2CN group, while that at 1140–1100 cm^{-1} is due to the $NCCO_2^-$ group. The position of this band (due to the C_1–N stretching mode), close to 1500 cm^{-1} has been used by several authors [2, 8, 10, 11] to explain the chelating ability of this sort of ligand and the multiplicity of this bond, and shows as well the acceptor properties of the Pt(II) species.

The assignation of the bands due to the $-CS_2$ moiety has caused a great controversy in the literature. Two bands that can be ascribed to the C–S stretching modes of this moiety are usually recorded. While several authors ascribed these bands to the C=S and C–S stretching modes [12, 13], very recently other authors [8, 14] ascribed these two bands to the symmetric and antisymmetric modes of this group, this ascription being, in our opinion, more reliable, as, in our previous studies on the crystallographic structure of the ligand, the C–S distances were nearly coincident, 171.7 and 171.8 pm, thus suggesting that both C–S bonds are identical, with a somewhat participation of a multiple bond. A further confirmation of this assumption comes from the X-ray photoelectron spectra of these compounds that show a single $S(2p_{3/2})$ signal, indicating the equivalence between both sulphur atoms (see below).

Finally, the band corresponding to the ν(Pt–S) stretching mode is recorded at 340–320 cm^{-1}, from comparison with data published by several authors for similar dithiocarbamate complexes fairly similar to those studied here.

The magnetic study carried out on these complexes indicates that all they are diamagnetic; together with the infrared data and the chemical analysis results, it can be concluded that the immediate environment of the Pt(II) species should be a near-square plane geometry. This geometry is very usual for d^8 ions; however, some sort of distortion exists from the ideal D_{4h} symmetry, due to the fact that the sulphur–sulphur distance between two sulphur atoms belonging to the same ligand is shorter than the sulphur–sulphur distance between two sulphur atoms belonging to two ligands coordinated to the same cation in *cis* positions, i.e. in a D_{2h} symmetry [15, 16].

Electronic spectra are essentially identical in all complexes, and their main features (number, position and intensity of the bands) have been summarized in Table 3.

Taking into account that the donating sulphur atoms in the dithiocarbamate complexes in someway determine the square-planar structure of complexes

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

Electronic transitions		λ_{max} (nm)	log ϵ
Band I	M ⟶ L	385	2.48
Band II	L ⟶ L*	342	3.21
Band III	L ⟶ M	303	2.90
Band IV	M ⟶ L	254	3.70
Band V	(unascribed)	210	3.41

with d^8 metal cations, the metal–sulphur bond has a π-type character, and so these complexes do not usually show Laporte-forbidden d–d bands, although four bands of this type would be expected for the D_{2h} symmetry.

Ascription of the bands has been carried out on the basis of the molecular orbitals calculations for PtS_4 in the literature [17, 18]. Band I, the weakest one, corresponds to a metal–ligand charge transfer process, and it has been previously recorded for dithiolates, dithiocarboxylates and dithiocarbamates; several authors [16, 19] have ascribed this band to transitions $^1A_{1g} \rightarrow {}^1B_{3u}$ and $^1A_{1g} \rightarrow {}^1A_{1u}$. According to data in the literature, band II corresponds to a $\pi \rightarrow \pi^*$ transition in the $S \cdots C \cdots S$ group [8]. Bands III and IV are L → M and M → L charge transfer bands, respectively. These bands are similar to the charge transfer bands observed for complexes of Pd(II) and Pt(II) cations in a near-square planar, D_{2h} environment, and have been ascribed [8, 19, 20] to transitions $^1A_{1g} \rightarrow {}^1B_{2u}$, $^1B_{3u}$, and $^1A_{1g} \rightarrow {}^1B_{1u}$, $^1B_{2u}$, $^1B_{3u}$, respectively. Finally, band V has not been undoubtedly ascribed in the literature to a particular electronic transition, as this band is not always recorded, and sometimes it has been ascribed to $\pi \rightarrow \pi^*$ transitions [8], while other authors have ascribed it [16] to d–p transitions, and it is even unascribed in some other cases [20].

Data for the ^1H and ^{13}C NMR spectra of complexes Pt(aa dtc)$_2$ are shown in Table 4. The observed shifts are very similar to those of free amino acids and the main differences are present in the $-S_2C-NH-CH-COOH$ grouping. In the ^1H NMR spectra, a deshielding of H(1) to values close to 4.5 ppm, similar to that described for other complexes of amino acid dithiocarbamates, is observed [6, 7].

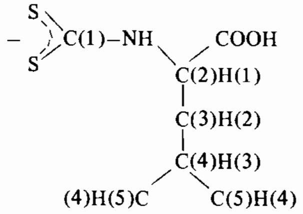
In the ^{13}C NMR spectra (as represented in Fig. 1), the hydrocarbonated moiety presents shifts lower than *c.* 2 ppm, and the carboxylic carbon shielding is *c.* 3 ppm, in comparison to the free amino acids, while a *c.* 173 ppm shift is displayed by the dithiocarbamate carbon. All these data agree with the proposed structures for these complexes. Unfortu-

TABLE 4. ^1H and ^{13}C NMR spectral data of the Pt(aa dtc)$_2$ complexes[a]

Complexes	H(1)	H(2)	H(3)	H(4)
^1H NMR[b] δ (ppm) [J (Hz)]				
Pt(gly dtc)$_2$	4.28s			
Pt(DL-ala dtc)$_2$	4.69q [7.1]	1.61d [7.1]		
Pt(DL-val dtc)$_2$	4.44d [6.0]	2.33m [6.7] [6.0]	1.06d [6.8] 1.04d [6.8]	
Pt(DL-leu dtc)$_2$	4.67dd [8.6] [6.3]	1.83m	1.83m	1.08d [5.8]

	COOH	C(1)	C(2)	C(3)	C(4)	C(5)
^{13}C NMR δ (ppm)						
Pt(DL-ala dtc)$_2$	173.71	214.62	52.62	17.44		
Pt(DL-val dtc)$_2$	172.37	214.80	62.84	33.30	19.43 18.57	
Pt(DL-leu dtc)$_2$	173.60	214.97	55.65	41.52	26.15	23.15 22.05

[a]Atom numbering:



[b]Symbols for multiplicities of the signals, s = singlet, d = doublet, q = quartet, m = multiplet, aa = α-amino acid.

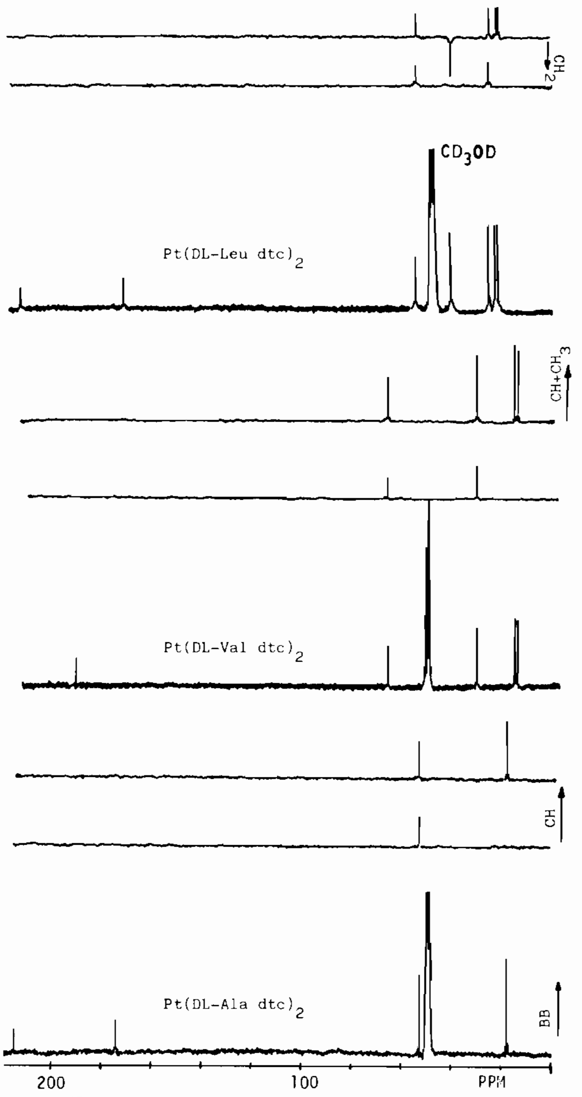
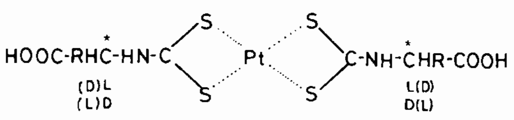


Fig. 1. ^{13}C NMR shifts of the complexes.

nately, the spectrum of the complex Pt(gly dtc)$_2$ has not been recorded, as the complex immediately decomposes in solution.

There is no spectroscopic evidence for the presence of the expected diastereoisomers for these compounds: LL (and its specular image, DD) and LD(DL), depending on the configuration of the Cα atom of the amino acid, existing in the ligand molecule (Scheme 1).

The distances existing between both ligands and the chiral centers make differences close to zero, and both hydrogen and carbon nuclei behave as magnetically equivalent in the diastereoisomer complexes, and duplication of the NMR signals is not observed.



Scheme 1.

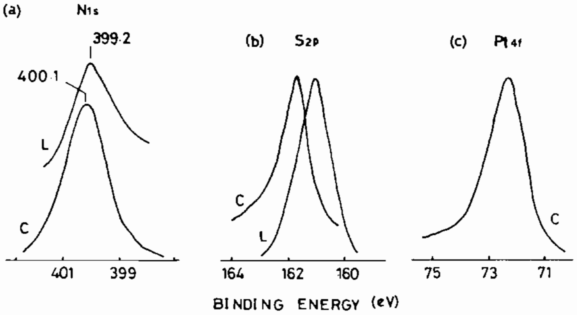


Fig. 2. X. p. spectra. (a) N(1s); (b) S(2p$_{3/2}$); (c) Pt(4f$_{7/2}$). L = ligands, C = complexes.

In a previous paper [21] the X-ray photoelectron spectra of the substances used as ligands in the present paper, in the form of barium salts, Ba(aa dtc)·3H$_2$O, have been described. However, a similar study has not been carried out in the case of the Pt(II) complexes studied here, as many peaks due to the support used in the UHV chamber (molybdenum) introduce some uncertainty in the origin of the signals recorded; this overlapping mainly affects signals due to oxygen and carbon. On the contrary, the value observed for the binding energy of the N(1s) electrons, 400.1 eV, is 0.9 eV larger (Fig. 2) than that recorded for the ligand, thus accounting for an increase of the bonding energy of the C—N with respect to that of the free ligand.

A similar behaviour is observed in the case of the signals due to the sulphur atoms: the S(2p$_{3/2}$) signal is recorded at 162.8 eV for the complex, 1.5 eV larger than that for the free ligand (Fig. 2), an increase fairly close to that reported in the literature (+1.2 eV) for compounds similar to those studied here [22]. Similarly, the value 72.3 eV recorded for the Pt(4f$_{7/2}$) level is in agreement with data previously reported [22, 23].

The thermal behaviour of the isolated complexes has been studied by TG and DSC. According to our results, the compounds are non-volatile, and a multistep decomposition path can be observed, which main features have been described in Table 5; however, these are not independent steps, but overlapping is usually observed, leading, in all cases, to formation of metallic platinum. On the contrary, Sharma [24] has reported that decomposition of dithiocarbamate complexes of Pt(II) lead to formation of non-stoichiometric platinum sulphide.

On the other hand, the thermal stability of these complexes decreases in the order Pt(gly dtc)$_2$ > Pt(DL-ala dtc)$_2$ > Pt(DL-val dtc)$_2$ > Pt(DL-leu dtc)$_2$, thus an inverse relationship between the molecular weight and the thermal stability exists. Thermal decomposition of the glycine complex starts above

TABLE 5. Thermal data for the complexes (°C)

	TG		Weight loss (%)		DSC	
	temperature (°C)	process	experimental	theoretical	temperature (°C)	process
Pt(gly dtc)$_2$	220–285	decarboxylation			250 (endo)	decarboxylation?
	285–375	pyrolysis			265 (exo)	pyrolysis
	375–380	pyrolysis			300 (exo)	pyrolysis
	380–500	pyrolysis	Pt(residue) 60.80	60.59	400 (exo)	pyrolysis
Pt(DL-ala dtc)$_2$	175–240	decarboxylation	16.93	16.82	205 (endo)	decarboxylation
	240–440	pyrolysis			240 (exo)	pyrolysis
	440–490	pyrolysis			390 (exo)	pyrolysis
			Pt(residue) 61.03	62.43	450 (exo)	pyrolysis
Pt(DL-val dtc)$_2$	170–220	decarboxylation	15.81	15.20	200 (endo)	decarboxylation
	220–355	pyrolysis			320 (exo)	pyrolysis
	355–460	pyrolysis			370 (exo)	pyrolysis
			Pt(residue) 66.74	66.31	420 (exo)	pyrolysis
Pt(DL-leu dtc)$_2$	150–210	decarboxylation	13.93	14.49	186 (endo)	decarboxylation
	210–350	pyrolysis			300 (exo)	pyrolysis
	350–540	pyrolysis			390 (exo)	pyrolysis
			Pt(residue) 67.16	67.86	440 (exo)	pyrolysis

220 °C, a temperature quite close to that of the decomposition of Pt(II) *N*-ethyl,*m*-tolyl-dithiocarbamate [25].

It is quite difficult to establish the mechanism followed by the decomposition reaction of these complexes; nevertheless, it seems to be very different from that displayed by the Ni(II) derivatives [26]. From the TG and DSC data, the first step in the decomposition of these compounds (except for the glycine derivative) seems to be a decarboxylation, between 150–285 °C (Table 5). The solids from decomposition during this first step are very unstable and rapidly decompose to yield three or even more exothermic effects in their DSC curves, due to pyrolysis of the organic residue. After this pyrolysis, metallic platinum is the final product of the decomposition. Weight loss data have been summarized in Table 5.

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