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Hydrophilic platinum complexes of N-2-hydroxyethyland N,N-di(2-hydroxyethyl)-N'-benzoylthiourea ligands. Crystal and molecular structure of N,N-di(2-hydroxyethyl)-N'-benzoylthiourea

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Abstract

The crystal and molecular structure of hydrophilic N,N-di(2-hydroxyethyl)-N'-benzoylthiourea (H_3L^4) has been determined. This ligand coordinates to Pt(II), Pd(II) and Ni(II) in a bidentate manner yielding essentially neutral complexes of the type cis-[Pt $(H_2L^4)_2$]. By contrast, N-(2-hydroxyethyl)-N'-benzoylthiourea (H_3L^5) behaves like a monodentate thiourea ligand and reacts with Pt(II) to yield a mixture of cis and trans complexes of [Pt $(H_3L^5)_2Cl_2$]. The (+)FAB mass spectrum of the latter complexes is also discussed.

Keywords: Crystal structures; Platinum-substituted thiourea complexes; Hydrophilic complexes

1. Introduction

The facile synthesis of N, N-dialkyl-N'-acylthioureas (HL) and N-alkyl-N'-acylthioureas (H_2L) from readily available starting materials allows for the preparation of a wide variety of ligands with interesting properties. The simplest of these ligands have attracted considerable attention as selective reagents for the liquid-liquid extraction and preconcentration of platinum group metals (PGMs) [1], as well as their potential chromatographic separation [2]. Despite the superficial similarity of the monoalkyl- (H₂L) and dialkyl-substituted (HL) ligands, these ligands show remarkably different coordination chemistry to Pt(II), Pd(II) and Ni(II). Particularly interesting is the hydrogen-bond controlled unidentate coordination of the potentially bidentate ligand, N-propyl-N'-benzoylthiourea (H_2L^1) , to Pt(II), to yield predominately cis-[Pt(H₂L¹)₂Cl₂], together with a small amount of the trans isomer [3]. By contrast, the N, N-di(n-butyl)-N'-benzoylthioureas (HL²) coordinate to Pt(II) to yield exclusively cis-[PtL²₂] complexes [4], a tendency mirrored for other d⁸ metals such as Pd(II) [5] and Ni(II) [6,7]. Recently, however, we characterized the first example of a trans-[PtL³₂] complex, where HL^3 is N,N-di(n-butyl)-N'-naphthoylthiourea [8].

As part of our interest in these ligands and the potential influence of intramolecular hydrogen bonding effects on their coordination of the PGMs, we have studied the coordination chemistry of the hydrophilic N,N-di(2-hydroxyethyl)-N'-benzoylthiourea (H₃L⁴) and N-(2-hydroxyethyl)-N'-benzoylthiourea (H₃L⁵) ligands (Scheme 1) with reference to the d⁸ metals Pt(II), Pd(II) and Ni(II). Hoyer and co-workers recently reported a study of the acid dissociation and stability constants of several related water-soluble di-substituted acylthioureas, including H₃L⁴, with a number of first row transition metal ions in dioxane/water solutions [9].





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We report here the characterization of some new water-soluble Pt(II) complexes of the ligands H_3L^4 and H_3L^5 (Scheme 1), as well as the crystal and molecular structure of the ligand H_3L^4 .

2. Experimental

2.1. Instrumentation and chemicals

All ¹H NMR spectra were recorded in 5 mm tubes using a Varian 400 MHz spectrometer at 25 °C. (+)FAB mass spectra of the [Pt(H₃L⁵)₂Cl₂] complex were recorded on a KRATOS MS-50 spectrometer (argon atom gun) using 3-nitrobenzylalcohol as matrix. Other (+)FAB mass spectra were obtained by courtesy of Dr L. Fourie, University of Potchefstroom, South Africa. All chemicals were used as received without further purification.

2.2. Preparation of ligands

The ligands were prepared according to the method of Douglass and Dains [10] in 70-80% yield. Pure compounds were obtained by recrystallization from ethanol.

 H_3L^4 : m.p. 120–122 °C (lit. 123–125 °C [9]). Anal. Calc. for $C_{12}H_{16}N_2O_3S$: C, 53.7; H, 6.0; N, 10.4. Found: C, 53.8; H, 5.8; N, 10.1%.

 $H_{3}L^{5}$: m.p. 124–127 °C. *Anal.* Calc. for $C_{10}H_{12}N_{2}O_{2}S$: C, 53.6; H, 5.4; N, 12.5. Found: C, 53.6; H, 5.0; N, 12.4%.

2.3. Preparation of metal complexes

2.3.1. $[Pt(H_2L^4)_2]$ and $[Pd(H_2L^4)_2]$

A solution of K_2PtCl_4 or K_2PdCl_4 (0.25 mmol) in an $H_2O/dioxane$ (1:1, vol./vol.) mixture was added dropwise to a warm (50 °C) solution of the ligand (0.5 mmol) in 20 ml dioxane–10 ml H_2O . After addition of the Pt/Pd containing solution, 0.5 mmol sodium acetate dissolved in a minimum volume of water was added and the reaction mixture was allowed to stir for 30 min at 50 °C. Upon addition of excess water the complex precipitate was collected by centrifugation, washed with cold water several times and dried at 50–60 °C to yield the analytically pure compound.

[Pt(H₂L⁴)₂]: yield 84%, m.p. 144–146 °C. Anal. Calc. for $C_{24}H_{30}N_4O_6S_2Pt$: C, 39.50; H, 4.1; N, 7.68. Found: C, 38.8; H, 4.1; N, 7.0%. (+)FAB (NOBA): m/z 731 (MH^+).

 $[Pd(H_2L^4)_2]$: yield 71%, m.p. 154–156 °C. *Anal.* Calc. for $C_{24}H_{30}N_4O_6S_2Pd$: C, 44.97; H, 4.7; N, 8.7. Found: C, 44.7; H, 4.6; N, 8.3%. (+)FAB (NOBA): m/z 641 (MH^+).

2.3.2. $[Ni(H_2L^4)_2]$

A solution of nickel acetate (0.25 mmol) in 5 ml methanol was added to a solution of H_3L^4 (0.5 mmol) in 10 ml methanol. The reaction mixture was stirred for 5 min at room temperature and then evaporated to dryness using a rotary evaporator. The crude product was recrystallized from aqueous ethanol to yield pale purple needles which were collected by filtration, dried at 60 °C and cooled under vacuum over silica gel.

Yield 64%, m.p. 161–163 °C. Anal. Calc. for $C_{24}H_{30}N_4O_6S_2Ni$: C, 48.58; H, 5.1; N, 9.44. Found: C, 47.7; H, 4.9; N, 9.0%. (+)FAB (NOBA): m/z 593 (MH^+).

2.3.3. $[Pt(H_3L^5)_2Cl_2]$

A solution of K_2PtCl_4 (0.26 mmol, 108 mg) in 10 ml 1 M HCl/dioxane (1:1 vol./vol.) was added dropwise to a 15 ml hot (70 °C), stirred solution of the same solvent mixture containing H_3L^5 (0.52 mmol, 116 mg) over a period of 10 min. The deep yellow mixture was allowed to stir for a further 15 min. Addition of 50 ml cold water and cooling in ice yielded a yellow precipitate which was collected by filtration and washed with several portions of cold water, followed by drying at 60 °C under vacuum for 24 h.

Yield 92%. Anal. Calc. for $C_{20}H_{24}N_4O_4S_2PtCl_2$: C, 33.62; H, 3.39; N, 7.84. Found: C, 34.24; H, 3.26; N, 7.69%. (+)FAB (NOBA): m/z 714.5 (MH^+) (see Section 3.4).

2.4. X-ray crystallography of N, N-di(2-hydroxyethyl)-N'benzoylthiourea $(H_{3}L^{4})$

Crystals of H₃L⁴, M = 268.33 g mol⁻¹, are orthorhombic, $P2_12_12_1$, a = 7.369(7), b = 17.508(5), c = 10.490(4) Å, V = 1353.4(14) Å³, Z = 4, $D_c = 1.317$ Mg m⁻³, F(000) = 568, λ (Mo K α) = 0.71069 Å, $\mu = 0.241$ mm⁻¹, T = 293 K.

2.5. Structure determination

A single crystal of dimensions $0.25 \times 0.28 \times 0.31$ mm was used for the data collection. Accurate cell parameters were determined by least-squares fitting of the setting angles of 24 reflections with $16 \le \theta \le 17^{\circ}$, automatically centred on an Enraf-Nonius CAD4 diffractometer. Intensities were collected with graphite monochromated Mo K α radiation, $\lambda = 0.71069$ Å, in the $\omega - 2\theta$ mode, scan width $(0.80 + 0.35 \tan \theta)^{\circ}$, range of reflections $2.26 \le \theta \le 29.97^{\circ}$. 2269 reflections were collected and used in the refinement, with index range $0 \le h \le 10$, $0 \le k \le 24$, $0 \le l \le 14$ and Np=176. Reference reflections were monitored for intensity and orientation control and showed no significant variations (0.5%). A Lorentz-polarization correction was applied to the data. The structure was solved using direct methods in SHELXS86 [11] and refined using SHELXL93 [12]. The final model included anisotropic refinement of all non-hydrogen atoms (based on F^2). The hydroxyl hydrogens and the hydrogen attached to N(8) were located in a difference electron density map and refined isotropically. Other hydrogens were placed in geometrically calculated positions and refined with a common isotropic temperature factor. At convergence, wR2 = 0.0935, conventional R = 0.0332 for 1962 reflections with $I > 2\sigma I$, S = 1.029, $(\Delta/\sigma)_{max} - 0.03(10)$, residual electron density was $-0.216 \le \Delta \rho \le +0.252$ e Å⁻³.

3. Results and discussion

3.1. Structure of ligands

The ¹H NMR spectrum of N,N-di(2-hydroxyethyl)-N'-benzoylthiourea (H_3L^4) in anhydrous DMSO-d₆ shows an interesting phenomenon in which two inequivalent proton resonances for the -OH protons are observed, the lower field resonances at 5.60 ppm being a broad unresolved ($\nu_{1/2}$ =53.6 Hz) peak, while the resonance at 4.85 ppm is a well-resolved triplet (${}^{3}J = 5.2$ Hz). The remaining exchangeable N(8)-H resonance is a broad signal at 10.86 ppm. Other ¹H NMR assignments are as given in Table 1. Apart from the expected restricted rotation about the C-N(10) bond, resulting in the inequivalence of the two 2-hydroxyethyl pendant arms, the broad unresolved -OH resonance compared to the well resolved triplet suggests substantially different rates of exchange for these two protons on the NMR timescale. We ascribe this phenomenon to the presence of an intramolecular hydrogen bond between one -OH moiety and the rest of the molecule.

Table 1			
¹ H chemical shift	data for ligands and	metal complexes in	DMSO-d ₆ at 25 °C

By contrast the ¹ H NMR spectrum of N-(2-hydroxy-
ethyl)-N'-benzoylthiourea (H_3L^5) shows a well-resolved
triplet at 4.98 ppm (${}^{3}J=4.8$ Hz), a poorly resolved
triplet at 11.04 ppm and a relatively sharp singlet at
11.29 ppm, in addition to other resonances assigned
in Table 1. The triplet at 4.98 ppm is assigned to the
-OH proton in slow exchange, while the other two
exchangeable resonances are assigned to the N(10)-H
and N(8)-H protons, respectively. The triplet structure
of the proton resonance at 11.04 ppm clearly arises
from the vicinal $({}^{3}J \sim 5.1 \text{ Hz})$ coupling between the
-CH ₂ protons of the hydroxyethyl moiety. From the
close similarity of the ¹ H NMR spectrum of H ₃ L ⁵ with
that of N-butyl-N'-benzoylthiourea, we infer an intra-
molecular hydrogen bond between the N(10)-H hy-
drogen and the carbonyl moiety of H ₃ L ⁵ analogous to
that observed in the crystal structure of N-butyl-N'-
benzoylthiourea [13] and N-propyl-N'-benzoylthiourea



[14]. It follows that the structure of H_3L^5 is better

As will become clear below, this structure has significant implications on the coordination chemistry of this ligand.

3.2. Crystal and molecular structure of H_3L^4

represented as

In order to elucidate the nature of the postulated intramolecular hydrogen bond for H_3L^4 , the crystal structure of this ligand has been determined. Fig. 1 shows the molecular structure of H_3L^4 revealing such a hydrogen bond between N(8) and O(13) with N(8)...O(13) = 2.729(3) Å, N(8)-H(8) = 0.864(1) Å and H(8)...O(13) = 1.91(3) Å, forming a seven-membered

Compound	H _{2,6}	H _{3,5}	H₄	(CH ₂) _{1'}	(-CH ₂)1*	(CH ₂) _{2'}	(CH ₂) ₂ .	-OH'	-OH"	N(8)-H	N(10)–H
H ₃ L ⁴	7.85	7.50	7.59	3.97	3.73	3.75	3.69	5.60	4.85	10.86	
$Pt(H_2L^4)_2$	8.14	7.51	7.61	3.96	3.84	3.73	3.69	5.00	4.92		
$Pd(H_2L^4)_2$	8.12	7.50	7.59	3.99	3.91	3.73	3.69	5.00	4.92		
$Ni(H_2L^4)_2$	8.31	7.73	7.60	4.46	4.28	3.81	3.69	5.00	4.86		
H ₃ L ⁵	7.91	7.50	7.63	3.65		3.65		4.98		11.29	11.04
$Cis-Pt(H_3L^5)_2Cl_2$ (74%)	7.91	7.63	7.50	3.66		3.61		3.56		11.31	11.03
Trans-Pt(H_3L^5)Cl ₂ (26%)	8.07	~ 7.63 ^b	7.76	3.76		3.68		3.56		11.34	11.21
H ₃ L ⁵ *	7.85	7.51	7.62	3.93 ^b		3.93 ^b		2.13		9.09	11.0
Cis-Pt(H ₃ L ⁵) ₂ Cl ₂ * (70%)	8.21	~7.51 ^b	~7.51 ^b	3.96		3.81		1.83 °		11.84	11.39 ^b
Trans-Pt(H ₃ L ⁵) ₂ Cl ₂ * (30%)	8.11	7.62	∼7.02 [⊾]	3.89		~ 3.96 ^b		1.80 °		11.59	11.39 в

* ¹H NMR spectra recorded in CDCl₃.

^b Peaks overlap.

^e Shift dependent on residual H₂O content in solvent.



Fig. 1. Molecular structure of N,N-di(2-hydroxyethyl)-N'-benzoyl-thiourea (H₃L⁴) showing the numbering scheme adopted. The hydrogen bond is indicated by a dashed line.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for the non-hydrogen atoms of H₃L⁴

	x	у	z	U _{eq} ^a
C(1)	7374(2)	4034(1)	- 311(2)	35(1)
C(2)	6919(3)	3618(1)	- 1390(2)	51(1)
C(3)	6014(4)	2931(2)	- 1268(3)	67(1)
C(4)	5538(4)	2664(2)	- 79(3)	69(1)
C(5)	5944(4)	3086(1)	995(3)	58(1)
C(6)	6873(3)	3774(1)	893(2)	42(1)
C(7)	8422(2)	4758(1)	- 509(2)	35(1)
O(7)	8445(3)	5091(1)	-1523(1)	52(1)
N(8)	9423(2)	4984(1)	526(2)	37(1)
C(9)	10407(2)	5657(1)	654(2)	34(1)
S(9)	9582(1)	6505(1)	203(1)	44(1)
N(10)	12016(2)	5572(1)	1221(2)	37(1)
C(11)	12869(3)	4818(1)	1431(2)	43(1)
C(12)	12375(3)	4453(2)	2687(3)	57(1)
O(13)	10558(3)	4173(1)	2600(2)	66(1)
C(21)	13083(3)	6230(1)	1657(2)	45(1)
C(22)	14289(3)	6560(1)	634(2)	48(1)
O(23)	15428(2)	5987(1)	103(2)	52(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Relevant bond lengths (Å) and bond angles (°) of H₃L⁴

Bond lengths		Bond angles	
C(7)-O(7)	1.213(2)	O(7)-C(7)-N(8)	123.2(2)
C(7)-N(8)	1.371(2)	O(7)-C(7)-C(1)	122.4(2)
N(8)-C(9)	1.391(2)	N(8)-C(7)-C(1)	114.3(2)
C(9)-N(10)	1.335(3)	C(7)-N(8)-C(9)	127.0(2)
C(9)-S(9)	1.672(2)	N(10)-C(9)-N(8)	114.3(2)
		N(10)-C(9)-S(9)	123.30(14)
		N(8)-C(9)-S(9)	122.35(14)
		N(10)-C(9)-N(8)	114.3(2)
		C(9)-N(10)-C(21)	121.8(2)
		C(9)-N(10)-C(11)	123.0(2)

ring involving a hydroxyethyl pendant arm and the N(8)-H moiety.

Table 2 lists the non-hydrogen atomic coordinates and Table 3 the relevant bond lengths and angles. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is definitely twisted as reflected by the torsion angles O(7)-C(7)-N(8)-C(9) and C(7)-N(8)-C(9)-S(9) of 8.9 and 44°, respectively. By comparison, the corresponding torsion angles for N,N-di(n-butyl)-N'-benzoylthiourea (HL²) and N,Ndi(n-butyl)-N'-naphthoylthiourea (HL²) and 0, -11.5and $-120, -109.5^\circ$, respectively, as obtained from the crystal structures of these molecules [15]. In the latter molecules the carbonyl and thiocarbonyl moieties are pointing in more or less opposite directions, at least in the solid state.

For H_3L^4 the C-N bond lengths are all shorter than the average single C-N bond length of 1.479 Å [16], being C(7)-N(8)=1.371(2) Å, C(9)-N(8)=1.391(1) Å and C(9)-N(10)=1.335(3) Å, thus showing varying degrees of double bond character in these C-N bonds. The partial double bond character of the C(9)-N(10) bond is further manifested by the magnetic inequivalence of the 2-hydroxyethyl moieties in the ¹H NMR spectrum of this ligand (Table 1).

The molecules of H_3L^4 pack in stacks of alternating orientation and are hydrogen bonded in a ribbon-like fashion approximately parallel to the z-axis. The intermolecular hydrogen bond linking adjacent molecules is between the O(13)-H group of a hydroxyethyl pendant arm and the O(23)-H group of an adjacent molecule with O(13)...O(23) = 2.739(3) Å, O(13)-H=0.822(1) Å and H(13)...O(23) = 1.96(2) Å. There is a second, weaker interatomic contact between O(23) and O(7) of 3.213(2) Å of two adjacent molecules in the solid state.

In DMSO-d₆ solution, only the intramolecular hydrogen bond between N(8)-H and O(13) is likely to persist, the consequences of which explains the different rates of hydrogen exchange observed for the two inequivalent hydroxyl protons as observed in the ¹H NMR spectrum above. The lability of the O(13)-H proton involved in the intramolecular hydrogen bond, is likely to be significantly different to that of the O(23)-H proton, so that the broad resonance at 5.60 ppm is assigned to the former moiety.

3.3. Coordination chemistry of H_3L^4

The di-substituted ligand H_3L^4 , readily forms neutral, slightly water-soluble complexes of the type $[M(H_2L^4)_2]$ (where M = Pt(II), Pd(II) and Ni(II)) by treatment of a solution of the metal chlorides/acetates with appropriate amounts of ligand in dioxane/water followed by deprotonation with sodium acetate. The ¹H NMR spectra of $[Pt(H_2L^4)_2]$ and $[Pd(H_2L^4)_2]$ of the unrecrystallized, analytically pure, complexes in DMSO-d₆ show these complexes to be isomerically pure, with ¹H NMR assignments as given in Table 1. Both complexes are assigned to have *cis* configuration on the basis of their ¹H NMR spectra and the fact that all previously reported d^8 metal complexes $[ML_2]$ obtained from N,N-dialkyl-N'-benzoylthioureas were of the *cis* configuration for M = Pt(II) [4], Pd(II) [5] and Ni(II) [6,7]. In this context it is important to note, however, that despite an overwhelming tendency to yield *cis* complexes with ligands of this type, we recently characterized the *trans*-bis(N,Ndibutyl-N'-naphthoylthioureato)platinum(II) complex by X-ray diffraction, which was isolated as the minor component from a mixture of the *cis* and *trans* complexes [8].

It is noteworthy that in both the ¹H NMR spectra of the $[Pt(H_2L^4)_2]$ and $[Pd(H_2L^4)_2]$ complexes, the hydroxyl proton resonances of both 2-hydroxyethyl pendant arms are well resolved triplets (³J = 5.6 Hz), in contrast to the spectrum of the uncomplexed ligand H₃L⁴, suggesting slow exchange on the NMR time scale in the metal complexes. Evidently the intramolecular hydrogen bond as observed for the uncomplexed ligand is not possible in the coordinated, deprotonated ligand.

The ¹H NMR spectrum of the analogous $[Ni(H_2L^4)_2]$ complex in DMSO-d₆ shows this complex to be essentially square planar, with a small degree of tetragonal distortion being suggested by the relatively broad resonances, as a result of the paramagnetism associated with Ni(II) compounds in octahedral symmetries [17]. This is understandable in view of the known tendency of analogous violet bis(N,N-diethyl-N'-benzoylthioureato)nickel(II) complexes to readily form green, octahedral adducts with strong donor ligands such as pyridine [18]. In the present case we postulate the existence of a planar-octahedral equilibrium involving the donor solvent DMSO-d₆, which must lie well toward planar complex geometry in the case of $[Ni(H_2L^4)_2]$, since the ¹H NMR resonances of the complex are only slightly affected (broadened and shifted downfield) by the paramagnetism associated with Ni(II) in tetragonally distorted/octahedral ligand fields [17]. In the absence of any evidence to the contrary, we assign the cis configuration to the $[Ni(H_2L^4)_2]$ complex.

3.4. Coordination chemistry of H_3L^5

As alluded to above, the coordination chemistry of H_3L^5 toward Pt(II) is profoundly different to H_3L^4 , in that an intramolecular hydrogen bond between N(10)–H and the carbonyl moiety forces this ligand into unidentate coordination, as has been previously demonstrated by the crystal structure of *cis*-bis(*N*-benzoyl-*N'*-propylthioureato)dichloroplatinum(II) [3]. Inspection of the ¹H NMR spectrum of analytically pure [Pt(H₃L⁵)₂Cl₂] in DMSO-d₆ (Table 1) shows this to be a mixture of ~74% *cis*- and 26% *trans*-[Pt(H₃L⁵)₂Cl₂]. This phenomenon is most clearly illustrated by the N–H resonances of these complexes given in Fig. 2, which shows two sets of N(8)–H and N(10)–H resonances, the latter resonance having a triplet structure



Fig. 2. ¹H NMR spectra of the low field region of (a) H_3L^5 and (b) cis-[Pt(H_3L^5)₂Cl₂] (74%) and *trans*-[Pt(H_3L^5)₂Cl₂] (26%) in DMSO-d₆ at 25 °C (assignments given in Table 1).

virtually identical to the uncoordinated ligand. We base our assignment of the *cis*- and *trans*-[Pt(H₃L⁵)₂Cl₂] complexes in the present case on the very similar ¹H NMR spectra obtained for the *cis*-bis(*N*-benzoyl-*N'*propylthioureato)dichloroplatinum(II) complexes in CDCl₃, in which the major isomer was established to have the *cis* configuration by X-ray diffraction.

The (+)FAB mass spectrum of a sample of $[Pt(H_3L^5)_2Cl_2]$ was found to be particularly informative, showing in addition to the MH^+ ion (m/z = 714.5), extensive evidence of self-assembly into dimeric species, in which both uni- and bidentate coordination of H_3L^5 is observed. As is evident from Fig. 3 in which assignments of the major (+)FAB peaks are given, it is clear that loss of Cl⁻ ions from the complex $[Pt(H_3L^5)_2Cl_2]$ results in species such as $[Pt(H_3L^5)_2Cl]^+$ (m/z = 679.3), in which one ligand moiety is presumed to coordinate in a bidentate mode to the Pt atom so stabilizing this species. Further loss of a Cl⁻ ion yields a species formulated to be $[Pt(H_3L^5)(H_2L^5)]^+$ $(m/z)^+$ = 642.2), in which both ligand moieties are presumed to chelate to the Pt(II) ion. The (+)FAB spectrum shows further that under conditions prevailing in the mass spectrometer vacuum chamber, several additional dimeric species are formed, in which Cl⁻ is postulated to act as a bridging ligand, something well known in the coordination chemistry of Pt(II) [19]. Thus species of types $[Pt_2Cl_2(H_3L^5)_3(H_2L^5)]^+$ (m/z = 1357.1), $[Pt_2Cl_3(H_3L^5)_3]^+$ (m/z = 1169.3), $[Pt_2Cl_2(H_1L^5)_2 (H_2L^5)$]⁺ (m/z = 1132.8) and [Pt₂Cl₂(H₃L⁵)(H₂L⁵)]⁺ (m/ z = 904.3) are all inferred from the (+)FAB spectrum, in which H₂L⁵ either coordinates in uni- or bidentate fashion to the metal ion, as illustrated in Fig. 3. These findings are supported by the remarkable complexity of the ¹H NMR spectrum obtained on addition of a base (e.g. triethylamine) to a solution of cis/trans-





Fig. 3. (+)FAB mass spectrum of $[Pt(H_3L^5)_2Cl_2]$, showing the observed m/z values rounded to the nearest mass unit together with assignments of possible species.

 $[Pt(H_3L^5)_2Cl_2]$. Evidently deprotonation of the unidentate coordinated ligand results in the formation of a complex mixture of a number of species, in which the ligand moiety is also coordinated in a bidentate mode. The complexity of the ¹H NMR spectrum is such that even at high field it is impossible to identify all the possible species present.

By contrast the (+)FAB spectrum of the *cis*-[Pt(H₂L⁴)₂] complex shows only one cluster of peaks centred around an m/z peak of 731, assignable to the MH^+ ion, and a typical fragmentation pattern with no evidence of any other complexes present; this is understandable in terms of the stability of the bidentate coordination of H₃L⁴ to Pt(II).

In conclusion we have shown that the coordination chemistry of H_3L^4 and H_3L^5 differs substantially with respect to platinum(II), in that the latter ligand behaves

more like a monodentate thiourea ligand, with the carbonyl atom being prevented from coordinating by an intramolecular hydrogen bond to yield a mixture of *cis* and *trans* complexes of $[Pt(H_3L^5)_2Cl_2]$. By contrast, the H₃L⁴ ligand always coordinates to Pt(II), Pd(II) and Ni(II) in a bidentate fashion, yielding essentially complexes of type *cis*- $[M(H_2L^4)_2]$.

These complexes are all reasonably soluble in mixtures of water and solvents such as methanol and acetonitrile, suggesting that mixtures of Pt(II), Pd(II) and Ni(II) complexes may be separable by means of C_{18} reverse phase HPLC. Preliminary work in this respect has confirmed this and work is in progress to explore the potential applicability of these hydrophilic ligands as reagents for the selective preconcentration and potential separation of the platinum group metals.

4. Supplementary material

Supplementary crystallographic data are available from K.R.K. on request. Arrangements to lodge these data with the Cambridge Crystallographic Data Centre will be made.

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