



Structural and spectral study of platinum(II) complexes of pyridil bis{3-piperidyl-, bis{hexamethyleneiminyl-, bis{N(4)-diethyl- and bis{N(4)-dipropylthiosemicarbazones}

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Abstract

Representative platinum(II) complexes of pyridil bis(N(4)-substituted thiosemicarbazones), in which the substituents replacing the NH₂ of the thiosemicarbazone moieties are piperidyl, H₂Plpip; hexamethyleneiminyl, H₂Plhexim; diethylamino, H₂Pl4DE; and dipropylamino, H₂Pl4DP, have been synthesized and characterized with IR, electronic, mass, and ¹H NMR spectra. Crystal structures have been solved for two platinum(II) complexes formed from H₂Pl4DP. [Pt(Pl4DP)] has square-planar N₂S₂ coordination (i.e. imine nitrogen and thiolato sulfur atoms) and [Pt₂(Pl4DP)Cl₂] has two PtNNSCl centers with the pyridine nitrogen, imine nitrogen and thiolato sulfur atoms coordinated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum(II); Pyridil; bis(Thiosemicarbazone); Crystal structures; Binuclear complexes

1. Introduction

The antitumor activity of bis(thiosemicarbazones) and their metal complexes has received considerable attention [1]. Since activity of heterocyclic thiosemicarbazones depends on the thiosemicarbazone's N(4)-substituent [2] (i.e. N(4)- refers to the IUPAC numbering system for thiosemicarbazones, C=N(1)–N(2)H–C(3)(S)–N(4)), bis{N(4) substituted thiosemicarba-

zones} and their metal complexes have been studied recently [3–11]. The previously studied bis(thiosemicarbazones) behave as dianionic, tetradentate N₂S₂ ligands with loss of the two N(2)H's upon coordination with nickel(II), copper(II), palladium(II) and platinum(II) [3–6,9]. We have reported previously the spectral and structural studies of nickel(II) [12], copper(II) [13] and palladium(II) [14] complexes of the following pyridil bis(thiosemicarbazones): 3-piperidyl, H₂Plpip; 3-hexamethyleneiminyl, H₂Plhexim; N(4)-diethyl, H₂Pl4DE and N(4)-dipropyl, H₂Pl4DP (Fig. 1). Here we report a similar study of the platinum(II) complexes of these four bis(thiosemicarbazones), which includes the crystal structures of two complexes of H₂Pl4DP, [Pt(Pl4DP)] and [Pt₂(Pl4DP)Cl₂].

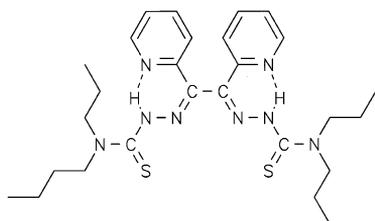


Fig. 1. Schematic representation of the pyridil bis(N(4)-dipropyl thiosemicarbazone H₂Pl4DP.

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2. Experimental

2.1. General

Elemental analyses were performed in a Carlos Erba 1108 microanalyser. IR spectra were recorded as KBr disks (4000–400 cm⁻¹) or polyethylene-sandwiched

Table 1
Crystal data and structure refinement for platinum(II) complexes of pyridil bis{N(4)-dipropylthiosemicarbazone, [Pt(PI4DP)] and [Pt₂(PI4DP)Cl₂]

Empirical formula	C ₂₆ H ₃₆ N ₈ PtS ₂	C ₂₆ H ₃₆ Cl ₂ N ₈ Pt ₂ S ₂
Color, habit	brown, prism	brown, plate
Formula weight	719.84	985.83
Temperature (K)	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	8.990(2)	11.645(6)
<i>b</i> (Å)	11.441(2)	12.042(3)
<i>c</i> (Å)	15.700(1)	13.081(5)
α (°)	78.52(1)	73.15(2)
β (°)	88.49(1)	85.51(4)
γ (°)	67.17(2)	71.95(3)
<i>V</i> (Å ³)	1456.1(4)	1668.9(11)
<i>Z</i>	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.642	1.962
Absorption coefficient (mm ⁻¹)	4.992	8.688
Crystal size (mm)	0.35 × 0.30 × 0.125	0.30 × 0.15 × 0.10
θ Range for data collection (°)	2.46–27.97	2.41–28.01
Index ranges	0 ≤ <i>h</i> ≤ 11, –13 ≤ <i>k</i> ≤ 15, –20 ≤ <i>l</i> ≤ 20	–15 ≤ <i>h</i> ≤ 14, –15 ≤ <i>k</i> ≤ 0, –17 ≤ <i>l</i> ≤ 16
Reflections collected	7433	8412
Independent reflections	6994 [<i>R</i> _{int} = 0.020]	8034 [<i>R</i> _{int} = 0.079]
Absorption correction	ψ -scan	ψ -scan
Max./min. transmission	0.521/0.274	0.967/0.729
Data/parameters	6994/418	8034/301
Goodness-of-Fit on <i>F</i> ²	1.218	0.962
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.031, <i>wR</i> ₂ = 0.089	<i>R</i> ₁ = 0.051, <i>wR</i> ₂ = 0.101
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.058, <i>wR</i> ₂ = 0.099	<i>R</i> ₁ = 0.209, <i>wR</i> ₂ = 0.132
Largest difference peak and hole (e Å ⁻³)	1.214 and –1.235	1.300 and –1.178

Nujol mulls (500–100 cm⁻¹) on a Mattson Instruments Cygnus 100 FTIR spectrophotometer using Nujol mulls between CsI plates; electronic spectra were acquired as nujol mulls adhered to filter paper with a Cary 5E spectrometer. NMR spectra were obtained as [DMSO-*d*₆] solutions with a Bruker WM-300 spectrometer, and chemical shifts are reported in parts per million downfield from Me₄Si. Mass spectra (FAB, 3-nitrobenzyl alcohol, Xe, 8 kV) were obtained on a Kratos MS-50 apparatus equipped with a DS-90 data acquisition unit.

2.2. Synthesis of the ligands and complexes

The synthesis of the pyridil bis{N(4)-substituted thiosemicarbazones} and their physical properties was reported previously [12]. The platinum(II) complexes

were prepared by boiling a pyridil bis(thiosemicarbazone) (0.04 mmol in 25 ml of 96% EtOH) under reflux with K₂PtCl₄ (solved in a small quantity of water) in a 1:1 molar for 4–5 h. The resulting solutions were cooled, filtered, and washed with *i*-PrOH. The yields of complexes were 54.9% for [Pt₂(PI4DP)Cl₂]·3H₂O, 65.1% for [Pt₂(PI4DE)Cl₂]·4H₂O, 95.6% for [Pt₂(Plpip)Cl₂]-[Pt(Plpip)] and 63.6% for [Pt₂(Plhexim)Cl₂]·4H₂O.

2.3. Crystal structure determination

Brown crystals of [Pt(PI4DP)] and [Pt₂(PI4DP)Cl₂], grown from EtOH, were mounted on glass fibers and used for data collection. Reflections were collected with a Nonius MACH3 diffractometer, Mo K α (λ = 0.71073 Å). Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data of 25 reflections from 11.162 < θ < 20.830° for [Pt(PI4DP)] and 9.390 < θ < 20.777° for [Pt₂(PI4DP)Cl₂]. The structures were solved by direct methods [15], which revealed the position of all non-hydrogen atoms, and refined on *F*² by a full-matrix least-squares procedure using anisotropic displacement parameters, except those of the propyl groups in [Pt₂(PI4DP)Cl₂] which showed disorder and were refined isotropically [16]. All hydrogens of [Pt(PI4DP)] were located from difference Fourier maps, except those of the methyl groups, and refined isotropically. The methyl hydrogens of [Pt(PI4DP)] and the hydrogens in [Pt₂(PI4DP)Cl₂] were located in their calculated positions (C–H, 0.93–0.97 Å) and refined using a riding model. Atomic scattering factors are from the International Tables for X-ray Crystallography [17] and molecular graphics are from PLATON-98 [18]. Summaries of X-ray data collection, data reduction and structure refinement results for the two complexes are given in Table 1.

3. Results and discussion

The stoichiometries, colors and partial elemental analyses for the platinum(II) complexes are listed in Table 2. The four complexes are stable in air, moderately soluble in polar solvents and insoluble in apolar solvents, and all but [Pt₂(Plpip)Cl₂][Pt(Plpip)] are isolated with hydrate water molecules. The mixed [Pt₂(Plpip)Cl₂][Pt(Plpip)] solid is not unique in this series complexes in that the crystal structures of both copper(II) centers of 2[Cu(PI4DE)]·[Cu(PI4DE)]₂ have been solved [13].

3.1. Crystal structure of [Pt(PI4DP)]

[Pt(PI4DP)], Fig. 2, has the same mode of coordination as the pyridil bis{N(4)-substituted thiosemicarba-

Table 2

Colors, partial elemental analyses and magnetic susceptibilities of for platinum(II) complexes of pyridil bis(thiosemicarbazones)

Compound	Color	Calc. (Found)			
		C	H	N	S
[Pt ₂ (P14DE)Cl ₂]-4H ₂ O	brown	26.4(26.0)	3.6(3.0)	11.2(10.8)	6.4(6.3)
[Pt ₂ (P14DP)Cl ₂]-3H ₂ O	brown	30.0(29.8)	4.1(3.4)	10.8(10.2)	6.2(5.5)
[Pt ₂ (Plpip)Cl ₂][Pt(Plpip)]	brown	35.1(36.4)	3.4(3.5)	13.7(13.8)	7.8(7.4)
[Pt ₂ (Plhexim)Cl ₂]-4H ₂ O	brown	29.6(29.3)	3.8(3.0)	10.6(10.3)	6.1(5.6)

zone} complexes of nickel(II) [12], three copper(II) complexes [13] and [Pd(Plhexim)] [14]. All have N₂S₂ coordination by the imine nitrogens and thiolato sulfurs of the thiosemicarbazone moieties, but not by the pyridine nitrogens, Fig. 1. Unfortunately, we have not been able to grow suitable crystals of H₂P14DP, but have solved the crystal structure of [Ni(P14DP)], which is monoclinic, *P*2₁/*c*, with three crystallographically unique molecules [12]. The Pt–N bonds are shorter than the Pt–S bonds (Table 3), but both are about 0.1–0.15 Å longer than the average of the analogous Ni–N and Ni–S bonds in [Ni(P14DP)] [12]. The C–S bonds, which are formally a double bond in H₂P14DP (the average of the C=S bonds in H₂Plpip [12], H₂P14DE [13], and H₂Plhexim [14] is 1.668(4) Å) and a single bond on complexation, averages 1.771(6) Å in [Pt(P14DP)]. The N13–C17 (and N23–C27) bond averages 1.368(5) Å in the three bis(thiosemicarbazones) [12–14], but formally becomes a double bond on complexation, and averages 1.335(7) Å in [Pt(P14DP)]. However, the imine C–N bond, which averages 1.296(4) Å [12–14], is only marginally longer at 1.313(7) Å and is similar to the average of 1.317(8) Å for [Ni(P14DP)] [12]. Other bonds of the thiosemicarbazone moiety in [Pt(P14DP)] are not significantly altered from the average of the three bis(thiosemicarbazones) [12–14]. In contrast, all of the bond angles of the thiosemicarbazone moieties undergo significant shift in [Pt(P14DP)] as was found for the other metal complexes [12–14].

The average N–M–S (Table 4) bite angle of [Pt(P14DP)] is smaller, 84.68(12)°, compared to [Ni(P14DP)], 87.6(2)°, and the N–M–N bite angle is also smaller for [Pt(P14DP)], 80.82(7)°, compared to 83.9(3)° for [Ni(P14DP)]. Therefore, the S–Pt–S angle is considerably larger, 109.80(5)°, than the S–Ni–S angle, 100.94(9)°. The average N–M–S *trans* angle is 165.49(13)° for [Pt(P14DP)] and 171.4(2)° for [Ni(P14DP)].

The coordination about Pt, S1–N12–N22–S2, is reasonably planar, i.e. RMS plane deviation is 0.0073 Å, and Pt is 0.0142(17) Å out of this plane (Table 5). The RMS planes of the thiosemicarbazone moieties make an angle of 7.41(14)° with the S1–N12–N22–S2 plane and are at an angle of 7.88(14)° with each other.

The pyridine rings RMS planes are at an angle of 41.93(16)° with the thiosemicarbazone moieties and 48.29(29)° to each other.

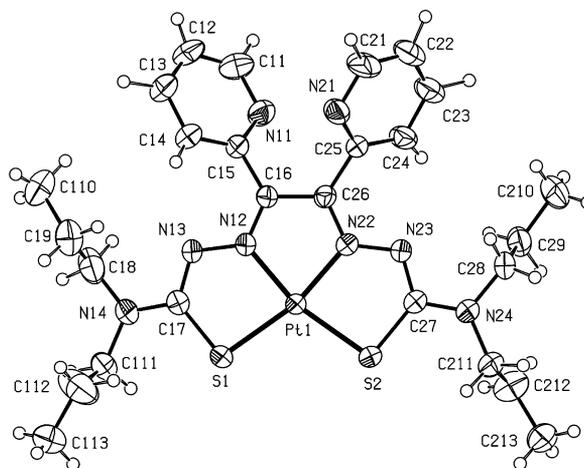


Fig. 2. Perspective view of [Pt(P14DP)] molecule, showing 50% probability ellipsoids for the nonhydrogen atoms and the numbering scheme of the atoms in the molecule.

Table 3

Bond distances (Å) for [Pt(P14DP)] and [Pt₂(P14DP)Cl₂]

	[Pt(P14DP)]	[Pt ₂ (P14DP)Cl ₂]
Pt1–N12	1.968(4)	1.941(2)
Pt1–S1	2.2841(15)	2.240(1)
Pt1/2–N22	1.968(4)	1.962(2)
Pt1/2–S2	2.2866(14)	2.250(1)
Pt1–C11		2.297(1)
Pt1–N11		2.023(2)
Pt2–N21		2.052(2)
Pt2–C12		2.294(1)
S1–C17	1.765(6)	1.755(3)
S2–C27	1.777(6)	1.773(3)
N12–C16	1.308(7)	1.332(3)
N12–N13	1.371(6)	1.373(3)
N13–C17	1.340(8)	1.344(3)
N14–C17	1.339(8)	1.339(4)
N22–C26	1.319(6)	1.329(3)
N22–N23	1.364(6)	1.332(3)
N23–C27	1.330(7)	1.340(4)
N24–C27	1.341(7)	1.298(4)

Table 4

Bond angles (°) for [Pt(PI4DP)] and [Pt₂(PI4DP)Cl₂]

	[Pt(PI4DP)]	[Pt ₂ (PI4DP)Cl ₂]
N11–Pt1–N12		80.88(9)
N11–Pt1–S1		166.17(6)
N12–Pt1–C11		175.89(7)
N11–Pt1–C11		97.25(7)
S1–Pt1–C11		96.55(4)
N12–Pt1–N22	80.83(17)	
N12–Pt1–S2	165.33(13)	
N22–Pt1/2–S2	84.55(13)	84.61(7)
N12–Pt1–S1	84.82(13)	85.41(7)
N22–Pt1–S1	165.65(13)	
S2–Pt1–S1	109.80(5)	
N22–Pt2–N21		81.53(9)
N21–Pt2–S2		166.11(5)
N22–Pt2–Cl2		178.14(7)
N21–Pt2–Cl2		96.88(7)
S2–Pt2–Cl2		96.99(5)
C17–S1–Pt1	94.2(2)	95.08(10)
C27–S2–Pt1/2	94.33(17)	94.72(11)
C16–N12–Pt1	115.7(3)	117.13(17)
N13–N12–Pt1	123.3(3)	123.37(16)
C26–N22–Pt1/2	114.7(3)	115.68(17)
N23–N22–Pt1/2	123.8(3)	124.44(15)
C16–N12–N13	120.8(4)	119.34(19)
N12–N13–C17	112.2(4)	111.8(2)
N13–C17–N14	115.1(5)	117.1(2)
N13–C17–S1	125.1(4)	124.1(2)
N14–C17–S1	119.8(5)	118.8(2)
C26–N22–N23	121.4(4)	119.8(2)
N22–N23–C27	112.7(4)	112.4(2)
N23–C27–N24	116.0(5)	116.5(3)
N23–C27–S2	124.6(4)	123.6(2)
N24–C27–S2	119.4(4)	119.9(2)

3.2. Crystal structure of [Pt₂(PI4DP)Cl₂]

A second crystal, [Pt₂(PI4DP)Cl₂], with a different mode of coordination by PI4DP has been obtained from a 2:1 molar mixture of K₂PtCl₄ to H₂PI4DP, Fig. 3. Coordination about both Pt centers is via the pyridine nitrogen, imine nitrogen and thiolato sulfur with a

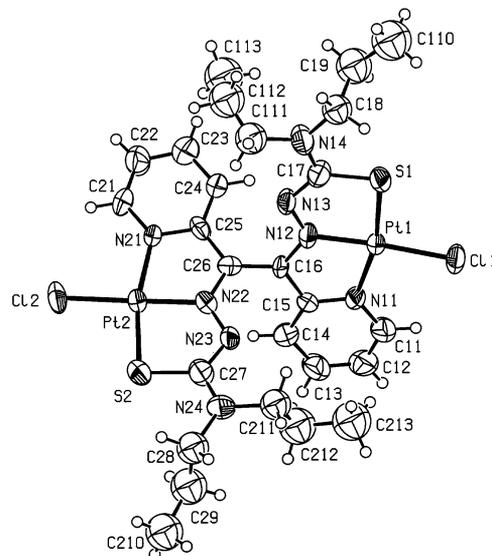


Fig. 3. View of the [Pt₂(PI4DP)Cl₂] complex showing the numbering scheme adopted for the atoms.

chloro ligand completing the coordination sphere, Fig. 3. In a related complex, [Pd₂(Plhexim)Cl₂] coordination about one of the Pd centers involves coordination by N23 rather than the expected N22 [14]. The Pt–N (pyridil) bonds are about 0.1 Å longer than the imine Pt–N bonds and the Pt–Cl bonds are about 0.05 Å longer than the Pt–S bonds. The Pd–S bonds average 2.245(4) Å for [Pt₂(PI4DP)Cl₂] compared to 2.2853(15) Å for [Pt(PI4DP)] and the Pd–N (imine) bonds are also shorter in [Pt₂(PI4DP)Cl₂], which probably results from the greater degree of chelation of [Pt(PI4DP)]. There are not significant differences in the bond distances of the thiosemicarbazone moieties of the two complexes. [Pt₂(PI4DP)Cl₂] and the Pd with the same mode of coordination in [Pd₂(Plhexim)Cl₂] have comparable bond distances; the M–N (pyridine) has the largest difference with [Pt₂(PI4DP)Cl₂] averaging 2.037(9) Å compared to 2.072(6) Å for [Pd₂(Plhexim)Cl₂].

Table 5

Root mean squared plane deviations and angles between [Pt(PI4DP)] and [Pt₂(PI4DP)Cl₂]

Compound	Plane	RMS deviation	Atom with greatest deviation	∠ to previous plane
[Pt(PI4DP)]	S1–N12–N22–S2	0.0073	N12/N22, 0.0086(0.0024)	
	C16–N12–N13–C17–N14–S1	0.0321	N13, 0.0546(0.0049)	7.41(0.14)
	C36–N22–N23–C37–N24–S2	0.0087	N22, 0.0177(0.0040)	7.88(0.14)
	N11–C11–C12–C13–C14–C15	0.0078	C12, 0.0097(0.0063)	41.93(0.16)
	N21–C31–C32–C33–C34–C35	0.0058	C35, 0.0087(0.0046)	48.29(0.29)
[Pt ₂ (PI4DP)Cl ₂]	N11–C11–C12–C13–C14–C15	0.0090	C13, 0.0140(0.0123)	
	C16–N12–N13–C17–S1–N14	0.0105	C16, 0.0146(0.0069)	2.57(0.89)
	C11–S1–N12–N11	0.0446	N12, 0.0530(0.0051)	6.04(0.58)
	C12–S2–N22–N21	0.0177	N22, 0.0210(0.0049)	60.55(0.20)
	C26–N22–N23–C27–S2–N24	0.0227	N22, 0.0363(0.0090)	3.46(0.53)
N21–C21–C22–C23–C24–C25	0.0090	C22, 0.0154(0.0124)	6.28(0.80)	

Table 6
IR assignments for platinum(II) complexes of pyridil bis{N(4)-substituted thiosemicarbazones}

Compound ^a	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	$\rho(\text{py})$	$\nu(\text{PtN})$	$\nu(\text{PtS})$	$\nu(\text{PtCl})$
H ₂ Pt4DP	1582m	806m	592w			
[Pt ₂ (Pt4DE)Cl ₂] \cdot 4H ₂ O	1600w, 1550s	742sh	619m	460m	332vs	313sh
[Pt ₂ (Pt4DP)Cl ₂] \cdot 3H ₂ O	1597w, 1545s	740sh	618sh	458m	338vs ^b	338vs ^b
[Pt ₂ (Plpip)Cl ₂][Pt(Plpip)]	1590sh, 1572w, 1544m	743sh	617sh 600w	461w	335sh	315vs
[Pt ₂ (Plhexim)Cl ₂] \cdot 4H ₂ O	1598w, 1534m	746sh	625m	467m	312vs ^b	312vs ^b

^a The hydrate waters have been omitted.

^b Composite band of $\nu(\text{PtS})$ and $\nu(\text{PtCl})$.

The bond angles that [Pt₂(Pt4DP)Cl₂] and [Pt(Pt4DP)] have in common, e.g. N12–Pd1–S1, are not significantly different nor are the angles within the thiosemicarbazone moieties. There are small deviations (i.e. 0.0446 and 0.0177 Å) from planarity for Cl1–S1–N12–N11 and Cl2–S2–N22–N21, which are at an angle of 60.55(0.20)° from each other compared to 53.34(0.11)° for [Pd₂(Plhexim)Cl₂]. The pyridine rings, due to pyridine nitrogen coordination, form much smaller angles with the thiosemicarbazone moieties, 2.57(0.89) and 6.28(0.80)°, than found for [Pt(Pt4DP)], and are comparable to the angles of [Pd₂(Plhexim)Cl₂]. The thiosemicarbazone moieties of [Pt₂(Pt4DP)Cl₂] are quite planar, with rms plane deviations of 0.105 and 0.0227 Å.

3.3. Spectral results

In the mass spectrum of [Pt₂(Plhexim)Cl₂] the molecular ion appears at $m/z = 981$ and a cluster of ions with significant intensity appears at m/z of 715 due to {Pt(Plhexim)}⁺. Also present are a cluster of ions at $m/z = 1661$, 1431 and 1226 with probable assignment of {Pt₃(Plhexim)₂}⁺ for the former. The mass spectrum of [Pt₂(Plpip)Cl₂][Pt(Plpip)] shows the molecular ion at $m/z = 1643$, a cluster of peaks centered at $m/z = 1607$ and 1376 due to [$M^+ - 35$] and [$M^+ - 265$], resulting from a loss of a Cl and two Cl's and a Pt, respectively. Also there are peaks at $m/z = 919$ and 688 due to {Pt₂(Plpip)Cl}⁺ and {Pt(Plpip)}⁺, respectively. The mass spectrum of [Pt₂(Pt4DP)Cl₂] has the molecular ion peak at $m/z = 986$ and ion fragment clusters at m/z values of [$M^+ - 35$], [$M^+ - 72$] and [$M^+ - 267$] the first two fragments due to loss of one and two chlorine atoms from the molecular ion and the latter is probably {Pt(Pt4DP)}⁺. Similarly, the mass spectrum of [Pt₂(Pt4DE)Cl₂] shows $m/z = 929$ due to its molecular ion, but only shows peaks of significant intensity at [$M^+ - 73$] and [$M^+ - 265$].

In the infrared spectrum of H₂Pt4DP $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ contribute substantially to bands at 1582 and 806 cm⁻¹, respectively, based on 2-benzoylpyridine 3-dipropylthiosemicarbazone [19], and both undergo shifts to lower energy on coordination in

[Pt₂(Pt4DP)Cl₂], Table 6. The spectra of [Pt₂(Pt4DE)Cl₂], [Pt₂(Plpip)Cl₂][Pt(Plpip)] and [Pt₂(Plhexim)Cl₂] show these two bands at similar energies. The spectra of the platinum complexes show a band at 1590–1600 cm⁻¹ due to $\nu(\text{N}=\text{C})$, which results on loss of the thioamide hydrogens from both thiosemicarbazone moieties. A broad band due to $\nu(\text{OH})$ is found at about 3450 cm⁻¹ in the complexes with hydrate water molecules. Coordination of the pyridine nitrogen causes a shift of the ring's out-of-plane deformation band from 592 cm⁻¹ to ca. 620 cm⁻¹. $\nu(\text{PtN})$ and $\nu(\text{PtS})$ have ranges of 458–467 and 312–338 cm⁻¹ based on studies of pyruvaldehyde bis(3-piperidylthiosemicarbazone) and platinum(II) [9]. The latter bands overlap or are shoulders to the $\nu(\text{PtCl})$ bands located at ca. 315 cm⁻¹ (Table 7).

The UV–Vis spectrum of the yellow H₂Pt4DP has a $\pi \rightarrow \pi^*$ band due to the pyridil rings at 36711 cm⁻¹, which is not altered significantly in [Pt₂(Pt4DP)Cl₂]. The pyridil and imine $n \rightarrow \pi^*$ transitions in H₂Pt4DP overlap and are centered at 28686 cm⁻¹ and the band associated with the thioamide function $n \rightarrow \pi^*$ transition is found at 26 838 cm⁻¹. This former band undergoes a small blue shift, and the latter band a larger blue shift in the spectrum of the four complexes and is found

Table 7
Electronic spectra (cm⁻¹) for pyridil bis(3-hexamethyleneiminylthiosemicarbazone) and platinum complex prepared with pyridil bis(thiosemicarbazones)

Compound	Intraligand and charge transfer	d → d
H ₂ Pt4DP	42 590, 36 711, 28 686, 26 838	
[Pt ₂ (Pt4DE)Cl ₂] \cdot 4H ₂ O	42 470, 36 860, 32 370, 24 120, 20 700	17 830, 16 200, 14 300
[Pt ₂ (Pt4DP)Cl ₂] \cdot 3H ₂ O	43 090, 35 370sh, 24 290, 20 830	17 640, 16 390, 14 420
[Pt ₂ (Plpip)Cl ₂][Pt(Plpip)]	40 750, 35 370, 27 580, 21290	20 100, 18 180, 14 840, 13 820
[Pt ₂ (Plhexim)Cl ₂] \cdot 4H ₂ O	41 890, 35 300, 23 990, 20 510	17 710, 16 640, 14 540

in the 32 000–36 000 cm^{-1} region. The spectrum of each platinum(II) complex shows a $\text{S} \rightarrow \text{Pt(II)}$ charge transfer band at ca. 24 000 cm^{-1} and the $\text{d} \rightarrow \text{d}$ bands are consistent with planar stereochemistry [20].

The ^1H NMR assignments for $\text{H}_2\text{Pl4DE}$ and $\text{H}_2\text{Pl4DP}$ are similar to the assignments made for H_2Plpip [12] and $\text{H}_2\text{Plhexim}$ [14]. The spectrum of $\text{H}_2\text{Pl4DP}$ (CDCl_3) indicates a mixture of isomers with a low field NH , 11.00 ppm, due to intramolecular hydrogen bonding to the pyridine nitrogen, as well as a high field NH , that is hidden by the pyridine hydrogens, with the former present in greater concentration. The NMR spectra [$^2\text{H}_6$ –DMSO] of the platinum(II) complexes are weak because of their lack of solubility; the most soluble is $[\text{Pt}_2(\text{Plpip})\text{Cl}_2][\text{Pt}(\text{Plpip})]$, or more likely, the $[\text{Pt}(\text{Plpip})]$ part of the mixture. The peaks for the pyridine rings are at 8.79(d), 8.09(t), 7.68(t) and 7.37(d) ppm and downfield from 8.29(d), 7.82(t), 7.36(t) and 7.29(d) ppm for H_2Plpip [12] and 8.09(d), 7.70(t), 7.61(t) and 7.00(d) for $[\text{Ni}(\text{Plpip})]$. The resonances for piperidine rings in what is likely $[\text{Pt}(\text{Plpip})]$ are at 3.80, 2.07 and 1.54 ppm compared to 3.71, 1.72 and 1.25 ppm for H_2Plpip and 3.68, 2.15 and 1.56 ppm for $[\text{Ni}(\text{Plpip})]$.

4. Conclusion

In contrast to the pyridil bis{N(4)-substituted thiosemicarbazone} complexes with nickel(II) [12] and copper(II) [13], $[\text{Pt}_2(\text{Pl4DP})\text{Cl}_2]$ involves pyridine nitrogens in the Pt(II) coordination spheres. However, this complex has coordination by the imine nitrogens to both platinum(II) centers in contrast to $[\text{Pd}_2(\text{Plhexim})\text{Cl}_2]$, which has two different coordination modes for its Pd(II) centers. Although the platinum(II) complexes all showed coordinated chlorine atoms, we were able to obtain a crystal of $[\text{Pt}(\text{Pl4DP})]$ and compare its bonding to $[\text{Ni}(\text{Pl4DP})]$ and $[\text{Pt}_2(\text{Pl4DP})\text{Cl}_2]$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC no. 145336 for $[\text{Pt}(\text{Pl4DP})]$ and CCDC no. 145337 for $[\text{Pt}_2(\text{Pl4DP})\text{Cl}_2]$. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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