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Platinum coordination compounds of thiosemicarbazide derivatives: a new class of platinum blues

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Platinum(II) forms blue 1:2 coordination compounds with 1-phenylthiosemicarbazide [H(1-PTSC)], 4-phenylthiosemicarbazide [H(4-PTSC)], 1,4-diphenylthiosemicarbazide [H(1,4-DPTSC)] and 4-(2-pyridyl)-thiosemicarbazide [H(4-(2py)-TSC)]. Electronic spectra of these compounds have been studied in different solvents. In all compounds, a band is observed in the 650–750 nm region that appears to be a metal-to-ligand charge transfer band. Infrared and proton NMR studies have been carried out to determine possible coordination sites and the nature of the complexes. IR spectra indicate bonding through sulfur and nitrogen and proton NMR spectra indicate bonding through the N¹ nitrogen.

Keywords: Platinum; Platinum blues; Substituted thiosemicarbazides

1. Introduction

Platinum blues have generated substantial interest not only because of their antitumor activity [1–5] but also for their brilliant colors. Whereas most complexes of platinum are colorless, yellow or orange, these compounds, involving various amide [6–9] and pyrimidine [10–19] ligands, are intense blue, blue–green or purple. Ambiguity regarding the structure and nature of these complexes has prevailed for some time because of the difficulty involved in isolating crystalline complexes. As a result, a variety of structures have been assigned to the platinum blues. The structure most generally accepted involves square planar platinum and chelating acetamido groups [20, 21], but other structures postulated involve six-coordinate dimers [22] and polymeric chains with bridging acetamido groups [7]. These compounds show certain distinctive features such as oligomeric structures with mixed oxidation states for platinum [12, 23–27]. With the synthesis of the first crystalline platinum blue, *cis*-diammine platinum α -pyridone blue [17], a clearer picture of this class of compounds emerged. The preparation and characterization of platinum α -pyridone blue, as well as physical

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and chemical studies of a variety of related pyrimidine blues and the original "Platinblau," established that these species were all amidate-bridged, mixed-valence [28], partially metal-metal bonded oligomers of varying chain lengths [29, 30].

Apart from the above-mentioned platinum blues containing amidate bridges, reports of the spectrophotometric determination of platinum using thiosemicarbazide and its derivatives involving blue solutions have been published [31–33]. However, the nature of these blue solutions has not been established. This study concerns this new class of platinum blues, studied by a combination of spectroscopic techniques.

2. Experimental

2.1. Materials and methods

Chloroplatinic acid was purchased from Johnson Matthey (UK) and was used to prepare a stock solution of platinum. All other chemicals were of reagent grade and were used without further purification, apart from solvents, which were purified according to standard methods. Electronic absorption, IR and proton NMR spectra were recorded on Hitachi U3210, Unicam 300S (KBr disks, 4000–300 cm^{-1}) and Bruker DPX-300 instruments, respectively. Microanalyses were carried out at the Indian Association for the Cultivation of Sciences, Jadavpur, Kolkata. Magnetic susceptibilities were determined by the Gouy method.

2.2. Preparation of ligands

2.2.1. 1-Phenylthiosemicarbazide [H(1-PTSC)] [34]. Potassium thiocyanate (5×10^{-2} mol) and an equivalent of phenylhydrazine hydrochloride were added to 50 cm^3 of water. The mixture was neutralized with KHCO_3 . About 125 cm^3 of ethanol was added to precipitate KCl, which was filtered off. The solution was then evaporated to dryness and the residue heated at 160°C until an exothermic reaction took place. The resulting product was recrystallized from 10–20 cm^3 of water; m.p. 168°C, yield 80%.

2.2.2. 4-Phenylthiosemicarbazide [H(4-PTSC)] [35]. Aniline (0.1 mol) was dissolved in 20 cm^3 of ammonia solution cooled in an ice bath. CS_2 (8 cm^3) was then added slowly, followed by 20 cm^3 of ethanol and the solution was stirred for 2 h. After allowing to stand for another 2 h, 0.1 mol of sodium chloroacetate dissolved in 10 cm^3 of water was added, followed by 10 cm^3 of 50% hydrazine hydrate. The compound precipitated out gradually and was filtered and washed with ethanol; m.p. 139°C, yield ca 75%.

2.2.3. 1,4-Diphenylthiosemicarbazide [H(1,4-DPTSC)] [36]. About 4.0 g of thiocarbanilide was heated with 7.0 g of phenylhydrazine and the mixture stirred until it crystallized suddenly to a paste; 15 cm^3 of methanol was then added with stirring and the mixture cooled to room temperature. The product was filtered off and washed with methanol; m.p. 174°C, yield ca 80%.

2.2.4. 4-(2-Pyridyl)thiosemicarbazide [H(4-(2py)-TSC)] [37]. To 10 g of 2-aminopyridine, 12.5 g (10 cm^3) of carbon disulfide was added, followed by potassium

hydroxide solution (6.5 g in 15 cm³ of water), and the mixture refluxed for 1 h. Then 7.0 g hydrazine hydrate was added and the resulting solution further refluxed for 1 h. Needle-shaped crystals separated out, were filtered off, washed thoroughly with water and recrystallized from ethanol; m.p. 194°C, yield ca 70%.

2.3. Preparation of platinum complexes

About 10.0 cm³ of an aqueous H₂PtCl₆ solution containing 1.60 mg of platinum per cm³ was diluted to 100 cm³ and the pH of the solution adjusted to between 6.0 and 6.5 with sodium acetate solution (10%). The solution was heated nearly to boiling and about 80 mg of the required thiosemicarbazide derivative dissolved in ethanol was added. The resulting solution was warmed on a water bath for 1 h. Blue to blue-green precipitates of the complexes were collected by filtration through a sintered glass frit, washed with hot water and dried at 110°C. Analyses (C, H, N, S, Pt) were consistent with a 1 : 2 metal : ligand ratio for all cases and with the simple stoichiometries Pt(1-PTSC), Pt(4-PTSC)₂, Pt(1,4-DPTSC)₂ and Pt[4-(2py)-TSC]₂. All complexes are diamagnetic.

3. Results and discussion

3.1. Electronic spectra

Absorption maxima in the electronic spectra of the platinum complexes in different solvents and their assignments are listed in table 1. Assignments are based on those of bis(maleonitriledithiolato)platinum(II) [38, 39], considering a planar, distorted D_{2h} symmetry applies to platinum(II) complexes of thiosemicarbazide derivatives. Electronic spectra show in general four maxima in the region 210–800 nm. Some complexes exhibit up to five bands. Of these, at least three are very intense, with $\epsilon > 1000 \text{ M}^{-1} \text{ cm}^{-1}$, and are most probably due to charge transfer transitions (M → L or L → M) or to transitions localized on the ligands (L → L). Weak bands with molar extinction coefficients less than 100 M⁻¹ cm⁻¹ and half bandwidth values greater than 5000 cm⁻¹ are assigned to Laporte-forbidden d–d transitions.

Table 1. Electronic absorption data for the complexes.

	λ_{max} (nm)				Assignment	
	C ₂ H ₅ OH	CHCl ₃	CH ₃ COOC ₂ H ₅	(CH ₃) ₂ SO		
Pt(1-PTSC) ₂	676	672	679	693	MLCT	a _{1g} → a _{2u} [*]
	436	435	436	437	d–d	a _{1g} → b _{1g}
	385	382	387	390	LMCT	a _{1g} → b _{1u}
	312	312			L → L*	a _{1g} → b _{2u}
	231				LMCT	a _{1g} → b _{2u}
Pt(4-PTSC) ₂	660	666	678		MLCT	a _{1g} → a _{2u} [*]
Pt(1,4-DPTSC) ₂	753	749	760	766	MLCT	a _{1g} → a _{2u} [*]
	430	431	429	431	d–d	a _{1g} → b _{1g}
	327		328	328	L → L*	a _{1g} → b _{2u}
	270				LMCT	a _{1g} → b _{1u}
Pt(4-2py-TSC) ₂	650		653	667	MLCT	a _{1g} → a _{2u} [*]

The most striking feature in the electronic spectra of the complexes is the blue band in the 650–760 nm region. Half bandwidths range between 2000 and 3000 cm^{-1} while extinction coefficients ($\text{M}^{-1}\text{cm}^{-1}$) vary from 6040 for $\text{Pt}(1\text{-PTSC})_2$ to 4497 for $\text{Pt}(1,4\text{-DPTSC})_2$ in ethanol solution. Considering the half bandwidth and the shift in position of the band with change of solvent, this may be assigned as a charge transfer band of the $\text{M} \rightarrow \text{L}$ type. It is unsymmetrical and broadened on the lower wavelength side, suggesting that it is probably an envelope of two bands due to electronic transitions of the MLCT type, $a_{1g} \rightarrow a_{2u}^*$ and $a_{1g} \rightarrow b_{2u}^*$. The second highly intense band, observed in the shorter wavelength region at around 35 000 cm^{-1} and above, is assigned to the high-energy, allowed $\text{L} \rightarrow \text{M}$ charge transfer transition, $b_{1u}(\sigma) \rightarrow b_{1g}$. $\text{L} \rightarrow \text{L}$ transitions are allowed, with the lowest energy band corresponding to $n \rightarrow \pi^*$ followed by $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$. These bands, although intense, are almost unaffected by change in solvent polarity. On comparing ligand absorption spectra with those of the corresponding platinum complex, the $\text{L} \rightarrow \text{L}$ band of lowest energy observed around 30 000 cm^{-1} in the complexes is at 32 051 cm^{-1} in $\text{Pt}(1\text{-PTSC})_2$ and at 30 581 cm^{-1} in $\text{Pt}(1,4\text{-DPTSC})_2$. The band is not observed in $\text{Pt}(4\text{-PTSC})_2$ and $\text{Pt}[4\text{-(2Py)-TSC}]_2$. This is most probably due to the very low solubility of these complexes in ethanol or chloroform. The tails of the intense absorption bands of ethyl acetate or dimethyl sulfoxide, in which these complexes are more soluble, obscure the spectra in this region.

Broad bands in the 430–440 nm region, with half bandwidths greater than 5000 cm^{-1} and very low extinction coefficients ($\epsilon < 100 \text{M}^{-1}\text{cm}^{-1}$), are assigned to the parity forbidden d–d transition $a_{1g} \rightarrow b_{1g}$. This band, in the yellow region of the spectrum, is almost unaffected by change in solvent polarity and is unambiguously assigned as the d–d transition. It is interesting to note a progressive bathochromic shift in the blue band (table 1; MLCT transition) with addition of phenyl groups to the thiosemicarbazide moiety. The absorption maximum of the root of the platinum thiosemicarbazide complex, $\text{Pt}(\text{TSC})_2$, is observed at 590 nm.

3.2. Infrared spectra

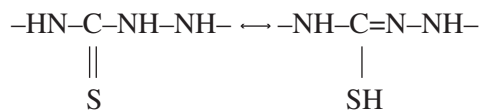
Significant bands observed in the IR spectra of the ligands and their complexes with assignments [40–43] are listed in table 2. Other peaks [$\nu(\text{C}-\text{C})$, $\nu(\text{C}-\text{H})$ of the benzene ring, $\nu(\text{C}-\text{H})$ out-of-plane, $\nu(\text{C}-\text{H})$ in-plane, $\nu(\text{N}-\text{N})$ and $\beta(\text{C}-\text{N}-\text{N})$ vibrations] are of course observed in both the reagent and complex. As their positions in the complex did not change significantly from those in the free ligands, these are not recorded. Broad bands between 3410 and 3100 cm^{-1} in the ligands are due to (N–H) stretching of NH_2 and NH groups. Complexation leads to a shift towards higher frequency. Moreover, they are split in the complexes. A similar observation was made for *trans*-bis(glycinato)platinum(II) [44]. The corresponding *cis* complex shows at least three bands due to N–H stretching. On this basis it may be assumed that in the thiosemicarbazide complexes of platinum, the hydrazinic $-\text{NH}_2$ or $-\text{NH}$ groups occupy *trans* positions. The number of bands in the complexes is usually greater than in the ligands. The $-\text{NH}_2$ bending mode is observed in the region 1650–1600 cm^{-1} . The $\nu(\text{C}-\text{N})$ band (Amide II [45]) is observed in the region 1570–1500 cm^{-1} in the ligands. This shifts to higher frequency upon complexation.

Bands involving $\nu(\text{C}-\text{S})$ are often difficult to assign [46]. Coordination of sulfur induces changes in positions and intensities of bands other than pure (C–S) stretching frequencies. The $\nu(\text{C}-\text{S})$ band is not found at a particular frequency.

Table 2. Characteristic infrared absorption data (cm^{-1}) for substituted thiosemicarbazides and their platinum complexes.

	$\nu(\text{N-H})$	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{S-H})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$
H(1-PTSC)	3410 3240b	1545 1475	1080 835	2540vw		
Pt(1-PTSC) ₂	3490 3280	1620	1070 730		530	440
H(4-PTSC)	3320b	1530 1500 1450	1030 1010 780	2535vw		
Pt(4-PTSC) ₂	3410	1525 1500	900 700		510	400
H(1,4-DPTSC)	3300 3230sh 3180	1545 1515	1100 1080 780	2550vw		
Pt(1,4-DPTSC) ₂	3380	1600 1505sh	1080 1030 700		490	395
H[4-2py-TSC]	3350 3100	1475 1510	1145 1100 790	2530vw		
Pt[4-2py-TSC] ₂	3350 3150	1505 1535	1105 1055 710		515	410

Because of coupled vibrations it may occur near $\nu(\text{C-N})$, aromatic $\nu(\text{C-C})$ and δNH_2 modes. In thiosemicarbazide, $\nu(\text{C-S})$ has been assigned [47] at 803 cm^{-1} and is reported to have more than 50% contribution from the (C-S) stretching mode. The premise that $\nu(\text{C=O})/\nu(\text{C=S})$ ranges from 1.38 to 1.5 [48] enables assignment of $\nu(\text{C-S})$ bands in the ligands and their platinum complexes. Bands having contributions from $\nu(\text{C-S})$ are given in table 2. A very weak band observed at around 2550 cm^{-1} is assigned to $\nu(\text{S-H})$, attributed to the presence of keto-enol tautomerism in the ligand. The weakness of the band is most probably due to the following equilibrium lying to the left-hand side.



Metal-nitrogen (M-N) and metal-sulfur (M-S) stretching frequencies have also been assigned. The $\nu(\text{M-N})$ vibration may be tentatively assigned [49] at around $510\text{--}535\text{ cm}^{-1}$. In several coordination compounds the $\nu(\text{M-S})$ band has been assigned [50, 51] at around $380\text{--}450\text{ cm}^{-1}$. In the complexes under study, the band observed in the region $395\text{--}440\text{ cm}^{-1}$ may therefore be assigned to the (M-S) stretch.

3.3. Proton NMR

Table 3 presents chemical shift data for ^1H NMR spectra of the substituted ligands and their platinum complexes. NMR spectra of the ligand reveal, in the case of H(1-PTSC),

Table 3. Proton NMR data for ligands and complexes. Chemical shifts (δ) are given in ppm, relative to TMS. Spectra were recorded in CDCl_3 .

	<i>o</i> - ϕ H	<i>m</i> - ϕ H	<i>p</i> - ϕ H	N ¹ H	N ² H	N ⁴ H
H(1-PTSC)	6.98	6.46	7.25	6.57	7.57	7.69
Pt(1-PTSC) ₂	7.15	7.06	7.20	7.22	absent	7.61
H(4-PTSC)	7.40	6.98	7.42	6.62	8.16	8.63
Pt(4-PTSC) ₂	7.18	6.82	7.59	8.85	absent	8.36
H(1,4-DPTSC)	6.86, 7.52	7.25, 7.29	7.15, 6.97	5.85	7.40	8.91
Pt(1,4-DPTSC) ₂	6.88, 7.44	7.25, 7.29	7.31, 6.97	7.98	absent	8.90
H(4-2py-TSC)				6.17	12.11	9.13
Pt(4-2py-TSC) ₂				8.51	absent	9.12

six signals. Signals at δ 6.98, 6.46 and 7.25 ppm are assigned to *ortho*, *meta* and *para* protons, respectively, on the aromatic ring. As is evident from table 3, they undergo little shift (0.22 ppm or less) in the platinum complex. N¹, N² and N⁴ protons are observed at δ 6.57, 7.57, 7.69 ppm, respectively. The position of the N⁴ proton is only slightly affected on complexation, the signal of the N² proton disappears and the position of the N¹ resonance shifts downfield shift by > 1.5 ppm, indicating that complexation occurs through N¹. This trend is more or less adhered to in the other ligands and their platinum complexes.

The above results show that in the complexes platinum is bonded through nitrogen and sulfur donors in the *trans* fashion. The intense blue color of the complexes may be attributed to low-energy electron transitions from the a_{1g} metal orbital to the a_{2u}^* ($d\pi^*$) orbital of sulfur. It appears that the HOMO of the metal is very close to the antibonding LUMO of sulfur in the thiosemicarbazide complexes. It is noted that the blue color of most of the platinum blues has been attributed to mixed valence oligomeric structures. However, the appearance of bands with absorption maxima at longer wavelengths is not uncommon with platinum complexes of sulfur donors. It has been observed that bis(maleonitriledithiolato)platinum(II) exhibits an absorption maximum at 520 nm. Shupack and coworkers [38] calculated the energy of the molecular orbitals and assigned the band to the $a_{1g} \rightarrow a_{2u}^*$ transition. A similar explanation for the occurrence of a low-energy transition may also be offered in the case of the substituted thiosemicarbazide complexes of platinum(II).

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