Synthesis and spectroscopic studies on platinum(II) complexes of thiosemicarbazone derivatives of p-anisaldehyde, p-tolualdehyde and p-vanillin

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The platinum(II) complexes of thiosemicarbazone derivatives of p-anisaldehyde (ATSCH), p-tolualdehyde (TTSCH) and p-vanillin (VTSCH) have been prepared and characterized by analytical, molar conductance, infrared, electronic, $^1$H and $^{13}$C NMR spectral data. Thiosemicarbazones exist in thione form and coordinate through thiolato/thiono sulphur and azomethine nitrogen. The chloro bridged dinuclear structures for $[\text{Pt(ATSCH)}\text{Cl}_2]$, $[\text{Pt(TTSCH)}\text{Cl}_2]$ and $[\text{Pt(VTSCH)}\text{Cl}_2]$ having four coordinate platinum(II) centres and square planar for $[\text{Pt(ATSCH)}\text{Cl}_2]$, $[\text{Pt(TTSCH)}\text{Cl}_2]$ and $[\text{Pt(VTSCH)}\text{Cl}_2]$ are suggested.

Platinum(II) complexes are interesting due to their biological role\(^1\) and medicinal properties\(^2\) -\(^4\). Cis-platin and a few thiosemicarbazones have been tested for combination chemotherapy for cancer\(^5\). The chemical\(^6\),\(^7\) and biological activities\(^8\) of thiosemicarbazones have been the subject of investigation in recent years. Besides, the thiosemicarbazones have been widely used as analytical reagents\(^9\). Platinum(II) complexes with bidentate\(^10\),\(^11\) and tridentate\(^12\),\(^13\) thiosemicarbazones have been reported. There are also a few reports on metal complexes with thiosemicarbazone derivatives of p-vanillin\(^14\),\(^15\) and p-anisaldehyde\(^16\),\(^17\). The present article describes the synthesis, IR, electronic, $^1$H and $^{13}$C NMR spectral properties of platinum(II) complexes of thiosemicarbazone derivatives of p-anisaldehyde (4-methoxy benzaldehyde), p-tolualdehyde (4-methyl benzaldehyde) and p-vanillin (4-hydroxy 3-methoxy benzaldehyde) abbreviated as ATSC, TTSCH and VTSCH respectively.

Materials and Methods

Preparation of thiosemicarbazones\(^16\),\(^17\)

**VTSCH (4-hydroxy 3-methoxy benzaldehyde thiosemicarbazone)**

To a boiling solution of p-vanillin (3.04 g, 20mmol) in ethanol (25 cm\(^3\)) was added dropwise a solution of thiosemicarbazide (1.82 g, 20mmol) in ethanol (50 cm\(^3\)) and the resulting solution was refluxed for a period of 2 h. The solution was then cooled and the crystals collected by filtration, washed with ethanol, followed by diethylether and dried over fused CaCl\(_2\). M.pt. 197-8°C. FAB (Pos) mass spectrum, m/z 226.0 (MH\(^+\)), Calcd molar mass 225.17 Anal. [Found: C=47.90, H=4.85, N=18.62; Calcd for C\(_9\)H\(_{11}\)N\(_3\)O\(_2\)S: C=48.00, H=4.89, N=18.66%]; IR/cm\(^{-1}\): \(v(\text{OH})\) 3530, \(v(\text{NH}_2)\) 3439, 3157, \(v(\text{NH})\) 3280, \(v(\text{C=N})\) 1611, \(v(\text{C=C})\) 1598, \(\delta(\text{NH}_2)\) 1587,1546, \(v(\text{NCS})\) 1462, 1443, 1428, 1376, \(v(\text{C=S})\) 838.

**ATSCH (4-methoxy benzaldehyde thiosemicarbazone)**

This ligand was prepared as described above using p-anisaldehyde. M.pt. 174-5°C. FAB (Pos) mass spectrum, m/z 210.0 (MH\(^+\)), calcd molar mass 209.17 Anal. [Found: C=51.62, H=5.20, N=21.68; Calcd for C\(_9\)H\(_{11}\)N\(_3\)S: C=51.68, H=5.26, N=21.75%]; IR/cm\(^{-1}\): \(v(\text{NH}_2)\) 3407, 3159, \(v(\text{NH})\) 3293, \(v(\text{C=N})\) 1607, \(v(\text{C=C})\) 1576, \(\delta(\text{NH}_2)\) 1538, 1513, \(v(\text{NCS})\) 1475, 1449, 1418, 1362, \(v(\text{C=S})\) 835.

**TTSCH (4-methylbenzaldehyde thiosemicarbazone)**

This ligand was prepared as described above using p-tolualdehyde. M.pt. 175-6°C. FAB (Pos) mass spectrum, m/z 194 (MH\(^+\)), calcd molar mass 193.26 Anal. [Found: C=55.88, H=5.67, N=21.68; Calcd for C\(_9\)H\(_{11}\)N\(_3\)SO: C=55.98, H=5.69, N=21.75%]; IR/cm\(^{-1}\): \(v(\text{NH}_2)\) 3404, 3158, \(v(\text{NH})\) 3244, \(v(\text{C=S})\) 1598, \(v(\text{C=C})\) 1568, \(\delta(\text{NH}_2)\) 1540, 1510, \(v(\text{NCS})\) 1475, 1464, 1410, 1370, \(v(\text{C=S})\) 830.

Preparation of platinum(II) complexes

$[\text{Pt(VTSCH)}\text{Cl}_2]$: \(\mu\text{-chloro-bis(4-hydroxy-3-methoxybenzaldehyde thiosemicarbazonato) diplatinum(II)}\) — p-vanillin thiosemicarbazone (VTSCH) and K\(_2\) Pt Cl\(_4\) (1:1 molar ratio) were dissolved in aqueous ethanol and the resulting mixture was refluxed for 2 h.
crystalline product was isolated and washed with ethanol, diethylether and dried over fused CaCl₂. Anal. [Found: C=23.60, N=9.20, H=2.26. Calcd for \( \text{Pt}_2\text{C}_8\text{H}_{20}\text{N}_6\text{S}_2 \): C=25.57, N=9.94, H=2.38%].

\( \text{M} =0.80 \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}, \text{IR/cm}^{-1}: \nu(\text{NH}) 3286br, \nu(C=N) 1574, \delta(\text{NH}) 1540, 1513, \nu(\text{NCS}) 3460, 3417, 3357, 3171, \nu(\text{NH}) 3288, \nu(\text{C} = \text{N}) 1574, \delta(\text{NH}) 1536, 1509, \nu(\text{NCS}) 1461, 1413, 1374; \nu(\text{C} = \text{S}) 829, 702, \nu(\text{Pt} = \text{N}) = 485, \nu(\text{Pt} = \text{S}) = 350.\)

\( \text{M} =0.65 \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}, \text{IR/cm}^{-1}: \nu(\text{NH}) 3343, 3325, 3148, \nu(C = N) 1587, \delta(\text{NH}) 1537, \nu(\text{NCS}) 1476, 1440, 1394, 1375, \nu(\text{C} = \text{S}) 805, 701; \nu(\text{Pt} = \text{N}) = 497, \nu(\text{Pt} = \text{S}) = 330, \nu(\text{Pt} = \text{Cl}) = 240.\)

[Pt(ATSCH)Cl₂]: Bis(4-hydroxy-3-methoxybenzaldene thiosemicarbazone) platinum(II) chloride—Aqueous ethanolic solutions of p-toluinaldehyde thiosemicarbazone (ATSCH) with \( \text{K}_2\text{PtCl}_4\) in 2:1 molar ratio as described above, yellowish brown crystals were obtained. Anal. [Found: C=30.08, N=11.70, H=3.07. Calcd for \( \text{PtC}_18\text{H}_{22}\text{N}_6\text{S}_2\text{Cl}_2 \): C=30.17, N=11.73, H=3.09%].

\( \text{M} =138 \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}, \text{IR/cm}^{-1}: \nu(\text{OH}) 3425, \nu(\text{NCS}) 3328, \nu(\text{NH}) 3175, \nu(\text{C} = \text{N}) 1596, \delta(\text{NH}) 1512, \nu(\text{NCS}) 1466, 1427, 1380, \nu(\text{C} = \text{S}) 821, 685, \nu(\text{Pt} = \text{N}) 496, \nu(\text{Pt} = \text{S}) = 370.\)

Dried samples were used for all physical and spectral measurements and carbon, hydrogren and nitrogen were analyzed using a Coleman Analyzer at RSIC, CDRI, Lucknow, India. Physical measurements, IR, electronic, \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were obtained as reported earlier. FTIR spectra were obtained on a Perkin-Elmer 1800 spectrometer at CDRI, Lucknow, India. Positive ion fast atom bombardment (FAB*) mass spectra were obtained with \( \text{m}/\text{z}\) nitrobenzyl alcohol as matrix.

**Results and Discussion**

The reactions of 4-methoxybenzaldene thiosemicarbazone (ATSCH) with \( \text{K}_2\text{PtCl}_4\) in the presence of hydrochloric acid gave \( [\text{Pt}(\text{ATSCH})\text{Cl}]\) and \( \text{Pt}(\text{ATSCH})_2\text{Cl}_2\).

\[
\text{ATSCH} + 2\text{K}_2\text{PtCl}_4 + \text{HCl} \rightarrow [\text{Pt}(\text{ATSCH})\text{Cl}] + 2\text{KCl} + \text{HCl}
\]

(1)

\[
2\text{ATSCH} + 2\text{K}_2\text{PtCl}_4 + \text{HCl} \rightarrow [\text{Pt}(\text{ATSCH})_2\text{Cl}_2] + 2\text{KCl}
\]

(2)

The TTSC (4-methylbenzaldene thiosemicarbazone) and VTSHC (4-hydroxy 3-methoxy benzaldehyde thiosemicarbazone) react in similar reaction conditions to produce (1:1) and (1:2) platinum(II) complexes respectively. The complexes are sparingly soluble in common organic solvents but soluble in DMF and DMSO. The electrical conductance measurements in DMF reveal the non-electrolytic

\[
[\text{Pt}(\text{ATSCH})\text{Cl}]_{\text{aq}}
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\[
[\text{Pt}(\text{ATSCH})_2\text{Cl}_2]_{\text{aq}}
\]
nature for [Pt(ATSC)Cl], [Pt(TTSC)Cl] and [Pt(VTSC)Cl], whereas the [((Pt(ATSC))Cl)2, (Pt(TTSC))Cl2 and [Pt(VTSC)Cl2] complexes exhibit (1:2) electrolytic nature.

The spectra of these thiosemicarbazones show three distinct bands in the region 3155-3160, 3240-3300 and 3400-3440 cm⁻¹. These bands are usually attributed to ν(OH) and ν(NH) stretching vibrations. Among these bands, the location of the middle one is the most sensitive to the aromatic part of the molecule since NH group is closer to the aromatic substituent than the N₂H₂ function. Thus, the middle band is assigned to ν(NH).

The IR spectrum of [Pt(VTSC)Cl] show only one broad band having maximum at 3286 cm⁻¹ and the spectrum of [Pt(ATSC)Cl] exhibits two sharp bands above 3100 cm⁻¹ assignable to νₜ(NH₂) and νₛ(NH₂) modes. The spectrum of [Pt(TTSC)Cl] differs from the spectra of other two complexes. The νₜ(NH₂) band is split due to probable interaction between two platinum(II) complex molecules. Crystallographic study on Ni(TTSC)₂ has indicated existence of twinned complexes. These observations provide sufficient evidence for probable deprotonation of NH group before coordination with platinum(II) ion. The spectrum of ATSCH also shows a band at 1607 cm⁻¹ assignable to ν(CN) vibration. On coordination it combines with the new ν(CN) band formed on loss of the NH proton to yield a band at 1600 cm⁻¹. Similar change has been observed for the other two platinum(II) complexes. A broad band at 835 cm⁻¹ as a result from coupled vibrations with large participation of the ν(CS) vibration has been located in the spectrum of ATSCH. This band disappears on coordination and is replaced by two bands at 832 and 704 cm⁻¹. Similar observations have been recorded for the spectra of other two platinum(II) complexes. A decrease in energy of this band is taken as an indication of metal-sulphur bond formation.

Both coordination modes are further supported by the presence of new bands in the far IR spectra of the complexes. Far IR spectra show new bands located at wavenumbers comparable with those previously attributed to ν(PTN), ν(PTS) and ν(PTCl) transitions. The earlier report suggests that the vibration energy for νₛ(PTCl) must be lower than νₜ(PTCl) due to the possible sharing of electrons between chloride and two platinum(II) ions. The reported value for νₛ(PTCl) in the spectra of K₂PtCl₄ (ref. 19) and an organometallic compound fall in the range 315-325 cm⁻¹. The values observed in the spectra of platinum(II) complexes in the range 230-260 cm⁻¹ suggest the bridging mode for chloride.

Infrared spectra of [Pt(ATSC)Cl]₂, [Pt(TTSC)Cl]₂ and [Pt(VTSC)Cl]₂. The νₛ(NH₂) band splits in the spectrum of [Pt(ATSC)Cl]₂ indicating intermolecular hydrogen bonding. The remaining spectra of the other complexes show increase in the energy of this vibration. The ν(NH) vibration energy decreases in the spectra of [Pt(ATSC)Cl]₂ and [Pt(VTSC)Cl]₂ but increases in the spectrum of [Pt(TTSC)Cl]₂. A group of bands resulting partially from coupled vibration of ν(NCS) modes and located between 1370-1470 cm⁻¹ in the spectra of thiosemicarbazones are also modified upon coordination with platinum(II) ions. The vibrational band in the region of 830-840 cm⁻¹ with predominant ν(CS) character also moves to lower energy region in the spectra of platinum(II) complexes indicating thione sulphur coordination. The observation of far IR bands in the spectra of platinum(II) complexes in the region of 482-496 and 335-370 cm⁻¹ due to ν(PTN) and ν(PTS) transitions respectively further suggest the involvement of azomethine nitrogen and thione sulphur coordination. Thus, thiosemicarbazones act as neutral bidentate chelating ligands. (Structure I).

The coupled vibrational character of nitrogen-hydrogen band together with hydrogen bond effects create serious problem in obtaining conclusive evidences of thiosemicarbazone deprotonation. On comparison of ¹H NMR spectra of thiosemicarbazones and (1:2) platinum(II) complexes recorded suggest that neutral form of ligands are present in [Pt(ATSC)Cl]₂, [Pt(TTSC)Cl]₂ and [Pt(VTSC)Cl]₂. The respective signal of NH group proton appears in the region 11.25-11.33 ppm in the ligand spectrum and it shifts to 12-12.50 ppm in the spectra of these platinum(II) complexes. The effects may result from changes in electron density after nitrogen-platinum(II) coordination.

The disappearance of this signal in the spectra of [Pt(ATSC)Cl]₂, [Pt(TTSC)Cl]₂ and [Pt(VTSC)Cl]₂ supports the presence of deprotonated form of thiosemicarbazones in these complexes. The two signals due to NH₂ protons are observed in the region 7.90-8.15 ppm and they shift upfield in the spectrum of [Pt(TTSC)Cl]₂ and downfield in the spectrum of [Pt(VTSC)Cl]₂. However, only one signal has been located in the spectrum of [Pt(ATSC)Cl]₂. The spectra of [Pt(ATSC)Cl]₂ and [Pt(VTSC)Cl]₂ show
Structures of Platinum(II) complexes

These signals at 8.20 and 8.50 ppm respectively indicating presence of unperturbed NH₂ groups. Moreover, the spectrum of [Pt(VTSC)Cl₂]₂ shows two signals for NH₂ group protons supporting intermolecular hydrogen bonding. A similar observation has been made during IR spectral study. The other proton signals are least affected. The observation of two signals due to CH₃ group protons could be attributed to the structural differences in two chelate rings in the platinum(II) complexes (Structure I).

The ¹³C NMR chemical shifts of thiosemicarbazones and their platinum(II) complexes have been obtained. The carbon signals for C=0 (177.44-177.81 ppm) and CH=N (142.17-143.28 ppm) groups are comparable with those reported earlier for thiosemicarbazones. In the spectra of [Pt(ATSC)Cl₂], [Pt(TTSC)Cl₂] and [Pt(VTSC)Cl₂] complexes, signal due to C=S moves upfield but signal due to CH=N moves downfield suggesting coordination involving azomethine nitrogen and thiolato sulphur. However, the spectrum of [Pt(VTSC)Cl₂]₂ exhibits signal due to C=S at 174.90 and 174.20 ppm and signal due to CH=N at 162.7 and 155.20 ppm respectively. The spectra of [Pt(ATSC)Cl₂] and [Pt(TTSC)Cl₂]₂ are quite different and show downfield shift of C=S signal probably due to increase in C=S bond order in cationic complexes. The difference in spectral changes could be attributed to the difference in the structure of thiosemicarbazone part of the complexes. The two signals due to CH₃ group could support the presence of two isomeric forms of the complexes. Thus, the observed spectral data suggest coordination through thione sulphur and azomethine nitrogen in the cationic platinum(II) complexes (Structure I).

The solution and solid state reflectance spectra of thiosemicarbazones and platinum(II) complexes have been recorded. Bands above 36000 cm⁻¹ are assigned to π-π* transitions of aromatic system. Lower energy absorption observed in the spectra of thiosemicarbazones around 30000-31000 cm⁻¹ result from π-π* (CH=N) transition. On metal coordination, this transition moves to lower energy indicating the electron density change caused by nitroge-platinum(II) bond formation. The smaller downward shift of π-π* (arom) transition is due to conjugation of π-orbitals of aromatic system and lone pair of electrons in azomethine group. The spectra of (1:2) cationic platinum(II) complexes exhibit only one composite spectral band probably due to the least difference in the energy levels for dₓz, dₓᵧ and dᵧ orbitals. The spectra of (1:1) neutral platinum(II) complexes show bands in the regions of 18500-19700, 20800-21800 and 29100-30200 cm⁻¹. These spectral bands are assigned to the transitions, A₁g →'A₂g + 'B₁g and 'A₁g →'E₁ in order of increasing energy. Thus, the comparison of electronic spectra of thiosemicarbazones and their platinum(II) complexes is able to provide some evidence about the mode of coordination. The ligand coordination takes place through thiolate/thione sulphur and azomethine nitrogen giving four coordinate platinum(II) centres (Structure I).

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