above, measurements of the electronic spectra of nickel complexes can not be used to identify binucleated structures. We have, therefore, no evidence at the moment on whether the nickelboron complex differs in structure from the other nickel group IV and group V metal complexes under investigation.

The financial support by the CSIR, New Delhi is gratefully acknowledged. One of us (A. K. B.) thanks the University of Kalyani for awarding a Junior Research Fellowship. Thanks are also due to Prof. P. L. Pauson of Strathclyde University, Glasgow, Prof. H. Werner of Würzburg University, West Germany and Dr. R. L. De of München University, West Germany for spectral and elemental analyses.

References

Palladium(II) & Platinum(II) Halide Complexes with 2,2''-Thiodiacetophenone Derivatives

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2,2''-Thiodiacetophenones (D) form 2:1 and 1:1 complexes with palladium(II) halides and platinum(II) chloride, having the general formulae MX2 (D)2 [M = Pd(II), X = CI, Br; M = Pt(II), X = CI] and [PtCl2(D)2] respectively. On the basis of IR and X-ray and electronic spectral data, these complexes have been assigned square planar stereochemistry, with coordination through sulphur atom. The carbonyl oxygen atoms are not involved in coordination. However, in [PtCl2(D)2] bridging through chloride ions gives a binuclear complex.
tered, washed with methanol, benzene and dried in vacuo at 80°C.

(b) Alternatively a solution of 1 (0.002 mol) in tetrahydrofuran (20 ml) was added to a stirred solution of palladium(II) chloride (0.001 mol) in methanol (25 ml) containing large amount of hydrochloric acid (1 ml) and the complexes, obtained were found to be identical (m.m.p. and spectral data) with those obtained in method (a).

Palladium(II) bromide complexes — Palladium(II) bromide was obtained from palladium(II) chloride by repeated treatment with hydrobromic acid (48%). To a solution of palladium(II) bromide (0.002 mol) in methanol (25 ml) was added a solution of 2 (0.002 mol) in tetrahydrofuran with constant stirring. The complexes were isolated as in method (a).

Platinum(II) chloride complexes — A solution of chloroplatinic acid (0.001 mol) in methanol (30 ml) was refluxed for 30 min to reduce platinum(IV) to platinum(II). To this a solution of the ligand (D) (0.002 mol) in THF (25 ml) was added dropwise with constant stirring. In the case of D-1 and D-3 the complexes separated out immediately but with D-2 the solution was refluxed for 30 min and the reaction mixture concentrated to one-third under reduced pressure. On cooling, the complex separated out which was isolated as in method (a).

The characterization data of the complexes (Table 1) indicate a 2:1 stoichiometry, PdX₂(D)₂ (where X = Cl, or Br) for the complexes of palladium(II) halides. However, platinum(II) chloride complexes of the molecular formulae PtCl₂(D)₂ (where D = D-2, D-3) or [PtCl₂(D-1)]₂ have been isolated. These complexes are stable in air and moisture and are either insoluble or sparingly soluble in methanol, ethanol, acetone, chloroform, benzene, nitrobenzene, DMF and DMSO. These complexes are nonelectrolytes in DMF and DMSO.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complex*</th>
<th>m.p.†</th>
<th>v(M-Cl)cm⁻¹</th>
<th>v(M-S)cm⁻¹</th>
<th>Found (Calc.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[PdCl₂(D-1)]₂</td>
<td>205-8</td>
<td>320s</td>
<td>350w</td>
<td>14.32 (14.47)</td>
</tr>
<tr>
<td>2.</td>
<td>[PdCl₂(D-2)]₂</td>
<td>210-13</td>
<td>320m</td>
<td>360mb</td>
<td>12.28 (12.60)</td>
</tr>
<tr>
<td>3.</td>
<td>[PdCl₂(D-3)]₂</td>
<td>235-40</td>
<td>330s</td>
<td>360w</td>
<td>12.15 (12.40)</td>
</tr>
<tr>
<td>4.</td>
<td>[PdCl₂(D-4)]₂</td>
<td>255-50</td>
<td>330m</td>
<td>360w</td>
<td>11.57 (12.01)</td>
</tr>
<tr>
<td>5.</td>
<td>[PdBr₂(D-1)]₂</td>
<td>210-15</td>
<td>320s</td>
<td>350w</td>
<td>12.83 (13.15)</td>
</tr>
<tr>
<td>6.</td>
<td>[PdBr₂(D-2)]₂</td>
<td>213-15</td>
<td>320m</td>
<td>360w</td>
<td>12.06 (12.30)</td>
</tr>
<tr>
<td>7.</td>
<td>[PdBr₂(D-3)]₂</td>
<td>252-55</td>
<td>320s</td>
<td>350w</td>
<td>10.95 (11.23)</td>
</tr>
<tr>
<td>8.</td>
<td>[PdBr₂(D-4)]₂</td>
<td>211-13</td>
<td>320m</td>
<td>360w</td>
<td>11.15 (11.44)</td>
</tr>
<tr>
<td>9.</td>
<td>[PtCl₂(D-1)]₂</td>
<td>216-17</td>
<td>305m</td>
<td>370w</td>
<td>35.85 (36.11)</td>
</tr>
<tr>
<td>10.</td>
<td>[PtCl₂(D-2)]₂</td>
<td>140-45</td>
<td>310m</td>
<td>370w</td>
<td>22.35 (22.62)</td>
</tr>
<tr>
<td>11.</td>
<td>[PtCl₂(D-3)]₂</td>
<td>255-57</td>
<td>315m</td>
<td>370w</td>
<td>20.18 (20.61)</td>
</tr>
</tbody>
</table>

*Colour of the complexes: Dark yellowish (Sl. No. 1); dirty yellow (2 and 9); yellow (3, 5-7); brownish yellow (4, 8); blackish brown (10); and brown (11)
† All these complexes melt with decomposition giving black residues.

† IR spectra (v_max in cm⁻¹) were recorded in nujol on Beckman-12 (200-600 cm⁻¹) and Spectromom (650-4500 cm⁻¹) instruments.
bridging and mononuclear structure(3) for rest of the platinum (II) and palladium(II) complexes.

The solid state electronic spectra of these complexes, recorded on Carl-Zeiss VSU-2 instrument show the following bands: (i) 37005-40815; (ii) 33670-36363; (iii) 29000-32580; and (iv) 19230- 23810 cm⁻¹. The intense band (i) is due to the internal ligand transition which appears at 39215 cm⁻¹ in the free ligand (2). The transitions (ii) and (iii) which also are of high intensity have tentatively been assigned to charge transfer mixed with internal ligand transition. The band (iv) of medium intensity has been assigned to $A_g \rightarrow$ $B_g$ transition in square planar platinum(II) and palladium(II) complexes.

Thermogravimetric and differential thermal analysis of [PdCl₂(D-4)₂]₂H₂O confirm the presence of two occluded molecules of water as the complex loses two water molecules at 80-100°C in TG while DTA shows no endothermic peak at this temperature. The endothermic peak in DTA at 280°C has been assigned to the loss of sulphur which has further been corroborated by TG as mass loss at this temperature corresponds approximately to the loss of sulphur. Further heating results in the loss of organic portion and halide ions with the formation of metal oxide at 600°C.

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References


Studies on Some Transition Metal Complexes of Schiff Bases Derived from Sulphaphenazole

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Complexes of the monovalent bidentate Schiff bases, 4-[5-(1-phenylpyrazolyl)sulphamyl]-2'-hydroxybenzylideneaniline (PSHBA) and 4-[5-(1-phenylpyrazolyl)sulphamyl]-2'-hydroxy-a-methylbenzylideneaniline (PShMBA) with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been prepared and characterised on the basis of elemental analyses, molar conductance, magnetic moment, infrared and electronic spectral studies. The stepwise stability constants of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes have also been determined using Calvin-Bjerrum potentiometric method in 25% (v/v) dioxane-water medium at an ionic strength 0.1 M (NaClO₄) and 27 ± 0.2°.

A SURVEY of the literature reveals that no work has so far been done on the coordination behaviour of the Schiff bases derived from sulphaphenazole such as 4-[5-(1-phenylpyrazolyl)sulphamyl]-2'-hydroxybenzylideneaniline (PSHBA) and 4-[5-(1-phenylpyrazolyl) sulphamyl]-2'-hydroxy-a-methylbenzylideneaniline (PSHMBBA). In continuation of our earlier studies on the sulphadrugs, we report here the preparation and characterisation of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes of these ligands (I). The complexes have also been studied in solution, employing Calvin-Bjerrum potentiometric titration technique as modified by Irving and Rossotti in 25% dioxane-water medium at an ionic strength 0.1 M (NaClO₄) and 27 ± 0.2°.

Sulphaphenazole was procured from M/s Ciba-Geigy Ltd., Bombay, and used as such. Salicylaldehyde, o-hydroxyacetophenone, sodium hydroxide, perchloric acid, sodium perchlorate, dioxane and metal salts were of AR grade. Solvents were purified by the standard methods.

Systronic digital pH-meter type 355 was employed for pH measurements (sensitivity, ±0.01 units) and calibrated at pH 4.05 and 9.18 using potassium hydrogen phthalate and borax buffer respectively. The molar conductance measurements were carried out on a Toshniwal conductivity-bridge type CL01. Magnetic measurements were carried out at room temperature (27°) in powder form by Gouy method using Hg[Co(NCS)₄] as the calibrant. The infrared spectra of the ligands and the complexes were recorded in KBr on a Perkin-Elmer 337 spectrophotometer. The electronic spectra of the complexes were recorded on a Beckman DU-2 (manual) spectrophotometer in methanol.

The Schiff bases, PSHBA and PSHMBA (m.p. 232° and 245° respectively) were synthesized by refluxing sulphaphenazole with salicylaldehyde and o-hydroxyacetophenone in ethanol in 1 : 1 ratio in the presence of anhydrous sodium acetate for 3-4 hr. The reaction mixture was poured into water and the precipitate obtained was crystallized from acetone.

Preparation of the complexes — The solution of the ligand in acetone was added dropwise with constant stirring to an aqueous solution of the metal ion in the ratio 2 : 1. On stirring the reaction mixture for 3-4 hr, the coloured complex separated out. The precipitated complex was filtered and washed with water, 50% ethanol and finally with ether and then