Magnetic & Spectral Studies on Dithiophosphinates of Ru(III), Rh(III) & Pd(II)

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New complexes of Ru(III), Rh(III) and Pd(II) of the type M(Etdtpi) or with di-(p-ethylphenyl)dithiophosphinic acid have been synthesised and characterised on the basis of elemental analyses, magnetic measurements, infrared and electronic spectral data. The octahedral Ru(III) compound is found to be paramagnetic with one unpaired electron while the octahedral Rh(III) and square-planar Pd(II) complexes are diamagnetic. Wherever possible 10Dq, B and β have been calculated and the values discussed with respect to the position of this ligand in the spectrochemical and nephelauxetic series of other dithi-ligands. Di-(3,4-dimethylphenyl)dithiophosphinato complexes of these metals together with a novel addition compound [Pd(3,4-Me2dtpi)2PPh3] are also described.

STABLE dithiophosphinates of nickel, and expansion of the coordinatively unsaturated NiS4 core to form penta- and hexa-coordinate complexes with nitrogen and oxygen donor molecules have been reported1-3. In this connection it was of interest to note that Ni(Etdtpi)2 (Etdtpi = di-(p-ethylphenyl) dithiophosphinate) was not sufficiently stable for isolation in the solid state and could be studied only in solution4. The present work was undertaken to see the behaviour of Etdtpi towards complex formation with second transition series metal palladium and to study the formation of any adducts by the PdS4 core. Complexes formed by the light platinum metals, Ru(III) and Rh (III), are also included to see the effect of substitution on phosphorus atom in relation to the magnitude of spectrochemical parameters.

Materials and Methods

The magnetic moment measurements were carried out at room temperature on a Gouy balance using Hg[Co(SCN)4] as the calibrant. UV-visible and IR spectra were recorded on Perkin-Elmer 402 and Beckmann IR-10 (200-800 cm-1) and Perkin-Elmer 297-B (625-4000 cm-1) Spectrophotometers. Molecular weights were determined by vapour pressure osmetry in benzene on a Knaur vapour pressure osmometer (Berlin) at different concentrations.

Preparation of the complexes — The compounds were synthesised employing similar procedures. Solutions of the metal chloride in methanol and the methanolic solutions of Me2dtpiH [di-(3,4-dimethylphenyl) dithiophosphinic acid] and EtdtpiH in 1 : 3 ratio were mixed followed by heating at 60°C for a few minutes with constant stirring. The resulting dark brown precipitate for Ru(III) and reddish brown precipitate for Rh(III) were filtered, washed with methanol and recrystallised from chloroform-methanol mixture. Identical methods were employed for Pd(II) compounds.

The addition compound [Pd(3,4-Me2dtpi)2PPh3] was synthesised by treatment of a suspension of [Pd(3,4-Me2dtpi)2] in chloroform with an excess of triphenylphosphine in methanol-chloroform at refluxing condition whereby a red solution was obtained which was allowed to evaporate at room temperature and finally dried in vacuo. After drying, it was recrystallised from benzene as a red crystalline product. Alternately, the addition compound was also synthesised by treatment of trans Pd[PPh3]2Cl2 with an excess of the ligand 3,4-Me2dtpi H in chloroform-methanol followed by refluxing, recrystallised as before and dried in vacuo.

Results and Discussion

All the complexes (Table 1) are soluble in common organic solvents and are monomeric. The X-ray powder diffraction pattern showed poor crystallinity. Ru(III) complexes — The dark brown complexes have room temperature magnetic moment around 1.9 B.M. which is equivalent to the magnetic moment of one unpaired electron, indicating no spin-spin interaction. The stereochemistry expected for d6 ruthenium(III) complexes is octahedral although a low symmetry distortion of geometric and electronic origin cannot be ruled out. In the visible spectra in chloroform the bands appearing at 18,520 and 18,720 cm-1 may be assigned to 1T2g -+ 1A1g and 1T2g -+ 2T1g transitions respectively. The values of 10Dq, B and β have been calculated as 20,230 cm-1, 295 cm-1 and 0.41 respectively. Thus the value of the Racah parameter B is found to be of the order of 41% of the free ion value, suggesting a significant covalency in the metal-ligand bond. The β values of these complexes are compared with other rhodium(III) derivatives of oxygen and nitrogen donor ligands and indicate pronounced nephelauxetic effects as in the...
case of other sulphur containing ligands. In the spectrochemical series these ligands are placed below dithiophosphates where oxygen is bonded to the phosphorus atom. This has been explained as due to the involvement of oxygen lone pairs in π-back donation to d-orbitals of phosphorus.

**Pd(II) complexes** — The deep brown Pd(Etdtpi)₂ and reddish brown Pd(3,4-Me₂dtpi)₂ are diamagnetic at room temperature suggesting a square planar geometry around the central metal atom as expected for a d⁸-configruration. The isolation of Pd(Etdtpi)₂ is of interest because it has not been possible to isolate the corresponding nickel compound in the solid state and reflects increase in the stability of complexes with sulphur donor ligands on going down from the first to the second transition series. Bands observed at 19,230 cm⁻¹ the visible spectrum in chloroform is assigned to ²A₁g → ²B₁g transition. Using equations given elsewhere the 10Dq value has been calculated as 21,330 cm⁻¹. This places dithiophosphinate in the spectrochemical series below dithiophosphates where oxygen is bonded to the phosphorus atom. This has been explained as due to the involvement of oxygen lone pairs in π-back donation to d-orbitals of phosphorus.

These dithiophosphinates of palladium do not reveal any expansion of the coordinatively unsaturated PdS₄ core on interaction with nitrogen and oxygen donor ligands. This is supported by the formation of addition compound with triphenylphosphine, a diamagnetic compound of formula Pd(3,4-Me₂dtpi)₂PPh₃ which is found to be monomeric. The infrared and electronic spectra were similar to those of Pd(Me₂dtpi)₂ as detailed in Table 2. The PMR spectra of Pd(3,4-Me₂dtpi)₂PPh₃ shows resonances for methyl and aromatic protons at δ 2.25 and 7.5-7.7 respectively. The corresponding chemical shifts of methyl and aromatic protons for Pd(3,4-Me₂dtpi)₂ are at δ 2.2-2.4 and 7.3-7.5 respectively. In view of the similarities in magnetic and spectral data of Pd(3,4-Me₂dtpi)₂ and adduct with triphenylphosphine, a square planar structure with PdS₄P chromophore is suggested for Pd(3,4-Me₂dtpi)₂PPh₃.

**Ultraviolet spectra** — The ultraviolet spectra of the compounds described above show certain common features. The solution spectra in chloroform show strong bands accompanied by well-defined shoulders around 40,000—35,000 cm⁻¹ characteristic of the presence of π-electron system. These bands have been assigned to intraligand π → π* transitions. The bands observed around 28,300 and 24,720 cm⁻¹ for Ru(III) compounds; 31,580 and 23,750 cm⁻¹ for Rh(III) compounds and 31,700 and 27,000 cm⁻¹ for Pd(II) compounds have been attributed to ligand → metal charge transfer transitions.

**IR spectra** — The infrared spectra of the complexes with both Me₂dtpi and Etdtpi are similar. The bands around 310-330 and 340-350 cm⁻¹ have been assigned to νₐ-M-S and νₐ-M-S respectively. Two types of bands of medium and high intensity are observed due to ν₋ₐ-S at 550-600 and 650-710 cm⁻¹ respectively. The spectra of Pd(Me₂dtpi)₃ and Pd(Me₂dtpi)₃PPh₃ are almost similar. This may be due to predominance of M-S vibrations of PdS₄P chromophore in Pd(Me₂dtpi)₃PPh₃.

References