

Complexes of Ethylene-1,2-bis-diphenylarsine with Pt(II & IV), Pd(II) & Ru(III)

R. K. PODDAR & U. AGARWALA

Department of Chemistry, Indian Institute of Technology, Kanpur

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Complexes of Pt(II), Pt(IV), Pd(II) and Ru(III) with ethylene-1,2-bis-diphenylarsine (EDA) are reported. Spectroscopic, magnetic, conductivity and other physical and chemical studies indicate the octahedral geometry for Pt(IV) and Ru(III) complexes and square planar geometry for Pt(II) and Pd(II) complexes. The ligand acts as bidentate in all these complexes.

THE complexing properties of ethylene-1,2-bis-diphenylarsine with Ru(II), Rh(I), Rh(II), Rh(III), Ir(I) and Ir(III) ions have been studied before^{1,2}. In this paper the preparations of the complexes of Pd(II), Pt(II), Pt(IV) and Ru(III) with this ligand are reported. Their structures have been proposed on the basis of analytical, spectral (visible and IR), magnetic, conductivity and other data. This ligand seems to act as a bidentate in all the complexes.

Materials and Methods

Ethylene-1,2-bis-diphenylarsine³ (hereafter referred to as EDA) and Ru(EDA)₂Cl₂ (ref. 1) were prepared according to the methods described in the literature. All the reactions were carried under nitrogen atmosphere.

The metal and halogen analyses were carried out according to the standard procedures^{4,5}. Molecular weights, infrared spectra, electronic spectra, magnetic measurements and conductivity measurements were obtained according to the methods described elsewhere². X-ray powder diffraction spectra were recorded on a XRD-6 X-ray diffractometer.

Dichloro mono(ethylene-1,2-bis-diphenylarsine)platinum(II), [Pt(EDA)Cl₂] — A solution of EDA (0.3 g) in ethanol (20 ml) was added to a solution of K₂PtCl₄ (0.2 g) in water (10 ml). The mixture was stirred for 24 hr at room temperature when a white precipitate was obtained. It was filtered, washed successively with ethanol and ether and dried under vacuum; m.p. 230° (Found: C, 41.6; H, 3.1; Cl, 9.2; Pt, 25.6, Req'd: C, 41.5; H, 3.2; Cl, 9.4; Pt, 25.9%).

Tetrachloro mono(ethylene-1,2-bis-diphenylarsine)platinum(IV), [Pt(EDA)Cl₄] — It was prepared as above, except PtCl₄ was used instead of K₂PtCl₄. The compound obtained was insoluble in most of the common organic solvents; m.p. >280° (Found: C, 37.7; H, 3.1; Cl, 16.9; Pt, 23.4. Req'd: C, 37.9; H, 2.9; Cl, 17.3; Pt, 23.7%).

Dichloro mono(ethylene-1,2-bis-diphenylarsine)palladium(II), [Pd(EDA)Cl₂] — A solution of EDA (0.5 g) in ethanol (20 ml) was added to a clear solution of PdCl₂ (0.1 g) and sodium chloride (0.06 g) in water (4 ml) (obtained by heating the mixture) and the

mixture stirred for 50 hr at room temperature when a yellow precipitate was obtained. It was filtered, washed successively, with water, ethanol and ether and dried under vacuum; m.p. >280° (Found: C, 46.8; H, 3.7; Cl, 10.5; Pd, 15.7. Req'd C, 47.0; H, 3.6; Cl, 10.7; Pd, 16.0%).

Hexachloro tris(ethylene-1,2-bis-diphenylarsine)dichlororuthenium(III), [Ru₂(EDA)₃Cl₆] — Dry chlorine and dry hydrochloric acid gas were bubbled through a solution of Ru(EDA)₂Cl₂ (0.25 g) in dry chloroform (35 ml). The yellow solution first turned green and finally brown. It was stirred for 1 hr and then concentrated on a water-bath whereby a brown compound separated out. It was washed with ethanol and ether and dried under vacuum; m.p. 180° (Found: C, 49.7; H, 4.1; Cl, 11.2; Ru, 10.6. Req'd: C, 50.0; H, 3.8; Cl, 11.4; Ru, 10.8%).

Reaction of Ru₂(EDA)₃Cl₆ with pyridine — Ru₂(EDA)₃Cl₆ (0.2 g) was dissolved in pyridine (10 ml) and the clear solution heated on a water-bath for 30 min. Excess pyridine was removed on the water-bath. The yellow compound, thus obtained was washed with ethanol and dried under vacuum; m.p. 240° (d) [Found: C, 52.6; H, 4.3; N, 3.2; Cl, 8.4; Ru, 12.2. Ru(EDA)(Py)₂Cl₂ requires: C, 52.9; H, 4.2; N, 3.4; Cl, 8.7; Ru, 12.4%].

Results and Discussion

The analytical data of the complexes show that they have different stoichiometries. Comparing the stoichiometries with the known preference of Pd(II) and Pt(II) for a coordination of four and of Pt(IV) and Ru(III) for a coordination of six, it would appear that the ligand is functioning as bidentate in these complexes.

The infrared bands found in the spectrum of the ligand were also present in the complexes, indicating the complex formation of the ligand with the metal ions. There were minor shifts (~10 cm⁻¹) in the positions of the bands due to ν_{As-C(Ar)}, on complexation. Similar results were obtained in the case of rhodium and iridium complexes². In all these complexes, no ν_{M-Cl} frequencies were identified because of the complexity of the spectra (the ligand bands were also present in the region 500-250 cm⁻¹).

Palladium(II) and Pt(II) complexes, viz. Pd(EDA)Cl₂ and Pt(EDA)Cl₂ are diamagnetic and non-conducting. This is in accordance with the results of the other known square planar complexes of Pd(II) and Pt(II). The molecular weight measurements for these complexes suggested them to be monomers. Monomeric and diamagnetic nature of these *d*⁸ complexes firmly supports square planar geometry for these complexes. It is further substantiated by the results of the visible spectra in chloroform solution. The spectra of these complexes showed a band at 27400 cm⁻¹. The extinction coefficient ($\epsilon = 7500$) of this band is of the order of 10⁴ in the case of Pd(II) complex similar to other *d*⁸ square planar complexes^{6,7}. This absorption band in the Pd(II) complex can be assigned to singlet-singlet $d_{xy} \rightarrow d_{x^2-y^2}$ transition in analogy with Pd(II) *d*⁸ square planar complexes^{6,7}. Dutta *et al.*⁸ observed a band at 27620 cm⁻¹ ($\epsilon = 4200$) in the spectrum of Pd(EDA)Cl₂ in dimethyl sulphoxide solution. The extinction coefficient ($\epsilon = 50$) of this band in the case of presently prepared Pt(II) complex is too low to be assigned to a singlet-singlet transition. This band has been assigned to a singlet-triplet transition. The singlet-singlet transition would appear towards higher energy side (above 30,000 cm⁻¹) which could be masked by the strong charge transfer band due to the complex. Thus on the basis of IR, visible spectral, magnetic and analytical data, a *cis*-square planar structure is proposed for the Pt(II) and Pd(II) complexes.

Platinum(IV) complex, Pt(EDA)Cl₄ is diamagnetic. Due to its insolubility in solvents like benzene, acetone, chloroform, dichloromethane and nitrobenzene, molecular weight and conductivity measurements could not be made. Platinum(IV) has a *d*⁶ configuration which corresponds to ¹A_{1g} ground state. Considering the ligand, to be bidentate and the preferred geometry for Pt(IV) complex to be an octahedral one, Pt(EDA)Cl₄ has been assigned an octahedral geometry. Since the complex is insoluble in most of the organic solvents, polymeric nature of the complex has been proposed. The visible spectrum of the complex in nujol mull shows a shoulder at 20,410 cm⁻¹ which is in accordance with the bands in other octahedral Pt(IV) complexes. This could be assigned to ¹A_{1g} → ³T_{1g}

or ³T_{2g} transition⁹. Based on the above results, an octahedral, ligand bridged, polymeric structure is proposed.

Ru₂(EDA)₃Cl₆ is a non-conducting complex, Ru(III) being a *d*⁵ system, is expected to give a paramagnetic complex. However, this complex was found to be diamagnetic. Similar to the Rh(II) complex, discussed elsewhere² the diamagnetism of Ru₂(EDA)₃Cl₆ could be explained on the basis of spin-spin interaction as a result of σ - or δ -bond formation. Its visible spectrum showed bands at 14,000, 16,000, 20,000 and 24,700 cm⁻¹. Since the energy level scheme for the diamagnetic *d*⁵ system has not been calculated, no definite assignment could be made for these bands. On the basis of the above results a dimeric distorted octahedral structure with the bridging ligand molecules has tentatively been proposed for the complex.

The formation of Ru(EDA)(Py)₂Cl₂ indicates that pyridine reduces Ru(III) to Ru(II) and gets coordinated to the metal ion forming Ru(EDA)(Py)₂Cl₂. The pyridine complex, thus obtained has similar geometry and structure as the complex Ru(EDA)(Py)₂Cl₂ obtained from Ru(EDA)₂Cl₂ and pyridine¹. The X-ray diffraction powder pattern, infrared and electronic spectra of this pyridine complex were superimposable to the one obtained from Ru(EDA)₂Cl₂ and pyridine. The structure and other physical studies of this complex has been discussed in detail in our previous publication¹.

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