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NOTES

Complexes of Palladium(II) and Platinum(II) with Some Bidentate Ligands

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$PdCl_2$ and K_2PtCl_4 react with some heterocyclic N-donor bases producing compounds of the type $MLCl_2$ where M=Pd(II) or Pt(II) and L=1,10 phenanthroline (*o*-phen), 2,2-bipyridyl (bipy) and 2,2-biquinoline (biqn). These compounds were characterised by elemental analyses, IR and UV-visible spectra. All the complexes have square planar geometry.

We have earlier reported diamagnetic Pd(II), Pt(II) and Pt(IV) complexes with imidazole and substituted imidazoles[1]. Our interest in platinum-metal complexes arose because a large number of these complexes were found to have anti-cancer activity[2-5]. Herein is reported the preparation and characterization of complexes of Pd(II) and Pt(II) with the bidentate ligands 1,10-phenanthroline (*o*-phen), 2,2′-bipyridyl (bipy) and 2,2-biquinoline (biqn).

Preparation of $PdLCl_2$ (L=*o*-phen, bipy, and biqn)

$PdCl_2$ (2 mmol)was digested with HCl several times, evaporated almost to dryness and extracted with ethanol. To this was added an ethanolic solution of the ligand (2 mmol) and the mixture stirred for a few minutes and allowed to stand. Light yellow crystals appeared. It was filtered out, washed several times with ethanol and dried over P_2O_5.

Preparation of $PtLCl_2$ (L=*o*-phen and bipy)

K_2PtCl_4 (2 mmol) was dissolved in water. The ligands (2 mmol) were also dissolved in hot and very dilute solutions of ethanol. Both the solutions were mixed together, stirred well and allowed to stand overnight. Yellow crystals deposited. These were filtered and dried as before.

Microanalytical data as well as metal analyses were in agreement with the general composition for the complexes $MLCl_2$ (M=Pd or Pt; L=*o*-phen, bipy or biqn) or $Pt(bipy)Cl_2 \cdot 4H_2O$. All the compexes were very stable, undecomposed even above 300°C. The molar conductivities have the values 10–20 mol^{-1} cm^2 ohm^{-1} in DMF at 25°C indicating non-electrolytic nature of the complexes.

The IR spectra of the ligands show band at *ca.* 620 cm^{-1} for the in-plane ring deformation. This shifts to 700 cm^{-1} for Pd(*o*-phen)Cl_2, to 715 cm^{-1} for Pd(bipy)Cl_2 to 740 cm^{-1} for Pd(biqn)C l_2 and to 700 cm^{-1}

for Pt(*o*-phen)Cl$_2$. The bands at 1600 cm^{-1} (*o*-phen), 1580 cm^{-1} (bipy) and 1595 cm^{-1} (biqn) for νC(aryl)$=$N also shift to higher frequency of 1710 cm^{-1} for Pd(*o*-phen)Cl$_2$, to 1620 cm^{-1} for Pd(bipy)Cl$_2$, to 1710 cm^{-1} for Pt(*o*-phen)Cl$_2$, but to lower frequency of 1580 cm^{-1} for Pd(biqn)Cl$_2$ indicating co-ordination of the nitrogens to the metal ion.

The new bands appearing in the regions 340 cm^{-1} (split) for Pd(*o*-phen)Cl$_2$, in 335 cm^{-1} for Pd(bipy)Cl$_2$, in 320 cm^{-1} for Pd(biqn)Cl$_2$, in 330 cm^{-1} for Pt(*o*-phen)Cl$_2$ and in 335 cm^{-1} for Pt(bipy)Cl$_2$ could be assigned to νM–Cl mode of vibration. The ν(M–N) mode of vibration appears below 300 cm^{-1}.

The electronic spectra of square planar Pd(II) and Pt(II) complexes are expected to show three d–d bands due to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1B_g$[8,9]. The electronic spectra of the complexes under study display bands at 28000 cm$^{=1}$ and 29411 cm^{-1} for Pd(*o*-phen)Cl$_2$, at 30,000 cm^{-1} and 32,000 cm^{-1} for Pd(bipy)Cl$_2$, at 26,000 cm^{-1} and 30,303 cm^{-1}) for Pt(*o*-phen)Cl$_2$. The third band may have merged with the high energy C.T. band. But in case of Pd(biqn)Cl$_2$ (27,070 cm^{-1}, 30,800 cm^{-1} and 35,260 cm^{-1}) and Pt(bipy)Cl$_2$ (25,641 cm^{-1}, 30,769 cm^{-1} and 31,746 cm^{-1}) all the three bands are observed. The C.T. bands are observed above 35,000 cm^{-1} region.

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