

NOTE

Synthesis and Characterization of Pd(II) and Pt(II) Complexes of 2-Pyridyl Methyl Ketazine

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2-Pyridyl methyl ketazine and its Pd(II) and Pt(II) complexes have been prepared and characterized by analytical, IR, magnetic and spectrophotometric studies. The ligand forms dinuclear complexes of the formula $[M_2(L)_3]X_4$ with bridged tetrafunctional co-ordination of each ligand in the *trans* configuration.

In earlier papers^{1,2}, it was shown that 2-pyridine aldazine acts as a chelating agent with Fe(II), Co(II) and Ni(II). In order to know the manner in which tetrafunctional azine ligands are coordinated and the properties of such complexes, studies have been carried out with a new azine ligand, 2-pyridyl methyl ketazine (L). Its Pd(II) and Pt(II) complexes are reported here. IR spectra indicate that the ligand forms chelate complexes with metal ion and the magnetic susceptibilities of the complexes over a range of temperature show the presence of anti-ferromagnetic exchange interaction in these systems.

All the chemicals used were of either E Merck or BDH quality. Ligand was prepared by the method reported by Busch *et al.*^{3,4}

2-Pyridyl Methyl Ketazine (L): 2-Acetyl pyridine (0.40 mol) was added to 25 mL of absolute alcohol along with 0.20 mol of hydrazine. After adding a few drops of glacial acetic acid, the mixture was heated to boiling and then cooled to room temperature. Some amount of distilled water was then added to the above solution and the whole solution was cooled in ice. A yellow solid gradually appeared which was allowed to stand for nearly 30 min during which a considerable amount of solid was formed and settled down. It was filtered, washed thoroughly with a small amount of distilled water and then dried in air and finally in *vacuo*.

Tris-(2-Pyridyl Methyl Ketazine) Di-palladium(II) Halides $[Pd_2(L)_3]X_4$: PdX_2 where X = Cl⁻, Br⁻, I⁻ (0.002 mol) and 2-pyridyl methyl ketazine (0.006 mol) were added to about 50 mL of water. The mixture was stirred at room temperature for 40 min and then warmed on water bath for 1h. On standing overnight, the precipitated product was obtained which was filtered, washed with water, then with ethanol and recrystallised from hot alcoholic solution. The product was then washed with ethanol, ether and dried in *vacuo*.

Tris-(2-Pyridyl Methyl Ketazine) Di-platinum(II) Halides $[Pt_2(L)_3]X_4$: These compounds were also prepared in a manner similar to the corresponding Pd compounds. K_2PtCl_4 was taken in place of green gray powder of $PtCl_2$.

2-Pyridyl methyl ketazine (L) forms complexes with Pd(II) and Pt(II) of the general formula $[M_2(L)_3]X_4$ where $X = Cl^-, Br^-, I^-$. The magnetic susceptibilities of Pd(II) and Pt(II) indicate that the metal ions are in an octahedral environment. The lower value is due to substantial spin-spin interaction between metal ions. The experimental values are 2.10 to 2.25 B.M. at 300 K per metal ion.

Infrared spectra as shown in Table-1 are quite similar to the corresponding complexes with other metal ions as discussed by various workers^{3,4}. For the complexes, the unsplit bands in the 1610–1565 cm^{-1} region and a pyridine ring breathing band shifted entirely from 1020 cm^{-1} to 990 cm^{-1} indicate symmetric bis-bidentate bonding. A band near 1600 cm^{-1} shows C=N coordination to metal(II) but bands near 1010 cm^{-1} suggest unsymmetric coordination of the ligand. It is particular to note that the CH_3 groups of the ketazine do not prohibit this manner of chelation even though considerable steric strain must be involved.

As can be seen from the spectral data, the logical conclusion relating to the structure of the complexes, *i.e.*, symmetric bi-bidentate bonding of the ligand with Pd(II) and Pt(II) and the most probable structures of the ligand and complexes may be represented as shown in Figs. 1 and 2.

TABLE-1
IMPORTANT IR BANDS (cm^{-1}) OF LIGAND AND METAL COMPLEXES

Compounds	$\nu(C=N)$	ν -(Pyridine)	Ring breathing	μ_{eff} (B.M.)
L	1610	1580, 1565	990	–
$[Pd_2(L)_3]Cl_4$	1625	1590, 1570	1010	2.25
$[Pd_2(L)_3]Br_4$	1620	1590, 1580	1020	2.20
$[Pd_2(L)_3]I_4$	1622	1585, 1570	1015	2.25
$[Pt_2(L)_3]Cl_4$	1615	1585, 1570	1013	2.15
$[Pt_2(L)_3]Br_4$	1618	1590, 1585	1012	2.10
$[Pt_2(L)_3]I_4$	1620	1588, 1585	1015	2.15

TABLE-2
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND THEIR ASSIGNMENTS

Complexes	${}^3B_{1g} \rightarrow {}^3E_g$	${}^3B_{1g} \rightarrow {}^3B_{2g}$	${}^3B_{1g} \rightarrow {}^3T_{1g}(F)$	${}^3B_{1g} \rightarrow {}^3T_{1g}(P)$
$[Pd_2(L)_3]Cl_4$	9,400	13,000	17,000	24,000
$[Pd_2(L)_3]Br_4$	9,420	13,010	17,100	24,200
$[Pd_2(L)_3]I_4$	9,450	13,250	17,650	24,350
$[Pt_2(L)_3]Cl_4$	9,450	13,400	17,750	24,375
$[Pt_2(L)_3]Br_4$	9,450	13,470	17,650	24,400
$[Pt_2(L)_3]I_4$	9,455	13,450	17,700	24,300

The complexes of Pd(II) and Pt(II) show transformation from octahedral to tetragonal symmetry. The orbitally excited triplet terms ${}^3T_{2g}$ and ${}^3T_{1g}$ split into ${}^3B_{1g} + {}^3E_g$ and ${}^3A_{1g} + {}^3E_g$ respectively and ${}^3A_{2g}$ term transforms to ${}^3B_{1g}$. Usually the splitting of the former term is appreciable enough to be observed experimentally. Bands observed near 9400 cm^{-1} and 13000 cm^{-1} are assigned to the

transition ${}^3B_{1g} \rightarrow {}^3E_g$ and ${}^3B_{1g} \rightarrow {}^3B_{2g}$. The transitions ${}^3B_{1g} \rightarrow {}^3T_{1g}(F)$ and ${}^3B_{1g} \rightarrow {}^3T_{1g}(P)$ are observed near 17000 and 24000 cm^{-1} respectively.

These visible spectra along with IR and magnetic moment data have supported the proposed structure of ligand as shown in Fig. 1 and complexes as shown in Fig. 2.

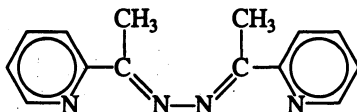
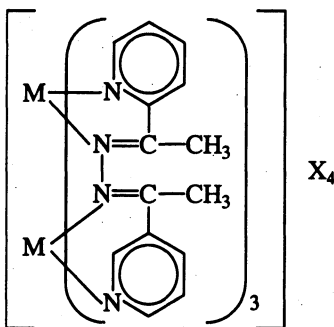


Fig. 1



M = Pd(II) or Pt(II) and X = Cl^- , Br^- , I^-

Fig. 2

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