

## References

- MERTZ, W. & SCHAWARZ, K., *Archs Biochem. Biophys.*, **58** (1955), 504.
- COLLINSON, C. N., in *Radioactive pharmaceuticals*, edited by G. A. Endreus (US Atomic Energy Commission, Oak Ridge), 1966.
- BAILER, C. J. (Jr), *Preparative inorganic reactions*, edited by W. L. Jolly (Interscience, New York), 1964.
- ROGINSKI, E. E. & MERTZ, W., *J. Nutr.*, **97** (1969), 525.
- FIGGIS, B. N., *Introduction to ligand fields* (Interscience, New York), 1960.
- COTTON, F. A., in *Modern coordination chemistry*, edited by J. Lewis & R. G. Wilkins (Interscience, New York), 1960.
- NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (Wiley Interscience, New York), 1960.
- GAMO, I., *Bull. chem. Soc. Japan*, **34** (1961), 760, 765, 1430.
- ROLLINSON, C. L. & ROSENBLUM, E. W., in *Coordination chemistry*, edited by S. Krishner (Plenum Press, New York), 1969.

**Complexes of Cu(II), Pd(II) & Pt(II)  
with Schiff Bases Derived from  
2-(2'-Aminoethyl)pyridine**

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**Cu(II), Pd(II) and Pt(II) complexes of tridentate Schiff base derived from 2-(2'-aminoethyl)pyridine; and salicylaldehyde or its derivatives (x-Salaep), o-hydroxyacetophenone (Hapaep), o-hydroxypropionophenone (Hppaep) and o-hydroxybutyrophenone (Hbpaep) have been obtained as coloured crystalline solids. On the basis of analytical, magnetic susceptibility, IR and electronic spectral data, the complexes have been assigned square-planar geometry. IR studies show that the metals are coordinated through the nitrogen atoms of the imine group and heterocyclic ring; and the oxygen atom of a phenolic group.**

**A** NUMBER of planar complexes of Cu(II), Pd(II) and Pt(II) of the type (MLX) where L is a mono-negative tridentate Schiff base and X is a mono-negative anion have been reported in recent years<sup>1-10</sup>. The present paper describes the preparation and characterization (elemental analysis, magnetic moment and electronic and IR spectral data), of Cu(II), Pt(II) and Pd(II) complexes with Schiff bases derived from 2-(2'-aminoethyl)pyridine and (i) salicylaldehyde, 5-chlorosalicylaldehyde, 5-nitrosalicylaldehyde or 5,6-benzosalicylaldehyde (Schiff bases abbreviated as x-Salaep); (ii) o-hydroxyacetophenone (Hapaep); (iii) o-hydroxypropionophenone (Hppaep); and (iv) o-hydroxybutyrophenone (Hbpaep).

**Preparation of complexes**—(i) The complexes with Schiff bases x-Salaep were prepared by the following general method:

To an aqueous solution of metal (II) chloride were added aqueous solution of sodium acetate and ethanolic solutions of salicylaldehyde or substituted salicylaldehydes and 2-(2'-aminoethyl)pyridine in 1:1 ratio. The reaction mixture was stirred for 5 hr at 60° when the colour of the solu-

tion gradually changed yielding crystals of the complexes. The complexes were recrystallized from organic solvents like ethanol, methanol or nitrobenzene (yield ~80%).

(ii) Complexes of Schiff base Hapaep were prepared as follows:

A mixture of o-hydroxyacetophenone (0.025 mole), 2-(2'-aminoethyl)pyridine (0.025 mole) and metal (II) chloride (0.02 mole) in ethanol (30 ml) was heated at 60° with stirring. To this a solution of potassium ethoxide (0.02 mole potassium in 20 ml EtOH) was added dropwise with constant stirring and the reaction mixture refluxed at 60° for 8 hr. The solution was allowed to stand overnight in a refrigerator when greenish, brown and reddish crystals of Cu(II), Pd(II) and Pt(II) complexes respectively were obtained. These were filtered off and recrystallized from ethanol, yield ~60%.

(iii) Complexes of Schiff base Hppaep were prepared by a procedure similar to that used for Hapaep complexes using o-hydroxypropionophenone (0.025 mole) and refluxing the reaction mixture at 60-70° for 12 hr. No crystalline compound separated even on keeping the reaction mixture in the refrigerator for several days. The solution obtained was evaporated under reduced pressure and again kept in refrigerator for a couple of days. The crude product so obtained was recrystallized twice from ethanol yielding dark green, brown and red crystals of Cu(II), Pd(II) and Pt(II) complexes respectively; yield ~55%.

(iv) Complexes of Hbpaep were prepared as above employing o-hydroxybutyrophenone (0.025 mole) and refluxing the reaction mixture at 60-70° for 24 hr. Concentration of the reaction mixture and subsequent refrigeration for several days resulted in the formation of complexes which were recrystallized from ethanol as pale yellow [Cu(II)], brown [Pd(II)] and red [Pt(II)] crystals in 40% yield.

**Copper(II) complexes**—Analytical results (Table 1) show the formation of 1:1 (metal-ligand) complexes in all the cases.

The magnetic moment values in the range 1.70-1.82 BM observed for Cu(II) complexes are very close to that expected for spin-only value indicating that the orbital contribution is almost quenched by the crystalline fields. As expected for planar complexes<sup>11-13</sup> of Cu(II) in general and in conformity with planar Cu(II) complexes of  $\beta$ -diketones<sup>14</sup>, the present Cu(II) complexes show a *d-d* band in the visible region 16780-16080  $\text{cm}^{-1}$  ( ${}^2B_{1g} \rightarrow {}^2E_g$ ) along with a shoulder in the region 19500-18000  $\text{cm}^{-1}$  ( ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ). However, it is interesting to note that the main absorption band in [Cu(x-Salaep)Cl] has been observed at higher energy (16780  $\text{cm}^{-1}$ ), than those of [Cu(Hapaep)Cl] (16550  $\text{cm}^{-1}$ ), [Cu(Hppaep)Cl] (16320  $\text{cm}^{-1}$ ) and [Cu(Hbpaep)Cl] (16080  $\text{cm}^{-1}$ ) and that the difference in the position of this band is ~230  $\text{cm}^{-1}$  in each of these complexes. This regular decrease could be related to the increasing steric hindrance in the series of ligands x-Salaep, Hapaep, Hppaep and Hbpaep. It may also be mentioned that the shoulder observed in the region 19500-18000  $\text{cm}^{-1}$  shifts towards lower frequency region in going from

[Cu(x-Salaep)Cl] (19500 cm<sup>-1</sup>) to [Cu(Hapaep)Cl] (19000 cm<sup>-1</sup>), [Cu(Hppaep)Cl] (18550 cm<sup>-1</sup>) and [Cu(Hbpaep)Cl] (18000 cm<sup>-1</sup>).

**Pt(II) and Pd(II) complexes** — All the complexes of Pd(II) and Pt(II) are diamagnetic. Three electronic spectral bands have been observed in the region 31080-31700, 33720-34360 and 39650-40500 cm<sup>-1</sup> for the Pt(II) complexes. First spin-allowed transition <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2g</sub> has been observed<sup>15</sup> around 25000 cm<sup>-1</sup> in [PtCl<sub>4</sub>]<sup>2-</sup> complexes. However, due to the difference in positions of halide and amine groups in spectrochemical series, this transition has been observed<sup>16</sup> around 34900 cm<sup>-1</sup> in the mixed chloro complex of 2-(2'-aminoethyl)pyridine, [Pt-(AEP)Cl<sub>2</sub>], which is the amine component of the present Schiff bases. The corresponding transition in the present mixed chloro Schiff base complexes of Pt(II) has been observed in the region 31080-31700 cm<sup>-1</sup>; lying about 6500 cm<sup>-1</sup> higher in energy than the corresponding transition in [PtCl<sub>4</sub>]<sup>2-</sup> complexes. Owing to the very little difference in the energies of b<sub>2g</sub> and e<sub>g</sub> levels; the above band may also be assigned as a combination of both <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>E<sub>g</sub> transitions<sup>17</sup>. The second band appearing in the region 33720-34360 cm<sup>-1</sup> may be due to the spin-allowed transition <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub>. The third band observed in the region 39650-40500 cm<sup>-1</sup> is of the ligand → metal charge-transfer type.

Only two bands in the regions 26500-27150 and 38000-38700 cm<sup>-1</sup> have been observed in the case of Pd(II) complexes. Following the assignment of Gray and Mason<sup>15</sup>, it can be assumed that the former band is a combination of all the three spin allowed transition and the latter band is of the ligand → metal charge-transfer type. This means that in case of Pd(II) complexes the a<sub>1g</sub> (z<sup>2</sup>) level has moved to higher energy relative to the corresponding Pt(II) complexes.

**IR spectra of the complexes** — The free ligands show νC=N in region 1644-1650 cm<sup>-1</sup>. On coordination νC=N is shifted to lower frequency side indicating coordination through imine nitrogen<sup>18</sup>. However, the reduction in this frequency is not large because of extended conjugation in the free ligands<sup>19-20</sup>. Further, the extent of decrease is lowest in Hbpaep complexes indicating that the steric hindrance in this complex is comparatively more.

Four bands have been observed in the regions 1597-1590 (I), 1565-1560 (II), 1475-1470 (III) and 1430-1428 (IV) in the Schiff bases which are shifted to 1616-1595 (I), 1590-1565 (II), 1487-1475 (III) and 1450-1432 cm<sup>-1</sup> (IV) respectively in the metal complexes. These bands may be assigned to a combination of νC=C and νC=N (pyridine) vibrations. The new bands in the complexes are nearly at the same positions as those of pyridinium ion<sup>21</sup> and the increase in their position from that of free ligand indicates coordination of pyridine to the metal atom<sup>22</sup>.

On complexation, the ring breathing modes appearing around 1010-1005 cm<sup>-1</sup> in the free ligands are replaced by a new band in the region 1020-1012 [Cu(II) complexes]; 1028-1020 [Pd(II) complexes] and 1038-1030 cm<sup>-1</sup> [Pt(II) complexes]. The increase in the frequency of this mode upon

TABLE 1 — ANALYTICAL DATA OF Cu(II), Pd(II) AND Pt(II) COMPLEXES

Compound	Calc. (Found) (%)				
	C	H	N	Cl	M
Cu(Salaep)Cl	51.85 (51.80)	4.02 4.22	8.94 8.85	10.93 10.86	19.59 19.51
Cu(5-Cl-Salaep)Cl	46.87 (46.78)	3.37 3.42	7.11 7.05	19.76 19.68	17.71 17.60
Cu(5-NO <sub>2</sub> -Salaep)Cl	45.53 (45.45)	3.27 3.38	11.38 11.28	9.60 9.52	17.20 17.08
Cu(5,6-Benzosalaep)Cl	57.75 (57.65)	4.03 4.22	7.48 7.40	9.47 9.35	16.97 16.88
Cu(Hapaep)Cl	53.25 (53.21)	4.46 4.52	8.28 8.22	10.48 10.44	18.78 18.71
Cu(Hppaep)Cl	54.54 (54.60)	4.86 4.90	7.95 7.92	10.03 9.95	18.03 17.98
Cu(Hbpaep)Cl	55.70 (55.75)	5.22 5.28	7.64 7.58	9.67 9.62	17.33 17.28
Pd(Salaep)Cl	45.76 (45.72)	3.56 3.58	7.62 7.58	9.65 9.62	29.04 28.95
Pd(5-Cl-Salaep)Cl	41.83 (41.65)	3.01 3.20	6.97 6.80	17.64 17.54	26.55 26.42
Pd(5-NO <sub>2</sub> -Salaep)Cl	40.76 (40.58)	2.93 3.04	10.43 10.50	8.59 8.44	25.87 25.72
Pd(5,6-Benzosalaep)Cl	51.78 (51.68)	3.62 3.72	6.71 6.68	8.49 8.52	25.55 25.42
Pd(Hapaep)Cl	47.25 (47.32)	3.97 3.92	7.34 7.28	9.29 9.22	27.97 27.88
Pd(Hppaep)Cl	48.59 (48.65)	4.33 4.38	7.08 7.00	8.96 8.99	26.97 26.77
Pd(Hbpaep)Cl	49.95 (49.89)	4.67 4.72	6.84 6.88	8.65 8.76	26.06 26.12
Pt(Salaep)Cl	36.87 (36.68)	2.87 2.95	6.14 6.07	7.77 7.62	43.03 43.62
Pt(5-Cl-Salaep)Cl	34.29 (34.10)	2.46 2.56	5.71 5.62	14.45 14.32	39.81 39.78
Pt(5-NO <sub>2</sub> -Salaep)Cl	33.56 (33.42)	2.41 2.48	8.36 8.28	7.05 7.12	38.97 38.83
Pt(5,6-Benzosalaep)Cl	42.72 (42.65)	2.98 3.02	5.53 5.48	7.07 7.02	38.58 38.35
Pt(Hapaep)Cl	38.33 (38.46)	3.21 3.28	5.96 5.88	7.54 7.44	41.54 41.48
Pt(Hppaep)Cl	39.70 (39.63)	3.54 3.65	5.78 5.66	7.32 7.46	40.33 40.28
Pt(Hbpaep)Cl	40.99 (40.85)	3.84 3.96	5.62 5.55	7.11 7.02	39.20 39.16

coordination is also indicative of pyridine coordination<sup>23</sup>.

The stretching and deformation modes of phenolic OH group appear around 3310-3300 and 1375-1370 cm<sup>-1</sup> respectively in the free ligands. These disappear in the spectra of the complexes indicating the formation of metal-oxygen bond. The νM-O band appears in the region<sup>24</sup> 540-525 cm<sup>-1</sup> in the spectra of complexes but it seems to be coupled with νM-N vibrations.

In the present studies, bands appearing in the region 340-325 and 305-270 cm<sup>-1</sup> have been assigned to νM-Cl and νM-N(Py) vibrations respectively.

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**References**

1. YAMADA, S. & YAMANOUCHI, K., *Bull. chem. Soc. Japan*, **42** (1969), 2562.
2. OEHMKE, R. W. & BAILAR (Jr), J. C., *J. inorg. nucl. Chem.*, **27** (1965), 2209.
3. SINN, E. & HARRIS, C. M., *Coord. Chem. Rev.*, **4** (1969), 391.

4. UHLIG, E. & SCHNEIDER, D., *Z. anorg. allg. Chem.*, **333** (1964), 90.
5. SRIVASTAVA, A. K., RANA, V. B. & MOHAN, M., *J. inorg. nucl. Chem.*, **36** (1974), 2118.
6. CHISWELL, B., LIONS, F. & TOMLINSON, M. L., *Inorg. Chem.*, **3** (1964), 492.
7. YAMADA, S., *XIII international conference on coordination chemistry, Poland*, Sept. 1970, 189.
8. BELL, C. F. & ROSE, D. R., *Talanta*, **12** (1965), 696.
9. CALLIGARIS, M., NARDIN, G. & RAMDACCIO, L., *Coord. Chem. Rev.*, **7** (1972), 385.
10. HOBDAV, M. D. & SMITH, T. D., *Coord. Chem. Rev.*, **9** 1972-73, 311.
11. PIPER, T. S. & BELFORD, R. L., *Molec. phys.*, **5** (1962), 169.
12. BELFORD, R. L. & BELFORD, G. G., *Theor. chim. Acta*, **3** (1965), 465.
13. FERGUSON, J., *Theor. chim. Acta*, **3** (1965), 287.
14. DIJKRAAF, C., *Theor. chim. Acta*, **3** (1965), 38.
15. MASON, W. R. & GRAY, H. B., *J. Am. chem. Soc.*, **90** (1968), 5721.
16. SHARMA, K. C., *Spectral data vis-a-vis nephelauxetic effect and stereochemistry of some metal complexes of nitrogen and oxygen donor ligands*, Ph.D. thesis, Meerut University, Meerut, 1974.
17. TEOTIA, M. P., *Physicochemical studies on the interaction of amino compounds with metals and metal cyanides* Ph.D. thesis, Meerut University, Meerut, 1973.
18. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (Wiley, New York), 1963.
19. LANE, L. W. & TAYLOR, L. T., *J. Coord. Chem.*, **2** (1973), 295.
20. SPENCER, C. T. & TAYLOR, L. T., *Inorg. Chem.*, **10** (1971), 2407.
21. GREENWOOD, N. N. & WADE, K., *J. chem. Soc.*, (1960), 1130.
22. FIGGINS, P. E. & BUSCH, D. H., *J. phys. Chem.*, **65** (1961), 2236.
23. SINHA, S. P., *Spectrochim. Acta*, **20** (1964), 879.
24. PERCY, G. C. & THORNTON, D. A., *J. inorg. nucl. Chem.*, **34** (1972), 3357.
25. CLARK, R. J. H. & WILLIAMS, C. S., *Inorg. Chem.*, **4** (1965), 350.
26. KRAUSS, F. & BRODKARB, F., *Z. anorg. allg. Chem.*, **165** (1927), 73.

### Oxovanadium(IV) & Bis(cyclopentadienyl)vanadium(IV) Complexes of Dithiocarbamate Ligands

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Complexes of oxovanadium(IV) and bis(cyclopentadienyl)vanadium(IV) with dithiocarbamate ligands, viz. N,N'-dibutyl-, piperidine-, morpholine- and pyrrolidine-dithiocarbamates, have been prepared. The complexes in the two series have the compositions  $\text{VO}(\text{L})_2$  and  $[(\text{cp})_2\text{V}(\text{L})][\text{Ph}_4\text{B}]^-$  (where L stands for dithiocarbamate ligands) and have been characterized with the help of elemental analyses, molar conductances, magnetic susceptibilities, and IR and electronic spectral data.

IN the course of our studies on the complexes of oxovanadium(IV)<sup>1</sup> with different types of ligands, we prepared several complexes containing sulphur as the donor atom<sup>2</sup>, and among these are many dithiocarbamate complexes of oxovanadium(IV) and bis(cyclopentadienyl)vanadium(IV) moieties [abbreviated as  $\text{VO}^{2+}$  and  $(\text{cp})_2\text{V}^{2+}$  respectively]. This note describes our work on dithio-

carbamate complexes. In recent past several papers appeared<sup>3-5</sup> which reported the preparation and characterization of some dithiocarbamate complexes of  $\text{VO}^{2+}$  and  $(\text{cp})_2\text{V}^{2+}$  moieties. Some of our work overlaps with their work. However, we include here only those compounds which have not been included in those papers.

Following dithiocarbamates were used: N,N'-dibutylthiocarbamate ( $\text{Bu}_2\text{dtc}$ ), piperidinedithiocarbamate (pipdtc), morpholinedithiocarbamate (mordtc), pyrrolidinedithiocarbamate (pyrdtc). Sodium salts of the ligands were prepared from carbon disulphide, the appropriate amines and sodium hydroxide essentially by the published methods<sup>6</sup>.

Bis(cyclopentadienyl)vanadium(IV) dichloride  $[(\text{cp})_2\text{VCl}_2]$  was prepared from  $\text{VCl}_4$  and sodium cyclopentadienide in benzene by a method described earlier<sup>7</sup>.

*Oxovanadium(IV) complexes (under dry nitrogen)* — A solution of  $\text{VO}^{2+}$  was prepared by dissolving  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  (0.02 mole) in 25 ml of warm water, to which was added 25 ml of ethanol (deaired) after dissolution of the sulphate had taken place. The  $\text{VO}^{2+}$  solution was then quickly added to an efficiently stirred solution of sodium salt(s) of the ligand(s) (0.04 mole) in 50 ml of 50% ethanol. The coloured precipitate was filtered off, washed with water, ethanol and diethyl ether and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ .

*Bis(cyclopentadienyl)vanadium(IV) complexes (under dry nitrogen)* — Solution containing stoichiometric amount of the ligand in 50 ml of distilled water was added with stirring to  $(\text{cp})_2\text{VCl}_2$  (1 g) in 150 ml of distilled water. The resulting solution was allowed to stand for 15-20 min and then directly filtered into an aqueous solution of  $\text{Na}(\text{Ph}_4\text{B})$ . The coloured powdery compound was separated by filtration, washed with water, ethanol and ether and dried at 60-65°C.

The present oxovanadium(IV)-dithiocarbamate complexes can be represented by the general formula,  $\text{L}_2\text{VO}$  (where L =  $\text{Bu}_2\text{dtc}$ , pipdtc, mordtc, or pyrdtc). On the other hand, bis(cyclopentadienyl)dithiocarbamate complexes can be represented by  $[(\text{cp})_2\text{VL}][\text{Ph}_4\text{B}]^-$  (where L = pyrdtc, mordtc, or pipdtc) (see Table 1). The  $\text{L}_2\text{VO}$  complexes are oxidized in air (rapidly when moist or in solutions). They are stable indefinitely when kept in nitrogen atmosphere. These oxovanadium(IV) complexes are soluble in common organic solvents, but insoluble in water. The pyridine solutions are deep green in colour, possibly due to the formation of addition complexes. On the other hand the  $[(\text{cp})_2\text{VL}][\text{Ph}_4\text{B}]^-$  complexes are stable in air and soluble in common organic solvents. Presumably the 'class-A' character of vanadium has been modified in the presence of cyclopentadienyl groups. The molar conductances of  $\sim 10^{-3}\text{M}$  solutions of  $[(\text{cp})_2\text{VL}][\text{Ph}_4\text{B}]^-$  complexes in nitromethane are in the range 53-58  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ . These values are all within the range reported<sup>8</sup> for 1:1 electrolytes in this solvent. The room temperature magnetic moments (Table 1) measured employing Grouy technique are in the range 1.66-1.79 BM indicating the presence of oxovanadium(IV) ion or V(IV) ion

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