Asian Journal of Chemistry Vol. 5, No. 1 (1993), 47–53

Synthesis and Characterization of Model Compounds—III Complexes of Iron(II), Iron(III), Cobalt(III), Nickel(II) and Copper(II) with *Syn*-Phenyl-α-Pyridyl Ketoxime

K. HUSSAIN REDDY

Department of Chemistry, Sri Krishnadevaraya University
Anantapur-515 003, India

Complexes of iron(II), iron(III), cobalt(III), nickel (II) and copper(II) with *Syn*-phenyl-α-pyridyl ketoxime (PPK) have been isolated and their structural properties investigated. The magnetic and electronic spectral data show that iron(II), and cobalt(III) complexes have pseudo octahedral and octahedral geometry respectively. Nickel(II) forms complex confirming the square-planar geometry. The binuclear nature and square-pyramidal geometry of copper complex are revealed from its magnetic and electronic spectral studies. The infrared spectral data indicate that PPK acts as uni-negative bidentate ligand by coordinating with azomethine nitrogen atom and heterocyclic ring nitrogen. The molar conductance data indicate ionic nature of iron, cobalt and nickel complexes.

INTRODUCTION

One of the major avenues of investigations of bio-inorganic chemistry involves an indirect approach, i.e., synthesis and characterization, physico-chemical study and reactions of so-called *model* compounds. An additional objective might be to mimic a simple natural system viz. iron porphyrins, cobalamins and mettallo enzymes. Schrauzer has carried out good amount of research[1] on bis(dimethylglyoximato) complex, which is most commonly known B_{12} model system. This type of complexes are often referred as cobaloximes. Some other model compounds have been discussed in a recent review[2]. The common feature of different model compounds is that each possesses a very strong equatorial ligand field formed by four nitrogen atoms which are in coordination with the central metal ion.

Although investigations of metal complexes with oximes have been extensive, studies on metal complexes in solid state with oximes of heterocyclic origin are rather limited[3–5], being mostly analytical in nature[6]. Recently we have reported synthesis and characterization of transition metal complexes of biomimetic N_2S_2 and N_2S_4 ligands[7]. In continuation of our efforts to study model compounds, synthesis and structural studies on transition metal complexes of *syn*-α-pyridyl ketoxime (PPK) are described here.

EXPERIMENTAL

The metal salts [$FeCl_2.4H_2O$, $FeCl_3$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and $NiCl_2.6H_2O$] used were of BDH (AR) or Merck (GR) grade.

Syn-phenyl-α-pyridyl ketoxime (PPK) was prepared from 2-benzoylpyridine by following procedure used by Trussel and Diehl[8]. The product was recrystallized from ethyl alcohol and got a material which melts at 151–153°C (lit. value 151–152°C).

The complexes were prepared by refluxing a mixture of ethanolic solution of the ligand and aqueous metal salt solution. The reaction mixture was concentrated and cooled when the crystals of the complexes separated out. The crude complex was dissolved in ethanol and reprecipitated by adding ether. Finally, the solid crystalline complexes were washed with methanol. All the complexes thus obtained were dried in vacuo over $CaCl_2$. In the preparation of complexes 1 : 2 (M:PPK) molar ratio was used.

The cobalt(III) complex of PPK was obtained by dissolving cobalt(II) chloride and the ligand in 1 : 2 molar ratio in 1 : 2 : 2 aq.-ethanol-ammonium medium and heating the solution on water bath for 1 hr., when spontaneous aerial oxidation took place leading to the isolation of the cobalt(III) complex of PPK which was subsequently dried in vacuo over $CaCl_2$.

Analyses, spectral and magnetic susceptibility measurements were described elsewhere[7,9–11].

RESULTS AND DISCUSSION

The analytical data (Table 1) show that the complexes have the formula $[Fe(PPK)_2(H_2O)_2]Cl$, $[Fe(PPK)_2(H_2O)_2]Cl_2$, $[Co(PPK)_2(H_2O)_2]Cl_2$, $Ni(PPK)_2]Cl$, and $[Cu_2(PPK)_4]$.

The molar conductance (Λ_M) values (given in parentheses) in dimethylformamide for $[Fe(PPK)_2(H_2O)_2]Cl$ (45) and $[Ni(PPK)_2]Cl$ (50) suggest the 1 : 1 electrolytic nature of iron(II) and nickel(II) complexes while molar conductances of iron(III) and cobalt(III) complexes are 145 and 165 ohm^{-1} cm^{-2} mol^{-1} respectively in support of 1 : 2 electrolytic nature[13].

Magnetic moments of iron(II) complexes are characteristic of high spin complexes[13]. The present iron(II) complex, however, shows a lower magnetic moment value of 3.9 B.M., which may be attributed to the quenching of orbital contribution possibly due to a lower site symmetry. It may be noted that the iron(III) complex of PPK showed magnetic

TABLE 1

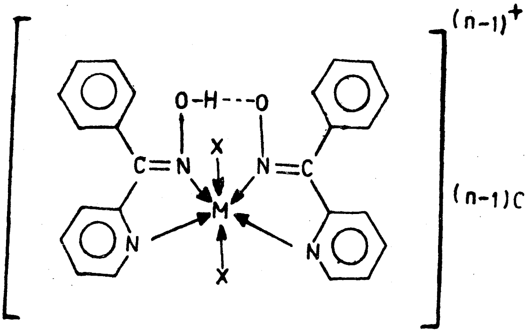
ANALYTICAL DATA OF PPK COMPLEXES

Complex	Colour	Analytical Data*, (%)				
		Carbon	Hydrogen	Nitrogen	Chlorine	Meta
$[Fe(PPK)_2(H_2O)_2]Cl$	Brown	26.80 (27.57)	4.35 (4.40)	10.50 (10.72)	6.10 (6.10)	10.50 (10.69)
$[Fe(PPK)_2(H_2O)_2]Cl_2$	Reddish Brown	25.95 (25.81)	4.25 (4.12)	9.50 (10.04)	12.50 (12.71)	9.60 (10.01)
$[Co(PPK)_2(H_2O)_2]Cl_2$	Dark-red	26.10 (25.67)	4.15 (4.10)	9.70 (9.98)	12.70 (12.64)	10.75 (10.50)
$[Ni(PPK)_2]Cl$	Orange-red	25.15 (24.43)	3.95 (3.88)	11.10 (11.44)	7.15 (7.28)	11.55 (11.05)
$[Cu_2(PPK)_4]$	Dark green	32.10 (31.41)	4.10 (4.14)	11.70 (12.21)	—	13.20 (13.86)

*Calculated values are in paranthesis.

moment (1.70 B.M.) which correspond to one unpaired electron for low spin iron(III) complex.

The electronic spectrum of iron(II) complex exhibits two bands at 10,000 and 10,990 cm^{-1} at room temperature. These spectral bands are characteristic of distorted octahedral iron(II) and are assigned[14] to components of the $^5T_{2g} \rightarrow {}^5E_g$. The splitting of this band may be due to a pronounced reduction in the ligand field symmetry caused by the greater steric requirements of the two ligand molecules. The doublet may be attributed to dynamic Jahn-Teller effect[15]. The intense band observed at 37,000 cm^{-1} in the spectrum is assigned to a charge transfer band $t_{2g}(Fe) \rightarrow \pi^*$ (PPK). The iron(III) complex reported herein is dark red, as is common for iron(III) compounds of oximes. This colour is usually ascribed to the presence of one or more low lying charge transfer absorption bands. Because of these very intense bands, one does not usually observe d-d transitions in the visible spectra of such compounds.



where, X = H_2O which is absent in Ni & Cu Complexes
n = Valence of M
M = Fe(II), Fe(III), Co(III), Ni(II) & Cu(II).

The cobalt(III) complex is diamagnetic and, therefore, it has octahedral structure. In the electronic spectrum of this complex a band at 25,970 cm^{-1} is attributed to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition[14], suggestive of octahedral environment[16,17] around cobalt atom.

A weak band at 15,380 cm^{-1} in the spectrum of nickel(II) complex can be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition and a strong band at 28,570 cm^{-1} can be assigned to charge transfer. This complex is found to be diamagnetic in favour of square planar structure[18].

The present copper complex is among the few typical copper(II) complexes in which the spin-paramagnetism is completely quenched ($\mu_{eff} = 0$) at room temperature. The diamagnetism may be due to metal-

metal interaction through super exchange phenomenon and/or the high polarizability[19] of ligand which supplies more electron density to copper ions and consequently the ions interact more strongly and consequently results in diamagnetic complex. The strong spin-spin interaction may take place by the overlap of strongly occupied $d_{x^2-y^2}$ orbital on the two cupric ions which give δ-type of bond[20] similar to that reported in copper(II) carboxylates *e.g.* $Cu(CH_3COO)_2H_2O$. A band at 14,580 cm^{-1} in the electronic spectrum of copper complex is attributed to d-d transitions[21,22] in favour of square pyramidal geometry[23] for this copper complex.

Infrared spectra

The ligand (PPK) exhibits band at 3180 cm^{-1} which may be assigned to the intermolecular hydrogen bonded ν(OH) of NOH group. The band at 1640 cm^{-1} has been assigned[24] to ν ($>C{=}N-$) and one appearing at 950 cm^{-1} to ν(N—O) (cf. ref. 25).

In all complexes, the ν(N—O) of the free ligand is shifted (20–35 cm^{-1}) to higher wave number indicating the coordination of metal ion through oxime nitrogen. The bonding is compatible with preferred mode of coordination of oxime[26].

In general, only small shifts in the vibrational frequencies of pyridine moiety are observed on complex formation. However, evidence of coordination of the pyridine ring is manifested by the changes of in-plane and out-of-plane vibrational modes at 620 and 450 cm^{-1}, respectively, in the free ligand, showing negative shift (*ca.* 20 cm^{-1}) in complexes which suggests the participation of heterocyclic ring nitrogen in coordination.

In far-IR spectra, the complexes exhibit bands around 270(w)[νM-py)] and 220(m) [ν(M-N)] which further substantiates the coordination of oxime nitrogen and nitrogen of pyridine ring.

The OH stretching band of PPK at 3180 cm^{-1} is shifted to around 1930 cm^{-1} in all complexes. This extraordinary low OH stretching frequency is attributed to strong interligand hydrogen bonding in analogy with well known observations of Runble and Parasol[27] $[Ni(DMG)_2]$ and Fujita *et al.* [28]$[CO(DMG)_2XY]$, where X, Y = Cl, Br, NO_2 or H_2O.

From the appreciation of results presented in elemental analysis, magnetic susceptibility measurements, conductivity data, electronic and infrared spectral data of the PPK complexes, the general structure (I) is assigned for the complexes (on page 50).

ACKNOWLEDGEMENTS

The author thanks the University Grants Commission, New Delhi for financial support. The author also thank the authorities of CDRI, Lucknow and RSIC, Madras for providing elemental analysis and spectral data, respectively.

REFERENCES

1. G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968).
2. A. Biggotto, G. Costa, G. Mestroni, G. Pellizer, A. Pexeddu, E. Reisenhofer, L. Stefani and G. Tauzer, *Inorg. Chim. Acta Rev.*, **4**, 41 (1970).
3. G. A. Nicholson, C. R. Lazarus and B. J. McCormick, *Inorg. Chem.*, **19**, 192, 195 (1980).
4. M. Mohan and M. Kumar, *Polyhedron*, **4**, 1929 (1985).
5. A. Chakravorthy, *Coord. Chem. Rev.*, **13**, 1 (1974).
6. R. B. Singh, B. S. Garg, and R. P. Singh, *Talanta*, **26**, 425 (1979).
7. A. Krishna, K. Hussain Reddy and D. Venkata Reddy, *Inorg. Chim. Acta*, **173**, 13 (1990).
8. F. Trussel and H. Diehl, *Anal. Chem.*, **31**, 1928 (1959).
9. K. Hussain Reddy and D. Venkata Reddy, *Indian J. Chem.*. **24A**, 154 (1985).
10. K. Giridhara Reddy, K. Hussain reddy and D. Venkata Reddy *Indian J. Chem.*, **25**, 982 (1986).
11. K. Hussain Reddy, *Currr. Sci. (India)*, **57**, 776 (1988).
12. W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
13. P. Gutlich, *Struct. Bonding*, **114**, 84 (1981).
14. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, London (1968).
15. B. N. Figgis, *Introduction to Ligand Fields*, 2nd Ed., Interscience, New York (1966).
16. D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, **A**, 146 (1966).
17. S. C. Chen and C. K. Poon, *J. Chem. Soc.*, **A**, 146 (1966).
18. K. K. Desai and H. B. Naik, *Indian J. Chem.*, **25A**, 291 (1986).
19. R. S. Nyholm, *Proc. Chem. Soc.*, **273**, (1961).
20. M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).
21. C. M. Harris, B. F. Hoskins and R. L. Martin, *J. Am. Chem. Soc.*, **81**, 3728, (1959).

22. I. P. Khuller and U. Agarwala, *Can. J. Chem.*, **53**, 1165 (1975).
23. A. Pignedoli and G. Peyronel, *Cazz. Chim. Ital.*, **92**, 745 (1962).
24. R. H. Holm, G. W. Everett (Jr.) and A. Chakravarthy, *Inorg. Chem.*, 7, 161 (1966).
25. A. Palam and H. Werbun, *Can. J. Chem.*, **32**, 858 (1954).
26. E. Frason, C. Panattoni and R. Zanettin, *Acta Crystallogr*, **12**, 201 (1959).
27. R. E. Rundle and M. Parasol, *J. Chem. Phy.*, **21**, 1487 (1952).
28. J. Fujita, A. Nakahara and R. Tsuchida, *J. Chem. Phys.*, **22**, 1541 (1955).

[*Received*: 10 April 1991; *Accepted*: 20 January 1992] AJC-389