

QUADRIDENTATE SCHIFF BASE LIGAND DERIVED FROM O-PHENYLENEDIAMINE WITH 2-FORMYL CYCLOHEXANONE IN THE NI(II), CU(II), CO(II), ZN(II), PB(II) AND UO₂(II) COMPLEXES

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ABSTRACT

Metal (II) chelates of Schiff base ligand derived from 2-formyl-cyclohexanone with o-phenylenediamine have been prepared and characterized. The isolated complexes are of the type $M(\text{PDBFCH}) \cdot x\text{H}_2\text{O}$ where $M = \text{Ni(II)}, \text{Cu(II)}, \text{Co(II)}, \text{Zn(II)}, \text{Pb(II)}$ and $\text{UO}_2(\text{II})$ whereas PDBFCH stands for the o-phenylenediamine bis(2-formylcyclohexylidene) Schiff base ligand. The trinuclear Cu(II) complex of the formula $\text{Cu}_2(\text{PDBFCH})_2 \cdot \text{CuCl}_2 \cdot 3\text{H}_2\text{O}$ was also prepared. The chelates were characterized by the elemental analyses, IR, PMR and UV-Visible spectra as well as conductivity and magnetic measurements. It has been found that the ligand behaves as ONNO quadridentate dibasic. Mode of bonding and geometrical structure are suggested and the non-electrolytic nature is proposed for these chelates.

Keywords: Isatin, Isonicotinoyl hydrazone, complexes.

INTRODUCTION

Chemistry of metal complexes with quadridentate Schiff base ligands has been extensively studied [1-10]. However little information was available in the literature concerning such type of complexes. Thus in connection with research projects being conducted in our laboratory on the metal complexes of Schiff bases derived from diamines [11-15], we report herein the chelating characters of Schiff base ligand derived from o-phenylenediamine with 2-formylcyclohexanone towards Cu(II), Ni(II), Co(II), Zn(II), Pb(II) and UO₂(II) ions. Hitherto such study could not be reported.

EXPERIMENTAL

All chemicals, metal salts and solvents were either Aldrich or BDH products. Preparation of 2-formylcyclohexanone was made according to the claisen condensation of cyclohexanone with ethyl formate in the presence of metallic sodium as reported in the literature [16].

Preparation of o-phenylenediamine bis (2-formylcyclohexylidene) Schiff base ligand; PDBFCH.

Twofold amount of 2-formylcyclohexanone (40 mmol) and one of o-phenylenediamine (20 mmol) were dissolved in 100 ml of hot ethanol. The reaction mixture was refluxed below 80°C for 4 hours. The precipitate that separated was filtered off, washed with ethanol and dried in vacuo over phosphorus pentoxide.

Preparation of the chelates

The following general procedure was adopted for the preparation of all the metal chelates: Metal salt solution (0.01 mol) of $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$, $\text{Pb(OAc)}_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in ethanol (50 ml) was added dropwise to a solution of PDBFCH Schiff base (0.01 mol), in ethanol (100 ml). Few drops of NaOH solution were added to the reaction mixture to make the resulting solution just alkaline. The reaction mixture in each case was then

kept under reflux with magnetic stirring for 3 hours. The solution was then reduced to a small volume and left to cool whereby the complexes separated. These were filtered off, washed with distilled water, and absolute ethanol followed by ether and then dried and preserved in a desiccator over silica gel.

Apparatus and physical measurements

The IR spectra of the metal complexes and their free ligand were measured using KBr disks with a Pye Unicam SP spectrometer. Electronic spectra in DMF were measured on Shimadzu UV-160A UV-Visible recording spectrophotometer. Molar conductivities were measured in DMF solution at 25°C with a YSI MODEL 35 Conductance Meter.

Magnetic measurements were carried out by Faraday technique at room temperature. The proton nuclear magnetic resonance spectra in DMSO-d₆ were measured on a Varian E.M. 390 NMR Spectrophotometer. Chemical shifts are reported in δ ppm downfield from internal TMS.

RESULTS AND DISCUSSION

The analytical data reported in Table (1) suggest that the reaction of o-phenylenediamine bis(2-formylcyclohexylidene) Schiff base, PDBFCH, with the investigated metal ions produces complexes of the type M(PDBFCH).xH₂O where M = Ni(II), Co(II), Cu(II), Pb(II), Zn(II), and UO₂(II). Conductance measurements in DMF indicate that the complexes are non-electrolytes.

Table 1. Analytical, magnetic and conductivity data of the metal chelates

Metal chelates	C% Found (calcd.)	H% Found (calcd.)	N% Found (calcd.)	μ_{eff} B.M	Λ ohm ⁻¹ .mol ¹ .cm ²
Ni(PDBFCH).2H ₂ O	57.68 (57.59)	6.41 (6.23)	6.82 (6.71)	-	5.32
Cu(PDBFCH).2H ₂ O	56.52 (56.93)	6.09 (6.16)	6.59 (6.64)	1.83	6.24
Co(PDBFCH).2H ₂ O	57.74 (57.56)	6.41 (6.23)	6.92 (6.71)	2.61	8.36
Zn(PDBFCH).3H ₂ O	54.61 (54.38)	6.52 (6.34)	6.15 (6.34)	-	14.21
Pb(PDBFCH).4H ₂ O	39.80 (39.92)	4.71 (4.99)	4.78 (4.65)	-	10.48
UO ₂ (PDBFCH).4H ₂ O	36.36 (36.14)	4.48 (4.51)	4.43 (4.21)	-	15.59
Cu ₂ (PDBFCH) ₂ CuCl ₂ .3H ₂ O	50.29 (50.02)	5.48 (5.21)	5.68 (5.83)	1.43	25.32

Infrared and PMR Spectra

The free ligand PDBFCH under this study can exist in three tautomeric forms as shown in Figure (1). The infrared spectrum of this ligand showed a broad

absorption around 3380 cm⁻¹ which may be due to hydrogen bonding ν (OH) in structure (II) or ν (NH) in (III). A more definite evidence for the presence of acidic proton may be deduced from the PMR spectrum. The ligand exhibited a doublet around 11.5 ppm which

may be attributed to NH or OH proton. Infrared spectrum of the ligand PDBFCH displayed also two bands in vicinity of 1650 and 1500 cm^{-1} which be assigned respectively to the perturbed $\nu \text{C}=\text{O}$ and the NH deformation mode. In all the metal chelates, the bands due to $\nu (\text{NH})$, $\nu (\text{C}=\text{O})$ and $\delta (\text{NH})$ are absent. On the other hand, an intense band in the 1600-1630 cm^{-1} region appears due to the stretching mode of the azomethine nitrogen ($\nu \text{C}=\text{N}$). In the PMR spectra of the diamagnetic chelates, the doublet around 11.5 ppm disappears. These observations suggest that the PDBFCH ligand coordinates as a dibasic ONNO quadridentate to the central metal ion in from (II) via the two bridging azomethine nitrogen atoms and the two negatively charged oxygen atoms of the deprotonated enolic form of cyclohexanone residues as shown in Figure (2).

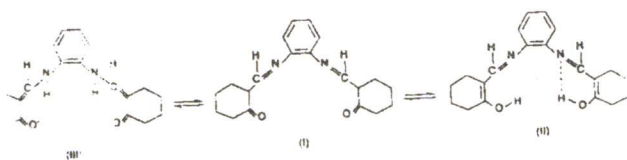


Figure 1. Tautomeric forms of PDBFCH free ligand.

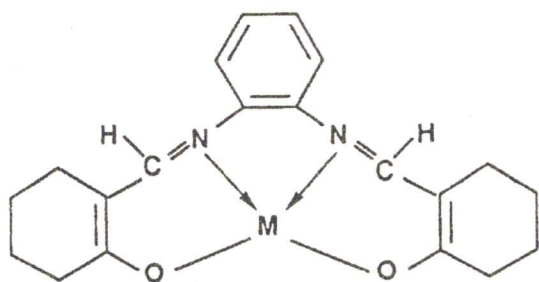


Figure 2. Metal complexes PDBFCH ligand.

The $\text{UO}_2(\text{II})$ ion is characterized by three vibrational frequencies, the symmetric (γ_1), asymmetric (γ_3) and the bending (ν_2) frequency [17,18]. Thus the two bands observed at 986 and 836 cm^{-1} in the IR spectrum of the $\text{UO}_2(\text{II})$ complex can be presumably attributed to γ_3 and γ_1 vibrations respectively. The band due to γ_2 vibration could not be noted as it appears in the lower region. A broad band around 3395-3460 cm^{-1} appears in all the IR spectra of the chelates. This band may be assigned to water molecule OH stretching frequencies

asserting the elementary analysis results that the water molecules are involved in the chemical composition of the chelates.

Magnetic moment and electronic spectra

The electronic spectrum of the uranyl chelate in DMF exhibits mainly one shoulder at 22790 cm^{-1} and two bands of moderate and high intensity at 28320 and 37520 cm^{-1} respectively. The latter one may be ascribed to charge transfer transition whereas the former may be due to the uranyl (O-U-O) ion in solution [19].

Copper(II) chelate was found to possess the room temperature magnetic moment value of 1.83 B.M which is very close to the spin-only value for a d^9 ion. The electronic spectrum displayed two weak and broad bands around 21200 and 15960 cm^{-1} which may be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions respectively in an idealised square planar symmetry. Ni(II) chelate showed the diamagnetic behaviour. The electronic spectrum of this chelate exhibited four bands at 187500, 20840, 26920 and 32690 cm^{-1} which may be assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1), ${}^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2), ${}^1A_{1g} \rightarrow {}^1E_g$ (ν_3) and $\pi-\pi^*(L)$ transitions respectively. The first two bands are of low intensity and are purely d-d transition while ν_3 is enveloped by a strong charge-transfer transition. These results suggest a square planar configuration for Ni(II) chelate. Cobalt(II) complex shows a magnetic moment value of 2.61 B.M. Its electronic spectrum displays two bands in vicinity of 16230 and 21260 cm^{-1} which may be assigned ${}^2A_{1g} \rightarrow {}^2B_{2g}$ and ${}^2A_{1g} \rightarrow {}^2E_g$ transitions respectively in square planar configuration around Co(II). The Zn(II) and Pb(II) chelates are diamagnetic in nature. The electronic spectral bands at 36420 and 24680 cm^{-1} for Zn(II) chelate and at 35850 and 23940 cm^{-1} for Pb(II) may be mainly attributed to L-L* transitions.

Trinuclear copper (II) chelate

It has been synthesized by adding $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) dissolved in the minimum quantity of water dropwise under stirring to DMF concentrated solution of $\text{Cu}(\text{PDBFCH}) \cdot 2\text{H}_2\text{O}$ (2 mmole). The reaction mixture was kept under reflux for about 4 hours. The analytical data obtained for the isolated solid product suggest the trinuclear, $[\text{Cu}(\text{PDBFCH})]_2 \text{CuCl}_2 \cdot 3\text{H}_2\text{O}$, structure as shown in Figure (3).

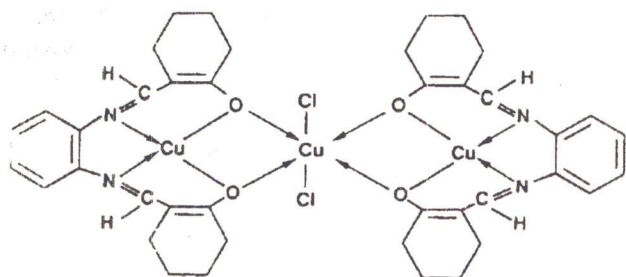


Figure 3. Trinuclear copper(II) chelate of PDBFCH ligand.

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