

Magnetic and structural aspects of tetranuclear complexes of bis-diacetylmonooxime-*p*-phenylenediamine with bivalent Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) metals

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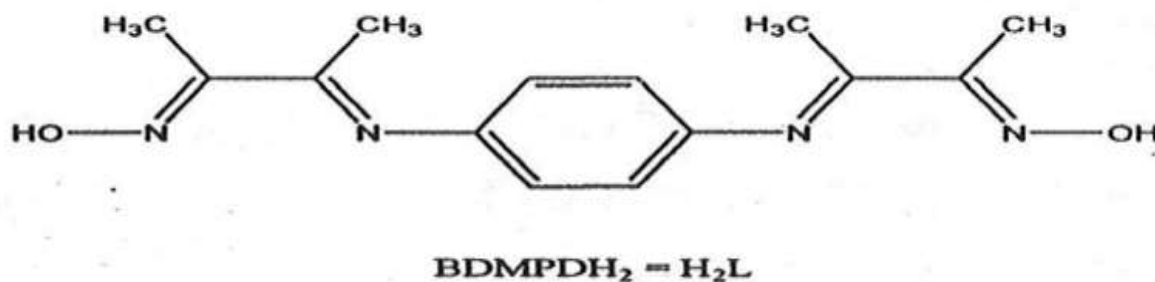
Abstract: The tetranuclear complexes of Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) with bis-diacetylmonooxime-*p*-phenylenediamine (BDMPDH₂) of composition [M₂(BDMPD)₂ (H₂O), (CuCl₂)] (M= Co²⁺ Ni²⁺ or Cu²⁺) and [M₂(BDMPD)₂ (CuCl₂)₂] (M-Zn²⁺ and Cd²⁺) has been prepared and characterized. The dinuclear chelate of bivalent metal has been found to coordinate with oxime group free oxygen (N-O) atom. The electrical conductance value suggested coordinated nature of chloride in complexes. The magnetic and electronic spectra of Co (II) and Ni (II) complexes are consistent with octahedral structure, while those of Zn (II) and Cd (II) possess tetrahedral structure.

Key words: *p*-phenylenediamine, diacetylmonooxime and (BDMPDH₂)

INTRODUCTION

It has been well established that transition and post transition metal chelate, complexes with bidentate and polydentate Schiff bases or ligands containing coordinated phenolic group or oxygen atoms further coordinated with metal atom to bonded oxygen atom, forming polynuclear complexes^[1-10]. Polynuclear complexes formed by chelate complexes have been studied extensively by Sinn Harris and others^[1-4]. Recently polynuclear chelates of transition metals have been studied due to their interesting structural variation^[5-10]. In present paper we report

the tetranuclear complexes of Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) with bis-diacetylmonooxime-p- phenylenediamine (BDMPDH₂).



MATERIALS AND METHODS

Preparation of ligand: The ligand BDMPDH₂ was prepared by condensing 0.1 mol of p-phenylenediamine with 0.2 mol of diacetylmonooxime in ethanol on refluxing on water bath. M.P. of ligand found 205°C. Nitrogen found 20.23%, required nitrogen for CHNO, (ligand) 20.43%. The reagents and chemical used were obtained from E. Merck or BDH.

Preparation of complexes M₂(BDMPD)_n(H₂O)_n (If MCo²⁺, Cu²⁺ or Ni²⁺; n = 4 and n = zero for Zn²⁺, Cd²⁺).

About 10 millimole of appropriate metal acetate or metal chloride was dissolved in aqueous methanol and treated with hot ethanolic solution of ligand in molar proportion in 30 ml methanol. The resulting solutions were refluxed on water bath at 60-70°C by adding aqueous solution of sodium acetate. The complex separated as flocculent precipitate on dilution with excess of water. The precipitate were digested for 15 minutes on a steam bath and collected on a filter. The products were washed with excess of water and dried over CaCl₂ in a desiccator. The elemental analysis (metals, carbon, hydrogen and nitrogen) of complexes were found in the expected range of composition of complexes and these are given in Table -1.

Preparation of complexes : [M₂(BDMPD)₂ (H₂O) (CuCl₂)₂]:

These polynuclear complexes were prepared by reaction of binuclear complexes [M₂(BDMPD)₂H₂O_n] (n = zero or 4) and (M=Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺ and Cd²⁺) with CuCl₂ in dry methanol.

Procedure:

About 10 millimole of binuclear complexes were suspended in dry methanol (20 ml) and treated with 20 millimole of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 20 ml hot dry methanol. The resulting mixture was refluxed on a steam bath in a R. B. flask for one hour when total content went into solution and from which tetranuclear product separated gradually. The products were collected on a filter, washed with methanol and dried over CaCl_2 . The results of chemical analysis are shown in Table - 1.

The chemical analysis of complexes formed by interaction of neutral bis chelate $[\text{M}_2(\text{BDMPD})_2]$ as well as with $[\text{M}_2(\text{BDMPD})_2(\text{H}_2\text{O})_4]$ (Co^{2+} Cu^{2+} Ni^{2+}) with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ corresponds to composition $[\text{M}_2(\text{BDMPD})_2 (\text{CuCl}_2)_2]$ ($\text{M} = \text{Cu}^{2+}$, Zn^{2+} and Cd^{2+}) and $[\text{M}_2(\text{BDMPD})_2(\text{H}_2\text{O})_4 (\text{CuCl}_2)_2]$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+}) respectively.

RESULTS AND DISCUSSION

It has been found that dinuclear metal chelates of bis-diacetylmonooxime-p-phenylenediamine (BDMPDH_2) of composition $\text{M}_2(\text{BDMPD})_2 (\text{H}_2\text{O})_n$ behave as ligand molecule Cu(II)Cl_2 through the uncoordinated oxime atoms and yield complexes with composition and $[\text{M}_2(\text{BDMPD})_2 (\text{H}_2\text{O})_4 (\text{CuCl}_2)_2]$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+}) and $[\text{M}_2(\text{BDMPD})_2 (\text{CuCl}_2)_2]$ ($\text{M} = \text{Zn}^{2+}$ or Cd^{2+}).

The complexes are stable to heat and do not lose water below $120-100^\circ\text{C}$ indicating coordinating nature of water molecule in complexes" and $[\text{M}_2(\text{BDMPD})_2(\text{H}_2\text{O})_4(\text{CuCl}_2)_2]$

The complexes have poor solubility in water but dissolve appreciably in dioxane, dimethyl formamide and pyridine.

The freshly prepared DMF solution of complexes show negligible electrical conductance value $12 (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$ suggesting coordination of chloride in complexes. The magnetic moment value of $[\text{Zn}_2(\text{BDMPD})_2 (\text{CuCl}_2)_2]$ and $[\text{Cd}_2(\text{BDMPD})_2 (\text{CuCl}_2)_2]$ for one metal atom corresponds to 1.84 BM, suggesting tetrahedral coordination. The magnetic moment value for one metal each in complexes $[\text{Ni}_2(\text{BDMPD})_2 (\text{H}_2\text{O})_2 (\text{CuCl}_2)_2]$ and $[\text{Co}_2(\text{BDMPD})_2 (\text{H}_2\text{O})_2 (\text{CuCl}_2)_2]$ are 2.63 and 3.54 BM respectively are consistent with octahedral coordination of metal atoms in polynuclear chelates^[13-17]. The electronic absorption spectrum of $[\text{Zn}_2(\text{BDMPD})_2 (\text{CuCl}_2)_2]$ shows a strong band at 440 nm and broad band near 630-650 nm suggesting tetragonal distortion in complexes. The IR spectra of free ligand shows

a band at 1634cm^{-1} assignable to $\nu(\text{C}=\text{N})$ stretch^[18]. Which is shifted to lower frequency in complexes suggesting coordination of ligand through (C=N). The $\nu(\text{N}-\text{O})$ of complexes shifted to lower wave number on coordination^[19-21]. The molecular weight determination determined by Rast method approximately consistent with tetranuclear structure of respective metal atom (Table - 2) from the physio-chemical studies. The following structures are suggested for complexes:

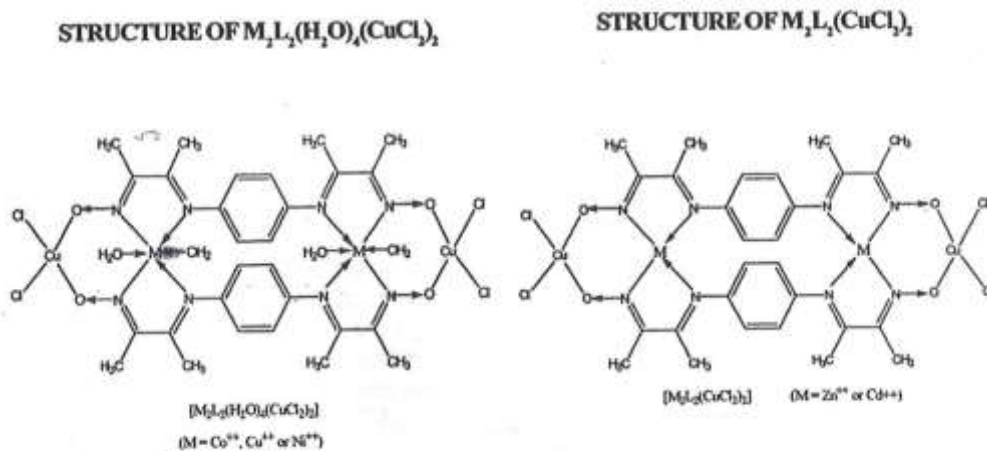


Table -1 : Analytical Results of Metals

Complex	% of elemental analysis, found (cal)					
	M	C	H	N	Cl	M'
$[\text{Co}_2(\text{BDMPD})_2(\text{H}_2\text{O})_4]$	11.60 (11.75)	33.60 (33.51)	4.25 (4.02)	11.20 (11.17)	14.20 (14.13)	12.70 (12.67)
$[\text{Ni}_2(\text{BDMPD})_2(\text{H}_2\text{O})(\text{CuCl}_2)_2]$	11.80 (11.70)	33.60 (33.53)	4.05 (4.02)	11.00 (11.17)	14.20 (14.14)	12.45 (12.67)
$[\text{Cu}_2(\text{BDMPD})_2(\text{H}_2\text{O})_4(\text{CuCl}_2)_2]$	25.30 (25.10)	33.45 (33.21)	3.70 (3.98)	11.20 (11.07)	14.05 (14.00)	
$[\text{Cd}_2(\text{BDMPD})_2(\text{CuCl}_2)_2]$	21.70 (21.65)	32.50 (32.39)	3.20 (3.11)	10.60 (10.79)	13.50 (13.66)	12.35 (12.24)
$[\text{Zn}_2(\text{BDMPD})_2(\text{CuCl}_2)_2]$	13.75 (13.83)	35.70 (35.61)	3.30 (3.41)	11.75 (11.87)	15.25 (15.02)	13.50 (13.46)

Table -2 : Physico chemical results of metals

Compound	Colour	Molecular wt. found (cal)	μ_{eff} at 304 k in BM	Molar electrical conductance value = ohm
[Co ₂ (BDMPD) ₂ (H ₂ O) ₄ (CuCl ₂) ₂]	Brown	990 (1013)	3.89	12
[Cu ₂ (BDMPD) ₂ (H ₂ O) ₄ (CuCl ₂) ₂]	Greenish Brown	1007 (1013)	1.84	8
[Cu ₂ (BDMPD) ₂ (H ₂ O) ₄ (CuCl ₂) ₂]	Yellowish brown	997 (1002)	2.89	8
[Cd ₂ (BDMPD) ₂ (CuCl ₂) ₂]	Greenish Yellow	940 (944)	1.83	9
[Zn ₂ (BDMPD) ₂ (CuCl ₂) ₂]	Greenish Yellow	1025 (1038)	1.89	12

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