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Synthesis of bimetallic bivalent metal complexes of Schiff base derivative from diacetylmonooxime and p-phenylene diamine

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Abstract
The bimetallic complexes of Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) with Schiff base of p-phenylenediamine with diacetyl monooxime ($BDMPDH_2$) composition $M_2(BDMPD)_2$ $(H_2O)n$ (n=4 for, Mn^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+} and n=zero for Zn^{2+}, Cd^{2+} or Hg_2) and M_2 $(BDMPDH_2)Cl_4$ have been prepared and characterised from magnetic susceptibility measurement and studies of IR and electronic spectra of complexes.

Keywords: P-phenylenediamine, diacetylmonooxime and ($BDMPDH_2$), metal complexes

Introduction
The Schiff bases and their metal complexes derived from α-α'-diketones and α -ketomonooxime have wide industrial and biological applications [1, 2, 3, 4, 5]. The coordination complexes of Schiff bases have been studied extensively due to their potential donor ability and strong complexing properties [6, 8, 9]. In present work we report the preparation and characterization of some bivalent metal complexes of bis- diacetylmonooxime-p-phenylenediamine ($BDMPDH_2$).
The ligand H_2L can remain in two tautomeric forms (X & Y) in which oxime group (C=NOH) may remain as N→O The ligand $BDMPDH_2$ contains four potential nitrogen atoms as donor sites, capable of forming bis chelate and bimetallic complexes. The hydroxime OH proton can be deprotonated in basic or neutral medium behaving as dianionic coordinating molecule.

Materials and methods
The Schiff base ligand of ρ-phenylenediamine with diacetylmonooxime ($BDMPDH_2$) was - prepared by refluxing ethanolic solution of reactant in equi-molar proportion by adding a few drops of acetic acid. The metal salts, diacetylmonooxime and ρ-phenylenediamine were obtained from either BDH or E Merck. Magnetic susceptibility was determined by Gouy method. IR and electronic absorption spectra of ligand and complexes were recorded at Shimadzu 2000; IR spectrophotometer.
Preparation of complexes, M_2 $(BDMPD)_2.nH_2O$ (M = Co^{2+}, Ni^{2+}, Cu^{2+} or Mn^{2+}; n = 4; when M=Zn^{2+}, Cd^{2+} or Hg+, n = zero) : 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 $CaCl_2$ 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, [M_2 $(BDMPDH_2)CI_4$] (M=Cu^{2+}, Zn^{2+}, Cd^{2+} or Hg^{2+}): About 10 millimole of metal chloride were dissolved in 20 ml hot dry methanol and treated drop wise with constant stirring a hot solution of 5 millimole of ligand in 10 ml hot methanol. The resulting solution was cooled with constant stirring when bimetallic tetrachloro-complexes separated gradually. The complexes were collected and analysed for metal, chlorine and nitrogen content of products. The colour, magnetic susceptibility value and electrical molar conductance values of complexes are shown in Table - 2.

Results and discussion
The analytical results of complexes of BDMPDH, correspond with compositions [$M_2(BDMPD)$, $(H_2O)_4$] (M = Co^{2+}, Mn^{2+}, Ni^{2+} or Cu^{2+}), [$M_2(BDMPD)_2$] (M=Zn^{2+}, Cd^{2+} or Hg^{2+}) and $M_2(BDMPDH_2)CI_4$ (M= Zn^{2+}, Cd^{2+} or Cu^{2+}). The complexes $M_2(BDMPD)_2$ $(H_2O)n$ (n=4 or zero) are formed in aqueous alcoholic basic medium while the tetrachloro binuclear complexes ($M_2(BDMPDH_2)CI$ (M= Cu^{2+}, Zn^{2+}, Cd^{2+} or Hg^{2+}) are formed in dry methanol. The complexes are quite stable in air and on heating aqua complexes [$M_2(BDMPD)_2$ (H_2O)] do not loss water below 100°c indicating coordinated nature of water in complexes. The complexes are almost insoluble in water but dissolve in ethanol and DMF. The DMF solution of complexes shows negligible electrical conductance value (Table 2) supporting nonionic nature of complexes [10] The zinc (II), cadmium (II) and mercury (II) complexes are diamagnetic and tetrahedral with sp^3 hybrid bonding. Manganese (II) complex $M_2(BDMPD)_2$, (H_2O), show room temperature magnetic moment value 5.87 BM suggesting octahedral structure. The molecular weight determination of complexes [$M_2(BDMPD)_2$] by Rast method in camphor correspond with bimetallic structure (Table - 2).
The electronic absorption spectrum of Ni (II) complexes [Ni_2L_2 (H_2O)] shows a strong band at 390 nm attributed to charge transfer transition. The complex [$Ni_2L_2(H_2O)_4$] is paramagnetic and shows magnetic moment value 3.14 BM similar to octahedral nickel (II) complexes. In visible region the electronic absorption bands at 420 nm, 592 nm and 782 nm are assigned to. t transitions $^3A_{2g}$→ $^3T_{1g}$ (P), $^3A_{2g}$→ $^3T_{1g}$

(F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) respectively in approximately 28 I octahedral field [11, 12, 13]. The copper (II) complex $[Cu_2(BDMPD)_2 (H_2O),]$ and $[Cu_2(BDMPDH_2)C1]$ show magnetic moment value 1.84 and 1.81 respectively supporting magnetically dilute nature of complexes [14]. The electronic absorption spectrum of $[Cu_2 (BDMPD)_2 (H_2O)_4]$ shows a broad medium absorption band near 610-614 nm attributable to $^2T_{2g} \rightarrow {}^2Eg$ transition in octahedral field.

The IR spectrum of ligand in KBr disc shows a broad band at 2940-3346 cm^{-1} attributable to, v(CH) phenyl, v(C-H) methyl and hydrogen bonded oxime (=NOH) group (OH) frequencies. The disappearance of v(OH) vibration in complexes $[M_2(BDMPD)_2 (H_2O)_4]$ and $M_2 (BDMPD)_2$ supported the deprotonation of (=NOH) proton, and coordination of oxime with nitrogen atom. The v(OH) of oxime is retained in complexes $M_2(BDMPDH_2)Cl$; indicating neutral coordination of ligand molecule. The v(C=N) of ligand was observed at 1634cm^{-1} which was shifted to lower wave number by 15-30 cm^{-1} supporting coordination of (C-N) imine nitrogen to metal atom [15, 16, 17, 18]. The ligand displays a number of strong to medium IR bands in fingerprint region due to various modes of phenyl ring vibrations and these are retained in metal complexes. From the studies of elemental analysis, metal: ligand ratio and physical data-

Table 1: Analytical results of complexes

Complex	% of elemental analysis, found (cal)				
	M	C	H	N	Cl
$[Co_2(BDMPD)_2(H_2O)_4]$	16.25 (16.05)	45.60 (45.78)	5.55 (5.49)	15.05 (15.26)	
$[Ni_2(BDMPD)_2(H_2O)_4]$	15.80 (15.99)	45.80 (45.81)	5.40 (5.49)	15.35 (15.27)	
$[Cu_2(BDMPD)_2(H_2O)_4]$	17.00 (17.09)	45.10 (45.21)	5.30 (5.42)	15.00 (15.07)	
$[Mn_2(BDMPD)_2(H_2O)_4]$	15.00 (15.12)	46.40 (46.28)	5.65 (5.55)	15.30 (15.43)	
$[Zn_2(BDMPD)_2]$	19.45 (19.37)	49.60 (49.79)	4.60 (4.77)	16.50 (16.59)	
$[Cd_2(BDMPD)_2]$	29.20 (29.22)	43.60 (43.71)	4.00 (4.19)	14.60 (14.57)	
$[Hg_2(BDMPD)_2]$	42.60 (42.42)	35.66 (35.56)	3.35 (3.41)	11.60 (11.85)	
$Cu_2(BDMPDH_2)Cl_4$	23.85 (23.40)	30.80 (30.95)	3.50 (3.34)	10.50 (10.32)	26.00 (26.10)
$Zn_2 (BDMPDH_2)Cl_4$	35.28 (35.08)	26.45 (26.23)	2.63(2.83)	8.60 (8.74)	22.10 (22.12)

Table 2: Magnetic suspectivility and electrical conductance value of complies

Compound	Colour	Molecular wt. found (cal)	μeff at 304 k in BM	Molar electrical conductance value = $ohm^{-1} mol^{-1}cm^2$
$[Co_2(BDMPD)_2(H_2O)_4]$	Buff colour	730 (734)	4.96	7
$[Ni_2(BDMPD)_2(H_2O)_4]$	Bluish green	728 (734)	3.14	6
$[Cu_2(BDMPD)_2(H_2O)_4]$	Brown	738 (734)	1.84	8
$[Mn_2(BDMPD)_2 (H_2O)_4]$	Cream	721 (728)	5.87	8
$[Cd_2(BDMPD)_2]$	White	760 (769)	Diamgentic	6
$[Zn_2(BDMPD)_2]$	White	670 (675)	Diamgentic	5
$[Hg_2(BDMPD)_2]$	White	------	Diamgentic	5
$Cu_2(BDMPDH_2)Cl_4$	Light brown	540 (544)	1.81	15
$Zn_2 (BDMPDH_2)Cl_4$	White	940 (944)	Diamgentic	21
$Cd_2(BDMPDH_2)Cl_4$	White	-------	Diamgentic	18
$Hg_2(BDMPDH_2)Cl_4$	White	-------	Diamgnetic	12

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