

Synthesis and Characterization of Some Transition Metal Complexes with Schiff Bases

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Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with Schiff base formed by condensation of S-ethyl dithiocarbamate and *p*-methoxy acetophenone have been synthesized. The complexes have been characterized on the basis of elemental analysis, magnetic susceptibility, molar conductance and spectral data.

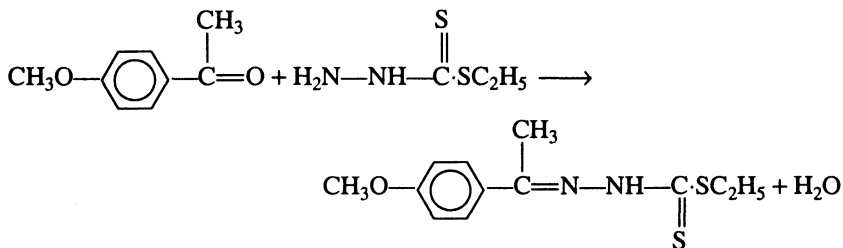
Key Words: Synthesis, Characterization, Complex, Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), Schiff base.

INTRODUCTION

Schiff bases derived from esters of dithiocarbazoic acid with aromatic carbonyl compounds are known to behave as bidentate chelating agents towards transition metal ions forming a five-membered chelate ring. In the present study, complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the above Schiff base, S-ethyl dithiocarbamate condensed with *p*-methoxy acetophenone hydrazone (AEdtCz), have been synthesized and characterized.

EXPERIMENTAL

All the chemicals were either BDH or AR grade and used as such. The Schiff base, *i.e.*, *p*-methoxyacetophenone hydrazone-N-[S-ethyl]dithio carboxylate, was synthesized by the simple condensation reaction between *p*-methoxy acetophenone and S-ethyl dithiocarbamate in ethanolic medium (Scheme-1).



Scheme-1

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Ethanol solution of *p*-methoxy acetophenone was mixed with the solution of *S*-ethylthiocarbamate in the same solvent in 1 : 1 molar proportion. The mixture was refluxed over a water-bath for 1 h. On cooling the reaction mixture, the Schiff base was separated out as yellow crystals. The crystals were filtered, recrystallized from a little alcohol and dried in an oven (m.p. $118 \pm 1^\circ\text{C}$). Analysis (%), Found (Calcd.): C = 54.10 (53.73), H = 6.00 (5.97), N = 10.50 (10.44), S = 23.70 (23.88).

Synthesis of metal-coordination compounds: About 100 mg of the Schiff base was dissolved in ethanol (30 mL) and this was added gradually to the ethanolic solution of the respective metal acetate, 50 mg in 20 mL ethanol, with constant stirring of the mixture. The crystals which were separated out were filtered off, washed thoroughly with ethanol and then dried in vacuum over P_4O_{10} .

RESULTS AND DISCUSSION

The complexes are insoluble in water but are moderately soluble in common organic solvents. The complexes are non-hygroscopic and air-stable for days together. The analytical data are presented in Table-1.

TABLE-1
ANALYTICAL DATA AND MOLAR CONDUCTANCE DATA OF
THE METAL COMPLEXES OF SCHIFF BASE

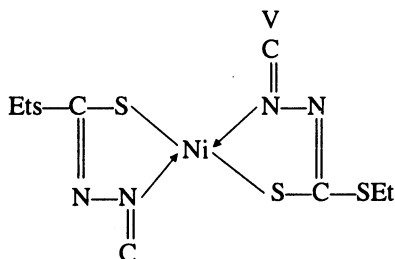
Complexes	Colour	μ_{eff} (B.M.)	Analysis (%), Found (Calcd.)					
			C	H	N	S	M	Ω
$\text{Co}(\text{AEtdtCz})_2$	Reddish brown	4.6	48.3 (48.57)	5.2 (5.10)	9.3 (9.44)	21.6 (21.58)	10.1 (9.94)	3.7
$\text{Ni}(\text{AEtdtCz})_2$	Brown	Diamag.	48.7 (48.59)	5.3 (5.10)	9.7 (9.44)	21.3 (21.59)	9.7 (9.90)	2.3
$\text{Cu}(\text{AEtdtCz})_2$	Green	1.5	48.5 (48.19)	4.9 (5.06)	9.5 (9.37)	21.2 (21.42)	10.4 (10.63)	4.9
$\text{Zn}(\text{AEtdtCz})_2$	Colourless	Diamag.	47.9 (48.04)	5.1 (5.04)	9.7 (9.34)	21.7 (21.35)	10.8 (10.90)	2.8
$\text{Cd}(\text{AEtdtCz})_2$	Pale yellow	Diamag.	44.7 (44.55)	4.7 (4.67)	8.4 (8.66)	20.0 (19.80)	17.2 (17.38)	3.4

These metal complexes register negligible molar conductance data in DMF solution indicating them to be all non-electrolytic in nature. In view of the N, S bidentate behaviour of the Schiff base as established on the basis of IR spectral studies all the bis complexes are 4-coordinate with chromophore (MN_2S_2). The Zn(II) and Cd(II) ions being d^{10} system, the complexes of these two metal ions are all diamagnetic.

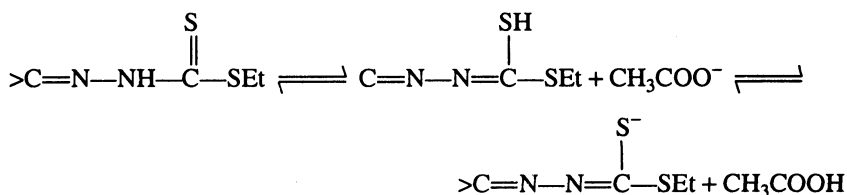
TABLE-2
 IR SPECTRAL BANDS (cm^{-1}) OF SCHIFF BASE AND ITS TRANSITION
 METAL(II) COMPLEXES

Compound	$\nu(\text{N—H})$	$\nu(\text{C—N})$	$\nu(\text{N—N})$	$\nu(\text{C= S})$	$\nu(\text{M—S})$
AEtdtCzH	3150 s	1590 s	1020 s	1000 s	—
Co(AEtdtCzH) ₂	—	1605 s	1030 br	970 s 990 s	430 w
Ni(AEtdtCzH) ₂	—	1610 s	1020 br	990 s 960 s	410 w
Cu(AEtdtCzH) ₂	—	1600 s	1020 br	985 s 970 sh	420 w
Zn(AEtdtCzH) ₂	—	1615 s	1025 br	990 s 970 sh	430 w
Cd(AEtdtCzH) ₂	—	1600 s	1030 br	980 s 960 s	410 w

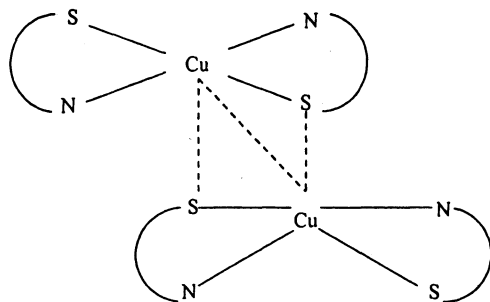
The Ni(II) and Co(II) complexes are diamagnetic. The diamagnetic behaviour in Ni(II) complex suggests that the spin-pairing in Ni(II) caused by strong ligand field and hence square-planar structure achieved by dsp^2 is $^1A_{1g}$ and one should expect three absorption bands corresponding to the $^1A_{1g} \rightarrow ^1A_{2g}$, $^1B_{1g}$ and 1E_g transition. However, in the case of ligands containing thiol group the high energy bands corresponding to the second and third transitions are invariably submerged under charge transfer or inter-ligand transitions and hence only the first band is observed. The neutral bis-ligand complexes of Ni(II) display the first band thereby indicating its square-planar geometry.



The electronic spectra of Co(II) complexes with Schiff base exhibit $^4A_2 \rightarrow ^4T_1(F)(\nu_2)$ and $^4A_2 \rightarrow ^4T_1(P)(\nu_3)$. The frequencies and intensities of the bands are typical of Co(II) in tetrahedral ligand field. Both the transitions hence deprotonation *via* enethiolization is enhanced.



The neutral bis ligand complexes of copper(II) are paramagnetic with magnetic moment values slightly less than spin-only values of 1.73 BM as expected for one unpaired electron. These subnormal magnetic moment values suggest the possibility of some sort of Cu-Cu interaction or association in these complexes. The X-ray structural analysis of the dimeric copper(II) dithiocarbamate complexes have shown that copper(II) ion is in a trigonal bipyramidal environment. Dimerization of copper(II) complexes with sulphur containing ligands is well known^{6,7}. The formation of dimers in case of copper(II) chelates of S-carboxydiethyl dithiocarbamic acid and diacetyl bis-thiosemicarbazone have been suggested to account for this ESR spectra^{6,7}. Sayed *et al.*⁸ have reported dimeric structure of copper(II) chelate with hydrazine-S-methyl dithiocarboxylate Schiff bases derived from acetone and acetophenone. Accordingly, the dimeric structure may be adopted for the copper(II) chelates investigated presently. The subnormal magnetic moments of these chelates are in agreement with such a dimeric structure due to possible Cu-Cu association resulting into partial spin-pairing.



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