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Synthesis And Physicochemical Elucidation Of Nickel (II) Complexes With Acetophenone Derivatives Of Dithiocarbazic Acid

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ABSTRACT

Nickel(II) complexes of the type $[Ni(L)_2X]$ *where L = ligand (acetophenone derivatives of dithiocarbazic acid) have been prepared by refluxing method. Ethanolic solution of ligand (L) was mixed with the 20-30 ml of hydrated nickel(II) chloride* $[NiCl_2.6H_2O]$ *and nickel(II) nitrate* $[Ni(NO_3)_2.6H_20]$ *solution in the same solvent. The resulting products have been characterized by elemental analysis, IR spectral studies as well as magnetic susceptibility measurements. Octahedral structure is proposed for the complexes.*

Keywords: Acetophenone derivatives, Ni(II) chloride, Dithiocarbazate, Physicochemical elucidation.

INTRODUCTION

Transition metals form a wide variety of complexes [1] with various ligands having various preparative methods and various structures. Several transition and inner-transition metal complexes with bi, tri and tetradentate organic acids or Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems, as anti-carcinogenic, anti-tuberculosis, antibacterial, antifungal and antitumor [2-6] etc., and represent interesting models for metalloenzymes which are efficient to catalyze the reduction of dinitrogen and dioxygen [7]. The above uniqueness made the transition metal chemistry of immense interest to the scientists.

Complexes of some metal ions with dithiocarbazic acid and its acetophenone derivatives have been synthesized and elucidated by using different physical tools and octahedral structure was proposed for all the complexes [8].

In present investigation acetophenone derivatives of dithiocarbazic acid derived by the reaction of acetophenone and t-butyl dithiocarbazate in ethanolic solution have been made to react with nickel(II) chloride and nickel(II) nitrate and the structure of the co-ordination compounds was investigated.

MATERIALS AND METHODS

All chemicals like t-butyl dithiocarbazate, $C_2H_5COCH_3$, H_2N-NH_2 , CS_2 , $NiCl_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ were either of B.D.H or A.R grade and used as such without further purification. IR data was recorded as KBr pellets on Perkin-Elmer 200 spectrometer in the wave range 4000-200 cm^{-1} at C.D.R.I. Lucknow. The

IR-spectra of some of the products were also recorded as Nujol mull from 4000-500 cm^{-1} at Delhi University, Delhi.

Magnetic moment data for Ni(II) complexes were measured at room temperature on Guoy balance using mercury tetra thiocyanate cobaltate $Hg[Co(NCS)_4]$ as standard. Analysis of C, H, N and S was done by micro-analytical method. Nickel was analyzed complexometrically. The amount of nickel was calculated by multiplying the weight of the precipitate by a chemical factor 0.20314. The molar conductance was determined in DMF / nitrobenzene using 10^{-1}M solution of the complexes by conductivity meter-bridge. t-butyl dithiocarbazate was prepared by known method [9-10].

Preparation of Ligands: The ethanolic solution of acetophenone was mixed with the solution of t-butyl dithiocarbazate in the same solvent in 1:1 molar proportion. The mixture was refluxed over water-bath for about an hour. Upon cooling to room temperature the Schiff base (ligand) was separated out as yellow crystals which were filtered off and the crude product was recrystallized from little alcohol, again filtered and dried in open. The yield was almost quantitative having m. p. 137°C.

$$C_6H_5\text{-}CO\text{-}CH_3 + H_2N\text{-}NH\text{-}CSSC(CH_3)_3 \text{ -------> } C_6H_5\text{-}C(CH_3)= N\text{- }NH\text{-}CSS\text{-}C(CH_3)_3 + H_2O$$

Preparation of Metal Complexes: An ethanolic solution of the ligand (10mM) was refluxed with appropriately hyderated nickel(ii) chloride (5mM) and nickel(ii) nitrate in the same solvent for half an hour with constant stirring. On cooling the solution mixture at room temperature crystals of the complex separated out. Ni(II) complex was found to get precipitated as brown (khaki) solid mass even on dilution of the reaction mixture with water. The complexes are insoluble in water but soluble in DMF. DMF solution of the complex is non-electrolytic in nature. These are non-hygroscopic and quite stable to air. The m. p. of the complexes is more than Ca. 125^0C. Beyond Ca. 125^0C the complexes decompose probably due to the aerial oxidation of their hydrazine moiety. The color of the complexes vary from green to brown. The synthetic analytical details are collected in table 1.

Table 1. Color, magnetic moment (μ_{eff}), synthetic analytical data and molar conductance of the complexes of t-butyl dithiocarbazate and its acetophenone derivatives.

Complexes	**Color**	**μ_{eff} (B.M)**	**Analytical data- Found (Calcd.)**						**Molar Condct. Ohm^{-1} cm^2 m^{-1}**
			%C	**%H**	**%N**	**%S**	**%M**	**%Cl**	
$C_{14}H_{10}O_2$			79.95 (80.23)	4.58 (4.65)	--	--	--	--	
$[Ni(t\text{-}BudtC_z)_2]$	Brown	Diam	31.00 (31.25)	5.52 (5.66)	14.80 (14.61)	33.53 (33.37)	15.52 (15.23)		1.30
$[Ni(t\text{-}BudtC_zH)_2Cl_2]$	Greenish	3.00	26.58 (26.32)	5.28 (5.15)	12.62 (12.34)	28.20 (27.98)	13.05 (12.80)	-- (15.49)	18.72
$[Ni(t\text{-}BudtC_zH)_2(NO_3)_2]$	Greenish Brown	2.93	23.52 (23.45)	4.80 (4.66)	16.32 (16.40)	24.78 (25.00)	11.58 (11.47)		19.51

( ) = Calculated values and B.M = Bohr Magneton.

Table 2. IR-spectral bands of Ni(II) complexes of t-butyl dithiocarbazate with their assignments

Band Position I	II	III	**Assignments**
3255m	3295m	3285m	asy (NH_2) vibration
3085m	3165m	3190m	sy (NH_2) vibration
---	3000m	3000m	(N-H) vibration
2900s	2900s	2900s	Nujol
1635s	1630s	1635s	(NH_2) vibration
1470s	1470s	1470s (Nujol)	(C-N) t-butyl vibration

1382s	1382s	1382s (Nujol)	$(NO_2)$of nitrate, vibration
---	---	1285m	sy (NO_2) of nitrate, vibration
1240m	1250m	1230m	Ý(NH_2)
1195s	1200s	1190s	(N-C-S) vibration
1075s br	1080s br	1065s	assy (CSS^-) + (N-N)
960br	965m	975m	(N-N) + assy (CSS^-)
925br	835m	820br	$N\text{-}CSSSC(CH_3)_3$
760br	750m	770m	sy (CSS^-)
710m	715br	720m	$C(CH_3)_3$ vibration

I = $[Ni(t\text{-}BudtC_z)_2]$, II = $[Ni(t\text{-}BudtC_ZH)_2Cl_2]$, III = $[Ni(t\text{-}BudtC_ZH)_2(NO_3)_2]$
Spectra taken as nujol mull.

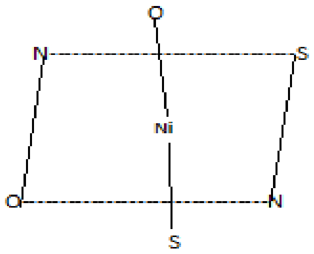
RESULTS AND DISCUSSION

Ni(II) yields 1 : 1 (M : L) complexes. The complexes are colored solids soluble in DMF and DMSO but insoluble in water. The complexes are non-hygroscopic and quite stable to air. The magnetic moment values of Ni(II) complexes indicate the paramagnetic [11] nature having $3d^84s^0$ electronic configuration. The elemental analysis of the complexes are in agreement with the values calculated for the molecular formula assigned to them. Their molecular conductance value in DMF (1.30–19.72 $ohm^{-1}cm^2$ $mole^{-1}$) indicate non-electrolytic nature of the complexes [12,13]

IR-Spectral Studies: IR-spectra give ample information to elucidate the way of bonding of the ligand to the metal ions. The main vibration frequencies of the ligands and their complexes are listed in Table-2 and Table-3. In case of ligand a very broad absorption band is observed in the 3µ region rendering the NH_2 and NH stretching vibration modes to be ill-defined. Regarding NH stretching vibration nujol mull is also not very informative. The free ligand shows three well-defined absorptions at 3300, 3110 and 2990 cm^{-1} assignable to NH_2 asymmetric, NH_2 symmetric and NH stretching vibrations respectively. Negative shift of $–NH_2$ group suggests that co-ordination is through nitrogen atom [14]. A band of medium intensity at 1520 cm^{-1} shows C-N stretching vibration mode. Spectra below 1500 cm^{-1} in the range of 1470-1495cm^{-1} shows C-N stretching Frequencies which is an evidence of NS bonded structure [15]. In NS bonded structure of t-butyl dithiocarbazate C-N stretching frequencies are expected below 1580 cm^{-1} which is indeed found to be so appearing as a strong band [16] at 1475 cm^{-1}. On the basis of above discussion the following tentative octahedral structure may be assigned for the complex.

Table 3. IR-spectral bands (cm^{-1}) of diagnostic values of the t-butyl dithiocarbazate and those of free ligand

Free Ligand Complexes	**asy (NH_2) sy (NH_2) and (N-H)**	**(C-N) or (C=N)**	**(C=S) or asy (CSS^-)**	**(N-N)**	**(M-N)**
$t\text{-}BudtC_ZH$	3300 sp 3110 br 2990 m	1520 m	995 vs	920 s	
$[Ni(t\text{-}BudtC_z)_2]$	3250 m 3080 m	1530 m	965 br 820 br	965 br	600 br
$[Ni(t\text{-}BudtC_zH)_2Cl_2]$	3290 m 3160 m 3000 m	1475 s	970 m 830 m	970m br	610 br or 580w
$[Ni(t\text{-}BudtC_ZH)_2(NO_3)_2$	3280 m 3190 w 3000 m	1475 s	980 m 820 br	980 br	610 br or 590 m



APPLICATIONS

These results are useful to elucidate the structures of the metal complexes and the complexes prepared with the new Schiff base could reasonably be used for the treatment of diseases like cancer, tuberculosis and diseases caused by bacteria.

CONCLUSIONS

In conclusion, the PPG has been employed as a novel, mild and highly efficient solvent system for the convenient preparation of benzimidazoles in excellent yields from o-phenyldiamine and a wide variety of aryl aldehydes using $ZnCl_2$ as catalyst. In addition low cost, recyclable solvent system and ready availability of catalyst, an environmentally benign procedure makes this methodology a useful contribution to the existing procedures available for the synthesis of benzimidazole derivatives.

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