

Synthesis and characterization of copper(II), nickel(II), cobalt(II), zinc(II) and cadmium(II) complexes of 5,6-diphenyl-3-(2'-hydroxyphenyl)-1, 2, 4-triazine

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A few complexes of the type $ML_2 \cdot nB$, [where $M = Cu(II)$, $Ni(II)$, $Co(II)$, $Zn(II)$, $Cd(II)$; $L = 5,6$ -diphenyl-3-(2'-hydroxyphenyl)-1, 2, 4-triazine (DPTH); $B = H_2O$; $n = 0, 2$] have been synthesized and characterized on the basis of elemental analysis, magnetic susceptibility, thermal studies and IR and electronic spectra. It is observed from the IR studies that the nitrogen in 2-position of DPTH is coordinated to the metal ion in all the cases.

Compounds containing 1, 2, 4-triazine moiety constitute a new class of biologically active compounds¹. The derivatives of 1, 2, 4-triazines are used as herbicides and anti-inflammatories². The industrial applications of 1, 2, 4-triazines and their derivatives are numerous^{3,4}. Studies on the coordinating ability of 1, 2, 4-triazine are much more limited and are known to coordinate through more than one nitrogen atom of the triazine group⁵. However, their coordinating ability with additional ligating groups has not been studied. In this note, we report the $Cu(II)$, $Ni(II)$, $Co(II)$, $Zn(II)$ and $Cd(II)$ complexes of 5, 6-diphenyl-3-(2'-hydroxyphenyl)-1, 2, 4-triazine(DPTH). The complexes have been characterized by elemental analysis, thermal analysis, magnetic moment and IR and electronic spectral measurements.

Experimental

Metals were estimated by incinerating the complexes with an excess of ammonium oxalate monohydrate. Elemental analysis were carried out at VHNSN College, Virudhunagar and the TG and DTG analysis were performed in nitrogen atmosphere on a Mettler TA3000 system with a scan rate of 10°min^{-1} . The magnetic susceptibility was measured in a Gouy balance at 8000G, calibrated against $Hg[Co(SCN)_4]$ at 302-304K. The electronic spectra were recorded in $CHCl_3$ using Shimadzu UV-160

double beam spectrophotometer. The IR spectra ($4000-200 \text{ cm}^{-1}$) were recorded in KBr disc on a Perkin-Elmer 577 grating spectrophotometer.

Synthesis of ligand

The ligand [5,6-diphenyl-3-(2'-hydroxyphenyl)-1,2,4-triazine] was synthesized as reported⁶ from salicylhydrazine, benzil and ammonium acetate in glacial acetic acid and recrystallized from DMF/EtOH (m.p. 174°C . Lit m.p. 174°C).

Synthesis of complexes

$M(DPT)_2 \cdot nH_2O$ [$n = 0$; $M = Cu(II)$, $Zn(II)$ and $Cd(II)$ and $n = 2$; $M = Ni(II)$ and $Co(II)$]

DPTH (2.5 mmol) was mixed with 120 ml of distilled ethanol and NaOH (8 ml, 0.025 M) in a beaker. It was heated over a water bath until the ligand dissolved and the colour changed from yellow to red orange. It was filtered to remove any suspended impurities and cooled to room temperature. To this was added metal(II) chloride/acetate (2 mmol) dissolved in 20 ml of water with constant stirring. The complex formed was filtered, washed with water, dilute ethanol and then dried *in vacuo*. [Yield: $Cu(DPT)_2$, 0.610g (55%); $Ni(DPT)_2(H_2O)_2$, 0.542g (47%); $Co(DPT)_2(H_2O)_2$, 0.621g (54%); $Zn(DPT)_2$, 0.563g (52%); $Cd(DPT)_2$, 0.558g (46%)].

Results and discussion

The characterization data of the complexes are presented in Table I. The ligand, DPTH is soluble in

Table I—Analytical data of the complexes

Complex (colour)	Found (Calcd.), %				$\mu_{\text{eff}}(\text{BM})$
	M	C	H	N	
$[Cu(DPT)_2]$ (Brown)	8.31 (8.9)	71.70 (70.82)	3.40 (3.96)	10.50 (11.78)	1.89
$[Ni(DPT)_2 \cdot 2(H_2O)]$ (Yellowish orange)	7.9 (8.58)	68.10 (67.85)	3.92 (4.06)	11.68 (11.30)	3.30
$[Co(DPT)_2 \cdot 2(H_2O)]$ (Brown)	8.8 (7.93)	68.93 (67.83)	3.98 (4.06)	11.85 (11.30)	5.05
$[Zn(DPT)_2]$ (Creamy white)	9.4 (9.16)	70.54 (70.64)	4.10 (3.95)	10.43 (11.76)	—
$[Cd(DPT)_2]$ (Creamy white)	14.1 (14.7)	65.70 (66.28)	3.94 (3.71)	10.80 (11.04)	—

ethanol, 1,4-dioxane, DMF and hot ethanol but insoluble in water. The complexes are freely soluble in chloroform, acetone, ethanol and DMF. The analytical data show that nickel(II) and cobalt(II) complexes have the composition $M(DPT)_2 \cdot 2H_2O$ while others have $M(DPT)_2$.

The copper complex of DPT has a magnetic moment of 1.89 B.M. typical of square-planar geometry⁷. Its electronic spectrum shows a broad band in the region 665-605 nm which is assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g}$ and 2E_g in a square-planar geometry with CuO_2N_2 chromophore⁸. The observed magnetic moment of nickel(II) complexes of DPT (3.3 B.M.) is indicative of an octahedral structure. The peaks in its electronic spectrum at 985, 495 and 350 nm may be assigned respectively to ${}^3A_{2g} \rightarrow {}^3T_{2g}(v_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(v_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (v_3) transitions characteristic of an octahedral geometry.

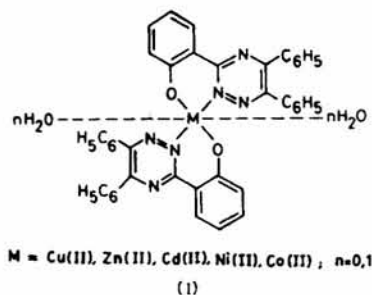
The magnetic moment of cobalt(II) complexes of DPT (5.05 B.M.) suggest that the cobalt(II) possesses an octahedral environment. Its electronic spectrum shows bands ~ 625 and 425 nm assigned respectively to ${}^4T_{1g} \rightarrow {}^4A_{2g}(v_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (v_3) for an octahedral splitting⁹.

The thermal studies of DPT metal(II) complexes shows stepwise decomposition depending upon the metal ion. Nickel(II) and cobalt(II) diaquo complexes undergo first stage decomposition to give anhydrous complexes. These anhydrous complexes and copper(II) complex undergo decomposition in the 300-500°C range by losing the phenoxide group first and subsequently to their oxides. Zinc(II) and cadmium(II) complexes undergo a single stage decomposition with a weight loss of 84.05 and 85.07% respectively in 200-400°C range. The results clearly indicate that the M-O bond breaks first since it is weaker than the M-N bond. The fact that the heterocyclic fraction decomposed after the fragmentation of phenoxide group indicates that the nitrogen of the heterocyclic ring is bonded to the central metal atom.

In the IR spectra of the ligand, a band at 3060 cm^{-1} is assigned to the hydrogen bonded $\nu(OH)$ of the ligand, the $\nu(C=N)$ and $\nu(N=N)$ bands occur at 1610 and 1580 cm^{-1} respectively^{10,11} whereas the phenolic $\nu(C-O)$ appears $\sim 1230\text{ cm}^{-1}$.

Upon coordination, the band due to $\nu(OH)$ disappeared and the $\nu(C-O)$ shifted to lower frequencies in all the complexes showing the complex formation through phenolic oxygen. Further, the change in the band position of $\nu(C=N)$ ($\Delta\nu = -25$

cm^{-1}) and $\nu(N=N)$ ($\Delta\nu = +5\text{ cm}^{-1}$) suggest the coordination of the heterocyclic ring through the nitrogen at 2-position. The bands due to $\nu(M-O)$ appears in the region $430-405\text{ cm}^{-1}$ and follows the expected order of stability¹² $Cd < Co < Ni < Cu > Zn$. The $\nu(M-N)$ appears in the range $590-585\text{ cm}^{-1}$ for all the metal complexes. The IR spectral data show that the nitrogen atom of 1, 2, 4-triazine group in the 2-position is coordinated to the metal ion along with phenolic oxygen. The magnetic and electronic spectra of copper(II) complex indicates that the copper(II) is in square-planar geometry. Nickel(II) and cobalt(II) possess octahedral geometry (Structure I). The cadmium(II) and zinc(II) can make use of their sp^3 hybridized orbitals for coordination to the ligand and hence tetrahedral structure may be assigned for these metal complexes.



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