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 ML₂.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 = H₂O; 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 compounds. The derivatives of 1, 2, 4-triazines are used as herbicides and anti-inflammatory agents. The industrial applications of 1, 2, 4-triazines and their derivatives are numerous. 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 group. 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 CHCl₃ using Shimadzu UV-160 double beam spectrophotometer. The IR spectra (4000-200 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 reported 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.nH₂O [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(H₂O)₂, 0.542g (47%); Co(DPT)₂(H₂O)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 1. The ligand, DPTH is soluble in

<table>
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<th>Table I—Analytical data of the complexes</th>
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<tr>
<td>Complex (colour)</td>
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<tr>
<td>Cu(DPT)₂</td>
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<tr>
<td>Ni(DPT)₂</td>
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<tr>
<td>Co(DPT)₂</td>
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<td>Zn(DPT)₂</td>
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<td>Cd(DPT)₂</td>
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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)$_2$.H$_2$O while others have M(DPT)$_2$.  

The copper complex of DPT has a magnetic moment of 1.89 B.M. typical of square-planar geometry. Its electronic spectrum shows a broad band in the region 665-605 nm which is assigned to $^2B_{1g} ightarrow ^2A_{1g}$, $^2B_{1g}$ and $^2E_g$ in a square-planar geometry with CuO$_2$N$_2$ chromophore. 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 to $^3A_{2g} ightarrow ^3T_{2g}$ ($v_1$), $^3A_{2g} ightarrow ^3T_{1g}$ ($v_2$), and $^3A_{2g} ightarrow ^3T_{1g}(P)$ ($v_3$) 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 $^4T_{1g} ightarrow ^4A_{2g}$ ($v_2$) and $^4T_{1g}(F) ightarrow ^4T_{1g}(P)$ ($v_3$) for an octahedral splitting.

The thermal studies of DPT metal(II) complexes show 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 loosing the phenoxide group first and subsequently to their oxides. Zinc(II) and cadmium(II) complexes undergo decomposition with a weight loss of 84.05 and 85.07% respectively in the 200-400°C range. The results clearly indicate that the M – N bond breaks first since it is weaker than the M – N bond. The fact that the heterocyclic fraction decomposed after the 300-500°C range by losing the phenoxide group suggests 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 v(OH) of the ligand, the v(C=N) and v(N= N) bands occur at 1610 and 1580 cm$^{-1}$ respectively whereas the phenolic v(C-O) appears ~ 1230 cm$^{-1}$. Upon coordination, the bands due to v(OH) disappeared and the v(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 v(C=N) ($\Delta v = -25$ cm$^{-1}$) and v(N= N) ($\Delta v = +5$ cm$^{-1}$) suggest the coordination of the heterocyclic ring through the nitrogen at 2-position. The bands due to v(M – O) appears in the region 430-405 cm$^{-1}$ and follows the expected order of stability Cd < Co < Ni < Cu > Zn. The v(M – N) appears in the range 590-585 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.

References