Complexes of chromium(III), cobalt(II), nickel(II), copper(II) & molybdenum(VI) with indane 1,3-dione-2-isonicotinoylhydrazone

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A new hydrazone derivative of indane 1,2,3-trione has been synthesized and characterized as indane 1,3-dione-2-isonicotinoylhydrazone (IIH). Complexes of IIH with chromium(III), cobalt(II), nickel(II), copper(II), palladium(II) and molybdenum(VI) have been prepared and characterized on the basis of elemental analysis, conductivity, magnetic, electronic and infrared spectral studies. IR spectral studies suggest that IIH acts as bidentate ligand in all complexes, the bonding sites being the enolic oxygen and azomethine nitrogen atoms.

Hydrazone derivatives containing additional donor sites such as $\equiv C=O$ and heterocyclic nitrogen have interesting ligational features. In continuation of our earlier studies on ninhydrin derivatives, we considered it worthwhile to prepare transition metal complexes of indane 1,3-dione-2-isonicotinoylhydrazone (IIH), a derivative of ninhydrin and a biologically active isonicotinic acid hydrazide.

In this note the results of the synthesis and structural characterization of chromium(III), cobalt(II), nickel(II), copper(II), palladium(II) and molybdenum(VI) complexes with the first hydrazone derivative of ninhydrin are described.

Synthesis of indane 1,3-dione-2-isonicotinoylhydrazone (IIH)

It was prepared by refluxing equimolar amounts of ninhydrin and isonicotinic acid hydrazide in 1:1 aqueous methanolic medium for 30 min. The yellow coloured precipitate was filtered off, washed with methanol and hot water and dried in vacuo; yield 72%; m.p. 209-210°C. Identity of IIH was confirmed by elemental analysis [Found: C, 63.40; H, 3.30 and N, 14.65%; calc. for $\text{C}_{13}\text{H}_{9}\text{N}_{3}\text{O}_{3}$: C, 64.52; H, 3.22, and N, 15.05%], infrared spectra [1705 ($\nu C=O$ of indane moiety); 1680 ($\nu C=O$ of amido group); 3340 and 3210 ($\nu NH$) and 1590 cm$^{-1}$ ($\nu C=N$ of azomethine group)], NMR spectra [pyridyl(4H), 8.20(d), 7.01(d), 6.18(d); indane (4H) 6.45(s) and amido NH, 5.65(s)] and mass spectra [78($\text{C}_{5}\text{H}_{5}\text{N}$) and 76($\text{C}_{6}\text{H}_{5}$)].

Synthesis of the complexes

Metal salt (2.5 mmol) dissolved in the minimum amount of water was added to a solution of indane 1,3-dione-2-isonicotinoylhydrazone (5 mmol) in 1:1 dimethylformamide (DMF)-methanol solvent medium. Then a few drops of 1 M sodium hydroxide in methanol were added and contents refluxed for 2 hr. On cooling, the product separated out; it was filtered in vacuo, washed with hot water, methanol and finally dried at 80°C for 2 hr. Yield and analytical data are given in Table 1.

The metal salts $\text{CrCl}_3\cdot6\text{H}_2\text{O}$; $\text{CoCl}_2\cdot6\text{H}_2\text{O}$; $\text{NiCl}_2\cdot6\text{H}_2\text{O}$; $\text{CuCl}_2\cdot2\text{H}_2\text{O}$; $\text{PdCl}_2$ and ($\text{NH}_4$)$\text{MoO}_4\cdot4\text{H}_2\text{O}$ used were of AR grade. All the chemicals used in this study were BDH reagents or reagents of equivalent quality.

Molar conductances of the complexes in DMF solutions ($\sim 10^{-3} M$) were measured with a Systronic 303, direct reading conductivity bridge. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) operating at field strength of 3 KG to 8 KG at room temperature. Electronic spectra were recorded on a Carl Zeiss DMR-21 recording spectrophotometer in solid state in the region 185-1200 nm. IR spectra were obtained in the range 4000 to 180 cm$^{-1}$ on a Perkin Elmer 983 G infrared spectrophotometer in KBr discs. $^1\text{H}$ NMR spectra were recorded in $d_6$-DMSO medium on Varian XL-300 spectrometer at room temperature.

Results and Discussion

Analytical data (Table 1) indicate the formation of 1:2 (M:IIH) complexes of molecular formula [M(IIH)$_2$(H$_2$O)$_2$]. All the complexes decompose in the 220-320°C temperature range. All complexes are insoluble in water and common organic solvents but soluble in DMF or DMSO and these are found to be nonelectrolytes in former solvent. Insufficient solubility of these complexes in suitable solvents precluded the determination of molecular weights.
Table 1—Colour, yield melting points, magnetic moment and analytical data of transition metal complexes of indane 1,3-dione-2-isonicotinoylhydrazone (IIH)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>m.p.,(°C)</th>
<th>μ_eff (BM)</th>
<th>Found (Calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(IIH)2CH2O]</td>
<td>Yellow</td>
<td>320</td>
<td>3.60</td>
<td>56.55 (54.43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(65)</td>
<td></td>
<td>2.80 (2.73)</td>
</tr>
<tr>
<td>[Co(IIH)2(H2O)3]</td>
<td>Brown</td>
<td>318</td>
<td>2.72</td>
<td>56.45 (55.30)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(70)</td>
<td></td>
<td>2.85 (3.07)</td>
</tr>
<tr>
<td>[Ni(IIH)2(H2O)3]</td>
<td>Deep-red</td>
<td>315</td>
<td>3.90</td>
<td>53.40 (55.32)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(72)</td>
<td></td>
<td>3.17 (3.07)</td>
</tr>
<tr>
<td>[Cu(IIH)2(H2O)3]</td>
<td>Brown</td>
<td>221</td>
<td>2.09</td>
<td>56.50 (54.91)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(73)</td>
<td></td>
<td>3.10 (3.05)</td>
</tr>
<tr>
<td>[Pd(IIH)2]</td>
<td>Parrot-green</td>
<td>235</td>
<td>Diamag.</td>
<td>59.17 (54.34)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(70)</td>
<td></td>
<td>2.33 (2.41)</td>
</tr>
<tr>
<td>[MoO2(IIH)2]</td>
<td>Grey</td>
<td>280</td>
<td>Diamag.</td>
<td>56.50 (52.63)</td>
</tr>
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Table 2—Electronic spectral data and ligand field parameters of [Ni(IIH)2(H2O)3] complex

<table>
<thead>
<tr>
<th>Spectral data</th>
<th>Observed</th>
<th>Calculated^14,15</th>
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<tbody>
<tr>
<td>ν1</td>
<td>8050</td>
<td></td>
</tr>
<tr>
<td>ν2</td>
<td>14285</td>
<td>13110</td>
</tr>
<tr>
<td>ν3</td>
<td>20830</td>
<td>22005</td>
</tr>
<tr>
<td>B_35</td>
<td>—</td>
<td>731</td>
</tr>
<tr>
<td>δν_0*</td>
<td>—</td>
<td>±1175</td>
</tr>
<tr>
<td>B_35**</td>
<td>—</td>
<td>0.705</td>
</tr>
<tr>
<td>10Dq</td>
<td>8050</td>
<td>8050</td>
</tr>
<tr>
<td>ν2/ν1</td>
<td>1.77</td>
<td>1.63</td>
</tr>
<tr>
<td>LFSE</td>
<td>—</td>
<td>23.0</td>
</tr>
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</table>

*Difference in the observed and calculated value of frequencies **Ratio of free ion and of complex.

The chromium(III) complex shows a magnetic moment value of 3.6 BM. Three bands are observed at 12195, 23250 and 35570 cm^{-1} in its electronic spectrum corresponding to $^4A_2g(F) → ^4T_2g(F)$; $^4A_2g(F) → ^4T_{1g}(F)$ and $^4A_2g(F) → ^4T_{1g}(P)$ transitions respectively in favour of octahedral geometry.

The magnetic moment of nickel(II) complex is found to be 3.9 BM in favour of octahedral geometry with $^3A_2g$ ground state. Bands at 10640(ν1), 16130(ν2) and 26315(ν3) are attributable to $^3A_2g(F) → ^3T_{2g}(F)$; $^3A_2g(F) → ^3T_{1g}(F)$ and $^3A_2g(F) → ^3T_{1g}(P)$ transitions respectively. The spectral data were used to compute ligand field parameters. The value of $B_{35}$ and 10Dq were used to calculate $ν_2$ and $ν_3$ and results are given in Table 2. The electronic spectral data together with reported magnetic moment values suggest an octahedral geometry for the present nickel(II) complex.

The magnetic moment value of copper(II) complex is found to be 2.09 BM, slightly higher than the magnetic moment value normally observed for copper(II) complexes. The magnetic moment of this complex indicates no metal-metal interaction. A strong band at 15380 cm^{-1} in the electronic spectrum of copper complex has been assigned to $^2E_g → ^2T_{2g}$ transition indicating the presence of copper in an octahedral field.

Palladium complex is found to be diamagnetic at room temperature. Three bands have been observed in the electronic spectrum at 16660, 24390 and 34480 cm^{-1}. The first low energy spin-allowed band has been assigned to $^1A_{1g} → ^1A_{2g}$ transition, similar to the assignment by Jorgensen for PdCl2^-. The bathochromic shift is expected because of the spectrochemical difference between the IIH and Cl^- . The second and third bands are spin allowed transitions which may be due to $^1A_{1g} → ^1B_{1g}$ and $^1A_{1g} → ^1E_{1g}$ transitions, respectively.

Molybdenum complex is found to be diamagnetic...
as expected for hexavalent molybdenum. The electronic spectrum of this complex exhibits a band at 410 nm (24390 cm\(^{-1}\)) with low molar extinction coefficient. As the optical density value is low and as there is no evidence for any \(d-d\) transitions over the visible range, this complex could be Mo(VI) species\(^{20}\), rather than Mo(V).

**Infrared spectral studies**

In the infrared spectrum of ligand (IIH) two \(\nu C=O\) frequencies are observed at 1705 and 1680 cm\(^{-1}\) attributable\(^{2,8,9,19,20}\) to C = O of indane and amido groups respectively present in the ligand. The appearance of latter band in the IR spectrum of ligand indicates that IIH remains in thione form at least in the solid state. In all complexes the former band is not shifted suggesting non-participation of indane oxygen in coordination. The amido-\(\nu C=O\) band disappears in the IR spectra of all complexes, and instead a new band due to \(\nu C=O\) is observed around 1095 cm\(^{-1}\) indicating enolization of IIH in the presence of metal ion and under the reaction conditions employed in the preparation of metal complexes. The enolization\(^{23}\) of ligand in the metal chelate is supported by the fact that the broad peaks at 3340 and 3210 cm\(^{-1}\) in ligand spectrum due to NH stretching disappear in all complexes.

A strong band observed in the IR spectrum of IIH at 1590 cm\(^{-1}\) due to azomethine group shifts (\(-10\) cm\(^{-1}\)) to lower frequency indicating the participation of azomethine nitrogen atom in complex formation\(^{24,25}\). A strong band at 1545 cm\(^{-1}\) in ligand spectrum is assigned to delocalized - C\(=\)N - present in isonicotinic ring of IIH. This band is not affected in spectra of all complexes indicating the non-participation of ring nitrogen atom in coordination.

A strong band at 925 cm\(^{-1}\) corresponds to trans dioxomolybdenum group present in Mo complex. In all complexes (except Pd and Mo), bands due to coordinated water molecules\(^{26-28}\), are observed in the regions 3215-3260, 1290, 880 and 760 cm\(^{-1}\) attributable to OH stretching, bending, rocking and wagging vibrations respectively. In chromium compound Cr - Cl vibration is also found at 310 cm\(^{-1}\).

The coordination of IIH through azomethine nitrogen and enolic oxygen is further corroborated by bands observed around 430 (\(\nu M=O\)) and 360 nm\(^{-1}\) (\(\nu M=N\)) in far IR spectra\(^{29}\) of all metal chelates.

ESR spectrum of copper complex shows two peaks at 2.33 and 2.09 corresponding to \(g_\perp\) and \(g_\parallel\) respectively.

On the basis of elemental analysis, conductivity, magnetic moment, electronic and infrared spectral studies, octahedral structure is assigned to chromium, cobalt, nickel and copper complexes while a square planar structure is suggested for the palladium complex.

**Acknowledgement**

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**References**