Diethylamino-oxyl derivatives of dialkytin(IV) have been synthesized and characterized on the basis of elemental analysis, molecular weight determination and IR data.

In continuation of our previous work on N,N-diethylhydroxylamine derivatives of titanium\(^1\), boron and aluminium\(^2\), the derivatives of dialkytin (IV) are reported in this note.

Dimethyl-, diethyl- and dibutyltin diisopropoxides and dibutyltin diethoxide, prepared by the standard method, react with diethylhydroxylamine to give products, \(R_2Sn(OR')_2+X[C_2H_5]_2NOH\) (Table 1). The reactions can be represented as follows:

\[
R_2Sn(OR')_2+x[C_2H_5]_2NOH \rightarrow \frac{R_2Sn(OR')_2+x[C_2H_5]_2NOH}{[ON(C_2H_5)_2]}+\frac{[ON(C_2H_5)_2]}{R'OH}
\]

\((R = \text{CH}_3, \text{C}_2\text{H}_5 \text{ and } \text{C}_4\text{H}_9; \ R' = \text{C}_2\text{H}_5 \text{ and } \text{C}_4\text{H}_9 \text{ and } x = 1 \text{ and } 2)\)

The general method of preparation of the compound is as follows: Dialkytin dialkoxides and diethylhydroxylamine were mixed in benzene in stoichiometric ratios and left overnight. Reaction mixtures were heated at a bath temperature of 80-90\(^\circ\)C for 4-8 hr. In reactions (1-3) the benzene was removed and the products distilled under reduced pressure. In other cases, insoluble products were separated by filtration and washed successively. Dialkytin derivatives (Table 1, Nos. 1-3) are liquids, miscible with organic solvents. These are volatile, can be distilled with slight decomposition under reduced pressure.

The molecular complexity of soluble diethylamino-oxyl derivatives of dibutylin(IV) was found to be about three as revealed by mol wt determination. Compounds derived from dimethyl- and diethyltin diisopropoxides are insoluble and can be considered to be polymeric.

IR spectra of the compounds exhibit \(v_{Sn-C}\) and \(v_{Sn-O}\) and \(v_{N-O}\) around 950 and 910 cm\(^{-1}\) respectively. The characteristic absorptions\(^4\) of isopropoxy group occur at 1140, 1055-1050 cm\(^{-1}\) and that of ethoxy group at 1180-1103 and 1010 cm\(^{-1}\). The bands in the regions 620-609 and 521-510 cm\(^{-1}\) have been assigned to \(v_{Sn-C}\) and \(v_{Sn-O}\) respectively.

References


Mn(II), Fe(II), Co(II), Ni(II) & Cu(II) Complexes with Benzoylhydrazine

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Benzoylhydrazine (BH) complexes of the types M(BH)\(_2\)SO\(_4\) \(_3\)H\(_2\)O where M = Ni(II), Co(II) or Fe(II); M'(BH)\(_2\)SO\(_4\) \(_2\)H\(_2\)O where M' = Cu(II) or Mn(II); M'(BH)\(_2\)Cl\(_2\) \(_3\)H\(_2\)O where M' = Ni(II), Co(II) or Mn(II) and Ni(BH)\(_2\)X where X = HgCl\(_2\), HgCl\(_2\)I\(_2\), HgI\(_2\), CdCl\(_2\) or CdI\(_2\) have been synthesized and characterized by analysis and physicochemical studies. The complexes are spin-free and octahedral where BH acts as a bidentate coordinating ligand. Molar extinction coefficient (\(3\)) and approximate oscillator strength (\(j\)) of the electronic bands have been calculated for complexes of the type M'(BH)\(_2\)Cl\(_2\). Sulphate group is bonded to metals directly or to BH by hydrogen bonding.

In continuation of our work\(^1\) on benzoylhydrazine (BH) complexes of Ti(IV) and some non-transition metal ions, the preparation and characteri-
zation of BH complexes with metal ions of first transition series are reported in this note.

Metal salts (EDH) of LR grade were used and benzoyl hydrazine (BH) was prepared as described by Curtius; m.p. 112° (lit. m.p. 111°). Metal complexes were synthesized by mixing ethanolic solutions of metal chlorides or aqueous solutions of metal sulphates and ethanolic solutions of BH in appropriate molar ratios. The metal chloride complexes were recrystallized from hot ethanol and the metal sulphate complexes, obtained as precipitates, were washed with dilute ethanol and dried in a desiccator.

For the syntheses of Ni(BH)\textsubscript{3}X complexes, Ni(BH)\textsubscript{3}Cl\textsubscript{2}·3H\textsubscript{2}O was dissolved in ethanol and an aqueous solution or ethanolic solution of K\textsubscript{2}HgCl\textsubscript{4}, K\textsubscript{2}HgCl\textsubscript{2}·12H\textsubscript{2}O, K\textsubscript{2}HgI\textsubscript{4}, K\textsubscript{2}CdCl\textsubscript{2}·12H\textsubscript{2}O or K\textsubscript{2}CdI\textsubscript{4} (prepared by mixing appropriate amounts of the salts) added to it. The precipitated complexes were washed with dilute ethanol and dried as mentioned above. Similar complexes were also prepared by reacting hot ethanolic solutions of Ni(BH)\textsubscript{3}Cl\textsubscript{2} and Hg(II) or Cd(II) salts in 1:1 molar ratio, cooling and crystallizing or precipitating the complexes with the addition of water.

Literature procedures\textsuperscript{4} were followed for gravimetric estimation of metals and anions. BH was estimated volumetrically using potassium iodate\textsuperscript{4} after acid hydrolysis. Estimation procedures were suitably modified to permit the estimation of BH in the presence of Fe(II), Cu(II) and I\textsuperscript{-} and the analysis of Ni(II) in the presence of Hg(II) and Cd(II).

Conductometric studies were carried out with Philips conductivity bridge (model 4494) using a dip type of cell. Spectrophotometric studies in solution and electronic spectra of some of the isolated products were carried out on a Perkin-Elmer spectrophotometer model 227. Nujol spectra of some insoluble complexes were recorded on Cary spectrophotometer model 14 and infrared (KBr) spectra on Perkin-Elmer grating spectrophotometer model 337. Faraday magnetic balance was used for the measurement of room temperature magnetic susceptibility.

It is evident from Table 1 that ionic complexes decompose above 240° without melting. Those having greater covalency due to either change in metal character or anion character melt with decomposition or melt below 200°.

The complexes, in general, are insoluble in organic solvents like benzene, chloroform, carbon tetrachloride, ether, nitrobenzene, etc. The metal sulphate complexes are insoluble in ethanol. Metal sulphate

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Melting/ decomposition point (°C)</th>
<th>Analysis (%)</th>
<th>Magnetic moment (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(BH)\textsubscript{3}Cl\textsubscript{2}·3H\textsubscript{2}O</td>
<td>Yellow brown</td>
<td>71</td>
<td>9-5 (9-3)</td>
<td>69-3 6-1</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{3}Cl\textsubscript{2}·3H\textsubscript{2}O</td>
<td>Light red</td>
<td>149</td>
<td>10-6 (9-9)</td>
<td>68-8 5-2</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{3}Cl\textsubscript{3}H\textsubscript{2}O</td>
<td>Blue</td>
<td>&gt;240</td>
<td>10-0 (9-9)</td>
<td>69-3 3-2</td>
</tr>
<tr>
<td>Mn(BH)\textsubscript{2}SO\textsubscript{4}·2H\textsubscript{2}O</td>
<td>Shining pale white</td>
<td>&gt;240</td>
<td>12-2 (11-9)</td>
<td>59-8 7-2</td>
</tr>
<tr>
<td>Fe(BH)\textsubscript{3}SO\textsubscript{4}·3H\textsubscript{2}O</td>
<td>Yellow</td>
<td>Not clear</td>
<td>9-5 (9-1)</td>
<td>66-9 5-9</td>
</tr>
<tr>
<td>Co(BH)\textsubscript{3}SO\textsubscript{4}·3H\textsubscript{2}O</td>
<td>Light red</td>
<td>&gt;240</td>
<td>9-7 (9-5)</td>
<td>65-7 5-3</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{3}SO\textsubscript{4}·3H\textsubscript{2}O</td>
<td>Light blue</td>
<td>&gt;240</td>
<td>9-4 (9-5)</td>
<td>65-8 3-2</td>
</tr>
<tr>
<td>Cu(BH)\textsubscript{3}SO\textsubscript{4}·2H\textsubscript{2}O</td>
<td>Blue</td>
<td>&gt;240</td>
<td>13-3 (13-5)</td>
<td>57-9 2-2</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{3}HgCl\textsubscript{4}</td>
<td>Light blue</td>
<td>&gt;240</td>
<td>7-0 (7-2)</td>
<td>49-4 3-2</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{3}HgCl\textsubscript{4}·H\textsubscript{2}O</td>
<td>do</td>
<td>193</td>
<td>5-8 (5-9)</td>
<td>40-7 3-1</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{2}HgI\textsubscript{4}</td>
<td>Light green</td>
<td>135</td>
<td>4-7 (4-9)</td>
<td>34-7 3-2</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{2}CdCl\textsubscript{4}·H\textsubscript{2}O</td>
<td>Light blue</td>
<td>200</td>
<td>6-4 (6-6)</td>
<td>44-8 3-2</td>
</tr>
<tr>
<td>Ni(BH)\textsubscript{2}CdI\textsubscript{4}</td>
<td>Light green</td>
<td>165</td>
<td>5-3 (5-5)</td>
<td>37-9 3-1</td>
</tr>
</tbody>
</table>

*Figures in parentheses are calculated values.
†% nickel in Ni(BH)\textsubscript{3}X complexes.
complexes, namely Cu(II) and Mn(II) complexes are insoluble, Ni(II) complex is slightly soluble while Co(II) and Fe(II) complexes dissolve freely in water. Metal chloride complexes, however, dissolve both in water and ethanol. Ni(BH)₃CdI₄ and Ni(BH)₃HgI₄ dissolve in ethanol but are insoluble in water. The other Ni(BH)₃X complexes are practically insoluble in the above solvents.

The conductometric titration curves of metal sulphates against BH show a sharp inflexion at 1:2 molar ratio in the case of Cu(II), a broad bulge at 1:3 molar ratio for Ni(II) and a slight inflexion at about 1:3 molar ratios for Co(II) and Fe(II). A similar titration of nickel chloride hexahydrate and BH in aqueous medium yields only a linear curve. In ethanol medium, however, inflexions at 1:1, 1:2 and 1:3 molar ratios show stepwise exchange of two water molecules by one BH molecule.

Visible spectra of the above ethanolic solutions show blue shift of $\lambda_{\text{max}}$ with increasing concentration of BH. For example, metal-ligand in 1:1 ratio shows $\lambda_{\text{max}}$ at 390 and 644 nm, in 1:2 ratio $\lambda_{\text{max}}$ shift to 320 and 606 nm respectively while in 1:3 ratio the absorption maxima undergo a further blue shift, appearing at 356 and 586 nm respectively. The solutions of ratios higher than 1:3 do not show any shift. From these observations and 1:3 composition of the Ni(II) complex, it can be safely inferred that the Ni(II) complex has a coordination number 6 with the ligand acting as a bidentate ligand.

Visible spectrum of Cu(II)-BH complex shows one broad band centred at 718 nm (13930 cm⁻¹) due to transition $^2T_{2g} \rightarrow ^2E_g$. Ni(II)-BH complex shows two bands at 586 and 354 nm due to transitions $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ in the region 750-350 nm. These two bands are comparable to those observed for octahedral complexes of Ni(II) with H₂O, NH₃ and C₆H₁₂(NH₂)₂ as ligands. The low values of $\epsilon_{\text{max}}$ (Table 2) for these bands also indicate octahedral stereochemistry, since the tetrahedral Ni(II) complexes show bands having high $\epsilon_{\text{max}}$ values. However, a solution spectrum of the Ni(II)-BH complex, obtained on Hitachi Perkin Elmer model 139, shows all the three expected bands due to transitions $^3A_{2g} \rightarrow ^3T_{2g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ at 870, 600 and 355 nm respectively for octahedral Ni(II). Visible spectra of Ni(BH)₃X complexes in nujol show bands around 600 nm confirming the presence of octahedral Ni(BH)₃⁺ complex cation in all of them. Co(II)-BH complex shows a band around 500 nm due to the transition $^4T_{1g} \rightarrow ^4T_{2g}(P)$ expected for octahedral Co(II) complexes. Oscillator strength values for some of the complexes are also given in Table 2.

Infrared spectra of BH and its metal complexes have been studied and BH has been reported to coordinate through $>\text{C}=\text{O}$ and NH₂ groups. The magnitude of shift in $>\text{C}=\text{O}$ stretching frequency has been related to the order of stability of the metal complexes of amides and ureas. The shift in $\nu\text{C}=\text{O}$ in BH complexes of Ni(II), Co(III) and Mn(II) can similarly be used to determine the stability order of $\text{Me-O}=\text{C}<}$ bond. The observed shifts in $\nu\text{C}=\text{O}$ of M"(BH)₃Cl₂ complexes (Table 2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\epsilon_{\text{max}}$ (litre mol⁻¹ cm⁻¹)</th>
<th>Oscillator strength (f)</th>
<th>$\nu\text{C}=\text{O}$ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(BH)₃Cl₂,3H₂O</td>
<td>228</td>
<td>420</td>
<td>4.42</td>
<td>1.97×10⁴</td>
</tr>
<tr>
<td>Co(BH)₃Cl₂,3H₂O</td>
<td>232</td>
<td>252</td>
<td>26550</td>
<td>23300</td>
</tr>
<tr>
<td>Ni(BH)₃Cl₂,3H₂O</td>
<td>232</td>
<td>255</td>
<td>28780</td>
<td>23840</td>
</tr>
<tr>
<td>Ni(BH)₃Cl₂,3H₂O</td>
<td>232</td>
<td>255</td>
<td>28780</td>
<td>23840</td>
</tr>
</tbody>
</table>

* $\nu\text{C}=\text{O}$ of BH = 1665 cm⁻¹.

\[ C_6H_5 \overset{\text{M=Ni(II), Co(II), Fe(II) and Mn(II)}}{\longrightarrow} \text{S} \overset{\text{X}=2\text{Cl}, \text{SO}_4^{2-}, \text{HgCl}_2^{2-}, \text{HgCl}_2^{2-}}{\longrightarrow} \text{HgI}_2^{2-}, \text{CdCl}_2^{2-} \text{or CdI}_2^{2-} \]
suggest the following stability order of M\(<\)O\(=\)C\(<\) bond: Ni(II)-BH\(>\)Co(II)-BH\(>\)Mn(II)-BH.

Sulphate group may be ionic, coordinated or bridged in metal complexes\(^{31}\). The absence of a band around 1220 cm\(^{-1}\) indicates the presence of a bridging sulphate group\(^{15,13}\). Moreover, sulphate group has a marked tendency to remain in unionized form in aqueous solution.\(^{14}\) This type of bonding of the sulphate group results in the appearance of a band around 1220 cm\(^{-1}\). The absence of this particular band in Mn(BH)\(_2\)SO\(_4\)·2H\(_2\)O shows bridging character of sulphate group. The presence of 1230 cm\(^{-1}\) band in Fe(II), Co(II) and Ni(II) complexes may be due to attachment of sulphate group to the ligand by hydrogen bonding. The appearance of 1230 cm\(^{-1}\) band in Cu(II) complex may be due to bonding of sulphate group to metal ion.

Water molecules are present in the lattice structures of all the complexes, because, neither there is any change in colour of the complexes on dehydration nor peak-by-peak comparison of the infrared spectra of aquated and dehydrated complexes shows any change in colour of the complexes on dehydration.\(^{11}\) Magnetic measurements show that all the complexes are spin-free and the magnetic moments fall to show magnetic moments very close to the spin-free planar Cu(II) complexes show magnetic moments of all the complexes, because, neither there is any disappearance of peaks assigned to coordinated water molecules.\(^{16}\)

Magnetic measurements show that all the complexes are spin-free and the magnetic moments fall to show magnetic moments very close to the spin-free planar Cu(II) complexes. The high magnetic moment of Mn(II) or by ion pairing involving hydrogen bonding with amine.\(^{14}\) The magnetic moment of Cu(BH)\(_2\)SO\(_4\)·2H\(_2\)O is high, because the square planar Cu(II) complexes show magnetic moments around 1·8 BM (ref. 18). The observed magnetic moment of Mn(BH)\(_2\)SO\(_4\)·2H\(_2\)O is high, because both tetrahedral and octahedral structures are expected to show magnetic moments very close to the spin-only values (5·92 BM).\(^{19}\) Recently, Frazer et al.\(^{20}\) have explained the high value of magnetic moment (3·0 BM) of Cu(II) complexes as due to the presence of some ferromagnetic impurities arising out of dimeric nature of the complexes. The high magnetic moment of Mn(II) complex, in the present case, can similarly be explained. Infrared and magnetic data discussed above indicates a dimeric nature for Mn(BH)\(_2\)SO\(_4\)·2H\(_2\)O. The following structures (I, II and III) are, therefore, proposed for the BH complexes.

Thanks are due to the authorities of Chemistry Department, Lucknow University, for laboratory facilities and CRDI, Lucknow for IR and electronic spectra.

References


Stabilities of Chelates of 2-Phenylacetohydroxamic Acid with Cu(II), Ni(II), Zn(II), Co(II), Mn(II) & Cd(II)

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Thermodynamic stability constants of the 2-phenylacetohydroxamic acid chelates with bivalent transition metals, Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\) and Cd\(^{2+}\), have been determined in aqueous medium adopting Irving and Rossotti pH-titration technique at 25°C ± 0·1°C and \(\mu = 0·1 M\) (NaClO\(_4\)). The stability constants are observed to follow the order Cu\(^{2+}\) > Ni\(^{2+}\) > Zn\(^{2+}\) > Co\(^{2+}\) > Cd\(^{2+}\) > Mn\(^{2+}\), in agreement with the Irving-William order.

HYDROXAMIC acids have been widely used\(^3\) as analytical reagents for a variety of metal ions. Though benzohydroxamic acid (BHA), N-phenylbenzohydroxamic acid, etc., chelates have been studied, both in solution and solid state, not much work has been reported on 2-phenylacetohydroxamic acid (PAHA) complexes. Thermodynamic stability constants of PAHA chelates with Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\) and Cd\(^{2+}\), in aqueous medium have now been determined adopting Irving and Rossotti\(^4\) pH-titration technique at 25°C ± 0·1°C and \(\mu = 0·1 M\).

The ligand was prepared by following one of the general procedures adopted for the preparation of hydroxamic acids\(^6\) recrystallized from dilute acetic acid and repeatedly washed with petroleum ether. Metal perchlorates were prepared and estimated by standard methods\(^6\). Experiments were carried out using a Leeds and Northrup pH meter fitted with glass and calomel electrodes. Following solutions (total vol. 100 ml) were titrated against carbonate-free 0·1M NaOH. (1) 0·005M perchloric acid + 0·1M sodium perchlorate; (2) 0·005M perchloric acid + 0·001M PAHA + 0·1M sodium perchlorate; and (3) 0·005M perchloric acid + 0·001M PAHA + 0·001M metal perchlorate + 0·1M sodium perchlorate. PAHA was taken ten times in excess to avoid the possible hydrolysis

NOTES