CADMIUM(II) COMPLEXES WITH DICYANDIAMIDE

Although complexation behaviour of cyanamide with transitional metal ions have been studied thoroughly, little work has been reported regarding the complexing ability of dicyandiamide with transitional and nontransitional metal ions. The present communication describes the preparation of Cd(II) complexes with monodentate dicyandiamide ligand.

Experimental

Methanolic solution of cadmium salts were mixed separately with dicyandiamide in methanol and refluxed for two hours. On cooling, white to yellowish white compounds separated out which were filtered off, washed with methanol, followed by ether and dried in vacuo.

Metal ion, nitrogen and halogen in the complexes were estimated by standard procedure. Conductance was measured in M/1000 acetone solution using a "Toshniwal" conductivity bridge. IR spectra were recorded in KBr phase using Unicam SP-200 spectrophotometer. The relevant analytical, conductance, and IR spectral data are recorded in Table I.

Results and Discussions

All the seven complexes have the composition [CdL2X2] and [CdL4] Y2, where L = dicyandiamide, X = Cl-, Br-, I-, SCN-, NO3-, Ac- and Y = ClO4-.

The compounds melt with decomposition and have low molar conductance values ($\Lambda_m$ being in the range of 5 to 12 mhos cm$^{-2}$) except the perchlorate complex indicating nonelectrolytic nature. $\Lambda_m$ for perchlorate complex is 145-6 mhos cm$^{-2}$ indicating it to be 1:2 electrolyte.

Infrared spectra of the complexes are quite informative. Thiocyanate complexes have two sharp bands $\sim$2080 and $\sim$820 cm$^{-1}$ attributable to $\nu$(C=S) and $\nu$(C=S) stretching modes of N-bonded terminal thiocyanate groups. In the present case an increase of 30-40 cm$^{-1}$ relative to free thiocyanate ion is indicative of N-bonded terminal thiocyanate group on the basis of earlier observation. In the nitrate complexes $\nu_4$ and $\nu_1$ bands (NO$_2$ asymmetric and symmetric stretch) appear in $\sim$1400 and 1270 cm$^{-1}$ region respectively. The position of $\nu_4$ and $\nu_1$ and their separation ($\Delta \nu$) of 130 cm$^{-1}$ suggest$^1$ the nitrate group to be monodentate. In the case of perchlorate complex a broad hump appears in 1150-1140 cm$^{-1}$ region indicative of an ionic perchlorate group which is in conformity with the conductance data. The asymmetric and symmetric stretching frequencies of acetate group in sodium acetate appear$^2$ at 1758 and 1414 cm$^{-1}$ respectively. These two bands move to slightly lower frequency region in cadmium acetate and shift to higher frequency in the complex.
TABLE I
Analyses, conductance and infrared spectral data (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Cd Found</th>
<th>% Cd Reqd.</th>
<th>% N Found</th>
<th>% N Reqd.</th>
<th>% Halogen Found</th>
<th>% Halogen Reqd.</th>
<th>(\Lambda_m) mhos cm(^{-2})</th>
<th>(\nu(C≡N)) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>.</td>
<td>.</td>
<td>66.22</td>
<td>66.61</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>2200</td>
</tr>
<tr>
<td>[CdL(_2)C(_2)]</td>
<td>31.58</td>
<td>31.98</td>
<td>31.58</td>
<td>31.86</td>
<td>19.63</td>
<td>20.17</td>
<td>12.0</td>
<td>2180</td>
</tr>
<tr>
<td>[CdL(_2)Br(_2)]</td>
<td>25.21</td>
<td>25.52</td>
<td>21.24</td>
<td>25.43</td>
<td>35.88</td>
<td>36.29</td>
<td>8.5</td>
<td>2185</td>
</tr>
<tr>
<td>[CdL(_2)]</td>
<td>20.82</td>
<td>21.03</td>
<td>20.64</td>
<td>20.96</td>
<td>47.28</td>
<td>47.50</td>
<td>7.0</td>
<td>2180</td>
</tr>
<tr>
<td>[CdL(_2)(SCN)(_2)]</td>
<td>28.05</td>
<td>28.34</td>
<td>34.95</td>
<td>35.30</td>
<td>.</td>
<td>.</td>
<td>10.4</td>
<td>2180</td>
</tr>
<tr>
<td>[CdL(_2)(NO(_2))(_2)]</td>
<td>27.36</td>
<td>27.78</td>
<td>34.38</td>
<td>34.60</td>
<td>.</td>
<td>.</td>
<td>5.0</td>
<td>2185</td>
</tr>
<tr>
<td>[CdL(_2)(Ac)(_2)]</td>
<td>27.83</td>
<td>28.20</td>
<td>27.83</td>
<td>28.10</td>
<td>.</td>
<td>.</td>
<td>8.5</td>
<td>2180</td>
</tr>
<tr>
<td>[CdL(_4)] (ClO(_4))(_2)]</td>
<td>17.07</td>
<td>17.35</td>
<td>34.28</td>
<td>34.59</td>
<td>.</td>
<td>.</td>
<td>145.6</td>
<td>2180</td>
</tr>
</tbody>
</table>

L = Dicyandiamide.

Dicyandiamide contains primary, secondary and tertiary nitrogen atoms as possible bonding sites to metal ions. The bond observed at 2200 cm\(^{-1}\) in the ligand is attributable to \(\nu(C≡N)\) vibration. In the complexes, this band has been shifted to lower frequency region \(\sim 2180\) cm\(^{-1}\), which indirectly supports the bonding of tertiary N-atom of C≡N group to the cadmium ion. The appearance of a strong band at 3200 cm\(^{-1}\) assignable to \(\nu(NH)\) vibration both in ligand and complexes suggests the non-coordination of \(-NH\) group and hence dicyandiamide acts as a monodentate ligand.

From analysis, conductance and IR spectral studies, the compounds are presumably tetrahedral environment around the metal ion.

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SURFACE HETEROGENEITY AND ELOVICH EQUATION

Gradient changes observed in the treatment of adsorption kinetic data through Elovich equation\(^{1-3}\)

\[
\frac{dq}{dt} = ae^{-a^2}
\]

where \(q\) is the amount adsorbed in ml NTP at time \(t\) have been the subject of critical examination in recent times and it is concluded that the breaks observed in Elovich plots are due to inherent nature of the mathematical form of the equation\(^4\) and not due to changes in adsorption mechanism at the point at which the change in gradient occurs. The purpose of this communication, therefore, to analyse the same kinetic data through both Elovich equation and by a procedure\(^5\) which can directly give the values of activation energy for adsorption and desorption simultaneously and to assess how far the gradient changes are due to changes in adsorption mechanism.

Hydrogen chemisorption kinetic data used for such an analysis have been obtained on a ZnO-MeO\(_3\) catalyst (the surface of this catalyst has been shown to be heterogeneous through temperature jump chemisorption of hydrogen\(^6\)) in a conventional volumetric adsorption apparatus by recording the volume uptake a, a function of time at various temperatures in the range 300 to 360°C.

The procedure used for the evaluation of the values of rate constants for adsorption and desorption processes is based upon the simple theory that the adsorption rate at any fixed value of coverage (\(\theta\)) is given by

\[
\left[ \frac{dq}{dt} \right]_\theta = k_a f(1 - \theta) p - k_d f(\theta)
\]

where \(k_a\) and \(k_d\) are adsorption and desorption rate constants. A plot of \(dq/dt\) at any fixed coverage will