Synthesis and characterization of nickel(II) and copper(II) complexes of cyclo(1,2)-dibiguanidinyl dibenzil and their adducts

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The syntheses of nickel(II) and copper(II) complexes with cyclo(1,2)-dibiguanidinyl dibenzil (H$_2$Mc, C$_{32}$H$_{26}$N$_{16}$) and of their adducts with pyridine and $\gamma$-picoline are described. H$_2$Mc forms a tetradentate dianion in the complexes. The adducts show changes in magnetic property with practically no change in spectra showing metalloporphyrin character.

The complexation reactions with transition and non-transition metal ions with biguanide and its different derivatives are well known. Being an amidine derivative, biguanide also gives Schiff base with metal ions which forms metal complexes, but in spite of having two amidine groups at its two ends, it is so far reported to form Schiff base linkage at one end only. A number of Schiff base containing macrocyclic metal chelates have been prepared by template synthesis. The present study has been undertaken to synthesise macrocyclic metal chelates where two biguanide units each with Schiff base linkages at its two ends are present. The preparation starts with guanidine in place of biguanide, as amine fragment that condenses with benzil to form an intermediate Schiff base and two such Schiff base molecules under the template action of a metal ion are made to cyclise together to generate biguanide bearing macrocyclic metal chelates. This synthesis reports the first macrocyclic compound that contains two biguanide moieties with Schiff base linkage at both ends of each of them.

**Experimental**

Guanidine hydrochloride (2 g, 0.02 mol) and sodium hydroxide (0.8 g, 0.02 mol) were refluxed in dry ethanol for some time. Sodium chloride which precipitated out was filtered off. To the boiling filtrate, benzil (2.1 g, 0.01 mol) was added in small portions over a period of ~ 1 hr. The mixture was refluxed for half an hour and cooled when a white solid (m.p. 299°C) crystallised out. It was filtered, washed with ethanol and dried. It was characterised as (1,2) diguanidinyl benzil (DGB) as shown by Eq. (1).

$$2\text{H}_2\text{NC}(-\text{NH})\text{NH}_2 + \text{O} = \text{C}(-\text{C}_6\text{H}_5)\text{C}(-\text{C}_6\text{H}_5)\text{=}\text{O} \rightarrow [\text{H}_2\text{NC}(-\text{NH})\text{N} = \text{C}(-\text{C}_6\text{H}_5)]_- + 2\text{H}_2\text{O} \ldots (1)$$

DGB and copper/nickel chloride in 2:1 mole ratio were refluxed in acetonitrile for a short period when the suspension became almost clear. It was filtered hot, mixed with a little ethanolic solution of guanidine and again refluxed for several hours. The macrocyclic biguanide complex of the metal was gradually formed with usual colour of the metal biguanide and simultaneous evolution of ammonia which was detected at the mouth of the condenser (Scheme 1). The copper complex was reddish violet whereas the nickel complex was orange to orange red. The complex was filtered, washed with acetonitrile and dried over fused CaCl$_2$. The macrocyclic biguanide being present as a dianion in the metal complex was abbreviated as H$_2$Mc.

Attempts to isolate the macrocycle from the metal complex by treatment with aqueous solution of KCN failed. However, the complex, on digestion with dil H$_2$SO$_4$ gave a white solid which on further treatment with aqueous solution of NaOH gave free H$_2$Mc as a very light creamish white solid (m.p. 314°C).

Pyridine and $\gamma$ picoline adducts of the macrocyclic biguanide complex of copper(II)/nickel(II) were prepared by refluxing each complex with the heterocyclic bases. The adduct was filtered, washed with ethanol containing a little pyridine/picoline followed by CCl$_4$ and dried over fused CaCl$_2$.

The analytical data of the ligands, metal complexes and their adducts are listed in Table 1. The observed nitrogens in the macrocycle and its complexes are generally lower than their expected values which might be due to partial deamination during refluxing. A Philips conductivity bridge, model GM 424 with a bottle type cell was used for conductance measurement in DMSO. The magnetic moment was measured using a PAR Vibrating...
Table 1—Characterisation data of nickel(II) and copper(II) chelates with 1,2-dibiguanidinyl dibenzil (H<sub>2</sub>Mc) and their adducts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (Calc.), %</th>
<th>µ&lt;sub&gt;eff&lt;/sub&gt; (B.M.)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>M</td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>DGB</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;Mc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(Mc)</td>
<td>8.96</td>
<td>62.25</td>
<td>20.23</td>
</tr>
<tr>
<td>Cu(Mc)</td>
<td>10.45</td>
<td>61.78</td>
<td>20.12</td>
</tr>
<tr>
<td>Ni(Mc)(py)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.55</td>
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<td></td>
</tr>
<tr>
<td>Ni(Mc)(y-pic)&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>Cu(Mc)(py)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>8.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(Mc)(y-pic)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>8.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DGB = C<sub>16</sub>H<sub>16</sub>N<sub>6</sub>; H<sub>2</sub>Mc = C<sub>32</sub>H<sub>56</sub>N<sub>10</sub>

Sample Magnetometer (VSM) model 155. The IR spectra were recorded in KBr/CsBr with a Beckan IR 20A spectrophotometer and the electronic spectra (reflectance) were recorded using Hitachi U-3210 spectrophotometer. The TGA and DTA of the adducts were carried out using a Shimadzu Thermal Analyser, DT 30. The metals were estimated by usual methods, elemental analysis by CHN Analyser and pyridine/picoline by TGA.

Results and discussion

The metal complexes are soluble in DMSO but insoluble in common solvents. Their conductances in DMSO at room temperature are in the range 2-26.5 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating them to be non-electrolytes.

The important IR bands (in cm<sup>-1</sup>) of DGB, H<sub>2</sub>Mc and metal complexes of H<sub>2</sub>Mc are as indicated. DGB: νC=N 1700, 1650; νN-H 3348, 3270; δ NH<sub>2</sub> 1580, 1530, 1490. H<sub>2</sub>Mc: νC=N 1680, 1638; νN-H 3315, 3240; δ NH<sub>2</sub> 1580, 1530, 1475. Ni(Mc): νC=N 1680, 1605; νN-H 3250; δ NH<sub>2</sub> 1570, 1540, 1480. Cu(Mc): νC=N 1690, 1595; νN-H 3240; δ NH<sub>2</sub> 1580, 1530, 1485. In all cases, there were two νC=N bands of which the higher frequency band is due to >C=NH group and the lower frequency band due to >C=N-C group. In the metal complexes, νC=N band due to >C=N-C group only shows appreciable lowering from that of H<sub>2</sub>Mc indicating their involvement in complexation. The νN-H and δ NH<sub>2</sub> bands in both H<sub>2</sub>Mc and its complexes virtually remain unchanged. It is very significant to note that both the νC=N band in H<sub>2</sub>Mc are appreciably lowered from their positions in DGB. The determination of molecular weight of H<sub>2</sub>Mc by Rast method gives a value 520 (550). If there had been no cyclisation of two DGB molecules, the observed molecular weight would be in the range of 292. This proves H<sub>2</sub>Mc to be a macrocycle.

The Ni(II) complex is diamagnetic and shows one broad absorption band ~ 473.6 nm. This indicates that the complex has a square planar geometry enforced by the macrocycle whose biguanide moiety is known to be planar. The Cu(II) complex of H<sub>2</sub>Mc is paramagnetic with µ<sub>eff</sub> = 1.78 B.M. and shows one absorption band ~ 535 nm again indicating a square planar geometry. Since macrocyclic complexes of both nickel and copper are free from anions, it is implied that the macrocycle is present as dianion in the complexes and it is formed by deprotonation from either the side chain - NH<sub>2</sub> or - NH - in the macrocycle ring with the negative charges being delocalised over the ring.

The TGA of each adduct shows loss of two molecules of pyridine/picoline at two different temperatures, the first molecule leaving ~ 100°-150°C and the second molecule ~ 250°-300°C. The adducts are very interesting from the point of view of their spectral and magnetic properties. The diamagnetic Ni(Mc), on additional ligation to Ni(Mc)L<sub>2</sub> (where L = pyridine/picoline) becomes paramagnetic with µ<sub>eff</sub> = 3.1 B.M. but its spectra practically remain unchanged from that of Ni(Mc) except that the band position is slightly shifted to a higher wavelength. This is somewhat contrary to
expectation because additional ligation will result in the formation of an octahedral geometry that is likely to show three or at least two absorption bands\textsuperscript{9}. The adducts of Cu(Mc) also behave identically. It may be pointed out that metalloporpyrins\textsuperscript{11} show analogous properties which are said to be due to its highly conjugated ring system which becomes more effective if electron attracting phenyl groups are present in the ring.

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References