Synthesis and structural characterization of a novel homo-binuclear complex [Cu(dinemac)(H₂O)₂][Cu(dipic)₂].3H₂O: Assembly of discrete cationic and anionic components in a 1D chain through H bonding

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This work describes the synthesis and structural characterization of a novel homo-binuclear copper(II) complex [Cu(dinemac)(H₂O)₂][Cu(dipic)₂].3H₂O (1), in which the macrocyclic cationic modules are assembled with the anionic components through H bonding. The X-ray structural analysis indicates that the central atoms Cu(1) and Cu(2) of the two independent cations lie on crystallographic centers of symmetry, and that the independent anion with its central atom Cu' is placed in a general position. The asymmetric unit of 1 consists of two halves of [Cu(dinemac)(H₂O)₂]⁺⁺ cations, a [Cu(dipic)]⁻ anion and three water molecules. The room temperature solid state EPR spectrum of the polycrystalline sample is typical for a non-distorted or exchange averaged mononuclear Cu(II) complex with gₑ = 2.14±0.005 and ΔHₑ = 9.5 mT.

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Crystal engineering of networks with desired functions and fascinating topological architectures has become an area of increasing interest in recent years. In this context, for the design and assembly of inorganic-organic hybrid materials exhibiting supramolecular structures, a macrocyclic complex can often be nicely employed as a discrete strategic module together with organic components. Such discrete modules are linked to larger networks through coordinate bonds, covalent bonds or other intermolecular secondary bonding interactions such as hydrogen bonding, π-π stacking, etc.

Hybrid solids containing Cu(II) macrocyclic complexes are a most unexplored class of molecular materials owing to their great reluctance to bind organic molecules from axial sites, due to the Jahn-Teller effect. Our main objective is, therefore, to attempt to synthesize such novel hybrids, which are often difficult to obtain in a conventional way.

Pyridine-2,6-dicarboxylic acid (dipic) is a versatile organic ligand which exhibits not only various coordination modes but also shows interesting biological activities. Furthermore, Cu(II) complexes with dipic ligand are not well explored and consequently we have paid our attention to dipic reactivity, especially in the Cu(II) macrocyclic environment. It is interesting to note that when dipic-bis(triethylammonium) salt (generated in situ) was added to [Cu(dinemac)](ClO₄)₂ in methanol-acetonitrile(1:2), mixture extracts some Cu(II) ions to form [Cu(dipic)]²⁻ ion leading to the formation of [Cu(dinemac)(H₂O)₂][Cu(dipic)].3H₂O, though it is expected that [Cu(dinemac)](ClO₄)₂ would be more stable than the corresponding dipic complex owing to the macrocyclic effect.

We report here the synthesis and structural characterization of a novel homo-binuclear copper(II) complex [Cu(dinemac)(H₂O)₂][Cu(dipic)₂].3H₂O (1), in which the macrocyclic cationic modules are assembled with the anionic components through H bonding.

Experimental

Materials such as aqueous formaldehyde (Merck, India, 36% copper(II) carbonate (Loba Chemie, India), nitroethane (Aldrich), pyridine-2,6-dicarboxylic acid (dipic) (Lancaster), perchloric acid (E-Merck, India) and hydrochloric acid (E-Merck, India) were of reagent grade and used as received. Ethylenediamine (E-Merck, India) and triethylamine (Ranbaxy, India) were distilled by refluxing over Na metal for about an hour before use. Cu(ClO₄)₂ was prepared from CuCO₃ by adding small amount of it with stirring in 50% HClO₄ till there were no effervescence of CO₂ and there was a slight excess of CuCO₃ in the solution. The solution was then filtered.
to remove unreacted CuCO₃ and concentrated over water bath which upon cooling gives CuClO₄₂6H₂O. [Cu(en)₂][ClO₄]₂ was prepared by addition of ethylenediamine to a methanolic solution of copper perchlorate, followed by cooling.⁸

Since perchlorate salts are potentially explosive, only small amounts of the materials should be handled with care.

Synthesis of 3,10-dimethyl-3,10-dinitro-1,4,8,11-tetraazacyclotetradecane copper(II) perchlorate, [Cu(dinemac)](ClO₄)₂ was carried out following the optimized method reported already.⁸

\[
\text{[Cu(dinemac)](H₂O)₂} \rightarrow \text{[Cu(dipic)]₂} \rightarrow \text{[H₂O]₂} \quad (1)
\]

Taking 0.40 mmol (0.205 g) of recrystallised [Cu(dinemac)](ClO₄)₂ in a 30 mL methanol-acetonitrile (1:2 v/v) mixture, 0.20 mmol (0.030 g) of dipic, dissolved in minimum volume of water using 0.20 mmol (0.020 g) of triethylamine was added drop-wise with constant stirring while the purple colour of the original solution changed to deep blue. After 30 min, the resulting deep blue solution was filtered. The filtrate was kept under ambient conditions. After a few days, suitable shining deep blue single crystals of 1 (highly insoluble in water and other organic solvents) were obtained from the filtrate and washed first with mother liquor, followed by diethyl ether and dried in air at room temperature. Yield 32% based on [Cu(dinemac)](ClO₄)₂. Anal. Calc'd. for C₂₆H₂₄Cu₂N₂O₁₁: C, 36.07; H, 4.85; N, 12.95; found: C, 36.76; H, 4.78; N; 13.04 %.

Physical measurements – Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyser. An infrared spectrum (400-4000 cm⁻¹) was recorded from KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. EPR spectra of polycrystalline samples were recorded using a Bruker EMX-220 digital X-band (ν=9.4 GHz) spectrometer. Processing and initial simulation of EPR spectra were carried out using Bruker's WIN-EPR and SimFonia software. Diamagnetic corrections were made using Pascal's constants.

Crystal structure determination of the complex – Intensity data of 1 were collected at 293(2) K on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ=0.71073Å) and the ω scan mode in the range 2.9520-54.5°. The intensities were corrected for Lorentz-polarization factors and semi-empirically for absorption using ψ scans. The minimum and maximum transmission factors were 0.135 and 0.108. The structure was solved by direct methods and all non-hydrogen atoms refined anisotropically by full matrix least-squares on \( R^2 \) with a riding model for hydrogen atoms, using SHELXL-97. Additional information concerning the data collection and refinement of the structure is compiled in Table 1.

Results and discussion
As we mentioned earlier, our intention was to synthesize hybrid materials using dipic as a guest ligand in the macrocyclic building block, but we observed an unusual dipic reactivity towards [Cu(dinemac)]⁺ precursor.

Description of the structure of [Cu(dinemac)-(H₂O)₂] [Cu(dipic)]₂H₂O (1)—The X-ray structural analysis indicates that the central atoms Cu(1) and Cu(2) of the two independent cations lie on crystallographic centers of symmetry and that of the independent anion with its central atom Cu' in a general position. This means that there is effectively one unit [(cation][anion)] in the asymmetric unit and \( Z=2 \) for the triclinic space group \( P\overline{1} \). Thus, the asymmetric unit of 1 consists of two halves of [Cu(dinemac)(H₂O)₂]⁺ cations, a [Cu(dipic)]₂⁻ anion and three water molecules. The important bond distances and angles are summarized in Table 2.

The coordination geometry about the copper atom of the cationic part of the complex is best described as

### Table 1 — Crystallographic data for 1

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{Cu₃H₄CuN}<em>2\text{O}</em>{17} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>865.76</td>
</tr>
<tr>
<td>( T (K) )</td>
<td>293 (2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( P\overline{1} )</td>
</tr>
<tr>
<td>( a (Å) )</td>
<td>9.482 (2)</td>
</tr>
<tr>
<td>( b (Å) )</td>
<td>13.877 (3)</td>
</tr>
<tr>
<td>( c (Å) )</td>
<td>13.947 (3)</td>
</tr>
<tr>
<td>( \alpha (°) )</td>
<td>88.52 (3)</td>
</tr>
<tr>
<td>( \beta (°) )</td>
<td>84.02 (3)</td>
</tr>
<tr>
<td>( \gamma (°) )</td>
<td>73.68 (3)</td>
</tr>
<tr>
<td>( V (Å³) )</td>
<td>1751.7 (6)</td>
</tr>
<tr>
<td>( Z )</td>
<td>2</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.64 × 0.59 × 0.27</td>
</tr>
<tr>
<td>20 Range (°)</td>
<td>2.94 – 45.0°</td>
</tr>
<tr>
<td>Refinements collected</td>
<td>4887</td>
</tr>
<tr>
<td>Independent reflecions</td>
<td>4555</td>
</tr>
<tr>
<td>( R ) indices (all data)</td>
<td>( R_1 = 0.114, wR_2 = 0.174 )</td>
</tr>
<tr>
<td>Final ( R ) indices</td>
<td>( R_1 = 0.065, wR_2 = 0.148 )</td>
</tr>
<tr>
<td>Goodness-of-fit on ( R^2 )</td>
<td>1.027</td>
</tr>
</tbody>
</table>
Table 2 — Selected bond distances (Å) and bond angles (°) for I⁺

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(11)</td>
<td>Cu(2)-N(3)</td>
</tr>
<tr>
<td>Cu(1)-N(12)</td>
<td>2.018(6)</td>
</tr>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.403(6)</td>
</tr>
<tr>
<td>Cu(2)-N(22)</td>
<td>2.045(6)</td>
</tr>
<tr>
<td>Cu(2)-N(21)</td>
<td>2.362(7)</td>
</tr>
<tr>
<td>Cu(2)-O(2)</td>
<td>2.362(7)</td>
</tr>
</tbody>
</table>

Symmetry transformation used to generate equivalent atoms: 
#1 = x+1, y-1, z-1; #2 = -x+1, y, z.

The anionic part of the complex [Cu(dipic)]²⁻ ion also exhibits a distorted octahedral geometry with four oxygen atoms comprising the basal plane whereas the axial sites are occupied by the two pyridine nitrogens of two dipic ligands. Such a bisdianionic binding mode was previously observed for [dipic]²⁻ in Fe(II) complex, but here for the first time for a Cu(II) complex. The Cu-O distances range from 2.172(5) to 2.233(6) Å, whereas the copper-nitrogen distances are almost identical with values of 1.935(7) and 1.928(6) Å. The difference in lengths for the individual Cu'-O' as well as the Cu'-N' bonds for the two identical ligands indicates that the Cu'(II) ion is not in a perfect centrosymmetric environment. The distortion of the coordination octahedron is due to deviation of the O(2')-Cu'-O(4') and O(1')-Cu'-O(3') axes from orthogonality. The deviation of Cu'(II) atom from equatorial plane is only ~0.018 Å.

Each axially occupied water molecule of the cationic moiety is involved in intermolecular hydrogen bonding with a neighboring carboxylato oxygen atom of the dipic ligand of the anionic segment, resulting a 1D chain (Fig. 1). The O1...O2' and O1...O72' distances are 2.761 and 2.675 Å respectively with O...H...O bond angles of 153.3 and 170.9°. The hydrogen-bonded 1D structure is unique in the way in which two giant discrete cationic and anionic segments, apparently incapable of achieving juxtaposition under normal circumstances, are assembled in a linear fashion.

Infrared spectroscopy—The IR spectrum shows a broad peak in the range 3520-3320 cm⁻¹, indicating...
the presence of water in the lattice. Two peaks at 1640(br) and 1370(s) cm\(^{-1}\) are assignable to \(v_{as}(C=O)\) and \(v_{s}(C=O)\) vibrations, respectively. The large separation between \(v_{as}(C=O)\) and \(v_{s}(C=O)\) suggests that each \(-COO^\cdot\) group of dipic ligand coordinates to the metal center in a monodentate fashion\(^{30}\). All the other peaks appeared more or less at their usual positions.

**EPR Study** — The room temperature solid state EPR spectrum of the polycrystalline sample of I is typical for a non-distorted or exchange averaged mononuclear Cu(II) complex. The EPR line is almost symmetrical, quasi-Gaussian with \(g_{av} = 2.146 \pm 0.005\) and \(\Delta H_{pp}=9.5\) mT. Since no “forbidden” half field (\(\Delta M=2\)) signals have been observed, it may be concluded that anti-ferromagnetically exchange coupled dinuclear species are not present at room temperature.

**Supplementary material**

Crystallographic data for the compound have been deposited with the Cambridge Crystallographic Data Centre (CCDC 239955). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk)

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**References**