Some New Bimetallic Tetrakis-dithiocarbamates

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Some new bimetallic tetrakis-dithiocarbamates of the type MM'(Et₂dtc)₄ [for M = Co(II), Cu(II), M' = Zn(II); for M = Co(II), Ni(II), Cu(II), M' = Hg(II); and for M = Pb(II), M' = Cd(II); Et₂dtc = dithylyldithiocarbamate] and Ag₂Cd(Et₂dtc)₄ have been prepared and characterised by analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral measurements.

In continuation of our earlier study on bimetallic tetrakis-dithiocarbamates we report herein the preparation and characterization of some bimetallic tetrakis-dithiocarbamates, MM'(Et₂dtc)₄ and Ag₂Cd(Et₂dtc)₄.

All the chemicals used were of BDH or equivalent grade. Sodium salt of diethyldithiocarbamate (NaEt₂dtc·3H₂O) was prepared as described earlier.

The starting complexes, Na₂[M'(Et₂dtc)₄], where M' = Zn(II), Cd(II) or Hg(II) were prepared in situ by the gradual addition of M'(NO₃)₂ solution in acetone-water mixture (80:20, v/v) to a solution of Na₂Et₂dtc in the above metal ions:.

The complexes thus precipitated were filtered immediately to avoid the formation of M(dtc)₂ and washed with the above solvent mixture and water and dried in vacuo.

The molar conductances, magnetic susceptibilities, electronic and IR spectra were measured as described in our previous paper.

The analytical data (Table 1) indicate that the complexes of the type, MM'(Et₂dtc)₄ and Ag₂Cd(Et₂dtc)₄ are formed, where M = Co(II), Ni(II), Cu(II) or Pb(II), M' = Zn(II), Cd(II) or Hg(II). All the complexes decompose in the temperature range of 135-199°C, are insoluble in water and common organic solvents (methanol, ethanol, benzene) but slightly soluble in CHCl₃, THF, DMF, DMSO and pyridine. The very low molar conductance values (0.18-0.64 Ω⁻¹ cm² mole⁻¹) in nitrobenzene are indicative of non-electrolytic nature of these complexes.

The magnetic moments of copper(II) complexes (1.71 and 2.0 BM) correspond to one unpaired electron. While the diamagnetism of nickel(II) complex and the magnetic moments of Co(II) complexes (2.41 and 2.83 BM) indicate square planar geometry around the above metal ions.

The diffuse reflectance spectrum of CoZn(Et₂dtc)₄ in nujol may be assigned to 2A₁g→2E₂g assuming square planar geometry around cobalt(II). The bands observed at 16340 and 19050 cm⁻¹ in the spectrum of NiHg(Et₂dtc)₄ in nujol may be attributed to the transition 2A₁g→2B₁g, 2A₁g→2A₂g and 2A₁g→2B₂g transitions respectively on the basis of square planar geometry around nickel(II).

Table 1—Analytical Data of the Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (Calc.) (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>M⁺</td>
<td>M⁺</td>
</tr>
<tr>
<td>CoZn(Et₂dtc)₄</td>
<td>Green</td>
<td>8.01</td>
</tr>
<tr>
<td>CoHg(Et₂dtc)₄</td>
<td>Green</td>
<td>7.02</td>
</tr>
<tr>
<td>NiHg(Et₂dtc)₄</td>
<td>Yellowish</td>
<td>7.05</td>
</tr>
<tr>
<td>CuZn(Et₂dtc)₄</td>
<td>Black</td>
<td>9.32</td>
</tr>
<tr>
<td>CuHg(Et₂dtc)₄</td>
<td>Black</td>
<td>7.01</td>
</tr>
<tr>
<td>Ag₂Cd(Et₂dtc)₄</td>
<td>White</td>
<td>23.92</td>
</tr>
<tr>
<td>PbCd(Et₂dtc)₄</td>
<td>White</td>
<td>22.56</td>
</tr>
</tbody>
</table>


The electronic spectra of cobalt(II) complexes in THF, DMF, DMSO and pyridine and those of nickel(II) and copper(II) in THF, DMF and DMSO are almost similar to those obtained in nujol indicating that square planar geometry around the above metal ions also persists in solutions. However, the spectrum of NiHg(Et₂dtc)₄ in pyridine exhibits three d-d
transition bands at 10260, 15750 and 21000 cm\(^{-1}\) assignable to \(^3A_{2g} \rightarrow ^3T_{2g}(F), ^3T_{1g}(F)\) and \(^3T_{1g}(P)\) transitions respectively in an octahedral geometry. The various ligand field parameters \(10D_q(10260 \text{ cm}^{-1}), B'(398 \text{ cm}^{-1}), \beta(0.38), \beta'(62.32 \%), \text{LFSE} (146.59 \text{ kJ mole}^{-1})\) and \(v_2/v_1\) ratio also support the octahedral geometry around nickel(II)\(^8\) in the above bimetallic complex. The spectra of copper(II) complexes in pyridine exhibit a broad band at 14045 cm\(^{-1}\) which is attributable to \(^2E_g \rightarrow ^2T_{2g}\) transition in distorted octahedral geometry around copper(II)\(^9\).

These observations reveal that the square planar geometry around Ni(II) and Cu(II) in the above bimetallic complexes changes to octahedral in pyridine by axial addition of two pyridine molecules\(^10\). However, all attempts to isolate bis-pyridine adduct failed. The reaction of pyridine with NiHg(Et\(_2\)dtc)\(_4\) yields Ni(Et\(_2\)dtc)\(_2\) and Hg(Et\(_2\)dtc)py. It is worthwhile to mention\(^10,11\) that nickel(II) dialkyl/diaryl-dithiocarbamates also do not yield any isolable addition compounds with Lewis bases\(^10,11\) and this inability of Ni(R\(_2\)dtc)\(_2\) to form adduct has been attributed to the donation of electrons from sulphur atom to non-bonding molecular orbital (\(^4P_z\)) of the metal, thereby decreasing its availability for axial interaction with bases. Probably for similar reason dialkyl/diaryl-dithiocarbamates of cobalt(II) and copper(II) and bimetallic tetrakis(dithiocarbamates) do not give addition compounds with Lewis bases.

The appearance of \(v(C=\bar{N})\) (thioueide band) band\(^12-14\) in the region 1410-1430 cm\(^{-1}\) midway between the reported values for \(v(C-\bar{N}) (1250-1350 \text{ cm}^{-1})\) and \(v(C=\bar{N}) (1640-1690 \text{ cm}^{-1})\), and a single band\(^15-17\) due to \(v(C=S)\) at 975-985 cm\(^{-1}\) in the IR spectra of bimetallic tetrakis(dithiocarbamates) indicate uninegative bidentate nature of dithiocarbamate anion in these complexes. The non-ligand bands occurring at 350 and 380-420 cm\(^{-1}\) are tentatively assigned to \(v(M-S)\) and \(v(M'-S)\) modes respectively. Based on analytical data and physicochemical studies on bimetallic tetrakis(dithiocarbamato complexes are proposed to have polymeric structures.

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References
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