Synthesis and characterization of transition metal complexes of bishomodihydro-tetraaza(14)annulene

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Bishomodihydrotetraaza(14)annulene [H₂(TAZM), IV], reacts with metal(II) acetates under inert and nonaquous conditions to afford the complexes [M(TAZM)]₂ (VI, M = Ni, Co, Cu). Treatment of the Co(II) complex with ammonia in the presence of air, results in the formation of an octahedral Co(II) complex which has been isolated as a tetraphenylborate salt [Co(TAZM)(NH₃)₂][BPh₄]. Elemental analyses, IR, UV and mass spectrometry have been used to assign the structures of the complexes.

Synthesis of complexes containing tetradeinate ligands, especially the macrocyclic ones, has evoked much interest due to their unique properties and their relation to biologically important systems. The preparations of these complexes fall, generally, into three main categories: first, synthesis involving complexation reactions; second, in situ or template effect synthesis, and third; synthesis involving modification of the macrocyclic ligand and/or the metal ion. The complexes reported here, which are derivatives of the tetraaza(14)-annulenes, were prepared by the first method. The aim of this work is to explore the potentials of (IV) in accommodating transition metal ions in its 14-membered ring cavity.

Experimental
All metal salts used were of AR grade and all organic solvents used were purified and dried according to literature methods. Electronic spectra were recorded on a Perkin-Elmer 330 spectrophotometer. IR spectra were obtained on a Perkin-Elmer 1420 ratio-recording infrared spectrophotometer. Metals were estimated by atomic absorption on a Perkin-Elmer 1100 atomic absorption spectrophotometer. An accurately weighed sample (about 20 mg) of each complex was taken into a small volumetric flask and dissolved with about 3 ml of conc. nitric acid in the case of nickel and copper complexes or with 3 ml of conc. sulfuric acid followed by 1 ml of 35% hydrogen peroxide in the case of the cobalt complexes. The flask was then filled to the mark with doubly distilled water. Atomic absorption measurements were then made. Mass and NMR spectra were measured on high resolution instruments at the University of Wurzburg. C, H and N analysis were performed at the Microanalytical Laboratory of the University of Wurzburg, West Germany.

Dihydrobromide salt of cis-cyclopropanediamine(I) and malondialdehyde dianil perchlorate(II). These were prepared according to literature procedures.

Bishomodihydrotetraaza(14)annulene (2HClO₄). (III).

The synthesis described for this compound was modified and scaled-up as follows: Malondialdehyde dianil perchlorate (II) (29.1 g, 90 mmol) and sodium acetate (15 g, 180 mmol) were placed in a R.B. flask (6 L) containing 4.5 L of 95% alcohol. The mixture was stirred till it became clear. Dihydrobromide salt of cis-cyclopropanediamine (I) (21.1 g, 90 mmol) was then added. Stirring in the dark at room temperature was continued for 4 days. The volume of the reaction mixture was reduced in vacuo to about 200 ml and then cooled at 0°C overnight when the first crop of the product was obtained. Similarly, a second crop was obtained. The combined products were recrystallized from 100 ml of boiling water (6 g of charcoal was added). The boiling filtrate was saturated with about 40 g of sodium perchlorate and upon cooling white needles of the title compound separated. These were filtered off, washed with a little ice-cold water and dried in vacuo, in the dark and in vacuo. M. p. 149-151°C, yield 3.5 g (85%).

Bishomodihydrotetraaza(14)annulene (2HClO₄), (IV):

Bishomodihydrotetraaza(14)annulene(2HClO₄), (III), (8 g, 19 mmol), 25 ml of dry methanol, and sodium methoxide (70 ml, 3 M) were stirred under nitrogen atmosphere for 15 min during which period the temperature was raised gradually to 70°C. Cooling the reaction mixture at 0°C overnight afforded pale yellow crystals. These were recrystallized from a minimum volume of dry methanol. The compound was stored in the dark and in vacuo. M. p. 149-151°C, yield 3.5 g, (85%).

Preparation of complexes of (IV): (VI, M = Ni, Co, Cu)

The appropriate hydrated metal(II) acetate (0.5 mmol) and ligand(IV) (108 mg, 0.5 mmol) were placed in a schlenk tube. Under argon atmosphere, 2 ml of
good quality dimethylformamide was added via syringe and the reaction mixture was then stirred at about 80°C for one hour. The reaction mixture was then cooled and 40 drops of degassed water were added via a syringe over a period of 5 h. The precipitated product was filtered off (under argon), dried and stored in vacuo.

Preparation of [Co(TAZM) (NH₃)₃][BPh₄]

During the preparation of the Co(II) complex described previously, after stirring for 1 h at 80°C, the reaction mixture was cooled to room temperature, exposed to air, and 3 drops of conc. ammonia solution were added. Stirring was then continued for another 3 h and 2 ml of saturated solution of sodium tetraphenylborate was added dropwise. The purple product thus obtained was filtered off, washed with ice-cold water (3 ml) and recrystallized from 50% methanol. M.p. 165-166°C, yield 429 mg (70%).

Results and discussion

The addition of a base (proton scavenger) to ligand (IV) is expected to facilitate the entry of a divalent metal ion into the cavity of the dianion (V) leading to the formation of a macrocyclic complex system (VI) (Scheme 1). This has been the strategy for the synthesis of complexes of (IV). Thus, attempts to introduce a divalent metal ion into the cavity of (IV) were based on the addition of a base such as potassium hydride, n-butyllithium or 1,8-diazabicyclo(5, 4, 0)undec-7-ene to a solution of (IV) to generate, in situ, the dianion (V) followed by the addition of the metal salt solution. In these attempts, bis(benzonitrile)palladium chloride⁸, palladium(II) chloride, palladium(II) acetate, platinum(II) chloride and Zeise's salt⁸ were used, and in addition, the reaction was carried out in various organic solvents such as benzene, methanol, ethanol, acetonitrile, THF and DMF. Inspite of numerous changes in the reaction conditions and working under extremely anhydrous and inert atmosphere, decomposition products were always obtained. This indicated that the dianion (V) might not be stable enough in the presence of metal ions such as Pd(II) and Pt(II) and probably decomposed prior to or during coordination. One probable reason for this decomposition is that Pd(II) and Pt(II) prefer square planar geometry¹⁰ and the four nitrogens in the ligand (IV) may not be planar. Alternatively, and what is more likely, ligand(IV) encompasses two malondialdehyde moieties and these are unstable particularly in the presence of platinum and palladium ions which may catalyze the decomposition. This was evidenced by the production of black powders in many of the attempted synthetic trials. Positions 3 and 5 in ligand (IV) are protected in the case of Holm macrocycle (VII)¹¹ and literature reports show that palladium and platinum complexes of ligand (VII) are accessible⁸,¹²,¹³.

When solutions of Ni(II), Co(II) and Cu(II) salts (not the acetates) were reacted with (V)¹⁴ under an inert atmosphere and at different temperatures, impure products were obtained probably due to instability of (V). To alleviate this problem, the preparation was repeated using pure metal acetates, ligand and good quality dimethylformamide in a small Schlenk tube under argon atmosphere. Pure crystalline products of (VI) (M = Ni, Co, Cu) were produced.

The nickel(II) complex was deep green in color and was soluble in most common organic solvents. Its mass spectra showed the molecular ion peaks at m/z = 272 (100%) as expected from its molecular formula. The ¹H-NMR spectral data for this complex were identical to those reported for the same complex prepared differently⁷. The IR spectrum of the complex showed the characteristic spectral pattern present in the spectrum of the ligand⁶ (in the region 700-1650 cm⁻¹) with minor shifts in the positions of the peaks. This together with the data presented in Tables 1 and 2 indicate structure (VI), (M = Ni) for the complex.

The cobalt(II) and copper(II) complexes were also soluble in most common organic solvents and their mass spectra showed the molecular ion peaks at m/z = 272 (100%) and 277 (100%), respectively as expected from their molecular formulae. The IR spectra for these complexes were similar to that of the nickel complex. These data indicate structure (VI), (M = Co, Cu) for the complexes (Tables 1 and 2). High resolution mass spectra of the three complexes showed their monomeric nature in the vapor phase, and in each case the most intense spectral peaks were those of the molecular ions. The observed and calculated
Table 1—Characterization data for the ligand and complexes

<table>
<thead>
<tr>
<th>Compd</th>
<th>Color</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
<th>Calc. (Found) (%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Ligand(IV)</td>
<td>pale-yellow</td>
<td>149-151</td>
<td>85</td>
<td></td>
<td>66.64</td>
<td>7.46</td>
<td>25.90</td>
<td></td>
</tr>
<tr>
<td>VI, M = Ni</td>
<td>deep-green</td>
<td>176-178</td>
<td>80</td>
<td></td>
<td>52.72</td>
<td>5.17</td>
<td>20.52</td>
<td>21.51</td>
</tr>
<tr>
<td>VI, M = Co</td>
<td>deep-red</td>
<td>154-155</td>
<td>88</td>
<td></td>
<td>52.75</td>
<td>5.16</td>
<td>20.51</td>
<td>21.57</td>
</tr>
<tr>
<td>VI, M = Cu</td>
<td>red-violet</td>
<td>195-196</td>
<td>86</td>
<td></td>
<td>51.88</td>
<td>5.08</td>
<td>20.17</td>
<td>22.87</td>
</tr>
<tr>
<td>[VI(NH₃)₂[BPh₄]M = Co</td>
<td>purple</td>
<td>165-166</td>
<td>70</td>
<td></td>
<td>69.02</td>
<td>6.44</td>
<td>13.41</td>
<td>9.41</td>
</tr>
</tbody>
</table>

a Sealed tube, uncorrected
b Based on that of (III) which is 47% on the basis of (I)

Table 2—Exact masses and electronic spectral data for the complexes

<table>
<thead>
<tr>
<th>Compd</th>
<th>Exact massa</th>
<th>λmax, cm⁻¹ (e)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI, M = Ni</td>
<td>272.05718</td>
<td>17483(243), 22989(sh, 5246), 24096</td>
</tr>
<tr>
<td></td>
<td>(272.05856)</td>
<td>(5829), 33113(14767), 38168(9715).</td>
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<tr>
<td>VI, M = Co</td>
<td>273.05502</td>
<td>20833(3624), 24096(5766), 24390</td>
</tr>
<tr>
<td></td>
<td>(273.05469)</td>
<td>(sh, 5772), 30769(sh, 9396), 31746</td>
</tr>
<tr>
<td>VI, M = Cu</td>
<td>277.05143</td>
<td>18183(1418), 27855(9705), 30120</td>
</tr>
<tr>
<td></td>
<td>(277.05111)</td>
<td>(sh, 10067), 34843(11007), 37736 (11141).</td>
</tr>
<tr>
<td>[VI(NH₃)₂[BPh₄]M = Co</td>
<td>17331(sh, 3213), 18868(4116), 20000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(9739), 29674(sh, 8434), 32787(7932).</td>
<td></td>
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</table>

a Exact masses were determined by high resolution mass spectrometry, uncorrected. b acetonitrile solution, dDMF solution.

molecular masses in the molecular ion regions were found to be in satisfactory agreement (Table 2). The electronic spectral data for the complexes (Table 2) were comparable to those of their analogs of the structurally similar ligand (VII). Addition of concentrated ammonia solution to a stirred (in the air) solution of the cobalt(II) complex produced, in the presence of ammonium tetraphenylborate solution, a compound which is believed to be an octahedral cobalt(III) complex of ligand(IV). Although, the mass and ¹H-NMR spectra of this complex could not be recorded due to volatility and solubility problems, the formulation [Co(TAZM)(NH₃)₂][BPh₄] for this complex seems to be realistic. This formulation is supported by elemental analyses (Table 1), electronic spectral data (Table 2) and the diamagnetic nature of the complex. In addition, the complex is a 1:1 electrolyte in DMF and its IR spectrum shows the characteristic envelope of peaks (700-1600 cm⁻¹) which are present in the IR spectra of the other complexes together with a broad absorption centered at ca. 3100 cm⁻¹ due to the N–H stretching.

Acknowledgement
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References
NOTES

14 Generated *in situ* from (IV) by the addition of a base such as the ones described in the text.