Synthesis and structural characterization of Cu(II) and Ni(II) complexes of antipyrine
schiff base derivatives

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The terfunctional schiff base ligands acetylaceton-4-aminoantipyrine, salicylal-4-aminoantipyrine and 2-hydroxy-1-naphthal-4-aminoantipyrine react with Cu(II) and Ni(II) metal ions in different stoichiometric ratios and at various pH values to yield complexes with different bonding features such as (i) neutral bidentate - coordination via. > C = O and > C = N-,(ii) neutral terdentate - coordination via. > C = O, -CH-NH- and quinonoid =0: from -OH,(iii) monovalent bidentate - coordination via. > C = N- and -O- from -OH and (iv) monovalent terdentate - coordination via. > C = N, > C = O and -O- from -OH.

The classical coordination chemistry of biologically active antipyrine with transition metals and lanthanides has been extensively studied1-9. In all the reported cases, the coordination possibilities of the schiff base ligands AcAAP, SAAP and HNAAP are restricted to terdentately bound complexes. Nevertheless, these ligands are also capable of behaving as neutral bidentates in their deprotonated form to coordinate with metal(II) ions.

In this note, we report the possibilities of these systems forming metal complexes by making use of different reaction conditions such as (i) the pH of the reaction solution (acidic, neutral or alkaline) and (ii) variable stoichiometries of substrates.

Experimental

All the chemicals and solvents used were of reagent grade. The ligands acetylaceton-4-aminoantipyrine (AcAAP), salicylal-4-aminoantipyrine (SAAP) and 2-hydroxy-1-naphthal-4-aminoantipyrine (HNAAP) were prepared by the condensation of 4-aminoantipyrine (AAP) with acetylacetone, salicylaldehyde or 2-hydroxy-1-naphthaldehyde according to the literature method5-8.

Preparation of complexes

Under acidic conditions (pH = 5-6)
A solution of hydrated metal(II) salt (0.01 mol) and the schiff base ligand in acetone were refluxed for 15-20 min in appropriate molar ratios. The solid product thus obtained upon cooling was filtered, washed with warm benzene, water and finally dried over CaCl₂ in a desiccator.

Under neutral conditions (pH = 7)
An ethanolic solution of the schiff base ligand was added to an equimolar aqueous solution of sodium acetate. To this solution, an ethanolic solution of metal(II) salt in appropriate molar ratio was added and boiled for 15 to 20 min. The pH of the reaction solution was monitored by an aqueous solution of sodium acetate and ethanol using a pH meter. The precipitated solid product thus obtained was purified as described above.

Under alkaline conditions (pH 8-9)
The preparation of the complexes was achieved by adopting the same procedure described above in ethanolic medium. The pH of the solution was rendered alkaline (8-9) using either NaOH (1N) or dil. NH₄OH. In most of the cases, the metal complexes precipitated within minutes, which were filtered, washed with cold ethanol and dried at room temperature. The physical measurements were carried out, as reported earlier8.

Results and discussion

A consequence of the monobasic nature of the ligands AcAAP - Acetylaceton-4-aminoantipyrine, SAAP-salicylal-4-aminoantipyrine and HNAAP-2-hydroxy-1-naphthal-4-aminoantipyrine with the metals Mn(II), Co(II), Ni(II) and Cu(II) at alkaline pH (~8-9) due to deprotonation of -OH into O-, is that the possibilities of coordination at the metal ion increase. Thus a second ligand such as an anion, or another molecule of the ligand itself, can enter the coordination sphere resulting in a 4 or 6 coordination geometry around the metal ion. Furthermore, 1:1 and 2:1 metal - ligand stoichiometries, can lead to the formation of complexes of the type [MLX] and [ML₂X₂] respectively at alkaline pH (~8-9) when NaOH (1N) is added. Interestingly, the same monobasic terdentate ligand at pH (~8-9) when NH₄OH is added, can form complexes of the type [ML₃] irrespective of the concentration of the substrates.

The IR spectra of these complexes viz. [MLX], [ML₂X₂] and [ML₃] show no bands ~ 3200 cm⁻¹ suggesting the absence of intra-ligand hydrogen
Table 1—Characterization data of representative nickel(II) or copper(II) complexes of acetylacetone-4-aminoantipyrine (AcAAP)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (Calc.), %</th>
<th>Electronic spectral bands (cm⁻¹)</th>
<th>Magnetic moment μ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>AcAAP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(AcAAP)Cl₂]⁺</td>
<td>14.3(14.2)</td>
<td>46.7(46.4)</td>
<td>4.4(4.4)</td>
</tr>
<tr>
<td>[Ni(AcAAP)Cl₂]²⁻</td>
<td>14.5(14.2)</td>
<td>46.13(46.4)</td>
<td>4.4(4.4)</td>
</tr>
<tr>
<td>[Ni(AcAAP) (H₂O)Cl₂]²⁻</td>
<td>15.3(15.2)</td>
<td>46.1(45.9)</td>
<td>4.4(4.3)</td>
</tr>
<tr>
<td>[Ni(AcAAP)Cl]²⁻</td>
<td>9.8(9.4)</td>
<td>61.5(61.3)</td>
<td>5.9(5.7)</td>
</tr>
<tr>
<td>[Ni(AcAAP)Cl₄]²⁻</td>
<td>15.7(15.5)</td>
<td>51.1(50.8)</td>
<td>4.9(4.8)</td>
</tr>
<tr>
<td>[Ni(AcAAP)Cl₂]⁴⁻</td>
<td>15.5(15.5)</td>
<td>50.6(50.8)</td>
<td>4.7(4.8)</td>
</tr>
<tr>
<td>[Ni(AcAAP)Cl₃]⁴⁻</td>
<td>16.8(16.6)</td>
<td>51.0(50.1)</td>
<td>4.7(4.7)</td>
</tr>
</tbody>
</table>

- neutral bidentate - coordination via C = O (pyrazolone ring) and C = N-, monomer
- neutral terdentate - monomer, coordination via C = O, C = N and -OH
- monobasic bidentate - coordination via -O- of -OH and C = N-
- monobasic terdentate - coordination via C = O, C = N and -O- of -OH, monomer
- monobasic terdentate - coordination via C = O, C = N and -O- of -OH, dimer

a - conversion of -O= to = O a resulting resonance from C = N- to NH

The in situ generation of acid prevents the deprotonation of -OH group and the ligands offer new possibilities yielding two types of complexes such as non-electrolytic mononuclear complex [MLX₂] and 1:1 electrolytic dinuclear complex [MLX₃]X₂.

These complexes show a broad band ~3600 cm⁻¹ instead of 3200 cm⁻¹ in the complexes, showing the non-involvement of -OH group on coordination.

The magnetic moments of the nickel(II) complexes (1,4) and (6) at room temperature are in the range 2.89 to 3.09 BM. These values are consistent with high spin d⁸ complexes. On the other hand, the nickel(II) complexes of the types (2,7) and the copper(II) complexes (3,8) show magnetic moments in the ranges 2.16 to 2.21 and 1.3 to 1.41 BM respectively. These values are lower than that predicted for low spin d⁸ metal ion respectively. The data indicate that all these complexes are probably dimeric similar to that found for the distinctly dimeric copper(II) acetate monohydrate with the attendant metal-metal interaction. The exchange interaction between the metal ions might occur through the phenoxide bridge (7 and 8) or through halide bridge (2 and 3).

While the Ni(II) complexes, 1,5 and 6 show a broad absorption band in the region 16500-16000 cm⁻¹ assignable to 3T₁g(F) --> 3T₂g(F) in a tetrahedral geometry, 4 exhibits two bands of lower intensity in the regions 15500-15000 and 23500 cm⁻¹ assignable to 3A₂g→3T₁g and 3A₂g→3T₁g(P) respectively in an octahedral geometry. Also the presence of an additional band below 10000 cm⁻¹ confirms the octahedral geometry for the latter Ni(II) complex 4. The molar con-
DUCTANCE data are in accord with a 1:1 composition for complexes (2, 3, 7 and 8) and a nonelectrolytic structure for the rest.

The analytical results of C, H, N and M (Table 1) of the complexes are in good agreement with the assigned structural formula. The overall reaction pattern is given in Scheme 1

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**References**