Cobalt(II), nickel(II), copper(II) and zinc(II) complexes of conjugated 3-(benzylidene/salicylidene)-β-diketones (having no enolisable γ-carbon proton) and their reactions

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Summary
The synthesis and structural characterization of new metal(II) chelates (M = CoII, NiII, CuII and ZnII) of neutral conjugated bidentate β-diketone ligands, having no enolisable γ-carbon proton, and their reactions are reported. The ligand systems chosen are Knoevenagal condensates of aromatic aldehydes with β-diketones, such as 3-(benzylidene/salicylidene) acetylacetone/benzoylacetonolacetates. The general composition of the chelates is [M(AA)B2C2] for 6-coordinate complexes and [M(AA)B2] for 4-coordinate complexes. (AA) is a neutral bidentate aldehyde-β-diketone condensate ligand; B is a monodentate anion and C is monodentate neutral ligand (H2O/Py). Bromination at α-methyl groups by NBS and PyHBr3, Schiff base condensation at β-carbonyl groups by amine bases and 1,2-addition reaction at the γ-carbon double bond are reported.

Introduction
The reactivity of Knoevenagel β-diketone condensates in the presence of metal ions has elicited much interest in connection with the synthesis of monoketoness'. However, the ability of these β-diketones in terms of chelation with metal ions has not been investigated so far. The ligand system after reduction by hydrogenation is capable of forming crystalline copper(II) chelates21 but not prior to reduction. Being incapable of enolisation, the condensates have not perhaps been considered earlier as potential ligands towards transition metal ions. In this paper we report the successful isolation and characterization of the title chelates and their subsequent reactions.

Experimental
The condensate ligand systems and the precursor neutral dichloro β-diketone metal(II) chelates (M = CoII and ZnII) were prepared by literature procedures3-4. 1H and 13C n.m.r. spectra were recorded on Bruker instrument in DMSO-d6. The uv-vis solution spectra were obtained using Shimadzu UV-160 spectrophotometer.

Preparation of the complexes

Diacetatodiaquo-3-(benzylidene)acetylacetono/benzoylacetonolacetone-copper(II)  
A mixture of 3-(benzylidene)β-diketone (0.01 mol) and piperidine (0.5 mol%) in CHCl3 (100 cm3) was gradually added to a suspension of Cu(OAc)2·H2O (0.01 mol) in CHCl3 (50 cm3) and stirred in a round bottom flask. The mixture was then boiled under reflux (2–3 h) until it became clear and then dark green. Upon concentration to one-third vol, followed by the addition of petroleum ether (3 vol) and subsequent cooling at 0°C (2 h), a blue crystalline solid product (4) precipitated. This product was removed by filtration, washed with 50% (v/v) EtOH–Me2CO and dried in vacuo. The same reaction, if carried out with CuCl2 instead of Cu(OAc)2·H2O, yielded no complex. Furthermore, the same ligand: BenAc/BenBz gave no complex with CoII and ZnII acetates. However, these metal complexes of CoII and ZnII could be successfully prepared from the precursor dichloro-β-diketono metal(II) chelate (2) using MeCN as the solvent in place of CHCl3. Attempts to prepare NiII analogue by the same procedure failed. Also when R1 = R2 = Ph no solid metal(II) complexes could be isolated.

Dichloro-3-(salicylidene)acetylacetono/benzoylacetonolmetal(II) complexes M = CoII, NiII, CuII and ZnII  
An EtOH solution (150 cm3) of 3-(salicylidene)-β-diketone (0.01 mol) and an aqueous solution (50 cm3) of NaOAc·H2O (0.01 mol) were mixed and heated on a steam bath for 1 h. To this an aqueous solution (50 cm3) of MCl2·nH2O was gradually added with constant stirring and the mixture was maintained at the reflux temperature for 2 h. The resulting crystalline product (5) was removed by filtration, washed with 50% (v/v) EtOH–Me2CO mixture and dried at 110°C. If metal(II) acetates were used as starting material, the corresponding complexes could not be prepared, but the CoII and ZnII salicylidene complexes were made successfully from (2) using the same reaction conditions as for (3).

Pyridine adducts
Crystalline pyridine adducts of (5) were prepared by dissolving the appropriate chelate in sufficient quantity of pyridine and evaporating the free pyridine under reduced pressure. The resulting solid (6) was washed thoroughly with EtOH and dried in vacuo.

Reaction of metal(II) chelates (5) at α, β and γ-carbon centres
Metal(II) conjugated condensate chelates (5) were subjected to bromination5,6 at the α-methyl groups using NBS or PyHBr3, Schiff base condensation7 of β-carbonyl groups with amine bases such as NH2OH, o-aminophenol and o-aminothiophenol, and 1,2-addition reaction8 across the double bond by NH2OH by adopting the usual procedures described elsewhere5-8.

Results and discussion
The novelty about the title complexes is that they may constitute the first instance of a β-diketone system devoid
of an enolisable \( \gamma \)-carbon proton yielding an isolable metal complex. By contrast, simple \( \beta \)-diketones are known to coordinate to almost every metal ion, forming stable complexes. Analytical and molecular weight data and their non-electrolytic behaviour in DMF and DMSO suggest a monomeric structure for complexes (4)–(11) and a dimeric structure for (12). The observed magnetic moments of copper(II) chelates corroborate with the above formulations. These results are represented in Scheme 1 and the analytical data for the copper(II) chelates, representative of the title metal(II) chelates, are compiled in Table 1.

Spectral characterization

The condensate chelates (4), (5) and (7) show two prominent peaks at 1665 and 1620 cm\(^{-1}\) corresponding to the \( \nu(C=O)\)-keto group and \( \nu(C=C)\)-olefinic double bond respectively. I.r. data on the carbonyl group frequencies of the free ligand with that of the complexes are given in Table 2 for various types of coordinating \( \beta \)-diketones\(^{9,10}\). The observed down field shift, going from free ligand to metal complexes \( \Delta \nu(C=O) \), suggests neutral ketonic coordination of carbonyl groups to the metal.

The principal n.m.r. features exhibited by the free ligand are retained in the spectra of the complexes (Table 3). The crystal field geometry of the above chelates around the central metal ion is inferred from the electronic spectra. The presence of a broad band at ca. 10000 cm\(^{-1}\) in all the complexes and their reaction

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Table 1. Analytical data for the copper(II) complexes representative of the title metal(II) complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Found (Calcd.)%</th>
<th>H</th>
<th>N</th>
<th>Br</th>
<th>( \mu_{\text{eff}} ) (BM)</th>
<th>Yield (%)</th>
</tr>
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<tr>
<td>(4)</td>
<td>([\text{Cu(BenAc)(OAc)}_2(H_2O)_2])</td>
<td>15.2</td>
<td>47.2</td>
<td>5.3</td>
<td>–</td>
<td>2.01</td>
<td>27</td>
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<tr>
<td>(5)</td>
<td>([\text{Cu(SalAc)}Cl_2])</td>
<td>18.9</td>
<td>43.0</td>
<td>3.6</td>
<td>–</td>
<td>2.00</td>
<td>65</td>
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<tr>
<td>(6)</td>
<td>([\text{Cu(SalAc)}Cl_2(py)_2])</td>
<td>12.6</td>
<td>52.9</td>
<td>4.5</td>
<td>5.71</td>
<td>1.93</td>
<td>95</td>
</tr>
<tr>
<td>(7)</td>
<td>([\text{Cu}(\text{Br}-\text{SalAc})Cl_2])</td>
<td>13.1</td>
<td>29.2</td>
<td>2.1</td>
<td>–</td>
<td>31.9</td>
<td>1.88</td>
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<tr>
<td>(8)</td>
<td>([\text{Cu}(\text{AP-SalAc})Cl_2])</td>
<td>14.5</td>
<td>64.7</td>
<td>4.6</td>
<td>6.2</td>
<td>1.96</td>
<td>71</td>
</tr>
<tr>
<td>(9)</td>
<td>([\text{CuTP-SalAc)}Cl_2])</td>
<td>13.7</td>
<td>60.7</td>
<td>4.1</td>
<td>5.7</td>
<td>2.01</td>
<td>65</td>
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<tr>
<td>(10)</td>
<td>([\text{Cu(NH-SalAc)}_2])</td>
<td>19.1</td>
<td>43.1</td>
<td>3.8</td>
<td>4.2</td>
<td>–</td>
<td>1.93</td>
</tr>
<tr>
<td>(11)</td>
<td>([\text{Cu}(\text{NH}_2\text{-SalAc)}_2])</td>
<td>12.7</td>
<td>57.4</td>
<td>5.6</td>
<td>5.5</td>
<td>–</td>
<td>1.97</td>
</tr>
<tr>
<td>(12)</td>
<td>([\text{Cu}_2(\text{NH}_2\text{-SalAc})_2\text{Cl}_2])</td>
<td>20.1</td>
<td>44.9</td>
<td>4.3</td>
<td>4.3</td>
<td>–</td>
<td>1.52</td>
</tr>
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Table 2. Shift of \( \nu(C=O) \) frequencies (cm\(^{-1}\)) upon metal ion coordination.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type</th>
<th>( \nu(C=O) ) (cm(^{-1}))</th>
<th>( \Delta \nu ) = ( \nu_1 - \nu_2 )</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>(1)</td>
<td>Simple enolic ( \text{eg: anionic coordination of acetyl acetone} )</td>
<td>1730</td>
<td>1560</td>
<td>140</td>
</tr>
<tr>
<td>(2)</td>
<td>Simple ketonic ( \text{eg: neutral coordination of acetyl acetone} )</td>
<td>1730</td>
<td>1720</td>
<td>10</td>
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<tr>
<td>(3)</td>
<td>Title conjugated ketonic ( \text{eg: neutral BenAc} )</td>
<td>1705</td>
<td>1660</td>
<td>45</td>
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