Synthesis & Characterisation of Copper (II) & Nickel (II) Complexes of Schiff Bases of Acetylacetone with S-Methyl-S’-benzyldithiocarbazate & S,S’-Dibenzyldithiocarbazate

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Schiff bases (I) derived from acetylacetone and S-methyl-S’-benzyldithiocarbazate and S, S’-dibenzyldithiocarbazate do not form complexes with Ni(II) chloride, bromide or nitrate, but with nickel(II) thiocyanate, these Schiff bases afford stable complexes of composition Ni(ONSR)NCS (ONSR = deprotonated ligands; R = CH₃, –CH₂C₆H₅). Magnetic and spectroscopic data suggest a square-planar structure for these complexes. With nickel(II) iodide, S-dealkylation of the ligand occurs with concomitant formation of nickel(II) complexes of the parent thioligand, 5,6-diaza-2-hydroxy-4-benzyl-7-thiono-8-thianona-2,4-diene (HONS). Magnetic and spectral data support a thiol sulphur-bridged dimeric structure for the Ni(ONS) complexes. Copper (II) complexes, Cu(ONSR)Br have normal room temperature magnetic moments and spectral data support square-planar structures for these complexes.

Although a considerable amount of data is available on the transition metal complexes of Schiff bases derived from salicylaldehyde and substituted salicylaldehydes and S-alkyldithiocarbazates¹, much less is known on the complexes of the Schiff bases of β-diketones with dithiocarbazic acid. Akbar Ali et al.² first reported the Schiff base of acetylacetone with S-methylthiodithiocarbazate, as an ONS tridentate ligand producing a ferromagnetic copper (II) complex. Later Akbar Ali and Teoh³ reported the Schiff bases derived from acetylacetone and N-methyl-S-alkyldithiocarbazates which behaved as ON bidentates with nickel (II), but as ONS tridentates with copper (II). Title investigation is a part of our general investigation on the complexes of Schiff bases of β-diketones and dithiocarbazic acid. The Schiff bases used in this study can be represented by the general structure (I).

\[
\text{H} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{N} \quad \text{E} \quad \text{S} \quad \text{C} \quad \text{H}_2 \text{C}_6 \text{H}_5
\]

Materials and Methods
IR spectra were recorded in KBr on a Perkin-Elmer 1330 spectrophotometer, reflectance spectra in nujol on a Cary model 319 spectrophotometer, absorption spectra in DMF on a Pye-Unicam model SP 8-400 spectrophotometer and ¹H and ¹³C NMR spectra on a Bruker WP-80 FT NMR spectrometer or a Varian EM 360A spectrometer with TMS as an internal standard. Magnetic and conductivity measurements were made as described before⁴.

Preparation of ligands: 5,6-Diaza-2-hydroxy-4-methyl-7-S-methyl-7-S-benzyl-3,4,6-triene (I, R = CH₃; abbreviated as HONSMe)
A solution of S-benzyldithiocarbazate⁵ (4 g) in ethanol (50 ml) was mixed with a solution of KOH (1.12 g) in the same solvent (50 ml). Methyl iodide (2.8 g) was added with stirring and the mixture allowed to stand for 30 min. To this was added acetylacetone (2 g) and left standing overnight. Water (100 ml) was added with stirring and the oily substance which had settled was collected. Since several attempts to induce crystallization of the oil did not meet with success, an alcoholic solution of the oil was used for the preparation of the metal complexes.

5,6-Diaza-2-hydroxy-4-methyl-7-S,S’-dibenzyldiene-2,4,6-triene (I, R = –CH₂C₆H₅, abbreviated as HONSBz)
This compound was prepared in a manner similar to the above S-methyl derivative except that benzyl chloride was used instead of methyl iodide.

Preparation of [Ni(ONSMe/BS)NCS]
Nickel (II) thiocyanate was prepared in situ by heating together nickel (II) nitrate hexahydrate (0.3 g) and potassium thiocyanate (0.1 g) in ethanol (30 ml) and filtering off the precipitate potassium nitrate. The filtrate was mixed with a solution of the ligand (0.3 g) in ethanol (20 ml) and the mixture heated on a water-bath for about 30 min. allowed to stand for 1 hr and the solid obtained was filtered off, washed several times with ethanol and dried in vacuo over silica gel; yield 0.6 g (Found: C, 43.15; H, 3.63; Ni, 14.08. Ni(ONSMe)NCS requires C, 43.92; H, 4.17; Ni,
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14.31%. Found: C, 50.42; H, 4.03; Ni, 11.92. Ni(ONSBz)NCS requires C, 50.83; H, 3.35; Ni, 12.31%.  

Reaction of NiI₂ with HONS(R = CH₃, CH₂C₆H₅)

A solution of nickel (II) iodide in ethanol was prepared by heating a mixture of nickel (II) nitrate hexahydrate (0.3 g) and sodium iodide (0.2 g) in ethanol (50 ml) and filtering off the precipitated sodium nitrate. The filtrate was mixed with a solution of the ligand (0.3 g) in the same solvent (30 ml) and gently heated on a water-bath for about 45 min. On being left to stand for about 1 hr a microcrystalline product had formed which was filtered off, washed several times with ethanol and dried in a vacuum desiccator over silica gel. Yield 0.7 g. (Found: C, 44.74; H, 3.87; Ni, 17.00. C₁₃H₁₅N₂S₂ONi requires C, 45.11; H, 4.34; Ni, 16.99%).

Results and Discussion

Though the Schiff bases (I) were obtained as oily substances, their complexes with Ni (II) and Cu (II) were obtained in a state of purity (Table I). It was interesting to observe that the formation of the nickel (II) complex was dependent on the nature of the anion being used. Thus Ni (II) chloride, bromide or nitrate failed to yield any compound with the ligands even after prolonged heating, whereas Ni (II) thiocyanate readily reacted with the ligands to afford crystalline complexes. Similar observations have also been reported by Akbar Ali⁶ who has attributed this anomalous behaviour to symbiotic effects.

The complex, Ni(ONSMe)NCS behaves as a non-electrolyte in DMF (Ω = 0.4 ohm⁻¹cm²mol⁻¹) and its IR spectrum displays a medium intensity band at 2070 cm⁻¹ due to vC-N mode of the N-bonded NCS group. The other relevant IR bands along with their tentative assignments are given in Table 2. The diamagnetism of NiLNCS complexes suggests a four-coordinate structure. The ¹H NMR spectra in DMSO-d₆ display -SCH₃, CH₃, CH₂S and phenyl proton resonances at δ 2.364, 2.49, 2.54, 3.90, and 7.34, respectively. The ¹³C NMR spectrum of Ni(ONSMe)NCS in DMSO-d₆ is dominated by solvent peaks. However, carbon resonances due to -CH₃ of the acetylacetone moiety are obtained at δ 22.165 and 20.269. The -SCH₃ signal is obtained at δ 17.614. The vinylic -CH and C=N carbon signals appear at δ 100 and 164, respectively. The electronic spectra of the thiocyanato complexes in DMF display bands at 560, 423 and 416 nm (Table I). Of these bands, the 560 nm band may be assigned to the d-d transition of square-planar nickel (II). The other bands are probably due to charge transfer (CT) transitions. The above magnetic and spectroscopic evidences support a four-coordinate square-planar structure for the Ni (II) complexes with the ligand acting as an ONS tridentate, the fourth coordination position being occupied by the thiocyanato group.

Reaction of Ni (II) iodide with the ligands in boiling ethanol yielded brown products which did not contain iodide as the anions. Analytical data support formulation of these compounds as Ni(ONS), where

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Decomp. point (°C)</th>
<th>B.M.</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(ONSMe)NCS</td>
<td>Brown</td>
<td>152</td>
<td>Diam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiONS NCS</td>
<td>Brown</td>
<td>202</td>
<td>Diam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiONS³</td>
<td>Dark-brown</td>
<td>140</td>
<td>Diam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiONS³</td>
<td>Dark-brown</td>
<td>148</td>
<td>Diam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(ONSMe)Br</td>
<td>Deep green</td>
<td>106</td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(ONSBz)Br</td>
<td>Brown</td>
<td>90</td>
<td>1.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Prepared from the reaction of NiI₂ with HONSMe.  
(b) Prepared from the reaction of NiI₂ with HONSBr.

<table>
<thead>
<tr>
<th>Compd</th>
<th>νC = N</th>
<th>νC = O</th>
<th>νM = O</th>
<th>νM = S</th>
<th>δmax (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(ONSMe)NCS]</td>
<td>1628m</td>
<td>1100m</td>
<td>602s</td>
<td>340w</td>
<td>560 (2.71), 430 (4.20), 420sh (4.1)⁷.</td>
</tr>
<tr>
<td>[Ni(ONSBz)NCS]</td>
<td>1616s</td>
<td>1142m</td>
<td>600sh</td>
<td>380w</td>
<td>526 (2.14), 432 (4.19), 416sh (4.06)⁷.</td>
</tr>
<tr>
<td>[NiONS³]</td>
<td>1602s</td>
<td>1130m</td>
<td>602</td>
<td>350w</td>
<td>580sh (2.24), ca. 430, 380sh⁷.</td>
</tr>
<tr>
<td>[NiONS³]</td>
<td>1622m</td>
<td>1125w</td>
<td>620m</td>
<td>335w</td>
<td>520sh (2.13), 430, 375sh².</td>
</tr>
<tr>
<td>[Cu(ONSMe)Br]</td>
<td>1620m</td>
<td>1128m</td>
<td>602m</td>
<td>360m</td>
<td>738 (1.41), 430sh (3.4), 280 (4.11)⁷.</td>
</tr>
<tr>
<td>[Cu(ONSBz)Br]</td>
<td>1620br</td>
<td>1155w</td>
<td>620w</td>
<td>340br</td>
<td>420sh (3.35), 288 (4.13)⁷.</td>
</tr>
</tbody>
</table>

*Other bands at 2140m (νC = N of NCS group), 780 (νC = S) and 722m (νC = S).
(a) Prepared by the reaction of NiI₂ with HONSMe.  
(b) Prepared by the reaction of NiI₂ with HONSBr.  
(c) In DMF.  
(d) As nujol mull.  
(e) log ε in parentheses.

| Table 2—IR* (νmax in cm⁻¹) and Electronic Spectral Data of the Complexes |
|-----------------------------|--------|--------|--------|--------|--------|
| Compd                       | νC = N | νC = O | νM = O | νM = S | δmax (nm) |
| [Ni(ONSMe)NCS]             | 1628m  | 1100m  | 602s   | 340w   | 560 (2.71), 430 (4.20), 420sh (4.1)⁷. |
| [Ni(ONSBz)NCS]             | 1616s  | 1142m  | 600sh  | 380w   | 526 (2.14), 432 (4.19), 416sh (4.06)⁷. |
| [NiONS³]                   | 1602s  | 1130m  | 602    | 350w   | 580sh (2.24), ca. 430, 380sh². |
| [NiONS³]                   | 1622m  | 1125w  | 620m   | 335w   | 520sh (2.13), 430, 375sh². |
| [Cu(ONSMe)Br]              | 1620m  | 1128m  | 602m   | 360m   | 738 (1.41), 430sh (3.4), 280 (4.11)⁷. |
| [Cu(ONSBz)Br]              | 1620br | 1155w  | 620w   | 340br  | 420sh (3.35), 288 (4.13)⁷. |

*Other bands at 2140m (νC = N of NCS group), 780 (νC = S) and 722m (νC = S).
(a) Prepared by the reaction of NiI₂ with HONSMe.  
(b) Prepared by the reaction of NiI₂ with HONSBr.  
(c) In DMF.  
(d) As nujol mull.  
(e) log ε in parentheses.
ONS represents the dinegatively charged parent thiol ligand, 5,6-diaza-2-hydroxy-4-methyl-7-S-benzyl-2,4-diene. The analytical data and other properties of the products seem to suggest that in the presence of Ni(II) iodide, S-dealkylation of the Schiff bases occurs with concomitant formation of the Ni(II) complex of the parent thiol ligand. Such S-dealkylation reactions of thioether ligands in the presence of Ni(II) iodide have also been recorded in literature. Several biologically important thioesters have also been cleaved in this manner. It is possible that the mechanism of S-dealkylation reaction is similar to that postulated for the Zeisel-cleavage of an ether by hydrogen halide.

The IR spectra of Ni(ONS) complexes display νC=N, νC-O, νM-O and νM-S bands at 1620, 1130, 600 and 350 cm⁻¹, respectively indicating that the S-dealkylated ligands behave as ONS tridentates. The diamagnetism of the complexes (Table 1) suggests that the thiol sulphur is involved in coordination since thios and not thioethers cause spin-pairing in complexes of nickel (II). The electronic spectra of the complexes (Table 2) display a band around 550 nm and two intense bands around 430 and 380 nm. The band at 550 nm may be assigned to the d-d transition of square-planar nickel (II). The other two bands are probably due to CT transitions. The diamagnetism and electronic spectra of Ni(ONS) suggest a four-coordinate square-planar configuration for these complexes. Since the metal to ligand ratio is 1:1, at least dimerisation is required to achieve four-coordination. The insolubility of these complexes in most of the non-polar solvents prevented us from measuring molecular weights. However, a sulphur-bridged dimeric structure (II), similar to that described for the closely similar nickel (II) complex of the Schiff base of 2,4-pentanediene and S-methylthiocarbazate, is proposed for the Ni(ONS) complexes.

The interaction of copper (II) bromide with the Schiff bases produced brown compounds, Cu(ONS)Br (Table I), which are non-electrolytes in DMF (Ω=0.2-0.3 ohm⁻¹ cm⁻² mol⁻¹). The appearance of νM-O, νC=N and νM-S around 600, 1600 and 342 cm⁻¹, respectively in the IR spectra of these complexes indicates that the Schiff base is coordinated to the copper (II) ion via the enolic oxygen, the azomethine nitrogen and one of the thioether sulphur atoms. The room temperature magnetic moments of 1.94 B.M. (Table 1) lie above the spin-only value and are normal for copper (II) complexes. The electronic spectrum of Cu(ONSMe)Br in DMF displays a broad band at 734 nm characteristic of square-planar copper (II). The spectrum of Cu(ONS)Br is dominated by intense CT bands extending up to the visible region. The magnetic and spectral data support a square-planar structure with the ligand acting as a uninegatively charged tridentate and the fourth coordination site being occupied by the bromide ion.

Acknowledgement

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References