Magnetic & Spectroscopic Studies on Metal Complexes of ONS Donor Ligands: Part II*—Nickel(II) & Copper(II) Complexes of Schiff Bases Formed by the Condensation of 2-Hydroxybenzaldehyde with S,S-Dibenzyl-dithiocarbazate & S-Methyl-S'-benzyl-dithiocarbazate

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Schiff bases formed by the condensation of 2-hydroxybenzaldehyde with S,S-dibenzyl-dithiocarbazate (HONSBz) and S-methyl-S'-benzyl-dithiocarbazate (HONSmMe) have been synthesized and characterised. The Schiff bases do not yield any complex when reacted with nickel(II) chloride, bromide or nitrate salts. However, HONSBz reacts with nickel(II) thiocyanate and nickel(II) iodide; S-debenzylation of the Schiff base occurs with the concomitant formation of the nickel(II) complex of the parent thiol ligand, S-benzyl-β-N-(2-hydroxyphenyl)methylendithiocarbazate. Magnetic and spectroscopic evidences support a thiol sulphur-bridged dimeric structure for the complex. With copper(II) chloride, the Schiff base HONSBz forms a crystalline compound of composition, Cu₂(ONSBz)₂Cl₂ (ONSBz = deprotonated form of the Schiff base). Magnetic and spectroscopic evidences support a chlorine-bridged trimeric structure. The Schiff base HONSmMe yields a brown thiocyanato complex, Ni(ONSmMe)NCS.H₂O, which is spin-paired and square-planar. In the presence of nickel(II) iodide, S-demethylation of the Schiff base occurs with the formation of nickel(II) complex of the parent thiol ligand. The copper(II) complexes, [Cu(ONSmMe)X] (X = Cl -, Br -) have also been isolated and characterised. Magnetic and spectral evidences support square-planar structures for these complexes.

Metal complexes of Schiff base ligands derived from S-methyl- and S-benzyl-dithiocarbazates have been the subject of considerable research over the past few years1-5. However, most of the ligands that have so far been investigated contain either a thiol or a thiketo sulphur as one of the donor atoms. Work on ligands containing thioether sulphur as one of the donors is relatively much less. As a part of our general investigation of metal complexes of ligands containing oxygen, nitrogen and sulphur donors, we report herein the results of our investigation of two new Schiff base ligands containing thioether sulphur as one of the ONS set of donor atoms.

Materials and Methods
The IR spectra were recorded in KBr on a Perkin-Elmer 1330 spectrophotometer. Electronic spectra were measured in the solid state with a Carl Zeiss PMQ II spectrophotometer equipped with a solid reflectance attachment; MgCO₃ was used as the reference; spectra in nujol were recorded on a Cary Model 319 spectrophotometer. Spectra in solution were measured using a Pye-Unicam Model SP8-400 spectrophotometer. The ¹H NMR spectra were measured by either a Bruker WP-80 FT NMR spectrometer or a Varian EM 360A spectrometer with TMS as an internal standard. The mass spectra were obtained on an AEI MS-12 mass spectrometer at 70eV in the temperature range 25'-40°C. Magnetic and conductivity measurements were made as described before6. Microanalyses for C, H and N were performed at the Microanalytical Laboratory, Department of Chemistry, University of Stirling, Scotland. Metal and halogen analyses were done as described before2.

Preparation of the ligands
Preparation of S,S'-dibenzy1-β-N-(2-hydroxyphenyl)methylendithiocarbazate (HONSBz)
Potassium hydroxide (0.56 g) was dissolved in absolute ethanol (50 cm³) and the solution was mixed with a solution of S-benzyl-dithiocarbazate (2.0 g) in the same solvent (30 cm³). Benzyl chloride (1.26 g) was added with stirring, over a period of ~20 min. 2-Hydroxybenzaldehyde (1.22 g) was then added and the reaction mixture was left overnight at room temperature. Addition of water (100 cm³) caused precipitation of a white product which on recrystallization from absolute ethanol gave beautiful fibre like crystals of the compound; yield, 3.0 g; m.p. 89°C. [Found: C, 66.8; H,
Preparation of S-methyl-S'-benzyl-N-(2-hydroxyphenyl)methylendithiocarbazate (HONSMe)

This compound was prepared in a similar manner except that methyl iodide (1.5 g) was added in place of benzyl chloride. The schiff base was isolated as an oily substance. Several attempts to crystallize the oil did not meet with success and consequently, an ethanolic solution of the oil was used for the preparation of metal complexes.

Reaction of nickel(II) thiocyanate with HONSBz

A filtered solution of the ligand (0.8 g) in absolute ethanol (50 cm³) was added with stirring to a solution of nickel(II) thiocyanate, prepared by heating nickel(II) nitrate hexahydrate (0.85 g) with potassium thiocyanate (0.3 g) in absolute ethanol (20 cm³) and filtering off the precipitated potassium nitrate. The reaction mixture was then refluxed for 4 h during which time the colour of the solution changed from green to brown. The mixture was then left to cool whereupon the reddish-brown crystalline product precipitated; it was filtered off, washed several times with ethanol and dried in vacuo [Found: C, 50.1; H, 2.9; N, 8.0. Calc. for C₁₅H₁₂N₂O₂S₂Ni: C, 50.2; H, 3.4; N, 7.8%].

Reaction of nickel(II) iodide with HONSBz

This reaction was carried out in a manner similar to that reported for nickel(II) thiocyanate except that sodium iodide was used instead of potassium thiocyanate. The product was obtained as a brown solid [Found: C, 49.9; H, 2.7; N, 7.6. Calc. for C₁₅H₁₂N₂O₂S₂Ni: C, 50.2; H, 3.4; N, 7.8%].

Preparation of Cu(ONSBz)₂Cl₂

The ligand (0.8 g) was dissolved in absolute ethanol (50 cm³) and the solution was added to a solution of copper(II) chloride dihydrate (0.52 g) in the same solvent (50 cm³). The dark-green reaction mixture was heated at reflux for one hour and then cooled. The dark-green crystalline product which had deposited was collected, washed repeatedly with ethanol and filtered in vacuo over P₂O₅ [Found: C, 47.5; H, 3.8; Cu, 17.4; Cl, 12.4. Calc. for C₁₅H₁₂N₂O₂S₂Cl₂Cu₂: C, 47.4; H, 3.4; Cu, 17.1; Cl, 12.7%].

Preparation of Ni(ONSBz)₂NCS

Nickel(II) nitrate hexahydrate (0.4 g) and potassium thiocyanate (0.1 g) were heated in absolute ethanol (20 cm³) for ~15 min and then cooled. The precipitated potassium nitrate was filtered off and the filtrate was mixed with a solution of the ligand (0.3 g) in ethanol (10 cm³). The mixture, on being heated on a water-bath for ~15 min, yielded a red crystalline product which was collected by filtration, washed and dried as before [Found: C, 46.5; H, 3.3; N, 9.7; Ni, 13.3. Calc. for C₁₅H₁₄N₂O₂S₂Ni: C, 47.2; H, 3.5; N, 9.7; Ni, 13.0%].

Results and Discussion

The schiff base, S,S'-dibenzyl-β-N-(2-hydroxyphenyl)methylendithiocarbazate (HONSbz) (I) was obtained as a beautifully crystalline solid.

The ¹H NMR spectrum of the schiff base in CDCl₃ displays the phenolic -OH signal at δ 11.40 ppm. In DMSO-d₆, this peak is somewhat broadened presumably due to the stronger hydrogen bonding in this solvent. Signals due to the protons of -CH=N-, phenyl and CH₂ groups appear at δ 8.55 (1H), 7.35...
Table 1 — Characterisation Data of the Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Dec. Temp(°C)</th>
<th>λ (ohm⁻¹cm⁻²mol⁻¹)</th>
<th>μ eff. (B.M.)</th>
<th>Electronic spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(ONS)]₆</td>
<td>Brown</td>
<td>144-150</td>
<td>5.2</td>
<td>Diam. Solid</td>
<td>556sh, 469</td>
</tr>
<tr>
<td>[Ni(ONS)]₄</td>
<td>Brown</td>
<td>150-152</td>
<td>6.2</td>
<td>Diam. Solid</td>
<td>556sh, 469</td>
</tr>
<tr>
<td>[Cu(ONSMe)]₂Cl₂</td>
<td>Brownish-green</td>
<td>125</td>
<td>113</td>
<td>1.76</td>
<td>Acetone² 750, 716, 640sh, 580sh, 345, 310</td>
</tr>
<tr>
<td>[Ni(ONSMe)NCS]</td>
<td>Red</td>
<td>138</td>
<td>0.1</td>
<td>Diam. Nujol</td>
<td>524sh, 420sh, 386, 259</td>
</tr>
<tr>
<td>[Ni(ONS)₃.H₂O]</td>
<td>Orange-brown</td>
<td>194</td>
<td>0.6</td>
<td>Diam. Nujol</td>
<td>550, 450, 385, 355, 275</td>
</tr>
<tr>
<td>[Cu(ONSMe)Cl]</td>
<td>Green</td>
<td>140</td>
<td>0.5</td>
<td>1.84</td>
<td>Nujol 650, 400, 310</td>
</tr>
<tr>
<td>[Cu(ONSMe)Br]</td>
<td>Dark-green</td>
<td>142</td>
<td>0.2</td>
<td>1.74</td>
<td>ca. 560, 388, 310</td>
</tr>
</tbody>
</table>

* Molar conductivity of -10⁻³M solution in DMF;

**μ eff. = 2.83 \( \sqrt{10^{6} \Delta T} \pm 0.02 \) B.M. at 298 K;

*Prepared by the reaction of HONSbz with Ni(NCS)₂;
*Prepared by the reaction of HONSbz with NiI₂, 6H₂O;
*Prepared by the reaction of HONSMe with NiI₂, 6H₂O;
* Spectrum of a saturated solution in acetone.

(14H, multiplet) and 4.4 (4H, doublet), respectively. The mass spectrum displays strong peaks for the molecular ion M at \( m/z = 392 \), and for the ions \( M-CH₂C₆H₄, (OH)C₆H₄CH = N - N - CS₂, N=C(SCH₂C₆H₄)₂ \) and \( \text{OHC}_6\text{H}_₄\text{CH} = N \), at 210, 269 and 121, respectively, in accordance with the structure 1.

The Schiff base HONSbz has five potential donor atoms; but, for steric constraints, a maximum of three donor atoms can coordinate to a metal ion simultaneously. The IR spectrum of the ligand shows \( \nu\text{O-H} \) at 3080 cm⁻¹ which disappears in the spectra of its metal complexes suggesting that the Schiff base loses the phenolic proton upon complexation with metal ions.

Reaction of the Schiff base with nickel(II) salts was found to be interesting in that the formation of a nickel(II) complex was dependent on the nature of the anion being used. Thus, nickel(II) chloride, bromide, nitrate and perchlorate salts failed to yield any compound with the ligand even after prolonged heating. However, NiI₂ and Ni(NCS)₂ on reaction with the ligand in ethanol readily gave crystalline compounds. Similar observations have been reported previously by Akbar Ali.⁴ According to the Ahrland, Chatt and Davies classification of metal ions⁹, the nickel(II) ion has been termed as a fairly hard ion and its complexing properties towards soft thioether ligands have been observed to be dependent on symbiotic effects⁸, whereby the iodo complexes form more readily than do the chloro and bromo analogues, the latter being difficult to isolate and apparently not forming in many cases.

Based on analytical data, the brown products obtained by the reaction of nickel(II) iodide and nickel(II) thiocyanate with the Schiff base HONSbz could be formulated as Ni(ONS) (where ONS = dinegatively charged Schiff base containing only one S-benzyl group). Molar conductance data in DMF (Table 1) suggest that these compounds behave essentially as non-electrolytes in this solvent. The IR spectrum of the product obtained from the reaction of nickel(II) thiocyanate with the ligand does not show the characteristic absorptions due to the NCS group. The analytical, conductivity and IR data suggest that in the presence of nickel(II) iodide and thiocyanate, S-debenzylation of the Schiff base occurs with the concomitant formation of the nickel(II) complex of the parent thiol ligand, S-benzyl-N-(2-hydroxyphenyl)methylene thiocarbazate in accordance with Scheme 1.

Similar S-dealkylation reactions of thioether ligands in the presence of \( d^8 \) metal ions to produce metal complexes of the corresponding thiol ligands have also been found to occur in many instances. Several biologically important thioesters have also been cleaved in this manner.⁰¹

\[
\text{NiI₂} + \text{HONSbz} \rightarrow \text{Ni(ONS)} \rightarrow \text{Ni(ONSMe)} \rightarrow \text{Ni(ONSMe)NO₃}
\]

**Scheme 1**
The IR spectra of Ni(ONS) complexes display $\nu$C = N at 1605, $\nu$C - O at 1525, $\nu$M - O at 3600 and $\nu$M - S at 355 cm$^{-1}$ respectively, indicating that the ligand behaves as a tridentate chelating agent coordinating via the phenolic oxygen, the azomethine nitrogen and one of the sulphur atoms. The diamagnetism of the complexes (Table 1) suggests that the thiol sulphur atom is involved in coordination, since thiols and not thioethers cause spin-pairing in complexes of nickel (II). The solid-state electronic spectra of Ni(ONS) display a shoulder at 556 nm and an intense band at 464 nm. The shoulder at 556 nm may be assigned to the d-d transition of square-planar nickel. The diamagnetism coupled with the electronic spectra support a square-planar structure 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 suitable non-polar solvents prevented us from measuring molecular weights. An oxygen-bridged (II) or a sulphur-bridged binuclear structure (III) is possible.

The IR spectra of these complexes may be used to distinguish between these two possible structures. It has been observed that the phenolic $\nu$C - O band in mononuclear copper(II) complexes of 1,2-bis(salicyaldimine)ethane occurs at about 1530 cm$^{-1}$. However, this band is raised by about 20-40 cm$^{-1}$ when these complexes form bi- or trinuclear complexes involving oxygen-bridging. This criterion has also been found to be diagnostic in distinguishing between bridging and non-bridging phenolic C - O groups. The IR spectra of Ni(ONS) complexes display the $\nu$C - O band at 1526 cm$^{-1}$ suggesting that the C - O group is not involved in bridging. Therefore, structure (II) is unlikely. The probable structure is (III) in which the nickel(II) ion achieves a four-coordinate square-planar configuration via sulphur bridges. Such a structure has in fact been proposed for the nickel(II) complexes of a closely related ONS ligand.

Reaction of the schiff base HONSbz with copper(II) chloride produces a dark-green compound. Analytical data support its formulation as Cu$_4$(ONSbz)$_2$Cl$_4$. The insolubility of the compound in most of the polar and non-polar organic solvents suggests its polymeric nature. Several structures (IV to VIII) may be envisaged for this complex.

The observed room-temperature magnetic moment of 1.76 B.M. (Table 1) excludes structure (IV), since such a bridging arrangement has already been shown to lead to a very strong antiferromagnetic interaction causing low room-temperature magnetic moments. The IR spectrum of the complex shows the phenolic $\nu$C - O at 1548 cm$^{-1}$ indicating the presence of a bridging phenolic C - O group. Accordingly, structure (V) is unlikely. The electronic spectrum of the complex (Table 1) does not resemble those of the known five-coordinate copper(II) complexes and consequently, structure (VI) is untenable. The presence of $\nu$M - S at 355 cm$^{-1}$ in its IR spectrum suggests the presence of metal-sulphur bonding. Also, the molar conductance value of 113 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in DMF (Table 1), although somewhat low for a bi-univalent electrolyte in the solvent, supports structure (VIII) rather than (VII). Therefore, structure (VIII) containing a four-coordinate square-planar structure with both oxygen...
and chlorine bridging would be consistent with the magnetic and spectral data.

The Schiff base, S-methyl-S'-benzyl-β-N-(2-hydroxyphenyl)methylendithiocarbazate, was obtained as an oil, and since repeated attempts to obtain this ligand in a crystalline form did not meet with success, an ethanolic solution of the ligand was used to prepare the metal complexes. Reaction of the Schiff base with the nickel(II) ion in the presence of chloride, bromide, perchlorate or nitrate as anions did not yield any metal complex. However, in the presence of nickel(II) thiocyanate, a red complex of composition Ni(ONSMe)NCS (ONSMe = deprotonated S-methyl Schiff base) was obtained. Its conductivity in DMF (Table 1) shows that it is a non-electrolyte in this solvent. Its IR spectrum displays a broad band at 2360 cm⁻¹ attributable to νC≡N of the S-bonded thiocyanate group. The C-S stretching frequency of the thiocyanate group occurs at 702 cm⁻¹ supporting the presence of an S-bonded thiocyanate group. The presence of νM–O, νC=N and νM–S at 592, 1600 and 348 cm⁻¹, respectively, indicates that the ligand is present in an ONS chelated form. The magnetic susceptibility, IR and electronic spectra are similar to those of the complex obtained from the reaction of nickel(II) iodide and HONSMe indicating that these are essentially the same compounds.

The interaction of copper(II) salts with the Schiff base HONSMe gave green compounds, Cu(ONSMe)X(X=Cl, Br), which were non-electrolytes in DMF (Table 1). The appearance of νM–O, νC=N and νM–S at ~600, 1600 and 342 cm⁻¹ in the IR spectra of the complexes indicate that the Schiff base is coordinated to the copper(II) ion via the phenolic oxygen, the azomethine nitrogen and one of the thioether sulphur atoms. The presence of νC=N bands at ~1525 cm⁻¹ in the IR spectra of the Cu(ONSMe)X complexes suggests that bridging C–O groups are not present. The room-temperature magnetic moments of 1.84 B.M. (Table 1) lie above the spin-only value of 1.73 B.M. and are normal for copper(II) complexes in the absence of antiferromagnetic interaction. The electronic spectra of the complexes in DMF display a broad d-d-absorption at ~600 nm. The magnetic moments and electronic spectra do not support tetrahedral structure for the complexes, since tetrahedral copper(II) complexes usually display magnetic moments of ~2.2 B.M. and they show no d-d bands in the range 1000–500 nm. The [Cu(ONSMe)X] complexes are, therefore, assigned square-planar structure with the ligand acting in a tridentate manner coordinating via the phenolic oxygen, the azomethine nitrogen and the S-methyl sulphur atom; the fourth-coordination position around copper(II) is occupied by a halide ion.

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References