Synthesis, characterization and thermal behaviour of ZnS₄P₂ chromophore as prototype

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Complexes of the type M(PPh₃)₂(dtc)₂, where M = Co(II), Ni(II), Zn(II) and Hg(II), PPh₃ = triphenylphosphine and dtc = sodium diethyldithiocarbamate, have been synthesized and characterized by elemental analysis, IR, UV-vis spectroscopy, TGA/DSC, magnetic moment and conductivity measurements. On the basis of these studies, an octahedral geometry has been proposed for all the complexes. The Zn-complex exhibits two-step thermogram leading to the formation of ZnS₄ as the end product at 900°C. Symmetrical bidentate coordination of the dithiocarbamate group has been observed in all the cases. Conductivity measurements of 1 mM solution of the complexes in DMSO show them to be non-electrolytes.

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Carbon disulphide is generally used for the preparation of thiocarbonyl, thioacyl, dithiocarbene, xanthates, cyanodithioimidocarbonate and dithiocarbanates¹³. Complexes with such ligands are used in vulcanization⁴, catalysis⁵ and in biology⁶. These bidentate sulfur systems may support unusual magnetic properties and are effectively used in the treatment of HIV-infected patients⁷. In fact, dithiocarbamates are strong chelators of heavy metals and employed in the quantitative/qualitative estimation of many metals like Ni, Cu, Zn, Hg, etc.⁸ Since the transition metal complexes with dithiocarbamates and xanthates are partially coordinatively unsaturated⁹, they can further coordinate with neutral molecules like pyridine, bipyridine or phenanthroline¹⁰. Although compounds with MS₂P₂ chromophore are known¹¹,¹², no compound with MS₄P₂ chromophore seems to have been reported so far. In continuation of our earlier studies¹³,¹⁴, we report here the synthesis and characterization of MS₄P₂ systems in order to ascertain the mode of linkage of dithiocarbamate moiety.

Materials and Methods

Hydrated metal chlorides (BDH), sodium diethyldithiocarbamates (Loba Chemie) and triphenylphosphine (Ranbaxy) were used as received. Methanol was used after distillation. Elemental analyses (C, H, N and S) were carried out with a Flash EA-1112 analyser, CE instrument. IR spectra (4000-400 cm⁻¹) were recorded on a FT-IR Perkin-Elmer BX as KBr disc. The conductivity measurements were carried out with a CM-82T Elco conductivity bridge in DMSO. The electronic spectra were recorded on a Cintra 5GBC spectrophotometer in DMSO. Magnetic susceptibility measurements were done with a Sherwood Scientific MSB Auto at room temperature. TGA/DSC was performed with a Universal V3.8 B TA SDT Q600 Build 51 thermal analyzer under nitrogen atmosphere using alumina powder as reference material. The heating rate was maintained at 10°C/min. Melting points were determined by the Wiswo melting point apparatus. The metal contents were estimated by complexometric titrations¹⁵.

Synthesis of Co(PPh₃)₂(dtc)₂

To a methanolic solution (30 mL) of CoCl₂(PPh₃)₂⁶ (1.31 g, 2 mmol) in a round bottom flask mounted on a magnetic stirrer was added dropwise a methanolic solution (20 mL) of sodium diethyldithiocarbamate (0.90 g, 4 mmol) at room temperature which instantaneously yielded a green precipitate. It was further stirred for 4 h. The precipitate was decanted, washed repeatedly with methanol and ether and dried over calcium chloride in vacuo (as depicted in Fig. 1). Yield: 68%.

Synthesis of Ni(PPh₃)₂(dtc)₂

A methanolic solution (20 mL) of sodium diethyldithiocarbamate (0.90 g, 4 mmol) was
transferred to a well-stirred blue solution of NiCl₂(PPh₃)₂ (2 mmol, 1.31 g) dissolved in 30 mL THF. It immediately afforded an olive-green precipitate at room temperature. The stirring was continued for 6 h and the precipitate was filtered, washed with methanol and dried over calcium chloride *in vacuo* (Fig. 1). Yield: 58%.

**Results and Discussion**

The complexes of the type [M(PPh₃)₂(dtc)] where M = Co(II), Ni(II), Zn(II), Hg(II) and dtc = S₂CN(C₂H₅)₂ can be conveniently obtained by the replacement of two chlorine atoms by the dtc group, Eq.(1). The complexes, thus obtained, are crystalline and are stable to heat and moisture. They decompose between 120-300 °C and above (Table 1). Their molar conductance of 1 mM solutions measured in DMSO indicated them to be non-electrolytes.

\[
\text{M(PPh₃)₂Cl₂ + 2NaCl → M(PPh₃)₂(dtc)₂ + 2NaCl} \quad (1)
\]

Dithiocarbamates may act both as a monodentate or a bidentate ligand. Bradley and Gitlitz have shown that the appearance of a solitary strong v(C-S) band in the 1000 ± 70 cm⁻¹ region is the characteristic of a bidentate dithiocarbamate group while the splitting of this band in the same region indicates monodentate binding of dithiocarbamate moiety. Brinkhoff and Grotens have also observed the v(C-S) band to appear in almost the same region. In the present study, we have observed a single sharp absorption band in the 987-1000 cm⁻¹ range assigned to v(C-S) confirming chelation of the dithiocarbamate to metal ions (Table 2).

A common thiourea band (S-C ====N)² has also been observed in the 1501-1519 cm⁻¹ range which is intermediate between C-N and C=O and might be due to delocalization of electrons over (S-C ====N) leading to an increase in π-bond character. For a symmetrically bound dithiocarbamate, this band

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>M. Pt. (°C)</th>
<th>Molar conductance (ohm cm²/m²)</th>
<th>Analysis, Found (Calcd), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(PPh₃)₂(dtc)₂</td>
<td>Green</td>
<td>&gt;300</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Ni(PPh₃)₂(dtc)₂</td>
<td>Olive-green</td>
<td>236</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Zn(PPh₃)₂(dtc)₂</td>
<td>Green</td>
<td>184</td>
<td>45.3</td>
<td></td>
</tr>
<tr>
<td>Hg(PPh₃)₂(dtc)₂</td>
<td>Yellow</td>
<td>120</td>
<td>41.4</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1 — Synthesis of the complex M(PPh₃)₂(dtc)₂, where M = Co(II), Ni(II), Zn(II) and Hg(II).**

Table 1 — Physical properties and analytical data of the complexes
 normally appears at higher wave numbers than in unsymmetrically bonded dithiocarbamate.

The M-S stretching mode falls in 200-600 cm\(^{-1}\) region. Generally, the \(\nu(M-S)\) depends upon the nature of the metal and the nature of substituents on the sulfur atom. In the present study, the \(\nu(M-S)\) were observed in the 490-506 cm\(^{-1}\) region. All the three fundamental vibrations of triphenylphosphine (\(q, r\) and \(t\)) showed only negligible change and are independent of the nature of the metal ion.

Three intense bands exhibited by Co(PPh\(_3\))(dtc)\(_2\) at 15,480; 20,781 and 24,272 cm\(^{-1}\) are attributed to three transitions from \(^4T_{1g}(F)\) ground state to \(^4T_{2g}(F), ^4A_{2g}(F)\) and \(^4T_{1u}(P)\) states, respectively, characteristic of the high-spin octahedral Co(II) complexes. \(D\) (1580 cm\(^{-1}\)) and \(B\) (753 cm\(^{-1}\)) are also in accordance with the octahedral environment of the Co(II) complexes. The room temperature magnetic moment of 4.39 BM further supports an octahedral arrangement around the Co(II) ion in Co(PPh\(_3\))(dtc)\(_2\).

The green Ni(PPh\(_3\))(dtc), exhibits three absorption bands at 12,898; 15,873 and 23,256 cm\(^{-1}\) corresponding to \(^4T_{2g}(F) \leftrightarrow ^4A_{2g}(F), ^4T_{1g}(F) \leftrightarrow ^4A_{2g}(F)\) and \(^4T_{1u}(P) \leftrightarrow ^4A_{2g}(F)\) transitions, respectively. The maxima between 29,548-33,300 cm\(^{-1}\) in the electronic spectrum of Ni(PPh\(_3\))(dtc), is ascribed to the intraligand transitions in the S\(_2\)CN\(^{-}\) group which has also been found by Pastorek in the case of...
[NiX(bz)Pd(tc)(PPh₃)] A magnetic moment value of 3.21 BM is also well within the specified range for octahedral coordination of Ni(II) ion in Ni(PPh₃)₂(dtc)₂. The value of Dₜ (1008 cm⁻¹) and B (793 cm⁻¹) are also in agreement with the octahedral geometry of the Ni(II) complexes. However, the diamagnetic Zn(PPh₃)₂(dtc)₂ and Hg(PPh₃)₂(dtc)₂ were proposed to be octahedral.

As all the complexes have similar ligand environment, the TGA/DSC plot of only a representative Zn-complex is reported. The complex, Zn(PPh₃)₂(dtc)₂ was heated up to 900°C (Fig. 2). The stepwise fragmentation pattern of Zn(PPh₃)₂(dtc)₂ is depicted in Fig. 3. The DSC curve of the sample depicts typical endothermic minima, the first of which occurs at 184°C. This endothermic peak corresponds to the melting of the complex, as the corresponding TGA curve shows no weight loss at this temperature. However, two distinct endothermic peaks represent the decomposition of the complex. The first peak is broad and large with a minimum at 346°C, while the second has a minimum at 784°C which is small and sharp. Thus, two different steps of decomposition corresponding to two different fragments can be vividly seen. The first step shows a weight loss of 71.3% corresponding to two triphenyolphosphine and four ethene molecules (Calcd 71.8%). The second decomposition step with a weight loss of about 6.8% is in agreement with the calculated value of 6.3% which is exactly equal to the weight loss of N₂ and two C₂H₄ molecules. The final residue of 21% at 900°C corresponds to the ZnS₄ formed (Calcd 21.7%) as the eventual product which is quite common in dithiocarbamato complexes.

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References