Synthesis and characterization of tris[butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamato]-cobalt(III) seskvitoluene

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A new bidentate ligand butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamate (bm$pdtc$) was prepared, as the sodium salt. In the reaction of hexaaminecobalt(III) chloride with Na$bm$pdtc, the corresponding $tris[bm$pdtc$]$ complex was prepared. The complex was characterized by elemental analysis, infrared, electronic absorption, $^1$H and $^{13}$C-NMR spectroscopy.

Keywords: cobalt(III) complex, dithiocarbamate, bidentate ligand.

Dithiocarbamates are organosulphur compounds with wide applications. They are used as accelerators in vulcanization, as high-pressure lubricants and as fungicides and pesticides. Also, dithiocarbamates are often used for the synthesis of transition metal complexes.1–15 As the dithiocarbamates themselves, dithiocarbamate-metal complexes have been used in agriculture for controlling insects and fungi, in the treatment of alcoholism, etc.3

Dithiocarbamates have been found to act almost as uninegative dibentate ligands, coordinating through both sulphur atoms, and both tetra- and hexa-coordinated complexes of many transition metal ions have been isolated.4,9–15 Little is known about mixed-ligand dithiocarbamate complex,13–15 and cyclam is a most useful macrocycle to form and stabilize those complexes.

In this work, a new bidentate ligand butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamate (bm$pdtc$) was prepared, as the sodium salt. In the reaction of hexaamminecobalt(III) chloride with the sodium bm$pdtc$ ligand, the corresponding [Co(bm$pdtc$)$_3$] complex
was obtained. The complex was characterized by elemental analysis, infrared, electronic absorption and \(^1\)H and \(^{13}\)C-NMR spectroscopy.

**EXPERIMENTAL**

**Materials**

Reagents, NaOH, CS\(_2\), diethylether, p.a., were obtained commercially (Merck) and used without further purification. The amine was obtained by the procedure described by Mićović et al.\(^{16}\)

**Preparation of sodium butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamate, Na\(bm\)pdtc\)**

The sodium salt of the ligand was prepared by treating 1.03 g butyl-(1-methyl-3-phenyl-propyl)-amine in 20.00 cm\(^3\) of dry diethylether with 0.48 cm\(^3\) (0.38 g) CS\(_2\) and adding 0.20 g NaOH with vigorous stirring over a 5 h period. Mole ratio amine : CS\(_2\) : NaOH = 1 : 1 : 1. Yield: 1.12 g (78.2 %). The crude, light yellow product was used directly for the synthesis of the corresponding complex.

**Preparation of tris\([\text{butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamato}\]\)cobalt(III), seskvitoluene, \([\text{Co(bm}\text{pdtc})_3]\).1.5 C\(_6\)H\(_5\)CH\(_3\)**

To a solution of 0.267 g (0.001 mol) of hexaamminecobalt(III) chloride in 10.00 cm\(^3\) of water, 0.910 g (0.003 mol) of sodium dithiocarbamate was added. The green trisdithiocarbamate cobalt(III) which immediately precipitated was extracted with toluene and evaporated under reduced pressure. The product was dried at 115 °C. Yield: 0.571 g (63.5 %). Anal. Calcd. for \([\text{Co(bm}\text{pdtc})_3]\).1.5 C\(_6\)H\(_5\)CH\(_3\): C, 62.95; H, 7.51; N, 4.23 %. Found: C, 62.66; H, 7.75; N, 4.14 %.

**Characterization**

The infrared spectrum was recorded on a Perkin-Elmer FTIR 31725-X spectrophotometer using the KBr pellet technique. The electronic absorption spectrum was recorded on a Varian GBC 911A spectrophotometer. A 1×10\(^{-3}\) molar solution of the complex in chloroform was used for this measurement. The \(^1\)H and \(^{13}\)C-NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer at room temperature. The chemical shifts were determined relative to TMS. Elemental analyses for C, H, N were performed by standard methods.

**RESULTS AND DISCUSSION**

**Electronic absorption spectrum**

The complex \([\text{Co(bm}\text{pdtc})_3]\) (Fig. 1) is diamagnetic and has an electronic spectrum which can be assigned to low-spin cobalt(III) in an octahedral environment.

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**Fig. 1. Possible structure of \([\text{Co(bm}\text{pdtc})_3]\) complex.**
Thus the peak at 636.5 nm and the shoulder at 490.0 nm arise from $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions, respectively.\textsuperscript{17} The other lower peaks are probably charge-transfer in origin.

Infrared spectrum

Two regions in the IR spectrum of the [Co(bm\textsuperscript{pdtc})\textsubscript{3}] complex have proven valuable in arguments concerning the electronic and structural characteristics of this compound. The presence of the thioureido band between 1530–1430 cm\textsuperscript{-1} suggest a considerable double bond character in the C\textsuperscript{=N} bond vibration of the S\textsubscript{2}C–NR\textsubscript{2} group.\textsuperscript{13} The band present in the 940 cm\textsuperscript{-1} range is attributed to the prevailing contribution of $\nu$(C\textsuperscript{=S}).\textsuperscript{15} Vibrations in these ranges have been used effectively in differentiating between monodentate and bidentate dithiocarbamate ligands.\textsuperscript{4,5,9–13} The presence of only one strong band supports bidentate coordination of the dithio ligand, whereas a doublet is expected in the case of monodentate coordination.\textsuperscript{6} The $\nu$(C\textsuperscript{=S}) and $\nu$(C\textsuperscript{=N}) stretching frequencies fall in the 1032 cm\textsuperscript{-1} (1001 cm\textsuperscript{-1} for the free ligand) and 1473 cm\textsuperscript{-1}, respectively. The methyl group in the complex, as a medium strong bands in the 2960 cm\textsuperscript{-1} range, can be related to the asymmetric CH\textsubscript{3} stretching vibration, while bands at 1380–1360 cm\textsuperscript{-1} are due to the degenerate symmetric vibrations of the methyl group.\textsuperscript{14}

\textsuperscript{1}H and \textsuperscript{13}C-NMR spectra

The $^1$H-NMR spectrum of tris(dithiocarbamato)cobalt(III) complex showed a pattern at $\delta$ 7.2 ppm, which may be assigned to the aromatic protons. The peak at $\delta$ 3.5 ppm belong to the tertiary proton (Table I). The resonance between $\delta$ 2.6–1.3 ppm may be assigned to methylene protons and at $\delta$ 0.9 ppm to methyl protons.\textsuperscript{16}

<table>
<thead>
<tr>
<th>$^1$H/(ppm)</th>
<th>$^{13}$C/(ppm)</th>
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</thead>
<tbody>
<tr>
<td>0.9 (C1, C14)</td>
<td>13.7 (C1)</td>
</tr>
<tr>
<td>1.3 (C2, C3)</td>
<td>20.5 (C2)</td>
</tr>
<tr>
<td>1.9 (C6)</td>
<td>32.7 (C3)</td>
</tr>
<tr>
<td>2.6 (C4, C7)</td>
<td>44.3 (C4)</td>
</tr>
<tr>
<td>3.5 (C5)</td>
<td>53.4 (C5)</td>
</tr>
<tr>
<td>7.2 (C9–C13)</td>
<td>36.6 (C6)</td>
</tr>
</tbody>
</table>

In the case of the $^{13}$C-NMR spectrum, the complex showed pattern at $\delta$ 205.9 (thiocarboxylato C), 141.6–125.9 (aromatic C), 53.7 (tertiary C), 53.4–30.9 (secondary C) and 18.6–13.7 (primary C).\textsuperscript{16}

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА
TRIC((1-METIL-3-FENIL-PROPIL)-DITIOKARBAMATO)KOBALT(III) SESKVITOLUENA

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Синтезисан је нови бидентатни лиганд бутил-(1-метил-3-фенил-пропил)-дитиокарбамат (bmFpdc), као натријумова со. Реакцијом хексаминкобалт(III)-хлорида и наведеног лиганда добијен је одговарајући комплекс [bmFpdc(buтил-(1-метил-3-фенил-пропил)-дитиокарбамат)кобалт(III)]. Комплекс је окarakтерисан елементалном анализом, инфрацрвеним, електрооско-апсорpcionим. $^1$H и $^{13}$C-NMR спектром.

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REFERENCES