

NOTE

**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 (bmΦpdtc) was prepared, as the sodium salt. In the reaction of hexaaminocobalt(III) chloride with NabmΦpdtc, the corresponding *tris*[butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamato]cobalt(III), [Co(bmΦpdtc)₃] complex was prepared. The complex was characterized by elemental analysis, infrared, electronic absorption, ¹H and ¹³C-NMR spectroscopy.

Keywords: cobal(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 (bmΦpdtc) was prepared, as the sodium salt. In the reaction of hexaamminocobalt(III) chloride with the sodium bmΦpdtc ligand, the corresponding [Co(bmΦpdtc)₃] complex

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was obtained. The complex was characterized by elemental analysis, infrared, electronic absorption and ^1H 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, $\text{Nabm}\Phi\text{pdtc}$

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

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 $[\text{Co}(\text{bm}\Phi\text{pdtc})_3] \cdot 1.5 \text{C}_6\text{H}_5\text{CH}_3$: 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 ^1H 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 $[\text{Co}(\text{bm}\Phi\text{pdtc})_3]$ (Fig. 1) is diamagnetic and has an electronic spectrum which can be assigned to low-spin cobalt(III) in an octahedral environment.

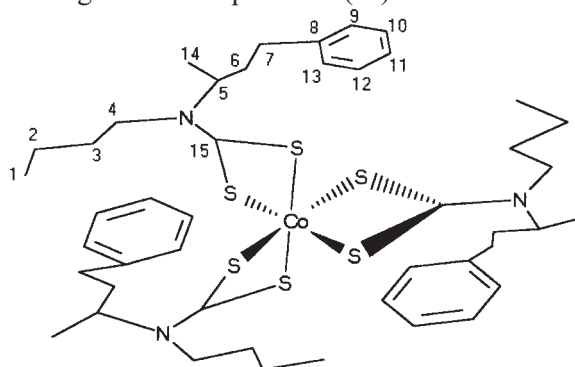


Fig. 1. Possible structure of $[\text{Co}(\text{bm}\Phi\text{pdtc})_3]$ complex.

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.¹⁷ The other lower peaks are probably charge-transfer in origin.

Infrared spectrum

Two regions in the IR spectrum of the $[\text{Co}(\text{bm}\Phi\text{pdtc})_3]$ complex have proven valuable in arguments concerning the electronic and structural characteristics of this compound. The presence of the thioureido band between $1530\text{--}1430\text{ cm}^{-1}$ suggest a considerable double bond character in the $\text{C}=\text{N}$ bond vibration of the $\text{S}_2\text{C}\text{--NR}_2$ group.¹³ The band present in the 940 cm^{-1} range is attributed to the prevailing contribution of $\nu(\text{C}=\text{S})$.¹⁵ Vibrations in these ranges have been used effectively in differentiating between monodentate and bidentate dithiocarbamate ligands.^{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.⁶ The $\nu(\text{C}=\text{S})$ and $\nu(\text{C}=\text{N})$ stretching frequencies fall in the 1032 cm^{-1} (1001 cm^{-1} for the free ligand) and 1473 cm^{-1} , respectively. The methyl group in the complex, as a medium strong bands in the 2960 cm^{-1} range, can be related to the asymmetric CH_3 stretching vibration, while bands at $1380\text{--}1360\text{ cm}^{-1}$ are due to the degenerate symmetric vibrations of the methyl group.¹⁴

${}^1\text{H}$ and ${}^{13}\text{C}$ -NMR spectra

The ${}^1\text{H}$ -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 $\delta 2.6\text{--}1.3$ ppm may be assigned to methylene protons and at $\delta 0.9$ ppm to methyl protons.¹⁶

TABLE I. ${}^1\text{H}$ - and ${}^{13}\text{C}$ -NMR chemical shifts (ppm) of the $[\text{Co}(\text{bm}\Phi\text{pdtc})_3]$ complex

${}^1\text{H}/(\text{ppm})$	${}^{13}\text{C}/(\text{ppm})$	
0.9 (C1, C14)	13.7 (C1)	30.9 (C7)
1.3 (C2, C3)	20.5 (C2)	141.6 (C8)
1.9 (C6)	32.7 (C3)	128.4 (C9, C10, C12, C13)
2.6 (C4, C7)	44.3 (C4)	125.9 (C11)
3.5 (C5)	53.4 (C5)	18.6 (C14)
7.2 (C9–C13)	36.6 (C6)	205.9 (C15)

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

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА
ТРИС[БУТИЛ-(1-МЕТИЛ-3-ФЕНИЛ-ПРОПИЛ)-ДИТИОКАРБАМАТО]КОБАЛТ(III)
СЕСКВИТОЛУЕНА

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Синтетисан је нови бидентатни лиганд бутил-(1-метил-3-фенил-пропил)-дитиокарбамат (bmФрdтс), као натријумова со. Реакцијом хексаамминкобалт(III)-хлорида и наведеног лиганда добијен је одговарајући комплекс *tris*[бутил-(1-метил-3-фенил-пропил)-дитиокарбамато]кобалт(III), [Co(bmФрdтс)₃]. Комплекс је окарактерисан елементалном анализом, инфрацрвеним, електронско-апсорпционим, ¹H и ¹³C-NMR спектрима.

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