

Synthesis And Characterization Of Mixed piperidine Dithiocarbamate-Phosphine Complexes Containing Co (II) and Ni(II)

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ABSTRACT

Complexes of the type $[M(PPh_3)_2(pddtc)Cl]$, where $M = Co(II)$ and $Ni(II)$, $[pddtc]$ = piperidinedithiocarbamate, and PPh_3 = triphenylphosphine have been synthesized and characterized by elemental analyses, IR, electronic, 1H NMR spectral data, magnetic moment and conductivity measurements. The spectroscopic evidence suggests that all the complexes have five coordinate geometry around the metal ion. The thermal studies reveal that the complex $[Co(PPh_3)_2(pddtc)Cl]$ decomposes in two stages while the DTA studies show that both weight loss steps are exothermic. The conductivity measurements data (1mmol solution) implies non-electrolytic behavior for all the complexes as evident by their low conductivity values obtained at room temperature. A symmetrical bidentate coordination has been observed for the dithiocarbamate moiety rendering the metal five coordinate.

KEYWORDS: spectroscopic measurements, dithiocarbamate, TGA, triphenylphosphine

INTRODUCTION

The transition metal complexes with easily replaceable tertiary phosphorus ligands are used in many homogeneous catalytic reactions.[1] To understand the proper mechanism of catalytic reactions, one must investigate the chemical properties and reactivity of the transition metal-phosphorous unit in detail. In this connection, insertion of a PPh_3 ligand is of significant interest.

Dithiocarbamates are known to inhibit the growth of bacteria and fungi.[2] Since the activity of the ligand is altered in the presence of metal ions it was thought worthwhile to study metal complexes of piperidine dithiocarbamate that also contain triphenyl phosphine.

Experimental

Piperidine, CS_2 (Fluka), THF (Merck), hydrated metal chlorides (BDH) were used as received. Elemental analyses (C, H, N, S) were carried out with a 1106 Carlo Erba analyzer. The metals were determined by complexometric titration using EDTA and chlorine was determined gravimetrically. The IR spectra ($4000-450\text{ cm}^{-1}$) were recorded on an Agilent technologies spectrometer using KBr discs. The conductivity measurements were carried out with a Systronics conductivity bridge in chloroform (Table I). Thermogravimetric analysis of $Co(II)$ complex and measurements of mass losses versus temperature (TGA), was determined using a SDT Q600 thermogravimetric analyzer under $N_2(g)$ (purge). The experiments were performed in $25-800^\circ C$ temperature range, heating rate at $5^\circ C/min$, 6.265 mg of sample was placed on a silica pan. Points of rapidly changing mass, slowly changing mass were identified from the TGA plot. Magnetic susceptibility measurements were done with a 155 Allied Research vibrating sample magnetometer at room temperature. 1H NMR spectra were recorded on a Bruker ACF 300 spectrometer at 300.12 MHz, using TMS as a reference in $DMSO-d_6$.

Synthesis of sodium salt of piperidine dithiocarbamate $Na(pddtc)$ where pd = piperidine and dtc = dithiocarbamate

To a methanolic solution (50 ml) of piperidine (1.0 ml, 10 mmol) carbon disulfide (0.61 ml, 10 mmol) was added dropwise with continuous stirring in an icebath followed by the addition of NaOH (0.4 g, 10 mmol) dissolved in minimum amount of aqueous methanol. The product obtained was filtered, washed with aqueous methanol and dried over phosphorous pentaoxide in vacuo.

Synthesis of $[M(PPh_3)_2(pddtc)Cl]$ where $M = Co(II)$ or $Ni(II)$

A solution of the sodium salt of piperidine dithiocarbamate (5 mmol) in THF (20 mL) was treated with 20 mL of a THF solution of $[(PPh_3)_2MCl_2]$ (5 mmol) in a 100 ml round bottomed flask. The mixture was continuously stirred over a period

of half an hour at room temperature. The precipitates thus obtained were filtered, washed with diethyl ether, recrystallized from CHCl_3 and dried in vacuo. Yield 69-71%

RESULTS AND DISCUSSION

The reactions of the complexes $[\text{Co}(\text{PPh}_3)_2\text{Cl}_2]$ and $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ with the sodium salts of piperidine dithiocarbamate (pddtc) yield $[\text{Co}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ and $[\text{Ni}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ respectively. They are formed by the replacement of chloride ions by dithiocarbamates according to the schemes shown in Figure.

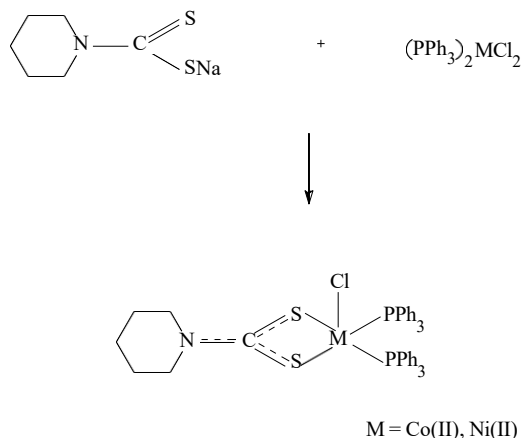


Fig. 1. Synthesis of $[\text{M}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$

The molar conductance of the complexes measured in DMF ($7\text{--}18 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) indicate that they are non-electrolytes. [3]

TGA

Thermal analysis of $[\text{Co}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ was done in the temperature range of $25\text{--}800^\circ\text{C}$, using a combined thermogravimetric analyzer and differential thermal analyzer. The thermogram may be divided into two major portions showing weight loss of various components. The first step shows a weight loss of about 3.67% in the temperature range of 100° to 160°C consistent with the loss of chlorine that would correspond to a calculated weight loss of 3.73%. The second step from 200° through 380°C shows a loss of 63.3%, which compares well with a weight loss of 63.9% for two molecules of triphenyl phosphine and piperidine moiety. At 380°C , the residue remaining is cobalt sulfide (21%). The metal sulfide was left as residue since the TGA has been carried out under nitrogen atmosphere. [4] The DTA studies show that both weight loss steps are exothermic.

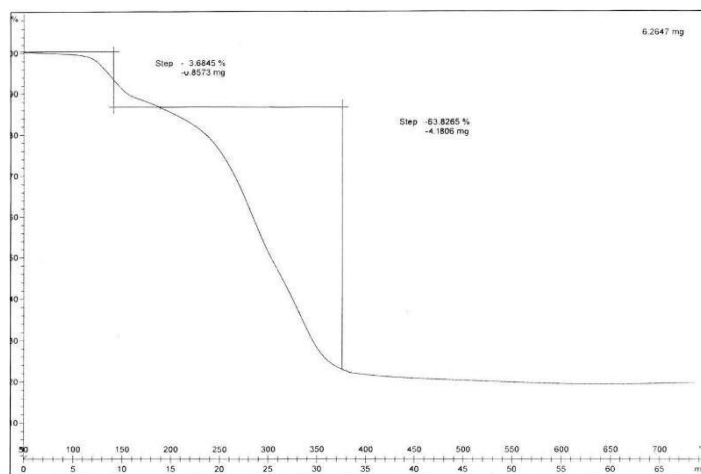
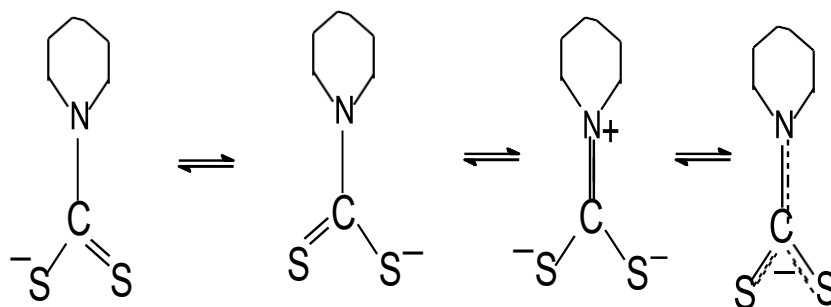


Fig. 2. TGA of $[\text{Co}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$

IR spectra

The IR spectral region $3300\text{--}3500\text{ cm}^{-1}$ of all the complexes, is devoid of any absorption indicating the absence of N–H groups. Attempts have been made to deduce the denticity of piperidine dithiocarbamate using $\nu(\text{C–N})$ and $\nu(\text{C–S})$. The $950\text{--}1050\text{ cm}^{-1}$ region has been shown to be reliable for determining the mono or bidentate nature of the ligand. According to Brinkhoff and Grotens,[5] the presence of only one strong C–S stretching vibration in the $950\text{--}1050\text{ cm}^{-1}$ region, is indicative of bidentate bonding of the dithiocarbamate ligand, while bonding is unidentate if this peak splits into two closely spaced bands. In the IR spectra of all the complexes, a strong absorption band is observed around 1000 cm^{-1} suggesting the bidentate nature of the piperidinedithiocarbamate rendering the metal five coordinate. A similar five coordinate organozirconium dithiocarbamate has been reported.[5] The thioureide bands appeared between 1423 and 1495 cm^{-1} , range which is intermediate between $\nu(\text{C=N})$ and $\nu(\text{C–N})$ indicating a partial double bond character between carbon and nitrogen. In both complexes bands in the range of $507\text{--}510\text{ cm}^{-1}$ are observed which may be assigned to a coordinated chloro group.[6] New absorption bands were also observed in complexes in the region $568\text{--}578\text{ cm}^{-1}$ and are assigned to M–S stretching frequencies.[7]



UV-Vis Spectra

The electronic spectra of all the complexes were recorded in CHCl_3 . The UV spectra of dithiocarbamate exhibited two bands in the range of 250 to 290 nm due to the $\pi\text{--}\pi^*$ transition of the N–C–S groups and a $n\text{--}\pi^*$ transition involving the lone pairs of electrons located on the sulfur atoms. These bands are shifted to higher wavelength after complexation, showing the involvement of NCS_2 group in coordination. The Co(II) complex shows three d–d bands at $24,330$, $16,556$, and $10,115\text{ cm}^{-1}$, a well-defined characteristic feature of a five coordinate system with square pyramidal geometry similar to that reported earlier.[7]

The solution spectrum of Ni(II) complex with piperidine dithiocarbamate exhibits two bands in the range of $17,060$ and $26,995\text{ cm}^{-1}$. This type of spectrum is consistent with a trigonal bipyramidal complex of Ni(II) . [8–9] Five coordinate complexes of Ni(II) are preferentially formed by multidentate ligands although unidentate ligands also yield a five coordinate complex where the lattice force can impose distorted structures as has been found in $[\text{Ni}(\text{CN})_5]^{3-}$ [10] Based on these results as well as on those of the microanalyses and magnetic study, we propose that the Ni(II) species in the complex has a trigonal bipyramidal structure.

Of the two idealized geometries, square pyramidal, C_{4v} and trigonal bipyramidal, D_{3h} the d^7 and d^8 ions can assume either a low or a high spin configuration according to whether the energy separation between the two highest orbitals in each symmetry is higher or lower than the spin pairing energy. It has been experimentally verified that with soft donor atoms such as P, low spin complexes are obtained, whilst with hard atoms formation of high spin complexes are preferred although the sulfur and halogen donor atoms yield both high and low spin complexes. In our case, low spin complexes are obtained with Ni(II) and Co(II) complexes containing sulfur, phosphorous and halogen donor atoms, which can be distinguished from their μ_{eff} value. The magnetic moment values of 2.2 BM for $[\text{Co}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ complex confirms the low spin square pyramidal geometry around the Co(II) ion, while the diamagnetic nature of Ni(II) complexes provide evidence for a low spin TBP structure.

It has been reported by Grotjah et al.[10] that the position of bulky ligands in five coordinate complexes depend on the electron count of the complex under consideration. For five coordinate d^8 complexes, both SQP and TBP structures are possible as has been found in the case of $[\text{Ni}(\text{CN})_5]^{3-}$ which exists in both these forms in equilibrium with each other. However, the TBP structure is found to be prevalent and is adopted by many Ni(II) complexes.

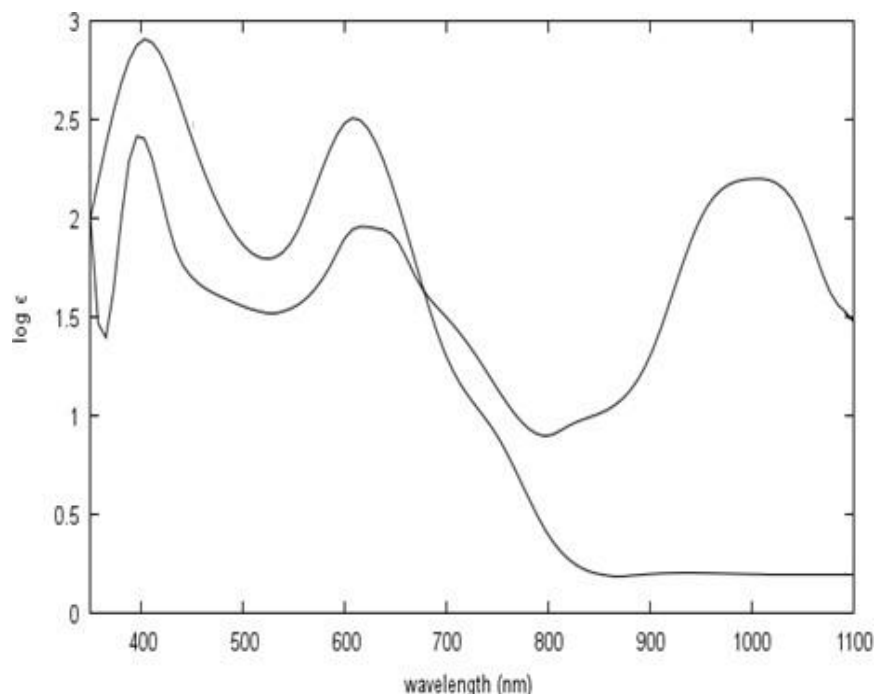


Fig.3. UV-Vis spectrum of $[\text{Ni}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ and $[\text{Co}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$

^1H NMR Spectra

The ^1H NMR spectra of $[\text{pddtc}]$ and $[\text{Ni}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ was recorded in $\text{DMSO}-d_6$. Depending on the chemical environment of the protons in $[\text{pddtc}]$ three signals were envisaged. They were found at C_1 (4H, br) at δ 2.77, C_2 (4H, q) at δ 1.51 and C_3 (2H, q) at δ 1.40. The ^1H NMR spectrum of $[\text{Ni}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ also exhibits three signals. They were found at δ 3.21 (4H, br, C_1 and C_1' protons), δ 1.73 (4H, q, C_2 and C_2' protons) and δ 1.51 (2H, q, C_3 protons). The protons in $[\text{Ni}(\text{PPh}_3)_2(\text{pddtc})\text{Cl}]$ are shifted to lower field than the protons in $[\text{pddtc}]$ which implies the partial drift of electron cloud of hydrogen towards the transition metal ions. The resonances due to the phenylic protons were found as a multiplet between δ 7.5 and 7.9.

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Table I. Physical Properties and Analytical Data for Metal Chelates

	Compounds (Formula weight)	Yield (%)	Colour	M.p. (°C)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	% Analysis Found (Calcd).				
						C	H	N	S	M
(1)	[Co(PPh ₃) ₂ (pddtc)Cl] (778.43)	71	Dark green	300 d	07	47.11 (46.97)	5.24 (5.52)	11.07 7.28 (10.96) (7.57)	24.17 (25.08)	
(2)	[Ni(PPh ₃) ₂ (pddtc)Cl] (778.19)	69	Light green	305 d	11	47.09 (47.07)	5.21 (5.19)	11.02 7.38 (10.96) (7.54)	24.13 (24.08)	

Table II. Important IR Bands (cm⁻¹) of Ligands and their Metal Chelates

	Compounds	$\nu(\text{C-N})$	$\nu(\text{C=S})$	$\nu(\text{M-Cl})$	$\nu(\text{M-S})$
(1)	[Co(PPh ₃) ₂ (pddtc)Cl]	1425 (s)	992 (s)	507	568
(2)	[Ni(PPh ₃) ₂ (pddtc)Cl]	1428 (s)	989 (s)	510	578

Table III. Magnetic Susceptibility, Electronic Spectra and Ligand Field Parameters of the Complexes.

	Compounds	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	Log ϵ (mol ⁻¹ cm ²)	Possible assignments
(1)	[Co(PPh ₃) ₂ (pddtc)Cl]	2.20	16,556 24,330 10,115	1.98 2.31 2.95	(e) ⁴ (b ₂) ² (a ₁) ¹ → (e) ³ (b ₂) ² (a ₁) ² (e) ⁴ (b ₂) ² (a ₁) ¹ → (e) ⁴ (b ₂) ² (b ₁) ¹ (e) ⁴ (b ₂) ² (a ₁) ¹ → (e) ⁴ (b ₂) ¹ (a ₁) ²
(2)	[Ni(PPh ₃) ₂ (pddtc)Cl]	Diamagnetic	17,060 26,995	2.42 2.95	(e'') ⁴ (e') ⁴ → (e'') ⁴ (e') ³ (a ₁ ') ¹ (e'') ⁴ (e') ⁴ → (e'') ³ (e') ⁴ (a ₁ ') ¹