

Nickel(II) cyclohexylethyldithiocarbamate complexes with monodentate P-donor ligands in the coordination sphere

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Abstract: A series of new Ni(II) dithiocarbamate compounds of the composition $[\text{NiX}(\text{cetdtc})(\text{PR}_3)]$ (X = Cl, Br, I, NCS; cetdtc = cyclohexylethyldithiocarbamate; R = phenyl, *n*-butyl) has been synthesized. All the isolated complexes have been characterized by elemental analysis, IR and UV/VIS spectroscopy, $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy, thermal analysis, magnetochemical and conductivity measurements. On the basis of the results of the physico-chemical study, all complexes are diamagnetic, non-electrolytes, with a square-planar NiS_2PX chromophore.

Keywords: nickel(II) cyclohexylethyldithiocarbamate complexes, monodentate P-donor ligands, synthesis, $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy.

INTRODUCTION

For several years considerable attention has been paid to dithiocarbamate compounds. Firstly, their biological effects have been researched, including anti-alkylation¹ anti-HIV properties² and antitumor activity against leucemic cells.³ Some dithiocarbamate complexes also have some practical applications. For example, they are used in agriculture as fungicides and pesticides.⁴

Furthermore, dithiocarbamates have been studied on account of their interesting coordination behaviour. In spite of the fact that many dithiocarbamate compounds with different transition metals are described in the chemical literature, we have only considered Ni(II) coordination compounds with non-symmetrical dithiocarbamates. We have principally searched for information on the synthesis and physico-chemical studies of the coordination compounds, such as the basic Ni(II) cyclohexylethyldithiocarbamate complex and Ni(II) dithiocarbamate complexes with monodentate P-donor ligands. Two relevant articles concerning the synthesis⁵ and structural characterization⁶ of $[\text{Ni}(\text{cetdtc})_2]$ (c = cyclohexyl; et = ethyl; dtc

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= S₂CN⁻ = dithiocarbamate) have been found. X-Ray structural analysis of this complex confirmed a four-coordinated nickel atom, which is bound by two dithiocarbamate ligands. Square-planar Ni(II) dithiocarbamate complexes of the general formula [Ni(R₁R₂dtc)(PR₃)₂]Y (R₁ = H, methyl, benzyl, cyclohexyl; R₂ = 2-hydroxyethyl, carboxymethyl, 3-(methylthio)-1-carboxypropyl, 2-(3-indolyl)-1-carboxyethyl, isopropyl, ethyl; R = phenyl, *n*-butyl; Y = ClO₄, BPh₄, PF₆),⁷⁻¹⁰ in which one of the dithiocarbamate ligand is replaced by two monodentate P-donor ligands, have been extensively studied. X-Ray structural analysis of [Ni(meadtc)(PPh₃)₂]ClO₄ (m = methyl; ea = 2-hydroxyethyl)⁸ and [Ni(bzⁱprdtc)(PPh₃)₂]ClO₄·0.5H₂O (bz = benzyl; ⁱpr = isopropyl)¹⁰ confirmed a slightly distorted square-planar coordination of the NiS₂P₂ chromophore. In addition to these compounds, complexes containing the dithiocarbamate ligand, monodentate P-donor ligand and a simple inorganic anion (Cl, Br, I or NCS) as an additional ligand in the Ni(II) coordination sphere have also been studied. Recently, square-planar coordination compounds of the general composition [NiX(R₁R₂dtc)(PR₃)₂] (X = Cl, NO₂, NO, Br, NCS, I; R₁ = H, benzyl; R₂ = 2-hydroxyethyl, methyl, ethyl, isopropyl, *sec*-butyl, *n*-butyl, isobutyl, *tert*-butyl, phenyl, *p*-chlorophenyl, *p*-methoxyphenyl, *p*-methylphenyl, 1-phenyl-2,3-dimethyl-1,5-dihydro-5-oxo-pyrazol-4-yl; R = phenyl, *n*-butyl)^{7,11-16} have been prepared and characterized. In the case of [NiX(bzⁱprdtc)(PPh₃)₂] (X = Cl, Br, I; bz = benzyl; ⁱpr = isopropyl)¹⁵ X-ray structural analysis showed the existence of a nickel atom with a coordination number four in a square-planar arrangement (NiS₂PX chromophore). However, no information on complexes of this type with the cyclohexylethyldithiocarbamate ligand were found in the literature.

In this paper, the synthesis and a physico-chemical study of several new Ni(II) cyclohexylethyldithiocarbamate complexes of the formula [NiX(cetdtc)(PR₃)₂] containing a monodentate P-donor ligand (PPh₃, P^{*n*}Bu₃) and a simple inorganic ligand (Cl, Br, I, NCS) in the nickel coordination sphere are reported. This work was also aimed at studying the influence of the cyclohexylethyldithiocarbamate ligand, monodentate P-donor ligands and simple X-inorganic ligands on the structure and properties of the newly synthesized complexes.

EXPERIMENTAL

Materials

N-cyclohexylethylamine (98 %), triphenylphosphine (99 %) and CDCl₃ (99.8 Atom % D) were purchased from Aldrich Co. Tributylphosphine (85 %) was from Fluka Co. The other reagents were supplied by Lachema Co. and were all of p.a. purity. The starting compounds [Ni(cetdtc)₂], [NiX₂(PPh₃)₂] and [NiX₂(P^{*n*}Bu₃)₂] were synthesized according to the procedures described in the literature.^{17,18}

Synthesis of [NiX(cetdtc)(PPh₃)₂] (X = Cl, Br, I, NCS)

The complexes were synthesized by the reaction of a suspension of fine pulverized parent complex [Ni(cetdtc)₂] (1 mmol) with pulverized [NiX₂(PPh₃)₂] (1 mmol) in chloroform (25 cm³). The mixture was intensively stirred at room temperature until dissolution of all the reaction compo-

nents. In all cases, the resulting solution was filtered and an excess of diethyl ether was added to the filtrate. The formed orange-violet precipitates were filtered off, washed with diethyl ether and dried under an IR lamp at 40 °C.

Synthesis of [NiX(cetdtc)(PⁿBu₃)] (X = Cl, Br, I, NCS)

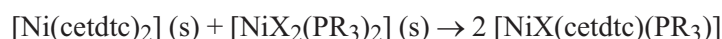
These complexes were prepared by the same procedure. To a suspension of finely pulverized [Ni(cetdtc)₂] (1 mmol) in chloroform (25 cm³), [NiX₂(PⁿBu₃)₂] (1 mmol) was added. The reaction mixture was stirred at room temperature until all the components had dissolved. The solution was filtered and left to crystallize at room temperature. In all cases, an oily product was obtained, which transformed into a powdered substance after addition of petroleum ether. The final orange-violet product was then filtered off, washed with petroleum ether and dried under an IR lamp at 40 °C.

Analytical methods and physical measurements

The content of nickel was determined by chelatometric titration using murexide as the indicator.¹⁹ Chlorine and bromine were determined according to the Schöniger method.²⁰ Elemental analyses (C, H, N, S) were performed on an EA 1108 instrument (Fisons). The room temperature magnetic susceptibilities of all compounds were measured using the Faraday method with Co[Hg(NCS)₄] as a calibrant on a laboratory designed instrument with a Sartorius 4434 MP-8 microbalance. The molar conductivities of 10⁻³ M solutions of all the complexes were measured with a Conductivity Hand-Held Meter LF 330 (WTW GmbH) at 25 °C. Diffuse-reflectance electronic absorption spectra (45000–11000 cm⁻¹) were carried out using a Specord M 40 instrument and IR spectra (4000–400 cm⁻¹) were recorded on a Specord M 80 instrument (Carl Zeiss, Jena) using nujol mulls. Thermal analysis was performed on an Exstar 6000, TG/DTA 6200 device (Seiko, Japan; sample weight 6.8–17.9 mg, temperature range 20–1100 °C, heating rate 2.5 °C/min; an air atmosphere). Melting points were determined by means of Boëtius instrument (VEB Wägetechnik Rapido, PHMK 79/2122). ³¹P{¹H}-NMR spectra were measured on a Bruker Avance 300 spectrometer operating at a frequency of 121.49 MHz. The measurement were performed at 300 K. All samples were prepared by dissolving the compounds in CDCl₃. 85 % H₃PO₄ was used as an external reference.

RESULTS AND DISCUSSION

The new coordination compounds were prepared by reaction between the parent Ni(II) dithiocarbamate, *i.e.*, [Ni(cetdtc)₂], and Ni(II) complexes of the type [NiX₂(PR₃)₂] in a chloroform suspension according to the following general scheme:



where X = Cl, Br, I, NCS and R = phenyl, *n*-butyl.

The complexes having PPh₃ ligand were obtained in form of orange-violet solids while the complexes bearing a PⁿBu₃ ligand separated from chloroform solution as oils. On account of this, petroleum ether was used in order to transform the oily products into orange-violet powdered substances. It is notable that the isolated coordination compounds were stable in air and soluble in most common organic solvents, such as chloroform, dichloromethane, nitromethane and acetone. They were insoluble in petroleum ether, diethyl ether and water. The colours, yields, analytical data and composition of all the complexes are given in Table I. The molar conductivities, spectral data, melting points (m.p.) and the results of the thermal analysis are summarized in Table II.

TABLE I. Colours, yields and chemical compositions of the isolated complexes

No.	Complex	Colour	Yield/%	Found (Calcd.)/%						X ^a
				Ni	C	H	N	S		
1	[NiCl(cetdic)(PPh ₃)] C ₂₇ H ₃₁ CINNiPS ₂	violet	60	10.2 (10.5)	57.8 (58.0)	5.4 (5.6)	2.5 (2.5)	11.1 (11.5)	6.5 (6.3)	
2	[NiBr(cetdic)(PPh ₃)] C ₂₇ H ₃₁ BrNiPS ₂	violet	58	9.9 (9.7)	53.8 (53.8)	5.2 (5.2)	2.2 (2.3)	10.1 (10.6)	13.9 (13.3)	
3	[Ni(cetdic)(PPh ₃)] C ₂₇ H ₃₁ INNiPS ₂	violet	75	9.4 (9.0)	49.0 (49.9)	4.9 (4.8)	2.3 (2.2)	9.7 (9.9)	–	
4	[Ni(NCS)(cetdic)(PPh ₃)] C ₂₈ H ₃₁ N ₂ NiPS ₃	orange	68	10.0 (10.1)	58.0 (57.8)	5.3 (5.4)	4.8 (4.8)	16.7 (16.6)	–	
5	[NiCl(cetdic)(P ⁿ Bu ₃)] C ₂₁ H ₄₃ CINNiPS ₂	red	86	11.8 (11.8)	50.0 (50.6)	8.8 (8.7)	2.8 (2.8)	12.8 (12.9)	7.8 (7.1)	
6	[NiBr(cetdic)(P ⁿ Bu ₃)] C ₂₁ H ₄₃ BrNiPS ₂	violet	83	10.9 (10.8)	45.9 (46.4)	8.2 (8.0)	2.3 (2.6)	11.0 (11.8)	14.2 (14.7)	
7	[Ni(cetdic)(P ⁿ Bu ₃)] C ₂₁ H ₄₃ INNiPS ₂	violet	75	9.8 (9.9)	43.2 (42.7)	7.5 (7.3)	2.8 (2.4)	10.4 (10.9)	–	
8	[Ni(NCS)(cetdic)(P ⁿ Bu ₃)] C ₂₂ H ₄₃ N ₂ NiPS ₃	orange	84	11.1 (11.3)	50.9 (50.7)	8.6 (8.3)	5.1 (5.4)	17.9 (18.5)	–	

^aX = Cl, Br

TABLE II. Molar conductivities, UV/Vis and IR spectral data, results of thermal analysis and melting points of the isolated complexes

No.	Complex	$\lambda_M^a/S \text{ cm}^2 \text{ mol}^{-1}$	UV/Vis ^b /10 ³ cm ⁻¹	IR ^b /cm ⁻¹		TA/°C		M.p./°C
				$\nu(\text{C}=\text{S})$	$\nu(\text{C}=\text{N})$	T_d	T_{en}	
1	[NiCl(cetdtc)(PPh ₃)]	6.3	19.0 28.4	992 w	1505 m	164	—	—
2	[NiBr(cetdtc)(PPh ₃)]	8.2	18.9 32.7	990 s	1510 m	170	—	—
3	[NiI(cetdtc)(PPh ₃)]	11.8	18.4 28.9	992 m	1520 w	140	—	—
4	[Ni(NCS)(cetdtc)(PPh ₃)]	3.9	20.7 36.4	995 m	1508 vs	173	163	165
5	[NiCl(cetdtc)(P ⁿ Bu ₃)]	3.8	19.9 33.3 36.4	995 m	1520 w	179	126	126
6	[NiBr(cetdtc)(P ⁿ Bu ₃)]	6.5	19.6 30.2 35.0	998 m	1522 w	177	123	123
7	[NiI(cetdtc)(P ⁿ Bu ₃)]	6.7	19.5 32.6	1000 m	1525 w	179	99	100
8	[Ni(NCS)(cetdtc)(P ⁿ Bu ₃)]	1.5	21.5 31.0 37.2	990 m	1530 w	164	127	128

^aMeasured in nitromethane solution, $[\text{Ni}^{2+}] = 10^{-3} \text{ mol dm}^{-3}$; ^bMeasured in nujol; T_d – beginning of the thermal decomposition; T_{en} – endo-effect

Magnetochemical and conductivity measurements

All the isolated complexes are diamagnetic substances. The values of the molar conductivities ($1.5 - 11.8 \text{ S cm}^2 \text{ mol}^{-1}$) in nitromethane solution correspond to non-electrolytes²¹. In view of this fact, it is supposed that Cl, Br, I and NCS anions are coordinated to the Ni(II), which was also confirmed by IR spectroscopy in the case of the NCS anion. The slightly higher values of the molar conductivities (Table II) can probably be explained by the partial dissociation of the complexes in the employed solvent. An identical phenomenon was encountered in a previous work,¹⁵ where the dissociation also increased in the order $\text{NCS} < \text{Cl} < \text{Br} < \text{I}$. The results of the magnetochemical and conductivity measurements allow the assumption of a square-planar arrangement of the NiS_2PX chromophore.

Spectroscopic characterization of the complexes

The IR spectra of the prepared compounds were not studied in detail. Only the bands characteristic for the dithiocarbamate ligand and NCS anion, which can coordinate to nickel *via* the nitrogen atom or *via* the sulfur atom, were monitored. In the IR spectrum of all of the complexes, maxima were found in the region $1505\text{--}1530 \text{ cm}^{-1}$ and $990\text{--}1000 \text{ cm}^{-1}$. They are typical for dithiocarbamates and can be attributed to $\nu(\text{C}\cdots\text{N})$ and $\nu(\text{C}\cdots\text{S})$ vibrations, respectively.^{13,22} In the case of $[\text{Ni}(\text{NCS})(\text{cetdtc})(\text{PPh}_3)]$ (**4**) and $[\text{Ni}(\text{NCS})(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$ (**8**) intensive bands were observed at $2080\text{--}2090 \text{ cm}^{-1}$ and $830\text{--}838 \text{ cm}^{-1}$, which correspond to $\nu(\text{C}\equiv\text{N})$, and $\nu(\text{C}\text{--}\text{S})$ vibrations, respectively. There is no doubt that the NCS anion is coordinated to nickel *via* the nitrogen atom.²³

The diffuse-reflectance electronic spectra of the complexes also support the assumption of a square-planar arrangement of the donor atoms around the central nickel atom. The absorption maxima in the region $18400\text{--}21500 \text{ cm}^{-1}$ may be assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ transition,²⁴ which is characteristic for square-planar Ni(II) complexes. The maxima between $28400\text{--}37200 \text{ cm}^{-1}$ are probably connected with intraligand transitions in the S_2CN^- group.¹³

The ${}^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the complexes were recorded in order to confirm the existence and coordination of the P-donor ligands (PPh_3 , P^nBu_3). In the ${}^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the free phosphorus ligands, only a single signal was found at -4.52 ppm (for PPh_3) and -30.07 ppm (for $\text{P}^n\text{-Bu}_3$). The ${}^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of compounds (**1**–**8**) consisted of singlets with large chemical shifts (Table III). In fact the shifts of the singlet signals were observed downfield from these of the corresponding free phosphorus ligands. This phenomenon is connected with the coordination of the phosphorus ligands and it has already been described in previous works.^{25,26}

It was not possible to prepare a single crystal suitable for X-ray structural analysis, from which all the experimental results as well as our general idea about the structure of the studied compounds could be unambiguously confirmed. However, on

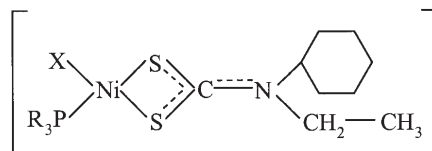


Fig. 1. Predicted structure of the complexes $[\text{NiX}(\text{cetdtc})(\text{PR}_3)]$ (**1–8**).

the basis of X-ray structural analysis of similar complexes $[\text{NiX}(\text{bz}^i\text{prdtc})(\text{PPh}_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{bz} = \text{benzyl}$, $^i\text{pr} = \text{isopropyl}$)¹⁵ it can be assumed that Ni(II) coordination compounds of the composition $[\text{NiX}(\text{cetdtc})(\text{PR}_3)]$ were synthesized (Fig. 1), in which the central nickel atom is coordinated by two sulfur atoms from one cyclohexylethylthiocarbamate ligand, one phosphorus atom from the monodentate P-donor ligand and one atom from the X-inorganic ligand ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) (the tetra-coordinated Ni(II) in the NiS_2PX chromophore).

TABLE III. $^{31}\text{P}\{^1\text{H}\}$ -NMR^a data of the isolated complexes

No.	Complex	δ/ppm
1	$[\text{NiCl}(\text{cetdtc})(\text{PPh}_3)]$	21.70 (s)
2	$[\text{NiBr}(\text{cetdtc})(\text{PPh}_3)]$	25.12 (s)
3	$[\text{NiI}(\text{cetdtc})(\text{PPh}_3)]$	31.52 (s)
4	$[\text{Ni}(\text{NCS})(\text{cetdtc})(\text{PPh}_3)]$	23.13 (s)
5	$[\text{NiCl}(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$	7.50 (s)
6	$[\text{NiBr}(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$	8.95 (s)
7	$[\text{NiI}(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$	13.04 (s)
8	$[\text{Ni}(\text{NCS})(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$	12.46 (s)

^aMeasured in CDCl_3 solution at 300 K; s-singlet

Thermal analysis

All the prepared complexes were examined by thermal analysis. Their thermal decomposition starts in the temperature interval 140–179 °C. In general terms, the course of the thermal decomposition of all the compounds is very similar; we depict the thermal analysis of $[\text{Ni}(\text{NCS})(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$ (**8**) for illustration in Fig. 2 as an example. In all cases, the decomposition is continuous without the formation of thermally stable intermediates. Hence it is not possible to obtain any reliable information about the course of the degradation. The existence of a small sharp endo-effect on the DTA-curves of the complexes (**4 – 8**) only is probably connected with the melting process. This observation was confirmed by the melting points determined on a Boëtius instrument (Table II).

The results of the physico-chemical study of the new Ni(II) cyclohexylethylthiocarbamate complexes are in good agreement with the experimental data re-

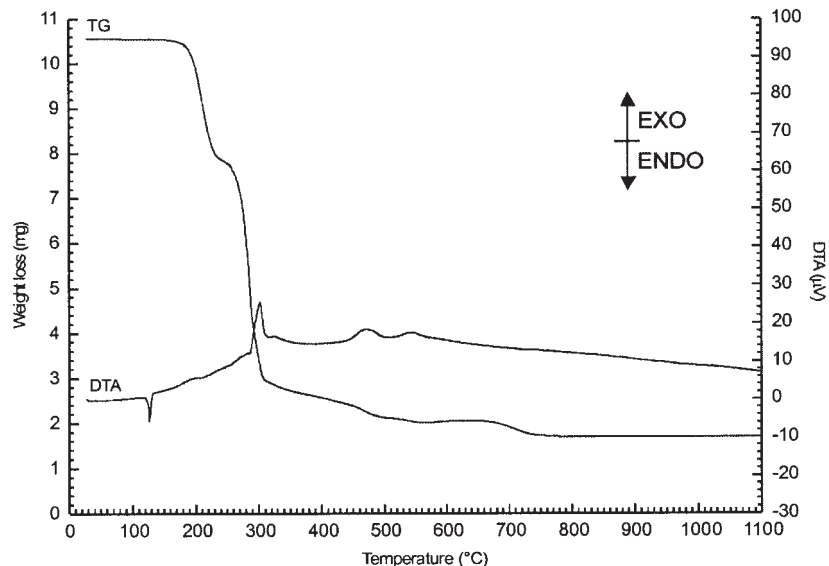


Fig. 2. Thermal analysis of $[\text{Ni}(\text{NCS})(\text{cetdtc})(\text{P}^n\text{Bu}_3)]$ (**8**).

ported in previous articles,^{13–16,27} which were aimed at the synthesis and structural characterization of coordination compounds with the same general formula $[\text{NiX}(\text{R}_1\text{R}_2\text{dtc})(\text{PR}_3)]$ containing different dithiocarbamate ligands. It can be concluded that the cyclohexylethyldithiocarbamate ligand, monodentate P-donor ligands and X-inorganic ligands have no significant influence on the shape of the coordination polyhedron.

ИЗВОД

НИКАЛ(II) ЦИКЛОХЕКСИЛЕТИЛДИТИОКАРБАМАТНИ КОМПЛЕКСИ СА МОНОДЕНТАТНИМ P-ДОНОРСКИМ ЛИГАНДИМА У КООРДИНАТНОЈ СФЕРИ

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Синтетизован је нов низ Ni(II) дитиокарбаматних једињења састава $[\text{NiX}(\text{cetdtc})(\text{PR}_3)]$ (X = Cl, Br, I, NCS; cetdtc = циклохексилетилдитиокарбамат; R = фенил, *n*-бутил). Сви изоловани комплекси карактерисани су елементалном анализом, IR и UV/VIS спектроскопијом, ^{31}P (^1H)-NMR спектроскопијом, термијском анализом, магнетохемијским мерењима и мерењима проводљивости. На основу физикохемијске анализе закључује се да су сви комплекси дијамагнетични, не-електролити и да имају квадратно-планарне хромофоре.

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