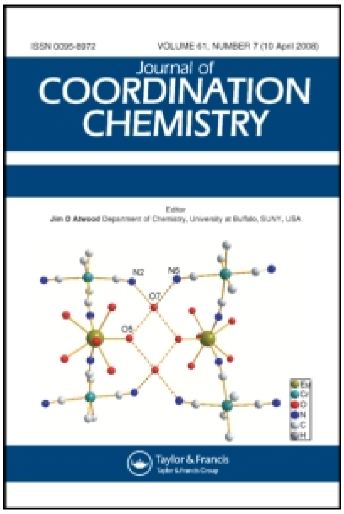

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Richard Pastorek[a]; Zdenêk Trávníĉek[a]; Pavel Ptoŝek[a]; Zdenêk Ŝindelá[a]; FrantiŜEk Bezina[a]; Jaromír Marek[b]
[a] Department of Inorganic and Physical Chemistry, Palacky University, Olomouc, Czech Republic [b] Department of Inorganic Chemistry, Masaryk University, Brno, Czech Republic

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PYRROLIDINEDITHIOCARBAMATE COMPLEXES OF NICKEL(II) WITH 1,4-*BIS*(DIPHENYLPHOSPHINO)BUTANE AS A MIXED P,P′-LIGAND

RICHARD PASTOREK[a,*], ZDENĚK TRÁVNÍČEK[a],
PAVEL PTOŠEK[a], ZDENĚK ŠINDELÁŘ[a], FRANTIŠEK BŘEZINA[a]
and JAROMÍR MAREK[b]

[a] *Department of Inorganic and Physical Chemistry, Palacký University, Křížkovského 10, 771 47 Olomouc, Czech Republic;* [b] *Department of Inorganic Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*

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Pyrrolidinedithiocarbamate nickel(II) complexes with 1,4-*bis*(diphenylphosphino)butane of composition $[Ni(plddtc)(dppb)]X \cdot H_2O$ and $[Ni_2(plddtc)_2(NCS)_2(dppb)] \cdot 2H_2O$ (pld $= C_4H_8$; dtc $= S_2CN^-$; dppb = 1,4-*bis*(diphenylphosphino)butane; X = Cl, Br, I, NO_3, ClO_4) have been synthesized. The compounds have been characterized by elemental analyses, IR and electronic spectroscopies, thermal analysis, magnetochemical and conductivity measurements. $[Ni(plddtc)(dppb)]I \cdot H_2O$ complex was studied by means of a single-crystal X-ray analysis. Crystals are orthorhombic, space group *Pnma*, with $a = 20.061(4)$, $b = 16.052(3)$, $c = 10.578(2)$ Å, $V = 3406.3(11)$ Å^3, $Z = 4$. The nickel(II) atom is coordinated by two phosphorus atoms from the dppb ligand [Ni–P = 2.1971(13) Å] and by two sulfur atoms from the pyrrolidinedithiocarbamate anion [Ni–S = 2.2151(13) Å] in a distorted square-planar arrangement. The iodide anion [Ni–I = 5.0476(13) Å] and the water molecule [Ni–O = 7.163(13) Å] are not bonded to nickel.

Keywords: Nickel(II); pyrrolidinedithiocarbamate; synthesis; X-ray structure

INTRODUCTION

As a part of a programme investigating the Ni(II)-dithiocarbamate complexes with P-donor ligands, we have reported[1] the syntheses and properties of complexes of composition $[NiX(plddtc)(PPh_3)]$ {X = Cl, Br;

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[*] Corresponding author.

PPh_3 = triphenylphosphine} and [Ni(plddtc)(dppe)]X · H_2O {X = Cl, Br, I, NCS, NO_3, ClO_4; dppe = 1,2-*bis*(diphenylphosphinoethane)}. These complexes are diamagnetic compounds in which the nickel atom is four coordinate in a distorted square-planar fashion. This was proven in the case of [NiBr(plddtc)(PPh_3)] by X-ray analysis. Unfortunately, the above nickel complexes with dppe have not been structurally characterized. The syntheses of these compounds extend the range of nickel pyrrolidinedithiocarbamate complexes with bidentate phosphorus donor ligands. In addition, the *bis*-(*tertiary* phosphines) are interesting for their coordination variability. They can bind to transition metal centres as bidentate P,P′-ligands or act as bridging ligands. Investigating of compositions and structures of nickel complexes with 1,4-*bis*(diphenylphosphino)butane is the subject of the present work.

EXPERIMENTAL

Materials

1,4-*bis*(diphenylphosphino)butane was supplied by Fluka Co. All other reagents were obtained from Lachema Co. and were of p.a. purity.

Syntheses

[Ni(plddtc)(dppb)]X · H_2O (X = Cl, Br, NO_3)

The complexes were prepared by a slight modification of the procedure described for similar complexes with dppe[1] [dppe = 1,2-*bis*(diphenylphosphino)ethane] in that fine, pulverized $NiX_2 \cdot nH_2O$ (X = Cl, Br, NO_3) (2 mmol) was added to fine, pulverized $[Ni(plddtc)_2]$[2] (2 mmol) in 100 cm^3 of absolute ethanol. The reaction mixture was refluxed for 4 hours, filtered hot and then the reaction solution was concentrated to small volume. An excess of water was added after cooling to 10°C and beige precipitates were obtained by freezing to −25°C. These were separated by filtration, dissolved in ethanol and then water was added again. After cooling in a freezer, the solids formed were filtered off, washed with water and dried under an IR lamp at 40°C.

[Ni(plddtc)(dppb)]X · H_2O (X = I, ClO_4)

A similar procedure to the above was used. The reaction mixture was filtered and the light-brawn solid (*X = I*) was obtained after three days at room temperature, while the orange substance ($X = ClO_4$) formed after cooling the reaction mixture. Compounds obtained were filtered off, washed with diethylether and dried under an IR lamp at 40°C. The complexes were recrystallized from ethanol and crystals suitable for a single-crystal X-ray analysis were obtained in the case of the iodide complex.

[$Ni_2(plddtc)_2(NCS)_2(dppb)$] · $2H_2O$

A similar procedure to the above was used, in that the reaction components were reacted in a 1 : 1 : 1 mol ratio. The purple substance formed during refluxing was filtered off and recrystallized from chloroform. It was then washed with diethylether and dried under an IR lamp at 40°C.

Physical Measurements

The nickel content was determined by chelatometric titration using murexid as indicator and halogens by the Schöniger method. C, H, N, S analyses were performed on an EA 1108 instrument (FISONS). Magnetochemical and conductivity measurements, IR and electronic spectroscopies, and thermal analyses were carried out as described previously.[1,3,4] In the case of the nitrate complex the IR spectrum was also recorded on an ATI Mattson Genesis Series FTIR Spectrometer using the KBr technique.

X-ray Crystallography

A crystal of dimensions 0.80 × 0.40 × 0.20 mm was mounted on a KUMA KM-4 diffractometer equipped with graphite monochromator. Intensities were recorded with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using an ω-2θ scan technique. Three standard reflections (200, 040, 004) were monitored after every 300 measurements; no significant changes in intensities were recorded. The unit cell dimensions were determined by least-squares refinement of 30 centred reflections in the $21.0 < 2\theta < 22.8°$ region. A total of 2732 reflections were collected of which 1753 reflections were classified as observed with $I > 2\sigma(I)$. The structure was solved by the heavy-atom method using the program SHELXS-86.[5] At the end of the isotropic refinement an empirical absorption correction using the program DIFABS[6] was applied ($R_{iso} = 0.100$ before and 0.079 after application). The minimum and maximum transmission factors were 0.366 and 1.000, respectively. The structure was refined anisotropically by full-matrix least-squares procedures on F^2 with $w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 3.0398P]$, where $P = (F_o^2 + 2F_c^2)/3$,

TABLE I Crystal data and structure refinement details for [Ni(plddtc)(dppb)]I · H_2O

Empirical formula	$C_{33}H_{38}INNiOP_2S_2$
Formula weight	776.31
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pnma*
Unit cell dimensions	$a = 20.061(4)$ Å $\alpha = 90.0°$ $b = 16.052(3)$ Å $\beta = 90.0°$ $c = 10.578(2)$ Å $\gamma = 90.0°$
Volume	3406.3(11) $Å^3$
Z	4
Density (calculated)	1.514 $Mg\,m^{-3}$
Absorption coefficient	1.719 mm^{-1}
$F(000)$	1576
Crystal size	0.80 × 0.40 × 0.20 mm
Theta range for data collection	2.03 to 25.06°
Index ranges	$-23 < h < 0$, $-19 < k < 0$, $-12 < l < 0$
Reflections collected	2732
Independent reflections	2731 [$R(int) = 0.0044$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2731/0/239
Goodness-of-fit on F^2	1.002
Final R indices [$I > 2\sigma(I)$]	$R = 0.033$, $R_w = 0.092$
R indices (all data)	$R = 0.077$, $R_w = 0.108$

using the SHELXL-93 program.[7] All H-atoms, except those of the water molecule, were found from difference Fourier maps. The H-atoms of the CH_2 groups of pyrrolidine were refined using a riding model. All parameters of the H-atoms bonded to carbons of phenyl rings were refined isotropically. ORTEP was used to draw the molecule.[8] Crystal data and structure refinement parameters for [Ni(plddtc)(dppb)]I · H_2O are listed in Table I. Atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms are given in Table II.

RESULTS AND DISCUSSION

Analytical data for the prepared complexes are listed in Table III. Other properties are summarized in Table IV.

All the complexes synthesized are diamagnetic and conductance studies show that they behave, except for **VI** which is a non-electrolyte, as 1 : 1 electrolytes.[9] The ionic nature of the NO_3 and ClO_4 anions is also supported by the IR spectra of **IV** and **V**. The strong band in the IR spectrum of [Ni(plddtc)(dppb)]NO_3 · H_2O at 1383 cm^{-1} indicates ionic nature of the NO_3 group.[10] Likewise, the unsplit strong maxima displayed at 1090 cm^{-1}

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Ni(plddtc) (dppb)]I · H_2O. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ni	4013(1)	2500	2490(1)	37(1)
S(1)	3679(1)	1629(1)	994(1)	51(1)
N	3007(3)	2500	−746(5)	49(1)
P(1)	4227(1)	1440(1)	3741(1)	45(1)
I	1534(1)	2500	1677(1)	75(1)
O	638(7)	2500	4695(10)	181(5)
C(1)	3395(3)	2500	240(6)	42(1)
C(2)	2724(3)	1734(4)	−1319(6)	72(2)
C(3)	2223(5)	2067(5)	−2237(8)	136(4)
C(4)	4804(3)	1557(4)	5068(5)	70(2)
C(5)	4519(5)	2099(4)	6127(6)	135(4)
C(11)	3467(2)	1017(3)	4432(5)	53(1)
C(12)	2852(3)	1299(3)	4043(6)	58(1)
C(13)	2270(3)	968(4)	4510(6)	76(2)
C(14)	2305(4)	348(5)	5381(7)	89(2)
C(15)	2907(5)	50(4)	5802(7)	88(2)
C(16)	3495(4)	381(4)	5322(6)	77(2)
C(21)	4573(2)	576(3)	2854(4)	46(1)
C(22)	4206(3)	−110(4)	2520(5)	58(1)
C(23)	4463(3)	−731(4)	1767(5)	67(2)
C(24)	5107(3)	−669(4)	1349(6)	72(2)
C(25)	5489(3)	−1(5)	1685(6)	71(2)
C(26)	5225(3)	628(4)	2417(5)	58(1)

TABLE III Analytical data for the complexes

Compound	*Found* (*Calcd.*) (%)					
	Ni	*C*	*H*	*N*	*S*	X^a
I [Ni(plddtc)(dppb)]Cl · H_2O	8.2(8.6)	57.1(57.9)	6.0(5.6)	1.7(2.0)	8.7(9.4)	4.6(5.2)
II [Ni(plddtc)(dppb)]Br · H_2O	7.7(8.0)	54.9(54.3)	5.5(5.2)	1.5(1.9)	8.1(8.8)	10.5(11.0)
III [Ni(plddtc)(dppb)]I · H_2O	7.5(7.6)	51.5(51.0)	5.1(4.9)	1.4(1.8)	7.7(8.3)	17.0(16.3)
IV [Ni(plddtc)(dppb)]NO_3 · H_2O	8.3(8.2)	55.8(55.7)	5.5(5.4)	3.7(3.9)	8.3(9.0)	
V [Ni(plddtc)(dppb)]ClO_4 · H_2O	8.2(7.8)	53.5(52.9)	5.2(5.1)	1.8(1.9)	8.7(8.6)	5.0(4.7)
VI [Ni_2(plddtc)$_2$(NCS)$_2$(dppb)] · $2H_2O$	12.4(11.9)	49.2(48.6)	4.7(4.9)	5.8(5.9)	19.7(19.5)	

[a] X = Cl, Br, or I.

(ν_3) and 622 cm^{-1} (ν_4) are connected with non-coordinated ClO_4^- in [Ni(plddtc)(dppb)]ClO_4 · H_2O.[11] The maxima at 1532–1537 cm^{-1} [ν(C$\overset{...}{-}$N)] and at 990–998 cm^{-1} [ν(C$\overset{...}{-}$S)] are characteristic for dithiocarbamates[12,13] and were observed in the IR spectra of all complexes. Coordination of the NCS group to the nickel through the nitrogen atom in [Ni_2(plddtc)$_2$(NCS)$_2$(dppb)] · $2H_2O$ is evident from bands at 2088 cm^{-1} and 840 cm^{-1} which belong to stretching modes C ≡ N and C–S, respectively.[14] This fact was already confirmed by X-ray diffraction studies of [Ni(NCS)(plddtc)(PPh$_3$)][3] and [Ni(NCS)(bu$_2$dtc)(PPh$_3$)][4] (bu = butyl).

TABLE IV Characteristic properties of the complexes

Compound	*Colour*	λ_M[a]	*IR* [cm^{-1}]		*UV/VIS*[d]		*TA* [°C]
		[S cm^2 mol^{-1}]	($C \overset{...}{=} S$)	($C \overset{...}{=} N$)	[$\times 10^3$ cm^{-1}]	T_s^e	*Plateau*
I	beige	101.3	995w	1536m	21.2 31.5	50	100–170
II	beige	99.9	995w	1534m	20.8 31.9	50	
III	light-brown	64.6[b]	990w	1534m	21.4 31.9	60	
IV	beige	133.9	996m	1532m	21.2 31.8	50	115–180
V	orange	137.4	996w	1534vs	21.2 32.0		
VI	purple	1.5[c]	998w	1537m	20.8 29.6	50	

[a] Measured in acetone solution, $[Ni^{2+}] = 10^{-3}$ mol dm^{-3}. [b] Measured in dimethylformamide solution, $[Ni^{2+}] = 10^{-3}$ mol dm^{-3}. [c] Measured in chloroform solution, $[Ni^{2+}] = 10^{-3}$ mol dm^{-3}. [d] Measured using the Nujol technique. [e] The beginning of thermal decomposition.

Square-planar coordination around nickel is also supported by diffuse-reflectance spectra. Medium to strong maxima were found in the 20 800–21 400 cm^{-1} region, which can be attributed to the $^1A_{1g} \rightarrow {}^1B_{1g}$ electron transition.[15] The maxima near 32 000 cm^{-1} are assignedable to the $n \rightarrow \pi^*$ intraligand transition on the sulfur atom in the S_2CN group.[12,16]

The structure of [Ni(plddtc)(dppb)]I · H_2O was confirmed by-single-crystal X-ray analysis. A perspective drawing of the centrosymmetric molecule is shown in Figure 1. Selected bond lengths and angles are given in Table V. As expected, the structure reveals a distorted square-planar arrangement of donor atoms. Thus, the central nickel atom is four-coordinated by two sulfur atoms and by two phosphorus atoms from plddtc and dppb, respectively. A degree of distortion in the NiS_2P_2 chromophore is obvious not only from differences in bond lengths and angles in the vicinity of the central atom (see Table V) but also from displacements of the Ni, P(1), S(1), P(1a) and S(1a) atoms from their least-squares best-fit plane. The deviations are as follows: Ni 0.054(1), P(1) −0.015(1), S(1) −0.012(1), P(1a) −0.015(1) and S(1a) −0.012(1) Å. The phenyl rings, C(11)–C(16) and C(21)–C(26), of the dppb ligand do not deviate significantly from planarity. The dihedral angle between the phenyl rings is equal to 74.1(2)° and they make angles with the Ni–P(1)–S(1)–P(1a)–S(1a) least-squares plane of 75.1(2)° and 89.7(1)°, respectively. Characteristic shortening of the interatomic distances in the S_2CN group (see Table V) compared to typical C–N (1.47 Å) and C–S (1.81 Å) single bonds[17] was found. This is connected with an increase of

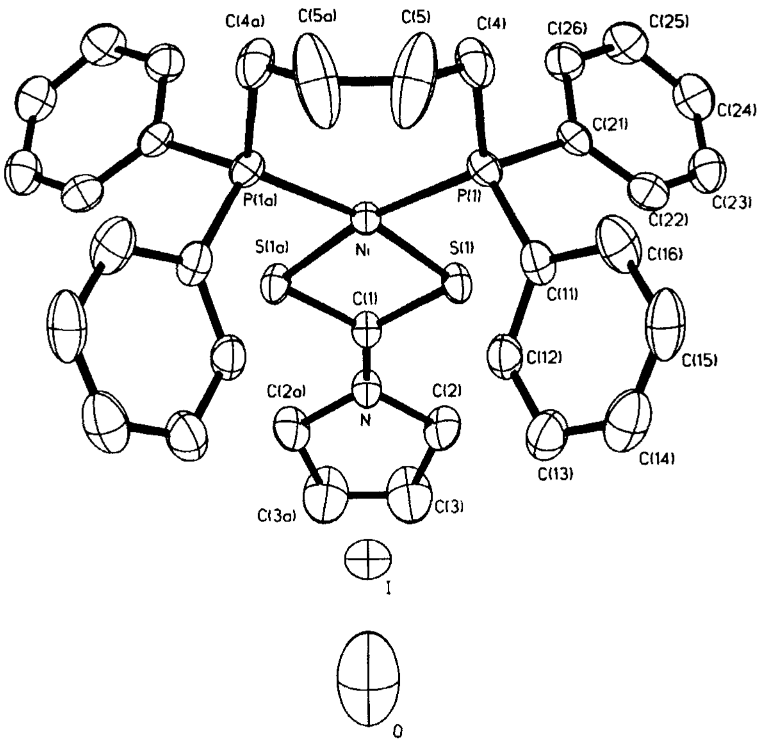

FIGURE 1 Molecular structure of the [Ni(plddtc)(dppb)]I · H_2O complex showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for the sake of clarity.

π-electron density over the group in dithiocarbamates. Displacement of iodide anion and the water molecule from the coordination sphere of nickel was also confirmed in [Ni(plddtc)(dppb)]I·H_2O. This is evident from interatomic distances between nickel and iodine [5.0476(13) Å], and nickel and oxygen [7.163(13) Å].

All the complexes begin to decompose in the 50–60°C range. They are less stable then the starting [Ni(plddtc)$_2$] complex which starts to react at 155°C. The first thermal step for **I** and **IV** is connected with the loss of the water molecules. This is seen in endothermic effects in DTA-curves (see Table IV). Existence of the anhydrous compounds was found in the 100–170°C and 115–180°C ranges, respectively. Decomposition of the other complexes, likewise further decay of **I** and **IV**, proceeds without formation of thermally stable intermediates. [Ni(plddtc)(dppb)]ClO$_4$·H_2O complex was not studied due to its possible explosive nature.

TABLE V Selected bond lengths, angles and other relevant interatomic parameters [Å, °] for [Ni(plddtc)(dppb)]I · H_2O

Ni-P(1a)	2.1971(13)	N-C(2a)	1.483(6)
Ni-P(1)	2.1971(13)	P(1)-C(21)	1.813(5)
Ni-S(1)	2.2151(13)	P(1)-C(11)	1.822(5)
Ni-S(1a)	2.2151(13)	P(1)-C(4)	1.830(5)
Ni-I	5.0476(13)	C(1)-S(1a)	1.707(4)
Ni-O	7.163(13)	C(2)-C(3)	1.496(8)
S(1)-C(1)	1.707(4)	C(3)-C(3a)	1.39(2)
N-C(1)	1.301(8)	C(4)-C(5)	1.529(9)
N-C(2)	1.483(6)	C(5)-C(5a)	1.286(14)
P(1a)-Ni-P(1)	101.46(7)	C(21)-P(1)-Ni	110.8(2)
P(1a)-Ni-S(1)	167.86(5)	C(11)-P(1)-Ni	111.6(2)
P(1)-Ni-S(1)	90.04(5)	C(4)-P(1)-Ni	120.4(2)
P(1a)-Ni-S(1a)	90.04(5)	N-C(1)-S(1a)	125.0(2)
P(1)-Ni-S(1a)	167.86(5)	N-C(1)-S(1)	125.0(2)
S(1)-Ni-S(1a)	78.24(7)	S(1a)-C(1)-S(1)	109.9(3)
I-Ni-O	28.81(9)	N-C(2)-C(3)	103.1(5)
C(1)-S(1)-Ni	85.3 (2)	C(3a)-C(3)-C(2)	110.9(4)
C(1)-N-C(2)	123.8 (3)	C(5)-C(4)-P(1)	112.5(5)
C(1)-N-C(2a)	123.8 (3)	C(5a)-C(5)-C(4)	124.7(4)
C(2)-N-C(2a)	111.9 (6)		

[a]Symmetry transformations used to generate equivalent atoms: x, $-y+1/2$, z.

Unfortunately, preparation of crystals suitable for a single-crystal X-ray analysis of $[Ni_2(plddtc)_2(NCS)_2(dppb)] \cdot 2H_2O$ failed. However, on the base of the above studies we suppose that in this dinuclear complex both central atoms have a square-planar arrangement of donor atoms. Thus, each nickel atom is coordinated by two sulfur atoms from dithiocarbamate, a nitrogen atom from an NCS group and the dppb ligand acts as a bidentate bridging ligand. We are continuing our studies using 1,6-*bis*(diphenylphosphino)-hexane.[18]

Supplementary Material

Lists of structure factors, all bond lengths and angles, atomic coordinates and equivalent isotropic displacement parameters of H-atoms, and anisotropic displacement parameters are available from Zdeněk Trávníček upon request.

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