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Nickel(II) Dithiocarbamates with Bis(2-diphenylphosphinoethyl)phenylphosphine

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A Ni(II) dithiocarbamates with the tridentate P,P,P-ligand of composition [Ni(pe$_2$dtc)(triphosI)]X (triphosI = $C_{34}H_{33}P_3$ = bis(2-diphenylphosphinoethyl)phenylphosphine, pe$_2$dtc = dipentyldithiocarbamate, X = Cl, PF_6, ClO_4), [Ni(bz$_2$dtc)(triphosI)]X (bz$_2$dtc = dibenzyldithiocarbamate, X = Cl, PF_6) and [Ni(cetdtc)(triphosI)]X (cetdtc = cyclohexylethyldithiocarbamate, X = Cl, PF_6, BPh_4, ClO_4) have been synthesized and studied by thermal analysis, IR and UV/VIS spectroscopy, $^{31}P\{^1H\}$-NMR spectroscopy, magnetochemical and conductivity measurements. All complexes are diamagnetic, 1:1 electrolytes. X-ray structural analysis was solved for the [Ni(pe$_2$dtc)(triphosI)]PF_6 and [Ni(bz$_2$dtc)(triphosI)]PF_6; the presence of NiS_2P_3 chromophore with penta-coordinated central nickel atom was confirmed.

Key words: Ni(II) dithiocarbamate, synthesis, physico-chemical study, X-ray structural analysis, $^{31}P\{^1H\}$-NMR spectroscopy

The reactions of basic Ni(II) dithiocarbamates [Ni(dtc)$_2$] with polydentate P-ligands have been recently studied with the aim of replacement of the sulfur atoms in the NiS_4 chromophore by the phosphorus and other atoms, including physico-chemical measurements. The diamagnetic square complexes of composition [Ni(dtc)(P,P)]X [1–16] with NiS_2P_2 chromophore (dtc = dithiocarbamate, P,P = bidentate P,P-ligand, X = anion) have been isolated. In some cases, the square-pyramidal diamagnetic compounds containing NiS_2P_2X chromophore of composition [NiX(dtc)(P,P)] [1,17] have been also prepared. For 1,4-bis(diphenylphosphino)butane and 1,6-bis(diphenylphosphino)hexane as a bidentate ligands, the diamagnetic binuclear complexes [Ni$_2$(μ-P,P)(dtc)$_2$X$_2$] with two square NiS_2PX chromophores and bridging P,P-ligand were synthesized [7,9,11,16,18].

The nickel dithiocarbamates with tridentate P,P,P-ligands in the coordination sphere were studied by our team only. In our previous papers [19,20] we published synthesis and physico-chemical study of the complexes [Ni(bz^{i}prdtc)(triphosI)]X (bz^{i}prdtc = benzylisopropyldithiocarbamate, X = Cl, PF_6, BPh_4, ClO_4), [Ni(tzdtc)(triphosI)]X (tzdtc = thiazolidinedithiocarbamate, X = Cl, PF_6), [Ni(hmidtc)(triphosI)]X (hmidtc = hexamethyleneiminedithiocarbamate, X = Cl, PF_6), [Ni(hmidtc)(triphosII)]X

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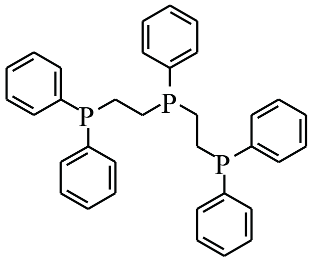
(triphosII = $C_{41}H_{39}P_3$ = 1,1,1-tris(diphenylphosphinomethyl)ethane, X = Cl, PF_6), [Ni(cetdtc)(triphosII)]X (X = Cl, PF_6, BPh_4, ClO_4) and [Ni(pe_2dtc)(triphosII)]X (X = Cl, ClO_4).



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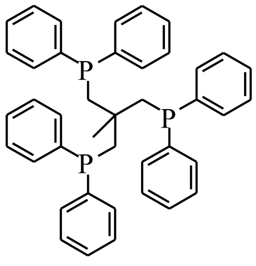

triphosII

All compounds are diamagnetic, 1:1 electrolytes with NiS_2P_3 chromophore (coordination number five for nickel atom).

The aim of this paper is to enlarge this study for other types of dithiocarbamates with triphosI ligand, including physico-chemical study of newly synthesized complexes and solving of X-ray structures of selected compounds to confirm the proposed coordination around the central atom.

EXPERIMENTAL

Materials and methods: Dibenzylamine (97%), N-cyclohexylethylamine (98%), $LiClO_4 \cdot 3H_2O$ and $CDCl_3$ (99.8%D) were supplied by Aldrich Co.; dipentylamine (97%), bis(2-diphenylphosphinoethyl)phenylphosphine (97%), K[PF_6], $NaClO_4 \cdot H_2O$ and CS_2 were obtained from Fluka Co. and all remaining reagents were products of Lachema Co. of p.a. purity.

The content of nickel was determined by chelatometric titration, using murexide as an indicator [21]. Chlorine was determined by the Schöniger method [22]. The C, H, N, S analyses were performed on an EA 1108 instrument (Fisons). The room temperature magnetic susceptibilities were measured by Faraday method, using Co[Hg(NCS)$_4$] as a calibrant on a laboratory designed instrument with the Sartorius 4434 MP-8 microbalance. Conductivities 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 on a Specord M 40 and IR spectra (4000–400 cm^{-1}) were recorded on a Specord M 80 (Carl Zeiss, Jena), using nujol mulls. The thermal analysis was performed on a Exstar 6000, TG/DTA 6200 device (Seiko, Japan) with gradient 2.5°C/min, sample weight 9.2–11.6 mg, between 20–1150°C. Melting points were determined by the Boëtius Rapido melting point apparatus (Wägetechnik PHMK 79/2122).

$^{31}P\{^1H\}$-NMR spectra were measured on a Bruker Avance 300 spectrometer, operating at frequency of 121.44 MHz. Measurements were performed at 300 and 320 K. All samples were prepared by dissolving of compounds in $CDCl_3$. 85% H_3PO_4 was used as an external reference.

Syntheses: [Ni(Ldtc)(triphosI)]Cl {L = pe_2(1), bz_2(4), cet(6)}: The suspension of fine powdered [Ni(pe_2dtc)$_2$] [23], [Ni(bz_2dtc)$_2$] [24], [Ni(cetdtc)$_2$] [24], respectively (1 mmol) and triphosI (1mmol) in 20 cm^3 dichlormethane was mixed at room temperature about 20 hours. The resulted violet colored solution was combined with active carbon and the mixture was filtered. During solvent evaporation and addition of diethyl ether, a violet solid substance appeared; it was isolated and dried under an infra-lamp at 40°C. Yields: 44% (1); 40% (4) and 78% (6).

[Ni(Ldtc)(triphosI)]X (L = pe_2, bz_2; X = PF_6, ClO_4): The suspension of fine powdered [Ni(pe_2dtc)$_2$] [23] or [Ni(bz_2dtc)$_2$] [24] (1 mmol) with triphosI (1 mmol) was stirred in 20 cm^3 methanol/acetone mixture (1:1). Resulted mixture was combined with fine powdered K[PF_6] (2), (5), $LiClO_4 \cdot 3H_2O$ (3), respectively (1 mmol). After 40 hours of stirring under reflux at room temperature, active carbon was added and the mixture was filtered. For [Ni(pe$_2$dtc)(triphosI)]PF$_6$ (2) and [Ni(bz$_2$dtc)(triphosI)]PF$_6$ (5) violet colored crystals, suitable for X-ray analysis were obtained. In the case of the perchlorate complex (3), a viscose substance resulted and the final violet product was obtained using ethanol. All compounds were washed by diethyl ether and dried under an infra-lamp at 40°C. Yields: 25% (2), 25% (3), 30% (5).

[Ni(cetdtc)(triphosI)]PF$_6$ (7): The solution of [Ni(cetdtc)(triphosI)]Cl$\cdot$H$_2$O in 10 cm^3 methanol (0.5 mmol) was stirred with solution of K[PF$_6$] (0.5 mmol) in 10 cm^3 H$_2$O. A dark violet substance was formed; it was washed by petroleum ether, filtered through active carbon, crystallized from methanol and dried under an infra-lamp at 40°C. Yield: 78%.

[Ni(cetdtc)(triphosI)]X {X = BPh$_4$ (8), ClO$_4$ (9)}: The suspension of fine powdered [Ni(cetdtc)$_2$] [24] (0.5 mmol) and triphosI (0.5 mmol) was mixed for 2 hours at room temperature in 10 cm^3 of dichlormethane (for X = ClO$_4$) or in 20 cm^3 of *n*-butanol/acetone (1:1) mixture (for X = BPh$_4$). The resulted solution was combined with the 0.5 mmol of appropriate salt (NaClO$_4\cdot$H$_2$O in 5 cm^3 methanol or Na[BPh$_4$] in 5 cm^3 *n*-butanol). For X = BPh$_4$ (8), during one hour a blue-violet substance appeared; it was filtered, washed by ethanol and petroleum ether. The violet perchlorate complex (9) was obtained after evaporation to a small volume and addition of petroleum ether. Both compounds were purified with active carbon, filtered and re-crystallized, using chloroform (8) or methanol (9) and dried under an infra-lamp at 40°C. Yields: 58% (8) and 52% (9).

X-ray crystallography: X-ray data collection of [Ni(pe$_2$dtc)(triphosI)]PF$_6$ (2) was performed on a KUMA KM-4 diffractometer with graphite monochromatized MoK$_\alpha$ radiation and area sensitive CCD-4 detector. The structure was solved by the heavy atom methods, using SHELXS-97 program [25]. No absorption corrections were applied. The structure was refined anisotropically by the full-matrix least-squares procedures, using program SHELXL-97 [26].

X-ray data of [Ni(bz$_2$dtc)(triphosI)]PF$_6$ (5) were collected by omega-scan technique on a four-circle κ-axis Xcalibur^{TM}2 diffractometer (Oxford Diffraction), equipped with Sapphire2 CCD detector, monochromator Enhance and Cryojet cooler system. Data collection for the complex was performed using MoK$_\alpha$ radiation at 100 K. CrysAlis program package (version 1.171.7, Oxford Diffraction) was used for data reduction. The structure of (5) was solved using direct methods [25]. Atoms forming the NiS$_2$P$_3$ chromophore and PF$_6$ anions were refined anisotropically on F^2, using full-matrix least-squares procedure [26], while all the remaining atoms were refined isotropically. The structure was solved in the chiral space group P2$_1$, as a racemic twin. The final R_{obs}-factor is equal to 0.1874. An application of anisotropic refinement of all non-hydrogen atoms did not lead to reduction of *R*-factors. We tried to measure several crystals of this complex, as well as to solve the structure in several different space groups and we always obtained comparable results. This fact may probably relate with a twinning of the crystals, which can be also evident from the value of $|E^2\text{-}1|$ = 0.591 (expected values are 0.968 for centrosymmetric and 0.736 for non-centrosymmetric space groups). The low quality of twinned data did not allow us to add hydrogen atoms to the model. The largest peak and hole on the final difference map were 2.56 [0.628 Å from Ni(1a)] and –2.30 [0.57 Å from Ni(1)] e.Å^{-3}. Nevertheless, in spite of bad statistical results, we assume that a manner of ligands coordination was unambiguously proved by X-ray analysis. Additional calculations were made using PARST program [27]. The X-ray results are given in Tables 2–5.

RESULTS AND DISCUSSION

All complexes exhibit the same coordination sphere with the uncommon NiS$_2$P$_3$ chromophore and coordination number five. This fact was confirmed by the physico-chemical measurements, namely by the X-ray structure analysis.

Composition and important physico-chemical results of complexes are summarized in Table 1. All compounds are diamagnetic, which is in good accord with the literature about low-spin penta-coordinated Ni(II) complexes [32,35]. The conductivity measurements show that λ_M values are in interval 104.7–146.3 S cm^2 mol^{-1}. This fact

Table 1.

Com-plex*	Color	λ_M (S cm^2 mol^{-1})	μ_{eff}/μ_B	IR (cm^{-1})					UV/VIS ($\times 10^3$ cm^{-1})				TA(°C)		
				$\nu(\text{C}\overset{\cdot\cdot}{-}\text{S})$	$\nu(\text{C}\overset{\cdot\cdot}{-}\text{N})$	$\nu_3(\text{ClO}_4)$	$\nu_4(\text{ClO}_4)$	$\nu(\text{PF}_6)$					T	E$_n$	E$_x$
(1)	violet	125.5	dia	995w	1510w	–	–	–	18.0				41.8	81.2	236.0
(2)	violet	140.0	dia	995m	1510s	–	–	840vs	14.3	18.3	24.5	30.0	234.6	210.6	264.6
(3)	violet	146.3	dia	995m	1510w	1075vs	625m	–	14.3	18.3	24.6	31.2		no study	
(4)	violet	104.7	dia	1000m	1510w	–	–	–	18.3	24.3	29.5		41.5	65.8	246.3
(5)	violet	114.4	dia	990w	1490m	–	–	830m	14.2	18.0	24.3		251.8	270.3	279.2
(6)	light-violet	113.0	dia	996m	1510m	–	–	–	18.5	36.0	39.0		49.1	61.8	207.8
(7)	dark-violet	113.3	dia	992w	1508w	–	–	830s	14.2	18.1	32.9		240.0	236.2	275.9
(8)	blue-violet	117.6	dia	998m	1508w	–	–	–	14.5	18.0	33.2		84.2	–	121.1
(9)	violet	125.8	dia	995m	1515w	1088s	620w		18.2	27.9	35.9	39.1		no study	

λ_M Molar conductivity in acetone solution (10^{-3} mol·dm^{-3}); T – start of thermal decomposition; E$_n$ – endo-effect; E$_x$ – exo-effect.
*(1) [Ni(pe$_2$dtc)(triphosI)]Cl·H$_2$O; (2) [Ni(pe$_2$dtc)(triphosI)]PF$_6$; (3) [Ni(pe$_2$dtc)(triphosI)]ClO$_4$·H$_2$O;
(4) [Ni(bz$_2$dtc)(triphosI)]Cl·H$_2$O; (5) [Ni(bz$_2$dtc)(triphosI)]PF$_6$; (6) [Ni(cetdtc)(triphosI)]Cl·H$_2$O;
(7) [Ni(cetdtc)(triphosI)]PF$_6$; (8) [Ni(cetdtc)(triphosI)]BPh$_4$; (9) [Ni(cetdtc)(triphosI)]ClO$_4$.

can be interpreted, according [30] as 1:1 electrolytes in acetone solution. Thus, we can conclude that the inorganic X anion is in all compounds out of the coordination sphere (see also IR spectroscopy).

Table 2. Crystallographic data for [Ni(pe$_2$dtc)(triphosI)]PF$_6$.

Molecular formula	$C_{45}H_{55}F_6NNiP_4S_2$
Formula weight	970.61
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2$_1$/n
Unit cell dimensions	a = 11.797(2) Å $\alpha = 90°$
	b = 21.685(4) Å $\beta = 94.31(3)°$
	c = 19.044(4) Å $\gamma = 90°$
Volume; Z; Calculated density	4858.0(16) Å^3; 4; 1.327 Mg/m^3
Absorption coefficient	0.671 mm^{-1}
F(000)	2024
Crystal size	0.40 × 0.40 × 0.20 mm
Θ range for data collection	2.55 to 28.59°
Index ranges	$-14 \leq h \leq 14$, $-25 \leq k \leq 20$, $-22 \leq l \leq 22$
Reflections collected/unique	34170 / 8541 [R(int) = 0.0785]
Completeness to Θ = 25°	99.8%
Max. and min. transmission	0.8774 and 0.7750
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8541/0/418
Goodness-of-fit on F^2	1.114
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0933, wR2 = 0.2843
R indices (all data)	R1 = 0.1330, wR2 = 0.3169
Largest diff. peak and hole	1.18 and –1.50 e· Å^{-3}

Table 3. Crystallographic data for [Ni(bz$_2$dtc)(triphosI)]PF$_6$.

Molecular formula	$C_{49}H_{47}F_6NNiP_4S_2$
Formula weight	1010.59
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2$_1$
Unit cell dimensions	a = 16.0394(5) Å $\alpha = 90°$
	b = 17.7755(4) Å $\beta = 90.086(3)°$
	c = 16.0828(4) Å $\gamma = 90°$
Volume; Z; Calculated density	4885.3(2) Å^3; 4; 1.464 Mg/m^3
Absorption coefficient	0.715 mm^{-1}
F(000)	2088
Crystal size	0.40 × 0.40 × 0.30 mm
Θ range for data collection	3.42 to 25.00°
Index ranges	$-19 \leq h \leq 18$, $-21 \leq k \leq 20$, $-11 \leq l \leq 19$
Reflections collected/unique	31343 /16066 [R(int) = 0.0285]
Completeness to Θ = 25°	99.6%
Max. and min. transmission	0.8141 and 0.7630
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	16066/1/432
Goodness-of-fit on F^2	1.172
Final R indices [$I > 2\sigma(I)$]	R1 = 0.1874, wR2 = 0.4176
R indices (all data)	R1 = 0.1881, wR2 = 0.4179
Largest diff. peak and hole	2.559 and –2.296 e·Å^{-3}
Absolute structure parameter	0.18(5)

Table 4. Selected bond distances and angles for [Ni(pe_2dtc)(triphosI)]PF_6.

Bond distances (Å)		Bond angles (°)	
Ni(1)–P(2)	2.1534(18)	P(2)–Ni(1)–P(1)	86.87(7)
Ni(1)–P(1)	2.1948(18)	P(2)–Ni(1)–S(1)	174.49(8)
Ni(1)–P(3)	2.254(2)	P(1)–Ni(1)–S(1)	95.29(7)
Ni(1)–S(1)	2.2388(19)	P(2)–Ni(1)–P(3)	88.28(7)
Ni(1)–S(2)	2.3035(19)	P(1)–Ni(1)–P(3)	121.82(7)
S(1)–C(1)	1.723(8)	S(1)–Ni(1)–P(3)	94.86(8)
S(2)–C(1)	1.708(7)	P(2)–Ni(1)–S(2)	97.69(7)
C(1)–N(1)	1.316(8)	P(1)–Ni(1)–S(2)	128.82(8)
		S(1)–Ni(1)–S(2)	77.01(7)
		P(3)–Ni(1)–S(2)	109.30(8)
		C(1)–S(1)–Ni(1)	86.6(2)
		C(1)–S(2)–Ni(1)	84.9(2)
		N(1)–C(1)–S(2)	126.3(6)
		N(1)–C(1)–S(1)	122.6(6)
		S(2)–C(1)–S(1)	111.0(4)

Table 5. Selected bond distances and angles for [Ni(bz_2dtc)(triphosI)]PF_6.

Bond distances (Å)		Bond angles (°)	
Ni(1)–P(2)	2.148(6)	P(2)–Ni(1)–P(1)	86.3(2)
Ni(1)–P(1)	2.222(7)	P(2)–Ni(1)–P(3)	89.7(2)
Ni(1)–P(3)	2.222(6)	P(1)–Ni(1)–P(3)	118.2(2)
Ni(1)–S(1)	2.250(5)	P(2)–Ni(1)–S(1)	175.7(3)
Ni(1)–S(2)	2.324(6)	P(1)–Ni(1)–S(1)	96.3(2)
S(1)–C(1)	1.752(18)	P(3)–Ni(1)–S(1)	92.1(2)
S(2)–C(1)	1.634(18)	P(2)–Ni(1)–S(2)	99.8(2)
Ni(1A)–P(2A)	2.165(6)	P(1)–Ni(1)–S(2)	124.2(2)
Ni(1A)–P(3A)	2.185(6)	P(3)–Ni(1)–S(2)	117.3(2)
Ni(1A)–P(1A)	2.200(6)	S(1)–Ni(1)–S(2)	75.89(19)
Ni(1A)–S(1A)	2.248(5)	P(2A)–Ni(1A)–P(3A)	87.9(2)
Ni(1A)–S(2A)	2.321(7)	P(2A)–Ni(1A)–P(1A)	86.8(2)
S(1A)–C(1A)	1.722(16)	P(3A)–Ni(1A)–P(1A)	124.0(3)
S(2A)–C(1A)	1.735(16)	P(2A)–Ni(1A)–S(1A)	177.8(2)
C(1)–N(1)	1.33(2)	P(3A)–Ni(1A)–S(1A)	92.2(2)
C(1A)–N(1A)	1.26(2)	P(1A)–Ni(1A)–S(1A)	95.0(2)
		P(2A)–Ni(1A)–S(2A)	101.6(2)
		P(3A)–Ni(1A)–S(2A)	114.8(2)
		P(1A)–Ni(1A)–S(2A)	120.9(2)
		S(1A)–Ni(1A)–S(2A)	6.46(19)

The X-ray structures of two complexes [Ni(pe_2dtc)(triphosI)]PF_6 (2) and [Ni(bz_2dtc)(triphosI)]PF_6 (5) have been solved. The final R-values for (2) are somewhat higher, probably in connection with the bad quality of experimental data (Rint = 0.0785). The basic crystallographic data are summarized in Tables 2, 3. The results obtained for both structures confirmed a five-coordinated central nickel atom in the distorted triangular bipyramid polyhedron. From Fig. 1, 2 it is apparent, that the axial positions are occupied by the S1 atom from dithiocarbamate ligand and by P2 atom from triphosI. The Ni1, S2, P1 and P3 atoms are nearly co-planar; the calculated [27] deviations from ideal LSQ-Ni1S2P1P3 plane are smaller than 0.02(1) Å (for 2), resp. 0.05(1) Å, (for 5). The assumption of the distorted triangular bipyramid coordination is in good agreement with calculations of angle structure parameter $\tau = (\beta - \alpha)/60 =$ 0.76 (2), resp. 0.85 (5) ($\tau = 1$ for triangular bipyramid; $\tau = 0$ for tetragonal pyramid coordination) [28]. The Ni–S and Ni–P bond lengths are not equal (the axial bond lengths are smaller than the remaining ones). A significant shortening of bond lengths in the S_2CN^- group, typical for dithiocarbamates (see Table 4, 5), was found. The common bond distances for σ-bond are [29]: C–N (1.47 Å); C–S (1.81 Å). This fact can be explained by a significant deal of the π-interactions in these bonds. The PF_6 ion is placed out of the coordination sphere; Ni1-P4 distance is about 6.68 Å for (2), resp. 9.42 Å and 7.35 for (5).

IR-spectra exhibit typical vibrations for dithiocarbamates: $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ at 1490–1515 cm^{-1} and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ at 990–1000 cm^{-1} [33]. For the complexes (3), (9) with ClO_4 the non-split maximum $\nu_3(ClO_4)$ at 1075 and 1088 cm^{-1}; $\nu_4(ClO_4)$ at 620 and 625 cm^{-1} were recorded, which indicates the ionic coordination of the ClO_4 group [31]. For complexes (2), (5) and (7) with hexafluorophosphate, the $\nu(PF_6)$ vibrations in the 830–840 cm^{-1} range were found [32].

The results of electronic diffuse-reflectance spectroscopy show absorption maxima near 14000, 18000 and 24000 cm^{-1}. Similar data were obtained by Ballester *et al.* [32] for low-spin penta-coordinated dithiocarbonates and xanthates of nickel(II) with triphosI of $[Ni(S_2COR)(triphosI)]^+$ and $[Ni(S_2COR)(triphosI)]$ types. These results are in good accord with [34]. The maxima over 30000 cm^{-1} can be assigned to intra-ligand transitions in the S_2CN^- group [33].

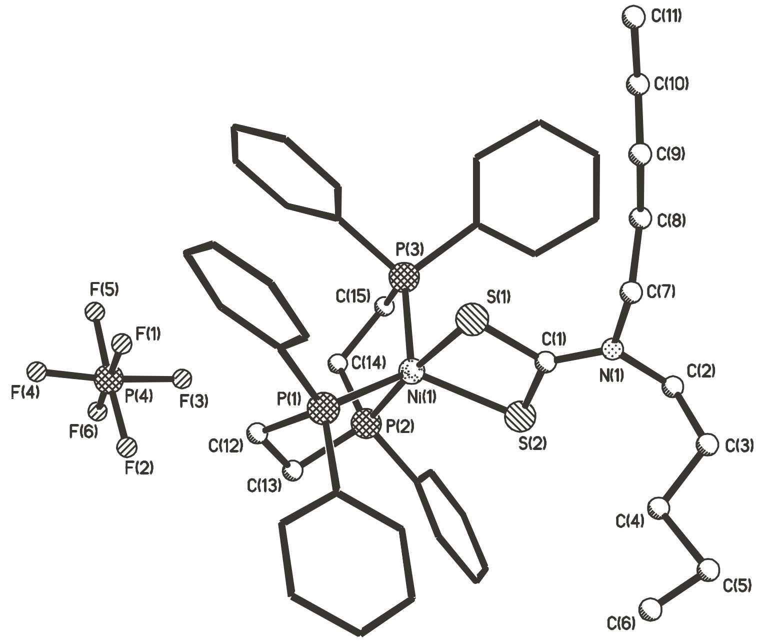

Figure 1. Molecule of $[Ni(pe_2dtc)(triphosI)]PF_6$.

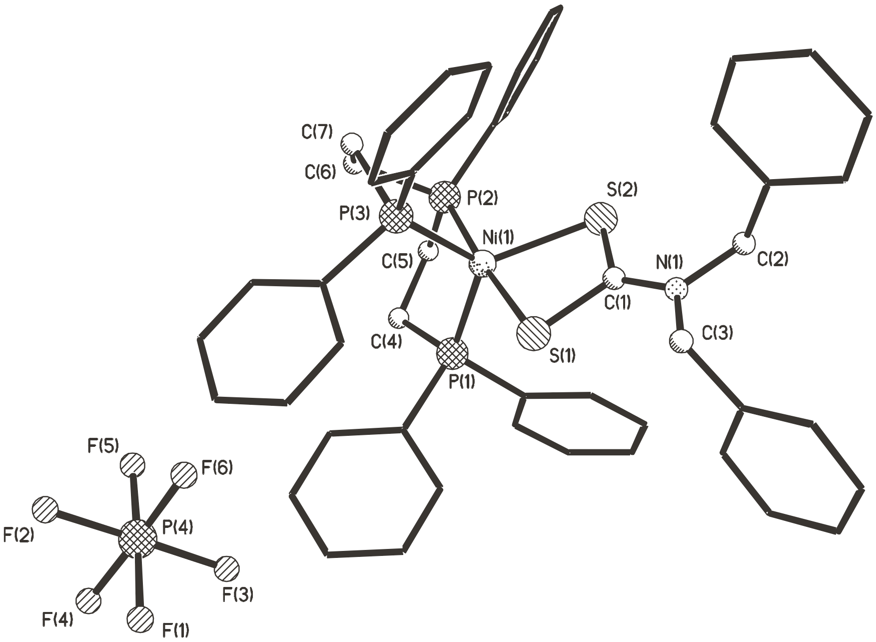

Figure 2. Molecule of [Ni(bz_2dtc)(triphosI)]PF_6.

$^{31}P\{^1H\}$-NMR spectra of the complexes, as well as the triphosI ligand, recorded at 300 and 320 K, are listed in Table 6. The free triphosI is characterized by the triplet at –15.85 ppm (central P atom) and by the doublet at –12.14 ppm (two terminal P atoms) at 300 K. The coordinated triphosI is characterized by the triplet in the 108.12–111.44 ppm range and by the doublet in the 41.33–42.35 ppm range [32]. These significant changes in chemical shifts for both signals confirm the coordination of all phosphorus atoms to nickel. Two overlapped doublets and two overlapped triplets were observed for the complexes (6)–(9), containing asymmetrical dithiocarbamate ligand cetdtc, in spectra at 300 K. For this reason, we have measured $^{31}P\{^1H\}$-NMR spectra at 320 K. This temperature increasing caused, that only one triplet and one doublet were observed. We suppose that this unusual behavior could be connected with a slow rotation of dithiocarbamato group along C$\overset{...}{-}$N bond, bearing particular multiple-character, which results in the formation of two isomers. At 320 K, the rotation is fast enough and only one form of the complex can be distinguished. This conclusion could be supported by the fact, that spectra of the complexes with coordinated symmetrical dithiocarbamates pe_2dtc and bz_2dtc, recorded at 300 and 320 K, did not vary from each other. A presence of the PF_6 anion in the complexes (2), (5) and (7) is evident from typical septet near –143 ppm ($^1J_{P\text{-}F}$ = 713 Hz).

Table 6. ^{31}P{^{1}H}-NMR[a] data.

Compound	300 K	320 K
triphosI	–15.85 (t, 1P, $^3J_{P-P}$= 28.22 Hz) –12.14 (d, 2P, $^3J_{P-P}$= 29.70 Hz)	–15.58 (t, 1P, $^3J_{p-p}$ = 28.51 Hz) –11.84 (d, 2P, $^3J_{p-p}$ = 28.51 Hz)
(1)	42.07 (d, 2P, $^3J_{P-P}$= 33.69 Hz) 110.40 (t, 1P, $^3J_{P-P}$ = 33.69 Hz)	41.32 (d, 2P, $^3J_{p-p}$ = 33.69 Hz) 109.61 (t, 1P, $^3J_{p-p}$= 33.69 Hz)
(2)	–143.64 (sept, 1P, $^1J_{P-F}$ = 712.82 Hz) 41.33 (d, 2P, $^3J_{P-P}$= 35.64 Hz) 109.38 (t, 1P, $^3J_{P-P}$= 35.64 Hz)	–143.76 (sept, 1P, $^1J_{P-F}$ = 712.82 Hz) 40.62 (d, 2P, $^3J_{P-P}$ = 34.16 Hz) 108.52 (t, 1P, $^3J_{P-P}$ = 34.16 Hz)
(3)	41.42 (d, 2P, $^3J_{P-P}$= 33.41 Hz) 109.87 (t, 1P, $^3J_{P-P}$= 33.41 Hz)	40.69 (d, 2P, $^3J_{p-p}$ = 33.41 Hz) 108.95 (t, 1P, $^3J_{p-p}$= 33.41 Hz)
(4)	42.35 (d, 2P, $^3J_{P-P}$= 33.41 Hz) 111.44 (t, 1P, $^3J_{P-P}$ = 33.41 Hz)	41.79 (d, 2P, $^3J_{p-p}$ = 33.41 Hz) 110.77 (t, 1P, $^3J_{p-p}$= 33.41 Hz)
(5)	–143.63 (sept, 1P, $^1J_{P-F}$ = 712.82 Hz) 41.50 (d, 2P, $^3J_{P-P}$= 34.16 Hz) 110.23 (t, 1P, $^3J_{P-P}$ = 34.16 Hz)	–143.74 (sept, 1P, $^1J_{P-F}$ = 712.82 Hz) 40.96 (d, 2P, $^3J_{P-P}$ = 34.16 Hz) 109.49 (t, 1P, $^3J_{P-P}$ = 34.16 Hz)
(6)	41.97 (d, 2P, $^3J_{P-P}$= 33.69 Hz) 42.23 (d, 2P, $^3J_{P-P}$= 33.69 Hz) 109.74 (t, 1P, $^3J_{P-P}$= 33.69 Hz) 110.00 (t, 1P, $^3J_{P-P}$ = 33.69 Hz)	41.41 (d, 2P, $^3J_{P-P}$ = 33.69 Hz) 109.03 (t, 1P, $^3J_{P-P}$ = 33.69 Hz)
(7)	–143.64 (sept, 1P, $^1J_{P-F}$ = 712.72 Hz) 41.42 (d, 2P, $^3J_{P-P}$= 35.64 Hz) 41.50 (d, 2P, $^3J_{P-P}$= 35.64 Hz) 108.84 (t, 1P, $^3J_{P-P}$= 35.64 Hz) 109.06 (t, 1P, $^3J_{P-P}$= 35.64 Hz)	–143.77 (sept, 1P, $^1J_{P-F}$ = 712.72 Hz) 40.76 (d, 2P, $^3J_{P-P}$ = 33.69 Hz) 108.02 (t, 1P, $^3J_{P-P}$ = 33.69 Hz)
(8)	41.82 (d, 2P, $^3J_{P-P}$= 33.69 Hz) 41.95 (d, 2P, $^3J_{P-P}$= 33.69 Hz) 108.12 (t, 1P, $^3J_{P-P}$= 33.69 Hz) 108.33 (t, 1P, $^3J_{P-P}$= 33.69 Hz)	41.18 (d, 2P, $^3J_{P-P}$ = 33.69 Hz) 107.37 (t, 1P, $^3J_{P-P}$ = 33.69 Hz)
(9)	41.50 (d, 2P, $^3J_{P-P}$= 34.16 Hz) 41.55 (d, 2P, $^3J_{P-P}$= 34.16 Hz) 109.24 (t, 1P, $^3J_{P-P}$= 34.16 Hz) 109.44 (t, 1P, $^3J_{P-P}$= 34.16 Hz)	40.82 (d, 2P, $^3J_{P-P}$ = 33.69 Hz) 108.47 (t, 1P, $^3J_{P-P}$ = 33.69 Hz)

[a] In $CDCl_3$ solution (δ in ppm); d – doublet; t – triplet; sept – septet.

Thermal analysis of complexes shows that very unstable are the [Ni(Ldtc)(triphosI)]Cl·H_2O compounds (1), (4) and (6) containing triphosI ligand. The decomposition starts between 41.5–49.1°C. Dehydration is accompanied by small endo-effects between 61.8–81.2℃; the plateau on the TG-curve for complexes (1), (4) in interval 88.0–149.5℃ and 96.9–158.6℃ were recorded, and can be assigned to non-solvated species. The complex (6) exhibits no plateau, due to continual decomposition. Thermally more stable are complexes (2), (5) and (7) with PF_6 ligand, which decomposed between 234.6–251.8°C. The endo-effects in interval 210.6–270.3°C are connected with melting (confirmed by estimation of melting points by Boëtius apparatus). All complexes exhibit exo-effects (between 121.1–279.2°C), which are connected with a mass increase. This fact is described in [36] and can be attributed to the oxygen-insertion into the Ni–P bond. The insertion is combined with the decomposition of the organic part of the molecule, without thermal stable intermediates [37] and this process was not studied. Complexes (3) and (9) with perchlorate were not studied, due to safety reasons (danger of explosion).

Supplementary data: Structure data has been deposited in the Cambridge Crystallographic Data Centre, Registry No. CCDC 215298 (2) and 225409 (5). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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