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Non-Symmetrical Nickel(II)dithiocarbamates with NiS_2P_2-Chromophore

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Non-symmetrically substituted Ni(II)dithiocarbamate complexes with NiS_2P_2 chromophore of composition $[Ni(bz^{i}prdtc)(PPh_3)_2]X$, $[Ni(bz^{i}prdtc)(PPh_3)_2]BPh_4\cdot 3H_2O$ ($bz^{i}prdtc^{-}$ = benzylisopropyldithiocarbamate, PPh_3 = triphenylphosphine, BPh_4^- = tetraphenylborate, X = ClO_4^-, PF_6^-), $[Ni(cetdtc)(PPh_3)_2]X$, $[Ni(cetdtc)(PPh_3)_2]PF_6$, $[Ni(cetdtc)(PBut_3)_2]X$ ($cetdtc^{-}$ = cyclohexylethyldithiocarbamate, $PBut_3$ = tributylphosphine, X = ClO_4^-, BPh_4^-) have been isolated. These complexes have been characterized by elemental analysis, IR and UV-VIS spectroscopy, thermal analysis, magnetochemical and conductivity measurements. X-ray structural analysis of $[Ni(bz^{i}prdtc)(PPh_3)_2]ClO_4\cdot 0.5H_2O$ confirms the NiS_2P_2 chromophore with a slightly distorted square arrangement around the central atom.

Key words: non-symmetrical dithiocarbamate nickel(II) complexes, synthesis, physicochemical study, X-ray structural analysis

There is only little information about non-symmetrically substituted Ni(II) dithiocarbamates with NiS_2P_2 chromophore available. For instance, complexes with a bidentate P-ligand 1,2-bis(diphenylphosphine)ethane (dppe) of the type $[Ni(R_1R_2Nadtc)(dppe)]ClO_4$ [1] have been described. Dithiocarbamates were derived from glycine (R_1 = H, R_2 = $C_2H_2O_2^-$), methionine (R_1 = H, R_2 = $C_5H_8O_2S^-$), tryptophan (R_1 = H, R_2 = $C_{11}H_9NO_2^-$) and sarcosine (R_1 = CH_3, R_2 = $C_2H_2O_2^-$); dtc^- = S_2CN^-. By X-ray structural analysis of $[Ni(MeEadtc)(dppe)]BPh_4\cdot CH_2Cl_2$ [2] (Me = methyl, Ea = 2-hydroxyethyl) it was confirmed a distorted square arrangement of NiS_2P_2 chromophore. As for monodentate ligands, only PPh_3 was used and complexes of the $[Ni(R_1R_2dtc)(PPh_3)_2]ClO_4$ type (R_1 = H, CH_3; R_2 = $C_2H_3O_2$, $C_5H_9O_2S$, $C_{11}H_{10}NO_2$) [1] have been isolated and X-ray structural analysis of $[Ni(MeEadtc)(PPh_3)_2]ClO_4$ [2] confirmed a distorted square coordination sphere as well.

We focused on nickel(II) benzylisopropyl- and cyclohexylethyldithiocarbamates and their reaction with monodentate P-ligands with the aim to study the influence of the dithiocarbamate, type of P-ligand and anion X on the structure and properties of newly synthesized complexes.

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EXPERIMENTAL

Materials and methods: Triphenylphosphine (99%) and $LiClO_4{\cdot}3H_2O$ were from Aldrich Co., tributylphosphine (85%), $NaClO_4{\cdot}H_2O$ and $K[PF_6]$ were from Fluka Co., the others from Lachema Co (p.a. purity). The content of nickel was determined by chelatometric titration using murexide as an indicator [3]; chlorine was determined by Schöniger method [4]. The 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 Faraday method with $Co[Hg(NCS)_4]$ as a calibrant. Conductivities were measured using a Conductivity Hand-Held Meter LF330 (WTW GmbH) at 25°C. Diffuse-reflectance electronic absorption spectra (45000–11000 cm^{-1}) were carried out on a Specord M40 (Carl Zeiss, Jena), IR spectra (4000–300 cm^{-1}) were recorded on a Specord M80 (Carl Zeiss, Jena) using nujol technique. The thermal analysis was performed on a Exstar 6000, TG/DTA 6200 (Seiko, Japan; sample weight 9.5–10.3 mg, temperature range 20–1150°C, gradient 2.5°C/min). Melting points were determined by Boëtius Rapido melting point apparatus (Wägetechnik PHMK 79/2106).

Syntheses: $[Ni(bz^{i}prdtc)(PPh_3)_2]X$, ($X = ClO_4^-, BPh_4^-, PF_6^-$): In the case of ClO_4^- salt the suspension of fine powdered initial complex $[NiCl(bz^{i}prdtc)(PPh_3)]$ [5] (1 mmol), PPh_3 (2 mmol) and $LiClO_4{\cdot}3H_2O$ (2 mmol) in 25 cm^3 methanol was stirred under reflux for 3 h. The resulting orange-colored crystalline substance was filtered, washed with n-hexane and dried at 40°C under an infra-lamp; yield 29%. In the case of BPh_4^- salt: $[NiCl(bz^{i}prdtc)(PPh_3)]$ (1 mmol), PPh_3 (2 mmol) in 5 cm^3 $CHCl_3$ and $Na[BPh_4]$ (1 mmol) in 5 cm^3 methanol were used; in the case of PF_6^- salt – as above, but instead $Na[BPh_4]$ – $K[PF_6]$ (1 mmol) and PPh_3 in 5 cm^3 acetone was used. After mixing appropriate solutions a slight dimness was observed that disappeared by adding $CHCl_3$. After reflux (4 h) red solutions were filtered and orange-brown ($X = BPh_4^-$), resp. red-violet ($X = PF_6^-$) substances were obtained by free crystallization over two days. The resulting compounds were washed with n-hexane and dried at 40°C. Yield: 28% and 26%, respectively.

$[Ni(cetdtc)(PPh_3)_2]X$, ($X = ClO_4^-, BPh_4^-, PF_6^-$): The complexes were synthesized by the reaction of a suspension of fine powdered $Na(cetdtc){\cdot}2H_2O$ [6] (1 mmol), PPh_3 (2 mmol), $NiCl_2{\cdot}6H_2O$ (1 mmol) in 30 cm^3 methanol. The mixture was stirred under reflux for 1.5 h and $NaClO_4{\cdot}H_2O$, resp. $Na[BPh_4]$ or $K[PF_6]$ (1 mmol) was added. After of 1 h reflux, red solutions ($X = ClO_4^-, PF_6^-$) were filtered and crystals were obtained by evaporation of solvent and decantation with n-hexane, filtration and washing with water and (after drying by air) with ether. In the case of $X = BPh_4^-$ an orange substance appeared during stirring under reflux; it was filtered, washed with n-hexane, toluene and ether. All samples were dried at 40°C. Yield: 58%, 56% and 57%, respectively.

$[Ni(cetdtc)(PBut_3)_2]X$, ($X = ClO_4^-, BPh_4^-$): The molar ratio of components is the same as above ($PBut_3$ instead of PPh_3 was used). Dark-red solutions were filtered; in the case $X = ClO_4^-$ an oily product was formed and an addition of petroleum ether was necessary to obtain an orange powder. The final product was obtained by re-crystallization from methanol. For $X = BPh_4^-$ orange colored crystals precipitated. Both products were washed with methanol and dried at 40°C. Yield: 33% and 39%, respectively.

X-ray crystallography: X-ray measurements were performed on a KUMA KM-4 diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using an area sensitive detector. The structures were solved by direct methods using the SHELXS-97 program [7]. The structures were refined anisotropically by the full-matrix least-square procedure on F^2 using a SHELXL-97 program [8]. Most H-atoms were found from difference Fourier maps and they were refined isotropically. Additional calculations were made using PARST 95 program [9]. Important crystallographic parameters are summarized in Table 2.

RESULTS AND DISCUSSION

Important results from physico-chemical measurements are given in Table 1. All compounds are diamagnetic and electrolytes 1:1 in acetone [10], which is in line with the assumption of the square coordination of NiS_2P_2. The complexes (1), (4) and (7) exhibit non-split maxima due to ionic character of ClO_4^- group: ν_3 (in interval 1076–1090 cm^{-1}) and ν_4 (620–622 cm^{-1}) [11]. The assumption of square polyhedron

Table 1. Results of physico-chemical studies.

Complex* Color	λ_M[a]	UV/VIS				IR (cm^{-1})				TA (°C)							
	(Scm^2 mol^{-1})	(×10^3 cm^{-1})				$\nu(C\cdots S)$	$\nu(C\cdots N)$	$\nu_3(ClO_4^-)$	$\nu_4(ClO_4^-)$	T		E_n		E_x			
(1) orange	124.9	15.4	19.8	29.4	31.2	995w	1510w	1076m	622w			no study					
(2) orange-brown	101.8		19.5		31.2	992m	1520m	–	–	58	66	79	109		133	159	254
(3) red-violet	120.0		19.6		31.0	995m	1525m	–	–	101		–				241	294
(4) orange	132.9		19.2		31.4	992s	1508s	1090vs	622m			no study					
(5) orange	103.3		19.2		31.2	995m	1522m	–	–	113[b]		119			115	131	167
(6) dark-orange	122.9		19.0	30.8	36.0	995m	1525m	–	–	142		–		197	217	226	279
(7) orange	127.8		20.2	23.9	33.3	1005m	1508s	1090vs	620m			no study					
(8) orange	104.3		19.5	23.4	33.1	970m	1512s	–	–	116[b]		116				123	148

[a] In acetone solution (10^{-3} mol·dm^{-3}); T – begin of thermal decomposition; [b] begin of mass increasing; E_n – endo-effect; E_x – exo-effect.

*(1) $[Ni(bz^iprdtc)(PPh_3)_2]ClO_4 \cdot 0.5H_2O$; (2) $[Ni(bz^iprdtc)(PPh_3)_2]BPh_4 \cdot 3H_2O$; (3) $[Ni(bz^iprdtc)(PPh_3)_2]PF_6$; (4) $[Ni(cetdtc)(PPh_3)_2]ClO_4$; (5) $[Ni(cetdtc)(PPh_3)_2]BPh_4$; (6) $[Ni(cetdtc)(PPh_3)_2]PF_6$; (7) $[Ni(cetdtc)(PBut_3)_2]ClO_4$; (8) $[Ni(cetdtc)(PBut_3)_2]BPh_4$.

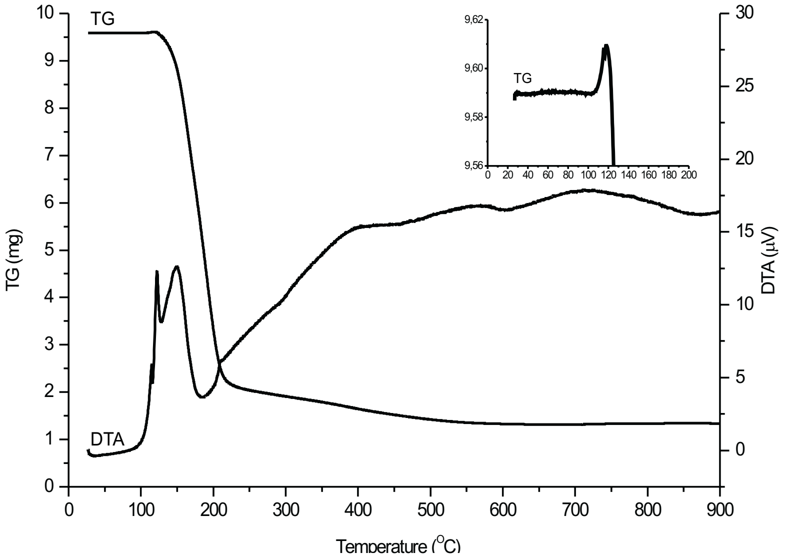

Figure 1. Thermal analysis of [Ni(cetdtc)(PBut$_3$)$_2$]BPh$_4$.

is supported also by electronic spectra in nujol – all compounds exhibit d-d absorptions (15400–23900 cm^{-1}) characteristic for $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions of low-spin square Ni(II) complexes [12]. The maxima over 30000 cm^{-1} can be assigned to intra-ligand transitions in the S$_2$CN$^-$ group [13]. IR-vibrations $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ (1508–1525 cm^{-1}) and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ (970–1005 cm^{-1}) typical of dithiocarbamates [13] were also observed in all complexes. Samples (3) and (6) exhibit very strong PF_6^- vibrations near 832 cm^{-1} and 830 cm^{-1}, respectively [14].

Thermal analysis was studied only for (2), (3), (5), (6) and (8); complexes with ClO_4^- were not examined for safety reasons. [Ni(cetdtc)(PBut$_3$)$_2$]BPh$_4$ (Fig. 1) exhibits a small sharp endo-effect at 116°C (melting point is 117°C). TG-curve recorded a slight mass increasing connected with a large exo-effect on DTA-curve (top at 123°C). This phenomenon was described for complexes containing Ni–P bonds [15] and can be explained by incorporation of oxygen into these bonds. Mass increasing is overlapped with decomposition of the organic part of the compound (exo-effect at 148°C). Complex [Ni(cetdtc)(PPh$_3$)$_2$]BPh$_4$ exhibits a sharp exo-effect at 115°C (insertion of oxygen), followed by a melting point (endo-effect at 119°C; apparatus: 121°C). Decomposition of the organic part is connected with a mass decreasing and two exo-effects (131°C and 167°C). Thermal behavior of [Ni(cetdtc)(PPh$_3$)$_2$]PF$_6$ complex is similar. Dehydration of [Ni(bz^{i}prdtc)(PPh$_3$)$_2$]BPh$_4$·3H$_2$O starts at 58°C and is connected with two endo-effects (the smaller at 66°; the bigger at 79°); the endo-effect at 109°C is due to the melting. A water-free complex is on TG-curve characterized by a plateau in interval 96–111°C ($\Delta M_{found/calcd}$ = 4.1/4.5%). A sharp exo-effect (insertion of oxygen) at 133° was also recorded, but no mass increasing appeared due to the fast thermal decomposition of the compound (exo-effects at 159°C and 254°C). [Ni(bz^{i}prdtc)(PPh$_3$)$_2$]PF$_6$ decomposes differently – neither exo-effect (incorporation of oxygen) nor endo-effect (melting of sample) were detected, only exo-effects (241°C and 294°C, decomposition of organic part) were found.

X-ray structural analysis of the $[Ni(bz^{i}prdtc)(PPh_3)_2]ClO_4{\cdot}0.5H_2O$ (Fig. 2) confirms the above conclusions (basic crystallographic data are collected in Table 2). The obtained results show that central atom of nickel possesses a distorted square coordination with nonequal Ni–S and Ni–P bond lengths and belonging angles. The deviations of ideal NiS_2P_2 plane (in Å) are calculated [9] for Ni: 0.007, S1: 0.137, S2: –0.139, P1: –0.124, P2: 0.107. Existence of π-bonds system in dithiocarbamate is illustrated by smaller bond distances of C1–N1 (1.304 Å), C1–S1(1.720 Å) and C1–S2 (1.719 Å) as compared to the literature values [16] for simple σ-bonds (C–N: 1.47 Å and C–S: 1.81 Å) (Table 3). The distance between chlorine and nickel (10.51 Å) shows that ClO_4^- is out of the nickel coordination sphere, which is in good agreement with physico-chemical measurements. No significant possible hydrogen bonds [9] were confirmed; one molecule of water has been found in the elemental cell.

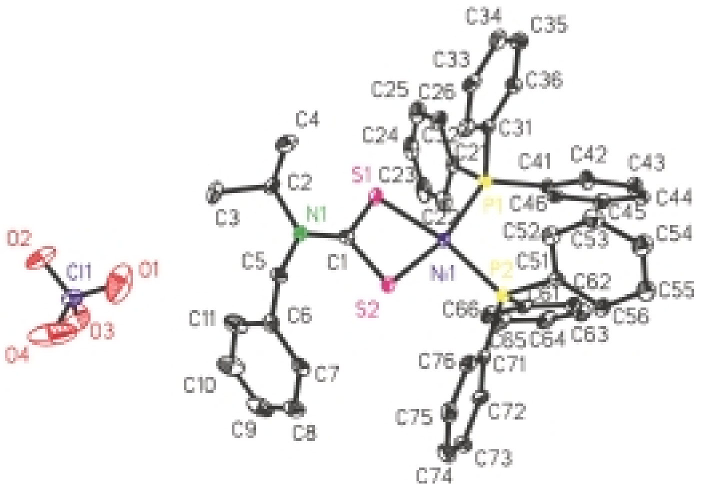

Figure 2. Molecule of $[Ni(bz^{i}prdtc)(PPh_3)_2]ClO_4{\cdot}0.5H_2O$ (solvent and H-atoms are omitted).

Thus, we can conclude that the type of dithiocarbamate, PR_3 and anion X^- exhibit a significant influence on the thermal behavior of complexes, but practically no influence on the shape of the coordination polyhedron.

Supplementary data: Material involving structure data has been deposited in the Cambridge Crystallographic Data Centre, Registry No. CCDC 186674. 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).

Table 2. Basic crystallographic data for [Ni(bz^{i}prdtc)(PPh$_3$)$_2$]ClO$_4$·0.5H$_2$O.

Molecular formula	$C_{47}H_{45}ClNNiO_{4.5}P_2S_2$
Formula weight	916.06
Temperature	120(2) K
Wavelength	0.71073 Å
Space group	$P\bar{1}$
Unit cell dimensions	a = 12.655(3) Å α = 92.80(3)° b = 12.884(3) Å β = 107.01(3)° c = 13.924(3) Å γ = 94.60(3)°
Volume; Z; density	2157.7(9) Å^3; 2; 1.410 Mg/m^3
Absorption coefficient	0.729 mm^{-1}
F(000)	954
Crystal size	0.35 × 0.25 × 0.05 mm
θ range for data collection	3.35 to 28.46°
Index ranges	$-16 \le h \le 10, -16 \le k \le 16, -17 \le l \le 18$
Reflections collected/unique	16390 / 9399 [R(int) = 0.0413]
Completeness to 2θ = 28.46°	86.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9399/0/576
Goodness-of-fit on F^2	0.967
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0387, wR2 = 0.0868
R indices (all data)	R1 = 0.0605, wR2 = 0.0944
Largest diff. peak and hole	0.611 and –0.444 e.Å^{-3}

Table 3. Important bond distances (Å) and angles (°) for [Ni(bz^{i}prdtc)(PPh$_3$)$_2$]ClO$_4$·0.5H$_2$O.

Bond distances		*Bond angles*	
Ni(1)–S(2)	2.1823(9)	S(2)–Ni(1)–P(2)	93.35(4)
Ni(1)–P(2)	2.1892(8)	S(2)–Ni(1)–P(1)	164.92(2)
Ni(1)–P(1)	2.2070(9)	P(2)–Ni(1)–P(1)	100.20(4)
Ni(1)–S(1)	2.2182(8)	S(2)–Ni(1)–S(1)	78.50(4)
P(1)–C(31)	1.813(2)	P(2)–Ni(1)–S(1)	169.53(3)
P(1)–C(21)	1.814(2)	P(1)–Ni(1)–S(1)	88.73(4)
P(1)–C(41)	1.818(2)	C(1)–S(1)–Ni(1)	85.75(8)
P(2)–C(51)	1.803(2)	C(1)–S(2)–Ni(1)	86.93(8)
P(2)–C(61)	1.812(2)	N(1)–C(1)–S(2)	124.97(18)
P(2)–C(71)	1.813(2)	N(1)–C(1)–S(1)	126.87(18)
S(1)–C(1)	1.720(2)	S(2)–C(1)–S(1)	108.13(12)
S(2)–C(1)	1.719(2)		
C(1)–N(1)	1.304(3)		

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