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Nickel(II)morpholinedithiocarbamate with Mixed P,P-Ligands

by R. Pastorek[1], J. Kameníček[*1], Z. Šindelář[1] and Z.) ák[2]

[1]*Department of Inorganic and Physical Chemistry, Palacký University, 771 47 Olomouc, Czech Republic*
[2]*Department of Inorganic Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*

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Ni(II)morpholinedithiocarbamate complexes with P,P-ligands in the coordination sphere of composition [Ni(morphdtc)(P,P)]X and [Ni_2(morphdtc)$_2X_2$(P,P)], resp. [(X = NCS^-, ClO_4^-, I^-; P,P = 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), 1,6-bis(diphenylphosphino)hexane (dpph), 1,1′-bis(diphenylphosphino)ferrocene (dppf); morph = C_4H_8O; dtc = S_2CN^-)] 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(morphdtc)(dppf)]$ClO_4 \cdot C_2H_5OH$ confirms the NiS_2P_2 chromophore with a slightly distorted square arrangement around central atom.

Key words: dithiocarbamate nickel(II) complexes, X-ray structural analysis, synthesis, thermal decomposition

Previously [1,2] we studied the possibility of replacement of some S-atoms from NiS_4 chromophore in the basic complex [Ni(morphdtc)$_2$] by other donor atoms. The diamagnetic square-planar complexes containing NiS_2PX chromophore of the type [NiX(morphdtc)(PPh_3)], (X = Cl, Br, I) have been prepared and the structure of the [NiBr(morphdtc)(PPh_3)] has been solved [1]. In the literature were found relatively few data about complexes with NiS_2P_2 chromophore. For instance, Ramalingam *et al.* [3] used triphenylphosphine as a monodentate P-ligand to obtain [Ni(morphdtc)(PPh_3)$_2$]ClO_4. Using of bidentate P,P-ligand was described for only the synthesis of [Ni(morphdtc)(dppe)]$ClO_4 \cdot CH_2Cl_2$ by Akilanen *et al.* [4]. Both complexes mentioned are diamagnetic with square coordination, which was confirmed by X-ray structural analysis. Our work is focused on P,P-ligands with the aim to study the influence of the type of P,P-ligand and anion X on the structure and properties of newly synthesized complexes.

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[*] Author for correspondence.

EXPERIMENTAL

Materials and methods: Dimethylformamide (dmf), 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), 1,6-bis(diphenylphosphino)hexane (dpph) and 1,1′-bis (diphenylphosphino)ferrocene (dppf) were from FLUKA Co., the others from LACHEMA Co. All reagents were of p.a. purity. The content of nickel was determined by chelatometric titration using murexide as an indicator. Chlorine and iodine were determined by Schöniger method [5]. 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 calibrant. Diamagnetic corrections were made with Pascal's constants [6]. Conductivities were measured using an OK 102/1 conductivity meter (Radelkis, Budapest) 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 stability was studied on a Q-1500 Derivatograph (MOM, Budapest; sample weight 150 mg, temperature range 20–900°C, gradient 2.5°C/min).

Syntheses: [Ni(morphdtc)(P,P)]X, (X = ClO_4^-, NCS^-, I^-): The suspension of fine powder of initial complex $[Ni(morphdtc)_2]$ [7] (1 mmol) in 50 cm^3 absolute ethanol with powdered $NiX_2{\cdot}nH_2O$ (1 mmol) and appropriate P,P-ligand (1 mmol) was stirred under reflux for six hours (in the case of complex 3 for twelve hours). The hot mixture was filtered. The crystals of complexes (3), (8) and (9) were obtained by free crystallization of the solution during 4–5 days. The substances were separated, washed with ether and dried at 40°C. In the case of complexes (1) and (2) the products were obtained by evaporation of solution to 20% of initial volume following by addition of water and stirring in refrigerator at –25°C. After separation the compounds were washed with water and dried at 40°C. The yield was about 60%.

$[Ni_2(morphdtc)_2X_2(P,P)]$: The molar ratio of components (1:1:1) was the same as above. In the case of complexes (4–6) the substances precipitated during reflux time. The products were separated from solution by filtration, washed with ethanol and ether and dried at 40°C. The complex (7) was obtained after evaporation to 20% of volume and filtration, washing with ether and drying.

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 $\omega/2\theta$ scan technique. The structures were solved by the direct methods using the SHELXS-97 program [8]. The structures were refined anisotropically by the full-matrix least-square procedure on F^2 using SHELXL-97 program [9]. Most H-atoms were found from difference Fourier maps and they were refined isotropically. Additional calculations were made using PARST 95 program [10]. Important crystallographic parameters are summarized in Table 1.

Table 1. Basic crystallographic data for $[Ni(morphdtc)(dppf)]ClO_4{\cdot}C_2H_5OH$.

Molecular formula	$NiFeC_{41}H_{42}NS_2P_2ClO_6$
Formula weight	920.83
Temperature	150(2) K
Wavelength	0.71073 Å
Space group	$P2_1/c$
Unit cell dimensions (Å), angles (°)	$a = 13.108(3)$; $\alpha = 90.0$
	$b = 10.280(2)$; $\beta = 99.34(3)$
	$c = 29.839(6)$; $\gamma = 90.0$
Volume; Z; density	3967.5(14) Å^3; 4; 1.542 Mg/m^3
Absorption coefficient	1.143 mm^{-1}
Reflections collected	5849
Independent reflections	5723 [R(int) = 0.0385]
Max. and min. transmission	0.8037 and 0.6905
Data/restraints/parameters	5723/0/653

Table 1 (continuation)

Goodness-of-fit on F^2	0.952
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0384, wR2 = 0.1107
R indices (all data)	R1 = 0.0947, wR2 = 0.1412
Extinction coefficient	0.0006(3)
Largest diff. peak and hole	0.513 and –0.644 e.Å^{-3}

RESULTS AND DISCUSSION

Important data from physico-chemical measurements are listed in Table 2. The [Ni(morphdtc)(P,P)]X complexes are diamagnetic, electrolytes 1:1 [11], which is in line with the assumption of the square coordination of NiS_2P_2. The ionic character of X^- is also confirmed by IR spectroscopy. The complexes with ClO_4^- exhibit characteristic non-split maxima ν_3 at 1085 cm^{-1} and ν_4 near 620 cm^{-1} [12]; the complexes containing NCS^- group exhibit vibration ν(CN) near 2055 cm^{-1} [13].

Binuclear complexes [Ni_2(morphdtc)$_2X_2$(P,P)] are also diamagnetic and except from (7) insoluble in common organic solvents (the conductivity cannot be measured). The value of λ_M of the [Ni_2(morphdtc)$_2$(NCS)$_2$(dppf)] in dimethylformamide is rather higher than should be for a non-electrolyte, but smaller then for 1:1 electrolyte [11]. This fact could be explained by partial dissociation of this complex in the solvent. In the IR-range of the complex (5) it was found a double maximum ν_3 at 1085 cm^{-1} and 1105 cm^{-1}, respectively, which can be interpreted according to [12] by coordination of ClO_4^- group to the central atom. The complexes (4) and (7) with X = NCS^- exhibit the IR-peaks belonging to ν(CN) near 2085 cm^{-1} and ν(CS) near 850 cm^{-1}. This fact supports the assumption of coordination of NCS^- to the nickel *via* nitrogen atom [13].

All experimental results show that all types of complexes have square arrangement of coordination sphere. This conclusion is supported also by the electronic spectra in nujol – with maxima due to d-d transitions of square Ni(II) complexes [14]. The maxima over 30000 cm^{-1} can be assigned to the intraligand transitions in the S_2CN^- group. IR-vibrations $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ (1515–1536 cm^{-1}) and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ (992–1005 cm^{-1}) typical for dithiocarbamates [15] were also observed for all complexes.

Thermal decomposition of hydrates begins in the interval 50–70°C. Dehydration of the (1), (2) and (4) complexes is connected with a small endo-effect between 120–135°C. The plateau in the case of (1) and (2) agrees with the elimination of water and formation of a non-hydrated intermediate. No other thermally stable intermediates were found (for complexes with ClO_4^- the thermal analyses cannot be performed for safety reasons).

[Ni(morphdtc)(dppf)]$ClO_4 \cdot C_2H_5OH$ was studied by X-ray structural analysis (basic crystallographic data are collected in Table 1). The obtained results (Table 3, Fig. 1) confirmed a distorted square coordination around nickel. The bond lengths in the chromophore are not equal and Ni, S and P atoms exhibit significant deviations

Table 2. Results of physico-chemical studies.

Com-plex*	Colour	λ_M (S cm^2 mol^{-1})	UV/VIS ($\times 10^3$ cm^{-1})					IR (cm^{-1})						T	Plateau (°C)	E
								ν(C$\cdots$S)	ν(C$\cdots$N)	ν(C≡N)	ν(C–S)	ν_3(ClO_4^-)	ν_4(ClO_4^-)			
(1)	dark-yellow	84^a		20.4		32.5		995vw	1525w	2052m	745vw			50	120–220	120
(2)	orange	81.7^a		21.0		32.2	41.2	995vw	1526m	2060s	748vw			60	120–200	
(3)	red	66.7^a		21.0		32.2		992w	1526s			1090vs	620m		no study	
(4)	yellow-brown	b	15.2	18.8	24.5	31.7	41.0	1005m	1515w	2080s	860vw			70	–	135
(5)	yellow-brown	b	15.0	18.9	24.6	30.5	40.0	1010m	1520m			1086s 1105s	622m		no study	
(6)	dark-violet	b		18.5	25.0	30.6	39.8	995w	1536w					60	–	
(7)	light-violet	38.1^a		18.4		31.8		992w	1528s	2098vs	838w			60	–	
(8)	red-violet	146^c		19.4		31.0	36.8	992s	1526s			1082vs	618s		no study	
(9)	dark-violet	65.3^a			20.5	31.4		992s	1520s		–		–	60	–	

^{a}In dimethylformamide solution (10^{-3} mol dm^{-3}), ^{b}insoluble in dimethylformamide and acetone, ^{c}in acetone solution (10^{-3} mol dm^{-3}),
T – begin of thermal decomposition, E – endoeffect

*(1) [Ni(morfdtc)(dppe)](NCS)·H_2O; (2) [Ni(morfdtc)(dppb)](NCS)·H_2O; (3) [Ni(morfdtc)(dppb)]ClO_4·H_2O; (4) [Ni(morfdtc)$_2$(NCS)$_2$(dpph)]·H_2O; (5) [Ni_2(morfdtc)$_2$(ClO_4)$_2$(dpph)]; (6) [Ni_2(morfdtc)$_2$$I_2$(dpph)]·2$H_2O$; (7) [$Ni_2$(morfdtc)$_2(NCS)_2$(dppf)]; (8) [Ni(morfdtc)(dppf)]ClO_4·C_2H_5OH; (9) [Ni(morfdtc)(dppf)]I.

from the ideal NiS_2P_2 plane (Ni: –0.0101 Å; S1: –0.0306 Å; S2: 0.0511 Å; P1: 0.0449 Å; P2: –0.0216 Å). The dihedral angle between NiS1S2C11 and NiS1S2P1P2 plane is 1.8(2)°. The bond lengths C11–N1 (1.317 Å); C11–S1 (1.713 Å) and C11–S2 (1.702 Å) in the dithiocarbamate group S_2CN^- are smaller as compared to the literature values [16] for simple σ-bonds (C–N: 1.47 Å and C–S: 1.81 Å) and confirm existence of π-bonds in this system. The distance between nickel and chlorine (8.34 Å) shows that anion ClO_4^- is not involved in the coordination sphere, which is in good agreement with all results of physico-chemical measurements. Possible hydrogen bonds formed by the O6 atom of solvent and the O5 atom from ClO_4^- group are given in Table 4.

Table 3. Important bond distances (Å) and angles (°) for [Ni(morphdtc)(dppf)]$ClO_4 \cdot C_2H_5OH$.

Bond distances		*Bond angles*	
Ni(1)–P(1)	2.1992(15)	P(1)–Ni(1)–S(1)	91.70(6)
Ni(1)–S(1)	2.2060(15)	P(1)–Ni(1)–P(2)	98.68(5)
Ni(1)–P(2)	2.2179(15)	S(1)–Ni(1)–P(2)	169.61(6)
Ni(1)–S(2)	2.2197(15)	P(1)–Ni(1)–S(2)	169.78(6)
S(1)–C(1)	1.723(5)	S(1)–Ni(1)–S(2)	78.57(5)
S(2)–C(11)	1.702(5)	P(2)–Ni(1)–S(2)	91.09(6)
P(1)–C(1)	1.791(5)	C(11)–S(1)–Ni(1)	85.70(17)
P(1)–C(21)	1.815(5)	C(11)–S(2)–Ni(1)	85.77(18)
P(1)–C(31)	1.824(5)	N(1)–C(11)–S(2)	125.6(4)
P(2)–C(6)	1.805(5)	S(2)–C(11)–S(1)	109.8(3)
P(2)–C(41)	1.820(5)	N(1)–C(11)–S(1)	124.6(4)
P(2)–C(51)	1.822(5)		
N(1)–C(11)	1.317(6)		

Table 4. Possible hydrogen contacts (distances in Å, angles in °) for [Ni(morphdtc)(dppf)]$ClO_4 \cdot C_2H_5OH$.

D–H	D ... A	H ... A	∠ D–H ... A
O6 -H6	O6 ...C11	H6 ...C11	O6 -H6 ...C11
.850(.065)	3.692(.073)	2.898(.018)	156.27(.67)
C42 -H42	C42 ...O6	H42 ...O6	C42 -H42 ...O6
.922(.257)	2.906(.029)	2.063(.356)	151.37(3.68)
C2 -H2	C2 ...O5	H2 ...O5	C2 -H2 ...O5
1.063(.730)	2.250(.078)	1.238(.315)	155.76(10.76)
C22 -H22	C22 ...O5	H22 ...O5	C22 -H22 ...O5
.939(.086)	2.125(.069)	1.312(.711)	140.82(5.39)

D donor; A acceptor.

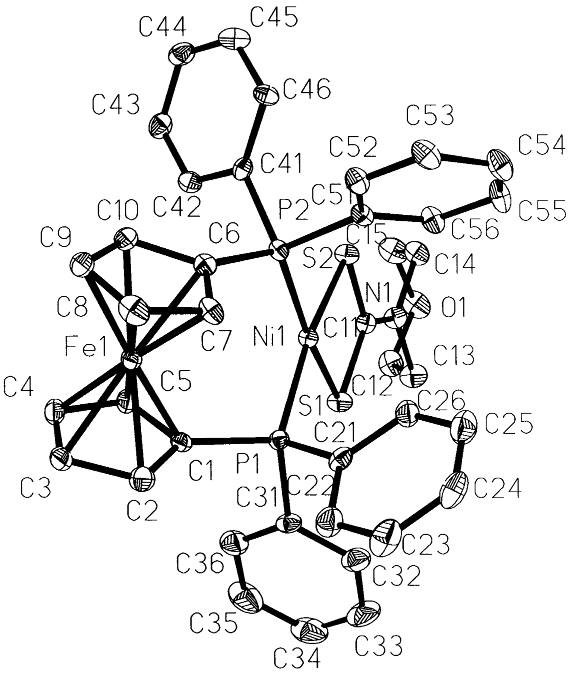

Figure 1. Molecule of [Ni(morphdtc)(dppf)]ClO_4 (solvent and H-atoms are omitted).

Some intermolecular contacts were observed; the interpretation of these bonds was made according [17]. The best convergence was reached by the assumption of two equivalent positions of three oxygen atoms (O2, O3, O4) from the ClO_4^- group with occupation factors 0.5. The structures of all complexes of the [Ni(morphdtc)(P,P)]X type seem to be similar – the X-ray structural analysis of the selected complex was solved and similar results are recently described, too [18]. In the binuclear complexes [Ni_2(morphdtc)$_2X_2$(P,P)], the P,P ligand is probably coordinated as a bidentate bridge *via* both P-atoms to the both Ni-atoms (each complex contains two square NiS_2PX chromophores). Unfortunately, our attempts to obtain the crystals suitable for X-ray analysis to confirm this structure were not successful.

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* Supplementary data

Material involving structure data has been deposited in the Cambridge Crystallographic Data Centre, Registry No: CCDC 143943.

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