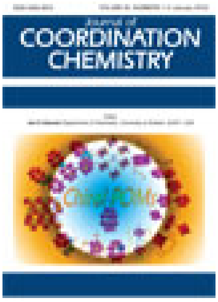

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Planar Ni(II) 1,2-dithiolenes involving tridentate P -donor ligands

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Planar Ni(II) 1,2-dithiolenes involving tridentate *P*-donor ligands

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A series of Ni(II) dithiolenes derived from maleonitriledithiol (mnt), benzene-1,2-dithiol (bdt), and toluene-3,4-dithiol (tdt) with potentially tridentate *P*,*P*,*P*-ligands *bis*(2-diphenylphosphino-ethyl)phenylphosphine (triphosI) and 1,1,1-*tris*-(diphenylphosphino-methyl)-ethane (triphosII) of the [Ni(*P*,*P*,*P*)(dithiol)] type have been synthesized. The compounds have been characterized by elemental analysis, IR and electronic spectroscopies, magnetochemical, and conductivity measurements. Single-crystal X-ray analysis of [Ni(triphosI)(mnt)] confirmed a planar geometry of NiP_2S_2 chromophore (one of *P*-atoms is not coordinated). Possible practical applications such as the use of these compounds as anticholinesterase agents were evaluated.

Keywords: Nickel(II); Dithiolenes; X-ray structure; Cholinesterase; Inhibitor

1. Introduction

In our previous work [1], we determined that a square-planar coordination polyhedron is very common for nickel dithiolenes with NiS_4 chromophore containing two *S*,*S*-ligands. Whereas a square-planar Ni(II)dithiocarbamate and dithiolate complexes with bidentate *N*-ligands [2], monodentate *P*- and bidentate *P*,*P*-ligands [3–10], were extensively studied; similar complexes with tridentate *P*,*P*,*P*-ligands were published

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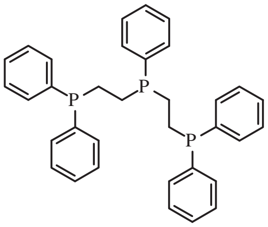
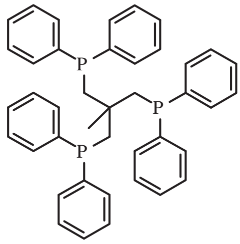
less commonly [11].



triphos I



triphos II

[Ni(dpdtc)(triphosI](PF_6) (dpdtc = dipentyldithiocarbamate) with coordination number five (NiS_2P_3 chromophore) was described, including X-ray analysis [12]. Some data of Ni(II) xanthates with triphosI and coordination number five, including X-ray structure of [Ni($S_2COC_6H_{11}$)(triphosI)][Ni($S_2COC_6H_{11}$)$_3$, were also reported [13].

Dithiocarbamate complexes, containing triphosII with coordination number four (MP_2S_2) and also five (MP_3S_2 chromophore) of general composition [M(S_2CHPEt_3) (triphosII](BPh_4)$_n$; M = Fe, Co, Ni; $n = 1,2$ were described by Bianchini *et al.* [14–16], including X-ray structures. Some isopropylxanthate and ethandithiolate Ni(II)-complexes of composition [Ni(Pr^ixa)$_2$(triphosII)] · H_2O and [Ni_2(edt_2)(triphosII) (H_2O)$_2$] (edt = $C_2H_4S^{2-}$) without X-ray structure confirmation have also been published [17, 18].

Some nickel complexes can be used as biologically active model compounds, also as superconductors, analytical reagents, polarization filters, pesticides, vulcanization catalysts, and special developers [19–25].

The aim of this work was the synthesis and physico-chemical study of a series of selected Ni(II) dithiolene complexes with bidentate *S*,*S*-ligands (bdt, tdt, and mnt) combined with potentially tridentate *P*,*P*,*P*-ligands (triphosI and triphosII), including X-ray analysis of a selected sample for unambiguous confirmation of coordination polyhedron around nickel. Potential applications as cholinesterase inhibitors are discussed.

2. Experimental

2.1. *Materials*

The following reagents (Sigma-Aldrich) were used for syntheses: *bis*(2-diphenylphosphino-ethyl)phenylphosphine ≥97%, 1,1,1-*tris*-(diphenyl-phosphinomethyl)-ethane, dimercaptomaleonitrile disodium salt hydrate ≥95%, toluene-3,4-dithiol ≥97%, benzene-1,2-dithiol ≥95%. All solvents were products of LACHEMA Brno. For the evaluation of cholinesterase activity, chemicals of analytical grade from Sigma-Aldrich were used.

2.2. *Physical measurements*

The nickel content was determined by chelatometric titration using murexide as indicator [26]. CHNS analyses were performed on a Fisons EA 1108 instrument; satisfactory analyses were obtained for all complexes (table 1).

Table 1. Analytical data.

Compound	M (g mol^{-1})	[Calcd/found] Ni (%)	C (%)	H (%)	S (%)	N (%)
I. [Ni(triphosI)(mnt)]	733.44	8.00/7.58	62.29/61.86	4.54/4.82	8.73/8.53	3.83/3.56
II. [Ni(triphosI)(bdt)]	733.48	8.00/8.13	65.57/64.98	5.09/5.12	8.73/9.13	/
III. [Ni(triphosI)(tdt)]	747.51	7.85/7.79	65.84/65.46	5.40/5.41	8.56/9.01	/
IV. [Ni(triphosII)(mnt)]	823.56	7.13/7.23	65.68/65.70	4.78/5.06	7.78/8.17	3.41/3.43
V. [Ni(triphosII)(bdt)]	823.60	7.13/7.10	68.60/68.77	5.27/5.28	7.77/8.15	/
VI. [Ni(triphosII)(tdt)]	837.63	7.00/6.95	68.80/68.71	5.54/5.86	7.64/8.02	/

Infrared (IR) spectra were recorded on a Nexus 670 FTIR spectrometer (ThermoNicolet) using a Smart Orbit diamond ATR technique (4000–200 cm^{-1}). Absorption electronic spectra (45,000–9090 cm^{-1}) were carried out on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer using dimethylformamide (DMF) as solvent (concentration of solutions: 1×10^{-3} mol dm^{-3}). Conductivities were measured with an LF 330/SET conductivity meter (WTW GmbH) at 25°C. The magnetic data were taken with the SQUID apparatus (MPMS-XL7, Quantum Design) using the RSO mode of detection. The susceptibilities were taken at $B = 0.1$ T. The powder samples were placed in gelatin capsules. ^{31}P-NMR spectra were recorded on a Varian VNMRS 600 spectrometer (conditions: pulse pw $45° = 5.3$; $t = 25°$C) using H_3PO_4 as a standard and dimethyl sulfoxide (DMSO) as solvent.

Multichannel spectrophotometer Sunrise (Tecan, Salzburg, Austria) was used for measuring cholinesterases activity. Previously optimized procedure [27, 28] was adopted in order to estimate anticholinergic properties; 96-wells photometric microplates made from polystyrene (Nunc, Rockilde, Denmark) were used.

Human recombinant acetylcholinesterase (AChE) and human plasmatic butyrylcholinesterase (BuChE; Sigma-Aldrich, Prague branche, Czech Republic) were suspended into phosphate buffer (pH 7.4) up to final activity 0.002 U µL^{-1}. Totally 5 µL of cholinesterase, 40 µL of freshly mixed solution: 5,5′-dithiobis(2-nitrobenzoic acid) [DTBN] – 0.4 mg mL^{-1} with phosphate buffer, and 5 µL of given concentration (10^{-3}–10^{-10} mol L^{-1}) of inhibitor were injected per well of a microplate. Enzymatic reaction was started with the addition of acetylthiocholine chloride (ATChCl) or butyrylthocholine iodide (BuCHI) – 1 mmol L^{-1} in phosphate buffer. Absorbance was measured at 412 nm after 5 min incubation with automatic shaking of the microplate. The achieved data were used for computing the percent of inhibition (I). It is expressed by equation:

$$I = 1 - \frac{\Delta A_i}{\Delta A_0} (\%) \tag{1}$$

where ΔA_i indicates absorbance change provided by cholinesterase exposed to potential anticholinergic compound and ΔA_0 indicates absorbance change caused by intact cholinesterase, i.e., phosphate buffer was applied as anticholinergic compound. IC_{50} was evaluated using Origin 6.1 (Northampton, MA, USA). Percents of inhibitions for the given anticholinergic compound were overlaid by proper curves chosen according to optimal correlation coefficient and IC50 was computed subsequently.

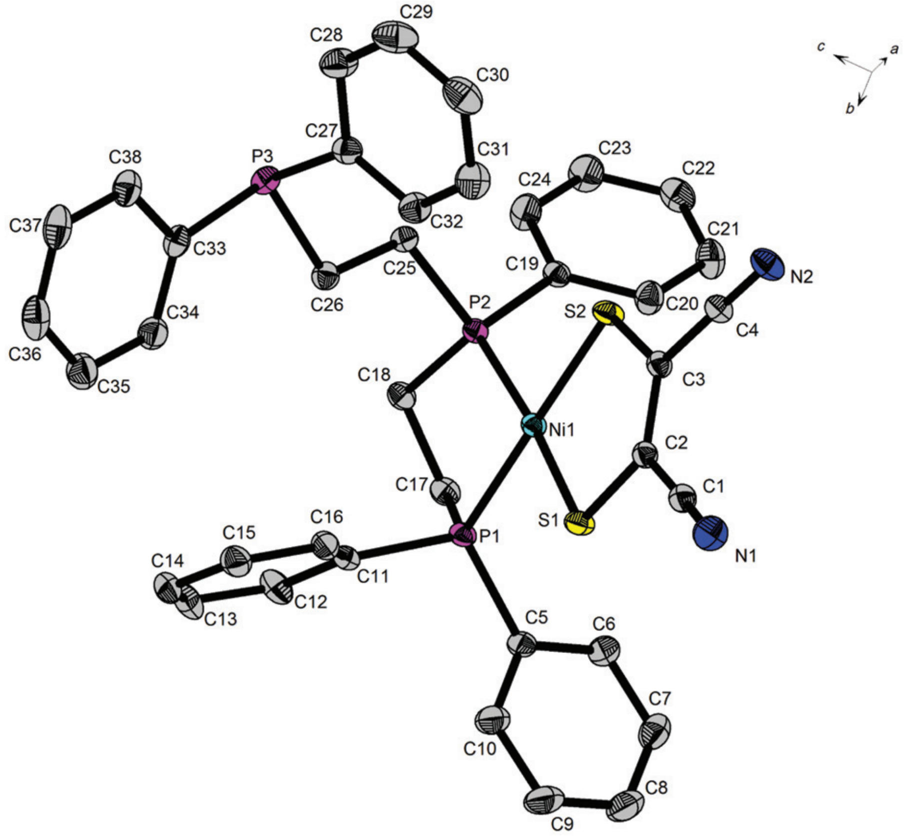


Figure 1. Drawing of [Ni(triphosI)(mnt)] with non-hydrogen atoms labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

2.3. *X-ray structure*

X-ray data collection for [Ni(triphosI)(mnt)] was performed on an Oxford Diffraction Gemini R four circle κ-axis diffractometer equipped with a Ruby CCD detector and a graphite monochromator, using Mo-Kα radiation at 293(2) K. CrysAlis program package (Oxford Diffraction, 2011) was used for data reduction [29]. The structure was solved by direct methods using SHELX [30, 31] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares. All hydrogen atoms were found from the Fourier map and were refined isotropically. Additional refinement and calculations were performed using the PLATON [32] and PARST programs [33]. DIAMOND was used for drawing (figure 1) [34]. Basic X-ray data are summarized in tables 2–4.

3. Results and discussion

Solution of metallic potassium (0.08 g, 200 mmol) in methanol (10 mL) were mixed with solution tdt (0.16 g, 100 mmol) or bdt (0.14 g, 100 mmol) in methanol (10 mL). Finally, $NiCl_2 \cdot 6H_2O$ (0.24 g, 100 mmol) in methanol (10 mL) and the appropriate

Table 2. Crystal data and structure refinement for [Ni(triphosI)(mnt)].

Empirical formula	$C_{38}H_{33}N_2NiP_3S_2$
Formula weight	733.40
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	10.31524(10)
b	16.7830(2)
c	22.3635(3)
α	90
β	95.5073(10)
γ	90
Volume (Å^3), Z	3853.71 (8), 4
Calculated density (Mg m^{-3})	1.264
Absorption coefficient (mm^{-1})	0.764
F(000)	1520
Crystal size (mm^3)	0.73 × 0.56 × 0.06
θ range for data collection (°)	3.44–29.50
Index ranges	$-13 \le h \le 14$; $-22 \le k \le 23$; $-29 \le l \le 30$
Reflections collected/unique	83,359/10,742 [R(int) = 0.0259]
Completeness to $2\theta = 25.00$ (%)	99.7
Max. and min. transmission	0.955 and 0.604
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10,742/0/415
Goodness-of-fit on F^2	0.991
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0276$, $wR_2 = 0.0771$
R indices (all data)	$R_1 = 0.0450$, $wR_2 = 0.0795$
Largest difference peak and hole (e Å^{-3})	0.280 and −0.193

Table 3. Selected bond lengths (Å) and angles (°) for [Ni(triphosI)(mnt)].

Ni(1)–S(1)	2.1529(4)	S(1)–Ni(1)–S(2)	92.998(14)
Ni(1)–S(2)	2.1506(4)	P(2)–Ni(1)–P(1)	86.361(14)
Ni(1)–P(2)	2.1777(4)	S(2)–Ni(1)–P(2)	90.232(14)
Ni(1)–P(1)	2.1747(4)	S(1)–Ni(1)–P(1)	90.644(14)
S(1)–C(2)	1.7412(14)	S(1)–Ni(1)–P(2)	175.101(15)
S(2)–C(3)	1.7373(13)	S(2)–Ni(1)–P(1)	174.984(15)
C(2)–C(3)	1.3468(19)	C(3)–S(2)–Ni(1)	102.95(5)
C(18)–P(2)	1.8368(14)	C(2)–S(1)–Ni(1)	102.64(5)
C(17)–P(1)	1.8243(14)	C(17)–P(1)–Ni(1)	106.33(5)
C(17)–C(18)	1.524(2)	C(5)–P(1)–Ni(1)	116.38(5)
C(19)–P(2)	1.8197(13)	C(11)–P(1)–Ni(1)	113.91(5)
C(25)–P(2)	1.8269(13)	C(19)–P(2)–Ni(1)	116.96(5)
C(5)–P(1)	1.8053(14)	C(25)–P(2)–Ni(1)	114.00(5)
C(11)–P(1)	1.8160(14)	C(18)–P(2)–Ni(1)	109.08(5)

P,*P*,*P*-ligand – triphosI (0.53 g), triphosII (0.62 g) – in dichloromethane (10 mL) was added. The mixture was stirred under reflux at 50°C for 24 h. The resulting solution was filtered and during 48 h a crystalline powder was precipitated. The solid was filtered off, washed with water, ethanol, and diethylether, and dried at room temperature (yields are 88–90%).

Complexes with mnt-ligand were synthesized by similar procedure with a solution of $Na_2(CN)_2C_2S_2$ (0.19 g, 100 mmol) in acetone (10 mL) mixed with $NiCl_2 \cdot 6H_2O$ (0.24 g, 100 mmol) in methanol (10 mL) and the appropriate *P*,*P*,*P*-ligand – triphosI

Table 4. Possible hydrogen bonds for [Ni(triphosI)(mnt)].

Donor–H	Donor···acceptor	H···acceptor	Donor–H···acceptor
C18–H18A	C18···N2(1)	H18A···N2(1)	C18–H18A···N2(1)
0.970(23)	3.318(22)	2.593(12)	131.67(18)
1.080		2.521	129.80**
C17–H17A	C17···S2(2)	H17A···S2(2)	C17–H17A···S2(2)
0.970(2)	3.888(7)	2.982(2)	155.85(13)
1.080		2.882	154.95**
C37–H37	C37···N2(3)	H37···N2(3)	C37–H37···N2(3)
0.930(18)	3.561(32)	2.719(20)	150.90(28)
1.080		2.589	149.29**

Number of possible hydrogen bonds: 3.
Equivalent positions: (1) $-x-1/2-1$, $y+1/2$, $-z-1/2-1$; (2) $x+1$, y, z; (3) $x-1/2$, $-y-1/2$, $z+1/2$.
**Values normalized in Refs [35, 36].

Table 5. Results of the physico-chemical study.

Compound	IR (cm^{-1})			UV-Vis (cm^{-1}) × 10^3	λ_M ($S\,cm^2\,mol^{-1}$)	μ_{eff} (BM)
	ν(C–S)	ν(P-$_{Phenyl}$)	ν(CN)			
I. [Ni(triphosI)(mnt)]	874m	1432s	2196s	27.34	1.78	dia
II. [Ni(triphosI)(bdt)]	884w	1434s		20.02; 11.48	5.78	dia
III. [Ni(triphosI)(tdt)]	871m	1434s		19.63; 11.18	3.56	dia
IV. [Ni(triphosII)(mnt)]	909m	1433s	2196s	26.82	3.12	dia
V. [Ni(triphosII)(bdt)]	918w	1434s		18.59; 11.47	2.25	dia
VI. [Ni(triphosII)(tdt)]	866m	1434s		18.31; 11.18	3.74	dia

(0.53 g) or triphosII (0.62 g) – in dichloromethane (10 mL) was added. The mixture was stirred under reflux at 50°C for 24 h. The resulting solutions were filtered. During 72 h, the precipitated crystals were filtered off, washed with water, ethanol, and diethylether, and dried at room temperature (yields for both compounds of 90%). Crystal of [Ni(triphosI)(mnt)] suitable for X-ray analysis was selected.

Selected data for the complexes are summarized in table 5. Results of IR-spectroscopy show that all complexes exhibit vibrations typical for dithiolates ν(C–S) at 866–918 cm^{-1} [37, 38]. For *P*-ligands, typical ν($P–C_{Ph}$) vibrations [39] were found at 1432–1434 cm^{-1} for all complexes (these vibrations for a single *P*-ligand are at 1432 cm^{-1}). A small shift can be assigned to chelate the nickel. The ν(C≡N) at 2196 cm^{-1} of **1** and **4** are typical with mnt [40, 41]. Planar coordination of nickel is also supported by UV-Vis absorbance spectroscopy; bands of bdt and tdt for complexes **2**, **3** and **5**, **6** observed at 18,310–20,020 cm^{-1} can be assigned to $^1A_{1g}$–$^1A_{2g}$ transitions typical of planar nickel(II) complexes [42]. The appropriate bands for **1** and **4** with mnt were not observed, probably due to CT overlap with maxima at 26,820 and 27,340 cm^{-1}. Also in agreement with a planar coordination sphere are the results of conductivity measurements (all complexes are non-electrolytes in DMF (concentration of solutions was 10^{-3} $mol\,dm^{-3}$)) [43].

All complexes (**1**–**6**) exhibit diamagnetic properties, which is also in accord with the supposed square-planar arrangement of NiS_2P_2 chromophore [44]. Thus, we conclude

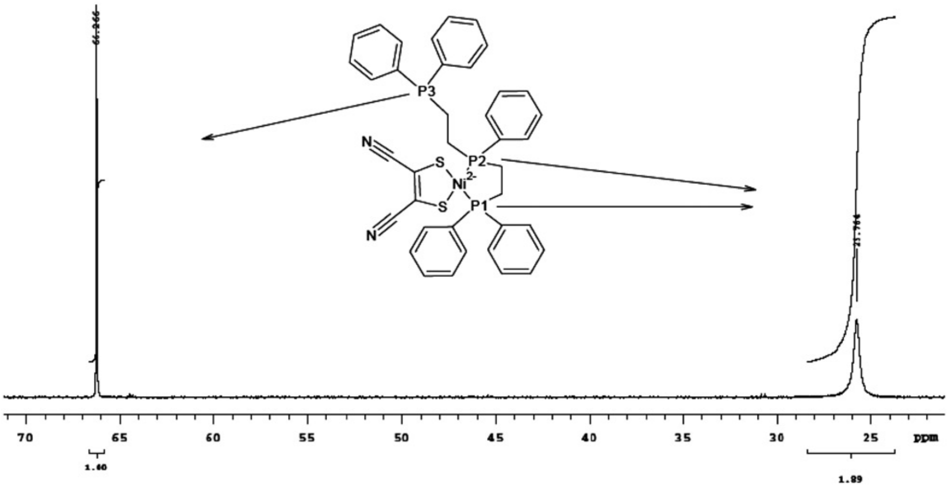


Figure 2. ^{31}P-NMR spectrum for [Ni(triphosI)(mnt)] complex.

Table 6. Anticholinesterase activity of the selected compounds.

	IC50 (μmol L^{-1})	
Compound	AChE	BuChE
[Ni(triphosII)(mnt)]	102 ± 20	247 ± 41
mnt	265 ± 52	15.7 ± 2.6
triphosII	a	a
$NiCl_2 \cdot 6H_2O$	a	a

a: no significant inhibition in the selected scale.

that both triphos ligands in all samples are coordinated to the central nickel atom *via* two *P*-atoms only (the third *P*-atom is not coordinated, so these potentially tridentate ligands behave as the bidentate ones). For definitive confirmation of this conclusion, the X-ray analysis for the selected sample was designed.

The X-ray structure of [Ni(triphosI)(mnt)] (figure 1, tables 2–4) confirmed a distorted square-planar geometry of NiS_2P_2 chromophore (triphosI is bidentate only; the third phosphine is not coordinated). Deviations of Ni1, S1, S2, P2, and P1 from an ideal NiS_2P_2 plane are less than 0.1 Å whereas deviation of non-coordinated P3 is about 4.28(1) Å; appropriate bond angles around nickel are 86.36(2)°–93.00(2)°. The dihedral angle are: for Ni1P2P1 and Ni1S1S2 planes, 5.22(3)°; for S1S2P2P1 and Ni1S1C2C3S2 planes, 2.74(2)°. Three intermolecular hydrogen bond interactions between hydrogen of phenyl rings and nitrogens of cyanos were identified in the structure. The disordered acetone was not possible to refine, so the PLATON/SQUEEZE procedure was used [32]. The volume of the void is 246 Å^3.

^{31}P-NMR spectra were recorded for the free triphosI ligand and also for [Ni(triphosI)(mnt)]. The free ligand chemical shift for P1 and P3 is $\delta = -13.641$ ppm (doublet) and for P2 $\delta = -16.915$ ppm (triplet) (Supplementary material). For [Ni(triphosI)(mnt)] the chemical shift for coordinated P1 and P2 is $\delta = 25.764$ ppm (integrated for two P) and for the non-coordinated P3 $\delta = 66.266$ ppm (integral for one atom, large peak) (figure 2). These results correspond to the above X-ray analysis.

Potency of the tested compounds to inhibit AChE and BuChE is depicted in table 6. [Ni(triphosII)(mnt)] was 2.5-fold stronger inhibitor of AChE than BuChE. The selectivity toward AChE is a promising advantage of the tested compound. Free mnt was a potent and selective inhibitor of BuChE. The inhibition was not retained once mnt is bound in [Ni(triphosII)(mnt)]. The inhibitory potency of [Ni(triphosII)(mnt)] was slightly under reported inhibition by reversible inhibitors tacrine and 7-methoxytacrine [27, 28].

Supplementary material

Crystallographic data of [Ni(triphosI)(mnt)] are deposited in Cambridge Crystallographic Data Centre, No. CCDC 846617. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +441223/336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgments

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