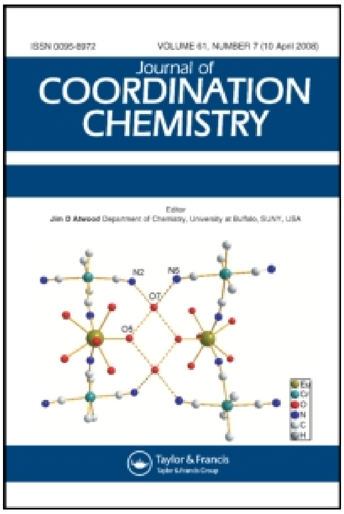


Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Planar Ni(II) 1,2-dithiolenes involving bidentate <i>N</i>-donor ligands

Jiří Kameníček[a]; Peter Herich[a]; Kamil Kuča[bc]; Daniel Jun[bc]; Milan Olšovský[d]
[a] Department of Inorganic Chemistry, Palacký University, CZ-771 47 Olomouc, Czech Republic [b] Faculty of Military Health Sciences, Center of Advanced Studies, University of Defence, Hradec Králové, Czech Republic [c] Faculty of Military Health Sciences, Department of Toxicology, University of Defence, Hradec Králové, Czech Republic [d] Faculty of Industrial Technologies TnUAD, Department of Chemistry and Technology of Polymers, SK-020 01 Púchov, Slovak Republic

To cite this Article Kameníček, Jiří , Herich, Peter , Kuča, Kamil , Jun, Daniel and Olšovský, Milan(2008) 'Planar Ni(II) 1,2-dithiolenes involving bidentate <i>N</i>-donor ligands', Journal of Coordination Chemistry, 61: 22, 3525 — 3533

To link to this Article: DOI: 10.1080/00958970802105326

URL: http://dx.doi.org/10.1080/00958970802105326

Journal of Coordination Chemistry
Vol. 61, No. 22, 20 November 2008, 3525–3533

Taylor & Francis
Taylor & Francis Group

Planar Ni(II) 1,2-dithiolenes involving bidentate *N*-donor ligands

JIŘÍ KAMENÍČEK*†, PETER HERICH†, KAMIL KUČA‡§,
DANIEL JUN‡§ and MILAN OLŠOVSKÝ¶

†Department of Inorganic Chemistry, Palacký University, Křížkovského 10,
CZ-771 47 Olomouc, Czech Republic
‡Faculty of Military Health Sciences, Center of Advanced Studies, University of Defence,
Třebešská 1575, CZ-500 01, Hradec Králové, Czech Republic
§Faculty of Military Health Sciences, Department of Toxicology, University of Defence,
Třebešská 1575, CZ-500 01, Hradec Králové, Czech Republic
¶Faculty of Industrial Technologies TnUAD, Department of Chemistry and Technology of
Polymers, Ivana Krasku 491/30, SK-020 01 Púchov, Slovak Republic

(*Received 13 November 2007; in final form 4 February 2008*)

A series of planar Ni(II) dithiolenes derived from maleonitriledithiole (mnt), benzene-1, 2-dithiole (bdt) and 1-toluene-3,4-dithiole (tdt) with bidentate *N*,*N*-ligands (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline, nphen = 5-nitro-1,10-phenanthroline) of the [Ni(*N*,*N*)(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(phen)(bdt)] confirmed a planar geometry of NiN_2S_2. Possible practical applications such as use for vulcanization catalytic agents and for their anticholinesterase activity were evaluated.

Keywords: Nickel(II); *N*,*S*-ligands; Vulcanization agents; Cholinesterase; Inhibitor

1. Introduction

A square-planar coordination polyhedron is very common for nickel dithiolenes with NiS_4 chromophores containing two *S*,*S*-ligands (bdt, tdt) of the $R[Ni(S,S)_2]$ and $R_2[Ni(S,S)_2]$ type, $R = NR_4^+$, PR_4^+ [1]. The situation is different for complexes where one *S*,*S*-ligand is replaced by a bidentate *N*,*N*- or *P*,*P*-ligand. Whereas a number of square-planar Ni(II) 1,1- and 1,2-dithiolenes with bidentate *P*,*P*-ligands have been reported [2, 3], similar complexes with coordination number four involving *N*,*N*-ligands are less common. For instance, two compounds of nickel with bdt and phen or nphen were reported [4] and the X-ray structure of [Ni(bpy)(bdt)], including a discussion of the possibility of photochemical oxidation [5, 6]. Nickel dithiolate complexes with the mnt

---

*Corresponding author. Email: kamen@prfnw.upol.cz

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802105326

ligand and oxidation activities were also published [7]. A range of practical applications were reported: toluene-3,4-dithiol analysis of blood for assessing carbon disulfide exposure [8]; nickel complexes used as biologically active model compounds (nickel hydrogenases [9]); possible uses as superconductors, analytical species, polarization filters, pesticides and vulcanization catalysts [10–12].

The aim of this work was synthesis and physico-chemical study of selected Ni(II) dithiolene complexes with bidentate *S*,*S*-ligands (bdt, tdt and mnt) and bidentate *N*,*N*-ligands (bpy, phen, nphen), including X-ray analysis of one. Practical applications (using samples as vulcanization accelerators and substances with anticholinesterase activity) are reported.

2. Experimental

2.1. *Materials*

For syntheses, the following reagents were used: 1,10-phenanthroline ≥99%, 2,2′-bipyridine ≥99% (LACHEMA Brno), 5-nitro-1,10-phenanthroline ≥97%, dimercaptomaleonitrile disodium salt hydrate ≥97%, toluene-3,4-dithiol ≥97%, benzene-1,2-dithiol ≥95% (SIGMA-ALDRICH).

All solvents were products of LACHEMA Brno.

For *in vitro* evaluation of anticholinesterase activity, chemicals of analytical grade from Sigma-Aldrich were purchased.

2.2. *Syntheses*

Complexes with bdt or tdt were obtained by mixing the appropriate ligand: tdt (0.16 g, 1 mmol) or bdt (0.14 g, 1 mmol) in a 1 : 1 dimethylformamide/butanol mixture (10 mL) with triethylamine (0.3 mL). Finally, $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) and appropriate *N*,*N*-ligand – bpy (0.31 g), phen (0.40 g) or *n*-phen (0.45 g) and dimethylformamide/butanol (10 mL) were added. The resulting mixture was stirred under reflux at 150°C for 20 min and then gradually cooled (50°C/30 min). The resulting powder was separated by filtration, washed with methanol and diethylether and dried at room temperature (yield: 85%). For compounds with mnt ligand, the solvent mixture of toluene (20 mL), dimethylformamide (10 mL), dichloromethane (10 mL) and hexane (10 mL) was used.

Crystals of [Ni(phen)(bdt)] for X-ray analysis were obtained in a similar way using a 1 : 1 dimethylformamide + butanol mixture (20 mL). The solution was heated up to boiling (cca 200°C), then slowly cooled and placed in a refrigerator (−12°C). Over two days, the prismatic crystals appeared and a single crystal suitable for X-ray analysis was selected.

2.3. *Physical measurements*

The nickel content was determined by chelatometric titration using murexide as indicator [13]. CHNS analyses were performed on a Fisons EA 1108 instrument;

satisfactory analyses for all above complexes were obtained (table 1). Room temperature magnetic susceptibilities were measured by the Faraday method using Co[Hg(NCS)$_4$] as a calibrant on a laboratory designed instrument with a Sartorius 4434 MP-8 microbalance. Conductivities were measured with an LF 330/SET conductivity meter (WTW GmbH) at 25°C. Diffuse-reflectance electron spectra (45,000–9090 cm^{-1}) were carried out on a Perkin-Elmer Lambda 35 UV/Vis spectrophotometer using nujol mulls. IR spectra (4000–450 cm^{-1}) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets.

In vitro anticholinesterase activity measurement was conducted as described earlier [14]. A solution of [Ni(bpy)(bdt)] of appropriate concentrations (concentration range from 10^{-7} to 10^{-1} M; 500 µL) was added to the suspension of rat brain homogenate (10% w/v in distilled water; 500 µL), solution of sodium chloride (3 M; 2.5 mL) and water (20 mL). Subsequently, a solution of acetylcholine iodide (0.02 M; 2.0 mL) was added (start of the enzyme reaction). The enzyme activity was immediately determined using an automatic titrator RTS 822 (Radiometer, Denmark). The IC$_{50}$ value of the [Ni(bpy)(bdt)] was calculated from a plot of percent inhibition of cholinesterase *vs* its concentration. To show that not only nickel causes the anticholinesterase activity, NiSO$_4$ was used as a standard for comparison. Nonlinear regression was performed using software for statistical analysis (GraphPad Prism version 4 for Windows, GraphPad Software, San Diego, California, USA, www.graphpad.com).

The feedback of selected substances on vulcanization was determined by the two-step technology according to the STN 62 1425 procedure in MATADOR Púchov, Slovakia using a BRABENDER mixing device (temperature 110°C; time of stirring 8 min) and compared with the standard technology. We studied the efficiency of samples as accelerators for sidewall mixture, which is utilized for production of sidewalls and clinchers of passenger car radial tires. As a comparable standard we prepared a mixture with Sulfenax CBS/MG, a commonly used accelerator in the sidewall mixtures. The preparation of rubber mixtures was made by the two-step mixing according to the Slovak standard STN 62 1425. In the second step of rubber mixture we tested sample accelerators and another vulcanizing admixture, vulcanizing agent (Sulfur N) inhibitor of overvulcanization (Duslin G80), which is used for the sidewall rubber mixture. The amount of sample was calculated in order to achieve an equal content in the mixture. The mixing of the second step was made at temperature of about 110°C of the laboratory mixing BRABENDER.

We recorded vulcanizing characteristics of the rubber mixtures at 150°C during 60 minutes in vulcameter Monsanto. All vulcanizing curves of rubber mixtures have

Table 1. Elemental analysis.

		Calcd/Found			
Compound	M [g mol^{-1}]	C (%)	H (%)	N (%)	Ni (%)
[Ni(bpy)(bdt)] (**I**)	355.11	54.18/54.04	3.41/3.35	7.89/7.59	16.53/16.70
[Ni(phen)(bdt)] (**II**)	379.13	57.02/57.18	3.19/2.79	7.39/7.46	15.48/14.78
[Ni(nphen)(bdt)] (**III**)	428.16	50.98/51.41	2.61/2.73	9.91/9.85	13.84/13.30
[Ni(bpy)(tdt)] (**IV**)	370.14	55.32/55.58	3.82/3.35	7.59/7.43	15.89/15.85
[Ni(phen)(tdt)] (**V**)V	393.16	58.04/57.97	3.59/3.33	7.13/7.25	14.92/14.67
[Ni(nphen)(tdt)] (**VI**)	443.19	52.08/52.61	2.99/3.07	9.59/9.50	13.39/13.32
[Ni(bpy)(mnt)] (**VII**)	355.07	47.36/47.31	2.84/2.47	15.78/15.38	16.58/16.31

an increasing torsional moment. The values of the vulcanizing parameters are comparable with the parameters of rubber mixture with Sulfenax CBS/MG, which was selected as reference material.

2.4. *X-ray crystal structure*

X-ray data collection for [Ni(phen)(bdt)] was performed on an Oxford Diffraction Xcalibur^{TM}2 four circle κ-axis diffractometer equipped with a Sapphire2 CCD detector, monochromator Enhance and a Cryojet cooler system using Mo-Kα radiation at 110(2) K. CrysAlis program package (1.171.7, Oxford Diffraction) was used for data reduction. The structure was solved by direct methods using SHELX programs [15, 16] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares procedures. All hydrogen atoms were found from the Fourier map and were refined isotropically. Additional calculations were performed using the PARST program [17]. Basic X-ray data are summarized in tables 3–5.

3. Results and discussion

Selected physical data for all complexes are summarized in table 2. All complexes except **VII** are diamagnetic as expected for a planar geometry around nickel [18]. The planar coordination of the nickel is also supported by UV/Vis reflectance spectroscopy; bands in the 16,800–23,000 cm^{-1} region can be assigned to the $^1A_{1g}$–$^1A_{2g}$ transitions, typical of planar nickel(II) complexes [19]. Conductivity measurements (all complexes are non-electrolytes [20]) are consistent with a planar coordination sphere.

For complex **VII** with mnt-ligand, a slight paramagnetism (under 0.66 BM) was found which cannot be eliminated by purification. The low-temperature dependence of magnetic susceptibility was measured (see figure 3). The result is that the compound behaves to 5 K according to the Curie–Weiss law; under this temperature, magnetic ordering occurs, maybe as a consequence of the polymeric character of the sample or due to intermolecular interactions. Detailed conclusions should be made using X-ray analysis, but all attempts to obtain appropriate single crystals were unsuccessful.

Table 2. Physico-chemical measurements.

Compound	λ_M (Scm^2 mol^{-1})	IR (cm^{-1})				UV/Vis (cm^{-1} × 10^3)		μ_{eff} (BM)
		ν(C–S)	ν(C=N)	$\nu(NO_2)$	ν(CN)			
I	0.8	872 m	1552 m			17.8	11.3	dia
II	1.4	836 s	1551 m			22.5	16.8	dia
III	1.4	840 s	1553 w	1531 s	1336 s	19.9	11.1	dia
IV	1.1	870 m	1542 w			19.9		dia
V	1.1	834 s	1541 w			23.0	17.3	dia
VI	2.7	841 s	1532 s	1532 s	1338 s	17.7	11.1	dia
VII	5.3	862 w	1509 s		2201 s	28.1	20.1	0.66–1.32*

*Temperature dependence of μ_{eff} see figure 3.

IR-spectroscopy shows that all complexes have vibrations typical of dithiolates ν(C–S) at 795–841 cm^{-1} and ν(C=N) at 1532–1553 cm^{-1} [21, 22]. Moreover, the ν(NO$_2$) for complexes with nphen ligand and ν(C≡N) vibrations for complexes with mnt ligand (see table 2) were recorded.

The X-ray structure of [Ni(phen)(bdt)] (see figure 1, tables 3–5) confirmed previous conclusions from physico-chemical methods about approximate square-planar geometry of NiS_2N_2 chromophore (the deviations of all atoms from an ideal NiS_2N_2 plane are less than 0.04 Å and the sum of d/s quadrates is 0.033). The S(1)Ni(1)S(2) angle is 90.47(2)° and N(1)Ni(1)N(2) is 84.18(7)°. Two intra-molecular and one inter-molecular hydrogen bond interactions (see table 5) were found in the structure.

For **II**, thermal analysis (figure 4) shows a small mass increase in the range 250–300°C (probably connected with reaction with oxygen, see a small *exo*-effect at 260°C) is accompanied with continual thermal decomposition (large *exo*-effect at

Table 3. Crystal and structure refinement data for [Ni(phen)(bdt)].

Empirical formula	$C_{18}H_{12}N_2S_2Ni$
Formula weight	379.13
Temperature (K)	110(2)
Wavelength (Å)	0.71073
Crystal system, space group	*Pbca*
Unit cell dimensions (Å)	
a	17.576(4)
b	8.612(2)
c	19.833(4)
Volume (Å^3)	3002.0(1)
Z, calculated density (Mg m^{-3})	8, 1.678
Absorption coefficient (mm^{-1})	1.569
F(000)	1552
Crystal size (mm^3)	0.30 × 0.25 × 0.20
θ range for data collection (°)	3.31 to 25.00
Index ranges	$-20 \le h \le 20$, $-10 \le k \le 9$, $-23 \le l \le 20$
Reflections collected/unique	17218/2637 [$R_{(int)} = 0.0421$]
Completeness to 2θ = 25.00° (%)	87.8
Max. and min. transmission	0.7443 and 0.6504
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2637/0/208
Goodness-of-fit on F^2	1.118
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0293$, $wR_2 = 0.0705$
R indices (all data)	$R_1 = 0.0303$, $wR_2 = 0.0712$
Largest diff. peak and hole (e Å^{-3})	0.357 and −0.236

Table 4. Selected bond lengths (Å) and angles (°) for [Ni(phen)(bdt)].

Ni(1)–N(1)	1.9315(19)	N(1)–Ni(1)–N(2)	84.18(7)
Ni(1)–N(2)	1.9372(18)	N(1)–Ni(1)–S(1)	92.36(6)
Ni(1)–S(1)	2.1338(7)	N(2)–Ni(1)–S(2)	92.98(5)
Ni(1)–S(2)	2.1326(7)	S(2)–Ni(1)–S(1)	90.47(2)
S(1)–C(1)	1.751(2)	N(1)–Ni(1)–S(2)	177.16(6)
S(2)–C(2)	1.750(2)	N(2)–Ni(1)–S(1)	176.54(5)
N(1)–C(7)	1.358(3)	C(1)–S(1)–Ni(1)	106.87(7)
N(1)–C(18)	1.333(3)	C(2)–S(2)–Ni(1)	106.81(8)
N(2)–C(8)	1.362(3)	C(7)–N(1)–Ni(1)	112.47(14)
N(2)–C(9)	1.337(3)	C(18)–N(1)–Ni(1)	130.25(16)
		C(8)–N(2)–Ni(1)	112.31(14)
		C(9)–N(2)–Ni(1)	130.84(15)

Table 5. Possible hydrogen bonds for [Ni(phen)(bdt)].

Donor-H	Donor ··· Acceptor	H ··· Acceptor	Donor-H ··· Acceptor
C9–H9	C9 ··· S2 (0)	H9 ··· S2 (0)	C9–H9 ··· S2 (0)
0.957(9)	3.129(46)	2.552(12)	119.02(11)
C18–H18	C18 ··· S1 (0)	H18 ··· S1 (0)	C18–H18 ··· S1 (0)
0.927(48)	3.090(15)	2.505(1)	121.30(16)
C11–H11	C11 ··· S1 (1)	H11 ··· S1 (1)	C11–H11 ··· S1 (1)
0.932(50)	3.669(67)	2.891(16)	141.79(21)

Number of possible hydrogen bonds 3.
Equivalent positions: (0) x, y, z; (1) $x - 1/2, -y + 1/2 + 1, -z$.

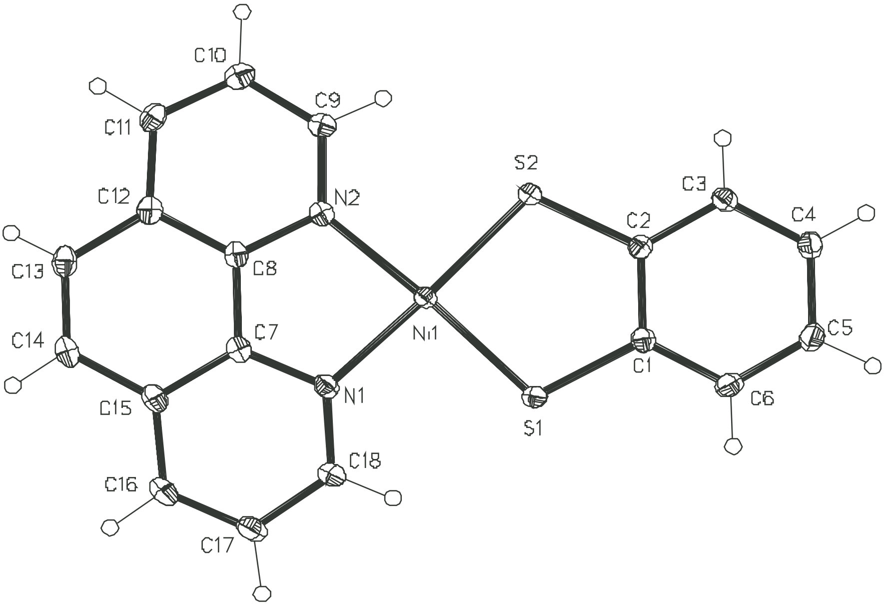


Figure 1. ORTEP of [Ni(phen)(bdt)] with the non-hydrogen atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

500°C due to the burning of sample). The plateau (530–650°C) corresponds to the formation of a NiS intermediate; the final product of thermal decomposition was found to be NiO (shown by X-ray powder diffraction).

Anticholinesterase activity of [Ni(bpy)(bdt)] and of $NiSO_4$ are shown in table 6 and figure 2. As clearly visible, the newly prepared complex [(Ni(bpy)(bdt)] reached almost two-fold higher inhibition potency compared with $NiSO_4$. Further investigation of the anticholinesterase activity of all compounds prepared in this study should be done. Because of the potency of **I** to inhibit cholinesterases, it could be considered as a potential drug for Alzheimer's or as prophylactics for nerve agents or pesticides poisoning [23].

The influence of selected complexes on vulcanization is summarized in table 7. Whereas [Ni(bpy)(mnt)] can be used as a vulcanization accelerator, [Ni(bpy)(tdt)] behaves as a vulcanization inhibitor.

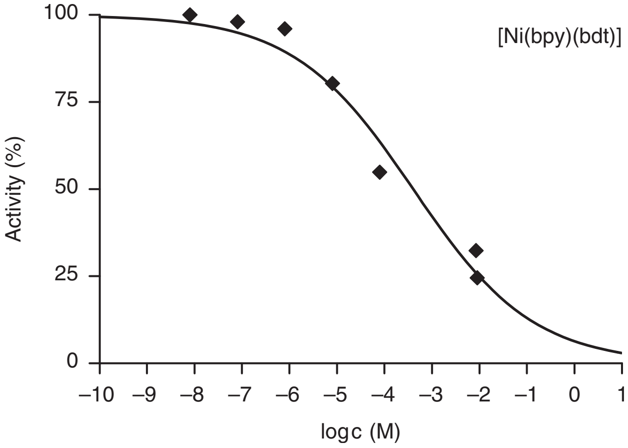


Figure 2. Anticholinesterase activity for [Ni(bpy)(bdt)].

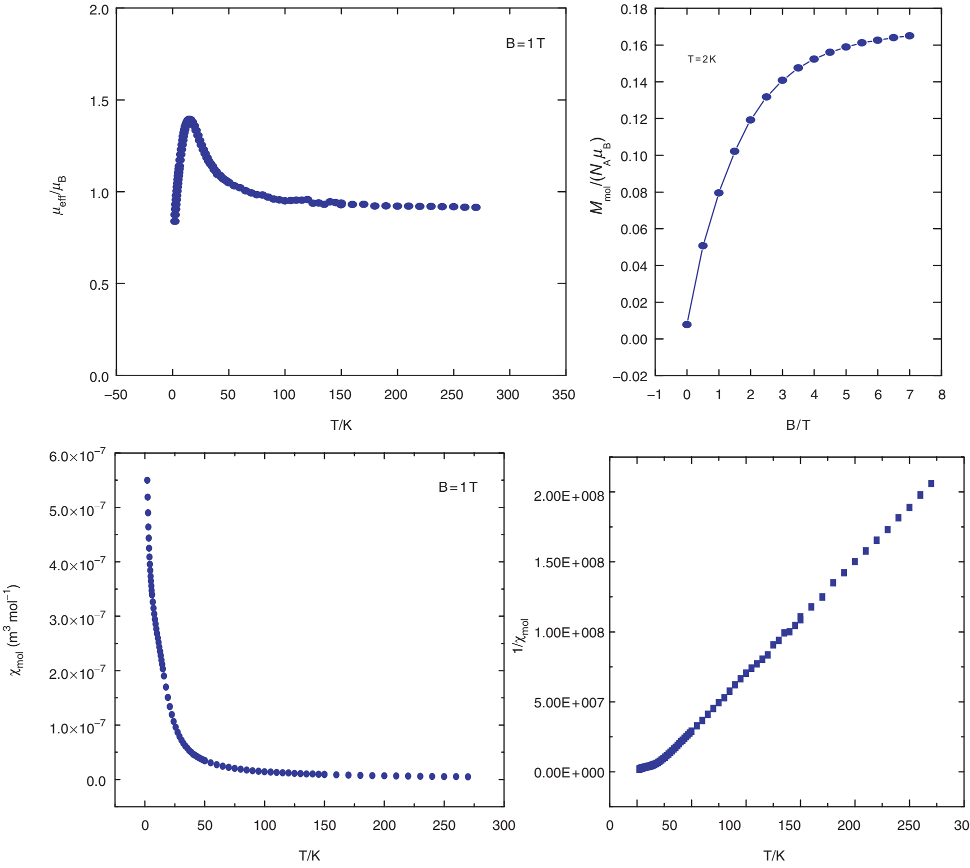


Figure 3. Magnetochemical measurements of [Ni(bpy)(mnt)].

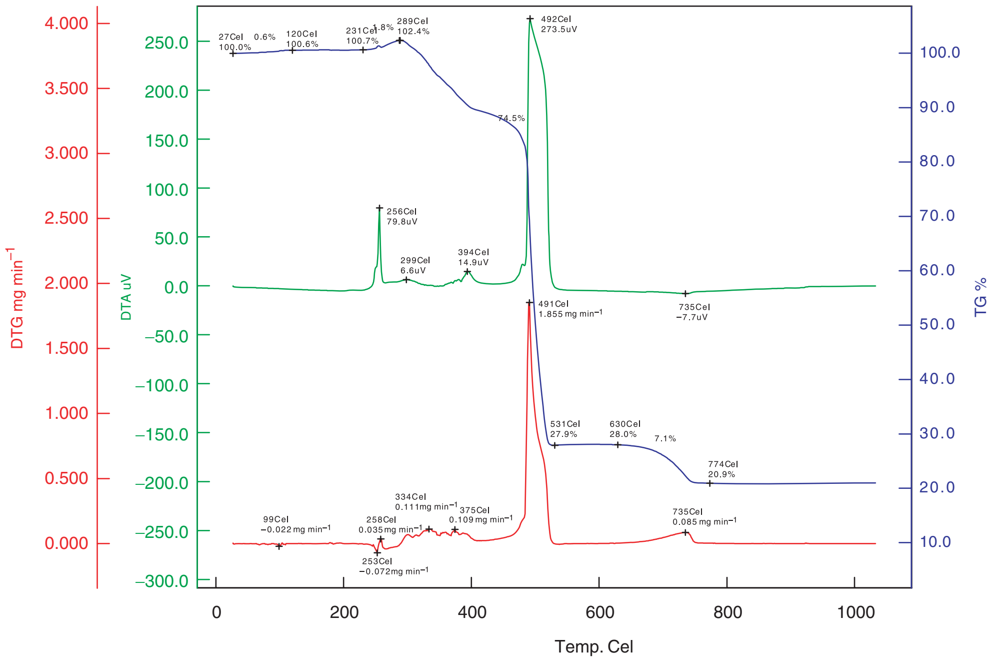


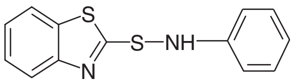
Figure 4. Thermal analysis of [Ni(phen)(bdt)].

Table 6. Anticholinesterase activity of the [Ni(bpy)(bdt)] complex.

Compound	IC_{50} [M]	95% CI (confidence interval) [M]
[Ni(bpy)(bdt)]	4.03×10^{-4}	1.35×10^{-4}–1.21×10^{-3}
$NiSO_4$	1.29×10^{-2}	1.99×10^{-3}–8.36×10^{-2}

Table 7. Vulcanization parameters.

Standard:
Sulfenax CBS/MG (N–cyclohexyl–2–benzothiazolsulfenamid CBS), CAS reg. No. 95-33-0



Vulcanization parameters	Standard	Complexes	
Parameter	Sulfenax CBS/MG	[Ni(bpy)(mnt)]	[Ni(bpy)(tdt)]
Ground I. stage (side of tire)	68.836 g	68.836 g	68.836 g
Mass of standard/sample	0.2886 g	0.2886 g	0.2886 g
Vulcanizing agent (Sulfur N)	1.1429 g	1.1429 g	1.1429 g
Inhibitor of overvulcanization (Duslin G-80)	0.0412 g	0.0412 g	0.0412 g
Vulcanization time t_{90}[min]	15.5–19.5	14.2	38.8
Start of vulcanization t_{02}[min]	6–10	5.1	7.0
Viscosity Mooney 100°C/1 + 4 min(ML)	51–68	51.1	55.8
Scorch time, 120°C [min]	30–50	30.0	43.6
Density II.° [g cm^{-3}]	1.11–1.14	1.12	1.12

Supplementary data

Crystallographic data are deposited in the Cambridge Crystallographic Data Centre, No. CCDC 665669. 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).

Acknowledgements

The authors would like to thank the grant No. ME865 (Ministry of Education, Youth and Sports, Czech Republic) for financial support, Prof. Z. Trávníček for X-ray measurements and data reduction, Ing. R. Herchel, Assoc. Prof. Z. Šindelář for magnetochemical measurements and Mgr. R. Štarha for thermal analysis.

References

[1] P. Solichová. Diploma thesis, Palacký University, Olomouc (2001).
[2] R. Pastorek, J. Kameníček, M. Pavlíček, J. Husárek, Z. Šindelář, Z. Žák. *J. Coord. Chem.*, **55**, 1301 (2002).
[3] J. Darkwa. *Inorg. Chim. Acta*, **657**, 137 (1997).
[4] K. Mrkvová, J. Kameníček, Z. Šindelář. *Acta Univ. Palacki. Olom., Chemica.*, **43**, 94 (2004).
[5] T.M. Cocker, R.E. Bachman. *Inorg. Chem.*, **40**, 1550 (2001).
[6] Ch. Makedonas, Ch.A. Mitsopoulou. *Eur. J. Inorg. Chem.*, **12**, 2460 (2006).
[7] T.-X. Fu, J. Tao, D. Li. *Wuli Huaxue Xuebao*, **20**, 843 (2004).
[8] W.M. Valentine, H.L. Valentine, K. Amarnath, V. Amarnath. *Toxicol. Sci.*, **50**, 155 (1999).
[9] E. Bowman, J. Reedijk. *Coord. Chem. Rev.*, **249**, 1555 (2005).
[10] P. Cassoux, L. Valade, H. Kobayashi, R.A. Clark, E. Underhill. *Coord. Chem. Rev.*, **110**, 171 (1991).
[11] R. Eisenberg. *Prog. Inorg. Chem.*, **12**, 295 (1970).
[12] W.E. Geiger, C.S. Allen, T.E. Mines, F.E. Senftleber. *Inorg. Chem.*, **16**, 2003 (1977).
[13] R. Přibil. *Komplexometrické Titrace*, p. 22, SNTL, Praha (1955).
[14] K. Kuča, J. Cabal, J. Patočka, V. Dohnal. *Lett. Drug Des. Discov.*, **1**, 97 (2004).
[15] G.M. Sheldrick. *Acta Crystallogr A.*, **46**, 467 (1990).
[16] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[17] M. Nardelli. *J. Appl. Cryst.*, **28**, 659 (1995).
[18] A.B. Nejding. *Magnetochimija Komplexnych Sojedinenij Perechodnych Metallov*, p. 165, Mir, Moskva (1970).
[19] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, p. 534, Elsevier, Amsterdam (1984).
[20] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[21] N.B. Colthup, L.H. Daly, S.E. Wiberley. *Introduction to Infrared and Raman Spectroscopy*, p. 204, Academic Press, New York and London (1964).
[22] D.M. Adams, E.A.V. Ebsworth. *Spectroscopic Properties of Inorganic and Organometallic Compounds*, Vol. 11, p. 316, Burlington House, London (1979).
[23] J. Patočka, K. Kuča, D. Jun. *Acta Medica (Hradec Králové)*, **47**, 215 (2004).