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Cyclohexylethyl- and Hexamethyleneimine Nickel(II)dithiocarbamates with 1,6-Bis(diphenylphosphino)hexane

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A binuclear diamagnetic Ni(II) dithiocarbamates with 1,6-bis(diphenylphosphino)hexane (dpph) as a bidentate bridging P,P-ligand of composition $[Ni_2(\mu\text{-dpph})(hmidtc)_2X_2]$ (hmidtc = hexamethyleneiminedithiocarbamate, dtc = S_2CN^-, X = Cl, Br, I, ClO_4, NCS); $[Ni_2(\mu\text{-dpph})(cetdtc)_2X_2]$ (cetdtc = cyclohexylethyldithiocarbamate, X = Cl, Br, I, NCS) and also the mononuclear diamagnetic complex $[Ni(cetdtc)(dpph)]ClO_4\cdot 2H_2O$ have been synthesized. The complexes have been studied by elemental analysis, IR and UV-VIS spectroscopy, thermal analysis, magnetochemical and conductivity measurements. X-ray structural analysis was solved for the $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$ and confirmed the presence of two NiS_2PBr chromophores bonded by the P-donor atoms of 1,6-bis(diphenylphosphino)hexane.

Key words: Ni(II)dithiocarbamate, synthesis, X-ray structure, physico-chemical study, X-ray structural analysis

Ni(II)-dithiocarbamates with 1,6-bis(diphenylphosphino)hexane as a bidentate P,P-ligand were recently studied only in our department. The diamagnetic square complexes with NiS_2P_2 chromophore of the composition $[Ni(Ldtc)(dpph)]ClO_4$ [1,2] (Ldtc = thiazolidine- or piperidinedithiocarbamate) were prepared. In most cases, dpph acts as a bidentate bridging P,P-ligand and the binuclear diamagnetic complexes $[Ni_2(\mu\text{-dpph})(Ldtc)_2X_2]$ (Ldtc = piperidine-, morpholine-, benzylisopropyl-, 4-aminoantipyrine- or pyrrolidinedithiocarbamate, X = Cl, Br, I, ClO_4, NCS) [2–4] are formed. We suppose, 1,6-bis(diphenylphosphino)hexane in these compounds is coordinated to the nickel atoms by the P-donor atoms and the dpph puts two square NiS_2PX chromophore into one diamagnetic species together. Conclusions above are proposed on the basis of the physico-chemical measurements. In this work there are confirmed also by the X-ray structure analysis results for $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$.

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EXPERIMENTAL

Materials and methods: 1,6-Bis(diphenylphosphino)hexane was supplied by Fluka Co.; all remaining reagents were obtained from Lachema Co. and were of p.a. purity. The content of nickel was determined by chelatometric titration using murexid as an indicator [5]. Chlorine and bromine were determined by the Schröniger method [6]. 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 9.3–18.2 mg, temperature range 20–1150°C. Melting points were determined by the Böetius Rapido melting point apparatus (Wägetechnik PHMK 79/2106).

Syntheses: [Ni$_2$(μ-dpph)(Ldtc)$_2$X$_2$] (Ldtc = hmidtc, cetdtc; X = Cl, Br, I, ClO$_4$, NCS).

The suspension of fine powdered [Ni(hmidtc)$_2$], resp. [Ni(cetdtc)$_2$] [7] (1 mmol) in 50 cm^3 absolute ethanol was mixed with powdered NiX$_2$·nH$_2$O (1 mmol) and 1,6-bis(diphenylphosphino)hexane (1 mmol) and stirred under reflux for 5 hours. The product was filtered, washed with ethanol and dried under an infra-lamp at 40°C. Complexes (1–5) were recrystallized from CHCl$_3$, compounds (6–9) from CHCl$_3$ + CH$_2$Cl$_2$ mixture (1:1). For [Ni$_2$(μ-dpph)(hmidtc)$_2$Br$_2$] · 2CHCl$_3$, it was possible to obtain a single crystal appropriate for X-ray analysis. Yields: 85% (1), 78% (2), 76% (3), 89% (4), 91% (5), 58% (6), 63% (7), 39% (8) and70% (9), respectively.

[Ni(cetdtc)(dpph)]ClO$_4$·2H$_2$O: The appropriate reaction components were used in the 1:1:1 ratio. During 5 h the solid substance appeared. The compound was filtered, washed by 96% ethanol and the crystallization was performed from chloroform solution using petrolether. The final product was dried at 40℃. Yield: 52%.

X-ray crystallography: X-ray data collection 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 direct methods using SHELXS-97 program [8]. No absorption corrections were applied. The structure was refined anisotropically by the full-matrix least-squares procedures using program SHELXL-97 [9]. Additional calculations were made using PARST program [10]. The X-ray results are given in Tables 2–4.

RESULTS AND DISCUSSION

Important physico-chemical results are summarized in Table 1. In accordance with the assumption of a square arrangement of the NiS$_2$PX chromophore, all compounds are diamagnetic. The mononuclear complex (10) is a 1:1 electrolyte in the acetone; the binuclear complexes (1–9) behave as non-electrolytes [11]. The compounds (6–9) are insoluble in the nitromethane; the molar conductivity values obtained in the dimethylformamide are slightly higher than it should be for non-electrolytes, but still lower than the values for 1:1 electrolytes in the literature (65–90 S cm^2 mol^{-1}) [11]. This fact can be explained by the partial dissociation of complexes in the dimethylformamide solution.

IR-spectra exhibit the vibrations typical for dithiocarbamates [12]: ν(C$\overset{...}{-}$N) at 1505–1528 cm^{-1} and ν(C$\overset{...}{-}$S) at 982–998 cm^{-1}, which were observed for all complexes. For the complex [Ni$_2$(μ-dpph)(hmidtc)$_2$(ClO$_4$)$_2$], the split maximum (ν_3 at 1080 and 1093 cm^{-1}) was recorded, which indicates the coordination of ClO_4^- group to the central atom, while for the [Ni(cetdtc)(dpph)]ClO$_4$ · 2H$_2$O the maximum is non-split due to the ionic character of this bond [13]. For complexes (5) and (9) with

Table 1. Results of physico-chemical studies.

Complex*	Colour	λ_M (S cm^2 mol^{-1})	IR (cm^{-1})						UV/VIS ($\cdot 10^3$ cm^{-1})			TA (°C)			
			$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{S})$	$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$	$\nu_3(\mathrm{ClO_4^-})$	$\nu_4(\mathrm{ClO_4^-})$	$\nu(\mathrm{C{\equiv}N})$	$\nu(\mathrm{C{-}S})$				T	P	E_n	E_x
(1)	violet	6.4[a]	998 w	1516 m	–	–	–	–	19.6		30.0	69.5	157–213	138	221
(2)	violet	8.2[a]	984 m	1526 m	–	–	–	–	19.4		29.2	85	129–190	107, 152	218
(3)	violet	4.8[a]	990 w	1520 m	–	–	–	–	18.6		31.0	45.5	–	70, 110	186
(4)	dark violet	7.6[a]	982 m	1514 m	1080 m 1093 m	615 m	–	–	19.8		31.2	not studied			
(5)	light red	5.5[a]	997 m	1520 s	–	–	2088 s	830 m	20.7		29.0	72	133–205	88, 174	215
(6)	violet	21.2[b]	995 w	1528 vw	–	–	–	–	19.5	24.6	29.9	225	–	–	248
(7)	violet	24.7[b]	992 w	1510 m	–	–	–	–	19.0		28.8	218	–	–	229
(8)	violet	25.8[b]	990 w	1508 w	–	–	–	–	18.5		30.3	185	–	–	203
(9)	red-brown	18.8[b]	992 w	1505 vs	–	–	2080 vs	840 w	20.2		30.5	213	–	202	219
(10)	brown	107.7[c]	994 s	1508 s	1076 vs	620 s	–	–	19.5	22.6	31.2	not studied			

[a] In nitromethane solution (10^{-3} mol·dm^{-3}); [b] In dimethylformamide solution ($5\cdot10^{-4}$ mol·dm^{-3}); [c] In acetone solution (10^{-3} mol·dm^{-3}).

T – begin of thermal decomposition; P – plateau; E_n – endo-effect; E_x – exo-effect.

*(1) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{hmidtc})_2\mathrm{Cl_2}]\cdot 2\mathrm{CHCl_3}$; (2) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{hmidtc})_2\mathrm{Br_2}]\cdot 2\mathrm{CHCl_3}$; (3) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{hmidtc})_2\mathrm{I_2}]\cdot \mathrm{CHCl_3}$; (4) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{hmidtc})_2(\mathrm{ClO_4})_2]$; (5) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{hmidtc})_2(\mathrm{NCS})_2]\cdot 2\mathrm{H_2O}$; (6) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{cetdtc})_2\mathrm{Cl_2}]$; (7) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{cetdtc})_2\mathrm{Br_2}]$; (8) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{cetdtc})_2\mathrm{I_2}]$; (9) $[\mathrm{Ni_2}(\mu\text{-dpph})(\mathrm{cetdtc})_2(\mathrm{NCS})_2]$; (10) $[\mathrm{Ni}(\mathrm{cetdtc})(\mathrm{dpph})]\mathrm{ClO_4}\cdot 2\mathrm{H_2O}$.

NCS$^-$ were found the vibrations $\nu(C\equiv N)$ at 2080–2088 cm^{-1} and $\nu(C–S)$ at 830–840 cm^{-1} typical for coordination of the NCS$^-$ group to nickel *via* the nitrogen atom [14]. All results above confirm the square arrangement of the coordination sphere.

Results above are in line with the electronic spectra results. The middle maxima between 18500–24600 cm^{-1} were found for all complexes, which can be assigned to the d-d electron transitions for Ni(II) complexes with square coordination [15]. The maxima over 30000 cm^{-1} can be assigned to intra-ligand transitions in the S_2CN^- group [12].

Thermal analysis of complexes containing hmidtc shows that the decomposition starts between 45.5–85°C with removing of chloroform (compounds 1–3) or water (5), which is accompanied by small endo-effects at 138°C (1), 107°C (2), 70°C, 110°C (3) and 88°C (5); the plateau on the TG-curve for complexes (1, 2, 5) are assigned to the non-solvated species. The endo-effects at 152°C (2) and 174°C (5) are without a mass loss on the TG-curve and could be connected with some structural changes. The complexes with cetdtc are thermally more stable – the beginning of decomposition is between185–225°C. The endo-effect at 202°C (9) was observed, due to the melting of compound (confirmed by the Böetius apparatus). All complexes exhibit a sharp exo-effect between 186–248°C connected with a mass increasing (Fig. 1). This fact is described in [17] and can be attributed to the oxygen insertion into Ni–P bond. The insertion is combined with the decomposition of organic part of molecule without thermal stable intermediates. Complexes with perchlorate were not studied for safety reasons.

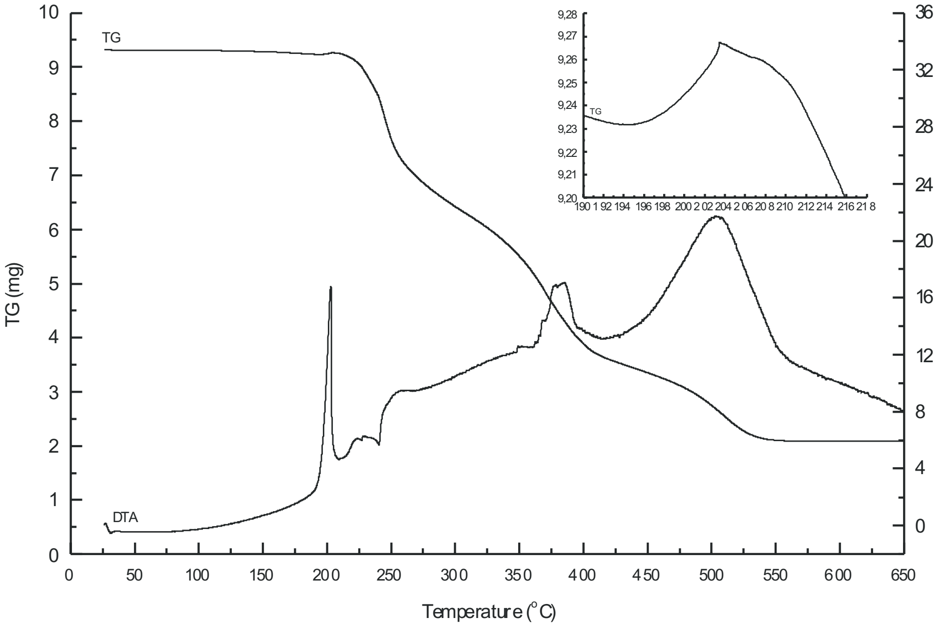

Figure 1. Thermal analysis of $[Ni_2(\mu\text{-dpph})(cetdtc)_2I_2]$.

The X-ray structure of the complex $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$ has been solved. The crystal is monoclinic and the basic crystallographic data are summarized in Table 2. The obtained results (see Table 3, Fig. 2) confirmed a distorted square coordination around central nickel atom. The Ni–S bond lengths are not equal and bond angles in the chromophore significantly differ from 90°. The deviations of atoms from an "ideal" LSQ plane NiS_2PBr are calculated [10]:

Ni(1): –0.024(7), S(1): 0.056(14), S(2): –0.008(15), P(1): 0.001(13), Br(1): 0.009(6) Å.

A significant shortening of bond lengths in the S_2CN^- group typical for dithiocarbamates (see Table 3) was found. The common bond distances for σ-bond are [16]: C–N (1.47 Å); C–S (1.81 Å). This fact can be explained by a significant contribution of the π-interactions in these bonds. Two solvent molecules of $CHCl_3$ are not in the coordination sphere of central atom (distance Ni–C is about 4.72 Å). 1,6-Bis(diphenylphosphino)hexane is coordinated *via* two P-donor atoms to the nickel atoms and provides the connection of both NiS_2PBr chromophores into one species. The distance between both nickel atoms is so large (10.92 Å) that no magnetic Ni-Ni exchange interaction was observed and the complex is diamagnetic. Four possible hydrogen bonds were calculated [10] and they are given in Table 4.

Table 2. Basic crystallographic data for $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$.

Empirical formula	$C_{46}H_{58}Br_2Cl_6N_2Ni_2P_2S_4$
Formula weight	1319.06
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 9.131(2) Å α = 90°
	b = 19.702(4) Å β = 90.84(3)°
	c = 15.096(3) Å γ = 90°
Volume	2715.5(10) $Å^3$
Z, Calculated density	2; 1.613 Mg/m^3
Absorption coefficient	2.707 mm^{-1}
F(000)	1340
Crystal size	0.35×0.35×0.25 mm
Theta range for data collection	3.34 to 28.45°
Index ranges	$-12 \le h \le 11; -25 \le k \le 26; -12 \le l \le 20$
Reflections collected/unique	21273/6281 [R(int) = 0.0494]
Completeness to 2Θ = 28.45°	89.1%
Max. and min. transmission	0.5509 and 0.4508
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6281/0/317

Table 2 (continuation)

Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0558, wR2 = 0.1160
R indices (all data)	R1 = 0.0686, wR2 = 0.1216
Largest diff. peak and hole	3.808 and –3.362 e. Å^{-3}

Table 3. Selected bond lengths and angles for $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$.

Bond distances (Å)		Bond angles (°)	
Ni(1)–S(1)	2.1707(12)	S(1)–Ni(1)–P(1)	98.34(5)
Ni(1)–P(1)	2.1741(12)	S(1)–Ni(1)–S(2)	78.97(4)
Ni(1)–S(2)	2.2032(12)	P(1)–Ni(1)–S(2)	177.13(5)
Ni(1)–Br(1)	2.3020(7)	S(1)–Ni(1)–Br(1)	171.15(4)
S(1)–C(1)	1.726(4)	P(1)–Ni(1)–Br(1)	89.98(4)
S(2)–C(1)	1.709(4)	S(2)–Ni(1)–Br(1)	92.65(4)
N(1)–C(1)	1.302(5)	C(1)–S(1)–Ni(1)	86.65(15)
		C(1)–S(2)–Ni(1)	86.04(14)

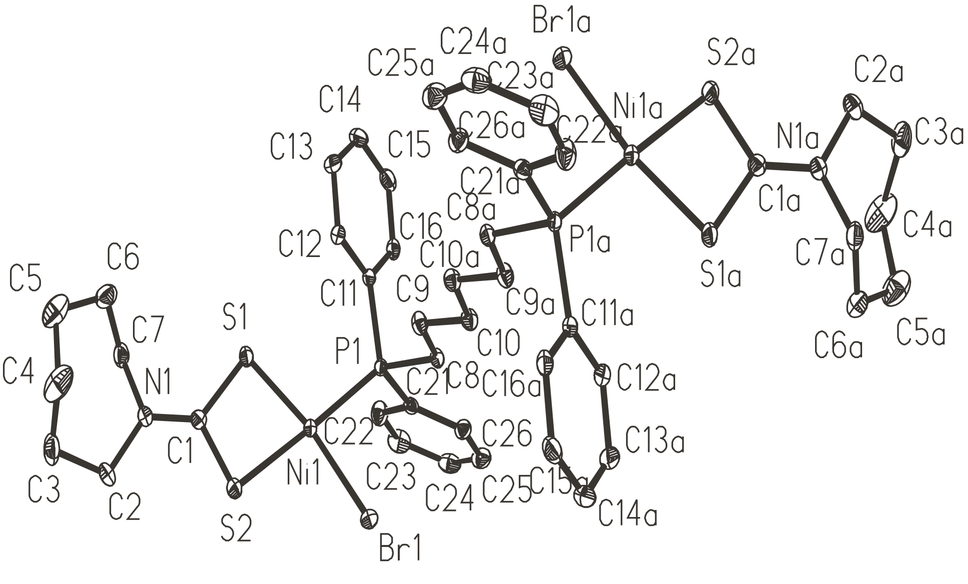

Figure 2. Molecule of $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$ (solvent and H-atoms are omitted).

Table 4. Possible hydrogen bonds for $[Ni_2(\mu\text{-dpph})(hmidtc)_2Br_2]\cdot 2CHCl_3$.

Donor-H (Å)	Donor...Acceptor (Å)	H...Acceptor (Å)	∠Donor-H...Acceptor (°)
C2 -H2A	C2 ....S2 (0)	H2A ...S2 (0)	C2 -H2A ...S2 (0)
.975(.169)	3.076(.007)	2.618(.042)	108.99(.22)
1.080		2.585	106.78 (**)
C7 -H7A	C7 ....S1 (0)	H7A ...S1 (0)	C7 -H7A ...S1 (0)
.933(.106)	3.053(.010)	2.720(.027)	101.94(.22)
1.080		2.694	98.89 (**)
C8 -H8A	C8 ....Br1 (0)	H8A ...Br1 (0)	C8 -H8A ...Br1 (0)
1.017(.198)	3.416(.012)	2.847(.160)	115.93(.33)
1.080		2.820	114.78 (**)
C12 -H12	C12 ....S1 (0)	H12 ...S1 (0)	C12 -H12 ...S1 (0)
.995(.111)	3.231(.008)	2.795(.149)	107.09(.25)
1.080		2.771	105.41 (**)

(**) Values normalized following G.A. Jeffrey & L. Lewis, *Carbohydr. Res*., (1978), 60, 179; R.Taylor, O.Kennard, *Acta Cryst*., (1983), B39, 133.

Equivalent positions:
(0) x, y, z
(1) x – 1/2, –y + 1/2, –z + 1/2.

Supplementary data: Material involving structure data has been deposited in the Cambridge Crystallographic Data Centre, Registry No. CCDC 201015. 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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REFERENCES

1. Pastorek R., Trávníček Z., Kvapilová E., Šindelář Z., Březina F. and Marek J., *Polyhedron*, **18**, 151 (1999).
2. Pastorek R., Trávníček Z., Marek J., Dastych D. and Šindelář Z., *Polyhedron*, **19**, 1713 (2000).
3. Pastorek R., Kameníček J., Šindelář Z. and Zák Z., *Polish J. Chem*., **75**, 363 (2001).
4. Pastorek R., Kameníček J., Husárek J. and Šindelář Z., *Acta Univ. Palack. Olom., Chemica*, **40**, 53 (2001).
5. Přibil R., *Komplexometrické titrace*, SNTL Praha 1955, p. 22.
6. Jureček M., *Organická analýza II*, ČSAV Praha 1957, p. 140.
7. *Gmelins Handbuch der Anorganischen Chemie, Nickel*, Teil C, Lief. 2, Verlag Chemie, GMBH, Weinheim, 1969, p. 996.
8. Sheldrick G.M., SHELXS-97; enhanced version of SHELX-S, *Acta Cryst*., **A46**, 467 (1990).
9. Sheldrick G.M., SHELXL-97, Program for crystal structure refinement. University of Göttingen, 1997.

10. Nardelli M., PARST 95, *J. Appl. Cryst.*, **28**, 659 (1995).
11. Geary W.J., *Coord. Chem. Rev.*, **7**, 81 (1971).
12. Tsipis C.A., Kessissoglou D.P. and Katsoulos G.A., *Chim. Chron., New Series*, **14**, 195 (1985).
13. Scholer R.P. and Merbach E.A., *Inorg. Chim. Acta*, **15**, 15 (1975).
14. Černikova I.E., Chartonik I.A., Umrejko D.S., Kavrikov A.B. and Afanov V.I., *Koord. Chim.*, **15**, 1695 (1989).
15. Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam 1984, p. 534.
16. Lide D.R. (Ed.), *Handbook of Chemistry and Physics*, 73rd Edition CRC Press Boca Raton, FL 1992.
17. Březina F. and Benátská E., *J. Thermal Anal.*, **22**, 75 (1981).