Tetracyanometallates with Complex Dien Cations: $[Ni(dien)_2][Ni(CN)_4] \cdot 2H_2O$ and $[Ni(dien)_2][Pd(CN)_4]$

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Abstract. The crystal structures of two square tetracyanocomplexes were determined. $[Ni(dien)_2][Ni(CN)_4] \cdot 2H_2O$ (NDNCH) and $[Ni(dien)_2][Pd(CN)_4]$ (NDPC) (dien = diethylene triamine) exhibit ionic structures consisting of *mer*-$[Ni(dien)_2]^{2+}$ cations and $[Ni(CN)_4]^{2-}$ or $[Pd(CN)_4]^{2-}$ anions, respectively. Moreover, the structure of NDNCH is completed by two water molecules of crystallisation. In both compounds hydrogen bonds contribute to the stabilisation of the structure. NDNCH dehydrates on air quickly yielding anhydrous $[Ni(dien)_2][Ni(CN)_4]$ (NDNC). Its thermal decomposition proceeds in a complicated process followed by aerial oxidation of metallic nickel to NiO.

Keywords: Nickel; Palladium; Crystal structure; Diethylenetriamine; Thermal properties

Tetracyanometallate mit komplexen dien-Kationen: $[Ni(dien)_2][Ni(CN)_4] \cdot 2H_2O$ und $[Ni(dien)_2][Pd(CN)_4]$

Inhaltsübersicht. Die Kristallstrukturen zweier quadratisch-planarer Tetracyanokomplexe wurden bestimmt. $[Ni(dien)_2][Ni(CN)_4] \cdot 2H_2O$ (NDNCH) and $[Ni(dien)_2][Pd(CN)_4]$ (NDPC) (dien = Diethylentriamin) zeigen ionische Strukturen, die aus *mer*-$[Ni(dien)_2]^{2+}$ Kationen und $[Ni(CN)_4]^{2-}$ bzw. $[Pd(CN)_4]^{2-}$ Anionen aufgebaut sind. Die Struktur von NDNCH weist darüberhinaus noch zwei Kristallwassermoleküle auf. In beiden Verbindungen tragen H-Brückenbindungen zur Stabilisierung der Strukturen bei. NDNCH verliert an Luft rasch Wasser und bildet wasserfreies $[Ni(dien)_2][Ni(CN)_4]$ (NDNC). Dessen thermische Zersetzung läuft in einem komplexen Prozess ab, gefolgt von Luftoxidation des gebildeten metallischen Nickels zu NiO.

Introduction

Recently, cyanocomplexes attract interest both of chemists and physicists due to their remarkable magnetic properties [1−4]. We are interested in low-dimensional magnetics based on cyanocomplexes. Previously we have described the preparation, structure and properties of cyanocomplexes containing mainly bidentate amine-type ligands like en (1,2-diaminoethane) or tn (1,3-diaminopropane) [5−7]. The obtained results and literature data [8] indicate that by the choice of suitable amine type ligands and the ligand/metal ratio it is possible to influence the dimensionality of the formed structure. It is known that dien (diethylenetriamine) may act as a tridentate ligand. It was used in various cyano complexes, like in molecular $Cu(dien)(mea)Ni(CN)_4 \cdot 2H_2O$ (mea = monoethanolamine) [9], one-dimensional (1D) $[Cu(dien)]_3[(Fe(CN)_6] \cdot 6H_2O$ [10] or in the 3D host-guest system $[Cd(dien)_2][Cd_2(dien)_2(CN)_3][Cd_8(CN)_{18}] \cdot 3H_2O$ [11]. The aim of the present work was to study the preparation, structure and properties of compounds obtainable from the aqueous systems $Ni^{2+}-dien-[M(CN)_4]^{2-}$, where M = Ni and Pd. From these systems at a Ni : dien molar ratio of 1:2 and higher $[Ni(dien)_2][Ni(CN)_4] \cdot 2H_2O$ (NDNCH) and $[Ni(dien)_2][Pd(CN)_4]$ (NDPC) can be isolated in the form of single crystals. As during our work a crystal structure determination of NDNCH at 20 °C was reported [12] with almost the same results, we have deposited our low-temperature data and restrict ourselves mainly to a short comparison along with the structure of NDPC, therefore.

Experimental Section

Syntheses

Single crystals of NDNCH suitable for X-ray studies were prepared by a modified method to that reported in [12]. The same method was used for preparation of single crystals of NDPC. The procedures were:

NDNCH: 10 ml of 0.1M $Ni(NO_3)_2$ solution (1 mmol) and 0.44 ml of dien (4 mmol) were mixed. To the resultant solution 10 ml of 0.1M $K_2[Ni(CN)_4]$ solution (1 mmol) was added. Finally, the formed violet solution was filtered and left for crystallisation. Large single crystals up to 5 mm appeared overnight. The product should be handled quickly due to dehydration.

NDPC: the same procedure was used with a solution of $K_2[Pd(CN)_4]$ instead of $K_2[Ni(CN)_4]$. Calc. (M_r = 475.54): C, 30.31; H, 5.51; N, 29.45%. Found : C, 30.49; H, 4.55; N, 29.06%.

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NDNC: the sample of NDNCH crystals were ground in an agate mortar and heated in an oven at 100 °C for one hour. Calc. (M_r = 427.81): C, 33.69; H, 6.13; N, 32.74%. Found : C, 33.75; H, 5.88; N, 32.33%.

IR spectroscopy

The IR spectra were measured on a Perkin-Elmer FT-IR instrument. Here are given the important well identifiable absorption bands:

NDNCH: ν(OH): 3642m, 3627wsh, 3565w, 3544wsh; ν(NH$_2$): 3328vs, 3267 vs, 3234vs, 3175 vs, 3155ssh; ν(CH$_2$): 2957s, 2919s, 2876s; ν(CN): 2121vs, 2113vs; δ(OH$_2$): 1693wsh, 1622msh; δ(NH$_2$): 1599m, 1582m; ρ(NH$_2$): 625m, 609m; δ(NC-CN): 525m, 514m, 486w; δ(Ni-CN): 412s cm^{-1}.

NDNC: ν(NH$_2$): 3337vs, 3310vs, 3274vs, 3246ssh, 3175msh; ν(CH$_2$): 2952msh, 2932m, 2877m; ν(CN): 2125ssh, 2117vs; δ(NH$_2$): 1579m; ρ(NH$_2$): 612m; δ(NC-CN): 519m; δ(Ni-CN): 417m cm^{-1}.

NDPC: ν(NH$_2$): 3339vs, 3314vs, 3273vs, 3171msh; ν(CH$_2$): 2973wsh, 2953msh, 2935s, 2879s, 2865s; ν(CN): 2136ssh, 2128vs; δ(NH$_2$): 1581s; ρ(NH$_2$): 611m; δ(NC-CN): 519m, 484w; δ(Pd-CN): 409m cm^{-1}.

Thermal analysis

The thermal behaviour of NDNC was studied on a Derivatograph OD-102 instrument (MOM Budapest). TG, DTG and DTA curves were recorded under following experimental conditions: TG = 100 mg, DTG = 1/5, DTA = 1/5, air atmosphere, ceramic crucibles, heating rate 10°/min, t_{max} = 1000 °C. The final product was examined by X-ray powder diffraction method using a DRON-2 diffractometer and CuK$_\alpha$ radiation.

X-ray crystallography

Data for NDNCH and NDPC (data are given in parentheses), respectively, were collected on a Enraf-Nonius (CAD4) four-circle diffractometer using graphite monochromated CuK$_\alpha$ (MoK$_\alpha$) radiation with λ = 1.54178 Å (λ = 0.71073 Å). Cell parameters were refined using 45 (25) reflections. Three control reflections were measured every two hours during data collection and no intensity decay was observed. For the crystal of NDNCH mounted in a glass capillary a numerical absorption correction was made using the measured crystal faces (the number in the parentheses are the distances (in mm) of the respective face from an arbitrary centre: 001 (0.025), $00\bar{1}$ (0.025), $1\bar{1}0$ (0.080), $\bar{1}10$ (0.080), 100 (0.20), $\bar{1}00$ (0.20). The absorption correction in the case of NDPC was based on ψ-scans.

The structures were solved by the heavy atom methods in *SHELXS86* [13], and refined using full-matrix least squares by *SHELXL97* [14]. The non-H atoms were treated anisotropically. The O2 atom in NDNCH was disordered, its less populated position (O21) was treated isotropically. Hydrogen atoms in NDNCH were treated riding on calculated positions, hydrogen atoms of the water molecule in NDNCH were found from a difference map. In NDNCH only isotropic displacement parameters of the hydrogen atoms common by groups were refined, while in NDPC also their positions were refined. Some further details along with the final values of crystallographic residuals are given in Table 1. Geometric parameters were calculated by using the program PARST [15] and the figures were drawn using the program DIAMOND [16]. The atomic co-ordinates of NDPC are collected in Table 2, selected geometric parameters are presented in Table 3, while the possible hydrogen bonds are gathered in Table 4.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-165239 (NDNCH) and CCDC-165240 (NDPC). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. Code +44(1223)336-033; E-mail: {HYPERLINK mailto: deposit@ccdc.cam.ac.uk]} deposit@ccdc.cam.ac.uk].

Results and Discussion

Using [Ni(dien)$_2$]$^{2+}$ cations and [Ni(CN)$_4$]$^{2-}$ and [Pd(CN)$_4$]$^{2-}$ anions, respectively, as building blocks two compounds with ionic structures crystallise from the aqueous solution. The results of structure analysis of NDNCH confirmed the identity of the isolated compound with the previously described one [12]. Its atomic co-ordinates and geometric parameters were deposited (see above).

The structure of the new compound NDPC is formed of [Ni(dien)$_2$]$^{2+}$ cations and [Pd(CN)$_4$]$^{2-}$ square anions (Fig. 1). The arrangement of the ions in the unit cell corresponds to the deformed NaCl structure type. Beside strong Coulombic attraction to the packing forces contribute also weak HBs of the N-H···NC type (Table 4). The cation like in NDNCH is *mer* isomer. Same type of cation was found e.g. in the trinuclear molecular tetracyanonickellate {[Ni(dien)]$_2$(C$_2$O$_4$)Ni(CN)$_4$} [17]. An *s-fac* isomer of the cation was found in the [Ni(dien)$_2$]CA · 2H$_2$O (CA = chloranilate) compound [12].

There exist three pairs of mean Ni-N bond distances, namely 2.08, 2.13 and 2.17 Å in the NiN$_6$ octahedron in NDPC (Table 3). The shortest Ni-N distances correspond to the bonds of the nickel central atom to the secondary amine group nitrogen atom. The corresponding Ni-N bond distances in NDPC are almost the same as in NDNCH despite the different temperature of data collection, and at the same time these values are somewhat shorter than the corresponding ones found in the previous structure determination of NDNCH [12]. The bond distances and angles in the chelate rings exhibit usual values [18]. The conformation of the chelate rings is the same (δλ) as in NDNCH.

The co-ordination of the palladium atom is exactly planar as required by symmetry ($\bar{1}$). All cyano groups are terminal, they are linked only by hydrogen bonds to water molecules or *dien* ligands. The geometric parameters in these anions are as usual [5, 19].

The NDNCH compound is very sensitive to handling, it readily decomposes on air due to dehydration. In the previous X-ray determination made on 20 °C [12] it was noted that a 20% lost of intensity of the control reflections was observed during data collection. It seems that the higher final value of R1 factor was influenced by partial deterioration of the single crystal. With our data, free refinement of the oxygen site occupation factors gave no indication of understoichiometry. As expected, our cell parameters of

Table 1 Crystal data and structure refinement for NDNCH and NDPC

Identification code	NDNCH	NDPC
Empirical formula	$C_{12}H_{30}N_{10}Ni_2O_2$	$C_{12}H_{26}N_{10}NiPd$
Formula weight	463.88	475.54
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions, a	8.8038 (10) Å	15.204(1) Å
b	8.8420(10) Å	9.5063(5) Å
c	15.8850(10) Å	15.363(1) Å
α	77.424(8)°	90°
β	88.961(11)°	112.102(6)°
γ	61.332(8)°	90°
Volume	1053.53(18) $Å^3$	2057.3(2) $Å^3$
Z	2	4
Temperature	213(2) K	293 K
Density (calculated)	1.462 Mg/m^3	1.535 Mg/m^3
Absorption coefficient	2.460 mm^{-1}	1.804 mm^{-1}
Crystal size mm^3	0.50 x 0.16 x 0.04	0.45 x 0.30 x 0.20
Theta range for data collection	2.86 to 64.98°	2.58 to 27.45°
Index ranges	$-8 \le h \le 10$ $0 \le k \le 10$ $-18 \le l \le 18$	$-19 \le h \le 19$ $-12 \le k \le 0$ $-19 \le l \le 19$
Reflections collected	3786	9399
Independent reflections	3540 [R_{int} = 0.0873]	4704 [R_{int} = 0.0320]
Max. & Min. Transmission	0.886, 0.563	0.810, 0.707
Goodness-of-fit on F^2	1.090	0.990
Final R indices [$I > 2\sigma_I$] R1 =	0.0620 [3540]	0.0326 [3026]
wR2 =	0.1712	0.0523
[all data] R1 =	0.0669	0.0697
wR2 =	0.1773	0.0603
Extinction coefficient	0.0026(7)	none
Largest diff. peak and hole	0.783 and −1.274 e/$Å^3$	0.467 and −0.316 e/$Å^3$

Table 2 Fractional atomic co-ordinates and equivalent isotropic thermal parameters $Å^2$ of NDPC.

Atom	x	y	z	U_{eq}
Pd1	0.0000	0.5000	0.5000	0.04315(9)
Pd2	0.5000	0.0000	0.5000	0.05418(10)
Ni	0.24367(3)	0.06646(4)	0.70543(3)	0.04263(10)
N1	0.3472(2)	0.1953(3)	0.68186(19)	0.0616(8)
N2	0.1722(2)	0.2567(3)	0.68514(19)	0.0603(8)
N3	0.11846(19)	−0.0004(3)	0.7289(2)	0.0571(7)
N4	0.3213(2)	0.0700(4)	0.85603(19)	0.0608(8)
N5	0.31431(17)	−0.1244(3)	0.72109(18)	0.0513(7)
N6	0.18257(19)	−0.0029(3)	0.56394(18)	0.0514(6)
C11	0.1104(2)	0.5294(3)	0.4624(2)	0.0524(8)
C12	−0.00104(19)	0.2999(3)	0.4628(2)	0.0484(7)
C21	0.3747(2)	0.0885(4)	0.4757(2)	0.0625(9)
C22	0.5140(2)	0.1265(4)	0.4035(3)	0.0749(11)
N11	0.1735(2)	0.5417(3)	0.4411(2)	0.0752(9)
N12	0.00041(18)	0.1853(3)	0.4425(2)	0.0681(8)
N21	0.3037(2)	0.1417(3)	0.4620(2)	0.0789(9)
N22	0.5198(2)	0.1995(4)	0.3477(2)	0.1127(15)
C1	0.3080(3)	0.3365(4)	0.6558(3)	0.0838(13)
C2	0.2413(4)	0.3701(4)	0.7043(3)	0.0789(12)
C3	0.1084(3)	0.2556(4)	0.7367(3)	0.0712(10)
C4	0.0542(3)	0.1213(5)	0.7153(3)	0.0730(11)
C5	0.3855(3)	−0.0516(5)	0.8825(3)	0.0746(11)
C6	0.3415(3)	−0.1722(4)	0.8183(3)	0.0689(10)
C7	0.2546(2)	−0.2178(4)	0.6461(3)	0.0587(9)
C8	0.2247(2)	−0.1386(4)	0.5550(2)	0.0579(9)

Table 3 Selected structure parameters Å, ° for NDPC.

Pd1-C11	1.989(3)	C12-Pd1-C11	88.11(11)
Pd1-C12	1.985(3)	C22-Pd2-C21	88.16(12)
Pd2-C21	1.985(3)	N11-C11-Pd1	177.9(3)
Pd2-C22	1.981(4)	N12-C12-Pd1	178.5(3)
C11-N11	1.131(4)	N21-C21-Pd2	178.7(3)
C12-N12	1.135(4)	N22-C22-Pd2	178.4(3)
C21-N21	1.138(4)		
C22-N22	1.132(4)		
Ni-N1	2.130(3)	N2-Ni-N1	81.49(12)
Ni-N2	2.072(3)	N2-Ni-N3	80.60(12)
Ni-N3	2.162(3)	N3-Ni-N4	89.21(11)
Ni-N4	2.166(3)	N5-Ni-N4	80.78(12)
Ni-N5	2.076(3)	N5-Ni-N6	81.66(11)
Ni-N6	2.122(3)	N1-Ni-N3	161.93(13)
N1-C1	1.462(5)	N6-Ni-N4	162.08(13)
N2-C2	1.455(5)		
N2-C3	1.464(4)		
N3-C4	1.477(5)		
N4-C5	1.469(5)		
N5-C6	1.464(4)		
N5-C7	1.468(4)		
N6-C8	1.469(4)		
C1-C2	1.502(6)		
C3-C4	1.488(5)		
C5-C6	1.497(6)		
C7-C8	1.500(5)		

NDNCH measured at low temperature are somewhat shorter (approx. 0.7%) than those reported in [12] which were measured at room temperature; consequently the cell volume measured at low temperature is smaller (1053.5(2) versus 1074.0(8) $Å^3$).

The IR spectra of all prepared compounds are very similar. The differences are mainly caused by the presence of water molecules in the dihydrate: four weak to medium absorption bands are observed in the region from 3642 to 3544 cm^{-1} due to symmetric and asymmetric ν(OH) stretching vibrations of the crystal water molecules. Moreover, the presence of water molecules manifests itself by two shoulders at 1693wsh and 1622msh due to δ(OH_2) defor-

Table 4 Possible hydrogen bonds in NDPC Å, °.

D-H	D···A	H···A	AD-H···A
N1-H1A 0.83(3)	N1···N22^{i} 3.058(4)	H1A···N22^{i} 2.28(3)	N1-H1A···N22^{i} 156(3)
N1-H1B 0.82(3)	N1···N21 3.228(4)	H1B···N21 2.55(3)	N1-H1B···N21 141(3)
N3-H3A 0.87(3)	N3···N12^{ii} 3.116(4)	H3A···N12^{ii} 2.28(3)	N3-H3A···N12^{ii} 161(3)
N3-H3B 0.81(3)	N3···N11^{i} 3.071(4)	H3B···N11^{i} 2.29(3)	N3-H3B···N11^{i} 161(3)
N4-H4A 0.90(3)	N4···N21^{i} 3.249(5)	H4A···N21^{i} 2.59(3)	N4-H4A···N21^{i} 131(3)
N4-H4B 0.83(3)	N4···N11^{i} 3.177(5)	H4B···N11^{i} 2.41(3)	N4-H4B···N11^{i} 154(3)
N5-H5 0.79(3)	N5···N22^{iii} 3.161(5)	H5···N22^{iii} 2.46(4)	N5-H5···N22^{iii} 148(3)
N6-H6A 0.92(3)	N6···N12^{ii} 3.248(4)	H6A···N12^{ii} 2.50(3)	N6-H6A···N12^{ii} 139(2)
N6-H6A 0.92(3)	N6···N12 3.235(4)	H6A···N12 2.66(3)	N6-H6A···N12 121(2)
N6-H6B 0.82(3)	N6···N21 3.147(5)	H6B···N21 2.45(4)	N6-H6B···N21 144(3)

Equivalent positions:
i x, 1/2-y, z+1/2
ii -x, -y, 1-z
iii 1-x, -y, 1-z

mation vibrations. These absorption bands are missing in the spectra of both anhydrous compounds, NDNC obtained by dehydration as well as NDPC.

The positions of the strong absorption bands due to ν(C≡N) stretching vibrations, characteristic for the cyano compounds, are almost the same in NDNCH (2121 and 2113 cm^{-1}) and dehydrated NDNC (2125 and 2117 cm^{-1}) and correspond well with the terminal character of the cyano ligands. The presence of two absorption bands can be explained by deviation of the anion site symmetry from ideal D_{4h}. Two absorption bands are also observed for the tetracyanopalladate compound; these are somewhat shifted to higher wavenumbers (2136 and 2128 cm^{-1}) according to the higher mass of palladium [20].

The dien ligands cause the presence of numerous absorption bands in the spectra of all compounds due to ν(NH), ν(CH), $\delta(NH_2)$, $\delta(CH_2)$ and other vibrations. The similarity of the IR spectra of both NDNC and NDPC and stereochemical considerations allow to conclude that the anhydrous compound $[Ni(dien)_2][Ni(CN)_4]$ (NDNC) exhibits an ionic structure like NDPC.

The thermal properties of the NDNC compound were studied. As can be seen from Fig. 2, this compound is stable up to 240 °C. In the temperature range 240−490 °C strong exothermic decomposition occurs. This decomposition is clearly a multistage process as suggested by the TG and indicated by the DTG curves. The first step is estimated to be 17.5%, but it does not correspond to the calculated weight loss (24.2%) of one *dien* molecule from the formula unit. So it can be concluded that contrary to the analogous compounds with etylenediamine $Ni(en)_xNi(CN)_4$ (x = 1−3) [21], it is not possible to prepare the $Ni(dien)Ni(CN)_4$ compound by solid state deamination reaction. On the other hand, the hydrate $Ni(dien)Ni(CN)_4 \cdot H_2O$ was isolated as precipitate from aqueous solution [22].

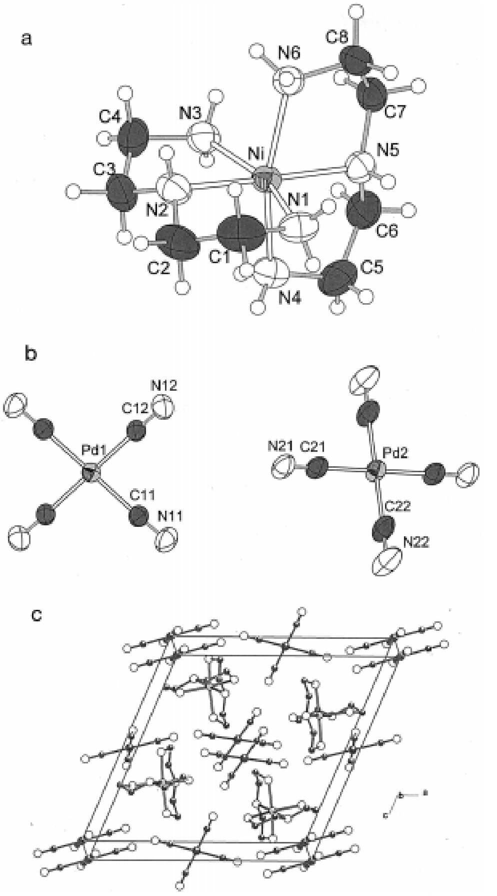

Fig. 1 Displacement ellipsoids drawing of **a)** the $[Ni(dien)_2]^{2+}$ cation, **b)** the centrosymmetrical $[Pd(CN)_4]^{2-}$ anions in NDPC along with the atom numbering scheme. Displacement ellipsoids at the 40% probability level. **c)** Unit cell of the NDPC structure. The hydrogen atoms are omitted for the sake of clarity.

The multistage decomposition with observed weight loss of 72.0% may correspond to the decomposition of both dien and cyano ligands leading under reductive conditions to the formation of metallic nickel (calc. 72.6%). This is further reoxidized by aerial oxygen as indicated by the observed weight increase of 6% up to 750 °C. The weight of the residue represents 35,0% of the initial weight; this is in line with the presence of NiO (calc. 34.9%) proved by the taken powder diffraction pattern.

The present work confirms generally close resemblance of the tetracyanonickellate and tetracyanopalladate compounds. The observed difference: formation of unstable dihydrate (Ni) and an anhydrous compound (Pd), respectively, under the same experimental conditions may reflect the different size of the respective complex anions.

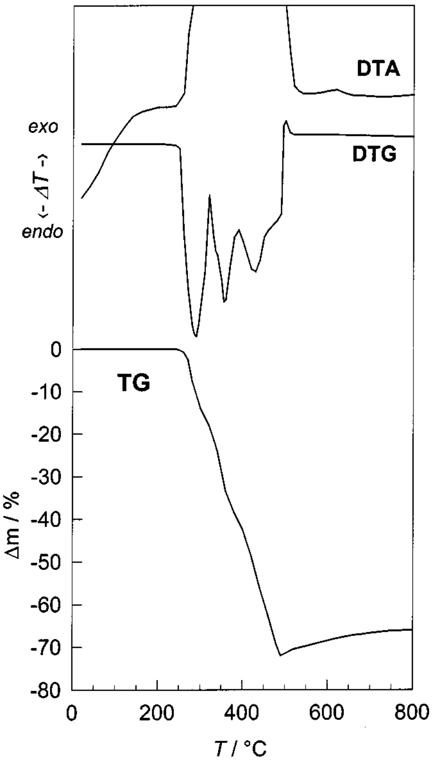

Fig. 2 TG, DTA and DTG diagrams for [Ni(dien)$_2$][Ni(CN)$_4$].

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