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NICKEL(II) COMPLEXES PREPARED FROM NNN TYPE LIGANDS AND PSEUDOHALOGENS*

Synthesis, structure and thermal decomposition

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Six nickel(II) complexes, using azide and thiocyanate ions, have been synthesized from bis-2,6(pyrazol-1-yl)pyridine (pp) and some methyl derivatives, 2-(3,5-dimethyl(pyrazol-1-yl)-6-(pyrazol-1-yl)pyridine (app) and bis-2,6(3,5-dimethyl(pyrazol-1-yl) pyridine (dmpp) in non-aqueous media. The complex structures were analyzed using elemental analysis, IR spectroscopy and thermogravimetry. Appropriate crystals of complex, containing azide $[Nipp(N_3)_2]{\cdot}MeOH$ (**I**) and thiocyanate $[Nidmpp(SCN)_2{\cdot}MeOH]$ (**VI**) were prepared and the molecular structures determined using X-ray diffraction. Complex **I** was seen to be dinuclear as stated in literature, space group $P2_1/n$, monoclinic, a=10.503, b=10.681, c=13.291 Å, β=106.56° and Z=2 whereas complex **VI** was found to be mononuclear, space group $P2_1/n$, monoclinic, a=8.646, b=12.614, c=20.697 Å, β=97.18° and Z=2. The Ni(II) coordination in both complexes were octahedral. Thermogravimetric studies showed azide containing structures to resemble the characteristics of explosive materials. Coordinative MeOH were seen to leave the structure in thiocyanate containing complexes, followed by irregular degradation above 300°C.

Keywords: *azide, crystal structure, nickel(II) complexes, synthesis, thermal analysis, thiocyanate*

Introduction

Bis-2,6(3,5-dimethyl(pyrazol-1-yl) pyridine (dmpp) is a terpyridyl type tridendate ligand synthesized at the beginning of the 1990's [1]. Due to the presence of 5 nitrogen donor atoms side by side in the three aromatic rings dmpp and similar molecules are denoted as strong ligands. Also the planar structure of the three donor atoms increase this effect. There are many similar studies and structures dealing with this subject. The structures of iron(II), copper(II) and cobalt(II) complexes of dmpp [2–4] and dinuclear structures of Ni(II) [5] have been reported in literature. There are also many studies dealing with the catalytic effect of some pyrazolyl pyridine complexes [6–11].

It has been established since 1986 that azide and thiocyanate ions form μ-bridges of end–end (1,1) and end–on (1.3) types [12, 13]. There are many examples in literature dealing with the 1,1 and 1,3 bridges formed by azide and thiocyanate ions [14–19].

In this this study bis-2,6(pyrazol-1-yl)pyridine (pp) and some methyl derivatives, 2-(3,5-dimethyl-(pyrazol-1-yl)-6-(pyrazol-1-yl)pyridine (app) and bis-2,6(3,5-dimethyl(pyrazol-1-yl) pyridine (dmpp) were synthesized with the intention of forming polynuclear nickel(II) complexes using azide and thiocyanate ions. X-ray studies revealed dinuclear complexes to form with azide ions and mono nuclear complexes to form with thiocyanate ions. Figure 1 gives the formulas of the ligands pp, app and dmpp.

Thermal analysis, especially thermogravimetry is an exceptionally effective method in determination of complex stoichiometry. The mass of the coordinatively bonded solvent molecules give very

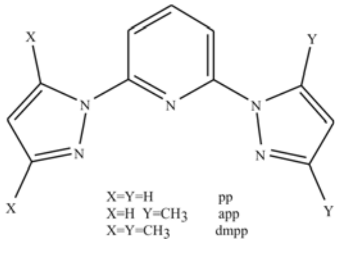

Fig. 1 The formulas of the ligands pp, app and dmpp

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beneficial results for the complex stoichiometry. The final mass of the residues is also very effective for stoichiometric determination. For this reason, TG and DTA methods were employed alongside elemental analysis and IR spectroscopy.

Experimental

Materials

Nickel(II) chloride hexahydrate (Aldrich), sodium azide (Sigma) and potassium thiocyanate (Sigma) were used without further purification. All other chemicals were of AR grade and used as received.

Caution. Although our samples were stable during handling, metal azido complexes are potentially explosive; only a small amount of material should be prepared and it should be handled with care.

Ligand synthesis

pp

Pyrazole (6.8 g, 0.1 mol) was dissolved in 100 mL of diethylene glycol dimethyl ether (diglym) at 50°C. Metallic Na (2.4 g, 0.104 mol) was added in small fragments and the solution was stirred for 2 h resulting in the formation of sodium pyrazolate. The unreacted sodium fragments were separated and 2,6-dichloropyridine (7.4 g, 0.05 mol) was added to the solution. The solution was stirred for two days in a temperature range of 110–130°C. The resulting mixture was poured into 600 mL of water-ice mixture and the resulting precipitate was filtered and dried under atmosphere conditions. The dry precipitate was crystallized in a MeOH:H_2O (1:2) mixture.

app

Pyrazole (6.8 g, 0.1 mol) was dissolved in 100 mL diglym at 50°C and metallic Na (2.4 g, 0.104 mol) was added in small fragment and the solution was stirred for 2 h resulting in the formation of sodium pyrazolate. The unreacted Na pieces were separated and 2,6-dichloropyridine (14.8 g, 0.1 mol) was added to the solution. The mixture was stirred for two days at 60°C on a water bath. The mixture was then poured onto 600 mL of an ice–water mixture and the resulting precipitate filtered and dried. The precipitate was identified as 2 pyrazol-1-yl-6- chloropyridine. An equimolar amount of 3,5-dimethylpyrazole was dissolved in diglym and reacted with 2.4 g of metallic sodium. 2-pyrazol-1-yl-6=chloro–pyridine was added to this solution and stirred for two days in the temperature range of 110–130°C. The mixture was then poured onto 600 mL of water-ice mixture and the resulting precipitate was filtered and dried. The dry crystals were recrystallized in a MeOH:H_2O (1:1) mixture.

dmpp

Bis-2,6(3,5-dimethyl(pyrazol-1-yl) pyridine, dmpp (9.6 g, 0.1 mol) was reacted with 2.4 g (0.104 mol) of metallic sodium for 2 h in 100 mL of diglym. The unreacted sodium particles were separated and 2,6-dichloropyridine (7.4 g, 0.05 mol) was added to the solution and stirred for 2 days at 110–130°C. This mixture was poured over 600 mL of iced water and the precipitate was filtered and recrystallized in a MeOH:H_2O (1:1) mixture.

Complex synthesis

Azide containing complexes: $[Nipp(N_3)_2]_2 \cdot MeOH$ (**I**), $[Niapp(N_3)_2]_2$ (**II**) and $[Nidmpp(N_3)_2]_2 \cdot 2MeOH$ (**III**)

The ligand of pp, app or dmpp (0.003 mol) is dissolved in 70 mL of MeCN and heated up to 45°C. To this, nickel(II) chloride hexahydrate (0.003 mol, 0.714 g) dissolved in 20 mL of methanol and sodium azide (0.006 mol, 0.390 g) dissolved in 10 mL of water was added. The medium temperature should not exceed 45°C, otherwise the crystals formed are very small. The solution was left to stand for 12 h and the resulting crystals are filtered and left to dry under atmospheric conditions. Elemental analysis results and some important IR data are given in Table 1.

Thiocyanate containing complexes: $[Nipp(SCN)_2 \cdot MeOH]$ (**IV**), $[Niapp(SCN)_2 \cdot MeOH]$ (**V**), $[Nidmpp(SCN)_2 \cdot MeOH]$ (**VI**)

The ligand of pp, app or dmpp (0.004 mol) was dissolved in 70 mL of MeCN and heated. To this was added the solutions of nickel(II) chloride hexahydrate (0.004 mol, 0.955 g) dissolved in 20 mL hot methanol and potassium thiocyanate (0.004 mol, 0.776 g) dissolved in 15 hot water. The mixture was left to stand for 2 days and the resulting crystals were filtered and left to dry under atmospheric conditions. Elemental analysis results and some important IR data are given in Table 1.

Measurement techniques

Elemental analysis was performed on a Eurovector 3018 C,H,N,S analyzer instrument. Nickel analysis was done gravimetrically using dimethylglyoxime. IR spectrums were obtained on a Mattson FTIR 1000 instrument using the KBr disk technique.

TG-DTA curves were obtained using a Shimadzu TG-60H instrument. Aluminium pans were used for curves obtained between room temperature and

Table 1 Elemental analysis results and important IR data of the complexes

Complexes	Elemental analysis								Important IR data/cm^{-1}							
	Expected/%				Found/%											
	C	H	N	Ni	C	H	N	Ni	ν_{OH}	$\nu_{C–H}$ aromatic	$\nu_{C–H}$ aliphatic	ν_{N_3}	ν_{SCN}	$\nu_{C=N}$	$\nu_{C=C}$	$\delta_{C–H}$ aromatic
[Nipp(N$_3$)$_2$]$_2$·MeOH [(C$_{11}$H$_9$N$_5$)Ni(N$_3$)$_2$]$_2$	37.34	3.39	39.91	15.21	36.94	3.02	40.63	16.08	–	3105 3059	–	2060 2081	–	1619	1590	777
[Niapp(N$_3$)$_2$]$_2$ [(C$_{13}$H$_{13}$N$_5$)Ni(N$_3$)$_2$]$_2$	40.88	3.43	40.32	15.36	41.42	3.36	41.26	15.74	–	3086 3041	2930	2046 2073	–	1618	1592	783
[Nidmpp(N$_3$)$_2$]$_2$·2MeOH [(C$_{15}$H$_{17}$N$_5$)Ni(N$_3$)$_2$]$_2$	42.09	4.47	35.98	13.72	41.83	4.42	36.20	14.39	–	3081 3068	2926	2045 2070	–	1618	1593	789
[Nipp(SCN)$_2$MeOH] (C$_{11}$H$_9$N$_5$)Ni(SCN)$_2$·MeOH	38.79	2.64	19.76	11.83	38.42	3.21	18.85	12.37	3358	3105	–	–	2097 2105	1618	1589	783
[Niapp(SCN)$_2$MeOH] (C$_{13}$H$_{13}$N$_5$)Ni(SCN)$_2$·MeOH	36.62	2.66	19.92	11.93	35.71	3.51	20.25	12.07	3360	3105 3059	2932	–	2097 2108	1618	1590	783
[Nidmpp(SCN)$_2$MeOH] (C$_{15}$H$_{17}$N$_5$)Ni(SCN)$_2$·MeOH	39.16	3.83	17.75	10.63	39.97	3.71	18.04	11.21	3400	3107	2928	–	2094 2108	1614	1590	787

450°C, whereas platinum pans were used for curves obtained between room temperature and 750°C. The curves were obtained under nitrogen atmosphere with a flow rate of 100 cm^3 min^{-1}. The heating rate was 10°C min^{-1} for the curves obtained between room temperature and C, and 5, 10, 20, 30°C min^{-1} for those obtained between room temperature and 450°C.

DSC curves were obtained on a Shimadzu DSC-60 instrument between room temperature and 450°C with a heating rate of 10°C min^{-1} under nitrogen atmosphere with a flow rate of 30 mL min^{-1}.

X-ray data were collected on an Oxford Diffraction Xcalibur (TM) Single Crystal X-ray Diffractometer [20] with MoK_{α} radiation using $\omega/2\theta$ scan mode low-temperature facilities. Unit cell parameters were refined from the setting angles of 25 centered reflections in the range of (**I**) $4.14 \leq \theta \leq 26.36$ and (**II**) $2.87 \leq \theta \leq 28.11$. Three standard reflections for every 120 min during data collection showed no significant intensity variations. The structures were solved by a combination of direct methods and Fourier techniques and refined by full-matrix least squares using the solution program SHELXS97 [21] in the WinGX package [22] and refined using SHELXL97 [21].

For complex **I**, all non-hydrogen atoms were refined with anisotropic thermal displacement parameters. All the hydrogen atoms were placed geometrically idealized positions and constrained to ride on their parent atoms with distances in the range 0.89–0.97 Å and with $U_{iso}(H)=1.2U_{eq}(C)$. For complex **VI**, the C18 atom is disordered. The disorder of atoms C18a and C18b were refined, with occupancies of 0.60(2) and 0.40(2), respectively. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Disordered atom hydrogens were placed geometrically idealized positions and constrained to ride on their parent atoms with distances in the 0.98 Å and with $U_{iso}(H)=1.5U_{eq}(C)$. Other hydrogen atoms were placed in calculated positions.

Results and discussion

Azide and thiocyanate ions are known for their inclination to form two types of μ-bridges: 1,1 and 1,3 [10]. The crystal structures of only two of the six syn-

Table 2 Crystallographic and experimental data for complexes **I** and **VI**

	Complex **I**	Complex **VI**
Formula	$C_{22}H_{22}N_{22}Ni_2O_2$	$C_{18}H_{23}N_7NiO_2S_2$
Formula mass	744.00	1002.48
Temperature/K	100(2)	100(2)
Wavelength/Å	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a/Å	10.503(1)	8.646(10)
b/Å	10.681(1)	12.614(10)
c/Å	13.291(2)	20.697(2)
β/°	106.56(1)	97.18(10)
Volume/$Å^3$	1429.2(3)	2239.5(4)
Z	2	2
Calculated density/Mg m^{-3}	1.729	1.487
Absorption coefficient/mm^{-1}	1.386	1.081
F(000)	760	1030
Crystal size/mm	0.30×0.30×0.10	0.35×0.24×0.10
$2\theta_{max}$/°	52.72	56.22
Index range	$-13 \leq h \leq 12$, $-13 \leq k \leq 13$, $-14 \leq l \leq 16$	$-7 \leq h \leq 11$, $-15 \leq k \leq 16$, $-26 \leq l \leq 26$
Number of reflections used	2921 ($I \geq 2\sigma(I)$)	3683 ($I \geq 2\sigma(I)$)
Number of parameters	250	305
R_{int}	0.037	0.0707
R	0.0337	0.0623
R_w	0.0828	0.1679
Goodness of fit	0.958	1.055
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e $Å^{-3}$	–0.511, 0.485	–0.435, 0.682

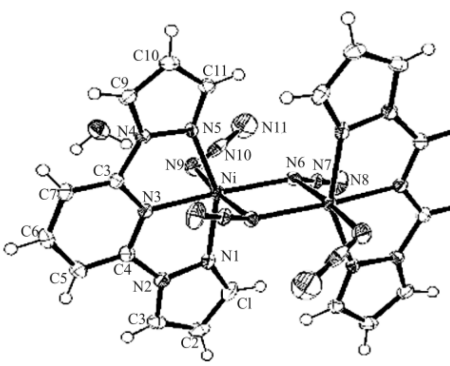

Fig. 2 The molecular structure and atomic labeling scheme of compound **I**. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labeled atoms by –x, –y, 1–z

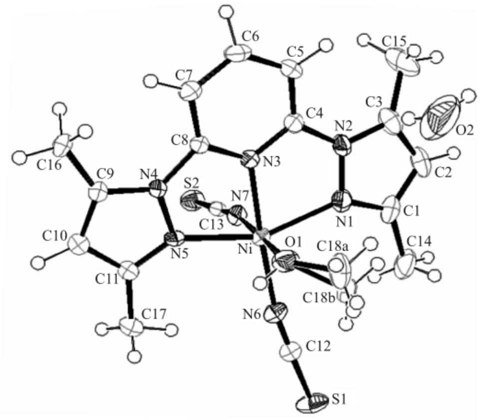

Fig. 3 The molecular structure and atomic labeling scheme of compound **VI**. Displacement ellipsoids are drawn at the 40% probability level

thesized complexes could be enlightened, of which one is dinuclear and the other mononuclear. Appropriate crystals for X-ray analysis could not be obtained with the other four. On the other hand, [Nidmpp$(N_3)_2$]$_2$·2MeOH (III), has previously been reported to be dinuclear in structure [5].

ORTEP drawing [23] of molecular structures and atomic labeling scheme of the compounds **I** and **VI** are shown in Figs 2 and 3. Crystallographic and experimental data for complexes **I** and **VI** are given in Table 2 and selected bond lengths and angles are given in Tables 3 and 4.

The figures show the Ni(II) ion to be in an octahedral coordination sphere in complexes **I** and **VI**. Complex **III**, previously reported in literature, has a similar coordination structure with complex **I**. The Ni(II) ions are seen to be coordinated by the the nitrogen donors of the ligand and two nitrogen of the azide ion in complex **I**. In addition, end – on coordination of one azide ion to the other Ni(II) ion, leads to the formation of μ-bridges and dinuclear structures.

Table 3 Selected bond lengths (Å) and angles (°) of the dinuclear Ni complex [Nipp$(N_3)_2$]$_2$·MeOH (**I**)

Ni	N1	2.112(2)
Ni	N3	2.023(2)
Ni	N5	2.132(2)
Ni	N6	2.054(2)
Ni	N9	2.101(3)
N1	N2	1.373(3)
N1	N2	1.386(4)
N4	N5	1.369(3)
N6	N7	1.208(3)
N7	N8	1.148(3)
N9	N10	1.035(3)
N10	N11	1.255(4)

N2	N1	Ni	112.13(15)
N4	N5	Ni	111.62(15)
N7	N6	Ni	128.64(18)
N8	N7	N6	176.9(3)
N10	N9	Ni	120.1(2)
N9	N10	N11	178.6(3)
N3	Ni	N6	167.65(9)
N3	Ni	N9	95.36(10)
N6	Ni	N9	96.81(10)
N3	Ni	N1	76.84(8)
N6	Ni	N1	105.25(8)
N9	Ni	N1	89.96(9)
N3	Ni	N5	76.52(8)
N6	Ni	N5	100.97(8)
N9	Ni	N5	91.64(9)

The Ni(II) ion in complex **I** ([Nipp$(N_3)_2$]$_2$·MeOH) is in the N_6 coordination sphere. The Ni–N lengths are between 2.132 and 2.032 Å. These coordination bond lengths are found to be about 0.1 Å longer with respect to the O_6, N_2O_4 and N_3O_3 coordination spheres. However, although nitrogen is a hard ligand, due to its high electron donating capability it can give electrons to the Ni(II) ion even from this distance resulting in longer bond lengths. The bond lengths observed in complex **I** are almost the same as those obtained for complex **III**, as given in literature [5]. The N6 and N3 atoms within the octahedral structure of complex **I** are in an axial position. On the other hand, N1, N5, N9 and N6' form the basal plane of the octahedron as the N3–Ni–N6 angle is largest in the octahedral structure with a value of 167.65°.

Table 4 Selected bond lengths (Å) and angles (°) of the mononuclear Ni complex [Nidmpp(SCN)$_2$MeOH] (**VI**)

Ni	N1	2.115(3)
Ni	N3	2.038(3)
Ni	N5	2.104(3)
Ni	N6	2.009(3)
Ni	N7	2.041(3)
Ni	O1	2.113(3)
N1	N2	1.386(4)
N1	N2	1.386(4)
N4	N5	1.388(4)
S1	C12	1.633(4)
S2	C13	1.638(4)

N2	N1	Ni	111.7(2)
N4	N5	Ni	112.58(19)
N6	Ni	N3	175.27(11)
N6	Ni	N7	91.13(12)
N3	Ni	N7	93.48(11)
N6	Ni	N5	104.22(12)
N3	Ni	N5	76.67(11)
N7	Ni	N5	91.90(11)
N6	Ni	O1	89.30(12)
N3	Ni	O1	86.13(10)
N7	Ni	O1	177.82(11)
N5	Ni	O1	85.92(11)
N3	Ni	N1	76.91(12)
N7	Ni	N1	91.75(12)
O1	Ni	N1	90.26(11)

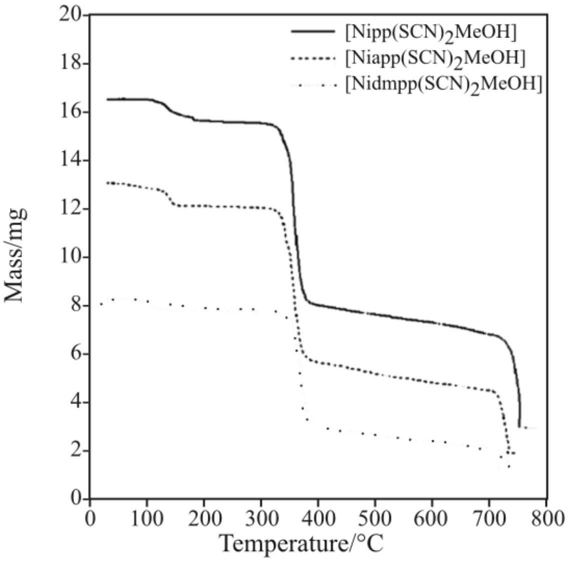

Fig. 4 TG curves of the [Nipp(SCN)$_2$MeOH] (**IV**), [Niapp(SCN)$_2$MeOH] (**V**) and [Nidmpp(SCN)$_2$·MeOH] (**VI**) complexes

Complex **VI** ([Nidmpp(SCN)$_2$·MeOH]), is mononuclear in structure as the thiocyanate ions have not formed a bridge. The nickel(II) ion is coordinated to the hard ends of the nitrogen atoms and the sixth coordination corner is occupied by a solvent molecule (MeOH). The coordination sphere of the complex is N$_5$O and the bond lengths are between 2.006 and 2.116 Å, with a mean bond length of 2.069 Å. The presence of an oxygen atom in the coordination sphere increases the coordination bond lengths as oxygen is a more hard donor with comparison to nitrogen. The methanol oxygen and O–Ni–N7 are in axial position whereas N6, N1, N3 and N5 compose the basal plane. The N7–Ni–O1 angle is close to 180°with a value of 177.72°.

Another important result obtained from the X-ray data is the state of the azide and thiocyanate groups. In complex **I** one of the azide groups forms a bridge (N6–N7–N8), whereas the other does not (N9–N10–N11). On the other hand in complex **VI** both thiocyanate groups don't form bridges. The N6–N7–N8 and N9–N10–N11 angles are quite close to one another with values of 176.86 and 178.62° respectively. The N9–N10 and N10–N11 distances are 1.035 and 1.255 Å, respectively, whereas the N6–N7 and N7–N8 distances are 1.208 and 1.148 Å respectively meaning the N–N distances on the μ-bridge are closer. This situation can be explained on the basis of the azide ion resonance boundary formulas.

$$N=N=N\leftrightarrow N-N\equiv N$$

a b

The bonds between the nitrogen atoms are double bonds in form (a) and thus their lengths should be close to each other. As a result form (a) is more appropriate a structure for a μ-bridge. On the other hand as no μ-bridges are formed at N9–N10–N11 form (b) is also a possibility. Thus, as one of the bonds approaches a triple bond and gets shorter the other is a single bond which should be longer. This can also be observed from the IR spectrums of complex **I** which gives two ν_{N_3} vibration bands at 2117 and 2195 cm^{-1}.

The nickel ions in both complexes have been coordinated by the nitrogen atoms of the azide and thiocyanate ions. As Ni(II) is a borderline acid coordination through the soft-end of the thiocyanate ions is not preferred, resulting in coordination through the hard-end [24]. There are examples of 1,3-μ-bridge coordination for Ni(II) with thiocyanate ions [25]. According to this literature dimerization can be expected for thiocyanate containing the folowing complexes over bridges.

Table 5 Thermoanalytical data

Complex	First thermal reaction MeOH or water loss			Second thermal reaction thermal decomposition	
	Temperature range/°C	Expected mass/ %	Found mass/ %	Temperature range/°C	Found mass loss/ %
[Nipp(N$_3$)$_2$]$_2$·MeOH	48–94 DTA peak: 74.29	4.84	4.65	199–202 DTA peak: 200.6	95.53
[Niapp(N$_3$)$_2$]$_2$	–	–	–	207–213 DTA peak: 209.6	98.22
[Nidmpp(N$_3$)$_2$]$_2$·2MeOH	76–134 DTA peak: 137.7	7.24	6.80	226–267 DTA peak: 242.5	86.82
[Nipp(SCN)$_2$MeOH]	81–191 DTA peak: 138	7.65	6.23	303–435 DTA peak: 345–356	46.84
[Niapp(SCN)$_2$MeOH]	73–164 DTA peak: 144	7.17	6.93	314–448 DTA peak: 343–358	50.49
[Nidmpp(SCN)$_2$MeOH]	75–158 DTA peak: 144	6.75	6.17	325–459 DTA peak: 376	58.74

Thermal analysis at this point is a very important tool. Figure 4 shows the TG curves of the [Nipp(SCN)$_2$MeOH], [Niapp(SCN)$_2$MeOH] and [Nidmpp(SCN)$_2$MeOH] complexes. All three complexes are seen to give similar curves. The 6% mass loss seen between 70–150°C, is probably due to the loss of the coordinative MeOH group in the structure.This is very high temperature proves that methanol is coordinated at Ni(II).

The essential mass loss is observed between 300–380°C; 46% for [Nipp(SCN)$_2$MeOH], 47% for [Niapp(SCN)$_2$MeOH] and 58% for [Nidmpp(SCN)$_2$MeOH]. Although these mass losses can be correlated to the large organic groups in the ligands, the values obtained are smaller than expected. In literature Pd(II) and Ni(II) complexes prepared with pyrazol type ligands and SCN$^-$ and N$_3^-$ ions, have been reported recently [26–28]. Similar comments are given for thermogravimetry in these studies. Table 5 gives the thermoanalytical data and Fig. 5 shows the DTA curves of the [Nipp(SCN)$_2$MeOH], [Niapp(SCN)$_2$MeOH] and [Nidmpp(SCN)$_2$MeOH] complexes. The decomposition process is a two-step endothermic reaction. During this process the ligand undergoes decomposition together with carbonization. The difference in the mass loss is probably due to the formation of carbonized residue. The Ni(II) oxide amounts are very close to the expected values (Ni(II) was converted to nickel oxide and all the carbonized residue was removed by flowing oxygen into the oven at 700°C).

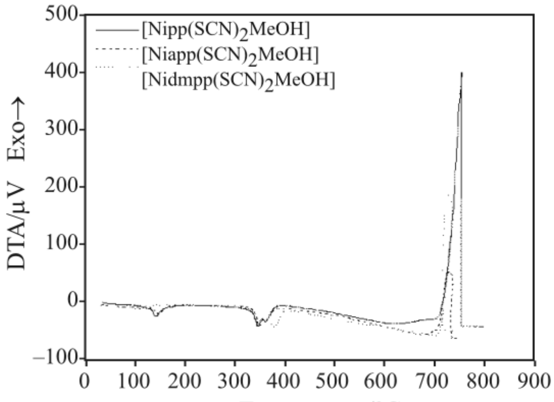

Fig. 5 DTA curves of the [Nipp(SCN)$_2$MeOH] (**IV**), [Niapp(SCN)$_2$MeOH] (**V**) and [Nidmpp(SCN)$_2$MeOH] (**VI**) complexes

The curves of [Nipp(N$_3$)$_2$]$_2$·MeOH, [Niapp(N$_3$)$_2$]$_2$ and [Nidmpp(N$_3$)$_2$]$_2$·2MeOH are as expected (Fig. 6). As the azide ion is an explosive compound, all complexes containing azides are also of ex-

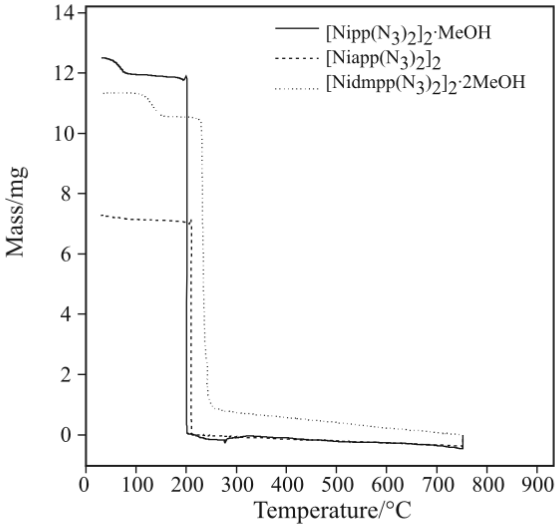

Fig. 6 TG curves of [Nipp(N$_3$)$_2$]$_2$·MeOH (**I**), [Niapp(N$_3$)$_2$]$_2$ (**II**) and [Nidmpp(N$_3$)$_2$]$_2$·2MeOH complexes (**III**)

plosive character and the curves resemble those of explosive materials. These complexes are seen to decompose exothermically without leaving any residue; between 198–200°C for $[Nipp(N_3)_2]_2\cdot$ MeOH, between 205–211°C for $[Niapp(N_3)_2]_2$ and between 235–245°C for $[Nidmpp(N_3)_2]_2\cdot$2MeOH. The effect of the number of methylene groups on the decomposition temperature is quite evident from the results. Curves and elemental analysis results showed $[Nipp(N_3)_2]_2\cdot$MeOH and $[Nidmpp(N_3)_2]_2\cdot$2MeOH to contain 1 and 2 mol of MeOH, respectively.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 606869 (I) and CCDC 606870 (VI) Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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