Preparation and Characterization of Macrocyclic Dinickel Complexes Coligated by Tetrazolate Ligands

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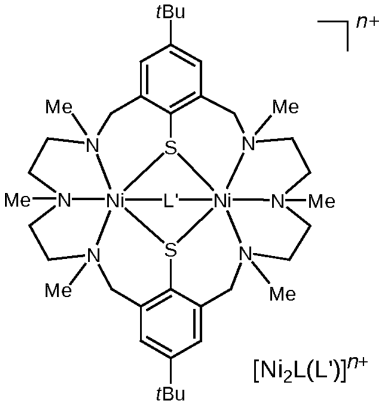
The dinuclear nickel(II) complex $[Ni_2LCl]^+$ (**1**), where $(L)^{2-}$ represents a 24-membered macrocyclic hexamine-dithiophenolate ligand, reacts readily with 5-R-tetrazolate ligands to give the complexes $[Ni_2L(RCN_4)]^+$, where R = H (**2**), Me (**3**), Ph (**4**). The new complexes were either isolated as perchlorate or tetraphenylborate salts and fully characterized by elemental analysis, UV/Vis, and IR spectroscopy. The structures of **2**$[BPh_4]\cdot MeCN$, **3**$[BPh_4]\cdot 2MeCN$, and **4**$[BPh_4]\cdot MeCN$ were determined by X-ray crystallography, showing that all tetrazolate units are in a 2,3-bridging mode to generate dioctahedral $N_3Ni(\mu\text{-}S)_2(\mu\text{-}N_4CR)NiN_3$ core structures. The RCN_4^- groups interact less strongly with the $[Ni_2L]^{2+}$ fragment than pyrazolate ligands $(CH)_3N_2^-$ as reflected in the longer Ni–N distances.

Key words: Macrocyclic Ligands, Nickel Complexes, Coordination Chemistry,
Tetrazolate Complexes

Introduction

Several examples of dinuclear $[Ni_2L(L')]^{n+}$ complexes supported by the macrocyclic hexaaza-dithiophenolate ligand L^{2-} have now been characterized (Scheme 1). These include complexes with $L' = Cl^-$ [1], OH^- [2], NO_2^-, NO_3^-, N_3^-, N_2H_4 [3], BH_4^- [4], various carboxylates [5 – 9], SH^-, S_6^{2-}, SPh^- [3, 10], and some biologically relevant molecules such as HCO_3^-, $H_2PO_4^-$ [11], and SO_4^{2-} [12]. In previous work, we have also described the synthesis of a few $[Ni_2L(L')]^{n+}$ complexes bearing small five- and six-membered N-heterocycles as coligands. The X-ray crystal structures of the pyrazolate ($(CH)_3N_2^-$, pz) and pyridazine ($(CH)_4N_2$, pydz) complexes $[Ni_2L(pz)]^+$ and $[Ni_2L(pydz)]^{2+}$ have been reported [3]. In view of the biological and medicinal importance of azoles [13], we considered it worthwhile to prepare further complexes of this type to gain more insight into the binding of these compounds towards the $[Ni_2L]^{2+}$ fragment. Here we describe the synthesis and characterization of three novel dinickel complexes bearing tetrazolate ligands and explore their structural features. A survey of the literature reveals that little is known of such coordination compounds [14].

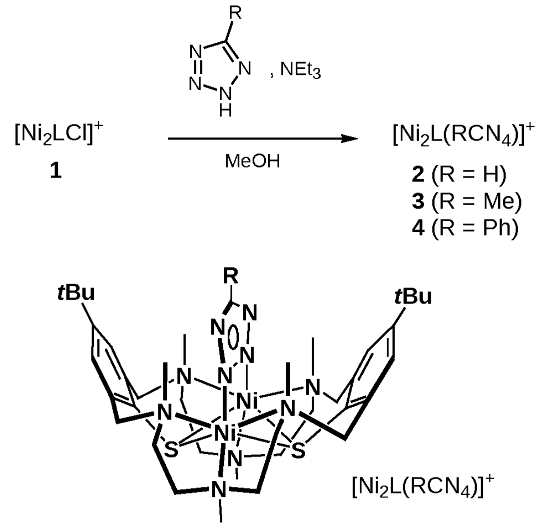


Scheme 1. Structure of dinuclear complexes $[Ni_2L(L')]^{n+}$ supported by the hexaaza-dithiophenolate ligand (L^{2-}) (L′ = coligand, $n = 1 - 2$).

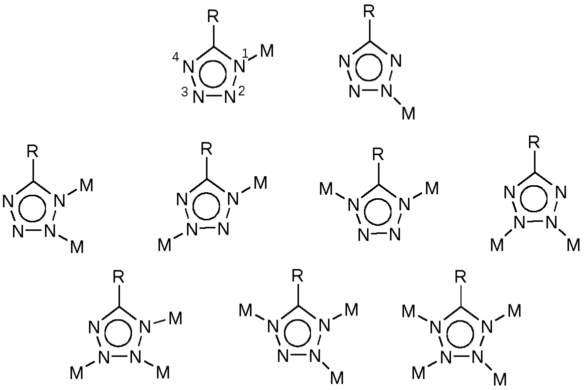
Results and Discussion

Synthesis and characterization of compounds

Tetrazole was prepared by a modified method based on the heterocyclization of triethylorthoformate with sodium azide and ammonium chloride [15]. The preparation of the 5-R-tetrazoles (R = Me, Ph) from the corresponding nitriles and sodium azide has been reported previously [16], as has the synthesis of the complex $[Ni_2LCl]ClO_4$ (**1**) [1], which was used as a starting material in this complexation study. All tetrazolates (prepared *in situ* from the free tetrazoles and triethylamine) were found to react smoothly with complex **1** in methanol over reaction times of several hours to give the green tetrazolate complexes **2**–**4**, which could be isolated as highly crystalline perchlorate salts in yields $> 80\,\%$ (Scheme 2). The behavior of the tetrazolate ligands is thus much like that of carboxylate ligands, which also readily displace the bridging halide ion in **1** [5]. Complexes **2**$[ClO_4]$–**4**$[ClO_4]$ are quite stable in solution and could therefore be subjected to salt metathesis with $NaBPh_4$ to generate the corresponding tetraphenylborate salts.



Scheme 2. Synthesis of tetrazolate complexes **2**–**4**.



Scheme 3. Coordination modes of tetrazolate ligands in metal complexes.

The new compounds are air-stable both in the solid as well as in solution, readily soluble in a variety of polar aprotic organic solvents such as dimethylformamide, acetonitrile, and dichloromethane, but less soluble in alcohols and virtually insoluble in water. Upon heating, they decompose without melting or exploding.

All compounds gave satisfactory elemental analyses and were characterized by IR and UV/Vis spectroscopy, and by X-ray structure analysis. In acetonitrile solution all complexes feature four intense UV/Vis absorption maxima in the range 250–500 nm, characteristic for nickel complexes of (L^{2-}) [10]. The ones at ~ 270 nm and ~ 300 nm can be attributed to $\pi - \pi*$ transitions within the aromatic rings of the supporting ligand, whereas those at ~ 330 nm and ~ 381 nm can be assigned to thiophenolate $\rightarrow Ni^{II}$ charge transfer absorptions. UV/Vis absorptions due to the tetrazolates were not detected. Above 500 nm, each complex exhibits two weak absorption bands at 619 ± 1 and 1135 ± 1 nm. A dependence of the band positions on the substituent in the 5-position of the tetrazolate ligand is thus not significant. The two bands can be assigned to the spin-allowed ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) transitions of a nickel(II) ($S = 1$) ion (in O_h symmetry for simplicity). The ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition is presumably obscured by the strong LMCT transitions. From the ν_1 transition one can obtain a rough estimate of the octahedral splitting parameters of $\Delta_{oct} \approx 8810$ cm^{-1}. Such low values for Δ_{oct} (*i. e.* Δ_{oct} $[Ni(H_2O)_6]^{2+}$ = 8500 cm^{-1} [17]) are quite typical for $[Ni_2L(L')]^+$ complexes containing $Ni^{II}N_4S_2$ chromophores (*i. e.* Δ_{oct} (L′ = pyrazolate) = 8475 cm^{-1}, Δ_{oct} (L′ = hydrazine) = 8977 cm^{-1}, Δ_{oct} (L′ = pyridazine) = 9132 cm^{-1} [3]).

The tetrazolate ligands have been shown to exhibit a rich variety of coordination modes [14]. As shown in Scheme 3 the tetrazolate can either coordinate by means of one, two, three or four endocyclic nitrogen atoms. The actual type of coordination depends on the electronic and steric characteristics of the substituent R and its capability to participate in binding with the metal ion. Additionally, in mixed ligand complexes the coligand also influences the coordination modes of tetrazolates [14]. Based on previous structures of hexaaza-dithiophenolate complexes $[Ni_2L(L')]^{n+}$ with N-heterocycles [3] one can assume a coordination of tetrazolate anions through two neighboring nitrogen atoms. In general, the 2,3-bridging mode [18] is favored over the 1,2-bridging mode [19] such that the former is expected for the present compounds. The crystal structure determinations described below have shown that this is indeed the case for all three complexes **2** – **4**.

Description of crystal structures

The structures of complexes **2**$[BPh_4]\cdot MeCN$, **3**$[BPh_4]\cdot 2MeCN$ and **4**$[BPh_4]\cdot MeCN$ were determined by single-crystal X-ray diffraction. ORTEP views of the molecular structures of the cations **2** – **4** are presented in Figs. 1 – 3. Selected bond lengths and angles are compiled in Table 1. The atomic numbering scheme used for the central $N_3Ni(\mu\text{-}S)_2(\mu\text{-}N_4CR)NiN_3$ core in **2** was also applied for **3** and **4** to facilitate structural comparisons. The data for $[Ni_2L(pz)]^+$ (**5**) and $[Ni_2L(pydz)]^{2+}$ (**6**) [3] are also included in Table 1 for comparison.

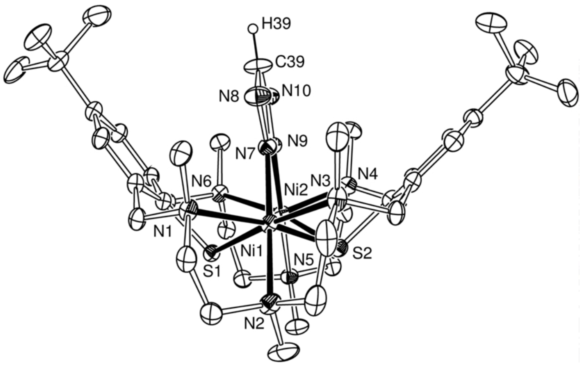


Fig. 1. Structure of cation **2** in crystals of **2**$[BPh_4]\cdot MeCN$ with thermal ellipsoids drawn at 30 % probability. Hydrogen atoms, except H(39), are omitted for reasons of clarity.

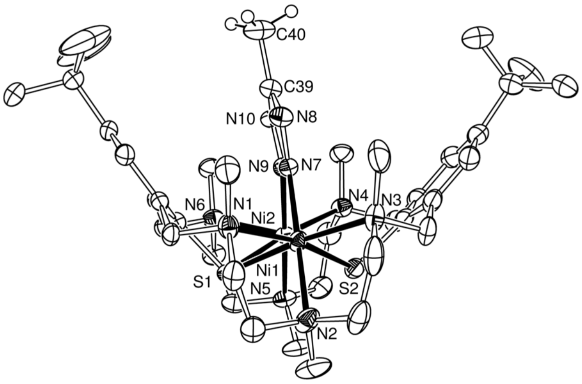


Fig. 2. Structure of cation **3** in crystals of **3**$[BPh_4]\cdot 2MeCN$ with thermal ellipsoids drawn at 30 % probability. Hydrogen atoms, except those bonded to C(40), are omitted for reasons of clarity.

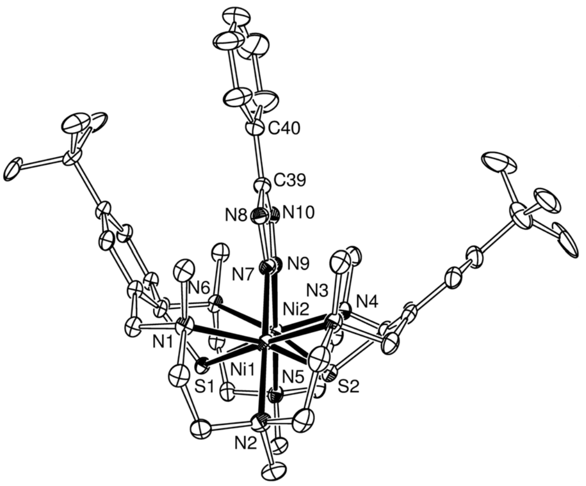


Fig. 3. Structure of cation **4** in crystals of **4**$[BPh_4]\cdot MeCN$ with thermal ellipsoids drawn at 30 % probability. Hydrogen atoms are omitted for reasons of clarity.

All tetrazolates bind to the $[Ni_2L]^{2+}$ fragment as bidendate bridges through their two ring nitrogen atoms N(7) and N(9). Consequently, the Ni···Ni distances are nearly identical in the three compounds (average 3.394(1) Å). The macrocycle assumes a bowl-shaped conformation, which is typical for $[Ni_2L(L')]^+$ complexes when coligated by multi-atom bridging ligands L′ [3, 20]. All tetrazolate units are essentially planar. The N–N and N–C distances of the tetrazolate rings in **2** – **4** differ significantly from the corresponding distances of the free 5-R-tetrazoles. Particularly affected are the N(7)–N(9) bonds. Thus, for 1-H-tetrazole and 5-methyltetrazole these bonds lengths are 1.295(3) Å [21] and 1.285(3) Å [22], much shorter than in **2** – **4**, averaging at 1.354(3) Å. Similar changes were observed for a related tetrazolate complex with 2,3-μ-coordination [18] albeit to a lesser extent. The larger differences in **2** – **4** presumably relate to the stronger Lewis acidity of the nickel(II) ions. All three N–N bond lengths in **3** are identical within experimental error, while they vary from 1.317(2) to 1.367(2) Å in **2** and from 1.317(4) to 1.360(4) Å in **4**.

The average Ni–N(heterocycle) bond lengths are 2.079(2) Å (**2**), 2.067(2) Å (**3**), and 2.061(3) Å

Table 1. Selected bond lengths (Å) in complexes **2** – **6**.

	2	**3**	**4**[a]	**5**	**6**
Ni(1)–N(7)	2.081(2)	2.063(2)	2.071(3)/2.065(3)	2.044(2)	2.117(2)
Ni(1)–N(1)	2.319(2)	2.306(2)	2.346(3)/2.317(3)	2.337(2)	2.343(2)
Ni(1)–N(2)	2.168(2)	2.162(3)	2.171(3)/2.159(3)	2.179(2)	2.132(2)
Ni(1)–N(3)	2.227(2)	2.232(3)	2.207(3)/2.221(3)	2.272(2)	2.281(2)
Ni(1)–S(1)	2.5152(7)	2.5044(8)	2.525(1)/2.532(1)	2.500(1)	2.453(1)
Ni(1)–S(2)	2.4626(7)	2.4664(8)	2.431(1)/2.443(1)	2.450(1)	2.450(1)
Ni(2)–N(9)	2.077(2)	2.071(2)	2.051(3)/2.055(3)	2.038(2)	2.138(2)
Ni(2)–N(4)	2.237(2)	2.204(2)	2.205(3)/2.210(3)	2.270(2)	2.338(2)
Ni(2)–N(5)	2.173(2)	2.170(2)	2.150(3)/2.154(3)	2.178(2)	2.126(2)
Ni(2)–N(6)	2.311(2)	2.324(2)	2.332(3)/2.338(3)	2.342(2)	2.268(2)
Ni(2)–S(1)	2.5194(9)	2.5012(8)	2.530(1)/2.515(1)	2.499(1)	2.450(1)
Ni(2)–S(2)	2.4509(6)	2.4699(8)	2.450(1)/2.441(1)	2.455(1)	2.451(1)
Ni–N[b]	2.239(2)	2.233(2)	2.235(3)/2.233(3)	2.263(2)	2.248(2)
$Ni–N^{het}$[b,c]	2.079(2)	2.067(2)	2.061(3)/2.060(3)	2.041(2)	2.128(2)
Ni–S[b]	2.4870(8)	2.4855(8)	2.484(1)/2.483(1)	2.476(1)	2.451(1)
Ni·Ni	3.455(1)	3.425(1)	3.443(1)/3.450(1)	3.389(1)	3.392(1)
N(7)–N(9)	1.367(2)	1.331(3)	1.346(4)/1.360(4)	–	–
N(7)–N(8)	1.325(2)	1.330(3)	1.333(4)/1.320(4)	–	–
N(9)–N(10)	1.317(2)	1.335(3)	1.328(4)/1.317(4)	–	–
C(39)–N(8)	1.331(3)	1.333(4)	1.341(5)/1.347(5)	–	–
C(39)–N(10)	1.341(3)	1.333(4)	1.347(5)/1.354(5)	–	–

[a] There are two crystallographically independent molecules A and B in the asymmetric unit. The second value refers to molecule B; [b] average values; [c] $Ni–N^{het}$ = N(heterocycle).

(**4**), intermediate between those in the pyrazolato and pyridazine complexes **5** (mean 2.043(2) Å) and **6** (mean 2.175(2) Å). This suggests that the binding affinity of the tetrazolate anions towards the $[NiL_2]^{2+}$ subunit is intermediate between that of pyrazolate and the neutral diazine heterocycles. There are no unusual features as far as bond lengths and angles around the Ni atoms are concerned. The average $Ni–N^{amine}$ and Ni–S distances are 2.239(2) and 2.4870(8) Å, respectively. Similar values have been observed in other Ni_2 complexes of L^{2-} with N donor ligands [3] (see also Table 1). Overall, the three structures clearly show that the $[Ni_2L]^{2+}$ units can expand their binding pockets sufficiently to accommodate 2,3-bridging tetrazolate ligands.

Conclusion

A series of novel dinuclear nickel(II) tetrazolate complexes supported by a hexaaza-dithiophenolate ligand have been synthesized and characterized, namely $[Ni_2L(HCN_4)]^+$ (**2**), $[Ni_2L(MeCN_4)]^+$ (**3**), and $[Ni_2L(PhCN_4)]^+$ (**4**). The crystal structures of the tetraphenylborate salts confirm the presence of 2,3-bridging tetrazolate units showing that the $[Ni_2L]^{2+}$ units can expand their binding pockets sufficiently to accommodate these ligands. Future work is focused on transformations of the tetrazolate moieties in the pockets of the complexes.

Experimental Section

Complex **1**$[ClO_4]$ ($[Ni_2LCl][ClO_4]$) [1], and the ligands (5-methyl- and 5-phenyltetrazole) [16] were prepared according to the literature procedures. All other compounds were purchased. Melting points were determined with a Waters VG-ZAB-HSQ instrument in open glass capillaries and are uncorrected, infrared spectra were recorded on a Bruker Vector27 FT-IR-spectrometer. Electronic absorption spectra were taken on a JASCO V670 UV/Vis spectrometer, elemental analyses on a VARIO EL-elemental analyzer.

CAUTION! *Perchlorate salts are potentially explosive. Only small quantities should be prepared and handled with appropriate care.*

Tetrazole (HCN_4)

Glacial acetic acid (150 mL) was added with strong stirring to a suspension of ammonium chloride (26.75 g, 0.5 mol), sodium azide (39.1 g, 0.55 mol) and triethylorthoformate (150 mL, 0.9 mol). The mixture was stirred on a boiling water bath for 2.5 – 3 h. Then the reaction mixture was cooled to r. t., treated with concentrated hydrochloric acid (7 – 10 mL) and filtered. The filtrate was evaporated to dryness on a rotary evaporator, and the residue was washed with dichloromethane and recrystallized from acetic acid. Yield: 25.2 g (72 %). M. p. 154 – 156 °C.

$[Ni_2L(HCN_4)][ClO_4]$ (2$[ClO_4]$)

To a solution of tetrazole (15.4 mg, 0.220 mmol) in methanol (30 mL) was added triethylamine (22 mg, 0.22 mmol). Complex **1**$[ClO_4]$ (184 mg, 0.20 mmol) was added and the resulting green solution stirred for 12 h. A solution of $LiClO_4 \cdot 3H_2O$ (321 mg, 2.00 mmol) in methanol (5 mL) was then added to the green solution. After further stirring for 2 h, the green precipitate was filtered off, washed with cold ethanol, and dried in air. Yield: 156 mg (82 %). M. p. 352 – 353 °C (decomp.). – IR (KBr): ν = 3442 (s), 2962 (s), 2868 (s), 2022 (w), 1632 (m), 1463 (s), 1428 (m), 1395 (w), 1363 (m), 1311 (w), 1264 (w), 1235 (w), 1200 (m), 1169 (w), 1153 (m), 1120 (s), 1098 (vs, $\nu_3(ClO_4^-)$), 1056 (s), 1040 (s), 1013 (w), 999 (w), 983 (w), 930 (w), 913 (m), 882 (w), 826 (m), 808 (w), 755 (w), 702 (w), 624 (m, $\nu_4(ClO_4^-)$), 565 (w), 544 (w), 493 (w), 418 (w) cm^{-1}. – UV/Vis (MeCN): λ_{max} (ε, mol^{-1} cm^{-1}) = 265 (sh, 17150), 302 (sh, 13305), 334 (11220), 380 (2364), 620 (31), 1135 (64) nm.

*[Ni$_2$L(HCN$_4$)][BPh$_4$] (**2**[BPh$_4$])*

A solution of $NaBPh_4$ (342 mg, 1.00 mmol) in methanol (5 mL) was added to a solution of **2**[ClO$_4$] (96 mg, 0.100 mmol) in methanol (50 mL) and stirred for 3 h at ambient temperature. The green solid was filtered, washed with ethanol and dried in air to give 107 mg (91 %) of **2**[BPh$_4$] as a green, air-stable, microcrystalline powder. M. p. 305 – 306 °C (decomp.). – IR (KBr): ν = 3442 (s), 3055 (m), 3033 (m), 2999 (m), 2965 (s), 2866 (s), 1940 (w), 1816 (w), 1631 (m), 1580 (m), 1481 (s), 1461 (s), 1427 (m), 1395 (w), 1363 (m), 1309 (w), 1265 (m), 1235 (m), 1201 (w), 1168 (m), 1153 (w), 1110 (w), 1074 (s), 1056 (s), 1040 (s), 999 (w), 982 (w), 929 (m), 912 (w), 883 (m), 844 (w), 825 (m), 808 (w), 748 (m), 733 (s, $\nu(BPh_4^-)$), 704 (s, $\nu(BPh_4^-)$), 668 (w), 630 (m), 612 (m), 564 (w), 543 (w), 493 (w), 468 (w), 416 (w) cm^{-1}. – UV/Vis (MeCN): λ_{max} (ε, mol^{-1} cm^{-1}) = 266 (20520), 275 (18490), 302 (sh, 13557), 334 (11384), 380 (2418), 623 (30), 1132 (63) nm. – Elemental analysis (%) for $C_{63}H_{85}BN_{10}Ni_2S_2$ (1174.74): calcd. C 64.41, H 7.29, N 11.92, S 5.46; found C 63.85, H 7.78, N 12.06, S 5.57.

*[Ni$_2$L(MeCN$_4$)][ClO$_4$] (**3**[ClO$_4$])*

This compound was prepared in analogy to **2**[ClO$_4$] using 5-methyltetrazole in place of tetrazole. Yield: 155 mg (80 %). M. p. 362 – 363 °C (decomp.). – IR (KBr): ν = 3443 (s), 2958 (s), 2869 (s), 2023 (w), 1631 (m), 1487 (s), 1462 (s), 1395 (w), 1364 (m), 1310 (w), 1264 (m), 1235 (m), 1200 (w), 1153 (m), 1120 (s), 1099 (vs, $\nu_3(ClO_4^-)$), 1078 (s), 1056 (s), 1041 (s), 1001 (w), 983 (w), 930 (w), 913 (w), 881 (w), 827 (m), 818 (m), 808 (w), 754 (w), 704 (w), 625 (m, $\nu_4(ClO_4^-)$), 565 (w), 543 (w), 493 (w), 418 (w) cm^{-1}. – UV/Vis (MeCN): λ_{max} (ε, mol^{-1} cm^{-1}) = 275 (sh, 13743), 300 (sh, 8958), 334 (7300), 386 (1544), 616 (23), 1132 (45) nm.

*[Ni$_2$L(MeCN$_4$)][BPh$_4$] (**3**[BPh$_4$])*

The preparation of this compound was similar to that used for **2**[BPh$_4$]. Yield: 106 mg (89 %). M. p. 333 – 334 °C (decomp.). – IR (KBr): ν = 3443 (s), 3055 (m), 3033 (m), 2998 (m), 2964 (s), 2866 (s), 1940 (w), 1817 (w), 1631 (w), 1580 (m), 1485 (s), 1461 (s), 1427 (m), 1395 (w), 1363 (m), 1309 (w), 1291 (w), 1264 (m), 1235 (m), 1199 (w), 1169 (w), 1153 (w), 1134 (m), 1110 (w), 1075 (s), 1056 (s), 1041 (s), 1000 (w), 982 (w), 929 (w), 912 (m), 882 (w), 843 (w), 825 (m), 807 (w), 733 (s, $\nu(BPh_4^-)$), 704 (s, $\nu(BPh_4^-)$), 669 (w), 630 (m), 612 (m), 564 (w), 543 (w), 493 (w), 470 (w), 417 (w) cm^{-1}. – UV/Vis (MeCN): λ_{max} (ε, mol^{-1} cm^{-1}) = 267 (19980), 275 (18131), 294 (sh, 13715), 334 (11203), 382 (2349), 620 (25), 1128(57) nm. – Elemental analysis (%) for $C_{64}H_{87}BN_{10}Ni_2S_2$ (1188.77): calcd. C 64.66, H 7.38, N 11.78, S 5.39; found C 63.47, H 7.30, N 12.05, S 4.62.

*[Ni$_2$L(PhCN$_4$)][ClO$_4$] (**4**[ClO$_4$])*

This compound was prepared in analogy to **2**[ClO$_4$] using 5-phenyltetrazole in place of tetrazole. Yield: 161 mg (78 %). M. p. 356 – 357 °C (decomp.). – IR (KBr): ν = 3442 (s), 2964 (s), 2901 (m), 2868 (s), 2023 (w), 1630 (m), 1462 (s), 1395 (w), 1363 (m), 1310 (w), 1264 (m), 1235 (m), 1201 (w), 1171 (w), 1154 (m), 1120 (s), 1099 (vs, $\nu_3(ClO_4^-)$), 1056 (s), 1040 (s), 1010 (w), 999 (w), 983 (w), 930 (w), 913 (w), 882 (w), 827 (m), 808 (w), 786 (w), 753 (w), 732 (w), 695 (m), 624 (m, $\nu_4(ClO_4^-)$), 565 (w), 545 (w), 492 (w), 418 (w) cm^{-1}. – UV/Vis (CH_3CN): λ_{max} (ε, mol^{-1} cm^{-1}) = 268 (18400), 300 (sh, 13775), 334 (11172), 384 (2334), 620 (28), 1128 (61) nm.

*[Ni$_2$L(PhCN$_4$)][BPh$_4$] (**4**[BPh$_4$])*

This compound was prepared in analogy to **2**[BPh$_4$]. Yield: 112 mg (90 %). M. p. 298 – 299 °C (decomp.). – IR (KBr): ν = 3442 (s), 3054 (m), 3031 (m), 2998 (s), 2964 (m), 2865 (s), 2812 (m), 1946 (w), 1882 (w), 1815 (w), 1630 (m), 1580 (m), 1461 (s), 1427 (m), 1395 (w), 1363 (m), 1308 (w), 1291 (w), 1265 (m), 1235 (m), 1200 (w), 1170 (w), 1153 (m), 1125 (w), 1110 (w), 1074 (s), 1055 (s), 1041 (s), 1010 (w), 999 (w), 982 (w), 929 (m), 912 (w), 882 (w), 843 (w), 825 (m), 807 (w), 785 (w), 732 (s, $\nu(BPh_4^-)$), 704 (s, $\nu(BPh_4^-)$), 669 (w), 629 (m), 612 (m), 565 (w), 543 (w), 492 (w), 470 (w), 417 (w) cm^{-1}. – UV/Vis (CH_3CN): λ_{max} (ε, mol^{-1} cm^{-1}) = 263 (sh, 23040), 274 (16320), 298 (sh, 11953), 334 (9607), 384 (2032), 616 (30), 1132 (59) nm. – Elemental analysis (%) for $C_{69}H_{89}BN_{10}Ni_2S_2$ (1250.84): calcd. C 66.25, H 7.17, N 11.20, S 5.13; found C 66.15, H 7.25, N 11.37, S 4.91.

Crystal structure determination

Single crystals of **2**[BPh$_4$] · MeCN, **3**[BPh$_4$] · 2MeCN and **4**[BPh$_4$] · MeCN were grown by recrystallization from acetonitrile. The data sets were collected at 213(2) K using a Stoe IPDS-2T diffractometer and graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The intensity data were

Table 2. Crystallographic data for **2**[BPh$_4$] · MeCN, **3**[BPh$_4$] · 2MeCN, and **4**[BPh$_4$] · MeCN.

Compound	2[BPh$_4$] · MeCN	3[BPh$_4$] · 2MeCN	4[BPh$_4$] · MeCN
Formula	$C_{65}H_{88}BN_{11}Ni_2S_2$	$C_{68}H_{93}BN_{12}Ni_2S_2$	$C_{71}H_{92}BN_{11}Ni_2S_2$
M_r	1215.81	1270.89	1291.91
Space group	$P\bar{1}$	$P2_1/c$	$P2/c$
a, Å	13.265(1)	15.060(2)	30.253(6)
b, Å	15.730(1)	27.916(3)	13.221(2)
c, Å	16.941(1)	16.658(2)	38.202(12)
α, deg	108.630(3)	90	90
β, deg	92.22(3)	107.01(2)	110.19(2)
γ, deg	107.46(2)	90	90
V, Å^3	3159.7(4)	6697.0	14341(6)
Z	2	4	8
$d_{\text{calcd.}}$, g cm^{-3}	1.278	1.260	1.197
Cryst. size, mm^3	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.25 × 0.20 × 0.15
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	0.711	0.674	0.630
θ limits, deg	2.04 – 26.06	1.76 – 26.81	1.71 – 24.63
Measured refl.	25362	50262	84185
Independent refl.	11582	14192	23998
Observed refl.[a]	8335	8783	15689
No. parameters	786	766	1622
$R1^{\text{a,b}}$ ($R1$ all data)	0.029 (0.070)	0.048 (0.089)	0.049 (0.119)
$wR2^{\text{a,c}}$ ($wR2$ all data)	0.041 (0.072)	0.099 (0.092)	0.084 (0.131)
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.32/−0.26	0.73/−0.34	1.25/−0.44

[a] Observation criterion: $I \geq 2\sigma(I)$; [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. ns2

processed with the program Stoe X-AREA. Structures were solved by Direct Methods [23] and refined by full-matrix least-squares on the basis of all data against F^2 using SHELXL-97 [24]. PLATON was used to search for higher symmetry [25]. H atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically. Selected crystallographic data are summarized in Table 2.

In the crystal structures of **2**[BPh$_4$] · MeCN and **4**[BPh$_4$] · MeCN two *tert*-butyl groups were found to be rotationally disordered. This disorder was refined by a split atom model yielding occupancy factors of 0.55/0.45, 0.56/0.44 (for **2**), 0.36/0.64 and 0.50/0.50 (for **4**), respectively. For **2**[BPh$_4$] · MeCN, the hydrogen atom H(39) was located unambiguously from final Fourier maps. Drawings were produced with ORTEP-III for Windows [26].

CCDC 673545 (**2**[BPh$_4$]$_2$ · MeCN), 673546 (**3**[BPh$_4$] · 2MeCN), and 673547 (**4**[BPh$_4$]$_2$ · 2MeCN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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