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## A Novel N(3),N(4)-Bridging Coordination Mode of 1-R-Tetrazole-5-thiolates – Synthesis, X-ray Diffraction, Magnetic Properties and Quantum-Chemical Study of a Macrocyclic Dinickel Complex Coligated by 1-Methyltetrazole-5-thiolate

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The dinuclear nickel(II) complex  $[Ni_2L(\mu-ClO_4)]ClO_4$ , where  $L^{2-}$  represents a 24-membered macrocyclic bis(triamine-thiophenolate) ligand, reacts with 1-methyltetrazole-5-thiol and triethylamine to give the complex  $[Ni_2L(\mu-SCN_4Me)]ClO_4$ , which was subjected to metathesis with NaBPh<sub>4</sub> yielding  $[Ni_2L(\mu-SCN_4Me)]BPh_4$ . This new complex was characterized by elemental analysis, UV/Vis/NIR and IR spectroscopy. The structure of  $[Ni_2L(\mu-SCN_4Me)]BPh_4$  was determined by X-ray crystallography, showing the 1-methyltetrazole-5-thiolate ligand in an N(3),N(4)-bridging mode gener-

### Introduction

1-Monosubstituted tetrazole-5-thiols (H1) attract considerable attention because of their interesting properties and applications. In particular, these tetrazoles are widely used in the surface treatment of materials. For example, 1phenyltetrazole-5-thiol (H1, R = Ph) is efficient both as a photographic stabilizer and as corrosion inhibitor.<sup>[1]</sup> 1-Alkyltetrazole-5-thiols have been shown to act as surfactants for the stabilization of CdS and Au nanoparticles.<sup>[2]</sup> Their efficiency in these processes is due to the formation of very stable tetrazole-5-thiolato complexes. The stability of such complexes is stipulated by high nucleophilicity and aromaticity of the corresponding thiotetrazolate anion, 1<sup>-</sup>, which is formed by deprotonation of H1 (Scheme 1).

Numerous investigations have been carried out in order to clarify the bonding between tetrazoles and metal surfaces,<sup>[1,3]</sup> and the structures and properties of tetrazole-5thiolato complexes have been studied intensively. It has been shown that the tetrazole-5-thiolates,  $1^-$ , can act as monodentate (S or N) or bidentate (N,N or N,S) ligands depending on the nature of the metal ions and coligands.

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[b] Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany Fax: +49-341-9736199 E-mail: b.kersting@unileipzig.de ating a bis(octahedral)  $N_3Ni(\mu-S)_2(\mu-SCN_4Me)NiN_3$  core. Quantum chemical calculations of the molecular electrostatic potential, natural population analysis and total energies of possible structures of  $[Ni_2L(\mu-SCN_4Me)]^+$  are in agreement with the structural data obtained. Temperature-dependent magnetic susceptibility measurements revealed that the Ni<sup>II</sup> ions in the dinuclear complex are weakly ferromagnetically coupled showing a coupling constant *J* of 19.5 cm<sup>-1</sup> (H =  $-2JS_1S_2$ ).



Scheme 1. Two resonance forms and deprotonation product of 1monosubstituted tetrazole-5-thiols.

However, to the best of our knowledge, only the coordination modes I–V have been reported to date (Figure 1). It is worth noting that mode I, exhibiting coordination through the sulfur atom, is strongly favoured.<sup>[1]</sup> In two examples additional semicoordination of the N(4) (II)<sup>[4]</sup> and N(3) atoms



Figure 1. Numbering scheme and coordination modes of 1-R-tetrazole-5-thiolates.

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Figure 2. Schematic presentation of the binding situation in complexes of  $[Ni_2L]^{2+}$  with tetrazole derivatives.

 $(III)^{[5]}$  has also been observed. Several structures contain tetrazole-5-thiolates exhibiting an N(4),S-bridging mode  $(IV)^{[6]}$  or an N(4)-coordination mode (V).<sup>[7]</sup>

In this investigation, we have tested the coordination mode of 1-methyltetrazole-5-thiolate,  $2^-$ , in a dinickel complex supported by a 24-membered macrocyclic bis(triamine-thiophenolate) ligand (L<sup>2–</sup>) and found a novel metalbinding mode of 1-R-tetrazole-5-thiolates, namely N(3),N(4)-bridging (VI). The [Ni<sub>2</sub>L]<sup>2+</sup> moiety has proved to be a good system for testing the coordination mode of coligands<sup>[8]</sup> since it provides two metal atoms in close proximity, which can be a simple approximation of a metal surface. 5-R-Tetrazolates (R = H, Me, Ph) have been also found to form [Ni<sub>2</sub>L( $\mu$ -RCN<sub>4</sub>)]X complexes (3) displaying an N(2),N(3)-bridging mode (Figure 2).<sup>[9]</sup> Herein, we describe the synthesis, analytical data, structure, magnetic properties and a quantum-chemical study of the novel mixed-ligand complex [Ni<sub>2</sub>L( $\mu$ -SCN<sub>4</sub>Me)]BPh<sub>4</sub> (5).

#### **Results and Discussion**

#### Synthesis and Characterization of the Complexes

Triethylammonium 1-methyltetrazole-5-thiolate (prepared in situ from H2 and triethylamine) was found to react smoothly with the complex  $[Ni_2L(\mu-ClO_4)]ClO_4$  in methanol over several hours. The perchlorate salt **4** was obtained in 79% yield. Salt metathesis of **4** with NaBPh<sub>4</sub> provided **5** in 86% yield (Scheme 2). The behaviour of the tetrazole-5thiolate is similar to that of 5-R-tetrazolate ligands which readily displace the bridging halide ion in  $[Ni_2L(\mu-Cl)]$  $ClO_4$ .<sup>[9]</sup> All complexes synthesized gave satisfactory elemental analyses and were characterized by IR and UV/Vis/NIR spectroscopy and mass spectrometry.

The electronic absorption spectra of compounds 4 and 5 were recorded in the range of 190–1600 nm in acetonitrile solution at ambient temperature. Spectra of both feature characteristic bands of nickel complexes of (L<sup>2–</sup>) coligated by tetrazolates.<sup>[9]</sup> Bands at ca. 195, 246, 276 and 305 nm are attributed to  $\pi$ - $\pi$ \* transitions within the aromatic rings of L<sup>2–</sup> and the BPh<sub>4</sub><sup>–</sup> anion, whereas those at ca. 330 and 396 nm can be assigned to thiophenolate $\rightarrow$ Ni<sup>II</sup> charge transfer absorptions. Similar to those of [Ni<sub>2</sub>L(µ-RCN<sub>4</sub>)]X



Scheme 2. Preparation of 4 and 5.

complexes, absorptions arising from the coligand were not observed.<sup>[9]</sup> The weak bands at ca. 640 and 1095 nm can be assigned to the spin-allowed  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  (v<sub>2</sub>) and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  (v<sub>1</sub>) transitions of the nickel(II) (S = 1) ions (in  $O_h$  symmetry for simplification). The  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  (P) transition is presumably obscured by the strong ligand-to-metal charge transfer bands. The UV/Vis/NIR spectroscopic data for both complexes are listed in detail in the Experimental Section.

#### Description of the Crystal Structure of 5.2MeCN

The structure of 5.2MeCN was determined by singlecrystal X-ray diffraction. The ORTEP view of the molecular structure of the complex cation is presented in Figure 3. Selected crystallographic data are given in Table 1. The 1methyltetrazole-5-thiolate anion,  $2^{-}$ , binds to the  $[Ni_2L]^{2+}$ fragment as a bidentate bridge through the two ring nitrogen atoms in 4- and 3-positions (numbered here as N7 and N8, respectively). The N(3), N(4)-bridging coordination mode observed is hitherto unknown for tetrazole-5-thiolates, but was reported recently for copper(II)<sup>[10]</sup> and cobalt(II)<sup>[11]</sup> chloride complexes of another 1,5-disubstituted tetrazole, 1,5-dimethyltetrazole. We attribute this different binding mode to electronic factors (see quantum chemical study) as well as steric hindrance caused by the interaction of the tetrazolate methyl group C40 and the sulfur atom S3 with the methyl groups C8, C14, C23 and C29 of the macrocyclic ligand.



Figure 3. ORTEP representation of the structure of  $[Ni_2L(\mu-SCN_4Me)]^+$  (5·2MeCN). Ellipsoids are represented at 50% probability. H atoms were omitted for clarity. Coordination bonds are depicted as solid lines.

Table 1. Selected interatomic distances [Å] and angles [°] for complex 5.2MeCN.

Bond/angle	Value Bond/angle		Value	
C39–N7	1.346(6)	N5–Ni2	2.196(3)	
C39-N10	1.320(6)	N6-Ni2	2.200(3)	
C39–S3	1.702(5)	N7–Ni2	2.181(3)	
N7–N8	1.422(5)	N8–Ni1	2.058(3)	
N8-N9	1.257(5)	S1-Ni1	2.501(1)	
N9-N10	1.360(5)	S1-Ni2	2.502(1)	
N1-Ni1	2.188(3)	S2-Ni1	2.419(1)	
N2-Ni1	2.152(3)	S2–Ni2	2.412(1)	
N3–Ni1	2.313(3)	Ni1…Ni2	3.4616(6)	
N4–Ni2	2.333(3)			
N7-C39-N10	108.5(4)	N3-Ni1-N8	94.0(1)	
N7-C39-S3	130.8(4)	N3-Ni1-S1	90.22(8)	
N10-C39-S3	120.6(3)	N8-Ni1-S1	83.4(1)	
C39–N7–N8	103.4(3)	N8-Ni1-S2	87.6(1)	
N7-N8-N9	111.5(3)	S1-Ni1-S2	78.36(3)	
N8-N9-N10	106.5(3)	N4-Ni2-N5	79.2(1)	
C39-N10-N9	110.1(3)	N4-Ni2-N6	101.8(1)	
Ni1-S1-Ni2	87.56(3)	N4-Ni2-N7	96.9(1)	
Ni1-S2-Ni2	91.54(3)	N4-Ni2-S1	88.90(8)	
N1-Ni1-N2	82.6(1)	N5-Ni2-N6	80.9(1)	
N1-Ni1-N3	100.3(1)	N5-Ni2-S1	97.80(9)	
N1-Ni1-N8	94.7(1)	N5-Ni2-S2	95.43(9)	
N1-Ni1-S2	91.23(8)	N6-Ni2-N7	96.2(1)	

The nickel atoms in 5·2MeCN show distorted octahedral coordination geometries. Each metal atom is surrounded by two bridging sulfur atoms and three nitrogen atoms of the macrocycle and one nitrogen atom of the tetrazolate group,  $2^-$ , typical for complexes of the type  $[Ni_2L(L')]^+$ . The macrocycle forms a bowl-shaped conformation typical for  $[Ni_2L(L')]^+$  complexes featuring multiatom bridging ligands.<sup>[12]</sup> In comparison to the Ni···Ni distance of  $[Ni_2L(\mu - RCN_4)]^+$  [average 3.394(1) Å], that found in 5·2MeCN is

significantly elongated [3.4616(6) Å]. The average Ni–N(heterocycle) bond length is 2.112 Å, which is slightly longer than those in  $[Ni_2L(HCN_4)]^+$  [2.079(2) Å],  $[Ni_2L-(MeCN_4)]^+$  [2.067(2) Å] and  $[Ni_2L(PhCN_4)]^+$  [2.061(3) Å].<sup>[9]</sup>

The tetrazolate unit is essentially planar, and the N-N, N-C and C-S distances of the tetrazole-5-thiolate moiety in 5.2MeCN can be compared with those of H2 and the potassium (18-crown-6)-1-methyl-1H-tetrazole-5-thiolate (6) described by Cea-Olivares et al.<sup>[13]</sup> The value of 1.702(5) Å determined for the length of the C-S bond in 5.2MeCN is between that for single (1.74-1.75 Å) and double (1.66–1.68 Å) C(sp<sup>2</sup>)–S bonds.<sup>[14]</sup> This is in good agreement with the values of 1.695(9) Å found for H2 and 1.708(4) Å found for 6 and indicates a ca. 50%  $\pi$ -bond character,<sup>[13]</sup> which remains unaffected by complex formation. The N9–N10 bond length of 1.360(5) Å is significantly shorter than that of 6 [1.390(6) Å] as well as that expected for N-N single bonds (1.41 Å).<sup>[14]</sup> In contrast, the N8-N9 and N7-C39 bonds [1.257(5) and 1.346(6) Å, respectively] are elongated [values for 6: 1.233(7) and 1.330(5) Å, respectively]. Nevertheless, the first can clearly be regarded as a true double bond (estimated at 1.24-1.26 Å).[14] As expected, the N7-N8 bond in 5.2MeCN [1.422(5) Å] is most affected by the coordination to the nickel centres [H2: 1.363(11); 6: 1.289(6) Å] and is only slightly shorter than the expected value for an N-N single bond. The endocyclic angles in 5.2MeCN range from 103.4 to 111.5° and differ only slightly from the value of an equilateral pentagon (108°). The values for the corresponding angles in 6 range from 104.5(4) to  $115.2(4)^{\circ}$ . In summary, these data suggest a similar  $\pi$ -electron delocalization in the tetrazole-5-thiolate of 5.2MeCN as in 6, interrupted along the N7-N8 bond, which is in good agreement with a  $\sigma$ -donor/ $\pi$ -acceptor binding of the anion  $2^{-}$  to the  $[Ni_2L]^{2+}$  moiety.

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#### Quantum-Chemical Study

Calculations of the molecular electrostatic potential (MESP) and natural population analysis (NPA) have been carried out for the anion  $2^-$  in order to study the possible metal coordination sites. The negative charge in 1-methyl-tetrazole-5-thiolate is strongly delocalized (Table 2). Hence, the structure of the investigated anion cannot be accurately described by a single localized Lewis structure, but should be considered as superposition of multiple Lewis structures 2a-e. We have employed natural bond orbital analysis to compare the relative accuracy of the five descriptions shown in Table 3.

Table 2. Atomic charges calculated for anion  $2^-$  and their labels as per IUPAC nomenclature as well as in the structure of crystals of  $5\cdot 2$ MeCN (second row).

Atom (IUPAC)	N(1)	N(2)	N(3)	N(4)	C(5)	S
X-ray label	N10	N9	N8	N7	C39	S3
NPA charge	-0.292	-0.154	0.120	0.389	+0.169	0.464

Structure 2a shows the smallest non-Lewis occupancy indicating the best Lewis structure. Nevertheless, the non-Lewis occupancy calculated for structure 2a is sufficiently large and shows strong delocalization. Therefore, it is necessary to consider other resonance structures in order to describe the discrepancy from the Lewis structure 2a. It is worth noting that the negative charge is localized on different atoms in each Lewis structure impeding the exact prediction of the coordination mode of  $2^{-}$  in complexes. Nevertheless, to some extent the coordination sites of molecules have been predicted correctly by analysis of MESP data.<sup>[15]</sup> The largest negative value of MESP is not necessarily adjacent to the atom with the largest negative charge. Figure 4 shows a contour map of MESP in the plane of the tetrazole ring of  $2^-$ . Local minima were detected next to each basic centre, the minimum near N(4) being the deepest, whereas the most negative charge is located on the sulfur atom (Table 2). The MESP minima near N(3) and S are approximately equal. The calculated MESP distribution is in good agreement with the coordination of the anion through N(3) and N(4) in crystals of 5.2MeCN. However, according to our calculations, coordination through the N(4) and S atoms is also possible. With respect to the calculated values of atomic charges, the latter coordination mode should be preferred.



Figure 4. MESP contour map calculated for anion  $2^-$  (positive values denoted by dashed lines).

The most precise prediction of the preferred coordination mode is given by comparing the relative energies of the structure of the corresponding complex, [Ni<sub>2</sub>L(µ-SCN<sub>4</sub>-Me)]<sup>+</sup>. Therefore, a geometry optimization of  $[Ni_2L(\mu SCN_4Me$ )]<sup>+</sup> coordinated through N(4) and N(3) of the tetrazole ring (mode VI) was carried out, which resulted in the same structure as determined by X-ray diffraction data. It is worth noting that a local minimum on the potential energy surface corresponding to the coordination of anion  $2^{-}$  through N(4) and S was not found. Unexpectedly, a geometry optimization starting from mode IV became a structure showing a complex coordinated through the S atom (mode I), with a nonbonding Ni–N(4) distance of 2.8 Å. It should be noted that bridging coordination of sulfur atoms has been previously reported for  $[Ni_2L(\mu-SH)]^+$ .<sup>[16]</sup> The calculated total energy of  $[Ni_2L(\mu$ -SCN<sub>4</sub>Me)]<sup>+</sup> with a binding mode I for the tetrazolate ring is 67.6 kJ mol<sup>-1</sup> higher than that with binding mode VI, which is in excellent agreement with the observed coordination mode of  $2^-$  in crystals of 5.2MeCN.

Table 3. Calculated total non-Lewis occupancy for anion 2-.

Structure		S <sup>©</sup> Me )/−N N N 2a	S N N N N 2b	S N N N S N S S C	S⊖ ⊕,Me ⊖N,N,N 2d	S N N N N N S N B N
Non-Lewis occupancy	е	1.391	1.644	1.801	1.577	2.425
	%	2.32	2.74	3.00	2.63	4.04



#### Magnetic Properties of 5.2MeCN

The plot of the temperature dependence of the effective magnetic moment,  $\mu_{\rm eff}$ , (per dinuclear complex) for compound 5·2MeCN, from data measured in an external magnetic field B = 1.0 T, is shown in Figure 5. At room temperature, the value of  $\mu_{eff}$  is 4.83  $\mu_B$  per dinuclear unit. With decreasing temperature, the  $\mu_{eff}$  value increases steadily to a maximum of 5.58 µ<sub>B</sub> (20 K). On lowering the temperature to 2.0 K, the value decreases to 4.73  $\mu_{\rm B}$ , presumably due to saturation effects or the zero-field splitting of nickel(II). The maximum value of the effective magnetic moment is in excellent agreement with the expected spin-only value of 5.60  $\mu_{\rm B}$  for  $S_{\rm T}$  = 2 resulting from ferromagnetic coupling of two Ni<sup>II</sup> ions ( $S_i = 1, g = 2.285$ ). Similar behaviour has also been observed for complexes 3.<sup>[17]</sup> The magnitude of the interaction was determined by least-squares fitting of the experimental magnetic susceptibility data to the spin Hamiltonian [Equation (1)]<sup>[18]</sup> over the temperature range of 2-330 K by using a full-matrix diagonalisation approach. Isotropic Heisenberg-Dirac-van Vleck exchange, the single zero-field splitting and the single-ion Zeeman interactions were taken into account. The introduction of a local axial zero-field splitting parameter (D) is appropriate for octahedral Ni<sup>II</sup> since the noncubic components of the ligand field may act on the <sup>3</sup>A<sub>2g</sub> ground-state to produce zero-field splitting, which may be of the same order of magnitude as  $J^{[19,20]}$  In Equation (1), the anisotropy axes z of the nickel(II) ions were assumed to be colinear, therefore the introduced D values should be regarded as "effective".



Figure 5. Temperature dependence of the effective magnetic moment  $\mu_{eff}$  (per dinuclear complex) for compound 5.2MeCN received from data measured at an external magnetic field B = 1.0 T (squares: experimental values; solid line: best theoretical fit).

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{ZFS} + \hat{H}_{Zee}$$

$$\hat{H}_{ex} = -2J_{12}\vec{S}_1 \cdot \vec{S}_2$$

$$\hat{H}_{ZFS} = \sum_{i=1}^2 D_i \left[ \hat{S}_{iz}^2 - \frac{1}{3}\vec{S}_i(\vec{S}_i + 1) \right]$$

$$\hat{H}_{Zee} = \sum_{i=1}^2 g_i \beta \vec{S}_i \cdot \vec{B}$$
(1)

Initially, identical D and g values for both of the two Ni<sup>II</sup> ions in 5·2MeCN were assumed. The coupling constant J was determined to be 19.5(5) cm<sup>-1</sup> and g (isotropic average)

to be 2.29. Effective absolute D values were determined to be 3.9(5) cm<sup>-1</sup>, though the derived value should be seen as indicative since temperature-dependent magnetic susceptibility measurements are not very appropriate for their determination.<sup>[21,22]</sup> Nevertheless, their inclusion significantly improved the low-temperature fit, while leaving the calculated J value almost unaffected. In a second approach, we took the slightly different coordination environment of the two Ni<sup>II</sup> ions into account and therefore allowed individual D and g values for each Ni<sup>II</sup> ion during the least-squares full-matrix diagonalisation. This resulted in the same values of J [19.5(5) cm<sup>-1</sup>] and |D| [3.8(5) and 4.1(5) cm<sup>-1</sup>, respectively] with respect to the limit of error, but in rather unreliable g values (2.388 and 2.182, respectively). In conclusion, the first approach for the determination of J proved to be a sufficient approximation in this case. The J and g values determined for 5 are otherwise similar to other bioctahedral nickel complexes supported by  $L^{2-}$  { $J = 6.7 \text{ cm}^{-1}$  for  $[Ni_2L(\mu-NO_2)]^+$ ,  $J = 7.9 \text{ cm}^{-1}$  for  $[Ni_2L(\mu-OAc)]^+$ , J =27.0 cm<sup>-1</sup> for  $[Ni_2L(\mu-BH_4)]^+$ .<sup>[8a]</sup> The superexchange-coupling mechanism thus presumably involves the bridging S atoms, although contributions from the tetrazolate ligand cannot be ruled out.[8b]

### Conclusions

We have presented the synthesis and characterization of a novel macrocyclic dinickel complex  $[Ni_2L(\mu-SCN_4Me)]$ -BPh<sub>4</sub> with 1-methyltetrazole-5-thiolate as a coligand. X-ray analysis of this complex displayed a novel coordination mode of the 1-methyltetrazole-5-thiolate ligand, namely N(3),N(4)-bridging. This is caused by electronic factors, revealed by quantum-chemical studies of the  $[Ni_2L(\mu-SCN_4Me)]^+$  cation, and steric hindrance caused by the interaction of the tetrazolate group with the macrocyclic ligand.

## **Experimental Section**

**General Remarks:** All reactions were carried out under dinitrogen by using standard Schlenk techniques. Complex  $[Ni_2L(\mu-ClO_4)]$ -ClO<sub>4</sub> was prepared according to the literature procedure.<sup>[23]</sup> All other compounds were purchased and used without further purification. Melting points were determined with an IA9100 instrument (Barnstead/Electrothermal) in open glass capillaries and are uncorrected. IR spectra were recorded from KBr pellets with a Bruker Vector 27 FTIR spectrometer. Electronic absorption spectra were measured with a JASCO V670 UV/Vis/NIR spectrometer. Elemental analyses were performed with a VARIO EL elemental analyzer. ESI mass spectra were recorded with a 7 Tesla APEX II instrument (Bruker Daltonics).

 $[Ni_2L(\mu-SCN_4Me)]ClO_4$  (4): Triethylamine (22 mg, 0.22 mmol) was added to a solution of 1-methyltetrazole-2-thiol (H2) (14.5 mg, 0.125 mmol) in methanol (20 mL).  $[Ni_2L(\mu-ClO_4)]ClO_4$  (110 mg, 0.113 mmol) was added, and the resulting green solution was stirred at room temperature for 20 h. A solution of LiClO<sub>4</sub>·3H<sub>2</sub>O (321 mg, 2.00 mmol) in methanol (5 mL) was added, and stirring was continued for 1 h. The resulting green precipitate of 4 was collected by filtration, washed several times with cold ethanol and diethyl ether and dried in vacuo to give 89 mg (0.089 mmol, 79%) of 4 as a light green, air-stable, microcrystalline powder; m.p. 284 °C (decomp.). IR (KBr):  $\tilde{v} = 2996$  (sh), 2956 (m), 2900 (m), 2868 (m), 1463 (s), 1427 (sh), 1395 (w), 1378 (w), 1362 (m), 1329 (m), 1292 (sh), 1267 (w), 1232 (m), 1200 (w), 1165 (w), 1152 (w), 1122 (s), 1108 (sh), 1095 (s), 1057 (m), 1043 (m), 999 (w), 981 (w), 928 (w), 913 (w), 881 (w), 827 (m), 818 (w), 807 (w), 754 (w), 742 (sh), 720 (w), 631 (sh), 624 (m), 600 (w), 567 (w), 540 (w), 493 (w), 479 (w), 438 (w), 417 (w) cm<sup>-1</sup>. UV/Vis/NIR (MeCN):  $\lambda_{max}$  ( $\varepsilon$ ) = 199 (55104), 248 (25755), 277sh (15823), 305sh (13044), 330 (9447), 396sh (1724), 641 (29), 927sh (27), 1097 (69) (103 m<sup>-1</sup> cm<sup>-1</sup>) nm. C<sub>40</sub>H<sub>67</sub>ClN<sub>10</sub>Ni<sub>2</sub>O<sub>4</sub>S<sub>3</sub> (1001.06): calcd. C 47.99, H 6.75, N 13.99; found C 47.96, H 6.57, N 13.08. ESI-MS+ (MeCN): m/z = 899.34 [C<sub>40</sub>H<sub>67</sub>N<sub>10</sub>Ni<sub>2</sub>S<sub>3</sub><sup>+</sup>].

[Ni<sub>2</sub>L(µ-SCN<sub>4</sub>Me)]BPh<sub>4</sub> (5): Complex 4 (100 mg, 0.100 mmol) was dissolved in methanol (50 mL), and a solution of NaBPh<sub>4</sub> (342 mg, 1.00 mmol) in methanol (5 mL) was added. The mixture was stirred at ambient temperature for 1 h. The green product was filtered, washed with cold ethanol, cold diethyl ether and dried in vacuo to give 105 mg (0.086 mmol, 86%) of 5 as a green, air-stable, microcrystalline powder; m.p. 260 °C (decomp.). IR (KBr):  $\tilde{v} = 3056$  (m), 3038 (m), 3000 (m), 2955 (s), 2902 (m), 2864 (s), 1580 (m), 1480 (s), 1462 (s), 1427 (m), 1394 (w), 1378 (m), 1362 (m), 1329 (s), 1309 (sh), 1292 (w), 1266 (m), 1231 (m), 1199 (w), 1165 (m), 1154 (m), 1134 (w), 1122 (w), 1109 (w), 1074 (m), 1056 (m), 1041 (m), 1000 (w), 981 (w), 928 (m), 914 (m), 891 (w), 881 (w), 845 (w), 826 (m), 819 (m), 809 (m), 754 (m), 732 (m), 707 (s), 667 (w), 628 (m), 612 (m), 567 (w), 536 (w), 473 (w), 414 (w) cm<sup>-1</sup>. UV/Vis/NIR (MeCN):  $\lambda_{\rm max}$  ( $\epsilon$ ) = 194 (168363), 246sh (35290), 276sh (16012), 305sh (12198), 332 (9093), 396sh (1808), 471sh (143), 638 (28), 919sh (25), 1094 (68  $\text{M}^{-1}$  cm<sup>-1</sup>) nm. C<sub>64</sub>H<sub>87</sub>BN<sub>10</sub>Ni<sub>2</sub>S<sub>3</sub> (1220.84): calcd. C 62.96, H 7.18, N 11.47; found C 62.39, H 6.84, N 11.10. ESI-MS+ (MeCN):  $m/z = 899.34 [C_{40}H_{67}N_{10}Ni_2S_3^+]$ .

Crystal Structure Determination: Single-crystals of 5.2MeCN were obtained by slow concentration of an acetonitrile/ethanol (1:1) solution of 5 at ambient temperature. Data collection was performed at 130(2) K with a Siemens Smart CCD area detector diffractometer by using monochromated Mo- $K_{\alpha}$  radiation (0.71073 Å) and ω-scan rotation mode. Data reduction was carried out with SAINT<sup>[24]</sup> and corrected for absorption by using SADABS.<sup>[25]</sup> The structure was solved by direct methods (SHELXS-97)<sup>[26]</sup> and refined by full-matrix least squares on the basis of all data against  $F^2$ using SHELXL-97.<sup>[27]</sup> PLATON<sup>[28]</sup> was used to search for higher symmetry. All non-hydrogen atoms were refined anisotropically. H atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystal data for 5·2MeCN:  $C_{68}H_{93}N_{12}Ni_2S_3B$ ,  $M_R = 1302.95$ , orthorhombic, space group *Pbca* (No. 61), a = 17.7371(3) Å, b = 17.5649(3) Å, c =41.8483(9) Å, V = 13037.9(4) Å<sup>3</sup>, Z = 8,  $\rho_{calcd} = 1.328$  g cm<sup>-3</sup>, T =130(2) K,  $\mu$ (Mo- $K_{\alpha}$ ) 0.725 mm<sup>-1</sup> ( $\lambda = 0.71073$  Å), 155004 reflections measured, 9351 unique, 7012 with  $I > 2\sigma(I)$ , refinement converged to R = 0.0552,  $wR = 0.0937 [I > 2\sigma(I)]$ ,  $GoF = 1.061, -19 \le$  $h \le 19, -19 \le k \le 19, -46 \le l \le 46, 2.54^{\circ} \le \theta \le 23.26^{\circ}, 772$ parameters and 0 restraints, min/max residual electron density +0.663/-0.506 e/Å<sup>3</sup>. CCDC-782779 contains the supplementary crystallographic data for 5.2MeCN. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

**Computational Details:** MO calculations were carried out by using the density functional theory B3LYP method<sup>[29]</sup> to study the coor-

dination features of the anion 2<sup>-</sup>. Our previous investigations<sup>[30]</sup> have shown the B3LYP/6-31G(d) level to provide data of calculated geometries of tetrazoles in good agreement with experimental findings. Nevertheless, in order to describe anions accurately use of a basis set that includes diffuse functions is required. Therefore, in the present work we have used the 6-31+G(d) basis set for geometry optimization, NPA and MESP calculations of the isolated anion 2-. We have used smaller basis sets for geometry optimization and total energy calculation of complex [Ni<sub>2</sub>L(µ-SCN<sub>4</sub>Me)]<sup>+</sup>. Nickel atoms were described by the standard LANL2DZ double- $\xi$  basis set, applying an effective core potential as suggested by Hay and Wadt.<sup>[31]</sup> All atoms of 2<sup>-</sup> were described by a 6-31G\* basis set, and STO-3G basis sets were used for the remaining atoms. The geometry of 2and its location relative to the macrocyclic hexaminedithiophenolate ligand was fully optimized, while the Cartesian coordinates of all atoms of  $[Ni_2L]^{2+}$  were fixed as those as in crystals of 5.2MeCN. In our calculations quintet configuration was considered for the complex [Ni<sub>2</sub>L(µ-SCN<sub>4</sub>Me)]<sup>+</sup>.

**Determination of the Temperature Dependence of the Magnetic Susceptibility:** Measurements of powdered polycrystalline **5**·2MeCN were carried out with a Quantum Design MPMS-XL7 SQUID magnetometer from 2 to 330 K and vice versa at an applied external field of 0.5 and 1.0 T, respectively, both in field cooling as well as in zero-field cooling mode. All obtained data were processed by using Bill's julX program<sup>[32]</sup> and were corrected for underlying diamagnetism by using Pascal's constants and for the contribution of the sample holder by subtraction of the previously determined holder average. With respect to the limit of error, all data gave the identical values mentioned above.

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- [1] P. N. Gaponik, S. V. Voitekhovich, O. A. Ivashkevich, *Russ. Chem. Rev.* 2006, *75*, 507–539.
- [2] a) S. V. Voitekhovich, D. V. Talapin, C. Klinke, A. Kornowski, H. Weller, *Chem. Mater.* 2008, 20, 4545–4547; b) M. N. Nichick, S. V. Voitekhovich, A. Shavel, A. I. Lesnikovich, O. A. Ivashkevich, *Polyhedron* 2009, 28, 3138–3142.
- [3] a) B. Pergolese, A. Bigotto, J. Raman Spectrosc. 2002, 33, 646–651; b) M. Mihit, S. El Issami, M. Bouklah, L. Bazzi, B. Hammouti, E. Ait Addi, R. Salghi, S. Kertit, Appl. Surf. Sci. 2006, 252, 2389–2395; c) H. Ma, T. Song, H. Sun, X. Li, Thin Solid Films 2008, 516, 1020–1024; d) K. F. Khaled, M. M. Al-Qahtani, Mater. Chem. Phys. 2009, 113, 150–158; e) M. Mihit, K. Laarej, H. A. El Makarim, L. Bazzi, R. Salghi, B. Hammouti, Arabian J. Chem. 2010, 3, 55–60.
- [4] C. Ma, J. Sun, Polyhedron 2004, 23, 1547-1555.
- [5] R. Cea-Olivares, O. J. Sandoval, G. Espinosa-Perez, C. Silvestru, *Polyhedron* **1994**, *13*, 2809–2818.
- [6] a) Y.-Q. Chen, J. Zhang, S. Cai, X.-F. Hou, H. Schumann, G.-X. Jin, *Dalton Trans.* 2007, 749–759; b) Y.-L. Wanga, Q. Shi, W.-H. Bi, X. Li, R. Cao, Z. Anorg. Allg. Chem. 2006, 632, 167–171; c) X.-L. Zhang, Y. Qiu, S. W. Ng, Acta Crystallogr., Sect. E 2006, 62, m3301–m3302; d) D. R. Whitcomb, M. Rajeswaran, J. Coord. Chem. 2006, 59, 1253–1260; e) V. W. L. Ng, S. L.

Kuan, W. K. Leong, L. L. Koh, G. K. Tan, L. Y. Goh, R. D. Webster, *Inorg. Chem.* **2005**, *44*, 5229–5240; f) H. Noth, W. Beck, K. Burger, *Eur. J. Inorg. Chem.* **1998**, 93–99.

- [7] a) J. Bravo, M. B. Cordero, J. S. Casas, M. V. Castano, A. Sanchez, J. Sordo, *J. Organomet. Chem.* **1996**, *513*, 63–69; b) S. Zhang, Y. Feng, *Chin. J. Chem.* **2009**, *27*, 877–881.
- [8] a) C. Loose, V. Lozan, J. Kortus, B. Kersting, *Coord. Chem. Rev.* 2009, 253, 2244–2260; b) V. Lozan, R. Syre, B. Kersting, *Z. Anorg. Allg. Chem.* 2008, 634, 2330–2336.
- [9] V. Lozan, S. V. Voitekhovich, P. N. Gaponik, O. A. Ivashkevich, B. Kersting, Z. Naturforsch., Teil B 2008, 63, 496–502.
- [10] L. S. Ivashkevich, A. S. Lyakhov, P. N. Gaponik, M. M. Degtyarik, O. A. Ivashkevich, S. I. Tiutiunnikov, V. V. Efimov, *Acta Crystallogr., Sect. C* 2006, *62*, m607–m609.
- [11] L. S. Ivashkevich, A. S. Lyakhov, A. P. Mosalkova, P. N. Gaponik, O. A. Ivashkevich, *Acta Crystallogr., Sect. E* 2009, 65, m236.
- [12] a) J. Hausmann, V. Lozan, M. H. Klingele, G. Steinfeld, D. Siebert, Y. Journaux, J. J. Girerd, B. Kersting, *Chem. Eur. J.* **2004**, *10*, 1716–1728; b) M. Gressenbuch, B. Kersting, *Eur. J. Inorg. Chem.* **2007**, 90–102.
- [13] R. Čea-Olivares, O. Jiménez-Sandoval, S. Hernández-Ortega, M. Sánchez, R. A. Toscano, I. Haiduc, *Heteroat. Chem.* 1995, 6, 89–97.
- [14] F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor. in *International Tables for Crystallography*, vol. C (Ed.: E. Prince), Kluwer Academic Publishers, Dodrecht, Boston, London, **2004**, pp. 790–811.
- [15] a) M. Alcami, O. Mo, M. Yanez, J. Phys. Chem. 1992, 96, 3022–3029; b) P. N. Gaponik, S. V. Voitekhovich, A. S. Lyakhov, V. E. Matulis, O. A. Ivashkevich, M. Quesada, J. Reedijk, *Inorg. Chim. Acta* 2005, 358, 2549–2557; c) P. N. Gaponik, M. M. Degtyarik, A. S. Lyakhov, V. E. Matulis, O. A. Ivashkevich, M. Quesada, J. Reedijk, *Inorg. Chim. Acta* 2005, 358, 3949–3957.
- [16] V. Lozan, B. Kersting, Inorg. Chem. 2008, 47, 5386-5393.

- [17] J. Lach, S. V. Voitekhovich, V. Lozan, P. N. Gaponik, O. A. Ivashkevich, J. Lincke, D. Lässig, B. Kersting, Z. Anorg. Allg. Chem. 2010, 636, 1980–1986.
- [18] C. J. O'Connor, Prog. Inorg. Chem. 1982, 29, 203-283.
- [19] A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* **1972**, *11*, 2884–2889.
- [20] O. Kahn, Molecular Magnetism, VCH, Weinheim, 1993.
- [21] D. M. Duggan, E. K. Barefield, D. N. Hendrickson, *Inorg. Chem.* 1973, 12, 985–991.
- [22] A. Meyer, A. Gleizes, J.-J. Girerd, M. Verdaguer, O. Kahn, Inorg. Chem. 1982, 21, 1729–1739.
- [23] Y. Journaux, V. Lozan, J. Klingele, B. Kersting, Chem. Commun. 2006, 83–84.
- [24] a) SMART, Area-Detector Software Package, Siemens Industrial Automation, Inc., Madison, WI, 1993; b) SAINT, Area-Detector Integration Software, Siemens Industrial Automation, Inc., Madison, WI, 1999.
- [25] G. M. Sheldrick, SADABS, An empirical absorption correction program [part of the SAINTPlus NT version 5.0 package (Program for Scaling and Correction of Area-detector Data), BRUKER AXS, Madison, WI], Göttingen, 1998.
- [26] G. M. Sheldrick, Acta Crystallogr., Sect. A 1990, 46, 467-473.
- [27] a) G. M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997; b) L. J. Farrugia, J. Appl. Crystallogr. 1997, 30, 565–566.
- [28] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2000.
- [29] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [30] a) V. E. Matulis, A. S. Lyakhov, P. N. Gaponik, S. V. Voitekhovich, O. A. Ivashkevich, *J. Mol. Struct.* 2003, 649, 309–314; b)
   A. S. Lyakhov, V. E. Matulis, P. N. Gaponik, S. V. Voitekhovich, O. A. Ivashkevich, *J. Mol. Struct.* 2008, 876, 260–267.
- [31] P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 270-283.
- [32] E. Bill, julX, Simulation of molecular magnetic data, version 1.4.1., MPI for Bioinorganic Chemistry, Mühlheim/Ruhr, 2008. Received: July 5, 2010

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