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Synthesis and Structure of a Macrocyclic Dinickel Complex Incorporating a Hypercoordinated Sulfenium(II) Cation

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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>Fig1.cdx Fig2.cdx</p>	



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3 **Synthesis and Structure of a Macrocyclic Dinickel Complex Incorporating**
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6 **a Hypercoordinated Sulfenium(II) Cation**
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9 Mathias Gressenbuch and Berthold Kersting*

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11 Received ...
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16 **Abstract.** The synthesis and structure of a macrocyclic dinickel complex incorporating a
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18 hypercoordinated sulfenium(II) cation are reported. The novel complex $[\text{Ni}_2\text{L}^3(\text{Cl})]^{2+}$ was
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20 obtained from a reaction of the per-hydroxyethylated N_6S_2 macrocycle H_2L^2 with
21
22 $\text{NiCl}_2(\text{H}_2\text{O})_6$ in the presence of air, and isolated as its ClO_4 or BPh_4 salt. The structure reveals
23
24 a three-coordinate sulfenium cation that is stabilized by two intramolecularly coordinating
25
26 amino groups. The N–S bonds are 2.087(7) Å and 2.105(6) Å and the N-S-N bond angle is
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28 168.2(2)°. The bonding is best described by a N,N-chelated sulfur(II) atom (3c-4e bond)
29
30 bearing two lone pairs and a formal charge of +1.
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37 **Keywords:** Macrocyclic ligands / Sulfenium Cation / Nickel / Crystal structure
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The synthesis and structural characterization of a number of hypercoordinated organo-selenium and -tellurium compounds have been reported [1]. Typical examples are the chalcogenenium cations **2** (RSe^+) and **3** (RTe^+) (Fig. 1) [2], both formally six-valence electron species, which are stabilized by two intramolecular $N \cdots E$ interactions ($E = Se, Te$).

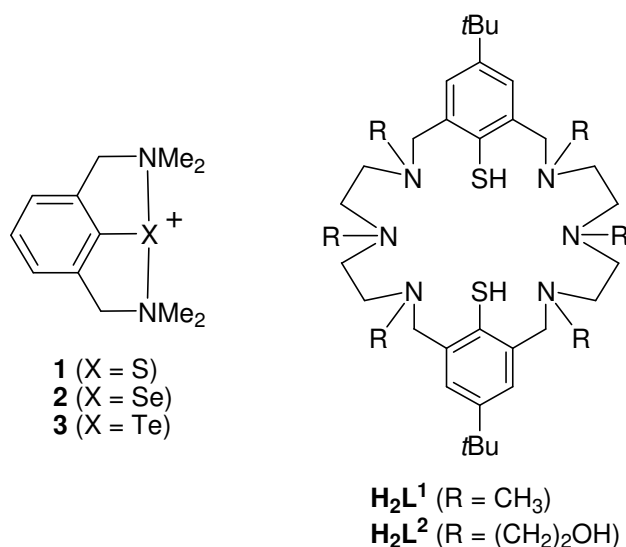


Fig. 1. Structures of compounds **1-3**, H_2L^1 and H_2L^2 .

While the chemistry of such hypercoordinate selenium and tellurium compounds is now fairly well-understood [3], surprisingly little is known about their corresponding sulfenium analogs (RS^+). Sulfenium cations are difficult to isolate as they are highly electrophilic and susceptible to nucleophilic attack, and only few cationic examples such as **1** have been structurally characterized to date [4]. In the course of our work on the coordination chemistry of macrocyclic amine-thiophenolate ligands H_2L^1 and H_2L^2 [5,6], we have now been able to isolate and structurally characterize a macrocyclic complex $[Ni_2L^3(Cl)]^{2+}$ (Fig. 2) incorporating such a hypercoordinated sulfur species. These results are described herein.

Results and Discussion

The dark green macrocyclic complex $[Ni_2L^3(Cl)]^{2+}$ was reproducibly obtained in ca. 80% yield by treatment of the protonated form of the per-hydroxyethylated macrocycle H_2L^2 [7]

with two equivalents of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ in methanol in the presence of NEt_3 and air at ambient temperature, followed by precipitation with LiClO_4 . This reaction is accompanied by an oxidation of the ligand (L^2)²⁻ to (L^3)⁻ [8]. Previously, only isothiazoles have been isolated from air-oxidation of macrocyclic amino-thiophenolates [9].

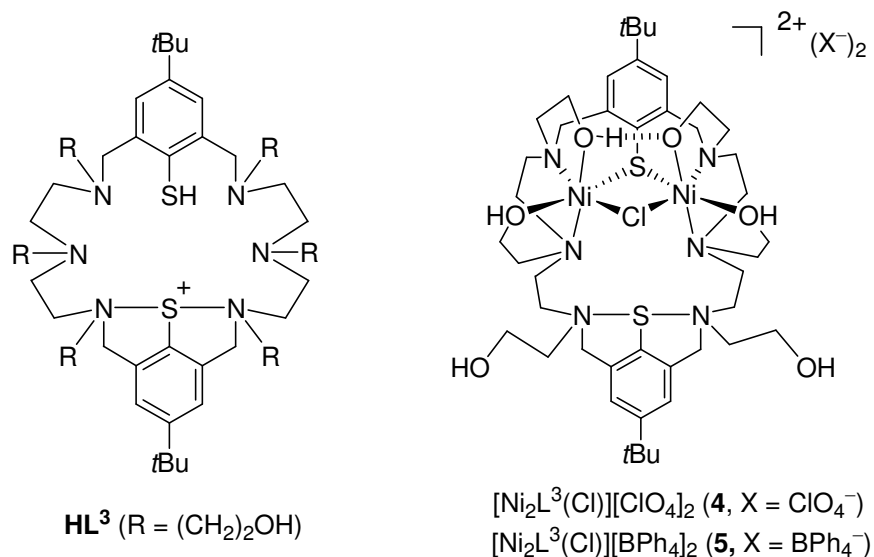


Fig. 2. Structures of the ligand HL^3 and its $[\text{Ni}_2\text{L}^3(\text{Cl})]^+$ complex in **4** and **5**.

The electrospray ionization mass spectrum (ESI-MS) of a dilute acetonitrile solution of **4** exhibited a molecular ion peak with the correct isotopic distribution for $[\text{Ni}_2\text{L}^3(\text{Cl})][\text{ClO}_4]^+$ ($m/z = 1097.31$), and elemental analysis agreed well with the formula $[\text{Ni}_2\text{L}^3(\text{Cl})][\text{ClO}_4]_2$. The $[\text{Ni}_2\text{L}^3(\text{Cl})]^{2+}$ cation was also isolated as its tetraphenylborate salt **5**.

Crystals of **5**·3MeOH are monoclinic, space group $P2_1/c$. The asymmetric unit contains a dicationic complex (Fig. 3), two tetraphenylborate anions (one of them disordered), and three methanol solvate molecules. Charge considerations imply the presence of one deprotonated hydroxyethyl arm (assuming the presence of two Ni^{2+} ions, a sulfenium (RS^+) cation, one thiophenolate residue, a chloride ion, two BPh_4^- anions, and the $\text{CH}_2\text{CH}_2\text{O}^-$ group). The latter is most likely coordinated to Ni2, as it accepts intra- ($\text{O1} \cdots \text{O6}$ 2.469 Å) and intermolecular hydrogen bonds ($\text{O6} \cdots \text{O5}'$ 2.548 Å). Such $\text{Ni}_2(\text{RO}-\text{H} \cdots \text{OR})$ structures are not unusual and occur in other dinuclear nickel(II) complexes [10]. In the present structure hydrogen bonds

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2
3 are also seen between the MeOH solvate molecules and the hydroxyethylarms of the
4
5
6 $[\text{Ni}_2\text{L}^3(\text{Cl})]^{2+}$ dication ($\text{O}2\cdots\text{O}7^{\text{MeOH}}$ 2.532 Å, $\text{O}3\text{a}\cdots\text{O}8^{\text{MeOH}}$ 3.140 Å, and $\text{O}4\cdots\text{O}9^{\text{MeOH}}$ 2.852 Å,
7
8 not shown in Figure 3). The Ni atoms have a distorted octahedral $\text{N}_2\text{O}_2\text{SCl}$ coordination
9
10 environment with normal bond lengths. The Ni \cdots Ni distance is at 3.397 Å.
11

12
13 The sulfenium cation is characterized by two intramolecularly coordinating amino groups.
14
15 The two hydroxyethyl groups on N3 and N4 are not coordinated to S2 ($\text{O}3\text{a}\cdots\text{S}2$ 3.804 Å,
16
17 $\text{O}4\cdots\text{S}2$ 4.967 Å), such that the sulfur atom is essentially three-coordinate. The N–S bonds
18
19 ($2.087(7)$ Å, $2.105(6)$ Å) and the N-S-N bond angle ($168.2(2)^\circ$) in **5** are very similar to those
20
21 in **1** ($2.063(1)$ Å, $2.063(1)$ Å, $168.54(9)^\circ$), as is the dihedral angle between the planes through
22
23 the N_2S and the aryl ring (14.6° in **5**, 14.3° in **1**). The bonding is best described by a N,N-
24
25 chelated sulfur(II) atom (3c-4e bond) bearing two lone pairs and a formal charge of +1 on the
26
27 basis of the current view of hypercoordinate species [11].
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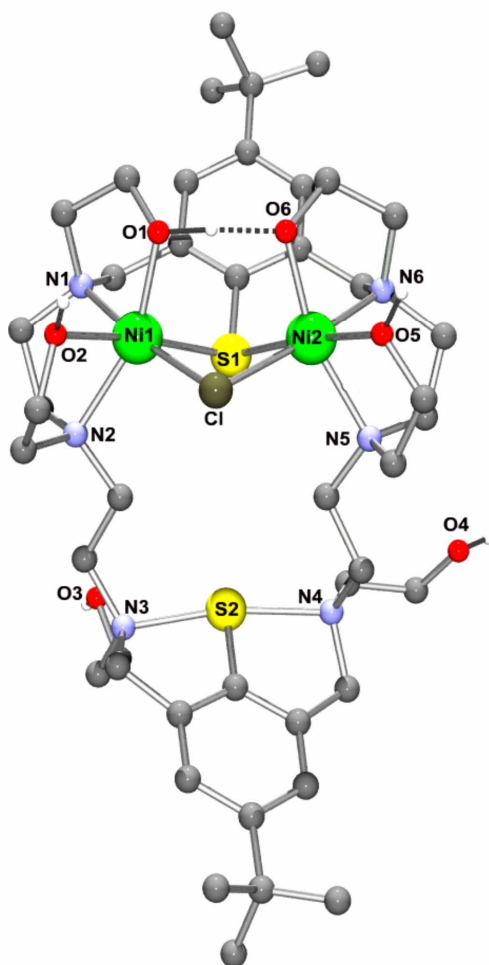


Fig. 3. Ball- and stick representation of the structure of the $[\text{Ni}_2\text{L}^3(\text{Cl})]^{2+}$ dication in crystals of $5(\text{MeOH})_3$. Hydrogen atoms have been omitted for clarity except for OH groups. The intramolecular hydrogen bond between O1 and O6 is shown as a dashed line.

Selected bond lengths [\AA] and angles [$^\circ$]: Ni1–O1 2.048(4), Ni1–O2 2.129(4), Ni1–N1 2.087(6), Ni1–N2 2.207(6), Ni1–S1 2.381(2), Ni1–Cl 2.438(2), Ni2–O5 2.085(5), Ni2–O6 2.053(4), Ni2–N5 2.169(5), Ni2–N6 2.091(6), Ni2–S1 2.422(2), Ni2–Cl 2.452(2), S1–C1 1.760(7), S2–C20 1.749(7), S2–N3 2.087(7), S2–N4 2.105(6); Ni1–Cl–Ni2 88.00(6), Ni1–S1–Ni2 90.02(6), N3–S2–N4 168.2(2)

In summary, the use of the perhydroxyethylated ligand H_2L^2 in place of H_2L^1 has enabled the isolation of a unique macrocycle incorporating a cationic aryl sulfenium ion in proximity to a dinickel(II) thiophenolate complex. The presence of the sulfenium ion and the nearby active coordination site at the Ni_2 center might enable molecular recognition of zwitterionic

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2
3 substrates within macrocyclic cavities. It is also tempting to investigate a possible
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5 stabilization of hypercoordinated S(IV) or S(VI) species by the CH₂CH₂OH functions. These
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7 topics will be addressed in ongoing studies.
8
9

10 11 12 **Experimental Part**

13
14
15 *General:* The ligand H₂L² was prepared as described in the literature [7]. The infrared spectra
16
17 were recorded as KBr discs using a Bruker VECTOR 22 FT-IR-spectrophotometer. Electronic
18
19 absorption spectra were recorded on a Jasco V-570 UV/vis/near IR spectrophotometer. ESI-
20
21 FTICR mass spectra were recorded with a Bruker-Daltonics Apex II instrument using dilute
22
23 MeCN solutions. **Caution !** *Perchlorate salts of transition metal complexes are hazardous*
24
25 *and may explode. Only small quantities should be prepared and great care taken.*
26
27
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31
32 **[Ni₂L³(μ-Cl)][ClO₄]₂ (4).** To a solution of H₂L²·6HCl (239 mg, 0.223 mmol) in methanol (20
33
34 mL) was added with stirring at room temperature a solution of [Ni(H₂O)₆]Cl₂ (106 mg, 0.446
35
36 mmol) in methanol (5 mL). A solution of NEt₃ (181 mg, 1.79 mmol) in methanol (1 mL) was
37
38 added to give a dark green solution. After stirring for 3 days at ambient temperature in air
39
40 solid LiClO₄·3H₂O (358 mg, 2.23 mmol) was added. The solution was concentrated under
41
42 reduced pressure to ca 25 % of its original volume, and left to stand in an open vessel to give
43
44 green crystals of the title compound, which were filtered, washed with cold methanol, and
45
46 dried in vacuum. The crude product was purified by recrystallization from methanol. Yield:
47
48 222 mg (83 %). C₄₄H₇₆Cl₃N₆Ni₂O₁₄S₂ (1200.98): calcd. C 44.00, H 6.38, N 7.00, S 5.34;
49
50 found: C 43.82, H 6.52, N 6.78, S 5.24.
51
52
53
54

55 **UV/Vis (CH₃CN):** λ_{max} (ε) = 646 (34), 859 (13), 1060 nm (42 M⁻¹cm⁻¹). **IR** (KBr, cm⁻¹): ν =
56
57 3424 s, 2957 m, 2926 m, 2866 m, 2361 vw, 2025 vw, 1631 w, 1454 m, 1398 vw, 1367 w,
58
59 1311 vw, 1262 vw, 1230 w, 1108(sh) vs, 1087 (vs, ν₃[ClO₄⁻]), 1004(sh) w, 964 vw, 910 w,
60
878 w, 763 vw, 742 vw, 715 vw, 677 vw, 628 (m, ν₄[ClO₄⁻]). **MS** (ESI⁺, CH₃CN): m/z

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3 1097.31 [(M-ClO₄)⁺, 80 %], 499.17 [(M-2ClO₄)²⁺, 100 %].
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8 **[Ni₂L³(μ-Cl)][BPh₄]₂ (5)**. A solution of NaBPh₄ (171 mg, 0.50 mmol) in methanol (2 mL)
9
10 was added to a solution of **4** (120 mg, 0.10 mmol) in methanol (20 mL) and stirred for 1 h.
11
12 The green product was filtered, washed with methanol and dried in air to give 136 mg (83 %)
13
14 of **6** as a green, air-stable, microcrystalline powder. C₉₂H₁₁₅B₂ClN₆Ni₂O₆S₂ (1639.53): calcd.
15
16 C 67.40, H 7.07, N 5.13, S 3.91; found: C 67.21, H 7.28, N 5.28, S 4.02.
17
18

19
20 **UV/Vis** (CH₃CN): λ_{max} (ε) = 651 (36), 863 (14), 1059 nm (48 M⁻¹cm⁻¹). **IR** (KBr, cm⁻¹): ν =
21
22 3515 w, 3055 w, 2965 w, 2901 w, 1947 vw, 1882 w, 1820 vw, 1611 w, 1580 w, 1478 w, 1455
23
24 w, 1427 w, 1394 w, 1367 w, 1349 w, 1315 w, 1265 w, 1229 w, 1181 vw, 1155 w, 1133 w,
25
26 1065 m, 1030 w, 1003 w, 966 w, 908 w, 882 w, 872 w, 847 w, 805 w, 755 w, 734 [s, ν(BPh₄⁻)],
27
28 704 [vs, ν(BPh₄⁻)], 625 w, 611 m. **MS** (ESI⁺, MeOH): *m/z* 1317.52 [(M-BPh₄)⁺, 60 %],
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30 499.17 [(M-2ClO₄)²⁺, 100 %].
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37 Single crystals suitable for an X-ray structure analysis were grown by slow evaporation of an
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39 methanol/acetonitrile (1:2) solution of complex salt **5**. The data set was collected at 213(2) K
40
41 using a STOE IPDS-2T diffractometer and graphite monochromated Mo-Kα radiation
42
43 (0.71073 Å). The intensity data were processed with the program STOE X-AREA. The
44
45 structure was solved by Direct Methods [12] and refined by full-matrix least-squares on the
46
47 basis of all data against *F*² using SHELXL-97 [13]. PLATON was used to search for higher
48
49 symmetry [14]. Drawings were produced with Ortep-3 for Windows [15]. Unless otherwise
50
51 specified the H atoms were placed at calculated positions and refined as riding atoms with
52
53 isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically.
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59 *Crystal data for 5·3MeOH*: C₉₅H₁₂₇B₂ClN₆Ni₂O₉S₂, *M*_r = 1735.64, monoclinic, space group
60
*P*₂₁/*c*, *a* = 21.939(2) Å, *b* = 18.348(1) Å, *c* = 22.962(2) Å, β = 96.66(1), *V* = 9181(1) Å³, *Z* =

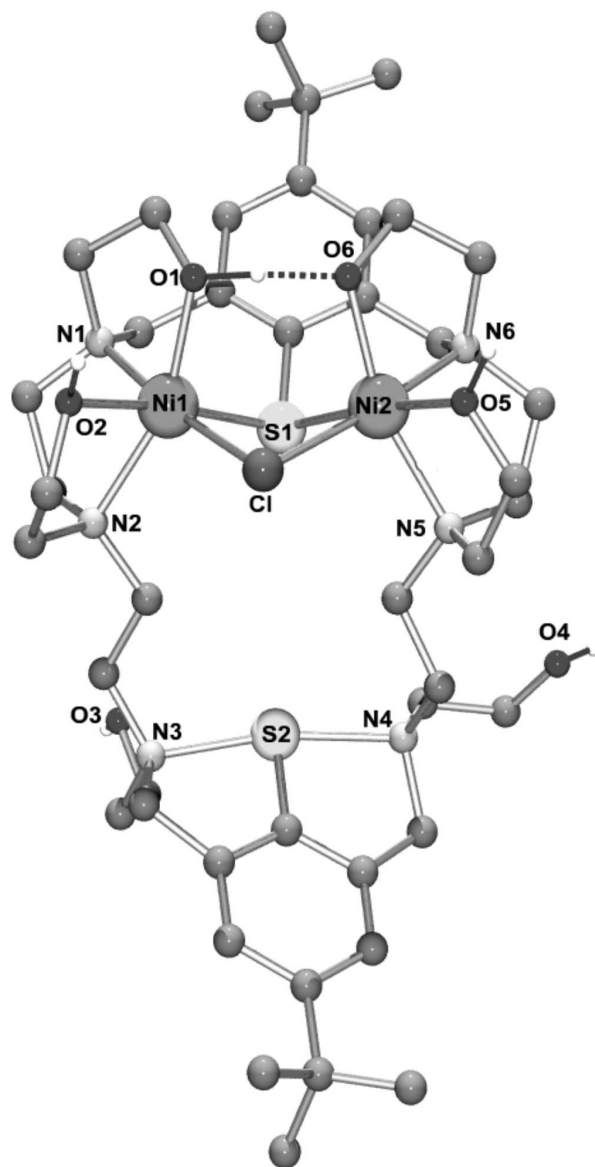
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3 4, $\rho_{\text{calcd}} = 1.256 \text{ g cm}^{-3}$; $\mu (\text{MoK}\alpha) = 0.544 \text{ mm}^{-1}$ ($\lambda = 0.71073 \text{ \AA}$); 61360 reflections measured,
4
5
6 15146 unique, 7410 with $I > 2\sigma(I)$, refinement converged to $R_1 = 0.0848$, $wR_1 = 0.2276$ (I
7
8 $2\sigma(I)$), $R_2 = 0.1384$, $wR_2 = 0.2494$ (all data); 931 parameters. The poor quality of the X-ray
9
10 data is a consequence of a disordered BPh_4^- ion, a disordered *t*Bu group, and a disordered
11
12 $\text{CH}_2\text{CH}_2\text{OH}$ group. The disorders were modeled by split atom models using SADI
13
14 instructions implemented in the SHELXTL software package. The hydroxyethyl OH
15
16 hydrogen atoms were located from final difference Fourier maps but their positions were
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18 refined as riding atoms with isotropic displacement parameters, min./max. residual electron
19
20 density = $+1.566/-3.396 \text{ e/\AA}^3$.
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25 CCDC-762675 contains the supplementary crystallographic data for this paper. These data
26
27 can be obtained free of charge from The Cambridge Crystallographic Data Centre via
28
29 www.ccdc.cam.ac.uk/data_request/cif.
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36 thank Prof. H. Krautscheid for providing facilities for X-ray crystallographic analyses.
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Ball and stick
304x541mm (96 x 96 DPI)