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Macrocyclic Nickel(II) Complexes Coligated by Hydrosulfide and Hexasulfide Ions: Syntheses, Structures, and Magnetic Properties of $[Ni^{II}_2L(\mu\text{-}SH)]^+$ and $[\{LNi^{II}_2\}_2(\mu\text{-}S_6)]^{2+}$

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The borohydride complex $[Ni^{II}_2L(\mu\text{-}BH_4)]^+$ (**3**) where L^{2-} represents a sterically demanding hexaaza-dithiophenolate ligand reacts rapidly with elemental sulfur in acetonitrile at ambient temperature to produce the cationic complexes $[Ni^{II}_2L(\mu\text{-}SH)]^+$ (**4**) and $[\{Ni^{II}_2L\}_2(\mu\text{-}S_6)]^{2+}$ (**6**). Both complexes were isolated as ClO_4^- or BPh_4^- salts and characterized by IR and UV/vis spectroscopy and X-ray crystallography. Complex **4** (also accessible from $[Ni^{II}_2L(ClO_4)]^+$ (**5**) and $Na_2S\cdot 9H_2O$) features an unprecedented $N_3Ni^{II}(\mu\text{-}SR)_2(\mu\text{-}SH)Ni^{II}N_3$ core structure, the hydrosulfide ligand being deeply buried in the binding-cavity of the bowl-shaped $[Ni^{II}_2L]^{2+}$ complex. In **6**, a helical S_6^{2-} chain, with a structure reminiscent to that of plastic sulfur, is almost completely encapsulated by two $[Ni^{II}_2L]^{2+}$ subunits. In contrast to other triply sulfur-bridged $N_3Ni^{II}(SR)_3Ni^{II}N_3$ structures whose ground states are typically of $S = 0$, **4** reveals an $S = 2$ ground-state which is attained by a ferromagnetic exchange interaction between the two Ni(II) ($S = 1$) ions ($J = 18$ cm^{-1}, $H = -2J\mathbf{S}_1\mathbf{S}_2$). Intradimer ferromagnetic exchange interactions are also present in **6** ($J = 23$ cm^{-1}). A qualitative explanation for this difference is offered.

Introduction

The study of the coordination chemistry of classical coordination compounds with deep binding cavities is an active research area.[1,2] Motivations in this area are diverse and include molecular recognition of neutral or charged guest molecules,[3,4] stabilization of unusual substrate coordination modes, isolation of reactive species,[5] promotion of reactions within their interiors,[6–11] and construction of more effective enzyme active site mimetics,[12] to name but a few. Various types of supporting ligands for such complexes have been developed. Most of them represent mononucleating systems derived from cyclodextrines,[6] calixarenes,[13] Schiff-base/calixarene hybrids, and some highly functionalized tripod ligands.[14–18] Much less is known of ligand systems that encapsulate polynuclear core structures, and the chemistry of such systems is not well explored.[19–21]

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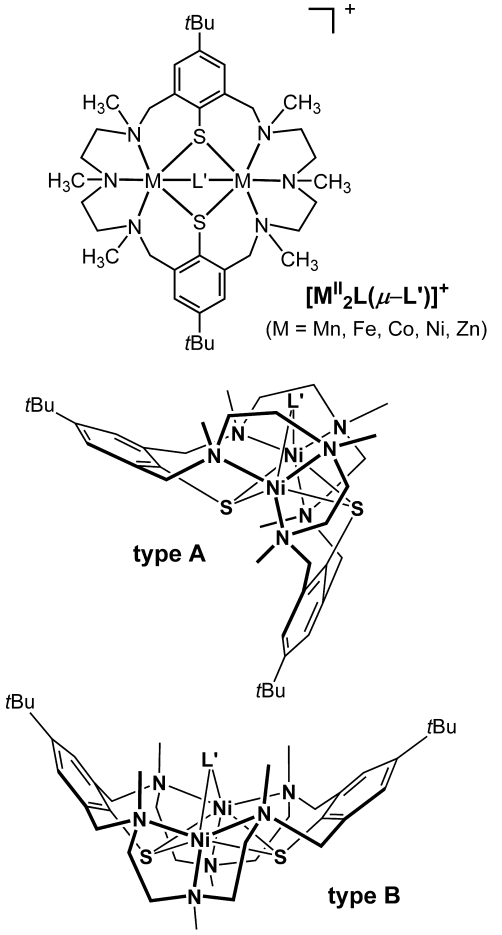

Figure 1. Cationic $[M^{II}_2L(\mu\text{-}L')]^+$ complexes supported by L^{2-} (L' = coligand), and schematic representation of their structures.

The coordination chemistry of binucleating hexaazadithiophenolate macrocycles has been reviewed.[22,23] The N_6S_2 ligand H_2L in its doubly deprotonated form supports the formation of dinuclear complexes of composition $[M^{II}_2L(\mu\text{-}L')]^{n+}$ (M = Mn, Fe, Co, Ni, Zn) whose two possible ligand conformations[24,25] are reminiscent of the "partial cone" (type A) and "cone" conformations (type B) of the calixarenes (Figure 1).[26] The coligands (L') include Cl^-,[27] OH^-,[28] NO_2^-, NO_3^-, N_3^-, N_2H_4,[29] carboxylates,[30–34] HCO_3^-, $H_2PO_4^-$,[30] ClO_4^-, ReO_4^-, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-},[35] alkylcarbonates ($ROCO_2^-$),[25,20] alkyl carbamates ($RNCO_2^-$),[36] and some five-membered N heterocycles.[37] Recently, we have reported the stabilization of quite reactive and unusual species such as $[Ni_2L(BH_4)]^+$,[38] and $[Co^{II}_2L(MoO_3OMe)]$.[39] As part of this program, we sought to extend our exploration to the syntheses of nickel complexes incorporating hydrosulfide (HS^-) coligands. Our motivation was 5-fold: (a) hydrosulfide complexes of labile transition-metal ions are rather scarce,[40–44] (b) the hydrosulfide ion is a biologically relevant molecule,[45] (c) nickel sulfur bonding is of importance in bioinorganic[46–48] and biomimetic chemistry,[49–57] (d) the chemistry of SH^- containing complexes is of relevance to metal sulfide hydrosulfurization catalysts,[58–60] and (e) coligands with "soft" donor atoms have not been incorporated in the binding pocket of the $[M^{II}_2L]^{n+}$ complexes.

A general problem associated with the preparation of hydrosulfide complexes is further aggregation which leads to the formation of polynuclear sulfido complexes and eventually to insoluble metal sulfides. Herein we demonstrate that the sterically demanding supporting ligand L^{2-} enables the isolation and characterization of the stable hydrosulfide

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complex $[Ni_2L(\mu\text{-}SH)]^+$ (**4**). A tetranuclear nickel(II) complex $[\{Ni_2L\}_2(\mu\text{-}S_6)]^{2+}$ (**6**) bearing a helical μ_4-hexasulfide ligand is also described as are results of temperature-dependent magnetic susceptibility measurements on **4**·BPh_4 and **6**·$(BPh_4)_2$.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk-line (Ar) techniques. Reagent grade solvents were used throughout. Melting points were determined in open glass capillaries and are uncorrected. Infrared spectra were recorded on a Bruker TENSOR 27 FT-IR-spectrometer. UV/vis spectra of solutions were measured on a Jasco 670 UV/vis/near spectrometer in the range 250−1600 nm at ambient temperatures. Elemental analyses were carried out with a VARIO EL elemental analyzer. The temperature-dependent magnetic susceptibility measurements were carried out on a SQUID magnetometer (MPMS 7XL Quantum Design) over the temperature range 2−300 K in an external magnetic field of 0.5 T. The experimentally determined susceptibility data were corrected for the underlying diamagnetism using Pascal's constants.

Starting Materials. The complexes $[Ni_2L(Cl)]ClO_4$ (**1**·ClO_4),[27] $[Ni_2L(BH_4)]ClO_4$ (**3**·ClO_4),[38] and $[Ni_2L(ClO_4)]ClO_4$ (**5**·ClO_4)[35] were prepared according to literature procedures. All other reagents were obtained from standard commercial sources and used without further purifications.

CAUTION! Perchlorate salts are potentially explosive and should therefore be prepared only in small quantities and handled with appropriate care.

$[Ni_2L(\mu\text{-}SH)]BPh_4$ (4·BPh_4). Method A. To a solution of $[Ni_2L(BH_4)]ClO_4$ (90 mg, 0.10 mmol) in acetonitrile (30 mL) was added a solution of elemental sulfur (3.2 mg, 0.10 mmol) in acetonitrile (10 mL), to produce a rapid color change from green to yellow-brown. The mixture was stirred for 1 h, $NaBPh_4$ (342 mg, 10.0 mmol) in MeOH (10 mL) was added, and the resulting solution concentrated to about half of its original volume. After standing for 2 days brown-yellow crystals of $[Ni_2L(SH)]BPh_4$ were collected by filtration. Yield: 80 mg (70%). M.p.: 244−245 °C. IR (KBr disk): ν = 2552 (vw, ν(SH)), 734 (s, $\nu(BPh_4^-)$), 705 cm^{-1} (s, $\nu(BPh_4^-)$). UV/vis(CH_3CN): λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$): 274 (16921), 304 (sh, 13080), 330 (10158), 662 (34), 1178 (53). ESI-MS (CH_3CN): m/z (rel. intensity) = 392.16 (60, $[Ni_2L]^{2+}$), 412.68 (100, $[Ni_2L(NCMe)]^{2+}$). Elemental analysis calcd (%) for $C_{62}H_{85}BN_6Ni_2S_3$ (1138.77): C 65.39, H 7.52, N 7.38, S 8.45; found: C 65.20, H 7.28, N 7.62, S 8.22.

Method B. A solution of Na_2S·$9H_2O$ (48 mg, 0.200 mmol) in methanol (5) was added to a green solution of $[Ni_2L(ClO_4)]ClO_4$ (99 mg, 0.100 mmol) in acetonitrile (40 mL). The mixture was stirred 3 h during which it became yellow-brown. A solution of $LiClO_4$·$3H_2O$ (160 mg, 1.00 mmol) was added and stirring was continued for another 2 h. The resulting precipitate of **4**·ClO_4 was filtered, washed with 2 mL of cold methanol and dried under vacuum. Yield: 71 mg % (77%). 303−304 °C (decomp). IR (KBr disk): ν = 2552 (vw, ν(SH)), 1094 (vs, $\nu_3(ClO_4^-)$), 627 cm^{-1} (s, $\nu_4(ClO_4^-)$). UV/vis(CH_3CN): λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$): 274 (16010), 301 (sh, 14138), 331 (10080), 663 (32), 1175 (49). Adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **4**·ClO_4 (92 mg, 0.10 mmol) in MeOH (50 mL) provides, after filtration, recrystallization, and drying under vacuum, 96 mg (84%) of **4**·BPh_4. The analytical data of this material are identical to that of the compound prepared by method A.

Table 1. Crystallographic Data for **4**·BPh_4·MeOH·$2H_2O$ and **6**·$(BPh_4)_2$·5MeCN

	4·BPh_4·MeOH·$2H_2O$	**6**·$(BPh_4)_2$·5MeCN
formula	$C_{63}H_{93}BN_6Ni_2O_3S_3$	$C_{134}H_{183}B_2N_{17}Ni_4S_{10}$
fw	1206.84	2609.03
space group	$P\bar{1}$	$P\bar{1}$
A (Å)	15.685(2)	15.8270(7)
B (Å)	16.161(2)	16.9597(7)
C (Å)	16.750(2)	26.675(2)
α (deg)	64.79(1)	100.618(7)
β (deg)	72.16(1)	99.450(8)
γ (deg)	66.73(1)	92.910(5)
V (Å^3)	3479.7(6)	6917.7(7)
Z	2	2
$D_{calcd.}$, (g/cm^3)	1.152	1.253
μ (mm^{-1})	0.675	0.740
$R1^a$ ($R1$ all data)	0.0561 (0.0809)	0.0567 (0.1222)
$wR2^b$ ($wR2$ all data)	0.1585 (0.1687)	0.1244 (0.1400)
max, min peaks, e$^-$/Å^3	1.609/−2.193	0.472/−0.361

^{a} $R1 = \Sigma|\,|F_o| - |F_c|\,|/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

$[\{Ni^{II}_2L\}_2(\mu\text{-}S_6)](BPh_4)_2$ (6·$(BPh_4)_2$). To a solution of $[Ni_2L(BH_4)]ClO_4$ (90 mg, 0.10 mmol) in acetonitrile (30 mL) was added a solution of elemental sulfur (9.6 mg, 0.30 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 30 min during which time the color turned from green to yellow-brown. Solid $LiClO_4$·$3H_2O$ (160 mg, 1.00 mmol) was added. The solution was concentrated to about 7−10 mL. The resulting orange-yellow solid was filtered, washed with cold ethanol, and dried in air. Yield: 62 mg (63% based on $[Ni_2L(BH_4)]ClO_4$). M.p.: 336−337 °C (decomp.). IR (KBr disk): ν = 1091 (vs, $\nu_3(ClO_4^-)$), 625 (s, $\nu_4(ClO_4^-)$), 468 (w, ν(SS)), 440 cm^{-1} (w, ν(SS)). UV/vis(CH_3CN): λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$) = 265 (18038), 304 (13710), 337 (8184), 647 (56), 1102 (72). The tetraphenylborate salt was prepared by salt-metathesis. To a solution of **6**·$(ClO_4)_2$ (196 mg, 0.100 mmol) in MeOH was added a solution of $NaBPh_4$ (342 mg, 1.00 mmol) in methanol (10 mL), and the resulting suspension was stirred for 2 h. The solid was filtered, washed with ethanol, and recrystallized from methanol/acetonitrile to give 180 mg (75%) of orange-colored crystals. M.p.: 231−232 °C (decomp.). IR (KBr): ν = 733 (s, $\nu(BPh_4^-)$), 704 (s, $\nu(BPh_4^-)$), 468 (vw, ν(SS)), 445 cm^{-1} (vw, ν(SS)). UV/vis(CH_3CN): λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$): 265 (24962), 273 (22884), 298 (17973), 335 (sh, 10742), 649 (58), 1105 (60). Elemental analysis calcd (%) for $C_{124}H_{168}B_2N_{12}Ni_4S_{10}$ (2403.8): C 61.96, H 7.04, N 6.99, S 13.34; found: C 61.71, H 7.23, N 6.69, S 13.09.

X-ray Crystallography. Crystals of **4**·BPh_4·MeOH·$2H_2O$ and **6**·$(BPh_4)_2$·5MeCN were both obtained by slow evaporation of a mixed methanol/acetonitrile solution. Crystal data and collection details are reported in Table 1.

The data sets were collected at 213(2) K using a STOE IPDS-2T diffractometer. Graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used throughout. The data were processed with the program STOE X-AREA.[61] Structures were solved by Direct Methods and refined by full-matrix least-squares with SHELXL-97 on the basis of all data using F^2.[62] H atoms were placed in calculated positions and treated isotropically using the 1.2-fold U_{iso} value of the parent atom except the methyl protons, which were assigned the 1.5-fold U_{iso} value of the parent C atoms. All non-hydrogen atoms were refined anisotropically. In the crystal structure of **4**·BPh_4·MeOH·$2H_2O$, one t-Bu group was found to be rotationally disordered over two sites. In the crystal structure of

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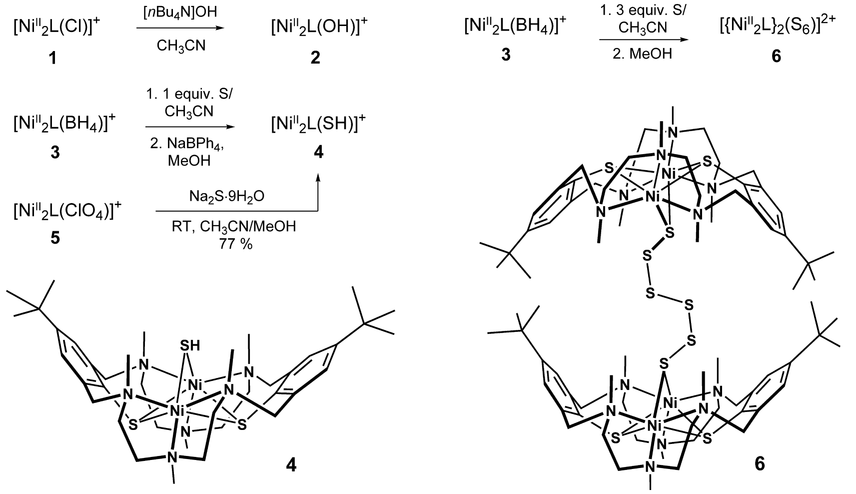
(61) *X-AREA*; Stoe & Cie: Darmstadt, Germany, 2001.

(62) Sheldrick, G. M. *SHELXL-97 Computer program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1. Preparation of Complexes **4** and **6**.



$6\cdot(BPh_4)_2\cdot5MeCN$, the S_6^{2-} group is also disordered over two sites. The disorder was modeled by using split atom models to give site occupancies of 0.71(1)/0.29(1) for the two *t*-Bu group orientations in **4** and 0.92(1)/0.08(1) for the two S_6^{2-} orientations in **6**, respectively. Drawings were produced with Ortep-3 for Windows.[63]

Results and Discussion

Synthesis and Characterization of Compounds. The synthetic procedures are depicted in Scheme 1. Initial attempts aimed at the synthesis of the hydrosulfide complex $[Ni_2L(SH)]^+$ (**4**) followed the method of preparing the hydroxide complex $[Ni_2L(OH)]^+$ (**2**) from $[Ni_2L(Cl)]^+$ (**1**) and $(n\text{-}Bu_4N)OH$,[27] but surprisingly, **1** proved to be substitutionally inert in reactions with $Na_2S\cdot9H_2O$ or $(Et_4N)SH$.[64] The reduction of elemental sulfur by the borohydride complex $[Ni^{II}_2L(BH_4)]^+$ (**3**)[38] was sought as an alternative procedure. Indeed, when green $\mathbf{3}\cdot ClO_4$ was treated with 1 equiv of S powder in CH_3CN, a yellow-brown solution forms immediately, and the desired hydrosulfide complex **4** can be isolated from methanol as a brown-yellow ClO_4^- salt in >70% yields. This reaction presumably involves thioborate/polysulfide intermediates (as in the $LiBH_4/S_8$ system)[65,66] which hydrolyze during workup to produce hydrosulfide anions which are trapped by the $[Ni^{II}_2L]^{2+}$ fragment. It should be noted that complex **4** is also obtained, in similarly high yields, from reactions in acetonitrile of the extreme labile perchlorato complex $[Ni_2L(ClO_4)]ClO_4$ ($\mathbf{5}\cdot ClO_4$) with 1 equiv of $Na_2S\cdot9H_2O$, followed by workup from methanol.

That polysulfide ions are indeed involved in these transformations was confirmed by the isolation of the hexasulfide complex $[\{Ni_2L\}_2(\mu\text{-}S_6)](BPh_4)_2$ ($\mathbf{6}\cdot(BPh_4)_2$). This material could be reproducibly obtained in yields as high as 70% when elemental sulfur is reacted with $\mathbf{3}\cdot ClO_4$ in MeCN in a 3:1 molar ratio followed by workup from wet methanol as indicated in Scheme 1. At larger (4:1) or smaller (2:1) S/**3** ratios a yellow-brown solid of unknown composition precipitates.

Table 2. Selected UV/Vis Data for Complexes **1**−**7**

complex	coligand	ν_2/nm	ν_1/nm	Δ_o/cm^{-1}	ref
1[a]	Cl^-	658 (41)	998 (67)	10020	27
2[a]	OH^-	655 (52)	1056 (40)	9470	30
3[a]	BH_4^-	650 (43)	1074 (77)	9311	38
4[b]	SH^-	663 (32)	1175 (49)	8511	this work
5[b]	ClO_4^-	578 (129)	1066 (86)	9381	38
6[b]	S_6^{2-}	647 (56)	1102 (72)	9074	this work
7[a]	SPh^-	667 (52)	1141 (68)	8764	69

[a] Data refer to the BPh_4^- salts. [b] Data refer to the ClO_4^- salts.

The complexes **4** and **6** are stable for weeks in the absence of air and protic reagents both in the solid state and in solution. This stability is quite remarkable given that hydrosulfide complexes of sterically less demanding ligands are readily transformed into polysulfides or metal sulfides.[43] In the presence of air the yellow-brown color of solutions of **4** and **6** fades away within about 24 h and green products of unknown compositions precipitate. The new compounds gave satisfactory elemental analyses and were characterized by spectroscopic methods (IR, UV/vis), and X-ray crystallography.

The ESI-MS of a freshly prepared acetonitrile solution of **4** shows two nickel-containing fragments at $m/z = 472.68$ and 412.68 neither of which is the parent peak. The infrared spectrum of $\mathbf{4}\cdot BPh_4$ in KBr shows a weak sharp ν(SH) band at 2552 cm^{-1} typical for complexes with SH^- groups.[67] For $\mathbf{6}\cdot(BPh_4)_2$ two weak IR bands appeared at 468 and 440 cm^{-1}, attributable to the S−S stretching modes of the S_6^{2-} unit. These values agree well with those reported for K_2S_6 and other compounds with a S_6^{2-} unit.[68] Electronic absorption spectra for $\mathbf{4}\cdot ClO_4$ and $\mathbf{6}\cdot(ClO_4)_2$ were registered in acetonitrile solution in the 250−1600 nm range. The data are collected in Table 2. Absorption data for other $[Ni_2L(L')]^+$ complexes relevant to the present study have been included for comparative purposes.

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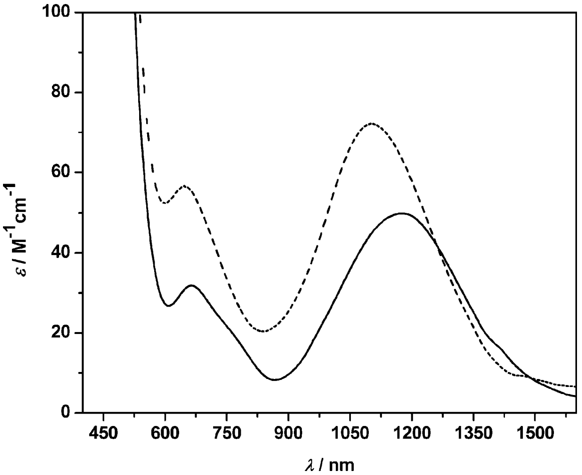

Figure 2. UV/vis spectra of $4\cdot ClO_4$ (solid line) and $6\cdot(ClO_4)_2$ (dashed line) in CH_3CN at room temperature. Concentrations: ca. 1×10^{-3} M.

Both complexes feature three intense absorption maxima in the UV at ~270 nm, ~300 nm, and 330 nm (not shown in Figure 2). These are characteristic for nickel complexes of L^{2-}. The former two can be attributed to π-π* transitions within the aromatic rings of the supporting ligand whereas the latter corresponds to a thiophenolate → Ni^{II} charge transfer absorption. Unfortunately, the ligand-to-metal charge transfer (LMCT) bands involving the SH^- and S_6^{2-} groups are not resolved.

Above 500 nm complex **4** exhibits two weak absorption bands at 663 and 1175 nm which 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.[70] The corresponding values for **6** are significantly blue-shifted to 647 and 1102 nm, respectively. The $^3A_{1g} \rightarrow {}^3T_{1g}$ (P) transition (expected below 400 nm) is obscured in each case by the strong LMCT transitions. From the ν_1 transition one can obtain rough estimates of the octahedral splitting parameters Δ_{oct} for **4** (≈8511 cm^{-1}) and for **6** (≈9074 cm^{-1}), respectively. Such low values for Δ_{oct} (i.e., Δ_{oct} (**4**, **6**) < $\Delta_{oct}[Ni(H_2O)_6]^{2+} = 8500$ cm^{-1}) are quite typical for $N_3Ni^{II}(\mu\text{-}SR)_3$ chromophores.[71] In general, thiolates induce only weak ligand field strengths because of their poor σ-donor bonding abilities. The same is true for the SH^- and S_6^{2-} ligands as indicated by the data in Table 2. **4** and **6** have the lowest Δ_{oct} values. In Table 2 are also included preliminary characterization data for the $[Ni^{II}_2L(\mu\text{-}SPh)]^+$ complex **7**.[69] The Δ_{oct} value for this complex (8764 cm^{-1}) lies between the values of **4** and **6**. On the basis of these data, the σ-donor bonding ability of the SR^- groups can be ranked as follows: $S_6^{2-} > SPh^- > SH^-$.

Table 3. Selected Bond Lengths (Å) for Complexes **4** and **6**

	4	**6**[a]
Ni(1)−S(3)/S(8)	2.532(1)	2.499(2) [2.494(1)]
Ni(1)−N(1)	2.255(3)	2.316(6) [2.211(6)]
Ni(1)−N(2)	2.179(3)	2.168(7) [2.171(4)]
Ni(1)−N(3)	2.373(3)	2.277(5) [2.378(8)]
Ni(1)−S(1)	2.4836(9)	2.495(2) [2.538(2)]
Ni(1)−S(2)	2.490(1)	2.481(2) [2.506(2)]
Ni(2)−S(3)/S(8)	2.521(1)	2.461(1) [2.460(2)]
Ni(2)−N(4)	2.316(4)	2.294(6) [2.250(8)]
Ni(2)−N(5)	2.190(3)	2.199(4) [2.177(7)]
Ni(2)−N(6)	2.339(3)	2.323(7) [2.378(6)]
Ni(2)−S(1)	2.456(1)	2.521(2) [2.501(2)]
Ni(2)−S(2)	2.4858(9)	2.509(2) [2.509(2)]
Ni−N[b]	2.275(4)	2.263(6) [2.261(7)]
Ni−S[b]	2.495(1)	2.494(2) [2.501(2)]
Ni···Ni	3.295(1)	3.348(1) [3.364(1)]

[a] Values in square brackets correspond to the second $[Ni_2L]^{2+}$ subunit. [b] Average values.

Table 4. Selected Bond Angles [deg] in **1**, **2**, **4**, and **6**

	1, X = Cl^-	**2**, X = OH^-	**4**, X = SH^-	**6**[a], X = S(3), S(8)
M−X−M	81.02(6)	93.3(3)	81.40(3)	85.21(6)
M−S−M	81.94(6)	76.96(9)	83.31(3)	84.0(6)
S−M−S	79.66(6)	82.15(9)	83.55(3)	82.83(6)
S−M−X^{cis}	82.54(7)	80.73(2)	79.81(3)	78.09(6)
N−M−N	87.4(2)	87.9(3)	85.7(1)	86.2(3)
N−M−S^{cis}	97.09(2)	95.98(2)	94.07(9)	93.8(2)
N−M−X^{cis}	93.86(2)	95.05(3)	101.53(9)	102.9(2)
N−M−S^{trans}	170.33(2)	172.78(2)	172.65(9)	172.0(2)
N−M−X^{trans}	163.8(2)	166.9(2)	177.34(9)	171.6

[a] Average values for the two $[Ni_2L]^{2+}$ subunits in **6**.

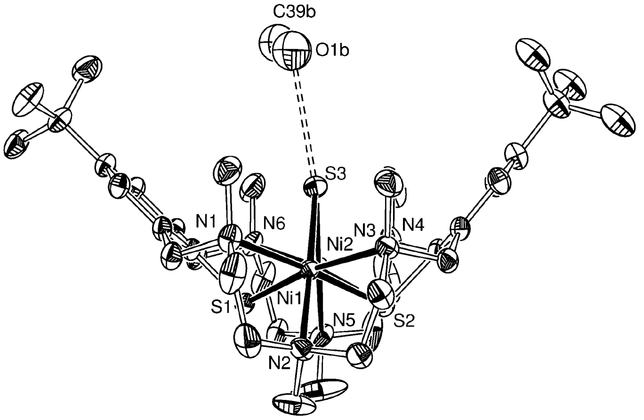

Figure 3. Structure of the hydrosulfide complex **4** in crystals of $4\cdot BPh_4\cdot MeOH\cdot 2H_2O$. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. The dashed line indicates a hydrogen bond between the SH moiety and the MeOH solvate molecule (S(3)···O(1b) 3.285 Å).

Description of Crystal Structures. The structures of complexes **4** and **6** were further substantiated by X-ray crystallography. Data collection and processing parameters are given in Table 1, selected bond lengths and angles in Tables 3 and 4. The atomic numbering scheme used for the central $N_3Ni(\mu\text{-}S)_3NiN_3$ core in **4** was also applied for **6** to facilitate structural comparisons.

$[Ni_2L(SH)]BPh_4\cdot MeOH\cdot 2H_2O$ ($4\cdot BPh_4\cdot MeOH\cdot 2H_2O$). This structure determination unambiguously confirmed the presence of the cationic hydrosulfide complex $[Ni_2L(\mu\text{-}SH)]^+$ (Figure 3). Although the SH hydrogen atom could not be located from difference Fourier electron density maps, its presence is implied by IR spectroscopy and charge consid-

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(69) Preliminary data of the crystal structure determination of $7\cdot BPh_4\cdot MeCN\cdot EtOH$: triclinic, space group $P\bar{1}$, $a = 15.953(3)$ Å, $b = 16.263(3)$ Å, $c = 16.398(3)$ Å, $\alpha = 63.81(3)°$, $\beta = 72.76(3)°$, $\gamma = 66.62(3)°$ Å, $V = 3465.9(2)$ Å^3, $Z = 2$, μ(Mo Ka) = 0.68 mm^{-1}, R1 = 0.0523 for 9571 $I > 2\sigma I$. Complex **7** is of type B. Its preparation and crystal structure will be reported in more detail in a subsequent paper.

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erations (assuming the presence of one dianionic L^{2-}, one BPh_4^-, one SH^-, and two Ni^{2+} ions). There is also a MeOH solvate molecule that lies in the vicinity of the SH unit ($S\cdots O^{MeOH}$ 3.285 Å) indicative of a weak $SH\cdots O^{MeOH}$ hydrogen bond.[72,73]

Unlike in isoelectronic $[Ni_2L(\mu\text{-}Cl)]^+$ (**1**) or in $[Ni_2L(\mu\text{-}OH)]^+$ (**2**), the macrocycle adopts the bowl-shaped conformation B as observed in $[Ni_2L(\mu\text{-}ClO_4)]^+$ (see Figure 1 for a schematic representation of the two conformations).[35] The presence of the type B conformation of L^{2-} in **4** presumably relates to the larger ionic radii of the SH^- group (OH^-: 1.19 Å, Cl^-: 1.67 Å, SH^- 1.93 Å).[74] Previous work has shown that the conformation of L^{2-} is coupled to the size of the coligand L′ in the $[Ni_2L(L')]^+$ complexes.[29,75] L^{2-} adopts the bowl-shaped conformation when L′ is large, the driving force being the more regular octahedral coordination environment about the Ni^{2+} ions. Similar arguments can be used to explain the different structures of **1**, **2**, and **4** (which bear all single-atom bridging ligands). Thus, upon going from the μ-OH complex **2** to the μ-Cl complex **1** the macrocycle maintains conformation A and the deviations of the L−M−L angles from the ideal values increase; particularly affected are the $N-M-X^{trans}$ angles. On the other hand, upon going from **2** to the SH complex **4**, L changes its conformation and the NiN_3S_3 polyhedra become more regular.

A number of dinuclear nickel complexes with $\mu\text{-}SR^-$ groups have been reported in the literature.[76,77] Pohl has reported a dinickel complex with two bridging SH groups.[78] As far as we are aware, **4** is the first dinickel complex with a single μ-SH group. The average Ni-SR(thiolate) bond length of 2.479(1) Å in **4** is quite typical for six-coordinate Ni^{II} thiolate complexes. For example, the Ni-μ-SPh bonds in the octahedral complexes $[Ni(\mathit{terpy})(\mu\text{-}SPh)_2]_2\cdot 6MeOH$[79] and $[Ni_2L(OAc)]BPh_4$[80] are 2.465(2) Å and 2.471(1) Å long, respectively. However, the Ni-μ-SH distances in **4** (mean 2.527(1) Å) are significantly longer than the Ni-μ-SR(thiolate) bonds. This is in good agreement with the notion that the SH^- ligands are weaker σ-donors than thiophenolates. It should be noted that the $Ni\cdots Ni$ distance in **4** at 3.295(1) Å is quite long for complexes containing face-sharing $N_3Ni(\mu\text{-}SR)_3NiN_3$ structures. In the trinuclear complexes $[\{Ni_2L''\}_2Ni]^+$ and $[\{Ni_2L''\}_2Ni]^{2+}$ (L″ = octadentate N_3S_3 ligand), the nickel atoms are separated by only 3.008(2) and 3.029(1) Å.[81] Likewise, for $[Ni_2L'''_3]^{2+}$ (L‴ = tridentate N_2S ligand) the $Ni\cdots Ni$ distance is 3.064(1) Å.[82] The Ni−S−Ni angles in these complexes range from 78.9 to 80.16° and are thus more obtuse than in **4** (83.3−81.4°).

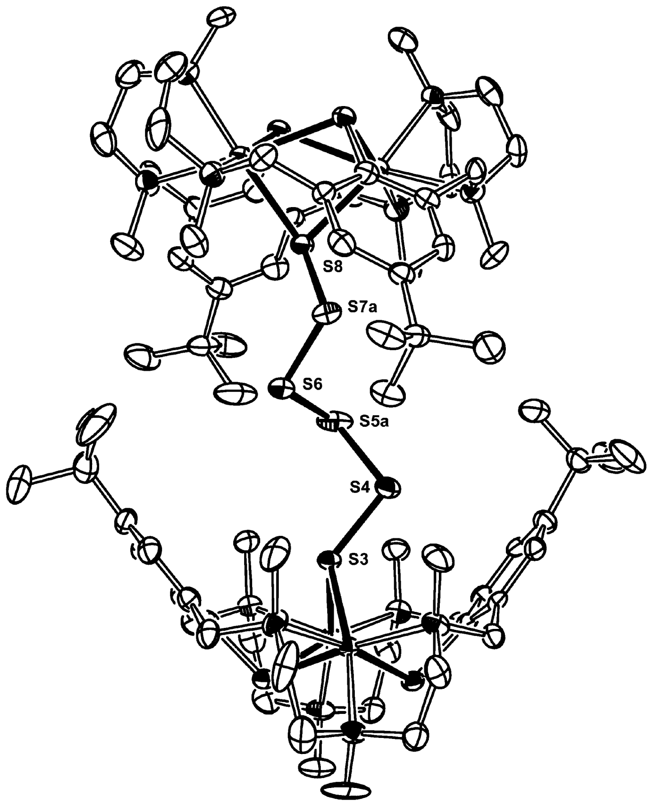

Figure 4. Structure of the $[\{Ni_2L\}_2(\mu\text{-}S_6)]^{2+}$ dication in crystals of **6**$\cdot(BPh_4)_2\cdot 5MeCN$. Thermal ellipsoids are drawn at the 30% probability level. Only one orientation of the disordered S_6^{2-} unit is displayed. Hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: S(3)−S(4) 2.076(2), S(4)−S(5a) 2.037(4), S(5a)−S(6) 2.083(3), S(6)−S(7A) 2.065(2), S(7A)−S(8) 2.063(3); S(3)−S(4)−S(5A) 103.8(1), S(4)−S(5A)−S(6) 107.5(1), S(5A)−S(6)−S(7A) 106.7(1), S(6)−S(7A)−S(8) 104.3(1); S(3)−S(4)−S(5A)−S(6) 76.4, S(4)−S(5A)−S(6)−S(7A) 94.3, S(5A)−S(6)−S(7A)−S(8) 83.6.

$[\{Ni_2L\}_2(S_6)]\cdot(BPh_4)_2\cdot 5MeCN$ (6(BPh$_4$)$_2\cdot$5MeCN). This salt crystallizes in the triclinic space group $P\bar{1}$. The structure consists of discrete tetranuclear $[\{Ni_2L\}_2(\mu\text{-}S_6)]^{2+}$ dications, tetraphenylborate anions, and acetonitrile solvate molecules. Figure 4 provides an ORTEP view of the structure of **6**. Two dinuclear $[Ni_2L]$ subunits are linked via a helical S_6^{2-} chain. Again, both $[Ni_2L]^{2+}$ subunits feature a bowl-shaped conformation for reasons likely to be similar to those detailed above for **4**. The average S−S bond length is 2.065(2) Å, and the dihedral S−S−S−S angles range from 76.4 to 94.3°. Similar values are observed in plastic sulfur[83] and other S_6^{2-} systems.[84–89]

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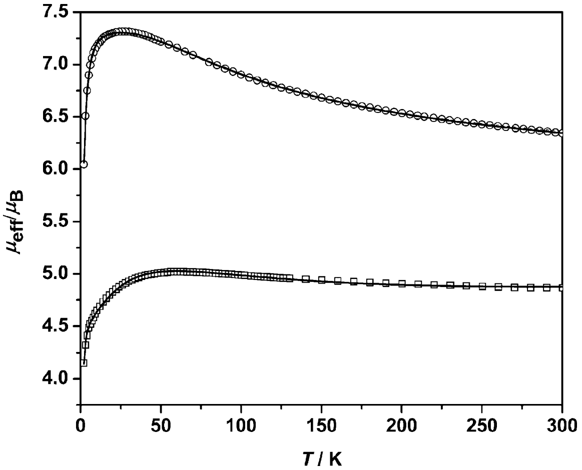

Figure 5. Temperature dependence of μ_{eff} for **4**·BPh_4 (open squares) and **6**·$(BPh_4)_2$ (open circles). The full lines represent the best theoretical fits to eqs 1 and 2. Experimental and calculated values are provided as Supporting Information.

It should be noted that the Ni-μ-S_6 bond lengths in **6** (mean 2.479(2) Å) are significantly shorter than the Ni-μ-SH bonds in **4** averaging 2.527(1) Å, an observation that correlates nicely with the stronger σ-bonding ability of the S_6^{2-} ion (vide infra). There are no unusual features as far as bond lengths and angles of the $[Ni_2L]^{2+}$ units are concerned. The average Ni−N (2.262(7) Å) and Ni−S (2.498(2) Å) bond lengths in **6** are similar to the values of the compound above. There are no significant intermolecular interactions between the Ni^{II}_4 complexes within the lattice. The shortest intermolecular Ni···Ni distance is at 7.711(1) Å. The present coordination mode of the S_6^{2-} dianion linking two binuclear $N_3Ni(\mu\text{-}SR)_3NiN_3$ cores is also without precedence in the literature.

Magnetic Properties of Complexes 4·BPh_4 and 6·$(BPh_4)_2$. Temperature-dependent magnetic susceptibility measurements for **4**·BPh_4 and **6**·$(BPh_4)_2$ were carried out to establish whether magnetic exchange interactions are present in these complexes. The temperature dependent susceptibility data for dry, powdered samples of the two complexes have been measured between 2.0 and 300.0 K by using a SQUID magnetometer in an applied external magnetic field of 0.5 T. The results are shown in Figure 5 in the form of μ_{eff} versus T plots.

For **4**·BPh_4, the effective magnetic moment (per dinuclear complex) increases from 4.86 μ_B at 300 K to a maximum value of 5.02 μ_B at 60 K, and then decreases to 4.15 μ_B at 2.0 K. Overall, this behavior indicates an intramolecular ferromagnetic exchange interaction between the two Ni^{II} ions that leads to an $S = 2$ ground-state of the hydrosulfide complex **4**. The decrease in μ_B at low temperatures is indicative of zero-field splitting of Ni^{II}. The effective magnetic moment of the tetranuclear complex **6**·$(BPh_4)_2$ also increases with decreasing temperature, reaching a maximum value of 7.32 μ_B at 28 K and then decreases again to 6.05 μ_B at 2.0 K. The value of μ_B at 28 K is in between a value of 9.84 μ_B calculated for an $S_T = 4$ ground-state resulting from the ferromagnetic coupling of four Ni^{II} ions ($S_i = 1$, $g_i = 2.20$) and a value of 6.22 μ_B for four noninteracting Ni^{II} ions. This behavior indicates the presence of weak ferromagnetic exchange interactions between the Ni^{II} ions in the binuclear $[Ni_2L]^{2+}$ entities and negligible coupling across the S_6^{2-} bridge. The former presumption is in good agreement with the results obtained for **4**, while the latter is not surprising in view of the long interdimer Ni···Ni distances ranging from 10.689 to 11.218 Å.

We tried to simulate the temperature dependence of the magnetic data of complex **4**·BPh_4 using the appropriate spin-Hamiltonian (eq 1)[90] which contains a Zeeman and a zero-field splitting term by using a full-matrix diagonalization approach. The introduction of a D parameter is appropriate for octahedral Ni^{II}, since the noncubic components of the ligand field may act on the $^1A_{2g}$ ground-state to produce a zero-field splitting which may be of the same order of magnitude as J.[91,92]

$$H = -2JS_1S_2 + \sum_{i=1}^{2}[D_i(\hat{S}_{iz}^2 - \frac{1}{3}S_i(S_i+1)) + g_i\mu_B B_\tau \hat{S}_{i\tau}] \quad (\tau = x, y, z) \qquad (1)$$

By taking into account the zero-field splitting and a small fraction ρ (0.035%) of a paramagnetic impurity with $S = 1$,[93] a good fit of the experimental data, shown in Figure 5 as a solid line, was possible over the full temperature range, yielding $J = +18$ cm^{-1}, $g = 2.23$, and $D = -82$ cm^{-1}. The latter value should be taken as indicative rather than definite, because temperature dependent magnetic susceptibility measurements are not very appropriate for the determination of D.[94,95] Nethertheless, J is not influenced markedly by the value of D and represents an accurate measure of the magnetic coupling in this complex. The J and g values determined for **4**·BPh_4 are quite typical for dinuclear nickel complexes supported by L^{2-} (e.g., $J = +6.7$ cm^{-1} for $[Ni^{II}_2L(NO_2)]^+$,[29] $J = +7.9$ cm^{-1} for $[Ni^{II}_2L(OAc)]^+$,[29] and $J = +27.0$ cm^{-1} for $[Ni^{II}_2L(BH_4)]^+$ [38]).

The magnetic susceptibility data for **6**·$(BPh_4)_2$ were analyzed by the spin-Hamiltonian in eq 2,[34] where J_1 and J_2 represent the intra- and interdimer exchange interactions in tetranuclear **6**. The D and g values were considered to be identical for all of the four Ni^{2+} ions. Notice that D represents an effective zero-field splitting parameter, since the zero-field splitting tensors of all ions are assumed to be colinear.

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$$H = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - 2J_2(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) + \sum_{i=1} [D_i(\hat{S}_{iz}^2 - \frac{1}{3}S_i(S_i + 1)) + g_i\mu_B S_{i\tau}B_\tau] \quad (\tau = x, y, z) \tag{2}$$

An excellent fit was obtained yielding $J_1 = +23$ cm^{-1}, $J_2 = 0$ cm^{-1}, $g = 2.12$, and $D = -8.5$ cm^{-1}. Again, the inclusion of the D parameter improves the low-temperature fit significantly, but it represents by no means an accurate value. Nevertheless, this analysis establishes clearly that magnetic exchange interactions via the hexasulfide moiety are not significant. The magnetic properties of complex **6** are solely based on the exchange couplings in the binuclear $[\mathrm{Ni_2L(SR)}]^+$ subunits.

There are not many examples of compounds reported in the literature which can be compared to the magnetic properties of **4** and **6**. The magnetic properties of two relevant linear trinuclear compounds $[\mathrm{L''Ni^{II}Ni^{II}Co^{III}L''}]$ (**8**) and $[\mathrm{L''Ni^{II}Ni^{II}Ni^{II}L''}]$ (**9**) containing triply thiophenolato-bridged $\mathrm{Ni^{II}}$ ions have been reported.[80] In complex **8** with a $\mathrm{N_3Ni^{II}S_3Ni^{II}S_3Co^{III}N_3}$ core a strong intramolecular antiferromagnetic exchange interaction is observed ($J = -61$ cm^{-1}). Similarly, for **9**, with a central $\mathrm{N_3Ni^{II}S_3Ni^{II}S_3Ni^{II}N_3}$ core, the electron spins on adjacent $\mathrm{Ni^{II}}$ ions couple antiferromagnetically ($J = -28$ cm^{-1}). In tris(μ-phenolato)-bridged complexes[71,96] or $\mathrm{Ni_3(acac)_6}$,[97] on the other hand, parallel spin alignment occurs. The change of the coupling type from antiferromagnetic in **8** and **9** to ferromagnetic in **4** and **6** may be traced to the widening of the Ni−S−Ni angles (average Ni−S−Ni for **4**: 82.7(1)°, **6**: 84.4°, **8**, **9** < 80°, [71]). The larger J value determined for **6** would be consistent with this in view. To date, a magneto-structural correlation for face-sharing bioctahedral $\mathrm{Ni^{II}_2}$ complexes has not appeared in the literature.

Conclusions

The main findings of the present work can be summarized as follows: (a) the steric protection−offered by the supporting ligand $\mathrm{L^{2-}}$ allows for the preparation and isolation of stable hydrosulfide complexes of labile transition metal ions; (b) the $[\mathrm{Ni_2L(BH_4)}]^+$ complex reacts rapidly with elemental sulfur and represents a versatile starting material for $[\mathrm{Ni_2L(\mu\text{-}SH)}]^+$; (c) polysulfide complexes such as $[\{\mathrm{Ni_2L}\}_2(\mu\text{-}\mathrm{S_6})]^{2+}$ are also accessible from $[\mathrm{Ni_2L(BH_4)}]^+$ and $\mathrm{S_8}$; (d) unlike in $[\mathrm{Ni_2L(\mu\text{-}Cl)}]^+$ (**1**) or in $[\mathrm{Ni_2L(\mu\text{-}OH)}]^+$ (**2**), the larger $\mathrm{SH^-}$ and $\mathrm{S_6^{2-}}$ ions induce the bowl-shaped macrocycle conformation of type B; (e) the SH and $\mathrm{S_6^{2-}}$ ions groups are characterized by their poor σ-donor bonding abilities; (f) **4** and **6** feature wider Ni−S−Ni angles than other $\mathrm{N_3Ni^{II}(SR)_3Ni^{II}N_3}$ structures. As a consequence, the orthogonality of the magnetic orbitals is not canceled and ferromagnetic pathways become available to produce a change of the sign of J; (g) magnetic exchange interactions via the hexasulfide moiety in **6** are insignificant. The magnetic properties of complex **6** are solely based on the exchange couplings in the binuclear $[\mathrm{Ni_2L(SR)}]^+$ subunits.

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Supporting Information Available: X-ray crystallographic data in CIF format. Derivation of the magnetic susceptibility expression for **4**·$\mathrm{BPh_4}$ and **6**·$\mathrm{(BPh_4)_2}$. Experimental and calculated magnetic susceptibility values (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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