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An Unsymmetrical Tripodal Ligand with NOS_2-Donor Set: Coordination Chemistry with Nickel(II) and Zinc(II)†

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The synthesis of the novel tripodal ligand $[N(CH_2CH_2CH_2OH)(CH_2CH_2SH)_2]$ H_3-**4** is reported. The aliphatic tetradentate ligand is equipped with an unsymmetrical NOS_2 donor set. It reacts with $Ni(OAc)_2 \cdot 4H_2O$ or $Zn(BF_4)_2 \cdot xH_2O$ to give the complexes $[Ni(H\text{-}4)]_2$ **5** and $[Zn(H\text{-}4)]_4$ **6**, respectively. The molecular structures of **5** and **6** have been determined by X-ray diffraction. In both cases multinuclear, μ-thiolato-bridged complexes, wherein the ligand coordinates with only three (NS_2) of the four donor groups, had formed. The dinuclear complex **5** adopts a butterfly geometry and contains nickel(II) ions in a square-planar NS_3 coordination environment. Cyclic voltammetry experiments indicate that the nickel centers in **5** are electron-rich but not overly sensitive toward oxidation. Complex **6** is tetranuclear and the four thiolato-bridged metal centers form a ring. It shows a distorted tetrahedral coordination geometry for the zinc(II) ions in an NS_3 coordination sphere. In both complexes the hydroxyl functionalized ligand arm of the tripodal ligand remains uncoordinated.

Introduction

The coordination chemistry of the metal ions in metalloproteines is dominated by amino, hydroxo, and mercapto groups of the amino acid side chains.[1] In many cases the existence of a binary N/O, O/S, or N/S coordination environment around the metal ion was demonstrated, while a ternary N/O/S coordination environment is rarely observed. Among the few examples for the latter are the nitrile hydratase[2] and the horseliver alcohol dehydrogenase.[3]

Tripodal ligands have proven useful for the modeling of active centers of metalloproteines. Besides tris(pyrazolyl)-borates[4] many symmetrical tripodal tetradentate ligands of the type $N[CH_2\text{-}(CH_2)_n\text{-}X]_3$ ($n = 1$: X = SH,[5a−d] SR,[6] NH_2,[7] NHMe, NMe_2,[8] OH;[9] $n = 2$: X = NH_2,[10] X = SH[5e]) and tripodal tris(oxime)amine ligands have been studied.[11] In addition, tripodal amine ligands of unsymmetrical topology (both C_2 and C_3 chains are present between the central nitrogen atom and X = NH_2) are known.[12] A few related

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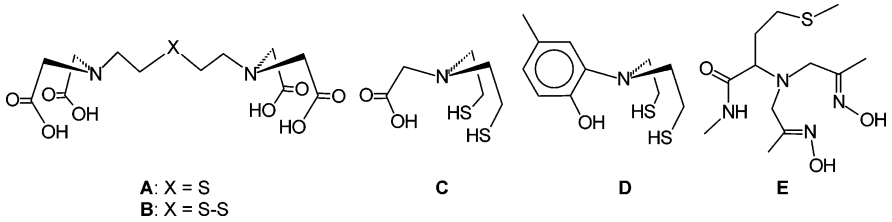

Figure 1. Ligands providing an NOS_2 donor set.

derivatives with phosphorus as central backbone atom have also been described.[13]

The substitution of the ligand arms in a tripodal ligand with different donor groups has recently attracted special interest since such derivatives are of particular interest for the modeling of unsymmetrically coordinated metal ions in the active centers of metalloproteines. Tripodal ligands of the type $CH_3C[(CH_2X)(CH_2Y)(CH_2Z)]$ (X, Y, Z = PR_2, PR'_2, NR_2, SR, and OR) have been reported by Huttner.[14] However, these ligands, some of which were prepared enantioselectively, form no mononuclear chelate complexes with all donor groups coordinated to the same metal center owing to the small size of the carbon backbone.

To our knowledge only a limited number of unsymmetrically substituted tripodal ligands with a central nitrogen donor atom and an NOS_2 donor set are known. Among the known examples are the heptadentate ligands **A** and **B**,[15] which both form dinuclear complexes, the tetradentate ligands **C**[16] and **D**,[17] and the tripod **E**[18] (Figure 1).

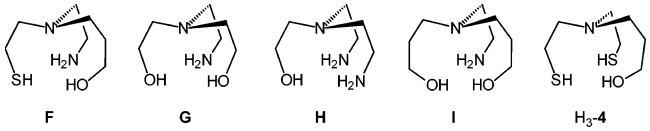

Figure 2. Topology of unsymmetrically substituted tripodal ligands.

Recently we reported on the synthesis and coordination chemistry of the tetradentate, purely aliphatic tripodal ligand **F** which is equipped with a completely unsymmetric N_2OS-donor set (Figure 2).[19] It was shown that this ligand reacts with nickel(II) to give a dinuclear complex that exhibits a remarkable reactivity toward oxygen. Aerial oxidation of the thiolate sulfur atom resulted in the unexpected formation of a sulfinate complex with an *O*,*O*-bound sulfinato group. The unusual reactivity of this complex prompted us to develop further representatives of unsymmetrically substituted aliphatic tripodal ligands. In a first study we reported on the synthesis, solution thermodynamics, and coordination chemistry of the unsymmetrically substituted ligands **G** and **H**,[20a] exhibiting N_2O_2[20b] and N_3O[20c−d] donor sets, respectively. Ligand **F** was further modified by introduction of propyl ligand arms for the *O*-donor functions, leading to ligand **I**.[21] Here we report the synthesis of the previously unknown tripodal NOS_2 ligand H_3-**4** (Figure 2). Ligand H_3-**4** is derived from the related N_2OS ligand **F** by substitution of the amine group for a thiol group. Ligand H_3-**4** exhibits an unsymmetrical topology regarding both the donor set (NOS_2) and the ligand arm lengths (two ethyl chains and one propyl chain). In addition, we present the coordination chemistry of H_3-**4** with nickel(II) and zinc(II).

Experimental Section

Materials and Analyses. All manipulations were carried out in an argon atmosphere. Solvents were purified by standard methods, freshly distilled, and degassed prior to use. Infrared spectra were recorded in KBr using a Perkin-Elmer IR 983 spectrometer. NMR spectra were recorded on a Bruker AM 250 spectrometer. Elemental analyses (C, H, N, and S) were performed on a Vario EL elemental analyzer. EI and +FAB mass spectra were taken on Finnigan MAT 112 or Finnigan MAT 711 instruments. The UV/vis spectrum of **5** was recorded in acetonitrile from 300 to 1100 nm at room

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temperature on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. The magnetism was measured with a JM MSB 1251 AUTO instrument. Cyclic voltammetry experiments were carried out with a Bank High Power Potentiostat Wenking HP 72 and a Bank Scan Generator Wenking model VSG 83 using a three electrode cell configuration (working electrode Pt; auxiliary electrode Pt; reference electrode Ag/AgCl/3 M KCl; $E_{Fc/Fc+} = 435$ mV). The experiments were performed with 0.1 M tBu$_4$NPF$_6$ as supporting electrolyte in acetonitrile with scan rates of 100 mV/s.

Ligand Synthesis. *N,N*-Bis(2-hydroxyethyl)-3-aminopropionic Acid Ethylester, 1. A sample of 12.01 g (0.12 mol) of acrylic acid ethylester was added to 10.51 g (0.1 mol) of diethanolamine (both freshly distilled) while the reaction flask was cooling in an ice bath. The mixture was allowed to warm to room temperature and was stirred at this temperature overnight. The excess of acrylic acid ethylester was removed in vacuo yielding 2.05 g (100%) of **1** as a colorless oil of purity sufficient for further reactions. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 4.16$ (q, 2H, OCH_2CH$_3$), 3.62 (t, 4H, NCH_2CH$_2$OH), 3.44 (s, 2H, OH), 2.88 (t, 2H, NCH_2CH$_2$COOEt), 2.66 (t, 4H, CH_2OH), 2.46 (t, 2H, CH_2COOEt), 1.30 (t, 3H, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): $\delta = 173.07$ (*C*OOEt), 60.53 (O*C*H$_2$CH$_3$), 59.44 (N*C*H$_2$CH$_2$OH), 56.02 (NCH$_2$*C*H$_2$OH), 49. 66 (N*C*H$_2$CH$_2$COOEt), 32.63 (*C*H$_2$COOEt), 13.97 (CH$_3$).

***N,N*-Bis(2-chloroethyl)-3-aminopropionic Acid Ethylester Hydrochloride, 2.** A 2.053 g (0.01 mol) sample of *N,N*-bis(2-hydroxyethyl)-3-aminopropionic acid ethylester **1** was dissolved in 50 mL of dry chloroform. To this solution was added dropwise 5.95 g (0.05 mol) of $SOCl_2$. After addition of the thionyl chloride the mixture was heated to reflux until the SO_2 evolution ceased. Upon cooling of the yellow solution to room temperature a colorless solid precipitated. Recrystallization of the solid from acetone yielded 1.950 g (70%) of bright white needles of the hydrochloride **2**·HCl. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 9.80$ (s, 1H, NH), 4.24 (q, 2H, OCH_2CH$_3$), 4.07 (t, 4H, CH$_2$Cl), 3.60 (t + t, 6H, NCH_2CH$_2$Cl and NCH_2CH$_2$COOEt), 3.09 (t, 2H, CH_2COOEt), 1.27 (t, 3H, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): $\delta = 169.60$ (*C*OOEt), 61.78 (O*C*H$_2$CH$_3$), 54.43 (N*C*H$_2$CH$_2$Cl), 49.47 (N*C*H$_2$CH$_2$COOEt), 36.34 (CH$_2$Cl), 28.96 (*C*H$_2$COOEt), 14.01 (CH$_3$). Anal. Calcd. for $C_9H_{18}Cl_3NO_2$ ($M_r = 278.61$): C, 38.80; H, 6.51; N, 5.03. Found: C, 38.50; H, 6.52; N, 5.11.

The ammonium salt **2**·HCl was deprotonated with dilute aqueous K_2CO_3 solution and extracted with diethyl ether. After removal of the solvent in vacuo the free amine was obtained as a colorless oil, which decomposed rapidly at room temperature.

WARNING: *β*-Chlorinated ethylamines are nitrogen derivatives of mustard gas which are known to be extremely carcinogenic.

***N,N*-Bis[(2-acetylthio)ethyl]-3-aminopropionic Acid Ethylester, 3.** *N,N*-Bis(2-chloroethyl)-3-aminopropionic acid ethylester **2** (13.93 g, 0.05 mol) and potassium thioacetate (13.705 g, 0.12 mol) were dissolved in 100 mL of dry DMF. The solution was stirred at ambient temperature for 60 min and for an additional 60 min at 60 °C. During that period a precipitate of KCl formed. All solvents were removed in vacuo and the residue was extracted three times with dietyl ether. Removal of the solvent yielded 13.9 g (86.6%) of **3** as an air-sensitive yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 4.09$ (q, 2H, OCH_2CH$_3$), 2.90 (t, 4H, NCH_2CH$_2$S), 2.79 (t, 2H, NCH_2CH$_2$COOEt), 2.60 (t, 4H, CH$_2$S), 2.39 (t, 2H, CH_2COOEt), 2.27 (s, 6H, CH_3C(O)SCH$_2$), 1.20 (t, 3H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): $\delta = 195.72$ (CH$_3$*C*(O)SCH$_2$), 172.24 (CH$_2$*C*OOEt), 60.29 (O*C*H$_2$CH$_3$), 53.10 (N*C*H$_2$CH$_2$S), 49.24 (N*C*H$_2$CH$_2$COOEt), 33.01 (*C*H$_2$COOEt), 30.49 (*C*H$_3$C(O)SCH$_2$), 27.16 (*C*H$_2$S), 14.14 (OCH$_2$*C*H$_3$).

3-Hydroxy-*N,N*-bis(2-mercaptoethyl)-propylamine, H_3-4. All functional groups in *N,N*-bis[(2-acetylthio)ethyl]-3-aminopropionic acid ethylester **3** were reduced simultaneously by use of $LiAlH_4$. A sample of 1.367 g (36 mmol) of lithium aluminum hydride ($LiAlH_4$) was suspended in 50 mL of dry THF. Compound **3** (3.215 g, 10 mmol, dissolved in 20 mL of dry THF) was added dropwise to the vigorously stirred suspension at 0 °C. The reaction mixture was stirred overnight at ambient temperature, and residual $LiAlH_4$ was carefully hydrolyzed with 2.7 mL (0.145 mol) of degassed water. All solids were removed by filtration under argon, and the residue was suspended in 50 mL of degassed THF. The suspension was saturated with CO_2 by addition of small pieces of solid carbon dioxide,[5] and filtered under argon. This procedure was repeated up to 5 times. Evaporation of the solvent in vacuo yielded 1.3 g (66.5%) of H_3-**4** as a clear colorless oil. Mass spectrum (EI-MS) [*m*/*z* (rel int)]: 195 (1.31, [M]$^+$), 148 (100, [M − CH$_2$SH]$^+$), 104 (10.13), 88 (10.27), 61 (23.31). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.71$ (t + s, 3H, CH_2OH + CH$_2$O*H*), 2.60 (m, 10H, NCH_2CH$_2$-CH$_2$OH + NCH_2CH$_2$SH + CH_2SH), 1.65 (m, 2H, CH$_2$CH_2CH$_2$), 1.52 (s, br, 2H, SH). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): $\delta = 62.95$ (CH$_2$OH), 57.11 (N*C*H$_2$CH$_2$SH), 53.15 (N*C*H$_2$CH$_2$CH$_2$OH), 28.71 (CH$_2$*C*H$_2$CH$_2$), 22.81 (CH$_2$SH).

Preparation of Metal Complexes. Synthesis of [Ni(H-4)]$_2$, 5. Triethylamine (218 mg, 2.2 mmol) and H_3-**4** (140 mg, 0.7 mmol) were dissolved in 20 mL of acetonitrile. This mixture was added dropwise to a hot (50 °C) solution of Ni(OAc)$_2$·4H$_2$O (178 mg, 0.7 mmol) in 30 mL of acetonitrile. The mixture immediately turned red, and after 15 min a brown precipitate had separated. The solid was collected by filtration. Recrystallization from warm acetonitril gave reddish brown crystals of [Ni(H-**4**)]$_2$, **5**. Yield 152 mg (86%). Mass spectrum (+FAB-MS, 3-nitrobenzyl alcohol/DMSO) [*m*/*z* (rel int)]: 503 (7.29, [{Ni(H-**4**)}$_2$ + H]$^+$). IR (ν, cm^{-1}): 3372 (s, OH), 2925, 2855 (s, CH), 1462 (m, CH), 1054 (m, CO). UV/vis (CH$_3$-CN, λ_{max}, nm) ϵ (10^3 cm^2·mol^{-1}): 370 (sh), 425 (sh), 545 (90.3), 790 (sh). Anal. Calcd for $C_{14}H_{30}N_2Ni_2O_2S_4$ ($M_r = 504.06$): C, 33.36; H, 6.00; N, 5.56; S, 25.44. Found: C, 33.39; H, 6.00; N, 5.87; S, 25.36.

Synthesis of [Zn(H-4)]$_4$, 6. Triethylamine (364 mg, 3.6 mmol) and H3-**4** (234 mg, 1.2 mmol) were dissolved in 10 mL of acetonitrile. This mixture was added dropwise to a solution of Zn(BF$_4$)$_2$·xH$_2$O (287 mg, 1.2 mmol) in 20 mL of acetonitrile resulting in the separation of a white precipitate. The solid was collected by filtration and dissolved in DMSO. Slow diffusion of diethyl ether into this solution gave colorless cubes of [Zn(H-**4**)]$_4$, **6**. Yield 123 mg (39.7%). Mass spectrum (+FAB-MS, 3-nitrobenzyl alcohol/DMSO) [*m*/*z* (rel int)]: 842 (4.45, [{Zn(H-**4**)}$_3$ + Zn]$^+$), 776 (3.23, [{Zn(H-**4**)}$_3$]$^+$), 581 (26.18, [{Zn(H-**4**)}$_2$ + Zn]$^+$), 519 (15.15, [{Zn(H-**4**)}$_2$ + H]$^+$), 258 (100, [{Zn(H-**4**)} + H]$^+$). IR (ν, cm^{-1}): 3354 (s, OH), 2924, 2850 (s, CH), 1449 (m, CH), 1084, 1054 (m, CO). Anal. Calcd for $C_{28}H_{60}N_4O_4S_8Zn_4$ ($M_r = 1034.76$): C, 32.50; H, 5.84; N, 5.41; S, 24.79. Found: C, 32.94; H, 5.98; N, 5.67; S, 23.53.

Crystal Structure Analyses. Crystals of **5** and **6** are stable in air. Suitable specimens were mounted on an Enraf-Nonius CAD-4 diffractometer at room temperature (**5**) or on a Nonius KappaCCD diffractometer with a rotating anode generator at 198(2) K (**6**). Important crystal and data collection details are summarized in Table 1. Raw data were reduced to structure factors by standard methods. An absorption correction using SORTAV[22] was applied to the raw data of **6** ($0.490 \le T \le 0.681$); no absorption correction was performed on the data for **5**. Both structures were solved by direct methods and refined on F^2 by the full-matrix least-squares

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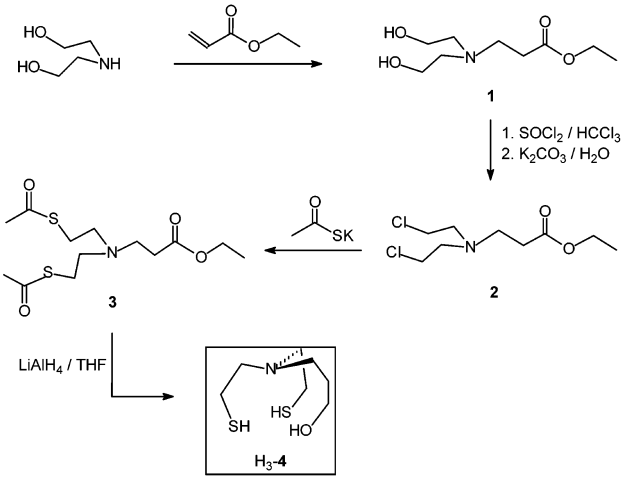
Table 1. Summary of Crystallographic Data for **5** and **6**

	5	**6**
formula	$C_{14}H_{30}N_2Ni_2O_2S_4$	$C_{28}H_{60}N_4O_4S_8Zn_4$
M_r	504.06	1034.76
cryst size [mm]	0.30 × 0.18 × 0.18	0.30 × 0.25 × 0.15
a [Å]	14.842(5)	14.594(1)
b [Å]	5.9083(10)	12.531(1)
c [Å]	23.241(2)	23.022(1)
α [deg]	90.00	90.00
β [deg]	99.07(2)	104.31(1)
γ [deg]	90.00	90.00
V [Å^3]	2012.5(8)	4079.6(5)
Z	4	4
space group	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)
ρ_{calcd} [g cm^{-3}]	1.664	1.685
μ Mo Kα [mm^{-1}]	2.296	2.771
λ [Å]	0.71073	0.71073
2θ range [deg]	$6 \le 2\theta \le 50$	$6 \le 2\theta \le 56$
unique data	1754	10028
obsvd data [$I \ge 2\sigma(I)$]	1462	8583
R	0.0423	0.030
wR^2	0.1052	0.068
no. of variables	110	437
peak/hole [e Å^{-3}]	0.73/−0.70	1.12/−0.50

Scheme 1. Preparation of the Ligand H_3-**4**



method using the SHELX[23,24] programs. Hydrogen atoms were added at geometrically idealized positions with fixed coordinates (**5**) or were refined using a riding model (**6**). Drawings were done with ORTEP.[25]

Results and Discussion

Ligand Synthesis. Ligand H_3-**4** was prepared in a four reaction sequence as depicted in Scheme 1. Starting from commercial diethanolamine addition of one equivalent of acrylic acid ethylester yields the tertiary amine **1**. The hydroxy groups were converted into chloride substituents by use of thionyl chloride giving **2**. Subsequent reaction with potassium thioacetate yields the dithioester substituted amine **3**. Finally, all donor groups were simultaneously liberated by reduction with $LiAlH_4$, which leads directly to the free ligand H_3-**4**.

A problem during the purification of H_3-**4** arises from the presence of acidic (SH) and basic (NR_3) functional groups in the same molecule leading to an equilibrium between the uncharged compound and the zwitterionic species. Generally, the position of the equilibrium shifts to the side of the zwitterionic product if the linker between the involved functional groups is shortened. It was shown previously[26] that this is due to an electrostatic interaction between the positively charged ammonium group and the negatively charged thiolato group, resulting in a stabilization of the zwitterionic molecule. Consequently, the SH groups of *β*- and *γ*-aminoalkylmercaptanes exhibit pK_a values which are surprisingly low in comparison to those of the unsubstituted aliphatic mercaptanes. However, the formation of zwitterionic H_3-**4** (hydrochloride and thiolate), which is only sparingly soluble in organic solvents, can be suppressed by the introduction of CO_2 during workup.[5]

Ligand H_3-**4** posseses both an unsymmetrical topology and donor set. Due to the different length of the ligand arms (two ethyl and one propyl chain) the ligand is capable of forming both five- and six-membered chelate rings upon complex formation. Furthermore, the alkyl arms are substituted by thiol or hydroxyl groups, respectively. Thus H_3-**4** is capable to provide a NOS_2 coordination environment for a metal ion without any sterical strain due to the length and the flexibility of the ligand arms.

Nickel and Zinc Complexes. The reaction of equimolar amounts of $[HNEt_3]^+_2[H\text{-}\mathbf{4}]^{2-}$ and $Ni(OAc)_2{\cdot}4H_2O$ in acetonitrile yielded a clear dark red solution from which reddish brown crystals precipitate within minutes (Scheme 2). The IR spectrum of these crystals shows no more resonance due to an SH vibration but a broad OH resonance was observed at 3372 cm^{-1}. No NMR spectra could be recorded due to the poor solubility of the complex. The FAB mass spectrum (positive ions) indicates that a dinuclear complex had formed. This was corroborated by an X-ray crystal structure analysis which showed the formation of complex $[Ni(H\text{-}\mathbf{4})]_2$ **5**.

Complex **5** resides on a crystallographic inversion center and consists of two, nearly square-planar $NiNS_3$ units sharing one edge of their coordination polyhedra (Figure 3). The folding angle between the planes defined by the four donor atoms measures 103.92°. Thus complex **5** adopts a butterfly geometry with *syn-endo* stereochemistry, which is typical for bridging, chelating thiolate ligands as demonstrated by Colpas et al.[7e] In addition, they pointed out that the folding arises from a combination of various factors such as the steric constraints of the ligand backbone, Ni−Ni interactions, and S−S interactions.[7e] In **5**, the folding along the S1−S1* axis brings the two nickel and the two sulfur atoms into close contact (Ni−Ni* 2.6962(9) and S1−S1* 2.867(2) Å). This is well below the sum of the van der Waals radii of the atoms involved and indicates weak interactions between Ni and Ni* as well as S1 and S1*. Altogether, complex **5** fits well in the series of similar $NiNS_3$ complexes reported previously.[7e,17]

As depicted in Figure 3 each nickel(II) ion in **5** is coordinated by one nitrogen, and one terminal and two bridging thiolato groups in a square-planar fashion. Selected

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(24) *SHELXL-97*; Sheldrick, G. M.; Universität Göttingen: Germany, 1997.
(25) *ORTEP-3*; Farrugia, L. J.; University of Glasgow: Scotland, 1999.
(26) (a) Franzen, V. *Chem. Ber.* **1957**, *90*, 623. (b) Benesch, R. E.; Benesch, R. *J. Am. Chem. Soc.* **1955**, *77*, 5877.

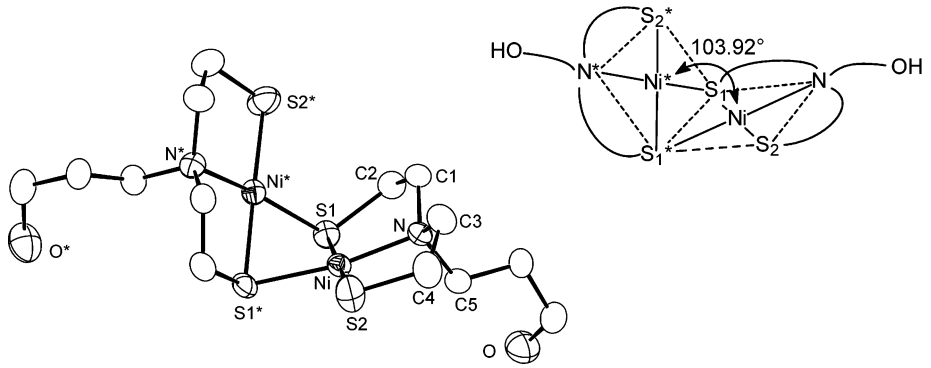

Figure 3. ORTEP plot of one molecule of complex **5**. Hydrogen atoms have been omitted.

Scheme 2. Preparation of the Ni(II) and Zn(II) Complexes of Ligand H_3-**4**

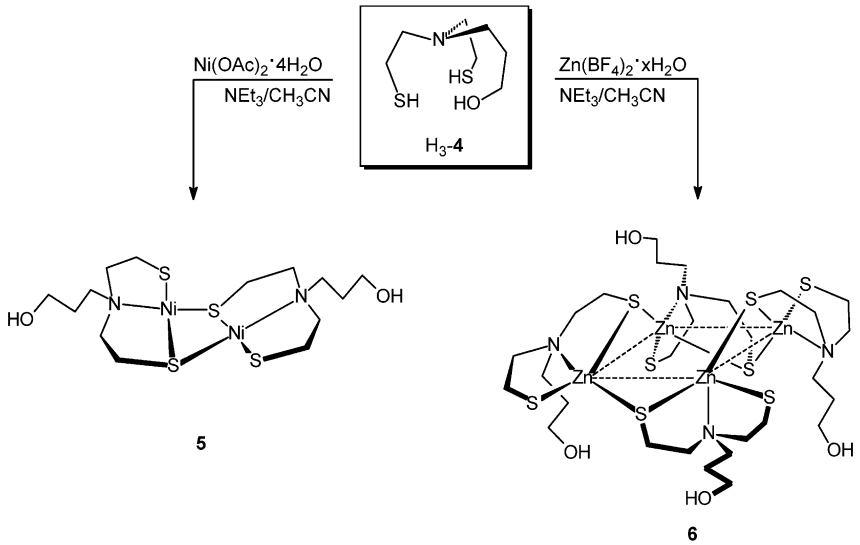

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **5**[a]

Ni···Ni*	2.6962(9)	S1−C2	1.827(4)
S1···S1*		S2−C4	1.823(5)
Ni−S1	2.2138(12)	N−C1	1.494(5)
Ni−S1*	2.1736(11)	N−C3	1.503(5)
Ni−S2	2.1573(13)	N−C5	1.497(5)
Ni−N	1.945(3)		
S1−Ni−S2	178.80(5)	Ni*−S1−C2	112.38(13)
S1−Ni−S1*	81.61(5)	Ni−S2−C4	98.80(15)
S1−Ni−N	89.03(10)	Ni−N−C1	106.9(2)
S2−Ni−S1*	98.05(5)	Ni−N−C3	110.5(2)
S2−Ni−N	91.18(10)	Ni−N−C5	107.3(2)
S1*−Ni−N	168.77(10)	C1−N−C3	107.8(3)
Ni−S1−Ni*	75.83(4)	C1−N−C5	112.3(3)
Ni−S1−C2	98.03(13)	C3−N−C5	111.8(3)

[a] Symmetry transformation used to generate equivalent positions: (*) $-x + 3/2, y, -z + 3/2$.

bond lengths and angles for **5** are shown in Table 2. The deviation from perfect square-planar geometry is best reflected by the angles N−Ni−S1* [168.77(10)°] and S1−Ni−S2 [178.80(5)°], whereas the N−Ni−S1 and N−Ni−S2 angles show only negligible distortion [89.03(10)° and 91.18(10)°]. A significant deviation from square-planar geometry was also observed for the angle S1−Ni−S1* of the Ni_2S_2 core [81.61(5)°]. The Ni−N bond distance measures 1.945(3) Å, while the Ni−S bond lengths are slightly longer and vary in a small range between 2.1573(13) and 2.2138(12) Å, with the shortest distance found for the terminal thiolato sulfur atom S2.

Another structural feature of **5** is the pendant hydroxypropyl arms. Recently we reported a similar situation for related nickel(II) complexes of a tripodal N_2OS ligand,[19] where the hydroxy group was also linked to the central nitrogen atom by a propyl chain. As observed for **5** this N_2-OS ligand used only three of the four donor groups while the hydroxypropyl arm remained protonated and was not involved in coordination. Theoretical[27] and solution thermodynamics[28] studies have shown that the stability of five-membered chelate rings is significant higher than that of six-membered rings. This was recently confirmed by a study of a series of copper complexes with tripodal tetramine ligands.[12c] In addition, coordination number four in complex **5** is also a consequence of the electronic situation at the nickel centers. Cyclic voltammetry experiments (vide infra) demonstrate that the highly thiophilic nickel(II) ions are electronically saturated by the soft, sulfur rich NS_3 coordination sphere. Thus the coordination of further donors, as observed for octahedral Ni^{II} complexes with amine ligation,[7e,12d] is not necessary.

(27) Hancock, R. D. *Acc. Chem. Res.* **1990**, *23*, 253.
(28) Dei, A.; Paoletti, P.; Vacca, A. *Inorg. Chem.* **1968**, *7*, 805.

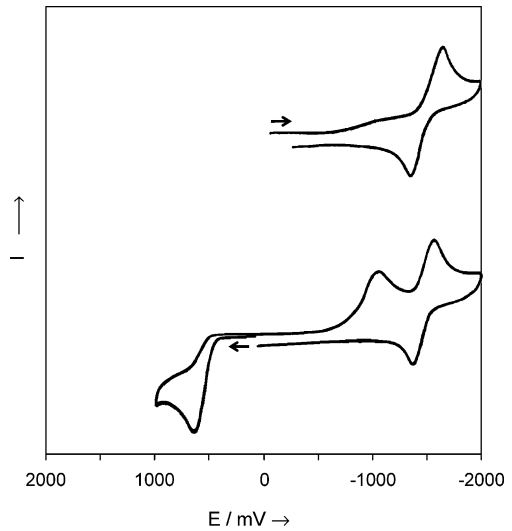

Figure 4. Cyclic voltammograms of **5**; *E* vs Ag/AgCl in acetonitrile. Top: scan to negative potential; bottom: full range scan starting to the anodic direction.

The cyclic voltammograms recorded for a solution of complex **5** are depicted in Figure 4. Starting in the cathodic direction (Figure 4, top) one quasireversible reduction peak is found at $E = -1420$ mV vs Ag/AgCl in acetonitrile, corresponding to the process $Ni^{II} + e^- \rightarrow Ni^{I}$. The Ni^{I} species is formed at a quite negative potential which indicates that the reduction does not happen readily. Upon application of a positive potential (Figure 4, bottom), an irreversible oxidation event is observed at $E = +665$ mV vs Ag/AgCl in acetonitrile. The low-potential oxidation step arises from the relatively facile oxidation of the nickel(II) ions, and, together with the quite negative reduction potential, it corroborates the assumption of an electron-rich metal center due to thiolate coordination. In contrast to the Ni^{I} complex the Ni^{III} species is not stable, but highly reactive. It rapidly decomposes to a nonidentified product which gives rise to an additional, irreversible reduction peak at the reverse scan at $E = -1080$ mV vs Ag/AgCl in acetonitrile (Figure 4, bottom).

When the scan limit was extended to more positive potentials (up to +2000 mV vs Ag/AgCl in acetonitrile) no additional oxidation events were observed. This corresponds to the observation that complex **5** is stable in air as a solid and in solution, and that no oxidation of the thiolato sulfur atoms to sulfinato groups occurs, as described previously for related thiolato complexes.[7e,19,29]

The molar susceptibility χ_M of **5** was determined by a magnetic susceptibility balance. A value of -108.5×10^{-6} $cm^3 \cdot mol^{-1}$ was found, clearly proving the expected diamagnetism for the square-planar Ni^{II} in **5**. A d^8 ion like nickel(II) in an square-planar ligand field gives rise to four spin-allowed absorption bands in the UV/vis spectrum.[30] In practice these transitions are scarcely observed as discrete absorption bands, but in many cases they overlap to one single signal between 450 and 600 nm, which causes the red to brown color of such complexes. In the UV/vis spectrum of **5** only one discrete absorption band is observed (545 nm, $\epsilon = 90.3 \times 10^3$ $cm^2 \cdot mol^{-1}$) resulting in the intensely red color of the complex. Further absorptions are observed as shoulders (370 nm, 425 nm) or as an ascent (790 nm).

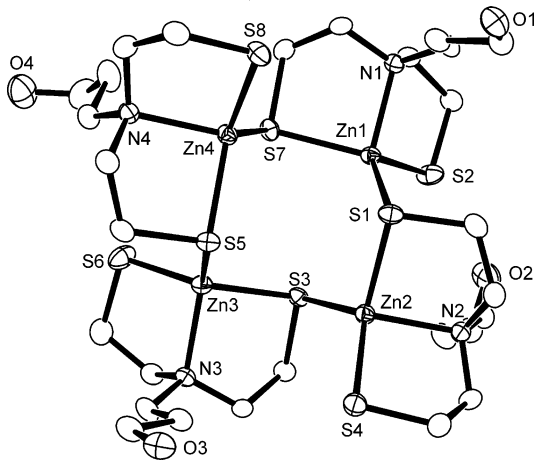

Figure 5. ORTEP plot of the tetranuclear complex **6**. Hydrogen atoms have been omitted.

As mentioned in the Introduction the active site of HLADH consists of a zinc(II) center that is tetrahedrally surrounded by an NOS_2 coordination environment. In this context it is interesting to know if the reaction of the NOS_2 ligand H_3-**4** with zinc(II) ions leads to a mononuclear complex with tetrahedral or trigonal-bipyramidal coordination geometry. Alternatively, the formation of a multinuclear, sulfur-bridged species similar to **5** can be expected. Owing to the Lewis acidity of zinc(II), chelating polyols such as triethanolamine are often deprotonated upon complex formation.[31] Such a deprotonation of the hydroxypropyl arm in H_3-**4** would strongly increase both its capability to coordinate and the stability of the resulting six-membered chelate ring, which might stabilize a mononuclear complex.

$Zn(BF_4)_2 \cdot xH_2O$ reacts with an equimolar amount of $[HNEt_3]^+_2[H\text{-}\mathbf{4}]^{2-}$ to give a fine white precipitate (Scheme 2). The IR spectrum of this solid is dominated by a broad absorption band at 3354 cm^{-1} arising from an OH vibration. No NMR spectra were recorded due to the low solubilty of complex **6**. The FAB mass spectrum (positive ions) indicates the formation of a multinuclear complex that is built up from [Zn(H-**4**)] units since the fragments $[\{Zn(H\text{-}\mathbf{4})\}_2 + H]^+$ and $[\{Zn(H\text{-}\mathbf{4})\}_3]^+$ are detected. Slow diffusion of diethyl ether into a DMF solution of the white precipitate yielded clear colorless crystals. The X-ray structure analysis of these crystals revealed that the tetranuclear complex $[Zn(H\text{-}\mathbf{4})]_4$ **6** had formed (Figure 5).

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(30) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1984.

(31) Hubert-Pfalzgraf, L. G. *Coord. Chem. Rev.* **1998**, *178*−*180*, 967.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **6**

Zn1−S1	2.3366(6)	Zn3−S3	2.3543(6)
Zn1−S2	2.2753(7)	Zn3−S5	2.3557(6)
Zn1−S7	2.3514(6)	Zn3−S6	2.2801(7)
Zn1−N1	2.126(2)	Zn3−N3	2.138(2)
Zn2−S1	2.3602(6)	Zn4−S5	2.3584(6)
Zn2−S3	2.3275(6)	Zn4−S7	2.3377(6)
Zn2−S4	2.2662(6)	Zn4−S8	2.2803(6)
Zn2−N2	2.154(2)	Zn4−N4	2.157(2)
S2−Zn1−S7	126.20(2)	S6−Zn3−S3	126.25(3)
S2−Zn1−S1	114.78(2)	S6−Zn3−S5	116.62(2)
S2−Zn1−N1	90.89(5)	S6−Zn3−N3	91.49(5)
S7−Zn1−S1	111.01(2)	S3−Zn3−S5	108.48(2)
S7−Zn1−N1	89.69(5)	S3−Zn3−N3	88.76(5)
S1−Zn1−N1	119.99(5)	S5−Zn3−N3	123.33(5)
S4−Zn2−S1	125.86(2)	S8−Zn4−S5	127.08(2)
S4−Zn2−S3	118.29(2)	S8−Zn4−S7	114.97(2)
S4−Zn2−N2	91.17(5)	S8−Zn4−N4	90.22(5)
S1−Zn2−S3	105.63(2)	S5−Zn4−S7	108.83(29)
S1−Zn2−N2	89.52(5)	S5−Zn4−N4	89.67(5)
S3−Zn2−N2	123.55(6)	S7−Zn4−N4	123.21(5)
Zn1−S1−Zn2	102.89(2)	Zn3−S5−Zn4	104.27(2)
Zn2−S3−Zn3	106.48(2)	Zn4−S7−Zn1	104.72(2)

Complex **6** crystallizes as μ-sulfur bridged tetramer. Similarly to **5**, one of the ethylthiolato arms of the ligand is terminally coordinated while the other one is used for the bridging of the [Zn(H-**4**)] units, resulting in the formation of a folded, tub-shaped Zn_4S_4 ring. The hydroxypropyl arm of the ligand is protonated and remains uncoordinated. Thus, the doubly deprotonated ligand H-$\mathbf{4}^{2-}$ provides an NS_3 coordination environment for Zn^{II}. The coordination geometry around zinc is best described as distorted tetrahedral. Within the four [Zn(H-**4**)] units the N−Zn−S angles vary between 88.76(5)° and 91.49(5)°, while the S−Zn−S angles are significantly larger [125.86(2)−127.08(2)°] due to the steric bulk of the thiolato sulfur atoms (Table 3). Within the Zn_4S_4 ring the Zn−S−Zn angles fall in the range of 102.89(2)−106.48(2)°, while the S−Zn−S angles are only slightly larger [range 105.63(2)−111.01(2)°]. Thus, the [Zn(H-**1**)] units are connected without any steric strain.

The Zn−N bond distances range from 2.126(2) to 2.157(2) Å. Two types of Zn−S bond lengths were observed, the shorter one connecting Zn to terminal sulfur atoms [range 2.2662(6)−2.2803(6) Å] and the longer one for the Zn-μSR bonds [range 2.3275(6)−2.3602(6) Å]. These parameters indicate quite symmetrical μ-SR bridges.

The most interesting structural features of **6** are the noncoordinated hydroxypropyl arms of the ligand that alternately stick out of the folded Zn_4S_4 ring. This behavior arises apparently from the same reasons as seen for complex **5**. The hydroxypropyl arm is not able to successfully compete for a coordination site at the metal center due to low stability of the six-membered chelate ring and the high bridging tendency of the soft thiolato sulfur atoms. Furthermore, the zinc atoms are electronically saturated by the sulfur rich NS_3 coordination sphere which makes the coordination of further ligands obsolete. All these effects lead to a small coordination number and a tetrahedral coordination geometry, but in contrast to the situation in HLADH, thiolato bridging and the formation of a tetranuclear species is preferred.

Conclusion

The coordination chemistry of ligand H_3-**4** helps to understand the gouverning principles for the formation of complexes with tripodal ligands. The coordination geometry of **5** and **6** is controlled by electronic effects since the ligand arms of H_3-**4** are highly flexible, and the ligand is capable of providing an NOS_2 coordination environment without any sterical strain. Owing to the sulfur rich donor set, the metal centers in **5** and **6** appear to be electronically saturated. Complexes with high coordination numbers, as observed for Ni^{II} complexes with N_4 ligands,[12d] do not form and the coordination geometry of small coordination number is preferred (square-planar or tetrahedral). In contrast to the coordination chemistry of tripodal N_4 ligands,[12] where the lengths of the ligand arms determine to a large extent the coordination geometry, the geometry and coordination number of complexes of H_3-**4** is controlled by the substitution pattern of the tripod.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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