

An Unsymmetrical Tripodal Ligand with an N₂OS Donor Set: Coordination Chemistry with Nickel(II) Ions and Aerial Oxidation to the Sulfinate Complex

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Abstract: The synthesis of the previously unknown tripodal ligand H₄-**1** is reported. The tetradentate ligand is equipped with a completely unsymmetrical N₂OS donor set. It reacts with Ni(OAc)₂·4H₂O or Ni(ClO₄)₂·6H₂O to give the multinuclear nickel(II) complexes [Ni(H-**1**-Imin)(OAc)]₂ (**2**) (which contains a coordinated Schiff base obtained by reaction of the primary amine with the acetone solvent) and [Ni₃(H₃-**1**)(H₂-**1**)]·ClO₄·H₂O·3 MeCN (**3**), respectively. A solution of **3** in DMF is readily oxidized upon exposure to air or by aqueous

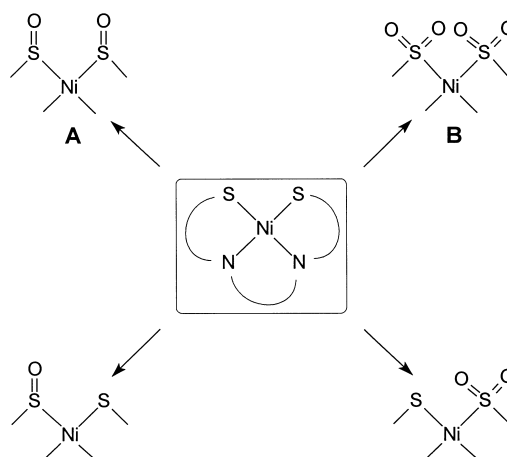
H₂O₂ to yield [Ni(H₂-**1**-sulfinate)]₂·2MeOH (**4**). The molecular structures of **2**–**4** have been determined by X-ray diffraction. Complex **2** exhibits a strongly distorted, octahedral coordination geometry around each nickel(II) ion. The primary amino group of the ligand in this case reacted with the solvent acetone to yield a Schiff base which is coordinated

to the metal center. The molecular structure of the trinuclear complex cation in **3** consists of two subunits: a nickel atom with a square-planar N₂S₂ coordination geometry and two other nickel atoms with a trigonal-bipyramidal N₂O₂S coordination environment. The dinuclear complex **4** shows distorted octahedral geometry around each nickel(II) ion. The thiolato groups of the ligands are oxidized to sulfinate groups which are *O,O*-bound to the nickel center. This coordination mode is unusual for nickel sulfinate complexes.

Keywords: N ligands · nickel · S ligands · tripodal ligands · structure elucidation

Introduction

The coordination environment of metal ions in metalloproteins is dominated by nitrogen, oxygen, and sulfur donor atoms of the amino acid side chains. The redox chemistry of coordinated thiol and thiolate ligands plays a key role in many biochemical processes.^[1] In contrast to the aerial oxidation of thiols and thiolates which yields disulfides via thiyl radicals, it is well known that transition metals catalyze the formation of sulfenates **A**, sulfinate **B**, and sulfonates (Scheme 1) from such groups. For example, such reactions are part of the metal-catalyzed oxidative degradation of cysteine.^[2] In addition, similar oxidation processes are discussed as important processes in the deactivation of sulfur-rich enzymes by air. The air



Scheme 1.

oxidation of thiolates has been modeled with various nickel and palladium complexes of the type [M(N₂S₂)] using linear N,S ligands. In these complexes the oxidation of the coordinated thiolato groups with peroxides or air resulted in the formation of sulfenato or sulfinate groups.^[3–5]

In all of these complexes the oxidized thiolate is coordinated through the lone pair of electrons of the sulfur atom. For nickel no example of *O*-bound sulfenato and sulfinate ligands is known to date. However, very recently the formation of an *O*-sulfinate iron complex was reported.^[6]

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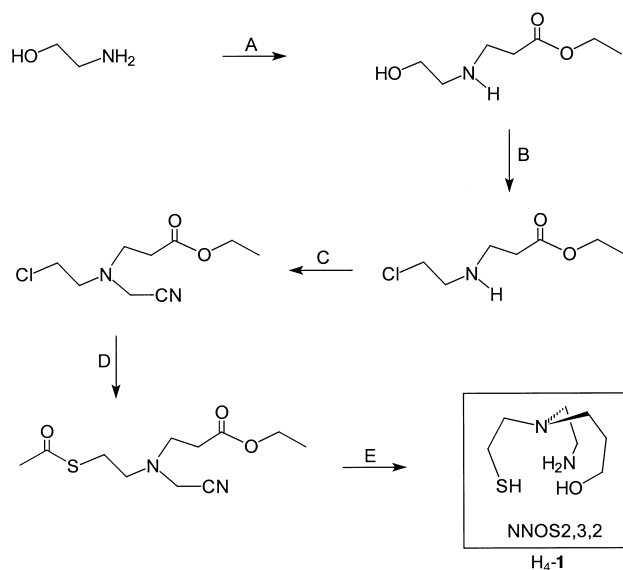
Tripodal ligands have proven useful in the modeling of the active centers of metalloproteins. Besides tris(pyrazolyl)borates^[7] many tetradentate ligands of the type $N[(CH_2-(CH_2)_n-X)]_3$ ($n=1$: $X=SH$,^[8] SR ,^[9] NH_2 ,^[5b,10] $NHMe$, NMe_2 ,^[11] OH ;^[12] $n=2$: $X=NH_2$ ^[13]) have been used as well as a few related derivatives with phosphorus as the central backbone atom.^[14] Most recently the synthesis and coordination chemistry of unsymmetrical tripodal amine ligands with ethyl and propyl arms has been presented.^[15] However, the substitution of all three ligand arms with three different donor groups has not yet been demonstrated, although such derivatives are of particular interest for the modeling of unsymmetrically coordinated active centers in metalloproteins such as nitrile hydratase^[6,16] and horse liver alcohol dehydrogenase (HLADH).^[17]

Tripodal ligands of the type $CH_3C[(CH_2X)(CH_2Y)(CH_2Z)]$ ($X, Y, Z = PR_2, PR'_2, NR_2, SR, \text{ and } OR$) have been reported by Huttner et al. and Liu et al.^[18] However, these ligands, some of which were prepared enantioselectively, rarely form mononuclear chelate complexes with all donor groups coordinated to the same metal center owing to the steric demand and small size of the carbon backbone.

Here we report the tripodal ligand **H₄-1**, which contains three differently substituted ligand arms (see Scheme 2) and an inflated (ethyl and propyl ligand arms) nitrogen-containing backbone. This ligand was developed for the preparation of chelate complexes in which all donor groups of one ligand molecule coordinate to the same metal center. In addition, we describe the coordination chemistry of **H₄-1** with nickel(II) ions and the oxidation of the coordinated ligand with air to yield a nickel sulfinate complex with an unusual coordination of the sulfinate group.

Results and Discussion

Ligand synthesis: Our strategy for the synthesis of the previously unknown tetradentate tripodal ligand **H₄-1** involved five reaction steps as depicted in Scheme 2. The



Scheme 2. Preparation of ligand **H₄-1**. Selected synthetic details. A: ethyl acrylate, 8 h, ambient temperature. B: 1. $SOCl_2$, toluene, $80^\circ C$; 2. K_2CO_3 . C: 1. $Na_2S_2O_7$; 2. CH_2O , 1 h; 3. KCN , $0^\circ C$. D: $KSac$, DMF , 45 min., $60^\circ C$. E: AlH_3 , THF .

Michael addition of one equivalent of ethyl acrylate to ethanolamine (step A) resulted in the formation of a secondary, β -hydroxylated ethylamine which was chlorinated by use of thionyl chloride (step B). Cyanomethylation of the secondary amine by a Strecker synthesis (step C) and subsequent substitution of the chlorine atom by a thiol ester (step D) yielded a suitable precursor for the ligand. Finally all protected donor groups were simultaneously liberated by reduction with AlH_3 (step E), leading directly to the free ligand **H₄-1**.

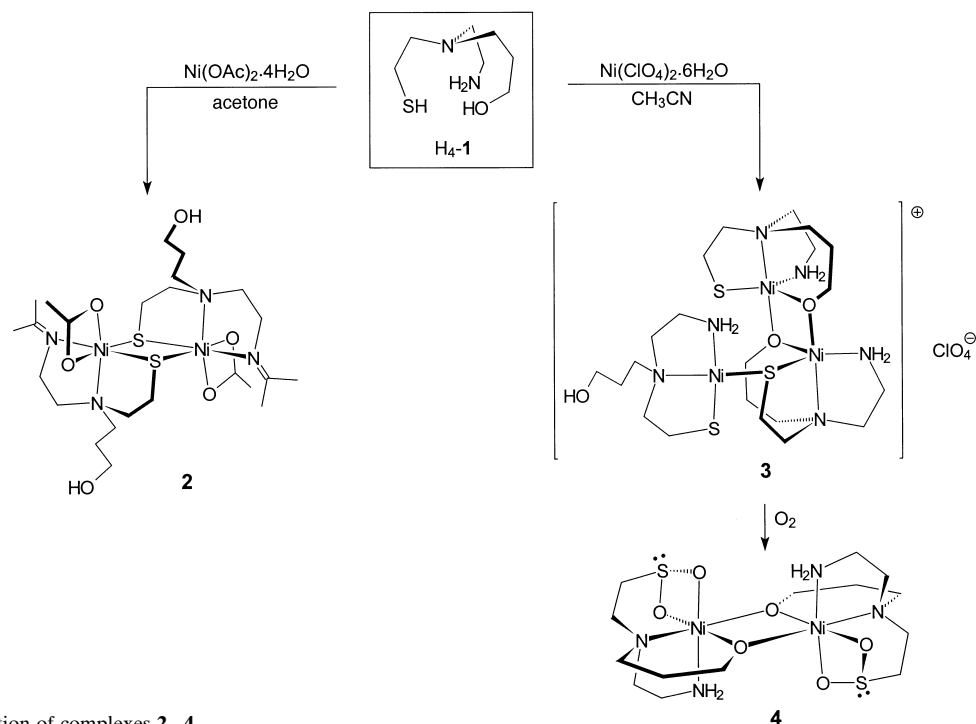
Ligand **H₄-1** contains three differently substituted ligand arms in addition to the central nitrogen donor atom. Furthermore, the ligand possesses an unsymmetrical topology with regard to the three alkyl chains, containing two ethyl and one propyl arm. This allows the formation of both five- and six-membered chelate rings upon complex formation. Owing to the flexibility and lengths of the alkyl arms, the ligand is capable of providing a N_2OS coordination environment for one metal ion without any steric hinderance. Ligand **H₄-1** is the first example of a saturated, sterically nonhindered, tripodal, tetradentate amine ligand with a completely unsymmetrical donor set, which potentially could lead to chiral mononuclear complexes upon coordination.

Coordination chemistry: The reaction of $[HNEt_3]^+[H_3-1]^-$ with an equimolar amount of $Ni(OAc)_2 \cdot 4H_2O$ in acetonitrile yielded a dark brown solution from which emerald cubes precipitated when acetone was added (Scheme 3). The X-ray crystal structure analysis proves the unexpected formation of the complex $[Ni(H-1-I \text{ min})(OAc)]_2$ (**2**) (Figure 1).

The dinuclear complex **2** resides on a crystallographic inversion center. Each nickel(II) ion is coordinated by two acetate oxygen atoms, two nitrogen atoms, and two bridging thiolate sulfur atoms of the ligand (Figure 1). Complex **2** exhibits a strongly distorted, octahedral $N_2O_2S_2$ coordination environment around the nickel atoms. The Ni_2S_2 core shows a negligible rhombic distortion. The core angle $S-Ni-S^*$ is $87.49(10)^\circ$, which is near the ideal value of 90° expected for a perfect octahedron. The $Ni-S$ and $Ni-S^*$ bond lengths differ only slightly ($Ni-S$ 2.418(3) and $Ni-S^*$ 2.388(3) Å). Thus the bridges are quite symmetrical.

As depicted in Figure 1, complex **2** contains two coordinated Schiff base groups. The Schiff bases must have formed from the complex obtained from **H₄-1** and the nickel precursor in acetonitrile upon addition of acetone. This is remarkable, and indicates that in the preliminary complex formed in acetonitrile the amino group was only weakly coordinated to the metal center. Furthermore the hydroxypropyl arm is not capable of successfully competing with the acetate ion for a coordination site at the metal center. Thus each **H₃-1** ligand anion uses only three of the four donor groups, while the hydroxypropyl arm is not coordinated and remains protonated.

Complex **2** is readily soluble in organic solvents as well as in water and exhibits an interesting solvatochromic behavior. While **2** dissolves in CH_2Cl_2 to give an intense green solution, the aqueous solution is cherry red. This change is also reflected in the UV/Vis spectra of **2**, in which both the number and the positions of the absorption bands change. In CH_2Cl_2



Scheme 3. Preparation of complexes 2–4.

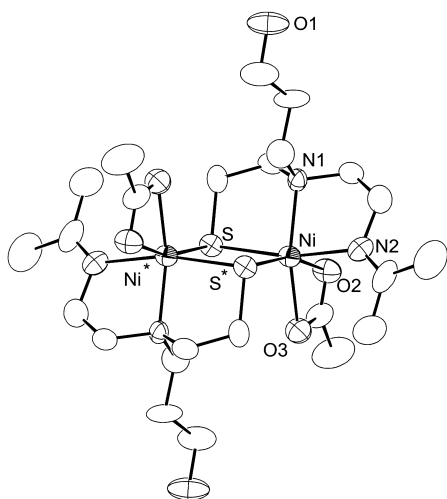


Figure 1. ORTEP plot of one molecule of **2**. Selected bond lengths [Å] and angles [°]: Ni–N1 2.094(9), Ni–N2 2.143(10), Ni–O2 2.210(7), Ni–O3 2.140(8), Ni–S 2.418(3), Ni–S* 2.388(3); N1–Ni–N2 81.2(4), N1–Ni–S 86.1(3), N1–Ni–S* 103.2(2), N1–Ni–O2 93.8(3), N1–Ni–O3 154.4(3), O2–Ni–O3 60.5(3), S–Ni–S* 87.49(10), Ni–S–Ni* 92.51(10). Symmetry code: (*) 1 – x, – y, – z.

three absorption maxima (400, 670, and 1060 nm) and, owing to the spin-forbidden transition ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$, a shoulder at about 500 nm are observed, which is typical for an octahedrally coordinated nickel(II) ion. In contrast, in water only one discrete absorption maximum at 508 nm and a shoulder at 360 nm was detected. Both the red color and the shape of the spectrum strongly indicate that the coordination geometry changes from octahedral to square planar when **2** is dissolved in water. We assume that this behavior is caused by dissociation of the acetate anions from complex **2** in water, resulting in the formation of a dinuclear complex dication with two square-planar coordinated nickel(II) ions. The red color of **2** in aqueous solution, which is typical for square-

planar nickel(II) ions,^[19] corroborates this assumption. In less polar solvents such as CH_2Cl_2 such a process does not take place, and thus the green octahedral species is observed.

The deprotonated ligand $[\text{H}_3\text{-1}]^-$ reacts with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile to give complex **3** as a dark brown crystalline solid (Scheme 3). In the course of the reaction various purple and green intermediates were observed. The FAB mass spectrum (positive ions) indicates a multinuclear complex (m/z 705 and 469). The X-ray structure analysis with single crystals revealed the presence of the trinuclear complex $[\text{Ni}_3(\text{H}_3\text{-1})(\text{H}_2\text{-1})_2]\text{ClO}_4$ (**3**) (Figure 2).

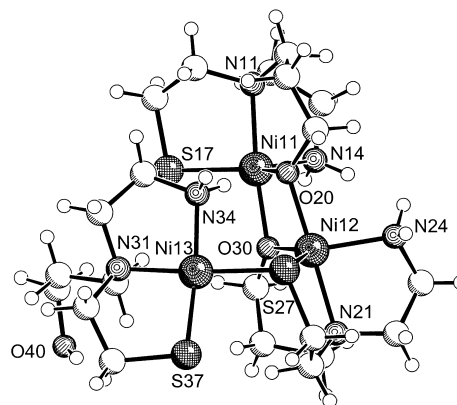


Figure 2. SCHAKAL plot of one complex cation of **3** (the asymmetric unit contains two nearly identical molecules; perchlorate anions and solvent molecules not shown for clarity). Selected bond lengths [Å] and angles [°]: Ni11–N11 2.102(5), Ni11–N14 2.046(5), Ni11–O20 1.985(3), Ni1–O30 1.993(4), Ni11–S17 2.292(2), Ni12–N21 2.140(5), Ni12–N24 2.048(5), Ni12–O20 2.017(4), Ni12–O30 1.913(4), Ni12–S27 2.336(2), Ni13–N31 1.944(5), Ni13–N34 1.945(5), Ni13–S27 2.184(2), Ni13–S37 2.150(2); N11–Ni11–N14 84.1(2), N11–Ni11–O20 95.5(2), N11–Ni11–S17 87.8(2), N11–Ni11–O30 171.5(2), O20–Ni11–S17 133.3(1), N21–Ni12–N24 83.9(2), N21–Ni12–O20 96.7(2), N21–Ni12–S27 87.8(1), N21–Ni12–O30 173.8(2), O30–Ni12–S27 128.50(15), N31–Ni13–N34 87.1(2), N31–Ni13–S27 172.5(2), N31–Ni13–S37 89.7(2), S37–Ni13–N34 169.7(2).

The molecular structure of the trinuclear complex **3** consists of two subunits. In the square-planar unit around Ni13 the ligand $[\text{H}_3\text{-1}]^-$ again uses only three of the four donor atoms to coordinate to the metal center. The hydroxyl-oxygen atom of the ligand (O40) does not take part in the coordination, which once again is an indication for the low stability of the six-membered hydroxypropyl chelate ring. Similar behavior of the tripodal tetramine ligands tren and trpn has recently been reported, where it was shown that the stability of the copper complex of the ligand trpn, which exclusively contains six-membered chelate rings, is about 10^5 times lower than the stability of the corresponding tren complex that contains only five-membered chelate rings.^[15c]

The fourth coordination site in the square-planar ligand arrangement around Ni13 is occupied by the thiolato-sulfur atom S27. Sulfur atom S27 belongs to a ligand coordinated to nickel Ni12. The nickel atoms Ni11 and Ni12 form a dinuclear, oxygen-bridged subunit $[\text{Ni}_2(\text{H}_2\text{-1})_2]$ in which each nickel(II) ion is coordinated by two nitrogen atoms, one thiolato group, and two bridging alkoxy groups in a distorted trigonal-bipyramidal fashion. The coordination geometry around Ni11 and Ni12 is best assigned by use of the τ -criterion^[20] ($\tau = 0.640$ (Ni11) and $\tau = 0.757$ (Ni12)). The trigonal-bipyramidal coordination environment around Ni11 and Ni12 is unusual especially when compared to the situation at Ni13, which is coordinated by the same ligand. A trigonal-bipyramidal coordination environment at nickel ions is normally enforced by the introduction of bulky groups at the terminal donor groups of a tripodal ligand.^[9] For a sterically nonhindered ligand like $\text{H}_4\text{-1}$ an octahedral (as in **2**) or a square-planar (like around Ni13 in **3**) coordination geometry would be expected. Furthermore, it is remarkable that the nickel atoms Ni12 and Ni13 are oxygen-bridged by the deprotonated hydroxypropyl arms of the ligand, and not, as one would expect, by the sulfur atoms of the thiolato groups. Apparently, the μ_2 -coordination of the alkoxy groups strongly contributes to the stabilization of the usually less stable six-membered chelate rings.^[11]

For the three nickel centers in **3** the bond lengths for comparable bonds are very similar. The Ni–O distances vary in a small range (Ni11–O20 1.985(3), N11–O30 1.993(4), Ni12–O20 2.017(4), Ni12–O30 1.913(4) Å), whereas the Ni–N bonds are slightly shorter in the square-planar subunit (1.944(5)–1.945(5) Å) than in the dimeric unit with penta-coordinate nickel atoms (2.046(5)–2.140(5) Å). Differences are more evident for the Ni–S bond lengths: They are significantly shorter in the square-planar unit (Ni13–S37 2.150(2), Ni13–S27 2.184(2) Å) than for the two nickel atoms the oxygen-bridged subunit (Ni11–S17 2.292(2), Ni12–S27 2.336(2) Å). Consequently, the μ_2 -sulfur bridge between Ni11 and Ni12 is also unsymmetrical.

In the cathodic direction the cyclic voltammogram of **3** displays one irreversible reduction peak ($E_{\text{pc}} = -1530$ mV vs. Ag/AgCl in acetonitrile) corresponding to the process $\text{Ni}^{\text{II}} + e^- \rightarrow \text{Ni}^{\text{I}}$. It is remarkable that all three nickel centers are reduced at the same potential. This changes upon application of a positive potential, where three hardly resolved, irreversible oxidation events are observed ($E_{\text{pa}} = 400, 1040, \text{ and } 1600$ mV). The corresponding broad wave seems to be the

overlapping of several redox processes that could not be resolved at different scan rates (10 to 1000 mV s^{-1}).

Solid **3** is stable in air; however, in solutions in DMF aerial oxidation of **3** takes place within one or two days to give the green complex $[\text{Ni}(\text{H}_2\text{-1-sulfinate})]_2 \cdot 2\text{MeOH}$ (**4**). With an equimolar amount of hydrogen peroxide (1% in water) this reaction occurs instantaneously (Scheme 3). Complex **4** crystallizes as green cubes from a mixture of methanol/THF. The X-ray crystal structure analysis of **4** shows that the thiolato groups in **3** were oxidized to sulfinato groups to give a μ_2 -alkoxo-bridged, inversion symmetric, dinuclear complex (Figure 3).

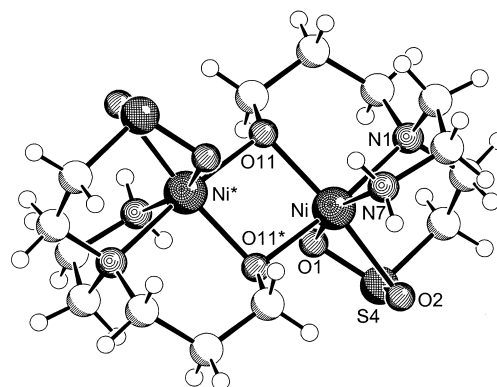


Figure 3. SCHAKAL plot of complex **4**. Selected bond lengths [Å] and angles [°]: Ni–N1 2.1527(11), Ni–N7 2.0614(12), Ni–O1 2.1281(10) Ni–O2 2.2315(10), Ni–O11 2.0075(9), Ni–O11* 2.0274(10); N1–Ni–N7 84.68(5), N1–Ni–O1 87.63(4), N1–Ni–O2 90.47(4), N1–Ni–O11 90.93(4), N1–Ni–O11* 173.67(4), O1–Ni–O2 66.98(4), O11–Ni–O11* 83.42(4), Ni–O11–Ni* 96.58(4). Symmetry code: (*) $-x, 1-y, 1-z$.

Both nickel(II) ions in **4** reside in the center of a distorted octahedron with an N_2O_4 coordination environment. The Ni_2O_2 core shows a small rhombic distortion and the N–O bonds are nearly equal in length (Ni–O11 2.0075(9), Ni–O11* 2.0274(10) Å). The Ni–O distances involving sulfinato oxygen atoms are slightly longer (2.1281(10) and 2.2315(10) Å). The Ni–N bond lengths vary in a small range between 2.0614(12) and 2.1527(11) Å; the shorter distance is found for the primary amino group.

The sulfinato groups in **4** are bound through an oxygen atom. This is unusual considering the fact that all nickel sulfinate complexes reported contain S-bound sulfinato groups which coordinate to the metal through the lone pair of electrons on the sulfur atom.^[3–5] Furthermore, the coordination of both oxygen atoms of the sulfinato groups as in **4** leads to highly strained four-membered $\overline{\text{Ni-O-S-O}}$ chelate rings. Thus *O,O*-bonding is not favored and one would expect that a rearrangement and formation of S-bound sulfinato groups would occur in order to attain less strained and more stable five-membered chelate rings; however, this was not observed. The situation in **4** differs from that found in the recently described iron *O*-sulfinato complex, in which only one of the oxygen atoms is coordinated to the iron atom.^[6]

We do not know the reason for the unusual coordination of the sulfinato groups in **4**. However, together with the striking reactivity of Ni-coordinated $[\text{H}_x\text{-1}]^{(4-x)-}$ (reaction with acetone to a Schiff base, oxidation by air), it appears to be one of

the fascinating characteristics that makes unsymmetrically substituted tripodal ligands of the type H₄-1 so interesting for the modeling of the coordination sphere of unsymmetrically coordinated (N₂OS coordination) metal centers in metalloproteins. Further investigations will show to what extent such ligands can contribute to the catalytic oxidation of mercaptans.

Experimental Section

General remarks: 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, S) were performed on a Vario EL Elemental Analyzer. EI and positive ion FAB mass spectra were recorded on Finnigan MAT 112 or Finnigan MAT 711 instruments. UV/Vis spectra were taken on a Perkin-Elmer Lambda 9 UV/Vis/NIR-Spectrophotometer. 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/3M KCl; $E_{\text{Fc}^+/0} = 435$ mV). The experiments were performed with 0.1M *t*Bu₄NPF₆ as the supporting electrolyte in acetonitrile with scan rates of 100 mV s⁻¹.

Ligand synthesis: A) Ethyl N-(2-hydroxyethyl)-3-aminopropionate: For reaction step A in the synthesis H₄-1, ethyl acrylate (80.096 g, 0.8 mol, freshly distilled) was added to ethanolamine (48.864 g, 0.8 mol; freshly distilled) while cooling the reaction mixture with ice. The mixture was stirred at room temperature overnight to yield a white waxlike solid (128.96 g; 100%) of sufficient purity for further reactions. ¹H NMR (250 MHz, CDCl₃): δ = 4.05 (q, 2H; OCH₂CH₃), 3.76 (t, 2H; NCH₂CH₂OH), 2.84 (t, 4H; NCH₂CH₂COO + NH + OH), 2.64 (t, 2H; CH₂OH), 2.44 (t, 2H; CH₂COO), 1.18 (t, 3H; CH₃); ¹³C{¹H} NMR (62.90 MHz, CDCl₃): δ = 172.56 (COO), 60.49 (OCH₂CH₃), 60.32 (NCH₂CH₂OH), 50.82 (NCH₂CH₂OH), 44.47 (NCH₂CH₂COO), 34.45 (CH₂COO), 14.00 (CH₃).

B) N-(2-chloroethyl)-3-aminopropionic acid ethyl ester hydrochloride: SOCl₂ (3.57 g, 0.03 mol) was added dropwise to a solution of ethyl N-(2-hydroxyethyl)-3-aminopropionate (3.224 g, 0.02 mol) in dry toluene (50 mL). The mixture was then heated to 80 °C until SO₂ evolution ceased. Upon cooling of the brown solution to room temperature a colorless solid precipitated. Recrystallization of this precipitate from acetone yielded bright white needles of the hydrochloride (2.635 g; 61%). ¹H NMR (250 MHz, CDCl₃): δ = 9.86 (s, 2H; R₂NH₂), 4.20 (q, 2H; OCH₂CH₃), 4.01 (t, 2H; CH₂Cl); 3.44 (t + t, 4H; NCH₂CH₂Cl + NCH₂CH₂COO), 3.06 (t, 2H; CH₂COO), 1.28 (t, 3H; CH₃); ¹³C{¹H} NMR (62.90 MHz, CDCl₃): δ = 170.63 (COO), 61.65 (OCH₂CH₃), 49.19 (NCH₂CH₂Cl), 43.65 (NCH₂CH₂COO), 38.51 (CH₂Cl), 30.35 (CH₂COO), 14.04 (CH₃). The ammonium salt was deprotonated with dilute K₂CO₃ solution and extracted with diethyl ether. After removal of the solvent in vacuo the free amine was obtained as a colorless and quickly degenerating oil. **CAUTION: β-Chlorinated ethylamines are nitrogen derivatives of mustard gas which are known to be extremely cancerogenic.**

C) Ethyl N-(2-chloroethyl)-N-(cyanomethyl)-3-aminopropionate: To a solution of sodium pyrosulfite (11.406 g, 0.06 mol) in water (15 mL) were added formaldehyde (4.870 g, 0.06 mol; 37% in water), ethyl N-(2-chloroethyl)-3-aminopropionate (8.982 g, 0.05 mol), DMF (8 mL), and KCN (3.907 g, 0.06 mol) dissolved in water (8 mL). During the addition the temperature was not allowed to rise above 0 °C. The resulting clear solution was stirred overnight at room temperature. During this period an oil had separated, which was extracted with chloroform (3 × 50 mL). The organic phases were combined, all solvents were removed in vacuo, and the oily residue dissolved in diethyl ether (30 mL). The diethyl ether phase was washed three times with a small amount of water (1% acetic acid) and dried over anhydrous MgSO₄. Removal of the solvent yielded a pale yellow oil (2.87 g; 22%). ¹H NMR (250 MHz, CDCl₃): δ = 4.14 (q, 2H; OCH₂CH₃), 3.68 (s, 2H; CH₂CN), 3.52 (t, 2H; CH₂Cl), 2.94 (t + t, 4H; NCH₂CH₂Cl + NCH₂CH₂COO), 2.52 (t, 2H; CH₂COO), 1.28 (t, 3H; CH₃); ¹³C{¹H} NMR (62.90 MHz, CDCl₃): δ = 171.45 (COO), 114.96 (CN), 60.70

(OCH₂CH₃), 55.62 (NCH₂CH₂Cl), 49.68 (NCH₂CH₂COO), 42.43 (CH₂CN), 41.29 (CH₂Cl), 33.08 (CH₂COO), 14.12 (CH₃).

D) Ethyl N-[(2-acetylthio)ethyl]-N-(cyanomethyl)-3-aminopropionate: Ethyl N-(2-chloroethyl)-N-(cyanomethyl)-3-aminopropionate (5.7 g, 26 mmol) and potassium thioacetate (3.654 g, 32 mmol) were dissolved in dry DMF (20 mL). The solution was stirred for 30 min at room temperature and for an additional 45 min at 45 °C. During that period a precipitate of KCl formed. All solvents were removed in vacuo and the residue was extracted three times with chloroform. Removal of the solvent yielded an air-sensitive and colorless oil (6.58 g; 98%). ¹H NMR (250 MHz, CDCl₃): δ = 4.14 (q, 2H; OCH₂CH₃), 3.62 (s, 2H; CH₂CN), 2.97 (t, 2H; NCH₂CH₂COO), 2.90 (t, 2H; NCH₂CH₂S), 2.57 (t, 2H; CH₂COO), 2.49 (t, 2H; CH₂S), 2.34 (s, 3H; SC(O)CH₃), 1.28 (t, 3H; CH₃); ¹³C{¹H} NMR (62.90 MHz, CDCl₃): δ = 195.41 (C(O)S), 171.48 (COO), 114.99 (CN), 60.62 (OCH₂CH₃), 53.45 (NCH₂CH₂S), 49.37 (NCH₂CH₂COO), 42.09 (CH₂CN), 33.05 (CH₂COO), 30.52 (SC(O)CH₃), 26.83 (CH₂S), 14.15 (CH₃).

E) 3-Hydroxy-N-(2-aminoethyl)-N-(2-mercaptoethyl)-propylamine (H₄-1): All functional groups in ethyl N-[(2-acetylthio)ethyl]-N-(cyanomethyl)-3-aminopropionate were reduced simultaneously by use of AlH₃. The AlH₃ was prepared from lithium aluminum hydride (LAH) (2.733 g, 72 mmol) and H₂SO₄ (3.065 g, 30 mmol; 96%) in dry THF (100 mL) as described.^[15b] The ester (2.58 g, 10 mmol) dissolved in THF (30 mL) was added dropwise to the vigorously stirred AlH₃ suspension. The reaction mixture was stirred for 48 h at ambient temperature, and residual AlH₃ was carefully hydrolyzed with degassed water (4.2 mL, 23 mmol). All solids were removed by filtration and washed with aqueous THF (5% water; 5 × 50 mL). The organic layers were combined, and all solvents removed in vacuo. Ligand H₄-1 was obtained as a white, air-sensitive solid (1.51 g; 84.8%). Elemental analysis calcd for C₇H₁₈N₂OS (178.29): C 47.16, H 10.18, N 15.71, S 17.98; found: C 47.25, H 10.15, N 15.56, S 17.37. ¹H NMR (250 MHz, CDCl₃): δ = 3.74 (s, 2H; CH₂OH), 2.84 (t, 2H; CH₂NH₂), 2.60 (m, 6H; NCH₂CH₂CH₂OH + NCH₂CH₂SH + CH₂SH), 2.50 (t, 2H; NCH₂CH₂NH₂), 2.24 (s, br, 4H; OH + NH₂ + SH), 1.68 (m, 2H; CH₂CH₂CH₂); ¹³C{¹H} NMR (62.90 MHz, CDCl₃): δ = 62.52 (CH₂OH), 57.35 (NCH₂CH₂SH), 56.54 (NCH₂CH₂NH₂), 53.00 (NCH₂CH₂CH₂OH), 39.66 (CH₂NH₂), 28.86 (CH₂CH₂CH₂), 22.36 (CH₂SH); MS (EI) *m/z* (%): 177 (43.69) [M - H]⁺, 148 (100) [M - CH₂NH₂]⁺, 131 (29.88) [M - H₂SH]⁺, 102 (36.66), 88 (30.78), 61 (27.01), 44 (65.57).

Preparation of nickel complexes: 2: H₄-1 (326 mg, 1.83 mmol) and triethylamine (182 mg, 1.8 mmol) were dissolved in acetonitrile (20 mL). This mixture was added dropwise to a solution of Ni(OAc)₂·4H₂O (448 mg, 1.8 mmol) in acetonitrile (20 mL). The solution immediately turned dark and a brown precipitate separated. The solid was collected by filtration and dissolved in methanol (5 mL). About 10 min after the addition of acetone (20 mL) to this solution, complex **2** separated as emerald cubes. Yield 460 mg (76.4%); elemental analysis calcd for C₂₄H₄₈N₄O₆S₂Ni₂ (670.20): C 43.01, H 7.22, N 8.36, S 9.57; found: C 42.95, H 7.16, N 8.26, S 9.76; MS (+FAB, 3-nitrobenzyl alcohol/DMSO) *m/z* (%): 549 (57.1) [M + H]⁺, 332 (11), 275 (100), 217 (49). IR (KBr): $\tilde{\nu}$ [cm⁻¹] = 3311 (s, OH), 2939, 2906, 2856 (s, C-H), 1651 (s, C=N), 1558 (s, C=O), 1041 (m, C-O), UV/Vis (CH₂Cl₂): λ_{max} [nm] = 400, 500 (sh), 670, 1060.

3: H₄-1 (326 mg, 1.83 mmol) was mixed with triethylamine (182 mg, 1.8 mmol). The mixture was added dropwise to a warm (40 °C) solution of Ni(ClO₄)₂·6H₂O (658 mg, 1.8 mmol) in acetonitrile (15 mL) resulting in the formation of purple and subsequently a green reaction product. Upon cooling of the solution to 3 °C a microcrystalline precipitate formed. The solid was separated by filtration. Slow recrystallization from warm acetonitrile yielded dark brown crystals (245 mg; 50.7%) that readily decomposed to give a fine powder when dried in vacuo. Elemental analysis calcd for C₂₁H₄₉N₆O₇S₃ClNi₃ (805.36): C 31.32, H 6.13, N 10.44, S 11.94; found: C 31.59, H 6.22, N 10.68, S 11.37; MS (+FAB, 3-nitrobenzyl alcohol/DMSO) *m/z* (%): 705 (7.6) [M]⁺, 469 (21); IR (KBr): $\tilde{\nu}$ [cm⁻¹] = 3337, 3283 (s, OH and NH₂), 2920, 2849 (s, C-H), 1461 (m, C-H), 1095 (vs, ClO₄), 623 (s, ClO₄); UV/Vis (CH₃OH): λ_{max} [nm] ϵ [10³ cm² mol⁻¹] = 470 (sh, 189.3), 625 (sh, 61.2), 1075 (32.2). **CAUTION: Perchlorate salts are potentially explosive. They should be handled in small amounts and with caution.**

4: a) Oxidation with hydrogen peroxide: For this oxidation **3** (80.5 mg, 0.1 mmol) was dissolved in methanol and treated with one equivalent of hydrogen peroxide (1% in water). The brown solution immediately turned

Table 1. Summary of the crystallographic data for 2–4.

	2	3	4
formula	C ₂₄ H ₄₈ N ₄ O ₆ S ₂ Ni ₂	C ₄₈ H ₁₀₉ N ₁₅ Cl ₂ Ni ₆ O ₁₅ S ₆ 2 equiv 3 · 3 CH ₃ CN · H ₂ O	C ₁₄ H ₃₂ N ₄ Ni ₂ O ₆ S ₂ · 2 CH ₃ OH
M _r	670.20	1752.03	598.06
T [K]	293(2)	198(2)	198(2)
cryst. size [mm]	0.20 × 0.20 × 0.20	0.60 × 0.25 × 0.10	0.60 × 0.40 × 0.30
a [Å]	11.202(1)	12.254(1)	7.662(1)
b [Å]	12.252(1)	13.229(1)	8.324(1)
c [Å]	12.352(1)	23.481(1)	10.085(1)
α [°]	90.0	89.73(1)	96.66(1)
β [°]	112.05(1)	79.76(1)	106.34(1)
γ [°]	90.0	81.58(1)	94.08(1)
V [Å ³]	1571.2(3)	3704.6(4)	609.4(1)
Z	2	2	1
space group	P2 ₁ /c (no. 14)	P $\bar{1}$ (no. 2)	P $\bar{1}$ (no. 2)
ρ _{calcd} [g cm ⁻³]	1.417	1.571	1.764
μ _{MoKα} [mm ⁻¹]	1.373	1.802	1.764
diffractometer	Enraf Nonius CAD-4	Enraf Nonius Kappa CCD	
λ [Å]	0.71073	0.71073	0.71073
2θ range [°]	2.4 ≤ 2θ ≤ 25.0	2.94 ≤ 2θ ≤ 30.54	2.97 ≤ 2θ ≤ 30.48
index range	±h, k, l	±h, ±k, ±l	±h, ±k, ±l
unique data	2026	21896	3618
obsd data			
[I ≥ 2σ(I)]	984	15490	3514
R	0.066	0.085	0.024
wR ²	0.107	0.230	0.063
no. of variables	172	735	155
largest diff.	0.36/–0.42	2.97/–2.49	0.40/–0.49
peak/hole [e Å ⁻³]	near disordered ClO ₄ ⁻		

green upon addition of the hydrogen peroxide. Slow diffusion of diethyl ether into the reaction solution yielded green cubes of 4.

b) Oxidation with air: A stream of air was bubbled through a solution of 3 (80.5 mg, 0.1 mmol) in DMF (5 mL). Within 24 h the color of the solution changed to green. Evaporation of the solvent and drying in vacuo yielded a green powder. Elemental analysis calcd for C₁₄H₃₂N₄O₆S₂Ni₂ (533.93): C 31.49, H 6.04, N 10.49, S 12.01; found: C 30.98, H 5.96, N 10.65, S 13.04; MS MS (+FAB, 3-nitrobenzyl alcohol/DMSO) m/z (%): 533 (2.6) [M+H]⁺, 267 (11).

X-ray structure analyses: Crystallographic data for complexes 2–4 are presented in Table 1. Crystals of 2 are air-stable. Diffraction data were collected at room temperature on an Enraf Nonius CAD-4 diffractometer. No absorption correction was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at geometrically idealized positions and were refined by using a riding model. Complexes 3 and 4 rapidly degenerate in air under loss of cocrystallized solvent. Suitable specimens were mounted at 198 K on a Nonius Kappa CCD diffractometer with a rotating anode generator. Diffraction data were collected at 198 K. Absorption corrections by SORTAV were applied to the raw data (0.411 ≤ T ≤ 0.840 for 3; 0.418 ≤ T ≤ 0.620 for 4). Two equivalents of 3 crystallize together with three molecules of acetonitrile and one molecule of water in the asymmetric unit. Both perchlorate anions and the acetonitrile molecules are disordered and were refined with geometric constraints and isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at geometrically idealized positions and were refined by using a riding model. No hydrogen atoms were localized for the water molecule. Complex 4 resides on an inversion center in the unit cell. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at geometrically idealized positions and were refined by using a riding model. The following programs were used: Data collection EXPRESS and COLLECT, data reduction MoIEN and DENZO-SMN, absorption correction for CCD data SORTAV, structure solution SHELXS-86 and SHELXS-97, structure refinement SHELXL-97, graphical presentation ZORTEP and SCHA-

KAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133073, CCDC-133074, and CCDC-133075. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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