$[Ni_5S(SBu^t)_5]^-$ and $[Ni_3S(SBu^t)_3(CN)_3]^{2-}$, novel complexes with sulfur-capped, thiolate-bridged polygonal metal frames

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$[Ni_5S(SBu^t)_5]^-$, an unprecedented pentanuclear sulfide thiolate cluster anion of fivefold symmetry containing a regularly shaped pentagonal nickel frame capped by a μ_5 sulfide ion, and $[Ni_3S(SBu^t)_3(CN)_3]^{2-}$, a related complex of threefold symmetry with additional cyanide ligands, are described.

The chemistry of nickel complexes with sulfur ligands has attracted much interest due to the unique biological function of nickel–sulfur sites in enzymes with hydrogenase activities.[1,2] Recently, we reported the synthesis and structure of the dinuclear complex anion $[Ni_2(SBu^t)_6]^{2-}$,[3] which is chemically related to the protein active site because its novel bitetrahedral Ni_2S_6 core contains a nickel ion linked to another one *via* two bridging thiolate ligands.[4] During our ongoing investigations of the reaction system $NiCl_2$–$NaSBu^t$ in acetonitrile, we have now synthesized two novel compounds with unprecedented coordination properties.

The reaction of $NiCl_2$ with 5 equiv. of $NaSBu^t$ in MeCN followed by the addition of 2 equiv. of $[PPh_4]Br$ yields after storage at −25 °C for 3–4 months, black crystals of $[Na(OPPh_3)_4][Ni_5S(SBu^t)_5]\cdot\frac{1}{2}C_6H_6\cdot\frac{1}{2}MeCN$ **1** as the only solid product in yields of *ca.* 35%. Under similar conditions, the presence of cyanide ions leads to the formation of the trinuclear compound $[PPh_4]_2[Ni_3S(SBu^t)_3(CN)_3]$ **3** which is isolated as the main product in form of dark-red crystals after diffusion of diethyl ether. The structures of **1** and **3** were determined by X-ray crystallography.†

Crystals of **1** contain discrete anions $[Ni_5S(SBu^t)_5]^-$ **2** with idealized C_{5v} symmetry, sodium cations coordinated by four $OPPh_3$ molecules, $[Na(OPPh_3)_4]^+$ and non-coordinating solvent molecules (see below). The structure of **2** is shown in Fig. 1.

The mixed-valent complex anion contains five Ni atoms, which define the vertices of a regular metal pentagon capped by a μ_5-S ion. The Ni–S bond lengths within the resulting flat Ni_5S pyramid range from 2.165(2) to 2.202(2) Å. In addition to the capping sulfide ion, each edge of the Ni pentagon is symmetrically bridged by a μ-SBu^t residue resulting in a trigonal-planar sulfur coordination for each Ni atom. The Ni–Ni distances within the metal pentagon (average 2.428 Å) are indicative of metal–metal bonds in accordance with an electron-delocalized system (mean oxidation state of Ni: +1.2). It is interesting that both metal atoms within the coordination sphere of a central Ni atom deviate only slightly from the plane defined by the S atoms.

Although the overall architecture of **2** is unique in nickel–sulfur chemistry, the metal atoms are in coordination environments similar to that observed for the set of six equivalent Ni atoms within the octanuclear complex anion $[Ni_8S(SBu^t)_9]^-$.[5] In both cases, the Ni atoms have three sulfur (thiolate : sulfide ratio 2 : 1) and two nickel neighbours each in nearly coplanar arrangements and within comparable distance ranges.

As far as we are aware, **2** is the first complex known to contain a μ_5-S ligand. However, comparable μ_5-Se ligands have been observed within the Ni–Se cluster frameworks of $[Ni_{34}Se_{22}(PPh_3)_{10}]$[6] and $[Ni_{20}Se_{12}(SeMe)_{10}]^{2-}$.[7] Both contain pentagonal Ni_5Se pyramids which resemble the Ni_5S unit present in **2**. Related Co_5Te fragments have also been identified in the cluster anion $[Co_{11}Te_7(CO)_{10}{}^{2-}]$.[8] Interestingly, in all these cases the compounds are mixed-valent with mean metal oxidation states ranging from +1.09 to +1.70.

The complex ion $[Na(OPPh_3)_4]^+$ exhibits no unusual structural features. The $OPPh_3$ ligands are most probably formed *in situ* as one product of the hydrolysis of $[PPh_4]^+$ cations, which were added to the reaction system as $[PPh_4]Br$. This reaction is probably caused by slow diffusion of water into the initially anhydrous system *via* greased joints. The other hydrolytic product is benzene, which is found to stabilize the crystal lattice together with acetonitrile. As a consequence of the incorporation of solvate molecules, one of the four independent $OPPh_3$ ligands is statistically disordered. Each sodium ion is surrounded by the oxygen atoms of four $OPPh_3$ ligands in a slightly distorted tetrahedral fashion. The Na–O distances depend on the P–O–Na angles, the individual distance/angle pairs are 2.209(5)/166.3(3), 2.23(2)/165(1), 2.241(5)/156.8(3) and 2.265(5) Å/140.4(3)°, respectively.

The complex anion **2** is the product of a complicated reaction, which must involve, besides the reduction of the metal, the elimination of a sulfide ion perhaps by condensation processes resulting in the formation of a corresponding thioether molecule. It is interesting that the formation of **2** takes place either with the simple starting components or by treating the

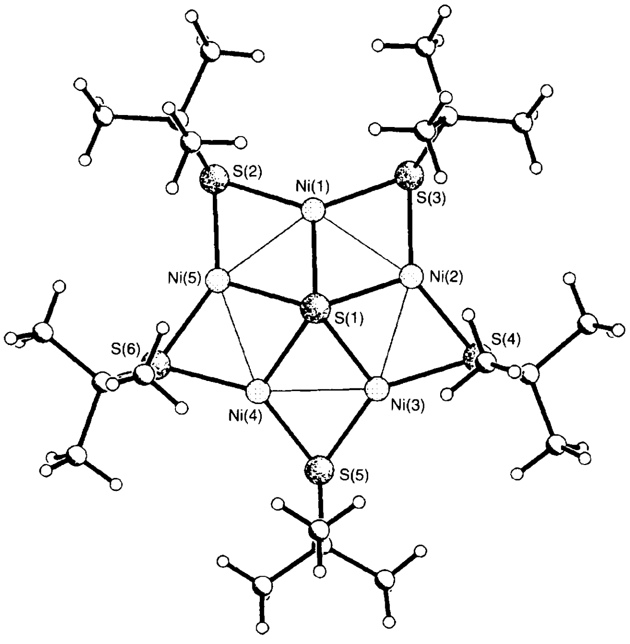

Fig. 1 Molecular structure of $[Ni_5S(SBu^t)_5]^-$ with atomic labels showing the overall fivefold symmetry. Mean distances (Å) and angles (°): Ni–Ni 2.428, Ni–S(1) 2.179, Ni–μ-S 2.163, Ni–S(1)–Ni 67.7, 128.6, Ni–μ-S–Ni 68.3, S(1)–Ni–μ-S 110.7, μ-S–Ni–μ-S 138.2.

previously isolated dinuclear complex $Na_2[Ni_2(SBu^t)_6]\cdot 4MeCN$[3] with Ph_4PBr in MeCN. However, if cyanide ions are introduced in this reaction system reduction of nickel is surprisingly prevented and the trinuclear complex **3** is isolated. The structure of the anion $[Ni_3S(SBu^t)_3(CN)_3]^{2-}$ **4** is depicted in Fig. 2.

Crystals of **3** contain discrete anions **4** of idealized C_{3v} symmetry and $[PPh_4]^+$ counter ions. The three Ni atoms form an equilateral triangle capped by a μ_3-S ion. Besides the capping sulfide ion, each edge of the Ni triangle is symmetrically bridged by a μ-SBu^t ligand. In addition, each Ni atom is terminally bonded to a cyanide ion resulting in a slightly distorted square-planar coordination with a S_3C donor set. A complex with non-bridging nitrogen donor functions is also known.[9] The central Ni_3S_4 core of **4** resembles the even more distorted ones found in the structurally related complex ions $[Ni_3S(SMe)_6]^{2-}$,[10] $[Ni_3S(SPh)_6]^{2-}$[11] and $[Ni_3S(SCH_2C_6H_4CH_2S)_3]^{2-}$[12] which have all-sulfur ligand spheres. Complexes with related M_3S_4 cores, but with tetrahedral metal stereochemistries are also known from other transition metals such as iron[13,14] or cobalt.[14,15]

The syntheses of the compounds reported here demonstrate that there are still surprises in store in transition-metal chemistry with thiolate ligands. Anion **2** is the first example of a new class of pentanuclear complexes, and other members should be expected. Furthermore, the isolation of the reaction products discussed here allows deeper insights into the complex reaction pathways within these reaction systems.

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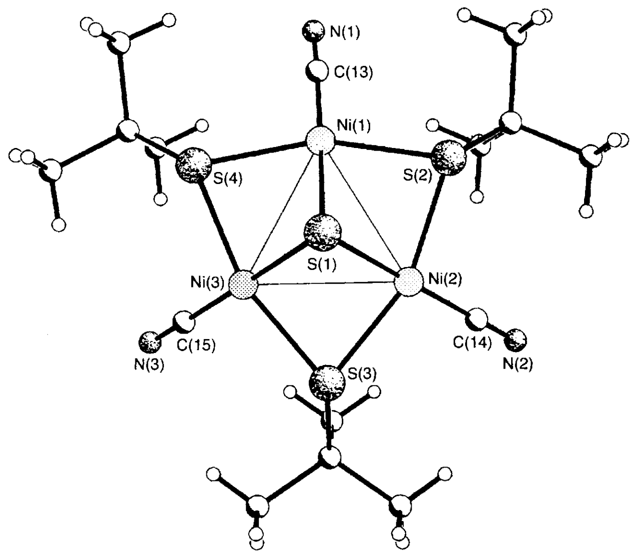

Fig. 2 Molecular structure of $[Ni_3S(SBu^t)_3(CN)_3]^{2-}$ with atomic labels showing the overall threefold symmetry. Mean distances (Å) and angles (°): Ni···Ni 2.825, Ni–S(1) 2.204, Ni–μ-S 2.206, Ni–C 1.868, Ni–S(1)–Ni 79.7, Ni–μ-S–Ni 79.6, S(1)–Ni–μ-S 78.8, μ-S–Ni–μ-S 156.9; S(1)–Ni–C 178.6, μ-S–Ni–C 101.2.

Footnotes

† *Crystal data.* Siemens P4RA four circle diffractometer, rotating-anode generator, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, scintillation counter, T = 150 K, empirical absorption correction; direct methods, full-matrix least-squares refinement, non-hydrogen atoms anisotropic, H atoms at idealized positions, one common isotropic temperature factor for H within each organic residue, solvate molecules isotropic (**1**), one extinction parameter, one scaling factor.

1: $C_{192}H_{219}NNa_2Ni_{10}O_8P_8S_{12}$, M = 3934.24, monoclinic, space group $P2_1/c$, a = 19.175(3), b = 14.214(3), c = 35.781(7) Å, β = 97.37(1)°, U = 9670 Å^3, Z = 2, D_c = 1.351 g cm^{-3}, μ(Mo-Kα) = 1.20 mm^{-1}, transmission range 0.665–0.540, $2\theta_{max}$ = 48°, ω-scan, crystal dimensions *ca.* 0.55 × 0.27 × 0.25 mm, 15179 unique reflections, $R(R_w)$ = 0.0646 (0.0573) for 10320 reflections with $I > 2\sigma(I)$, 1141 variables.

3: $C_{63}H_{67}Ni_3N_3P_2S_4$, M = 1232.51, triclinic, space group $P\bar{1}$, a = 11.240(2), b = 11.839(2), c = 23.152(4) Å, α = 100.02(1), β = 92.01(1), γ = 99.56(1)°, U = 2985 Å^3, Z = 2, D_c = 1.371 g cm^{-3}, μ(Mo-Kα) = 1.17 mm^{-1}, transmission range 0.744–0.655, $2\theta_{max}$ = 54°, ω-scan, crystal dimensions *ca.* 0.65 × 0.42 × 0.35 mm, 13026 unique reflections, $R(R_w)$ = 0.0347 (0.0372) for 10202 reflections with $I > 2\theta(I)$, 682 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/24.

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