$[Ni_4(S_2)(SCH_2CH_2S)_4]^{2-}$, the First Polysulphide–Thiolate Complex of a Transition Metal and $[Ni_3(SCH_2CH_2S)_4]^{2-}$, a Related Linear Trinuclear Nickel Thiolate

Wolfgang Tremel, Bernt Krebs, and Gerald Henkel*

Anorganisch-Chemisches Institut der Universität, Correnssstrasse 36, D-4400 Münster, West Germany

$[Ni_4(S_2)(SCH_2CH_2S)_4]^{2-}$, which can be obtained by reaction of $NiCl_2$, $Na_2(SCH_2CH_2S)$, and Na_2S_2, is the first complex that contains polysulphide and thiolate ligands simultaneously; the related trinuclear thiolate $[Ni_3(SCH_2CH_2S)_4]^{2-}$ has a linear metal frame and is formed in the absence of Na_2S_2.

The chemistry of transition-metal complexes with sulphur ligands has attracted much attention in the past, and a variety of homo- and hetero-nuclear transition metal–sulphur clusters with biological or industrial relevance have been prepared (see for example ref. 1 and references cited therein). While these investigations have focused predominantly on iron in the first transition series, a comparably extensive chemistry of nickel has not been developed as yet, although the biological significance of nickel–sulphur complexes[2] and the importance of nickel promotors in heterogeneous catalysis based on transition metal sulphides[3] has been recognised. In particular, there is a lack of knowledge concerning structural and chemical properties of homonuclear nickel–thiolate and nickel–sulphide–thiolate clusters, respectively, and only few complexes containing bridging SR^- ligands have been reported.[4]

In the search for nickel–sulphide–thiolate complexes which derive from metal–sulphur core units different from the pyramidal Ni_3S portion observed in $[Ni_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ (S_2-o-xyl^{2-} = o-xylene-α,α'-dithiolate),[5] Ni^{II}/edt^{2-}/X reaction systems [edt^{2-} = ethane-1,2-dithiolate, X = S^{2-}, $S_2{}^{2-}$, $S_x{}^{2-}$ (x>2), S_8, SR^-, edt^{2-}] employing the bidentate edt^{2-} ligand have been explored. Whereas the S_2-o-xyl^{2-} ligand supports, as previously demonstrated, not only the square-planar[5] but also the tetrahedral stereochemistry,[6] the edt^{2-} ligand was chosen because its intraligand S · · · S separation fits perfectly well into planar NiS_4 units but does not allow an undistorted tetrahedral Ni–S co-ordination.

We report here the synthesis and structure of $[Ni_4(S_2)(edt)_4]^{2-}$ (**1**), which is one of the two structurally defined complexes containing both disulphide and thiolate ligands simultaneously known so far {the other one is $[Mo_3(S_2)_3S(edt)_3]^{2-}$ [7]}, and of $[Ni_3(edt)_4]^{2-}$ (**2**), a novel homoleptic nickel thiolate. The tetranuclear cluster (**1**) was initially obtained from the Ni^{II}/edt^{2-}/$S_2{}^{2-}$ systems containing a 1:2:1 ratio of the reactants in methanol and could be isolated as $[Ph_4P]_2[Ni_4(S_2)(edt)_4]\cdot MeOH$ (**3**) on addition of Ph_4PBr. In subsequent optimization processes a more rational synthetic procedure has been developed which, according to equation (1), results in improved (50%) yields after recrystallization from dimethylformamide (DMF)–MeOH.

$$4\,NiCl_2 + 4\,Na_2edt + Na_2S_2 \rightarrow Na_2[Ni_4(S_2)(edt)_4] + 8\,NaCl \qquad (1)$$

The electronic spectrum of (**1**) in DMF is characterized by absorptions at $\lambda_{max.}$ 453 nm (ε 9000) and 354 nm (sh). Complex (**1**) is essentially diamagnetic. The cyclic voltammogram shows one irreversible reduction wave at −1.79 V.†

The trinuclear thiolate (**2**) could be isolated from the reaction system Ni^{II}/edt^{2-} (2:3) as green water-soluble crystals of $[Ph_4P]_2[Ni_3(edt)_4]$ (**4**) on addition of Ph_4PBr. Analytical and spectroscopic data [$\lambda_{max.}(\varepsilon)$: 662 (1200), 526 (2600), 443 (3900), 316 (16900) nm; diamagnetic] indicate the complex to be identical with a side product of the Ni^{II}/edt^{2-}/$S_2{}^{2-}$ (1:2:1) system.

$[Ni_4(S_2)(SCH_2CH_2S)_4]^{2-}$
(**1**)

$[Ni_3(SCH_2CH_2S)_4]^{2-}$
(**2**)

$[Ph_4P]_2[Ni_4(S_2)(SCH_2CH_2S)_4]\cdot MeOH$
(**3**)

$[Ph_4P]_2[Ni_3(SCH_2CH_2S)_4]$
(**4**)

$[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$
(**5**)

The structures of (**3**) and (**4**) were determined by X-ray

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† On a platinum electrode *vs.* saturated calomel electrode in DMF, 100 mV/s, solutions *ca.* 0.001 M in electrolyte and *ca.* 0.05 M in $Bu^t{}_4NClO_4$.

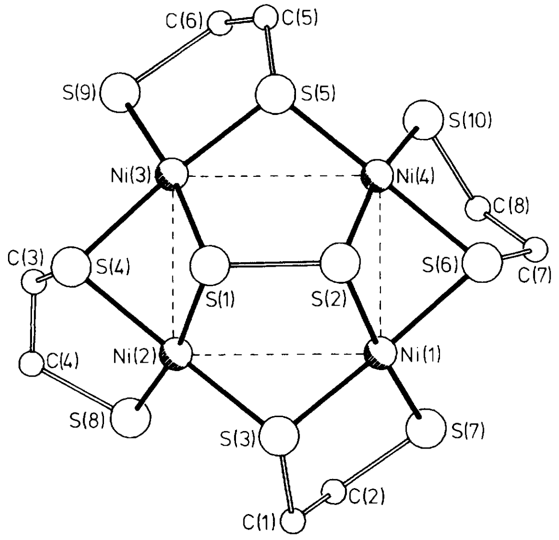

Figure 1. Structure of the tetranuclear $[Ni_4(S_2)(SCH_2CH_2S)_4]^{2-}$ anion (**1**) without H atoms. Metal co-ordination: distances, Ni(1) · · · Ni(2) 3.329(2), Ni(1) · · · Ni(4) 2.822(1), Ni(2) · · · Ni(3) 2.869(1), Ni(3) · · · Ni(4) 3.344(2), mean Ni(1)–S 2.185, mean Ni(2)–S 2.177, mean Ni(3)–S 2.182, mean Ni(4)–S 2.193 Å; angles (arranged into sets of 4 and 2, respectively), S–Ni(1)–S 92.6 and 172.2, S–Ni(2)–S 90.2 and 170.5, S–Ni(3)–S 90.0 and 172.4, S–Ni(4)–S 90.3 and 167.6°.

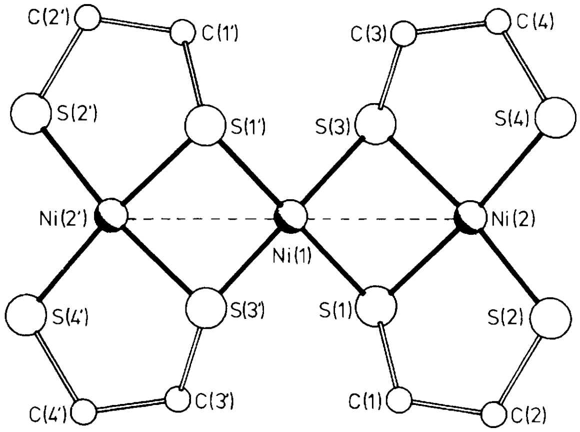

Figure 2. Structure of the trinuclear $[Ni_3(SCH_2CH_2S)_4]^{2-}$ anion (**2**) without H atoms; the primed atoms are related to the unprimed ones by a centre of inversion. Metal co-ordination: distances, Ni(1) · · · Ni(2) 2.856, mean Ni(1)–S 2.200, mean Ni(2)–S 2.183 Å; angles (arranged into sets of 4 and 2, respectively), S–Ni(1)–S 90 and 180, S–Ni(2)–S 89.9 and 172.7°.

crystallography.‡ In crystals of (**3**) isolated anions (**1**) are separated by Ph_4P^+ cations and discrete MeOH molecules. Though the anions occupy crystallographically equivalent sites, *ca.* 15% of them, (**1a**), are rotated with respect to the remaining ones, (**1b**), in such a way that the positions of two nickel atoms and all of the non-bridging sulphur atoms coincide in both orientations. These positions are occupied by Ni(1), Ni(3), S(7), S(8), S(9), and S(10). Consequently, two different sets of atomic positions for the anions (**1a**) and (**1b**) are present with occupancies of 0.15 and 0.85, respectively. These sets could be resolved with respect to the metal–sulphur frames, but owing to the small scattering cross section of carbon only (**1b**) could be completely defined. The geometrical data of (**1**) given in this paper thus refer to (**1b**). The anion (**1**) consists of four nickel atoms, four edt^{2-} ligands, and a bridging $S_2{}^{2-}$ group. Its projection is shown in Figure 1.

The metal-sulphide frame has the mixed Ni_4S_2 prismane type structure with four nickel atoms in a rectangular arrangement [mean Ni · · · Ni 2.846 (×2), 3.337 (×2) Å]. The sulphur atoms of the central $S_2{}^{2-}$ ligand [S(1) and S(2), S–S 2.084(3) Å] are bonded to two different nickel atoms each (mean Ni–S 2.217 Å). In addition, the nickel atoms are bridged by four thiolate S atoms [S(3), S(4), S(5), and S(6), mean Ni–S 2.177 Å] and complete their ligand spheres by bonds to the remaining four thiolate S atoms [S(7), S(8), S(9), and S(10), mean Ni–S 2.166 Å]. Thus each edt^{2-} ligand furnishes one terminal and one bridging S atom to the polycyclic Ni_4S_{10} core which consists of two five-membered Ni_2S_3 and two four-membered Ni_2S_2 rings folded along their Ni · · · Ni diagonals with square-planar NiS_4 co-ordination sites. The architecture of the Ni_4S_{10} core observed in (**1**) has not been found previously in any discrete cluster nor, to our knowledge, is it part of the structure of any sulphide mineral.

Crystals of (**4**) consist of isolated anions (**2**) and discrete Ph_4P^+ cations. The anions (**2**) occupy crystallographic inversion centres. As a result, the metal frame of the complex which consists of three nickel atoms and four edt^{2-} ligands is strictly linear [Ni · · · Ni 2.856(1) Å]. The structure of (**2**) is depicted in Figure 2.

The central nickel atom is chelated by two identical $Ni(edt)_2$ entities with square-planar NiS_4 centres [mean Ni(2)–S 2.183 Å, mean S–Ni(2)–S 89.9 (×4), 172.7° (×2)] such that Ni(1) is surrounded by four coplanar bridging thiolate S atoms [mean Ni(1)–S 2.200 Å]. The three NiS_4 units are condensed *via* opposite edges of the central NiS_4 site to form a Ni_3S_8 frame in a chair-like conformation with angles of 116.8° between adjacent NiS_4 units.

It is particularly informative to compare the trinuclear Ni_3S_8 moiety of (**2**) with the Ni_3S_8 frame of the related complex $[Ni_3(S_2\text{-}o\text{-}xyl)_4]^{2-}$ (**5**).[8] The bent arrangement of the Ni atoms in (**5**) [Ni · · · Ni 3.074 Å, Ni · · ·Ni · · · Ni 131.34°] is a result of an Ni_3S_8 frame in a boat-like conformation and can be attributed to the steric requirements of the $S_2\text{-}o\text{-}xyl^{2-}$ ligands. The same arguments can be used to explain why the

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‡ *Crystal data.* Syntex P2₁ four circle diffractometer, Mo-K_α radiation, graphite monochromator, scintillation counter, 2θ—θ scan mode, T = 150 K, empirical absorption corrections.

Compound (**3**): $C_{57}H_{60}Ni_4OP_2S_{10}$, M = 1378.41, triclinic, a = 11.506(6), b = 11.902(6), c = 23.152(13) Å, α = 104.10(4), β = 97.23(4), γ = 105.73(4) °, space group $P\bar{1}$, Z = 2, D_c = 1.583 g cm^{-3}, μ(Mo-K_α) = 17.3 cm^{-1}, $2\theta_{max.}$ = 44°, crystal dimensions 0.20 × 0.15 × 0.10 mm, 7161 unique reflections, R (R_w) = 0.057 (0.057) for 5715 reflections with $F > 3.92\sigma(F)$ {699 variables, H atoms fixed at idealized positions with isotropic temperature factors tied to the equivalent isotropic temperature factors of the C atoms to which they are bonded [$U(H) = 1.2U_{eq.}(C)$], all other atoms with the exception of the resolved atoms of (**1a**) refined with anisotropic temperature factors together with an overall scale factor}.

Compound (**4**): $C_{56}H_{56}Ni_3P_2S_8$, M = 1223.56, triclinic, a = 9.974(3), b = 11.303(4), c = 13.840(5) Å, α = 105.91(3), β = 98.91(3), γ = 112.62(2)°, space group $P\bar{1}$, Z = 1, D_c = 1.535 g cm^{-3}, μ(Mo-K_α) = 14.6 cm^{-1}, $2\theta_{max.}$ = 54°, crystal dimensions 0.30 × 0.20 × 0.20 mm, 5784 unique reflections, R (R_w) = 0.038 (0.039) for 4531 reflections with $F > 3.92\sigma(F)$ {313 variables, H atoms fixed at idealized positions with isotropic temperature factors tied to the equivalent isotropic temperature factors of the C atoms to which they are bonded [$U(H) = 1.2U_{eq.}(C)$], all other atoms refined with anisotropic temperature factors together with an overall scale factor}.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

co-ordination modes of the ligands in (**5**) (two of them with a total of four Ni–S bonds each, the other two without bridging S groups) are different from those found in (**2**) (four equivalent ligands).

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