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Synthesis and Structure of $[Ni_3(\mu_3\text{-}S)(o\text{-}\{SCH_2\}_2\text{-}C_6H_4)_3]^{2-}$, a New Type of Trinuclear Nickel–Sulfide–Thiolate Cluster

WOLFGANG TREMEL, BERNT KREBS and GERALD HENKEL*

Anorganisch-Chemisches Institut der Universität Münster, Corrensstr. 36, D-4400 Münster, F.R.G.

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Introduction

During recent years considerable interest has been shown in finding synthetic routes for transition metal–sulfur compounds as models for the active sites of metalloproteins [1]. The discovery of 3Fe–3S clusters in several iron–sulfur proteins [2] has stimulated research in the field of iron–sulfide–thiolate chemistry. In the course of developing preparative routes to 3-Fe complexes, which might serve as synthetic analogues of the active sites of iron–sulfur proteins such as *Desulfovibrio gigas* Fd II [3] or *Azotobacter vinelandii* Fd I [4], the reactions of Fe(II) and Co(II) salts with *o*-xylenedithiolate (S_2-*o*-xyl^{2-}) or durene-α,α'-dithiolate (S_2-dur^{2-}) and sodium hydrosulfide have been shown to produce the trinuclear cluster anions $[Fe_3(\mu_3\text{-}S)(o\text{-}\{SCH_2\}_2\text{-}C_6H_2R_2)_3]^{2-}$ {R = CH_3 (*1a*) [5] or R = H (1b)} [6, 7] and $[Co_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3]^{2-}$ (*2*) [6, 7]. However the corresponding $[Ni_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3]^{2-}$ cluster (*3*) is still unknown. The synthesis and structure of the title compound shows *1* and *2* to be examples of a more general cluster type $[M_3(\mu_3\text{-}S)(o\text{-}\{SCH_2\}_2\text{-}C_6H_2R_2]^{2-}$ with M = Mn, Fe, Co, Ni [8]. Interest in nickel sulfur chemistry has grown as the presence of nickel in several hydrogenases has been established recently [10].

We have investigated the reaction system $NiCl_2$/Na_2S_2-*o*-xyl/X (X = S^{2-}, PhS^-, S_2-*o*-xyl^{2-}, $R_2NCS_2^-$). This communication reports the preparation and structural investigation of the trinuclear $[Ni_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3]^{2-}$ cluster anion. In addition the trinuclear Ni–thiolate cluster $[Ni_3(S_2\text{-}o\text{-}xyl)_4]^{2-}$ was isolated [11].

Experimental

Preparations and manipulations were conducted under a pure dinitrogen atmosphere using degassed solvents.

A solution of 5.10 g (30 mmol) H_2S_2-*o*-xyl and 1.38 g (60 mmol) Na in 100 ml of methanol was added to a solution of 3.90 $NiCl_2$ (30 mmol) in 50 ml of methanol. After stirring for 20 min, a solution of 0.56 g NaSH (10 mmol) and 0.23 g Na (10 mmol) in 50 ml of methanol was added producing a brown slurry. The mixture was stirred for 16 h and filtered. Upon addition of 2.20 g NMe_4Cl (20 mmol) in 50 ml of methanol black crystals of $[Ni_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3][NMe_4]_2\cdot MeOH$ appeared. The product was collected by filtration, washed with methanol, and dried. Pure material can be obtained by recrystallization from acetonitrile. *Anal.* Calcd for $C_{33}H_{52}N_2Ni_3OS_7$: C, 44.37; H, 5.87; N, 3.16. Found: C, 43.48; H, 6.08; N, 3.10. The electronic spectrum of *3* in acetonitrile is characterized by absorptions at 796, 604, 476, and 335 nm.

Crystal data: $C_{33}H_{52}N_2Ni_3OS_7$, $M = 893.34$ a.m.u., monoclinic, $a = 953.8(3)$ pm, $b = 2721.6(7)$ pm, $c = 1596.1(5)$ pm, $\beta = 103.52(2)^\circ$, $V = 4028.4 \times 10^6$ pm^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.473$ g cm^{-3}, $\mu(\text{Mo-K}_\alpha) = 17.7$ cm^{-1}, T = 140 K. Intensity data were collected on a SYNTEX $P2_1$ four-circle diffractometer with Mo-K_α radiation (graphite monochromator, scintillation counter, ω-scan, $(\sin\theta)/\lambda_{max} = 0.57$ Å^{-1}, empirical absorption correction). The structure was solved by direct methods and Fourier procedures. Least-squares refinements converged at $R(R_w) = 0.035(0.033)$ for 4755 reflections ($F_0 > 3.92\ \sigma(F_0)$). The positional and thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

Results and Discussion

The structure of the anion is shown in Fig. 1. Though it has no crystallographically imposed symmetry, the point symmetry of the Ni_3S_7 frame may be considered to be C_{3v}. The three Ni atoms form an equilateral triangle (Ni–Ni: 281.8 pm) with the central μ_3-S atom on the local threefold axis above the metal centre. In addition, each edge of the metal triangle is bridged symmetrically by one of the two S atoms of a thiolate group, while the second S atom is terminally bound, completing the coordination sphere of Ni towards an approximately square planar environment of four sulfur atoms. In this structural feature *3* differs fundamentally from *1* and *2*, where a tetrahedral coordination is adopted by Fe(II) and Co(II). Within experimental error each Ni atom and the four surrounding sulfur atoms are coplanar, distortions from ideal square planar stereochemistry are assumed to be generated by geometric limitations of the ligands. The Ni–Ni distances (mean: 281.8 pm) are shorter than those found in other completely

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*Author to whom correspondence should be addressed.

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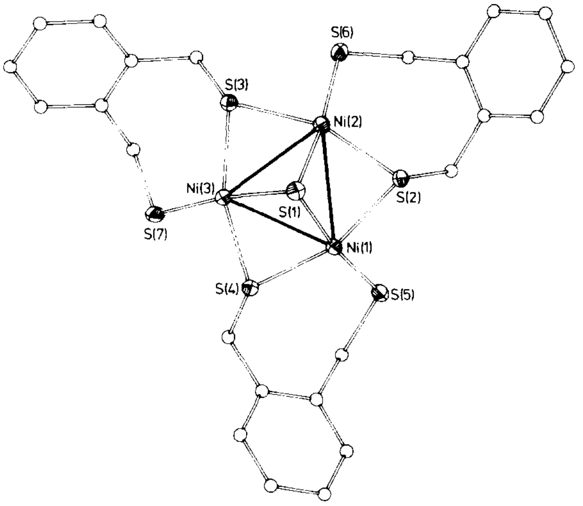

Fig. 1. Structure of the $[Ni_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3]^{2-}$ anion in crystals of $[(CH_3)_4N]_2[Ni_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3]\cdot MeOH$; vibration ellipsoids of the Ni and S atoms with 50% probability. Selected distances [pm] ($\sigma = 0.1$ pm): Ni(1)–Ni(2) 284.0; Ni(1)–Ni(3) 281.7; Ni(2)–Ni(3) 279.8; Ni(1)–S(1) 221.1; Ni(1)–S(2) 220.3; Ni(1)–S(4) 221.4; Ni(1)–S(5) 219.2; Ni(2)–S(1) 221.5; Ni(2)–S(2) 220.4; Ni(2)–S(3) 218.8; Ni(2)–S(6) 219.0; Ni(3)–S(1) 221.9; Ni(3)–S(3) 220.1; Ni(3)–S(4) 220.3; Ni(3)–S(7) 218.6.

sulfur-coordinated polynuclear Ni complexes, *e.g.* 290.4 pm in $[Ni_3S_2(NS_3)_3]^-$ [12], 292 pm in $[Ni(SC_2H_5)_2]_6$ [13], and 307.4 pm in $[Ni_3(S_2\text{-}o\text{-}xyl)_4]^{2-}$ [11]; the Ni–S–Ni angles vary from 78.25 to 80.25°. The average values of the Ni–S bond lengths are within the expected limits (Ni–μ_3S: 221.5 pm, Ni–μ_2S: 220.2 pm, Ni–S: 219.0 pm), however they are clearly divided into different sets for triple and double bridging and terminal sulfur atoms, respectively.

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8 A simple MO model indicates that the formation of the corresponding $[Zn_3(\mu_3\text{-}S)(S_2\text{-}o\text{-}xyl)_3]^{2-}$ should not be as favoured as corner-sharing ZnS_4 arrangements. In fact, reaction of $ZnCl_2/Na_2S_2\text{-}o\text{-}xyl/NaSH$ (3:3:1) affords a 'superadamantane-type' $[Zn_{10}S_4(S_2\text{-}o\text{-}xyl)_8]^{4-}$ anion, analogous to the recently reported $[Zn_{10}S_4(SPh)_{16}]^{4-}$ [9]; W. Tremel, B. Krebs and G. Henkel, results to be submitted for publication.

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