# Formation and Structure† of $[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]^{2-}$, a Cyclic Trinuclear Metal–Sulphide–Thiolate Cluster with Simple Monofunctional Thiolate Ligands

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The reaction of $NiCl_2$ with Na(SMe) in acetonitrile (molar ratio 1 : 4.4) gives the trinuclear cluster $[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]^{2-}$ (**2**) in 12% yield. It can be isolated as black crystals of $[NMe_4]_2[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]$ (**3**) in the presence of $NMe_4Cl$. The crystal and molecular structure of (**3**) has been determined from *X*-ray diffraction data. Crystals are cubic, space group $P2_13$, with $a = 13.801(4)$ Å and $Z = 4$. The structure was solved by direct methods and refined to $R$ ($R'$) = 0.018 (0.014) on the basis of 1 029 observed reflections with $I > 1.96\sigma(I)$. Anion (**2**) is the first example of a cyclic trinuclear metal–sulphide–thiolate complex which contains simple monofunctional ligands and thus is not stabilized by chelating thiolate groups. It consists of three Ni atoms, one triply bridging suphide ion, and six $MeS^-$ ligands in two different co-ordination modes. The electronic spectrum is consistent with a diamagnetic $d^8$ system. Structural changes related to the steric requirements of the ligands are discussed.

Transition-metal complexes containing sulphide ions and thiolate ligands simultaneously constitute a continuously growing family of polynuclear compounds in metal–sulphur chemistry. With respect to trinuclear species with thiolate bridges and tetrahedral or square-planar co-ordination sites sharing common edges, two fundamental cluster principles have been recognized. One (type I, tetrahedral co-ordination) is derived from the widely distributed metal–sulphur cubane-type $M_4(\mu_3\text{-}S)_4$ cage[1] and is observed in $[M_3(\mu_3\text{-}S)L^1{}_3]^{2-}$ [$L^1$ = *o*-phenylenedimethanethiolate(2−)] with M = Co[2,3] or Fe[3,4] and in $[Fe_3(\mu_3\text{-}S)L^2{}_3]^{2-}$ [$L^2$ = 4,5-dimethyl-*o*-phenylenedimethanethiolate(2−)],[5] and the other (type II, square-planar co-ordination) is derived from the sulphur cubane-type $M_6(\mu_3\text{-}S)_8$ cage[6] and is observed in $[Ni_3(\mu_3\text{-}S)L^1{}_3]^{2-}$ (**1**).[7] In both cases the trinuclear clusters known so far are stabilized by 1,4-dithiolate ligands ($L^1$ or $L^2$) which form seven-membered chelate rings each providing one thiolate bridge and one terminally bonded thiolate function.

We report here the unexpected formation of $[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]^{2-}$ (**2**), which is the first cyclic trinuclear metal–sulphide–thiolate complex with simple monofunctional thiolate ligands, and the structure of $[NMe_4]_2[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]$ (**3**).

## Experimental

*Synthesis.*—All operations were carried out in a pure dinitrogen atmosphere using solvents degassed prior to use. Sodium methanethiolate was prepared from dimethyl disulphide and sodium in tetrahydrofuran and isolated as a white solid.[8]

To a stirred suspension of $NiCl_2$ (0.65 g, 5 mmol) in acetonitrile (60 cm³) was added solid Na(SMe) (1.54 g, 22 mmol). After 20 h, a dark precipitate was removed containing *ca.* 10% of the overall Ni. The brown filtrate was treated with an excess of solid $NMe_4Cl$ and stored at room temperature. A few days later black crystals started to separate slowly from the solution. They were collected by filtration, washed with diethyl ether, and dried *in vacuo*; yield 0.13 g (12%) of $[NMe_4]_2[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]$ (**3**) (Found: C, 26.0; H, 6.60; N, 4.65. Calc. for $C_{14}H_{42}N_2Ni_3S_7$: C, 26.3; H, 6.60; N, 4.40%). From the brown filtrate an insoluble and unreactive brown product, presumably a polymeric thiolate, which contained *ca.* 75% of the total Ni separated on standing at room temperature. The electronic spectrum of compound (**3**) in dimethylformamide (dmf) is characterized by absorptions at $\lambda_{max.}$ 338 ($\varepsilon$ 2 637) and 484 nm (810 dm³ mol⁻¹ cm⁻¹).

*Structure Determination.*—*X*-Ray diffraction data were collected with an automated Syntex $P2_1$ four-circle diffractomer. The unit-cell dimensions with standard deviations were derived from a least-squares fit from the angular positions of 15 centred reflections in the range $20 \leqslant 2\theta < 30°$. Crystal data and details of the data collection and structure refinement are given in Table 1. An empirical absorption correction ($\psi$ scan) was applied. After averaging, the intensities were corrected for Lorentz and polarization effects. Direct methods provided the positions of the nickel and the sulphur atoms. Subsequent least-squares refinement cycles followed by Fourier difference syntheses revealed the positions of all other atoms in the unit cell. Final full-matrix refinement cycles (Ni, S, C anisotropic, H isotropic) converged to $R = 0.018$ and $R' = 0.014$. Both the $[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]^{2-}$ anions as well as the $NMe_4{}^+$ cations occupy three-fold rotation axes in the crystal. Further details concerning the data reduction and refinements including definitions of the $R$ values *etc.* can be found in ref. 8. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

## Results and Discussion

The reaction of $Ni^{II}$ with aliphatic thiolates $RS^-$ can easily be directed towards polymeric insoluble products of general formula $[Ni(SR)_2]_n$. In certain cases, however, polynuclear nickel thiolates could be isolated and structurally characterized which are either members of the open-chain family $[Ni_n(SR)_{2n+2}]^{2-}$ with $n$ = 2,[9,10] 3,[9,11,12] or 6[13] or of the cyclic family $[Ni_n(SR)_{2n}]$

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† Bis(tetramethylammonium) tri-μ-methanethiolato-$\mu_3$-sulphido-tris(methanethiolatonickelate).

*Supplementary data available:* Bond distances and valence angles of the $NMe_4{}^+$ cations, anisotropic thermal parameters, and observed and calculated structure factors can be ordered from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, quoting reference number CSD 52653, the names of the authors, and the title of the paper.

with $n$ = 4,[14,15] 5,[15] 6,[16–18] or 8.[19] A characteristic property of all these complexes is the square-planar $NiS_4$ stereochemistry which is also observed in the mononuclear complex[10] $[Ni(SCH_2CH_2S)_2]^{2-}$ but which is avoided in the anion $[Ni(SPh)_4]^{2-}$ in favour of a tetrahedral $NiS_4$ co-ordination.[20] The question concerning the thermodynamically stable co-ordination in monomeric nickel complexes with simple aliphatic thiolate ligands is still a central problem in nickel chemistry because the ligand $^{-}SCH_2CH_2S^{-}$ does not allow an undistorted tetrahedral co-ordination due to its short intraligand S $\cdots$ S bite. The initial goal of our work was directed towards the synthesis of simple monomeric nickel complexes with sterically unencumbered aliphatic thiolate ligands. The investigation of the reaction system $NiCl_2$–Na(SMe) in acetonitrile shows, however, that even if a slight excess of Na(SMe) is used (ratio 1:4.4) the formation of an insoluble and unreactive product, probably a polymeric thiolate, is the preferred reaction. When $NMe_4^+$ cations are present after mixing $NiCl_2$ and Na(SMe) a side product consisting of $[NMe_4]_2[Ni_3(\mu_3\text{-S})(\mu\text{-SMe})_3(SMe)_3]$ (**3**) precipitates slowly.

In crystals of compound (**3**) the isolated anions (**2**) are separated by $NMe_4^+$ cations. The positional parameters for all atoms are given in Table 2, bond lengths and valence angles in Table 3. The cation has the expected structural properties and calls for no special comment. The anion (**2**) consists of three nickel atoms, six $MeS^-$ ligands, and one triply bridging sulphide ion. The Figure shows the anion projected along the three-fold axis. The overall architecture of the Ni–S framework is similar to that found in compound (**1**) and can be described in terms of three roughly planar $NiS_4$ co-ordination sites which are condensed *via* adjacent edges to form a polycyclic system with a triply bridging S atom.

Due to geometrical restrictions introduced by the bridging sulphur atoms, the $NiS_4$ units are not strictly planar. Deviations from the mean plane are −0.060 Å for Ni and 0.152, 0.158, −0.152, and −0.101 Å for S(2), S(2$^{i}$), S(1), and S(3), respectively. As a consequence, the bridging S atoms are only 0.051 Å from the plane defined by the three equivalent nickel atoms. The six $MeS^-$ ligands are present in two different co-ordination modes reflecting the number of planar $NiS_4$ sites to which they are bonded. These numbers are 1 for the terminally bonded atoms S(3) and 2 for the bridging atoms S(2).

The ground-state symmetry of compound (**2**) is expected to be $C_{3v}$ in solution. In the crystal we observe a slight pertur-

**Table 1.** Summary of crystal data and details of data collection and structure refinement for $[NMe_4]_2[Ni_3(\mu_3\text{-S})(\mu\text{-SMe})_3(SMe)_3]$

| | |
|---|---|
| Formula | $C_{14}H_{42}N_2Ni_3S_7$ |
| $M$ | 639.03 |
| Crystal system | cubic |
| Space group | $P2_13$ |
| $a$/Å | 13.801(4) |
| $U$/Å$^3$ | 2 628.6 |
| $Z$ | 4 |
| $D_c$/g cm$^{-3}$ | 1.61 |
| $T$/K | 150 |
| $F$(000) | 336 |
| Crystal dimensions/mm | 0.28 × 0.28 × 0.28 |
| Radiation (graphite monochromator) | Mo-$K_\alpha$ ($\lambda$ = 0.710 69 Å) |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 26.5 |
| Scan mode | $\theta$—2$\theta$ |
| Scan speed (intensity dependent)/° min$^{-1}$ | 4—30 |
| Background/scan time | 0.5 |
| Scan range/° | 2 + $K_\alpha$ splitting |
| (sin $\theta$)/$\lambda$ cut-off/Å$^{-1}$ | 0.64 |
| Index range | +$h$, +$k$, +$l$ |
| Total no. of data collected | 2 280 |
| No. of unique data | 1 080 |
| No. of observed data [$I > 1.96\sigma(I)$] | 1 029 |
| No. of variables | 127 |
| $R$, $R'$ | 0.018, 0.014 |

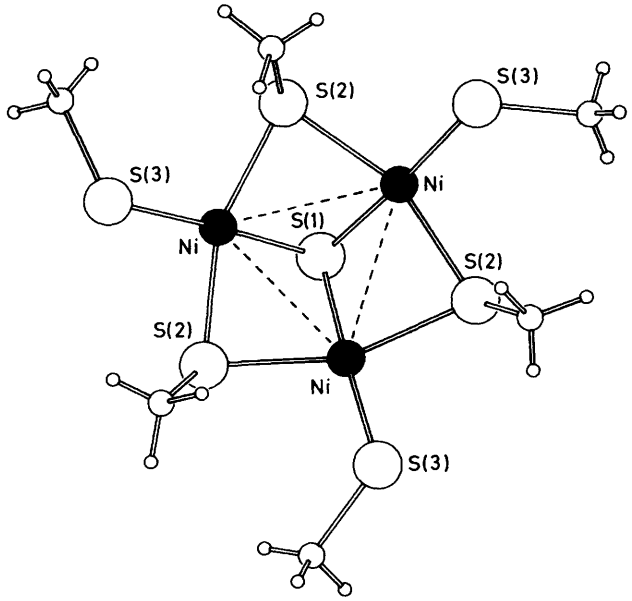

**Figure.** Structure of the anion $[Ni_3(\mu_3\text{-S})(\mu\text{-SMe})_3(SMe)_3]^{2-}$ in crystals of $[NMe_4]_2[Ni_3(\mu_3\text{-S})(\mu\text{-SMe})_3(SMe)_3]$ projected along the three-fold axis, with atomic labelling scheme

**Table 2.** Atomic co-ordinates with standard deviations for $[NMe_4]_2[Ni_3(\mu_3\text{-S})(\mu\text{-SMe})_3(SMe)_3]$

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Anion | | | | Cations | | | |
| Ni | 0.917 36(2) | 0.973 53(2) | 1.083 39(2) | N(1) | 0.473 6(2) | 0.4736 | 0.473 6 |
| S(1) | 0.931 36(5) | 0.931 36 | 0.931 36 | C(3) | 0.509 7(2) | 0.478 2(2) | 0.371 9(2) |
| S(2) | 0.851 10(5) | 1.100 59(5) | 1.016 51(5) | C(4) | 0.535 9(2) | 0.5359 | 0.5359 |
| S(3) | 0.898 51(5) | 1.005 44(5) | 1.238 01(5) | H(3a) | 0.464(2) | 0.444(2) | 0.334(2) |
| C(1) | 0.868 3(2) | 1.206 7(2) | 1.090 4(2) | H(3b) | 0.567(2) | 0.451(2) | 0.369(2) |
| C(2) | 0.777 4(2) | 1.050 3(2) | 1.257 3(2) | H(3c) | 0.512(2) | 0.544(2) | 0.349(2) |
| H(1a) | 0.809(2) | 1.212(2) | 1.125(2) | H(4) | 0.508(2) | 0.530(2) | 0.601(2) |
| H(1b) | 0.872(2) | 1.254(2) | 1.052(2) | N(2) | 0.204 4(2) | 0.2044 | 0.2044 |
| H(1c) | 0.924(2) | 1.201(2) | 1.135(2) | C(5) | 0.264 6(2) | 0.126 1(2) | 0.161 8(2) |
| H(2a) | 0.780(3) | 1.093(3) | 1.300(3) | C(6) | 0.266 5(2) | 0.266 5 | 0.2665 |
| H(2b) | 0.742(3) | 1.001(3) | 1.279(3) | H(5a) | 0.231(2) | 0.091(2) | 0.127(2) |
| H(2c) | 0.750(3) | 1.079(3) | 1.214(3) | H(5b) | 0.292(2) | 0.090(2) | 0.216(2) |
| | | | | H(5c) | 0.318(2) | 0.157(2) | 0.128(2) |
| | | | | H(6) | 0.233(2) | 0.320(2) | 0.295(2) |

**Table 3.** Bond distances (Å) and angles (°) with standard deviations for $[NMe_4]_2[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]$ *

| | | | |
|---|---|---|---|
| $Ni \cdots Ni^{i}$ | 2.855(1) | $Ni \cdots Ni^{i} \cdots Ni^{ii}$ | 60.0 |
| Ni–S(1) | 2.186(1) | S(1)–Ni–S(2) | 81.1(1) |
| Ni–S(2) | 2.182(1) | $S(1)–Ni–S(2^{i})$ | 81.0(1) |
| $Ni–S(2^{i})$ | 2.187(1) | S(1)–Ni–S(3) | 175.8(1) |
| Ni–S(3) | 2.194(1) | $S(2)–Ni–S(2^{i})$ | 158.2(1) |
| | | S(2)–Ni–S(3) | 101.6(1) |
| | | $S(2^{i})–Ni–S(3)$ | 97.1(1) |
| | | $Ni–S(1)–Ni^{i}$ | 81.5(1) |
| | | $Ni–S(2)–Ni^{i}$ | 81.6(1) |
| S(2)–C(1) | 1.800(3) | Ni–S(2)–C(1) | 111.0(1) |
| | | $Ni^{i}–S(2)–C(1)$ | 109.9(1) |
| S(3)–C(2) | 1.802(3) | Ni–S(3)–C(2) | 108.8(1) |
| C(1)–H(1a) | 0.95(3) | S(2)–C(1)–H(1a) | 103(2) |
| C(1)–H(1b) | 0.84(3) | S(2)–C(1)–H(1b) | 107(2) |
| C(1)–H(1c) | 0.99(3) | S(2)–C(1)–H(1c) | 113(2) |
| | | H(1a)–C(1)–H(1b) | 108(3) |
| | | H(1a)–C(1)–H(1c) | 112(3) |
| | | H(1b)–C(1)–H(1c) | 113(3) |
| C(2)–H(2a) | 0.84(4) | S(3)–C(2)–H(2a) | 108(3) |
| C(2)–H(2b) | 0.89(4) | S(3)–C(2)–H(2b) | 107(3) |
| C(2)–H(2c) | 0.81(4) | S(3)–C(2)–H(2c) | 120(3) |
| | | H(2a)–C(2)–H(2b) | 109(4) |
| | | H(2a)–C(2)–H(2c) | 101(4) |
| | | H(2b)–C(2)–H(2c) | 112(4) |

* Symmetry transformation: i *z*, *x*, *y*; ii *y*, *z*, *x*.

**Table 4.** Summary of average Ni–S bond lengths for the anions $[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]^{2-}$ (**2**) (this work) and $[Ni_3(\mu_3\text{-}S)L^1{}_3]^{2-}$ (**1**)[7]

| | Average length/Å | |
|---|---|---|
| Bond | (**2**) | (**1**) |
| $(\mu_3\text{-}S)$–Ni | 2.186 | 2.215 |
| $(\mu\text{-}S)$–Ni | 2.185 | 2.202 |
| $S_{term.}$–Ni | 2.194 | 2.189 |
| $(Ni–S)_{overall}$ | 2.187 | 2.202 |

bation with respect to the methyl groups which is probably due to crystal-packing forces. The nickel atoms form a regular triangle [Ni $\cdots$ Ni 2.855(1) Å] and are symmetrically bridged by a $\mu_3$-S atom resulting in a central pyramidal $Ni_3S$ cluster core with Ni–S 2.186(1) Å. The height of the pyramid is 1.436 Å. In addition, each edge of the triangle is bridged by a thiolate group. The three thiolate bridges are nearly symmetric and are identical by symmetry [Ni–S 2.182(1) and 2.187(1) Å, respectively], and within the limits of experimental errors are equal in length to the bonds formed by the triply bridging S atom. It is interesting that the bonds to the terminal ligands [2.194(1) Å] are slightly longer.

In this context it is particularly instructive to compare the unrestricted $Ni_3S_7$ framework of compound (**2**) with the related framework of the restricted complex (**1**).[7] Though the metal–sulphur framework is a (distorted) section of the cubanoid $S_8M_6$ cage in both cases, significant differences become evident if equivalent nickel–sulphur bond lengths are compared. Table 4 summarizes Ni–S bond distances averaged over equivalent bonds in (**1**) and (**2**). It is clear that the bonds to the terminal ligands are of roughly the same length in both complexes, but if we look at the bonds associated with the sulphur bridges we find them to be longer in (**1**) than in (**2**). If these differences are not the result of crystal-packing forces, the introduction of sterically unencumbered groups leads to a decrease in the mean nickel–sulphur distance of *ca.* 0.014 Å on going from the restricted bifunctional ligand $L^1$ to the simple monofunctional methanethiolate ligand.

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