# The Synthesis and Structural Characterization of $Zr_3(S)(Bu^tS)_{10}$. A Zr–S Cluster that Contains Thiolate Ligands in Three Different Modes of Co-ordination

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The synthesis and structural (crystallographic and spectroscopic) characterization of the new $Zr_3(S)(Bu^tS)_{10}$ cluster is described.

The importance of certain monomeric zirconium compounds in the activation and reduction of carbon monoxide is well documented.[1] The rarity of soluble polynuclear Zr clusters and the potential employment of such species in small molecule activation has prompted us to initiate studies towards the synthesis and characterization of Zr clusters.

Recently we reported[2] on the synthesis and structural characterization of the $Zr_3S_3(Bu^tS)_2(BH_4)_4(thf)_2$ and $Zr_6S_6(Bu^tS)_4(BH_4)_8(thf)_2$ (thf = tetrahydrofuran) aggregates as the first examples of polynuclear Zr clusters that contain aliphatic-thiolate and sulphide ligands. The sulphur ligands in both of these compounds structurally support hexagonal bipyramidal $Zr_3(\mu_3\text{-}S)_2(\mu_2\text{-}SR)_2(\mu_2\text{-}S)$ cores that contain puckered $Zr_3(\mu_2\text{-}SR)_2(\mu_2\text{-}S)$ equatorial planes.

In this communication we report on the synthesis and structure of $Zr_3(S)\ (Bu^tS)_{10}$, a new trinuclear Zr cluster that contains the $Zr_3(\mu_3\text{-}S)(\mu_3\text{-}SR)\ (\mu_2\text{-}SR)_3$ core and displays three modes of ligation for the $Bu^tS^-$ ligands.

A clear yellow solution of $Zr(CH_2Ph)_4$[3] in dry toluene reacts instantly with four equivalents of $Bu^tSH$ and after *ca.* 5 min a yellow solid is precipitated. Following filtration, concentration of the yellow-orange filtrate, and cooling, the crude product is obtained in excellent yield. Long yellow needles are obtained by cooling (at −20 °C) concentrated diethyl ether solutions of this compound. The 360 MHz n.m.r. spectrum of the compound in toluene solution shows four resonances in a 3 : 3 : 3 : 1 ratio at δ 1.81, 1.93, 2.01, and 2.32, respectively.

*Crystal Data:* yellow needles of $Zr_3(S)(Bu^tS)_{10}$ (**1**) are monoclinic, space group $P2_1/c$, $a = 22.009(8)$, $b = 11.372(4)$, $c = 26.980(7)$ Å, $\beta = 101.93(3)°$; $Z = 4$. Single-crystal, *X*-ray diffraction data were collected on a Syntex P2$_1$ four-circle diffractometer using Mo-$K_\alpha$ radiation. The data were collected at −104 °C using a flow of boiling liquid nitrogen. The solution of the structure by a combination of heavy atom Patterson, direct methods, and Fourier techniques and refinement by full-matrix least-squares methods was based on 3966 unique reflections $[F^2 > 3\sigma(F^2)]$. Anisotropic temperature factors for the Zr and S atoms, and isotropic temperature factors for the carbon atoms were used and with all atoms present in the asymmetric unit, refinement has converged to $R = 0.072$.†‡

**Table 1.** Interatomic distances (Å) and angles (°) in the $Zr_3(\mu_3\text{-}S)(\mu_3\text{-}SBu^t)(\mu_2\text{-}SBu^t)_3(SBu^t)_6$ (**1**), and $Zr_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(SBu^t)_2(BH_4)_4(thf)_2$[a] (**2**) trinuclear complexes.

| | (**1**) | (**2**) |
|---|---|---|
| Zr–Zr | 3.722 (3, 6)[b,c] | 3.47 (3, 12) |
| Zr–$\mu_3$-S | 2.601 (3, 5)[d] | 2.594 (6, 18) |
| Zr–$\mu_3$-SR | 2.765 (3, 5)[e] | — |
| Zr–$\mu_2$-SR | 2.627 (6, 7)[f] | 2.641 (4, 8) |
| Zr–SR$_t$ | 2.423 (6, 8)[g] | — |
| | | |
| Zr–Zr–Zr | 60.0 (3, 2)[h] | 60.0 (3, 3.0) |
| Zr–$\mu_3$-S–Zr | 91.4 (3, 2)[i] | 84.1 (6, 2.0) |
| Zr–$\mu_3$-SR–Zr | 84.5 (3, 2)[j] | — |
| Zr–$\mu_2$-SR–Zr | 90.3 (3, 1.2)[k] | 85.0 (1) |
| RS$_t$–Zr–SR$_t$ | 94.4 (3, 1.7)[l] | — |

[a] From ref. 2. [b] Range 3.715(2)—3.733(2). [c] In parentheses the first entry represents the number of independent distances or angles averaged; the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation $\sigma = [\Sigma_{i=1}^{N} (x_i - \bar{x})^2/N(N-1)]^{1/2}$. [d] Range: 3.597(5)—2.600(5). [e] Range: 2.761(5)—2.770(5). [f] Range: 2.600(5)—2.642(5). [g] Range: 2.403(6)—2.440(5). [h] Range: 59.8(1)—60.3(1). [i] Range: 91.1(2)—91.4(2). [j] Range: 84.4(1)—84.9(1). [k] Range: 88.1(2)—91.4(1). [l] Range: 91.7(2)—95.9(2).

The structure of (**1**) contains the $Zr_3(\mu_3\text{-}S)(\mu_3\text{-}SR)(\mu_2\text{-}SR)_3$ core that roughly can be described as a hexagonal bipyramid where three $\mu_2$-$Bu^t$ thiolates bridge the Zr atoms in a puckered equatorial plane, and a $\mu_3$-$S^{2-}$ and a $\mu_3$-$Bu^tS^-$ ligand serve as 'capping' ligands on the axial positions (Figure 1). The core

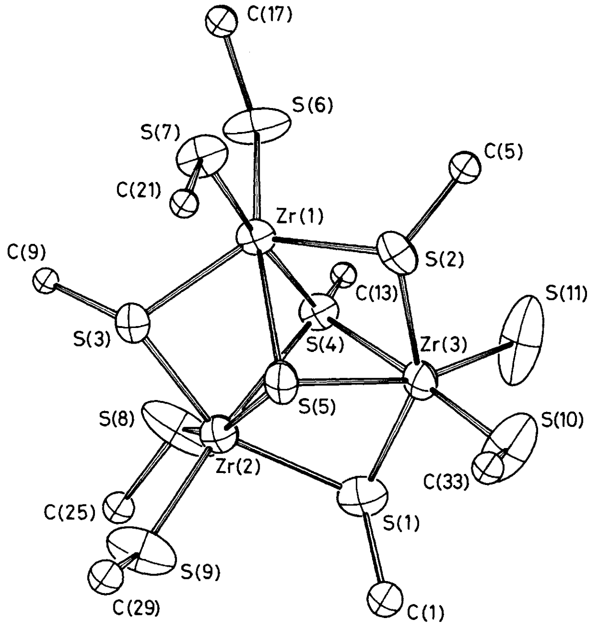

**Figure 1.** Structure of the $Zr_3(S)(Bu^tS)_{10}$ cluster. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-4794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965) represent the 33% probability surfaces. Only the tertiary carbon atoms of the t-butyl groups are shown with artificially small temperature factors for clarity.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The elemental analysis obtained was not inconsistent with the formulation. In calculating the elemental composition half a molecule of diethyl ether was included since $Et_2O$ co-crystallised in the lattice of (**1**).

can be described also as the result of the cofacial fusion of three octahedrally co-ordinated $\mathrm{ZrS_6}$ units.

A comparison of the structural parameters within the $\mathrm{Zr_3(\mu_3\text{-}S)(\mu_2\text{-}SR)_3}$ cores in (**1**) and the $\mathrm{Zr_3S_3(Bu^tS)_2(BH_4)_4(thf)_2}$ cluster (**2**) shows similar Zr–$\mu_3$–S and Zr–$\mu_2$-SR distances but greatly different Zr–Zr distances (Table 1). In both (**1**) and (**2**) the Zr–Zr distances at 3.722(6) and 3.471(2) Å definitely are non-bonding and very likely are determined by predominant Zr–Zr repulsions, subject to steric considerations. The longer Zr–Zr distances within the $\mathrm{Zr_3}$ triangular unit in (**1**) do not appear to affect the Zr–Zr distances within the core but rather seem to correlate with the oblique Zr–$\mu_2$-SR–Zr and Zr–$\mu_3$-S–Zr angles. These angles, 90.3(1.2) and 91.4(2)°, are significantly larger than the corresponding angles in (**2**), 85.0(1) and 84.1(2.0)° respectively. The Zr-$\mu_3$-S–Zr angle with the $\mathrm{S^{2-}}$ ligand in (**1**), 91.4(2)°, is much larger than the Fe–$\mu_3$-S–Fe angle in the $\mathrm{Fe_4S_4}$ cores of the $\mathrm{(Fe_4S_4L_4)^{2-}}$ 'cubanes'[4] (~75°), and nearly 25° larger than the Mo–$\mu_3$-S–Mo angle in the $\mathrm{(Mo_3S_2Cl_9(^{3-}}$ trianion.[5]

The structure of (**1**) presents an opportunity to examine the bonding of a thiolate ligand bound in three different co-ordination modes within the same molecule. A nearly linear increase in the Zr–S distances is observed [2.423(8); 2.627(7); 2.765(5) Å] as the co-ordination mode of the thiolate ligand changes from terminal to $\mu_2$ and to $\mu_3$ bridging. This behaviour has a precedent in the structures of the $\mathrm{[M_4(SR)_{10}]^{2-}}$ 'adamantanes.' In the latter the mean value of the M–S bond lengths with the six $\mu_2$ bridging $\mathrm{RS^-}$ ligands invariably is larger than the value of the M–S bond lengths with the $\mathrm{RS^-}$ terminal ligands.[6] The very long Zr–$\mu_3$-SR distances in (**1**) are nearly 0.3 Å longer than the sum of the Zr and S covalent radii (2.49 Å), and suggest that the $\mu_3$-$\mathrm{RS^-}$ bridge may be a site of unusual reactivity.

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