# Preparation and Crystal Structure of the Unprecedented Octameric Zinc–Aminothiolate Complex $[Zn_8\{S(CH_2)_3NMe_2\}_{16}]$

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$[Zn_8\{S(CH_2)_3NMe_2\}_{16}]$, prepared by anodic oxidation of zinc in acetonitrile containing 3-dimethylamino-1-propanethiol, contains zinc atoms coordinated tetrahedrally by either four sulphur or one nitrogen and three sulphur atoms; the aminothiolate ligands function variously as terminal, $\mu_2$-bridging, or both chelating and bridging ligands.

It is now well established that zinc–cysteine coordination occurs in many important metalloproteins with different values of $n$ in the $Zn(cys\text{-}S)_n$ centres.[1] It has also recently been suggested that $[Zn(cys\text{-}S)_2(his)_2]$ coordination plays an essential structural role in many protein–DNA interactions.[2] Interest in zinc–thiolate chemistry[3] is fuelled by the absence of simple structural analogues of the active centres in cases where the structure of the zinc-containing protein has already been determined by X-ray diffraction,[4] and by the search for synthetic models for species in which coordination around zinc has only been proposed.[5]

We are engaged in a study of aliphatic mercaptoamine ligands, which can coordinate to metal atoms either through sulphur only, as monofunctional thiols with a solubilizing amino group, or alternatively through both sulphur and nitrogen, as chelating ligands. We report here the synthesis and crystal structure of the novel octameric complex of a γ-mercaptoamine ligand, $[Zn_8\{S(CH_2)_3NMe_2\}_{16}]$. The zinc complex of the β-mercaptoamine analogue, $[Zn\{S(CH_2)_2NMe_2\}_2]$, which closely resembles models proposed for zinc coordination in $[Zn(cys\text{-}S)_2(his)_2]$ centres,[5] consists of discrete mononuclear molecules.[6]

The anodic oxidation of zinc in acetonitrile solution containing 3-dimethylamino-1-propanethiol, an excess of triethylamine and tetraethylammonium perchlorate, was carried out over a period of 24 h with a constant potential of 24 V. The addition of diethyl ether and subsequent extractions with n-hexane yielded a colourless powder, which was recrystallized from dry methanol to give single crystals. Satisfactory elemental analysis results were obtained. The IR spectrum in the range 3000–900 $cm^{-1}$ is practically identical to that of the free ligand, $HS(CH_2)_3NMe_2$; bands appearing between 3000 and 2600 $cm^{-1}$ suggested that coordination of the ligand was through the sulphur atoms only.[7] The spectrum in the range below 400 $cm^{-1}$ includes metal–ligand vibrations, but this range is complex, with many weak bands, and we have not been able to make definite assignments.

The structure of $[Zn_8\{S(CH_2)_3NMe_2\}_{16}]$, determined by X-ray crystallography,† consists of discrete octameric molecules, as shown in Fig. 1. The molecule has $S_4$ symmetry, and so there are two crystallographically independent zinc atoms. There is a central eight-membered $Zn_4S_4$ ring, in which the four symmetry-equivalent zinc atoms lie almost in a plane (deviations ±0.187 Å from the mean plane) and the sulphur atoms lie alternately on either side of it (at ±1.393 Å). Each pair of adjacent zinc atoms of this central ring is further linked by a S–Zn–S fragment, thus giving rise to four six-membered $Zn_3S_3$ rings fused to the central ring. These six-membered rings have a boat conformation, and also lie alternately above and below the mean plane of the four central zinc atoms. Of the two crystallographically independent zinc atoms, Zn(1) is coordinated tetrahedrally by four sulphur atoms, and Zn(2) is coordinated by one nitrogen and three sulphur atoms.

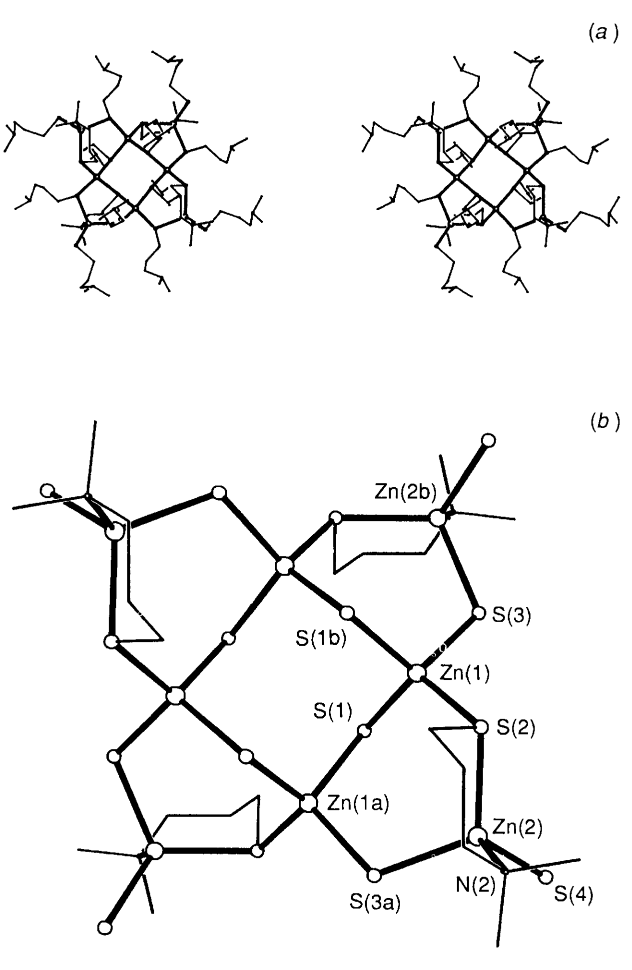

**Fig. 1** The molecular structure of $[Zn_8\{S(CH_2)_3NMe_2\}_{16}]$ at 120 K: (*a*) a stereo view of the complete molecule excluding hydrogen atoms; (*b*) the central core with C and N atoms shown only for the chelating ligands, and with the atom labelling scheme. Key dimensions: Zn(1)–S(1) 2.326(2), Zn(1)–S(2) 2.352(2), Zn(1)–S(3) 2.364(2), Zn(1)–S(1b) 2.343(2), Zn(2)–S(2) 2.335(2), Zn(2)–S(4) 2.256(2), Zn(2)–S(3a) 2.363(2), Zn(2)–N(2) 2.147(6) Å; S(1)–Zn(1)–S(2) 116.0(1), S(1)–Zn(1)–S(3) 105.4(1), S(2)–Zn(1)–S(3) 109.6(1), S(1)–Zn(1)–S(1b) 110.5(1), S(2)–Zn(1)–S(1b) 104.2(1), S(3)–Zn(1)–S(1b) 111.2(1), S(2)–Zn(2)–S(4) 121.1(1), S(2)–Zn(2)–S(3a) 114.1(1), S(4)–Zn(2)–S(3a) 112.4(1), S(2)–Zn(2)–N(2) 95.4(2), S(4)–Zn(2)–N(2) 107.5(2), S(3a)–Zn(2)–N(2) 102.8(2), Zn(1)–S(1)–Zn(1a) 106.2(1), Zn(1)–S(2)–Zn(2) 111.5(1), Zn(1)–S(3)–Zn(2b) 113.3(1)°.

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† *Crystal data* for $C_{80}H_{192}N_{16}S_{16}Zn_8$: $M = 2414.5$, tetragonal, $I\bar{4}$, $a = 20.253(6)$, $c = 14.257(6)$ Å, $U = 5848.0$ Å$^3$, $Z = 2$, $D_c = 1.371$ g cm$^{-3}$, λ(Mo-Kα) = 0.71073 Å, $\mu = 1.97$ mm$^{-1}$, $F(000) = 2560$, $T = 120$ K. Data were measured with on-line profile fitting[10] on a Stoe-Siemens diffractometer equipped with a Cryostream cooler.[11] The structure was determined by direct methods and refined[12] to a minimum of $\Sigma w\Delta^2$ $[\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 621 - 994G + 896G^2 - 1358H + 789H^2 + 732GH$, $G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}]$[13] from 3143 reflections with $2\theta < 45°$ and $F > 4\sigma_c(F)$ ($\sigma_c$ from counting statistics only). Anisotropic thermal parameters were refined for all non-H atoms, H atoms were constrained. Final $R = 0.0482$, $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.0460$, $S = 1.06$, for 272 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Of the four crystallographically independent ligands, two function exclusively as bridging ligands with an uncoordinated nitrogen atom: S(1) bridges two equivalent zinc atoms within the central eight-membered ring, while S(3) bridges between the two different types of zinc atom. One ligand serves not only as a Zn–S–Zn bridge [S(2) between Zn(1) and Zn(2)], but also as a chelating ligand to Zn(2) through both sulphur and nitrogen. The fourth ligand is terminally bonded through sulphur S(4) to Zn(2), with an uncoordinated nitrogen atom.

The bond lengths around Zn(1) are all similar, each sulphur acting as a $\mu_2$-bridge to another zinc atom. Angular distortions from ideal tetrahedral geometry are only small. Distortions are larger at Zn(2), the smallest angle being that for the chelating ligand. The shortest Zn(2)–S bond is to the terminally coordinated S(4) ligand.

This structure is totally unprecedented among group 12 metal complexes with any type of thiolate ligands. It is also the first example of a complex in which a mercaptoamine ligand functions, within the same structure, as a terminal ligand, a bridging ligand, and simultaneously a chelating and bridging ligand. A zinc thiolate cluster structure with stoichiometry $Zn_8S_{16}$ has been reported for $[ClZn_8(SPh)_{16}]^-$,[8] {the same framework occurs[9] in $[SCd_8(SePh)_{16}]^{2-}$}. The structure is, however, quite different from the one we report here: it has two tetrahedra of zinc atoms, one inside and the other outside an icosahedron of twelve chemically equivalent bridging S atoms; the remaining four thiolate ligands are terminal, and the whole cluster is centred on a chloride ion. The closest Zn···Zn distances are similar in both octanuclear zinc cluster structures, since in both cases they are largely dictated by the geometry of $\mu_2$-thiolate bridging. In the present structure, Zn(1)···Zn(1a) is 3.734 Å, Zn(1)···Zn(2) is 3.875 Å, and Zn(1)···Zn(2b) is 3.947 Å; each of these is equal to three other Zn···Zn distances within the cluster, by symmetry.

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