$[ClZn_8(SPh)_{16}]^-$, A New, Highly Symmetrical Cage Containing Metal Atoms Inside and Outside an Icosahedron of Ligands; *X*-Ray Crystallographic Study

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Summary In the molecular cage $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$ the central chlorine atom is surrounded by a tetrahedron of zinc atoms, which is enclosed by an icosahedron of bridging benzenethiolate ligands, which links to an outer tetrahedral array of ZnSPh groups, the symmetry of the complete cage, excluding only the four outer phenyl-groups, is very close to that of the cubic point group *T*.

A MIXTURE of $Zn(NO_3)_2 \cdot 6H_2O$ (21 mmol), benzenethiol (51 mmol), tripropylamine (50 mmol), tetramethylammonium chloride (19 mmol), methanol, and acetone, under nitrogen at room temperature, crystallised two products. After yielding the first microcrystalline product, probably $(Me_4N)_2[Zn_4(SPh)_9Cl]$, the undisturbed reaction mixture produced well-developed colourless crystals in very low yield over a period of three weeks. Characterisation of this second product by *X*-ray diffraction† has revealed the occurrence of a new molecular cage with the composition $[ClZn_8(SPh)_{16}]^-$.

Although this cage possesses only low crystallographic symmetry (C_2), it approximates closely to a much higher cubic symmetry of order 12 and the cage structure is described here in terms of its idealised point group, *T*.

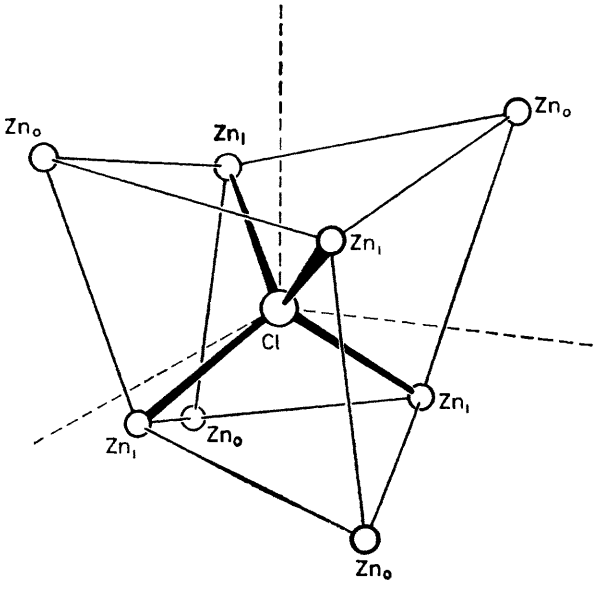

FIGURE 1. The $Cl(Zn_{inner})_4(Zn_{outer})_4$ bitetrahedron in $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$.

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† *Crystal data*: space group *Pbcn*, $a = 2349{\cdot}3(3)$, $b = 2972{\cdot}6(4)$, $c = 1783{\cdot}5(2)$ pm, $D_m = 1{\cdot}43(1)$ kg dm^{-3}. *M* determined crystallographically = 2·68 kg mol^{-1} ($Z = 4$), *M* for a possible formulation $(Pr_3NH)(Pr_3N)[ClZn_8(SPh)_{16}] = 2{\cdot}593$ kg mol^{-1}, 6424 intensity measurements (Cu-K_α), 2715 observed $[I > 2\sigma(I)]$ reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Consider a body-centred cube $ClZn_8$, which is decomposed into two tetrahedra $Cl(Zn_{inner})_4(Zn_{outer})_4$ by extending four zinc atoms out along the threefold axes until all the Zn_{inner}–Zn_{outer} edge lengths are equal (see Figure 1) to the length (385 pm) of the face-diagonal of the original cube. In the resulting Zn_8 polyhedron (a tetracapped tetrahedron) the four Zn_{inner} atoms are bonded to Cl (Cl–Zn 236 pm). A bridging benzenethiolate ligand is added across each of the twelve Zn_{inner}–Zn_{outer} edges, such that the twelve sulphur atoms constitute an icosahedron. Finally, one terminal benzenethiolate ligand is added to each of the four outer zinc atoms, resulting in the structural formulation $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$.

The Zn_{inner} and Zn_{outer} atoms are situated, respectively, inside and outside faces of the S_{12} icosahedron. Each zinc atom has tetrahedral co-ordination, with three bonds to the bridging benzenethiolate ligands and the fourth to Cl for Zn_{inner} and to the terminal benzenethiolate for Zn_{outer}. Figure 2 shows the $ClZn_8S_{16}$ framework of the cage, with the cubic axes (see Figure 1) marked.

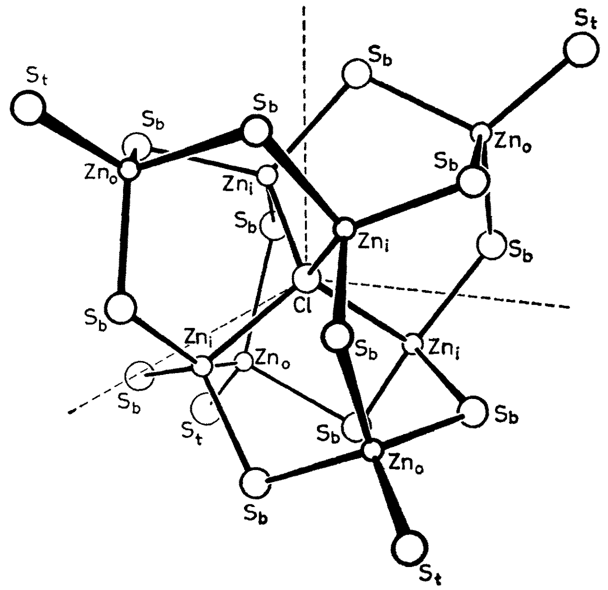

FIGURE 2. The $ClZn_8S_{16}$ core of $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$: Zn_i, Zn_o, S_b, S_t are Zn_{inner}, Zn_{outer}, bridging SPh, and terminal SPh, respectively.

The actual locations of the $ClZn_8S_{16}$ atoms are within 0·1 Å of the co-ordinates idealised according to the symmetry of point group *T*. Further, the phenyl-rings of the twelve bridging benzenethiolate ligands do not break this approximate high symmetry of the $ClZn_8S_{16}$ core. This result is illustrated in Figure 3 which is a view along one of the pseudo-threefold axes of $[ClZn_4(\mu\text{-}SPh)_{12}(ZnS)_4]$. The phenyl-groups on the terminal ligands necessarily break the *T* symmetry and are omitted from Figure 3.

The $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$ structure is unique in two ways. First, the ClZ_8S_{16} cage is unprecedented; these cage atoms do not constitute a fragment of a close-packed structure. Second, the high symmetry of the array of phenyl-rings on the bridging benzenethiolate ligands has not been found in other benzenethiolate–metal cage structures.[1] Two features of the $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$ structure have appeared in other compounds: (i) the icosahedron of the bridging sulphur donor atoms occurs in $[ClCu^{I}_{8}L_{12}Cu^{II}_{6}]$,[2] $[ICd_8(SCH_2CH_2OH)_{12}]^{3+}$,[3] and the three clusters $[Cu_8(S\text{–}S)_6]^{4-}$ with 1,1- and 1,2-dithiolate ligands S–S,[4] but $[ClZn_4(\mu\text{-}SPh)_{12}(ZnSPh)_4]^-$ is the first example where all the ligands are non-chelating; (ii) the central internal ligand with tetrahedral co-ordination by zinc is known in $SZn_4[S_2AsMe_2]_6$[5] and $OZn_4(O_2CCH_3)_6$.[6]

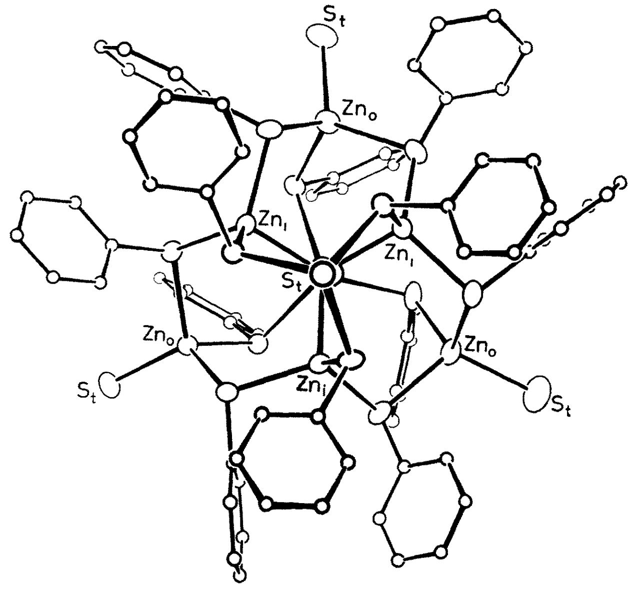

FIGURE 3. View along one pseudo-threefold rotation axis of $[ClZn_4(\mu\text{-}SPh)_{12}(ZnS)_4]$: the phenyl groups on S_t are omitted.

We previously suggested that in the case of copper(I) with trigonal-planar co-ordination by thiolate a $[Cu_8(SR)_{12}]^{4-}$ cube/icosahedron cage would be insufficiently rigid for independent existence.[1a] The present results reveal a structural modification which can stabilise an icosahedron-based cage for a metal adopting tetrahedral co-ordination. The structural principle which appears is the degeneration of a single large convex polyhedral surface containing both metals and bridging ligands into an 'onion' of concentric polyhedra containing alternately ligands and metals.

The crystallographic analysis has determined unequivocally the structure of the cage. A refined model of the cage anion only, with the ligands as librating rigid bodies, yields $R = 0{\cdot}12$ for 2646 observed reflections with $\sin\theta/\lambda > 0{\cdot}1$. The cation in the crystal appears only as a poorly resolved electron density, separate from the anions, and unequivocal identification of the cation by *X*-ray crystallography alone is not possible. Attempts to develop a reproducible synthesis of this compound have not yet been successful, precluding precise chemical analysis The unlikely possibility that the central ligand is an adventitious S^{2-} instead of Cl$^-$ cannot be refuted with the available data

The support of the Australian Research Grants Committee and the assistance of Dr A D Rae with the constrained refinement, are gratefully acknowledged

(*Received, 12th May* 1980, *Com* 505)

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