

$[S_4M_{10}(SPh)_{16}]^{4-}$ ($M=Zn, Cd$), a Molecular Fragment of the Sphalerite MS Lattice: Structural Congruence of Metal Sulphides and Metal Thiolates

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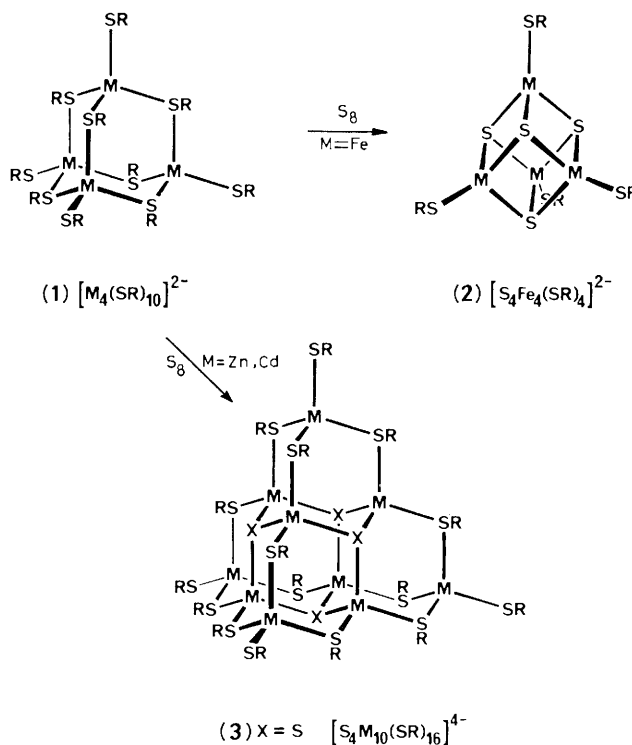
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Treatment of $[M_4(SPh)_{10}]^{2-}$ ($M = Zn, Cd$) with sulphur yields $[S_4M_{10}(SPh)_{16}]^{4-}$ with a molecular structure *tetrahedro-(μ_3 -S)₄-octahedro- M_6 -truncated tetrahedro-(μ -SPh)₁₂-tetrahedro-(MSPh)₄*, in which the $M_{10}S_{20}$ array is congruent with a fragment of the sphalerite lattice.

The ions $[M_4(SPh)_{10}]^{2-}$, $M = Fe$,¹ Co ,² Zn ,^{3,4} and probably Cd , possess the molecular structure *octahedro-(μ -SR)₆-tetrahedro-(MSR)₄*, (1), in which the M_4S_{10} core is structurally equivalent to a unit cell of the cubic zinc sulphide (sphalerite) lattice. Holm *et al.*⁵ have shown that $[Fe_4(SPh)_{10}]^{2-}$, on treatment with sulphur, is converted only, and without detectable intermediates, into $[Fe_4S_4(SPh)_4]^{2-}$, which has the well-known *tetrahedro-(μ_3 -S)₄-tetrahedro-(FeSR)₄* structure type, (2).

In contrast to this, we find that the zinc and cadmium ions $[M_4(SPh)_{10}]^{2-}$ † react with sulphur in acetonitrile to yield the larger molecular ions $[S_4M_{10}(SPh)_{16}]^{4-}$, (3), as colourless crystals with Me_4N^+ .

The essential structure of the ion is shown in Figure 1.‡ There are six central metal atoms bridged by four triply-bridging sulphide ions, four outer metal atoms each connected by three doubly-bridging thiolate ligands to a face of the central M_6 octahedron, and four outer terminal thiolate ligands. The sulphur atoms of the twelve bridging thiolate



† $(Me_4N)_2M_4(SPh)_{10}$ isolated from a mixture of $PhSH$, Et_3N , hydrated metal nitrate, and Me_4NCl (150, 150, 50, and 60 mmol respectively) in methanol (200 ml), recrystallised from acetonitrile-toluene.

‡ *Crystal data:* $(Me_4N)_4[S_4Cd_{10}(SPh)_{16}]$ (Zn analogue isostructural), $M = 3295.6$, tetragonal, space group $I42m$ (disordered structure), $a = 2014.0(2)$, $c = 1689.6(1)$ pm, $D_{obs} = 1.593(7)$, $D_{calc} = 1.597$ g cm⁻³, $Z = 2$; 916 observed reflections ($Mo-K\alpha$); In refinement Cd , S anisotropic, C , N isotropic thermal parameters, $R = 0.042$, $R_w = 0.051$. Satisfactory CHN analytical data have been obtained. 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. The structure factor table is available as Supplementary Publication No. SUP23466 (5 pp.) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index Issues.

ligands comprise a truncated tetrahedron. In terms of expanding concentric polyhedra the molecule is described as *tetrahedro-(μ_3 -S)₄-octahedro- M_6 -truncated-tetrahedro-(μ -SPh)₁₂-tetrahedro-(MSPh)₄*. The $M_{10}S_{20}$ molecular framework has S_4 crystallographic symmetry and virtual T_d symmetry, and constitutes a larger fragment of the sphalerite lattice. There are two types of cadmium atom, Cd_{inner} [$Cd(1)$, $Cd(2)$] and Cd_{outer} [$Cd(3)$], two types of thiolate sulphur, $S_{bridging}$ [$S(2)$, $S(3)$, $S(4)$] and $S_{terminal}$ [$S(5)$], and one type of sulphide

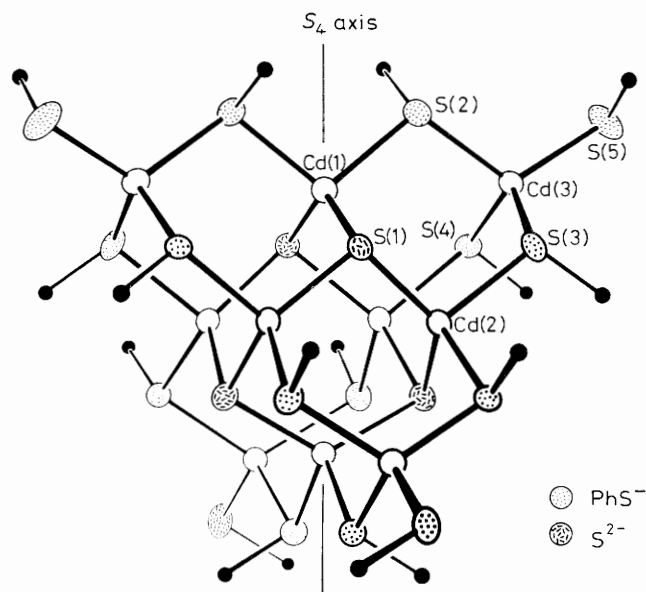


Figure 1. The $[S_4Cd_{10}(SPh)_{16}]^{4-}$ ion ($M = Cd$), including only the C_x atoms of the phenyl substituents, and showing the crystallographic S_4 axis.

ion [S(1)]. Mean dimensions (sample standard deviations in parentheses) are: Cd_i-S_{br} 260.3(1.1), Cd_i-S 247.9(9), Cd_o-S_{br} 256.6(1.6), and Cd_o-S_t 245.9 pm; $Cd_i-S_{br}-Cd_o$ 107.0(1.4) and Cd_i-S-Cd_i 100.7(1.5)°.

The configurational isomerism due to inversion at doubly-bridging thiolate allows 186 isomers, none of which requires unfavourable steric interference of substituents. The high symmetry of the ion and of its counteranion accounts for the observed crystallographic disorder, which involves mirror reflection.

The cation $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ has a molecular structure⁶ with a similar sphalerite basis for the $Cd_{10}S_{16}$ array, but modified by additional co-ordination of all ligand OH functions to eight of the cadmium atoms [$4 \times Cd_{outer} \times CdS_4O$ co-ordination, $4(Cd_{outer}) \times CdS_3O_3$]. In solution this molecule reacts with an excess of thiolate which probably displaces hydroxy-co-ordination at the four outer cadmium atoms to give uncharged molecules $Cd_{10}(SR)_{20}$.⁷ Stereochemical analysis of possible intramolecular interactions between substituents R confirms the feasibility of molecules $M_{10}(SR)_{20}$, (**4**) \equiv (**3**); $X-SR$], with simple monofunctional thiols. The positions at the centres of the faces of the tetrahedrally-shaped mole-

cule $M_{10}(SR)_{20}$ are the more sterically congested, and are occupied by the bridging sulphide ligands in $[S_4M_{10}(SPh)_{16}]^{4-}$.

In view of the occurrence of molecules $[M_4(SPh)_{10}]^{2-}$, $[S_4M_{10}(SPh)_{16}]^{4-}$, and probably $M_{10}(SR)_{20}$, all with structures which are fragments of the MS structure when $M = Zn, Cd$, it is reasonable to postulate that the ligating properties of S^{2-} and RS^- are sufficiently similar for them to be interchangeable (taking account of differing connectivities to metal) within this structure type. Homologues of $[S_4M_{10}(SPh)_{16}]^{4-}$, as thiolate coated fragments of metal sulphide, may exist. Extensive occurrence of congruent structures is unlikely, and should $[SM_8(SR)_{16}]^{2-}$ occur with the same structure as $[ClZn_8(SPh)_{16}]^{8-}$ it would contravene this structural relationship. However, the proposed structural correspondence between non-molecular metal sulphides and molecular sulphido-metal-thiolates is supported and extended by the molecule $[S_6Co_8(SPh)_8]^{4-}$, which has the structure of the non-molecular sulphide pentlandite Co_9S_8 .⁹ In broad terms this view of corresponding structures is comparable with that¹⁰ of large metal cluster molecules as fragments of bulk metal, terminated by carbon monoxide or other ligands,^{11,12} and with that of metal alkoxides as models for metal oxides.¹³

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