

The Stereochemistry of $(\mu\text{-SR})_3\text{M}_3$ Cyclic Molecules, with Reference to the Molecular Structures of $(\mu\text{-SPh})_3\text{Cu}_3(\text{PPh}_3)_4$ and $[(\mu\text{-SPh})_3\text{Fe}_3\text{Cl}_6]^{3-}$

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In the cyclic molecule $(\mu\text{-SPh})_3\text{Cu}_3(\text{PPh}_3)_4$ possessing a twist conformation different from the planar $(\mu\text{-SPh})_3\text{Fe}_3$ ring in $[(\mu\text{-SPh})_3\text{Fe}_3\text{Cl}_6]^{3-}$, the Cu-S-Cu angles vary from 87 to 124°, but correlate well with the inclination of the S-C bonds to their Cu-S-Cu planes, a pattern which is pertinent to the conformations of similar cycles in metallo-cysteine proteins.

The $[(\mu\text{-SPh})_3\text{Fe}_3\text{Cl}_6]^{3-}$ ion (**1**) has been recently reported,¹ with a remarkable structure in which *all* atoms of the $(\mu\text{-SPh})_3\text{Fe}_3$ cyclic core are coplanar. This is in stark contrast to the non-planar cycle with chair conformation observed for the few molecules²⁻⁴ known to contain the $(\mu\text{-SR})_3\text{M}_3$ cycle un-

supported by additional bridging or chelating groups. Furthermore, many metal thiolate cages are composed of *condensed* $(\mu\text{-SR})_3\text{M}_3$ and $(\mu\text{-SR})_2(\mu_3\text{-S})\text{M}_3$ cycles, all in the chair conformation,⁵⁻⁷ and consequently the $(\mu\text{-SR})_3\text{M}_3$ chair has been regarded as a paradigmatic structural unit, and has been

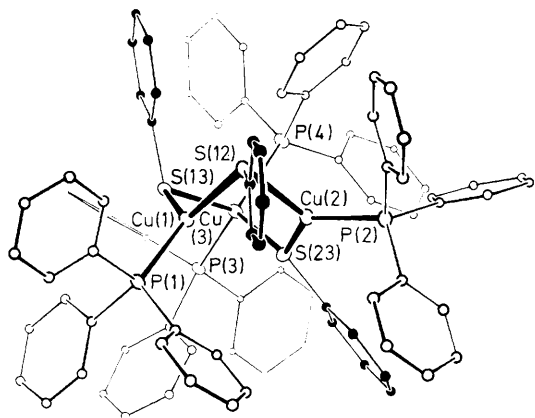
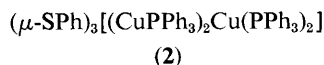
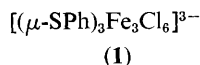


Figure 1. The $(\mu\text{-SPh})_3\text{Cu}_3(\text{PPh}_3)_4$ molecule (2) viewed almost parallel to the Cu_3 plane.

incorporated into the current model for a $(\mu\text{-S-cys})_3\text{Cd}_3(\text{S-cys})_6$ (cys = cysteinato) aggregate in cadmium metallothionein.⁸



A second unusual feature of (1) is the planar stereochemistry at the sulphur atom of the doubly bridging thiolate. Amongst numerous instances of thiolate ligands bridging two metals there is only one other reported occurrence of this planar stereochemistry, in $(\mu\text{-SPh})_2\text{Cu}_2(\text{PPh}_3)_4$,⁹ where it is enforced by phenyl ring crowding over the surface of the molecule.

Colourless crystals of $\text{Cu}_3(\text{SPh})_3(\text{PPh}_3)_4(\text{CHCl}_3)_{1.6}$, obtained from CuSPh plus Ph_3P (≤ 1.5 equiv.) in chloroform-propanol, contain the cyclic $(\mu\text{-SPh})_3[(\text{CuPPh}_3)_2\text{Cu}(\text{PPh}_3)_2]$ molecule, (2).† Two copper atoms possess trigonal planar $\text{S}_2\text{-Cu-P}$ co-ordination while the third $[\text{Cu}(3)]$ is tetrahedrally coordinated, *i.e.*, as S_2CuP_2 . The side view in Figure 1 shows that the core is distinctly non-planar and not in a chair conformation.

The significance of this structure derives from the dissymmetry of the $\text{S}_3\text{Cu}_3\text{P}_4$ core [see Figures 1 and 2(a)]. The major distortion occurs in the Cu-S-Cu angles which are all quite different (87, 105, and 124°) despite the absence of any abnormality in Cu-S distances or other dissymmetry of individual $(\mu\text{-SPh})\text{Cu}_2$ bridges. The torsional angles for the six Cu-S bonds, given in Figure 2(b), show that the Cu_3S_3 ring most closely approximates a slightly twisted boat conformation.¹⁰ Note, however, that the unique diagonal of this conformation is not $\text{Cu}(3)\text{-S}(12)$ (as might be expected from the twofold

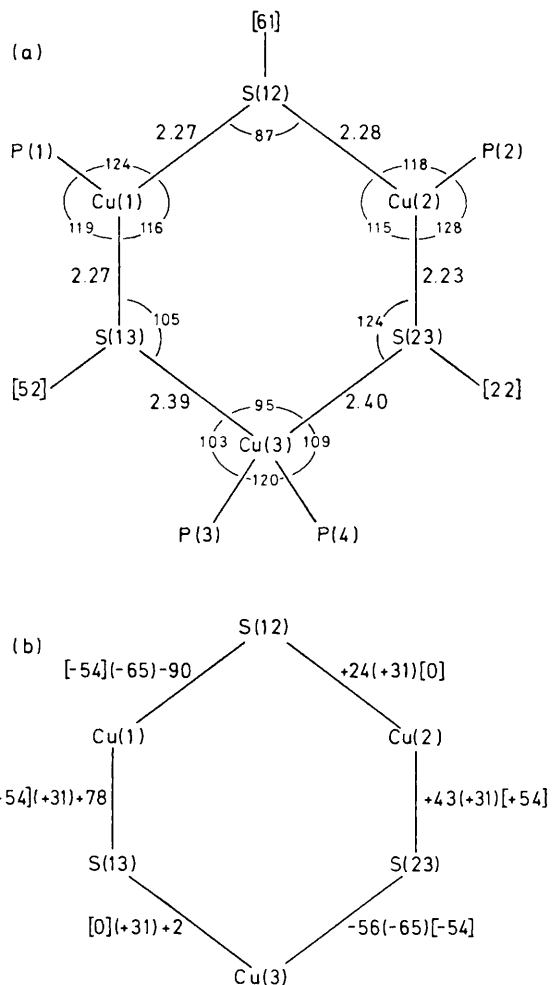


Figure 2. (a) Selected bond distances (Å) and angles ($^\circ$) for $(\mu\text{-SPh})_3\text{Cu}_3(\text{PPh}_3)_4$ (2). The angles in square brackets are the inclinations of the S-C bonds to their Cu-S-Cu planes. (b) Torsional angles for the Cu_3S_3 ring, in comparison with idealised values for the twist conformation (round brackets) and the boat conformation (square brackets).

symmetry of the $\text{S}_3\text{Cu}_3\text{P}_4$ connectivity) but $\text{Cu}(1)\text{-S}(23)$, because this twist conformation allows isoclinal¹¹ rather than pseudoaxial directions for the bulky PPh_3 ligands on $\text{Cu}(3)$.

There are significant relationships between the orientations of the SPh ligands and the stereochemistry at sulphur. The angles ϕ of inclination of each S-C ligand to its Cu-S-Cu plane vary widely [see Figure 2(a)], but are systematically related to the Cu-S-Cu angles (θ). This relationship is graphically displayed in Figure 3, which also includes mean values of ϕ and θ for $(\mu\text{-SPh})\text{M}_2$ bridges in condensed $(\mu\text{-SPh})_3\text{-M}_3$ cycles in the cages $[(\text{Cu}_4(\text{SPh})_6)]^{2-}$,⁵ and $[\text{M}_4(\text{SPh})_{10}]^{2-}$ and their derivatives⁶ (where ϕ and θ are close to the tetrahedral ideal of 54.7 and 109.5°). There is clear general correlation of ϕ and θ over a wide range of stereochemistry at the sulphur of the bridging thiolate. The wide angle (139 and 142°) Fe-S-Fe bridges in (1), with $\phi = 0^\circ$, also follow this correlation.‡

From these observations and patterns it may be postulated that for isolated $(\mu\text{-SR})_3\text{M}_3$ cycles, the M-S-M angles, and consequently the cycle conformations, are quite variable and

† Crystal data: $\text{C}_{90}\text{H}_{75}\text{Cu}_3\text{P}_4\text{S}_3(\text{CHCl}_3)_{1.6}$, $M = 1758.3$, space group $P\bar{1}$, $a = 13.432(4)$, $b = 13.815(2)$, $c = 25.164(2)$ Å, $\alpha = 94.80(1)$, $\beta = 94.73(1)$, $\gamma = 111.66(1)^\circ$, $Z = 2$, $D_m = 1.36$, $D_c = 1.36$ g cm^{-3} ; 5984 observed, absorption corrected data ($\text{Cu-K}\alpha$) from two crystals; (decay $1 \rightarrow 0.85$ each). Refinement with Cu , S , and P anisotropic, Ph as rigid groups, and CHCl_3 with site occupancies; $R = 0.071$ and $R_w = 0.103$.

The atomic co-ordinates 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 wide-angle inter-cage $(\mu\text{-SPh})\text{Zn}_2$ bridge in *catena*- $(\mu\text{-SPh})_6(\mu\text{-SPh})_6\text{Zn}_3(\text{SPh})(\text{MeOH})$,^{6b} $\theta = 140^\circ$, $\phi = 21^\circ$, is acyclic.

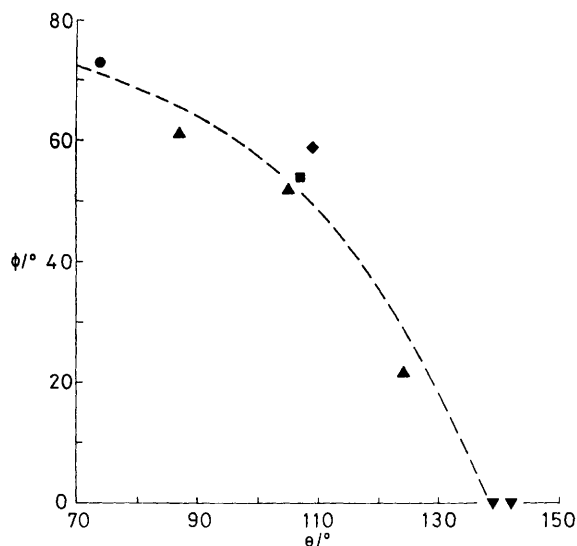


Figure 3. The correlation between the inclination ϕ of the S-C bond to the M-S-M plane and θ the M-S-M angle, for the cycles $(\mu\text{-SPh})_3\text{M}_3$: ▲ values for $(\mu\text{-SPh})_3\text{Cu}_3(\text{PPh}_3)_3$; ▼ values for $[(\mu\text{-SPh})_3\text{Fe}_3\text{Cl}_6]^{3-}$ (ref. 1); ■ mean value for $[\text{M}_4(\text{SPh})_{10}]^{2-}$ (ref. 6); ◆ mean value for $\text{Zn}_3(\text{SPh})_6(\text{MeOH})$ (ref. 6b); ● mean value for $[\text{Cu}_4(\text{SPh})_8]^{2-}$ (ref. 5).

are strongly dependent on the directions of approach of the C-S bonds to the cycle. These stereochemical principles should be pertinent to the conformations of $(\mu\text{-S-cys})_3\text{M}_3$ cores in metallo-cysteine proteins, where there are constraints on the spatial array of the ligating cysteinyl residues.

Note that a unique cycle stereochemistry does not necessarily obtain for a given set of C-S bond directions, and indeed a non-planar cycle could occur with the trigonal coplanar set of C-S bonds in (1).

In (2) there is additional correlation of the rotational conformation of the phenyl group about the S-C bond and the stereochemistry at sulphur. Thus the angle ψ between the

normal to the S-Ph ring plane and the bridged Cu-Cu vector follows ϕ : ψ data pairs are 61, 10; 53, 60; and 22, 78°. The unusual ϕ , ψ values of 0, 90° for (1) are consistent with this pattern.

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