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Tetrahedral, octahedral, cubal and centered cubal dithiolate clusters and cages of Cu(I) and Ag(I)

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Abstract:
In the absence of halides, anionic sulfur containing ligands generally produce multi nuclear products with Cu^I and Ag^I. For example, Cu^{II} and Ag^I acetates react with mercaptothiazoline, HMT, to produce tetranuclear Cu^I and Ag^I clusters which polymerize, $[M_n(MT)_4]_n$. Tetranuclear dithiocarbamates, $M_4(DTC)_4$, and dithiophosphates, $M_4(DDP)_4$, are important commercial chemicals with $Cu_4(DDP)_4$ functioning as an important anti-oxidant in motor oils. Cu^I-S clusters also have been implicated in biological redox chemistry. With the *i*-MNT ligand, hexa- and octanuclear complexes are also known. This paper summarizes the current knowledge of the synthesis and structural chemistry of Cu^I and Ag^I with 1,1-dithiol ligands. Clusters and cages such as $[Cu_6(S_2P(O^iPr)_2)_6]$ and $\{Cu_8[S_2P(O^iPr)_2]_6S\}$ are described along with their structural relationship to $[Zn_4(S_2P(OEt)_2)_6S]$.

Introduction

Compounds formed from Zn^{II} with dithiolate ligands such as the dialkyldithiocarbamates, DTC, and dithiophosphates, DDP, have long been important in technology (ref. 1). Cu^I derivatives of the dialkyldithiophosphates more recently have become important anti-oxidation additives (ref 1(b)). Cu^I-S clusters also have been implicated in biology as anti-oxidants (ref. 2) . Yet, little is known concerning the role of the metal ion in these processes. However, CuDDP (the technical name used for the Cu^I dialkyldithiophosphate formed with a $C_{8\text{-}12}$ alcohol), has become so important that a $129 Million patent infringement law suit was lost over its use recently (ref. 3). Both Cu^I and Zn^{II} complexes with these types of sulfur ligands can be mononuclear, usually with bases also bonded to the metal ions as in $[(Ph_3P)_2CuDTC]$, or polynuclear as has been described for $[Cu_4(DTC)_4]$ (ref. 4) and will be discussed here. The structure of the tetranuclear $[Cu_4(^iPr\text{-}DDP)_4]$, Fig.1, is similar (ref. 5) to that of the dithiocarbamates (ref. 6). This structure demonstrates that the sulfur atoms in these 1,1-dithiolate complexes behave as unidentate, μ_1, or bidentate, μ_2, centers and that the Cu^I is 3-coordinate, essentially sitting in the plane of the three S atoms. As we shall see, this CuS_3 coordination dominates the chemistry of Cu^I. Amma showed (ref. 7) many years ago that CuS_4 coordination is also found in some Cu^I -sulfur clusters. A long Cu-Cu distance of nearly 4.0 Å was observed in the thiourea complex he studied (ref. 8).

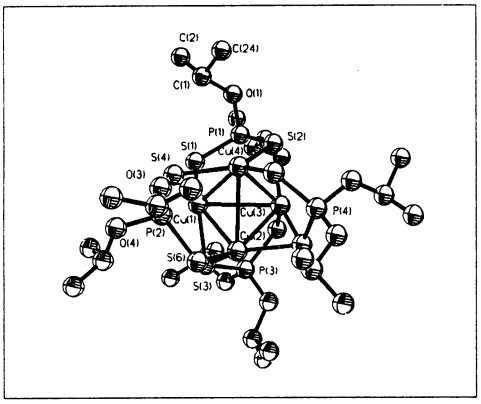

Fig. 1. $[Cu_4(S_2P(O^iPr)_2)_4]$ cage.

Dance recently reviewed (ref. 9) metal chalcogenide cluster chemistry including the beautiful mega clusters of Fenske such as $[Cu_{20}Se_{13}PEt_3)_{12}]$ in which the Cu^I atoms are both 3- and 4-coordinate. This material contains a cube of Cu^I atoms

with a Se in its center. Unfortunately the process of predicting structures expected for metal-chalcogenide complexes remains crude. As Dance states the electron counting procedures used to predict structure in other cluster chemistry "surrenders its predictive power". Theoretical studies by Avdeef (ref. 10), using SCF methods, showed clearly that little metal-metal bonding occurs in the cubane Cu^I cluster of the *i*-MNT ligand, $[S_2CC(CN)_2]^{2-}$, $[Cu_8(i\text{-MNT})_6]^{4-}$, characterized by us nearly 30 years ago (ref. 11). In the cubane cluster anion the S atoms are all μ_2 and the Cu^I atoms are three coordinate, separated from each other by about 2.8 Å. The lowest lying orbitals available to accept electron density from added donors are largely p_z in nature relative to the trigonal coordination about the Cu^I. This theoretical study implied that a two or an eight electron donating anion such as H^- or Cl^- could occupy the center of the cube symmetrically, although no such compound was known at the time.

A schematic representation of tetra-, hexa-, and octanuclear structural types is presented in Fig. 2. In this scheme the μ_2 S atoms are represented by the arrowheads. Two distinct structural types are drawn for hexanuclear clusters with six bidentate ligands in which each metal atom is three coordinate but the ligands are (μ_2,μ_1). Recent work in our laboratory has demonstrated that the hexanuclear Cu^I and Ag^I dialkyldithiophosphates are not isostructural but have the two distinct arrangements sketched in Fig. 2B,2C. This paper describes the synthesis of 1,1-dithiolate clusters, some of their chemistry, and the connections which exist between the various cluster structures. It points out structural relationships of hexanuclear Cu^I complexes with those of the cubane and centered cubane complexes, and also the tetranuclear basic Zn^{II} structure of $[Zn_4(DDP)_6S]$, Fig. 3, and its oxygen analog, $[Zn_4(DDP)_6O]$ which is an end product found when ZDDP (the technical name for the zinc dialkyldithiophosphate) is used as an oil additive.

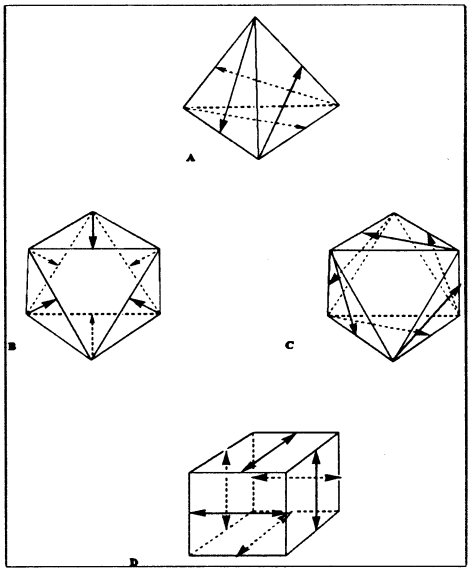

Fig. 2. Drawings of A, tetrahedral (S_4); B, C, octahedral (D_{3d}) and (S_6), the two known geometries; and D, cubic (T_h) dithiolate clusters. Arrowheads represent the μ_2 S atoms of the ligands with tails being unsaturated μ_1 S atoms.

Syntheses

Tetranuclear 1,1-dithiolate and related complexes of Cu^I generally are synthesized from Cu^{II} starting materials, the ligand being sacrificially oxidized in the process, **1**. While examining the related chemistry of 2-mercaptothiazoline, a N,S-coordinating ligand, $HS\text{-}C_3NSH_4$, (HMT), which was known to give an insoluble Cu^I N-bonded complex when the HMT ligand was reacted with Cu^{II}

$$\mathbf{1} \qquad 4\,Cu^{II} + 8\,S_2CR_2 \longrightarrow [Cu_4(S_2CR_2)_4] + 2[R_2C(S)S\text{-}]_2$$

salts, it became clear that a butterfly tetranuclear cluster of Cu^I was produced which was polymeric in the solid state (ref. 12). Two of the Cu^I atoms are 3-coordinate and two are 4-coordinate with weak intercluster bonding. Addition of PPh_3 or $AsPh_3$ to a suspension of $[Cu_4(MT)_4]_n$ in CH_2Cl_2 led to the isolation and characterization by crystallography of the cluster $(PPh_3)_2Cu_4(MT)_4$ in which the phosphines replaced the intercluster linkages. With pyridine as the base, a polymer was characterized $[pyCu_4(MT)_4]_n$ in which one of the wing-tip Cu^I atoms still was involved with intercluster linkages. It was important to avoid halide salts of Cu^{II}, or ethanol as a solvent with $Cu(OAc)_2{\cdot}H_2O$ as the salt, to avoid the formation of other products. The reduction of the Cu^{II} to a Cu^I cluster is both solvent and anion dependent. In acetonitrile the cluster formation is complete. Furthermore is was possible to synthesize and structurally characterize the mixed Ag^I, Cu^I cluster in this manner, in which the 4-coordinate wing-tip positions are Ag^I atoms and the butterfly body atoms are 3-coordinate Cu^I, with no apparent disorder. Clearly the synthetic procedures which here-to-fore had produced only tetranuclear clusters of Cu^I with dithiocarbamates and dithiophosphates had to be re-examined. It was already known that anionic tetra-, hexa- and octanuclear clusters of Ag^I could be isolated using the *i*-MNT ligand.

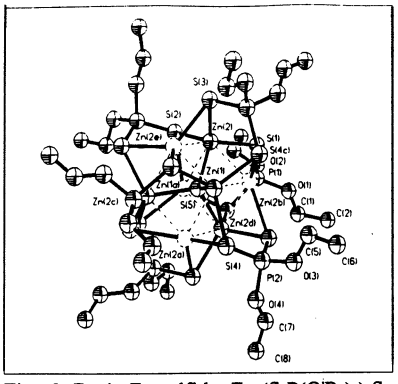

Fig. 3. Basic Zn sulfide, $Zn_4(S_2P(O^iPr)_2)_6S$. Dashed positions generated by inversion.

The original synthetic studies of $[Cu_8(i\text{-}MNT)_6]^{4-}$ had been done starting with Cu^{II} salts. No tetranuclear $[Cu_4(i\text{-}MNT)_4]^{4-}$ was known. However, Coucouvanis had shown (ref. 13) that it was possible to obtain linked tetranuclear clusters from an acid reaction with the octanuclear $[Cu_8(^tBu\text{-}DED)_6]^{4-}$, DED = $[S_2CC(COO^tBu)_2]^{2-}$. Furthermore, the sulfur-rich DED complex led to the formation of a tetranuclear complex (ref. 14) with three $[S,^tBu\text{-}DED]^{2-}$ ligands, with each of the Cu_4 tetrahedral edges of the anion $[Cu_4(S,^tBu\text{-}DED)_3]^{2-}$ containing μ_2 S atoms. Each Cu^I atom in these structures remains 3-coordinate. It quickly became clear that many new tetra-, hexa-, and octanuclear Cu^I and possible also Ag^I clusters might be synthesized using different conditions. A listing of the possible topological bonding arrangements possible assuming that each metal atom is only 3-coordinate and that the S atoms of the sulfur ligand can be $\mu_{1\text{-}3}$ is presented in Table 1. It will be noted that a number of different arrangements are possible for each nuclearity. This table does not take into account that different stereochemical structures may be found with the number of $\mu_{1\text{-}3}$ listed. For example, the structures represented in Fig. 4 obey the coordination rules but contain more than one S atom bridging the metal atoms. Starting with $[Cu^I(CH_3CN)_4]PF_6$ and the $[^nBu_4N]^+$ salt of the ligand in acetonitrile, it was possible to isolate in poor yield and crystallographically characterize the anion $[Cu_4(i\text{-}MNT)_4]^{4-}$. Its structure is the typical M_4L_4 entity seen previously for the $[Cu_4(DTC)_4]$ and related clusters, Fig. 2, A.

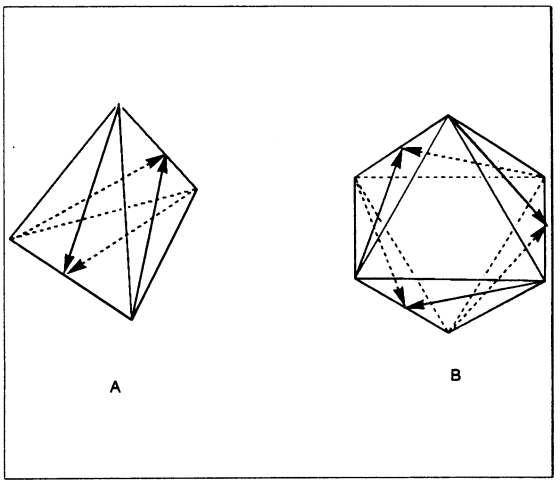

Fig. 4. Tetrahedral, A, and Octahedral, B, geometries with double bridging between Cu^I atoms.

However, following the lead of Coucoucvanis and adding powdered sulfur to the cubane $[Cu_8(i\text{-}MNT)_6]^{4-}$ cluster in acetonitrile, with some KOH(aq) present, the new hexanuclear, sulfur-rich cluster anion $[Cu_6(S,i\text{-}MNT)_6]^{6-}$, Fig. 5, was obtained. The surprising feature here is the nearly planar hexagonal arrangement of the Cu^I atoms. This anion reacts cleanly in acetone with 6 molar equivalents of Ph_3P to eliminate Ph_3PS and the tetranuclear cluster in high yield. Upon isolation of this product, it was possible to study its further conversion into the cubane (ref. 15). Before this reaction is briefly discussed, additional structural features found with the *i*-MNT complexes need to be described.

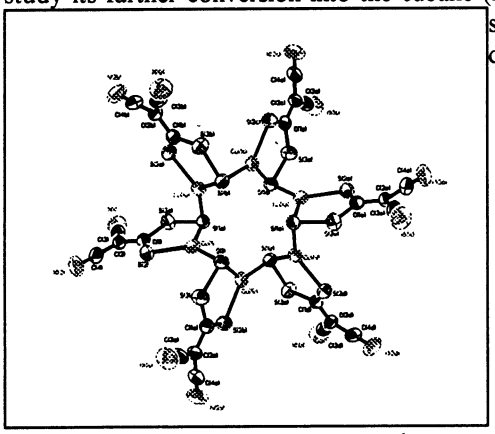

Fig. 5. Structure of S-rich $[Cu_6(S,i\text{-}MNT)_6]^{6-}$

In acetonitrile, $AgNO_3$ reacts with the $[Bu_4N][i\text{-}MNT]$ to produce $[Ag_4(i\text{-}MNT)_4]^{4-}$ which is isostructural with the Cu^I analogue, Fig. 2,A. Dietrich (ref. 16) had isolated the hexanuclear anion $[Ag_6(i\text{-}MNT)_6]^{6-}$ and the octanuclear anion $[Ag_8(i\text{-}MNT)_6]^{4-}$ by a similar synthesis. Both anions have been structurally characterized. This Ag_8 cluster is isostructural with the Cu^I cubane while the hexanuclear complex has the approximate D_{3d} geometry sketched in Fig, 2 B. It is this structure (ref. 17) which needs further elaboration. Notice that the μ_1 S atoms of Fig. 3 B are in an equatorial belt with all six bridging S atoms occupying opposite triangular faces of the metal octahedron. It is

Table 1. Topological arrangements for Chelating S ligands.

M	L	SA	S	μ_1	μ_2	μ_3
2	2	4	6	3	0	1
				2	2	0
3	3	6	9	4	1	1
				3	3	0
4	4	8	12	6	0	2
				2	3	1
				4	4	0
4	3	6	12	4	0	2
				1	4	1
				0	6	0
6	6	12	18	9	0	3
				8	2	2
				7	4	1
				6	6	0
8*	8	8	24	0	0	8
8	8	16	24	8	8	0
	6	12	24	0	12	0

* Only one S atom per ligand

$S = 3\mu_3 + 2\mu_2 + \mu_1$ (Sites, three for each metal atom)

$SA = \mu_1 + \mu_2 + \mu_3$ (Number of S atoms, two per ligand)

$S - SA = \mu_2 + 2\mu_3$

apparent that the equatorial S atoms can function as chelating ligands to other metal centers. Upon addition of $[Ag(PPh_3)_2]NO_3$ to this anion in acetonitrile in 2:1 or 3:1 molar ratios, high yields of $[Ag_8(i\text{-}MNT)_6(PPh_3)_4]^{4-}$ and $[Ag_9(i\text{-}MNT)_6(PPh_3)_6]^{3-}$, respectively, can be isolated as their $[BzEt_3N]^+$ salts. The structure of $[Ag_8(i\text{-}MNT)_6(PPh_3)_4]^{4-}$ is presented in Fig.6.

Cluster Geometries

Synthesis of the $[Ag_6(S_2P(O^iPr)_2)_6]$ cluster (ref. 18) in acetonitrile with a D_{3d} M_6S_{12} arrangement like the $[Ag_6(i\text{-}MNT)_6]^{6-}$ prompted us to examine further what possible M_6L_6 structures of the octanuclear species are reasonable. Using straight chain alkyls we had already reported that hexanuclear Cu^I dialkyldithiophosphates can be formed (ref. 19). Indeed, the S_6 structure of the complex is represented by Fig. 2 C. Thus at least two different geometries exist. How many others can be expected? Complete topological analysis indicates that two additional reasonable structures with no double S bridges and only 3-coordinate Cu^I are plausible. A sketch of their geometries is seen in Fig. 7. Assuming the existence of double S bridges, two additional structures are reasonable. None of these species have been observed to date with Cu^I or Ag^I. Without double S bridges and only 3-coordination, only these four, Fig. 2B,C and Fig. 7, geometrical structures, D_{3d}, S_6, C_{2h} and C_2 are reasonable for the octahedral complexes of the bidentate dithiolate ligands.

Cluster Rearrangements

As stated above, Liu had observed (ref. 20) that the tetranuclear anion $[Cu_4(i\text{-}MNT)_4]^{4-}$ slowly converts into the homocubane $[Cu_8(i\text{-}MNT)_6]^{4-}$ in CH_2Cl_2 and other solvents. Careful studies of this system showed that oxidation accelerated the rearrangement. A summary of the various reactions are presented in Fig. 8. Might there be a similar cluster expansion with the dithiocarbamates and the dithiophosphates under oxidizing conditions? By reacting $[Cu(CH_3CN)_4]PF_6$ with $(NH_4)[S_2P(O^iPr)_2]$ in CH_2Cl_2 with added water containing an oxidant, the centered cubane cluster $\{Cu_8[S_2P(O^iPr)_2]_6S\}$ was obtained in about 6% yield (ref. 19). The same type of cluster and its related Cl centered cluster, $\{Cu_8[S_2P(OEt)_2]_6(Cl)\}^+$, had been obtained previously (ref. 21) (ref. 22) by the fortuitous reaction of $CuCl_2{\cdot}2H_2O$ with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2[\mu\text{-}SOP(OEt)_2]\text{-}[S_2P(OEt)_2]_3(O)_2$. From Mo, the products were reported to be dark red colored. Our first synthesis involving only Cu^I yielded a deep blue product. Subsequently our group was able to reproduce the reaction in the absence on Cu^{II} to obtain a colorless product. Based on the electronic structure of the components in these clusters, no color (or perhaps a light

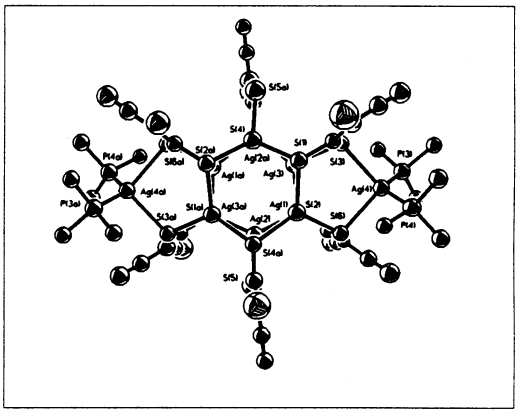

Fig. 6. **$[Ag_6(i\text{-}MNT)_6(AgL_2)_2]^{4-}$.**

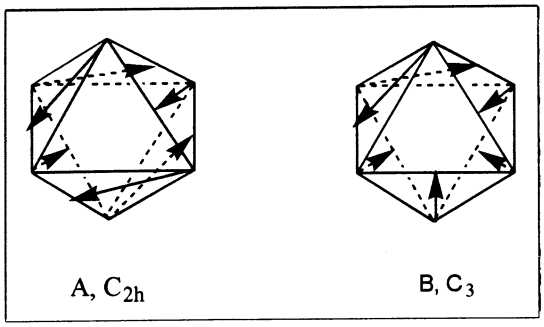

Fig. 7. Two additional geometries not observed.

yellow color) is expected for these complexes. Clearly the clusters are prone to associate with other metal ions in a manner yet to be determined. The Chinese Academy of Sciences group in Fuzhou (ref. 23) subsequently has established a multi-metal cluster chemistry involving bridging sulfido ligands. In our group the synthesis (and characterization by crystallography) of colorless $[Cu_8(S_2P(O^iPr)_2)_6(Br)]Br$ has been achieved in various yields (20-90%) from $[Cu(CH_3CN)_4]PF_6$ and $(NH_4)S_2P(O^iPr)_2$ by the addition of $[BzEt_3N]Br$ in CH_2Cl_2 and addition of slightly basic(pH ~ 8) water containing added bleach.

Structural Relationships

The centered cubane cluster observed in $\{Cu_8[S_2P(O^iPr)_2]_6S\}$ contains an icosahedron of S atoms surrounding a cube of Cu^I atoms which has a S atom inside the cube. Electronically the S atom is S^{2-} to balance the charge

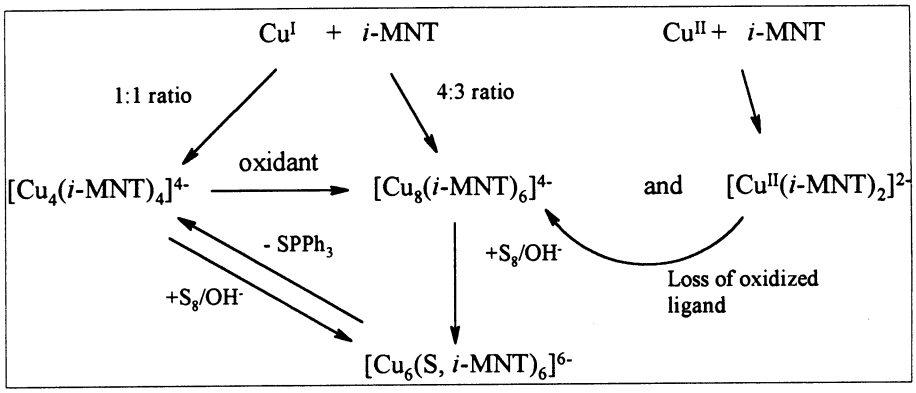

Fig. 8. Summary of the reactions of the *i*-MNT complexes.

since the dithiolate ligands are uni-negative. Overall, the I_h symmetry of the icosahedron and the O_h symmetry of the cube are lost in the idealized structure which contains only those symmetry features both groups have in common, namely those of T_h. This is the idealized symmetry of $[Cu_8(i\text{-MNT})_6]^{4-}$.

Careful re-examination of the structure of $[Cu_6(S_2P(O^iPr)_2)_6]$ described originally (ref. 19) to be $[Cu_6(S_2P(O^iPr)_2)_6]\cdot 2H_2O$ showed that the "water" are small amounts (~ 4%) of disordered Cu atoms. If all sites are completely occupied, the structure of the Cu_6S_{12} core becomes that of the centered cubane, with the center S atom absent, Fig.9. There is a slight 0.02 Å shrinkage of the Cu-Cu distances in the $[Cu_6(S_2P(OEt)_2)_6]$ cage compared with $[Cu_6(S_2P(O^iPr)_2)_6]$ or $[Cu_8[S_2P(O^iPr)_2]_6Cl]^+$, but overall the cage size remains constant. Even more interesting is the fact that the $Zn_4S_{12}S$ cage in the basic ZnDDP, $[Zn_4(S_2P(OEt)_2)_6S]$, is essentially like these other two products, Fig. 10. The dithiophosphate icosahedron of S atoms containing a atom centered tetrahedron, a disordered octahedron or a centered cube become the thermodynamic products of the oxidation of the anti-oxidants ZDDP and CuDDP. We suspect that these cages are also efficient metal ion traps for ions like Fe^{3+}, Cu^{2+}, etc.

Acknowledgments

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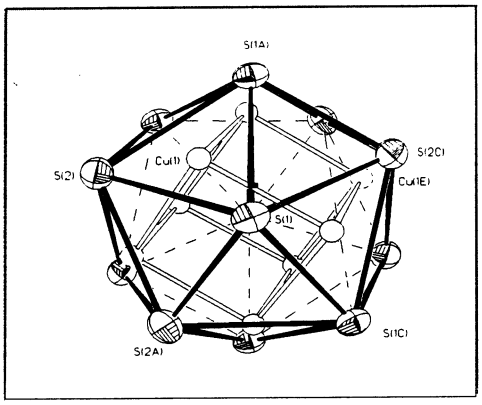

Fig. 9. The icosahedral S atom arrangement about Cu_6DDP_6.

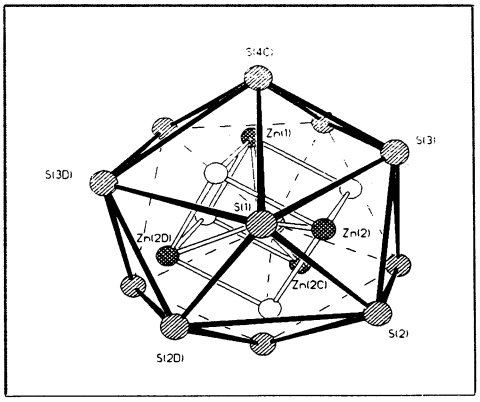

Fig. 10. Icosahedron of S atoms about $[Zn_4(DDP)_6S]$.

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