

Copper(I), Lithium, and Magnesium Thiolate Complexes: An Overview with Due Mention of Selenolate and Tellurolate Analogues and Related Silver(I) and Gold(I) Species

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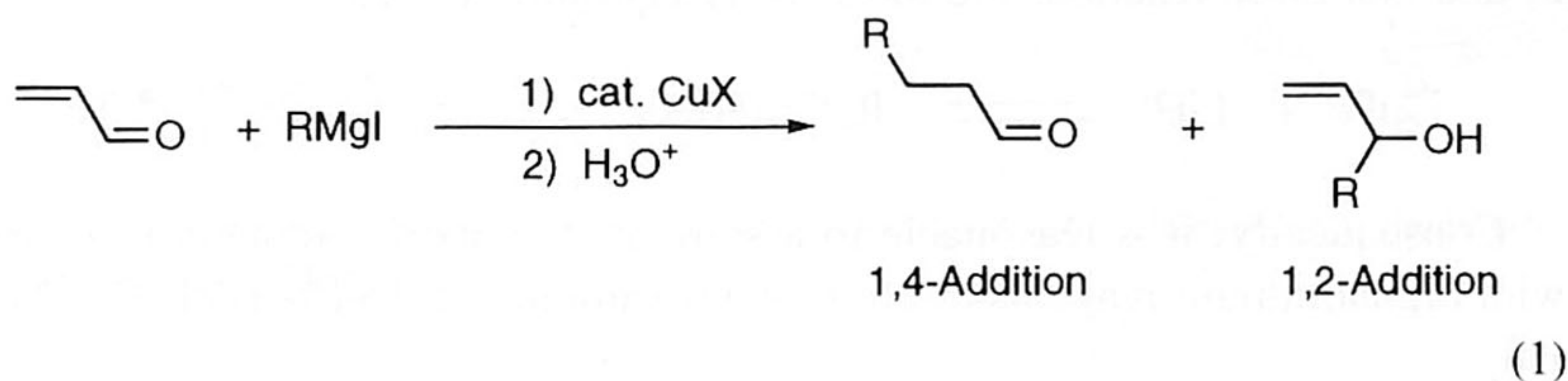
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I. INTRODUCTION

It has long been known that thiolate ligands (RS^-), which are formally derived from thiols (RSH) by deprotonation, are well suited to form metal complexes (1). Specific reviews of this area have covered the structural chemistry of metal thiolates (1a), the coordination chemistry of metal thiolates from a bioinorganic perspective (1b), transition metal thiolates (1c), and, most recently, early transition metal thiolates (1d). Because of potential thione–thiol tautomerism, a review dealing with complexes of heterocyclic thione donors (1e) is also relevant. This chapter concentrates on thiolate complexes of copper(I), lithium, and magnesium, but we also mention, for comparison or contrast, many related species of silver(I) and gold(I) and of some complexes that contain selenolate and tellurolate ligands. However, it should be emphasized that we have not attempted a comprehensive literature search outside the primary field of interest.

This chapter on thiolate ligands was motivated by the fact that metal thiolate species are finding increasing application in fields such as medicine, materials science, and organic synthesis. In particular, the recent use of thiolates in the copper-mediated reactions of organolithium and Grignard reagents (i.e., RLi and $RMgX$) makes an overview that links copper, lithium, and magnesium opportune (2). In this area, the unique capabilities of the sulfur atoms of a thiolate ligand for bonding as a terminal or a bridging center provides an interesting variety of structures which, when the underlying structural themes are understood, should provide a basis for the development of new thiolate ligands for application in enantioselective synthesis. In this chapter, we present our ideas regarding these underlying themes.

From a historic perspective, in 1936 Gilman and Straley (3) discovered that catalytic amounts of a copper salt lead to an increased reactivity of Grignard reagents. A little later, in 1941, Kharasch and Twaney (4) found that Grignard reagents react with α,β -unsaturated ketones to afford products that result from 1,4-addition instead of the normally observed 1,2-addition (Eq. 1). Since then, various researchers have studied the application of cuprates $[\text{LiCuR}_2]$ in numerous organic C—C bond formation reactions (5–9).



After the first preparation of the Gilman reagent, $[\text{LiCuMe}_2]$, House et al. (10) used cuprates in organic synthesis, and found that only one-half of the organic groups are transferred. In order to reduce the loss of the often valuable organic groups, mixed cuprates $[\text{LiCuR}^t\text{R}^f]$ were introduced in which R^t is the valuable transferable group and R^f is a cheap and expendable nontransferable group that remains in the copper reagent. Many modifications of the latter R^f group have been reported over the years and examples of such groups include alkynyl (11), cyclopentadienyl (11b), halide (12), cyanide (13), silyl (14), hydride (15), amide (16, 17), phosphide (18), alcoholate (16, 19), and thiolate ligands (16).

Although Posner et al. (16) reported in 1973 that copper(I) thiophenolate, $[\text{Cu}(\text{SPh})]$, can be used as a stoichiometric catalyst in cuprate-mediated reactions in order to prevent the loss of the valuable group R^t (i.e., PhS^- is the nontransferable group R^f), the idea of using a well-chosen nontransferable arenethiolate group in cuprate-catalyzed organic synthesis found its first application as late as 1989 (2a). In later publications, Knotter et al. (2b, 20) reported the use of catalytic amounts of copper(I) arenethiolates with potentially intramolecularly coordinating amine functionalities in the enantioselective conjugate 1,4-addition of Grignard reagents to an α,β -unsaturated enone (i.e., benzylidene acetone). Since then, copper(I) arenethiolate catalysts have also been applied in various heterocuprate mediated organic reactions and recent examples of the successful use of copper(I) arenethiolate catalysts with Grignard reagents in organic syntheses include: (a) the 1,4-addition to acyclic (2b, 20, 21) and cyclic (22) α,β -unsaturated enones, (b) the 1,6-addition to $\alpha,\beta,\gamma,\delta$ -unsaturated enyne esters (23), (c) the selective α - or γ -nucleophilic substitution of allylic acetates (24), and (d) cross-coupling reactions with primary alkyl halides (25).

The successful application of copper(I) arenethiolate catalysts in organic chemistry thus led to a rapid growth of this field of research. However, whereas the influence of the arenethiolate backbone on the selectivity of organic conversions was studied in detail (2, 20–25), little is known about the influence of this backbone on the structure of the copper(I) arenethiolate itself, let alone on that of the kinetically active (key)intermediates.

It is well known that organocopper complexes [CuR] react with organolithium reagents [LiR'] to afford the corresponding cuprates [LiCuRR'] (Eq. 2) and that these reactions are most likely equilibria (2, 26).



Consequently, it is reasonable to assume that copper(I) arenethiolates react with organolithium reagents to afford heterocuprates [LiCu(SAr)R] (Eq. 3) (2, 16).



The presence of equilibria in the former reaction (Eq. 2) as well as the similarity between organocopper and copper(I) arenethiolate complexes leads one to the assumption that in the reaction of a copper arenethiolate with an organolithium reagent it must be also possible to have reverse formation of the cuprate species (i.e. reaction of organocopper with lithium arenethiolate as shown in Eq. 3). A similar line of reasoning is applicable to reactions involving organomagnesium and magnesium arenethiolate complexes.

Complexes of lithium and magnesium with monoanionic thiolate ligands are scarce, and the influence of intramolecular coordination on the structure and stability of these species has not been systematically studied. In this area, there is one report of a unique mixed-organo(arenethiolato) cluster containing copper and magnesium, that is [Cu₄Mes₄][Mg(SAr)₂]₂ (Fig. 1) (20), and its description as either a cuprate, [Cu₄Mes₄(SAr)₂][Mg(SAr)]₂, or a coordination complex, [Cu₄Mes₄][Mg(SAr)₂]₂, is of interest not only from a structural point of view, but also for understanding the kinetically active species formed in a mixture of copper(I) arenethiolate catalyst, Grignard reagent, and enone substrate.

Within this overview of copper(I), lithium, and magnesium thiolate complexes, one of the aims is to highlight the influence that (intramolecular) nitrogen coordination exerts on the structure of such species, since intermolecular (auxiliary) coordination of heteroatoms often leads to poorly defined species. An example of this poor "species definition" is the reaction behavior of polymeric copper(I) thiophenolate, [Cu(SPh)], with triphenylphosphine: Several P-coordinated aggregates with variable stoichiometry were reported (Scheme 1) (27–29). This behavior makes it difficult to study one specific species in copper(I) thiolate catalyzed organic reactions since equilibria are likely to occur.

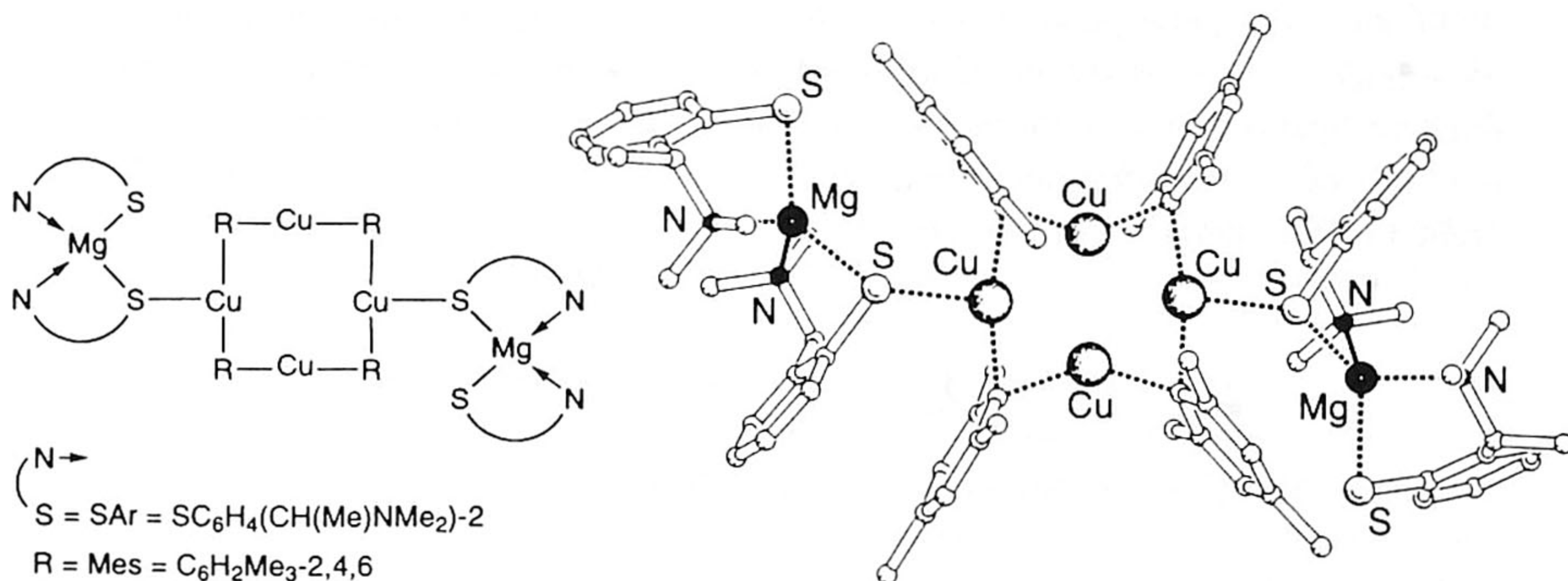
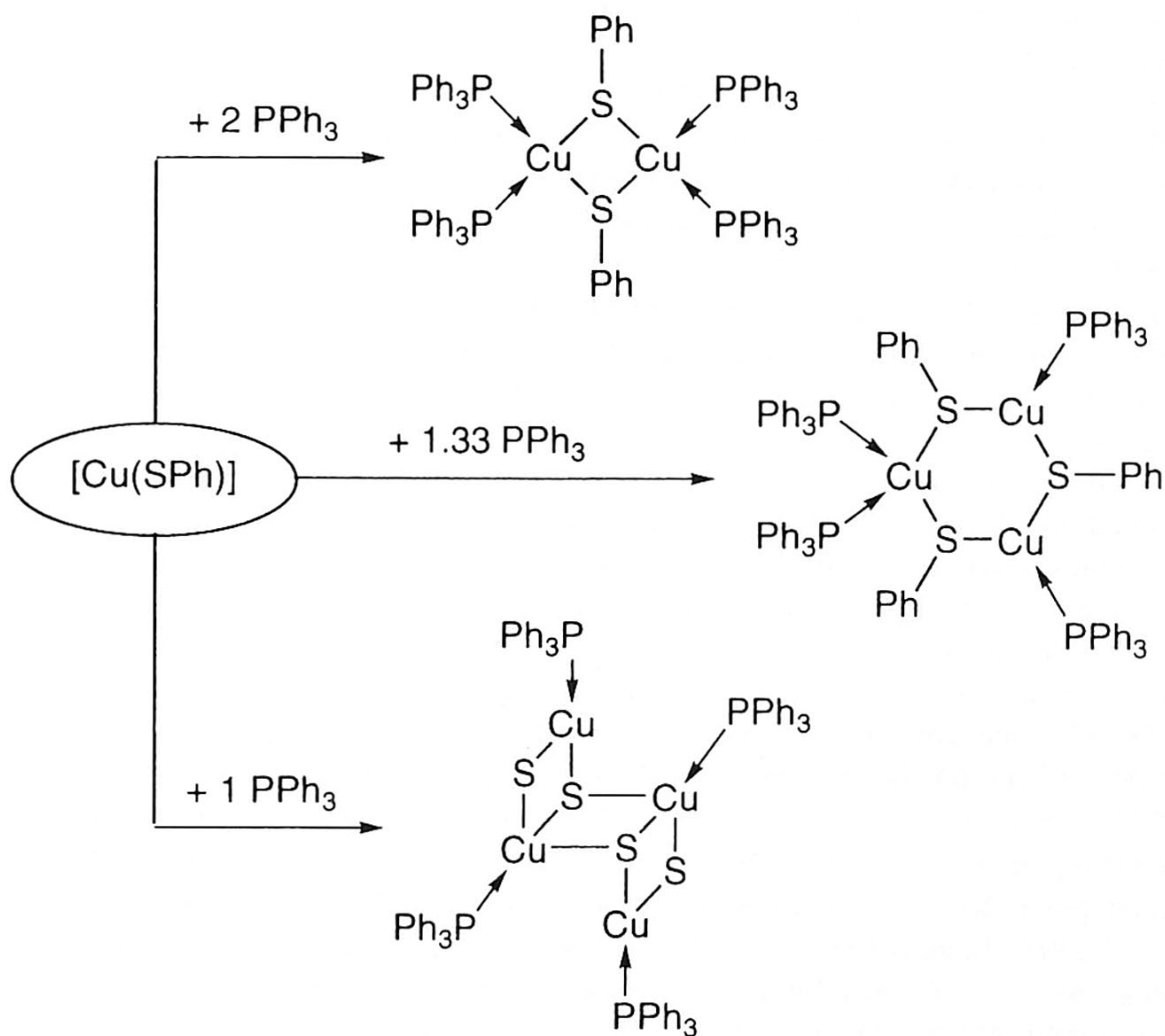


Figure 1. Schematic representation and molecular structure of $[Cu_4Mes_4][Mg(SAr)_2]_2$ (hydrogen atoms are omitted for clarity).



Scheme 1. Examples of PPh_3 coordinated copper(I) thiophenolate aggregates.

Finally, one anticipates that from this structural data, together with the accumulated data from spectroscopic and chemical studies on well-defined isolated complexes, that it should be possible to make meaningful postulates regarding the structures and reactivity of key intermediates in copper(I) arenethiolate catalyzed organic reactions.

II. COPPER(I) THIOLATE COMPLEXES

A. Copper, Silver, and Gold Thiulates in Perspective

The great interest in copper(I) arenethiolates stems, not only from their recent application in organic synthesis (16, 20–25) and from the unique and sometimes puzzling variation in their structural formats, but also from their relevance to the structure and function of the active sites in metalloproteins (30) such as the blue copper proteins, which involve Cu—S binding. Moreover, copper arenethiolate complexes can sometimes behave as semiconductors (31), while thermolysis of such species can offer a low-temperature route to novel solid state chalcogenide materials (32). The complexation of thiolate ligands to silver(I) has been studied in detail (33–35), but only a few structurally characterized species are known and, where relevant, these have been included in this chapter. Gold(I) thiulates have been extensively studied in relation to chemotherapy for arthritis (36). These studies have spawned an enormous literature in this area (37). The mechanism of the action of gold-containing pharmaceuticals is not clear, but interaction of gold(I) centers with the thiol groups of proteins and enzymes seems critical. A limited number of simple gold(I) thiolate structures is known and reference is made to some of them where deemed necessary.

The organothiolate anion RS^- is a ligand that is sometimes classified as a pseudohalide, comparable with ligands such as Cl^- , Br^- , and I^- , and its metal complexes are of fundamental chemical interest (1). One of the pseudohalide attributes of the RS^- ligand is the formation of metal thiolate complexes that are similar to metal halides, but with the difference that thiulates are stronger Brønsted bases than halides. For example, there is a great similarity between the solid state structures of the dianionic complexes $[Cu_4(SPh)_6]^{2-}$ and $[Cu_4I_6]^{2-}$ (38). The thiolate ligand (RS^-) has the advantage over the related sulfido ligand (S^{2-}) that by variation of the group R the redox properties of the metal atom in its complexes can be tuned. In this way, complexes have been synthesized that are reported to mimic the blue copper protein and metallothionein proteins (39).

Thiolate ligands have a reputation for bridging metal atoms, a reputation engendered by the insolubility of copper(I) thiolate complexes $[Cu(SR)_n]_p$ in common organic solvents that is presumed to be the result of polymeric structures (1a). However, the great difficulty in obtaining structural information on

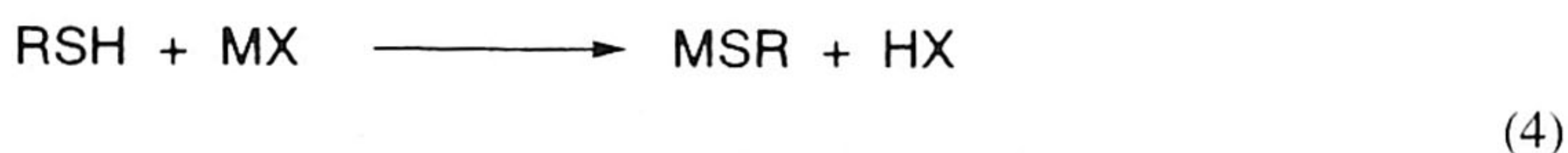
(copper) thiolate complexes, that is caused by insolubility and poor crystal habit, has in a number of cases been overcome by either the use of auxiliary coordinating ligands or by appropriate variation of the group R of the thiolate ligand. The latter variations include the introduction of bulky (40) or intramolecularly coordinating (41) substituents as well as the introduction of stereogenic centers in cases where metal arenethiolates have been used as chiral catalysts (2, 20, 21, 42).

B. Synthesis of Copper(I) Thiolates

Several methods have been applied to prepare copper(I) thiolates in a pure form. As a result of the high thermal stability of such complexes, a copper(I) thiolate can generally be prepared in a number of ways, which is in contrast to the preparation of organocopper species where, due to their low thermal stability, specific protocols are often necessary to successfully isolate the target compound (43).

1. Synthesis via Deprotonation of Thiols

As a consequence of the inertness of copper(I) thiolates toward protic media, the synthesis of these complexes can often be carried out in solvents such as methanol or ethanol and a very simple synthetic procedure is the reaction of the thiol (RSH) with a suitable copper source (either Cu^{I} or Cu^{II}) in the presence of a base (Eq. 4). A complication of this method is the tendency of copper to bind to more than one thiolate ligand and, therefore, instead of the neutral copper(I) thiolate $[\text{Cu}(\text{SR})]$ anionic species such as $[\text{Cu}(\text{SR})_2]^-$ or $[\text{Cu}(\text{SR})_3]^{2-}$ are frequently isolated (44, 45).



$\text{MX} = \text{Cu}(\text{O}_2\text{CMe})_2, \text{Cu}(\text{NO}_3)_2, \text{AgNO}_3, \text{Cu}_2\text{O}, \text{CuO}, \text{CuCl}$

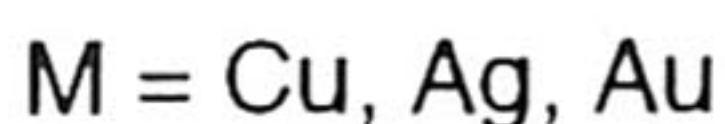
$\text{R} = \text{alkyl, aryl}$

Examples of the successful application of this method are the use of copper(II) acetate for the preparation of neutral complexes $[\text{Cu}(\text{SR})]$ ($\text{R} = \text{aryl, alkyl}$; no base needed) (46), and the use of copper(II) nitrate for the synthesis of anionic species $[\text{Cu}_4(\text{SPh})_6]^{2-}$ and $[\text{Cu}_5(\text{SPh})_7]^{2-}$ (47, 48), as well as of the cationic species $[\text{Cu}^{\text{I}}(\text{SC}_5\text{H}_4\text{NH})_3]^+$ (49). The latter complex is interesting in that each thiolate ligand is neutral due to protonation of the pyridine nitrogen atom. Similarly, silver nitrate has been used to prepare several neutral alkylthiolato silver complexes (33). The use of copper(I) oxide was reported in the synthesis of a family of copper(I) arenethiolates containing intramolecularly

coordinating amine substituents, one example being $[\text{Cu}_3(\text{SC}_6\text{H}_4(\text{CH}(\text{R})\text{NMe}_2)_2)_3]$. Since H_2O is formed in this synthetic route a base is not necessary, although one is actually present in the ortho substituent (20, 50). The use of copper(II) oxide was also reported, but in this case a mixed-valence species $[\text{Cu}_8^{\text{I}}\text{Cu}_6^{\text{II}}(\text{SR})_{12}]\text{Cl} \cdot 3.5\text{SO}_4$ was isolated (51). Finally, in the preparation of $[\text{Cu}_8(\text{SC}_6\text{H}_2\text{-}i\text{-Pr}_3\text{-}2,4,6)_8]$, copper(I) chloride was used but, due to its low solubility, it was necessary to also use a base as a coordinating solvent (usually acetonitrile) and a high reaction temperature (reflux) (52). In many of these syntheses an inert atmosphere is required to prevent the oxidation of the thiol (31). The reaction of an arenethiol with CuCl has also been used to prepare the oligomeric complexes $[\text{CuSC}_6\text{H}_4\text{S}]_n$ and $[\text{CuSC}_6\text{H}_4\text{SCu}]_n$, which both display semiconducting properties (31). More recently, organocopper compounds $[\text{CuR}]_n$ and copper alkoxide complexes $[\text{CuOR}]_n$ have found employment in the preparation of copper(I) thiolates: the reaction of *tert*-amylmercaptide ($\text{Et-CMe}_2\text{SH}$) with mesitylcopper cleanly affords $[\text{Cu}(\text{SCMe}_2\text{Et})]$ (53), while the reaction of arenethiols with copper *tert*-butoxide cleanly affords the corresponding copper arenethiolates $[\text{Cu}(\text{SAr})]_n$ (54).

2. Electrochemical Synthesis

An extension of the preparative route via thiol deprotonation (Section II.B.1) is the electrochemical synthesis of copper(I) thiolates. In this latter method, acetonitrile solutions of either a thiol or a disulfide (and a coordinating ligand) are electrolyzed using a platinum cathode and a copper anode (Eq. 5) (55–57). This particular route can be easily extended to the synthesis of both silver(I) and gold(I) thiolates (55).



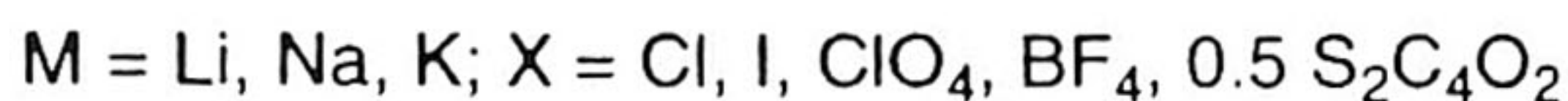
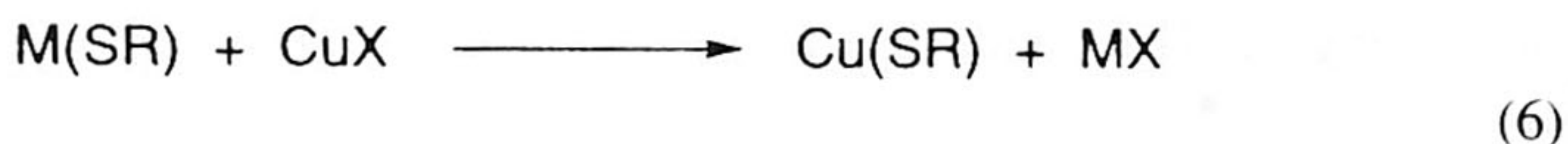
(5)

The yields in this type of synthesis are generally better than 90% (based on dissolved anode material) and the isolated material is of high purity (55). Anionic species $[\text{Cu}(\text{SR})_n]^{1-n}$ with $n > 1$ are generally not isolated and both copper alkyl- and arenethiolates are accessible in this way. Moreover, this technique also allows access to copper selenolates $[\text{Cu}(\text{SeR})]$ (57).

One example of a copper thiolate synthesis exists in which a disulfide reacts directly with metallic copper without the necessity of an externally applied potential: CF_3SSCR_3 and Cu^0 cleanly afford the copper(I) perfluoro-alkylthiolate complex $[\text{Cu}_{10}(\text{SCF}_3)_{10}(\text{MeCN})_8]$ (58).

3. Synthesis via Transmetalation

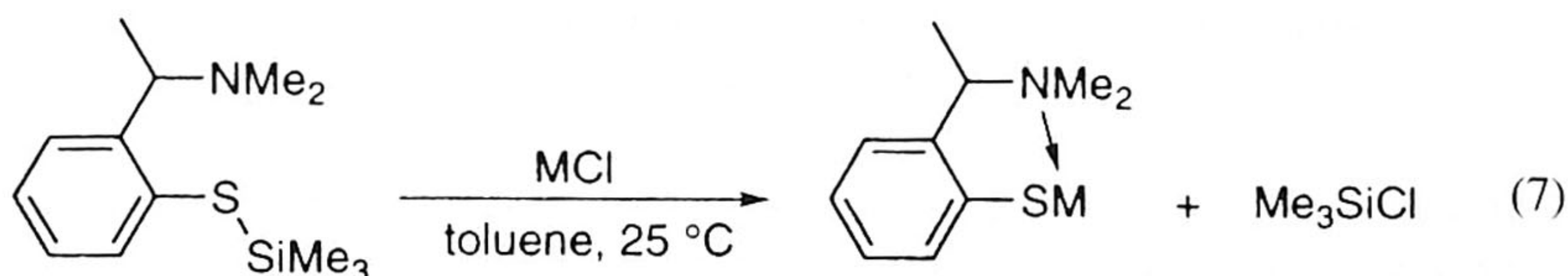
Copper(I) thiolates can be prepared by transmetalation of Group 1 (IA) metal thiolate complexes with suitable copper halide salts whereby the halide ligand is selectively transferred to the more electropositive metal (Eq. 6).



The copper salts most commonly used in this synthetic route are the sparingly soluble species CuCl (59), CuBr (60), and CuI (61). More soluble precursors, such as $[(PPh_3)CuCl]$ (62), $[Cu(MeCN)_4]ClO_4$ (63, 64), and $[Cu(MeCN)_4]BF_4$, have also been frequently used (65, 66). Less frequently used precursors include the copper bis(dithiosquarate) dianion $[Cu(S_2C_4O_2)_2]^{2-}$ (45) and copper(II) dichloride (67). As is the case in synthetic routes employing corresponding thiols (Sections II.B.1 and II.B.2), anionic species such as $[Cu(SR)_2]^-$, $[Cu(SR)_3]^{2-}$, and $[Cu_4(SR)_6]^{2-}$ are also formed, but in this case mixed-arenethiolatocopper copper halide aggregates, such as $[Cu_8(SR)_3Br_5]$ (60) and $[Cu_3(SR)_3]_4[CuI]_4$ (61), can also be isolated. Moreover, copper thiolates prepared this way sometimes retain the Group 1 (IA) metal salts MX, which are generated by this route, and, for example, in catalytic applications of these thiolate species the presence of such extraneous salts is highly undesirable (20, 50, 68).

4. Synthesis via Trimethylsilyl Arenethioethers

A synthetic procedure for copper(I) thiolates that avoids the formation of Group 1 (IA) metal salts is the reaction of trimethylsilyl arenethioethers (Me_3SiSAr) with copper(I) chloride (Eq. 7) (68, 69). From this reaction the only side product is volatile chlorotrimethylsilane, which can be easily removed in vacuo.

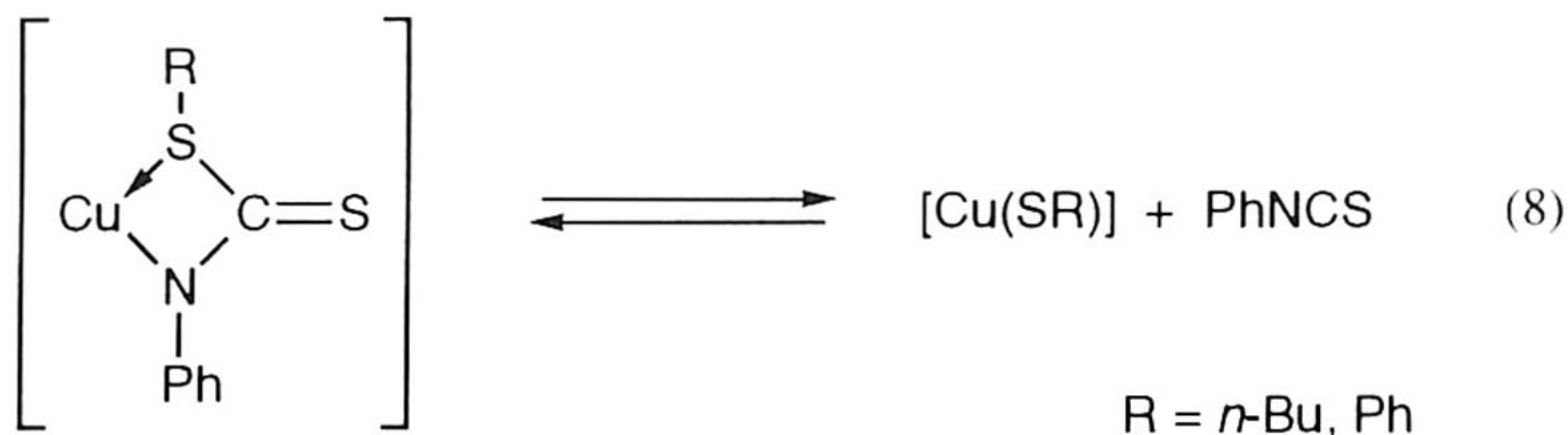


A second advantage of this synthetic route is its wide applicability. Besides CuCl, other metal halide species such as MeZnCl (68), ZnCl₂ (70), $[PdCl_2(MeCN)_2]$ (71), and $[AuCl(tht)]$ (72) can also be used, leading to the

corresponding pure metal arenethiolate in virtually quantitative yield. However, when applied for the synthesis of copper(I) species, this method is limited to arenethiolate ligands containing potentially coordinating substituents (69). Fenske et al. (73) applied a similar approach to prepare copper(I) sulfide, selenide, and telluride cage clusters in the presence of auxiliary phosphine ligands and, alternatively, sulfide clusters $[M_6S_{17}]$ ($M = Nb$ or Ta) have been prepared by reacting $M(OEt)_5$ with $(Me_3Si)_2S$ (74).

5. Miscellaneous

It was reported that copper dithiocarbamato complexes $[Cu(RSC(S)NPh)]$ [formed from $CuCl$ or $CuBr$, $RSC(S)N(H)Ph$ and NEt_3 in acetonitrile] can eliminate $PhNCS$ both in solution and in the solid state to afford the corresponding copper(I) thiolates $[Cu(SR)]$ (Eq. 8) (75).

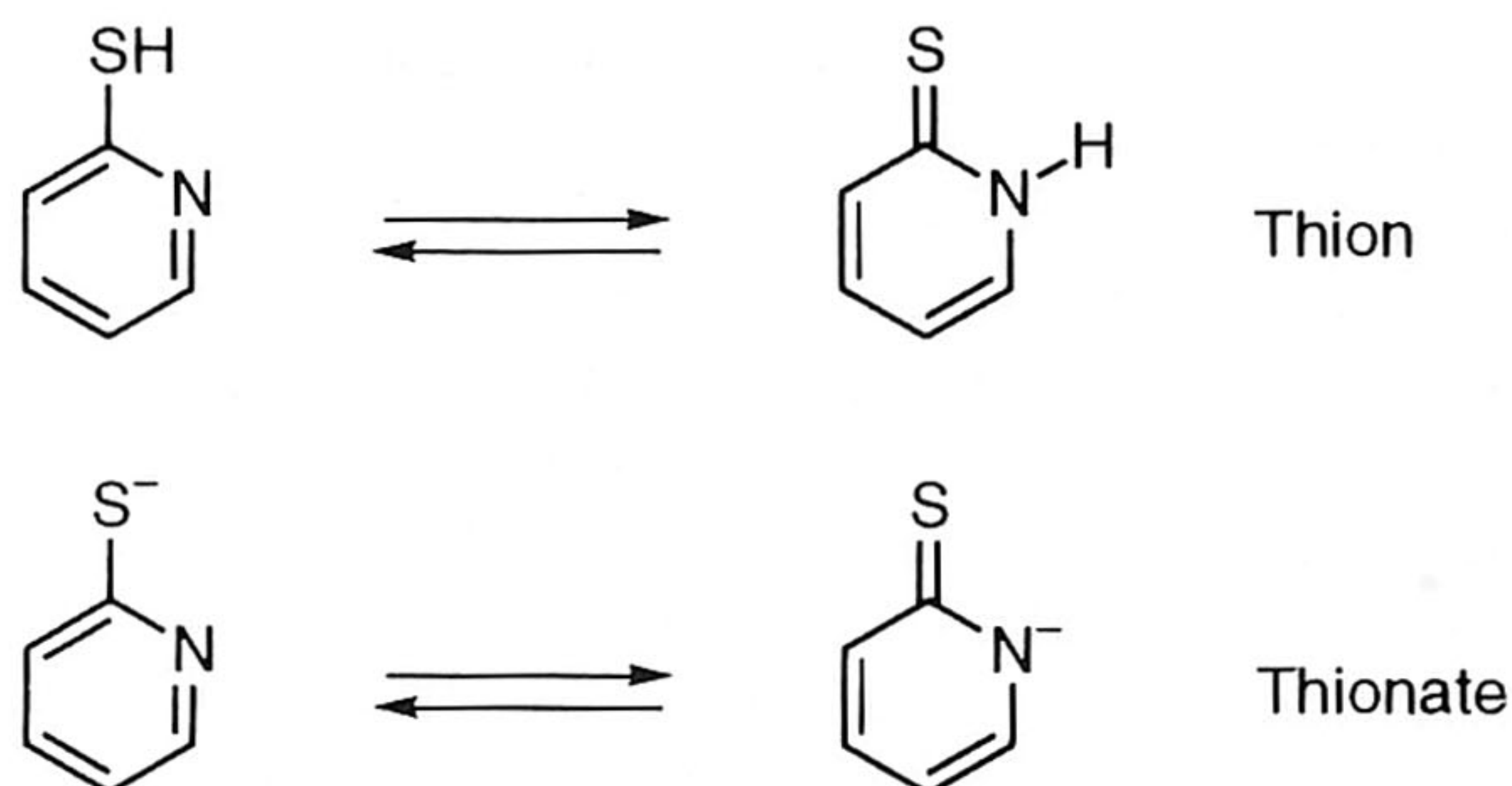


This method has not been extensively applied because the group R in the dithiocarbamato copper(I) complexes has a large influence on the stability of the complexes $[Cu(RSC(S)NPh)]$. In the case where R is $n\text{-Bu}$, the elimination reaction is successful though rather slow (few hours), but with R being Me the dithiocarbamato complex is stable and cannot be used to afford $[Cu(SMe)]$. In contrast, when R is Ph , the dithiocarbamato copper complex is so unstable that $[Cu(SPh)]$ is isolated quantitatively. Interestingly, in some cases the elimination reaction has been shown to be reversible since addition of an excess of $PhNCS$ can lead to reformation of the dithiocarbamato complex $[Cu(RSC(S)NPh)]$ (75).

C. Structures of Copper(I) Arenethiolates with Intramolecular Coordination

In this chapter, the term copper(I) thiolate is taken in its broadest sense of being any species in which a Cu^I ion is coordinated to one or more sulfur atoms of an SR unit. For comparative reasons, some examples of thione and thionate complexes (Scheme 2) are also included since in their deprotonated form thiones can be considered as anionic ligands ArS^- . The coordination behavior of thione ligands toward metals was reviewed some years ago (1d).

The various complexes covered here include $[Cu_n(SR)_n]$ species, which will



Scheme 2. Resonance equilibria of thione and thionate ligands.

be termed pure copper(I) thiolates, ionic species $[\text{Cu}_n(\text{SR})_m]^{n-m}$ with $m > n$ (that often result when other ligands are absent) and species that also contain discrete auxiliary donor ligands such as phosphines or amines. However, the primary class of copper(I) thiolates to be discussed is that in which the thiolate ligand has a heteroatom containing function that can coordinate intramolecularly to the metal center. These intramolecularly coordinated copper(I) thiolates sometimes also contain auxiliary neutral donor ligands.

Copper(I) thiolates have a wide variety of structures and in almost all cases are found as aggregated species in which the sulfur atoms bridge two or more copper atoms. Table I lists structurally characterized neutral copper(I) thiolate

TABLE I
Neutral Copper(I) and Silver(I) Thiolate Complexes without Coordinating Ligands

Entry	Compound ^a	References
1	$[\text{Cu}_3(\text{SC}(\text{SiMe}_3)_3)_3]$	76
2	$[\text{Ag}_3(\text{SC}(\text{SiMe}_2\text{Ph})_3)_3]$	33
3	$[\text{Cu}_4(\text{SC}_6\text{H}_3(\text{SiMe}_3)_{2-2,6})_4]$	77
4	$[\text{Cu}_4(\text{SC}_6\text{H}_3-i\text{-Pr}_3-2,4,6)_4]$	52b
5	$[\text{Cu}_4(\text{SSi}(\text{O}-t\text{-Bu})_3)_4]$	78
6	$[\text{Ag}_4(\text{SC}(\text{SiMe}_3)_3)_4]$	33
7	$[\text{Ag}_4(\text{SCH}(\text{SiMe}_3)_2)_4]$	33
8	$[\text{Ag}_4(\text{SC}_6\text{H}_4\text{SiMe}_3-2)_4]$	40
9	$[\text{Au}_4(\text{SC}(\text{SiMe}_3)_3)_4]$	79
10	$[\text{Cu}_6(\text{SeC}_6\text{H}_2-i\text{-Pr}_3-2,4,6)_6]$	80
11	$[\text{Au}_6(\text{SC}_6\text{H}_2-i\text{-Pr}_3-2,4,6)_6]$	81
12	$[\text{Cu}_8(\text{SC}_6\text{H}_2-i\text{-Pr}_3-2,4,6)_8]$	52
13	$[\text{Ag}_8(\text{S}-t\text{-Bu})_8]$	82
14	$[\text{Ag}_8(\text{SC}(\text{Me})\text{Et}_2)_8]$	83
15	$[\text{Cu}_{12}(\text{SC}_6\text{H}_4\text{SiMe}_3-2)_{12}]$	40, 84
16	$[\text{Ag}_{12}(\text{S}-c\text{-Hex})_{12}]$	85
17	$[\text{Ag}(\text{SC}_6\text{H}_2-i\text{-Pr}_3-2,4,6)]_\infty$	86

^aIsopropyl = *i*-Pr; *tert*-butyl = *t*-Bu; methyl = Me; ethyl = Et; cyclohexyl = *c*-hex; phenyl = Ph.

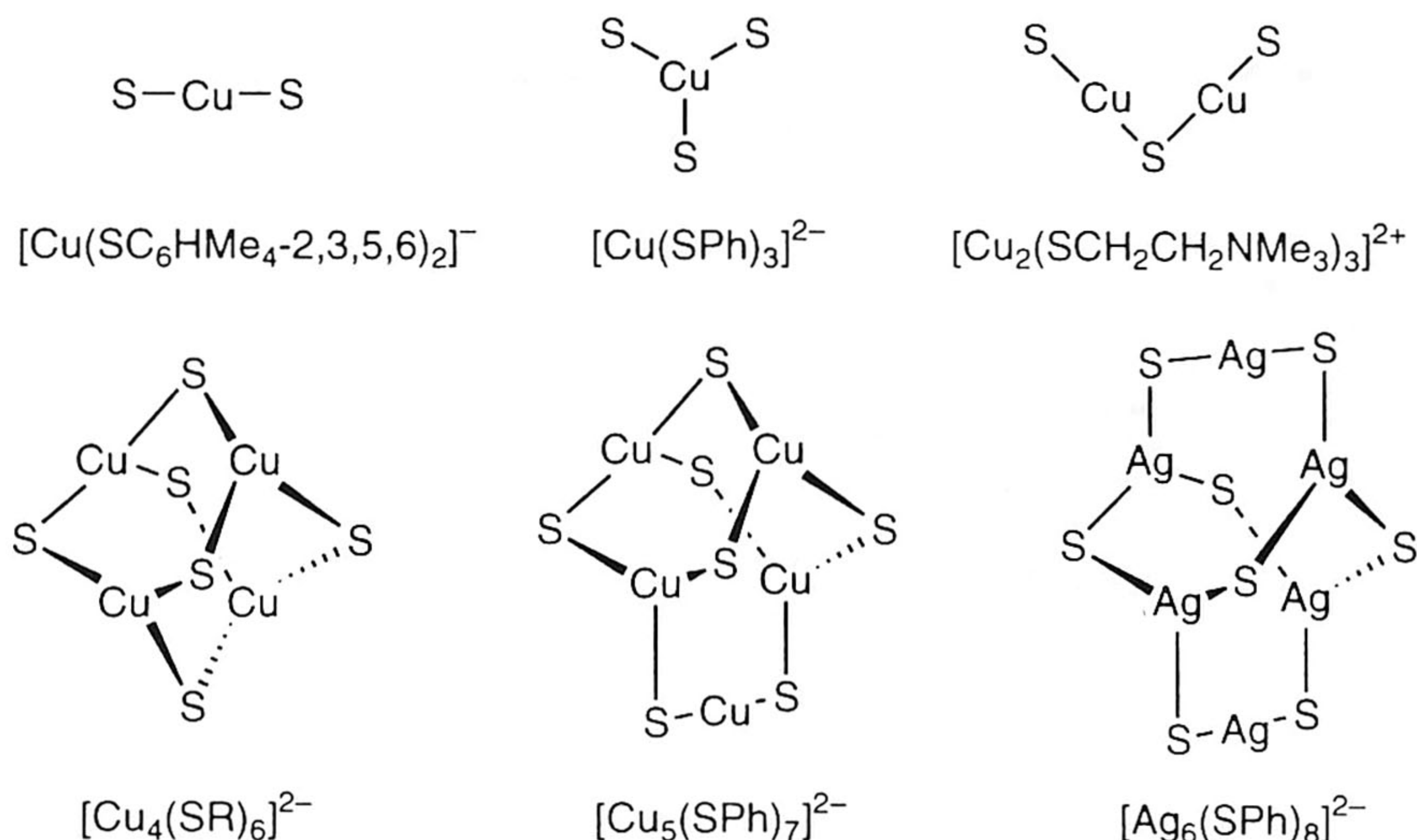
complexes of the type $[\text{Cu}_n(\text{SR})_n]$, while the aggregates $[\text{Cu}_n(\text{SR})_n]^{m-m}$ (usually anionic with $m > n$) in which the thiolate has no potentially coordinating functions are listed in Table II. An earlier review of complexes of this type appeared in 1986 (1a). Some examples of the structural formats found for these anionic cage aggregates are illustrated in Scheme 3. Tables I and II and Scheme 3 also include some closely related silver(I) and gold(I) species.

The structures of copper(I) thiolates in which the only other donor functions present are those of the auxiliary ligands (Table III) often resemble structures of those species in which the arenethiolate ligands have a heteroatom containing function that can coordinate intramolecularly to the metal center (Table IV). There are some structurally characterized mixed-organo(arenethiolato)copper(I) and arenethiolatocopper copper halide aggregates in which intramolecular coordination is present. These aggregates are collected in Table V, which allows some direct comparisons to be made between the two types of species. For ease

TABLE II
Ionic copper(I) and Silver(I) Thiolate Complexes without Coordinating Ligands

Entry	Compound	References
1	$[\text{Cu}(\text{SPh})_2]^- (\text{N}^+\text{Bu}_4)^+$	44
2	$[\text{Cu}(\text{SC}_6\text{F}_5)_2]^- (\text{pyH})^+$	87
3	$[\text{Cu}(\text{SC}_6\text{HMe}_{4-2,3,5,6})_2]^- (\text{N}^+\text{Pr}_4)^+$	65
4	$[\text{Ag}(\text{SC}_6\text{HMe}_{4-2,3,5,6})_2]^- (\text{N}^+\text{Pr}_4)^+$	65
5	$[\text{Au}(\text{SC}_6\text{H}_2-i\text{-Pr}_{3-2,4,6})_2]^- (\text{NH}_4)^+$	81
6	$[\text{Cu}(\text{SPh})_3]^{2-} (\text{NEt}_4)_2^+$	62
7	$[\text{Cu}(\text{SPh})_3]^{2-} (\text{PPh}_4)_2^+$	45
8	$[\text{Cu}(\text{SC}_6\text{H}_4\text{N}(\text{H})\text{C}(\text{O})-t\text{-Bu})_3]^{2-} (\text{NEt}_4)_2^+$	88
9	$[\text{Cu}(\text{SC}_5\text{H}_4\text{NH})_3]^+ (\text{NO}_3)^-$	49
10	$[\text{Cu}_4(\text{SPh})_6]^{2-} (\text{NMe}_4)_2^+$	89a
11	$[\text{Cu}_4(\text{SPh})_6]^{2-} (\text{NMe}_4)_2^+ \cdot \text{EtOH}$	89b
12	$[\text{Cu}_4(\text{SPh})_6]^{2-} (\text{PPh}_4)_2^+$	45, 48b
13	$[\text{Cu}_4(\text{SMe})_6]^{2-} (\text{NMe}_4)_2^+$	89b, 90
14	$[\text{Cu}_4(\text{SEt})_6]^{2-} (\text{PPh}_4)_2^+$	91
15	$[\text{Cu}_4(\text{dmit})_3]^{2-} (\text{N}^+\text{Bu}_4)_2^+$	64
16	$[\text{Cu}_4(o\text{-(SCH}_2)_2\text{C}_6\text{H}_4)_3]^{2-} (\text{PPh}_4)_2^+$	66
17	$[\text{Cu}_5(\text{S}-t\text{-Bu})_6]^- (\text{HNEt}_3)^+$	92
18	$[\text{Cu}_5(\text{S}-t\text{-Bu})_6]^- (\text{NEt}_4)^+$	90, 92, 93
19	$[\text{Cu}_5(\text{SPh})_7]^{2-} (\text{NMe}_4)_2^+$	47, 48a, 90
20	$[\text{Ag}_5(\text{SPh})_7]^{2-} (\text{NMe}_4)_2^+$	47
21	$[\text{Ag}_6(\text{SPh})_8]^{2-} (\text{NMe}_4)_2^+$	94
22	$[\text{Cu}_7(\text{SEt})_8]^- (\text{PPh}_4)^+$	91
23	$[\text{Cu}_8(\text{DTS})_6]^{4-} (\text{PPh}_4)_4^+$	95
24	$[\text{Cu}_8(\text{DED})_6]^{4-} (\text{NBu}_4)_4^+$	95
25	$[\text{Ag}_{12}(\text{SPh})_{16}]^{4-} (\text{NMe}_4)_4^{+a}$	94

^aComprises two linked $[\text{Ag}_6(\text{SPh})_8]^{2-}$ cages.



Scheme 3. Some structural formats of anionic copper(I) thiolates.

TABLE III
Copper(I), Silver(I), and Gold(I) Thiolates with Auxiliary Donor Ligands

Entry	Compound	Reference
1	$[Cu(SPh)(SO_2)(PPh_2Me)_3]$	46
2	$[Cu(SC_6F_5)(HB(3,5-i-Pr_2pz)_3)]$	96
3	$[Cu(SCPh_3)(HB(3,5-i-Pr_2pz)_3)]$	96
4	$[Cu(SC_6H_4NO_2-4)(HB(3,5-Me_2pz)_3)][KNO_3]$	59
5	$[Au(SC_6H_2Et_3-2,4,6)(PPh_3)]$	97
6	$[Au(SC_6H_2-i-Pr_3-2,4,6)(PPh_3)]$	97
7	$[Cu_2(SPh)_2(PPh_3)_4]$	27
8	$[Cu_2(SC_6H_4Me-2)_2(phen)_2]$	55
9	$[Cu_2(SC_6H_4Me-2)_2(Me_2phen)_2]$	98
10	$[Cu_2(SPh)_2(RC \equiv CR)_2]^a$	99
11	$[Cu_2(SC_5H_4NH)_6]^{2+}$	100
12	$[Cu_2(SePh)_2(PPh_3)_3]$	57
13	$[Au_2(SPh)_2(PPh_3)_2]$	97
14	$[Cu_3(SPh)_3(PPh_3)_4]$	28
15	$[Cu_4(SPh)_4(PPh_3)_4]$	29
16	$[Cu_4(S-t-Bu)_4(PPh_3)_2]$	101
17	$[Cu_4(SC(Me)_2Et)_4(dppm)_2]$	56
18	$[Cu_4(SC(=S)C_6H_4Me-2)_4(dppm)_2]$	102
19	$[Ag_6(SC_6H_4Cl-4)_6(PPh_3)_5]$	103
20	$[Au_6(S_6C_6)(PPh_3)_6]^a$	104
21	$[Ag_8(SC(Me)Et)_8(PPh_3)_2]$	105
22	$[Cu_{10}(SCF_3)_{10}(MeCN)_8]$	58
23	$[Ag_{14}(S-t-Bu)_{14}(PPh_3)_4]$	105
24	$[Cu(SPh)(Me_2phen)]_\infty$	63

^a3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne = $RC \equiv CR$ and S_6C_6 is benzenehexathiolate.

TABLE IV
 Copper(I) and Silver(I) Thiolates with Intramolecular Coordination

Entry	Compound	Reference
<i>Neutral Complexes</i>		
1	[Cu{SC(=NPh)(OC ₆ H ₃ Me ₂ -2,6)}(PPh ₃) ₂]	106
2	[Cu ₂ {SC(=NPh)(OC ₆ H ₂ - <i>t</i> -Bu ₂ -2,6-Me-4)} ₂ (P(OMe) ₃) ₂]	106
3	[Au ₂ (SCH ₂ CH ₂ PEt ₂) ₂]	107
3	[Cu ₃ (SC ₆ H ₄ NMe ₂ -2) ₃]	69
4	[Cu ₃ {SC ₆ H ₄ ((<i>R</i>)-CH(Me)NMe ₂ -2)} ₃]	50
5	[Cu ₃ {SC(H)Me(η ⁵ -C ₅ H ₃ PPh ₂ -2)Fe(η ⁵ -C ₅ H ₅) ₃ }]	54a
6	[Cu ₄ (mimt) ₄]	108
7	[Cu ₄ {SC ₆ H ₄ (CH ₂ N(Me)CH ₂ CH ₂ OMe-2)} ₄]	68
8	[Cu ₄ (SC ₃ H ₄ NS) ₄ (py)] _∞	109
9	[Cu ₄ (SC ₃ H ₄ NS) ₄ (PPh ₃) ₂]	109
10	[Ag ₄ (SC ₃ H ₄ NS) ₄ (PPh ₃) ₂]	109
11	[Cu ₂ Ag ₂ (SC ₃ H ₄ NS) ₄ (PPh ₃) ₂]	109
12	[Cu ₄ {SC(=NPh)(OC ₆ H ₃ Me ₂ -2-6)} ₄]	106
13	[Cu ₆ (SC ₅ H ₄ N) ₆]	110
14	[Cu ₆ (dmpymt) ₆]	111
15	[Cu ₆ (Me(OH)pymt) ₆] ^a	112
16	[Cu ₆ (SC ₅ H ₃ N(SiMe ₃)-6) ₆]	113
17	[Ag ₆ (SC ₅ H ₃ N(SiMe ₃)-6) ₆]	113
18	[Cu ₆ (SC ₉ H ₆ N) ₆] ^a	114
19	[Cu ₆ (SC(O)NEt ₂) ₆]	115
20	[Cu ₆ (<i>n</i> -BuSC(S)NPh) ₆]	75
21	[Ag ₆ (SC(S)N- <i>n</i> -Pr ₂) ₆]	116
22	[Cu ₈ (SC(Me) ₂ Et) ₄ (S ₂ CSC(Me) ₂ Et) ₄] ^b	117
23	[Cu ₉ (S-1-C ₁₀ H ₆ NMe ₂ -8) ₉]	69
24	[Cu(SC ₉ H ₇ N)(ClO ₄)] _∞ ^c	114
<i>Ionic Complexes</i>		
25	[Cu ₃ (SCH ₂ CH ₂ S) ₃] ³⁻ (Me ₃ NCH ₂ Ph) ₂ ⁺ Na ⁺ · MeOH	67
26	[(S ₆)M(S ₈)M(S ₆)] ⁴⁻ (PPh ₄) ₄ (M = Cu or Ag)	118
27	[Cu ₃ (S ₄) ₃] ³⁻ (PPh ₄) ₂ ⁺ (NH ₄) ⁺	118a
28	[Cu ₃ (S ₆) ₃] ³⁻ (PPh ₄) ₂ ⁺ (NH ₄) ⁺	119
29	[Ag ₈ (SC ₅ H ₃ N(SiMe ₂ Ph)-3) ₆] ²⁺ [Ag(NO ₃) ₂] ₂ ⁻	120
<i>Mixed-Valence Complexes</i>		
30	[Cu ^I ₈ Cu ^{II} ₆ (SC(Me) ₂ CH ₂ NH ₂) ₁₂ Cl] · 3.5SO ₄	51

^a4-hydroxy-6-methylpyrimidine-2-thionate = Me(OH)pymt, quinoline-2-thionate = SC₉H₆N, quinoline-2-thione = SC₉H₇N.

^bFormed by insertion of CS₂ into [Cu(SC(Me)₂Et)]_n; the Cu—S—C(S) unit can formally be interpreted as a four-membered chelate.

^cThione complex.

TABLE V
Mixed-Organo(arenethiolato)copper(I) and Arenethiolatocopper Copper Halide Species

Entry	Compound	Reference
1	$[\text{Cu}_3(\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2-Cl-5})_2(\text{Mes})(\text{PPh}_3)]$	20
2	$[\text{Cu}_4(\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2-Cl-5})_2(\text{Mes})_2]$	20
3	$[\text{Cu}_6(\text{SC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2})_4(\text{C}\equiv\text{C-}t\text{-Bu})_2]$	21
4	$[\text{Cu}_6\{\text{SC}_6\text{H}_4((S)\text{-CH}(\text{Me})\text{NMe}_2\text{-2})\}_4(\text{C}\equiv\text{C-}t\text{-Bu})_2]$	121
5	$[\text{Cu}_6(\text{S-1-C}_{10}\text{H}_6\text{NMe}_2\text{-8})_4(\text{C}\equiv\text{C-}t\text{-Bu})_2]$	69
6	$[\text{Cu}_8(\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2,6})_3\text{Br}_5]$	60
7	$[\text{Cu}_3(\text{S-oxazoline})_3]_4[\text{CuI}]_4$	61

of discussion, the complexes in this chapter are described in order of their aggregation state.

1. Monomeric Complexes

There are no known monomeric species, that is $[\text{Cu}(\text{SR})]$, when the thiolate ligand has no substituents present for intramolecular coordination. All monomeric species are of the type $[\text{Cu}(\text{SAr})\text{L}_n]$ in which there is an auxiliary donor ligand L. Several species were reported where n is 3 with ligands such as phosphines and amines [Fig. 2(a)]. The only reported example of a monomeric copper(I) thiolate in which, besides auxiliary coordination (of two PPh_3 ligands), there is also intramolecular coordination (of one N-donor group) is the complex $[\text{Cu}\{\text{SC}(=\text{NPh})(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})\}(\text{PPh}_3)_2]$ (106). In all monomeric complexes $[\text{Cu}(\text{SAr})\text{L}_3]$, the copper atom has a tetrahedral geometry. Some typical Cu—S bond lengths of these species are listed in Table VI.

Recently, we reported the use of the bis(alkynyl)titanocene complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$ as a molecular tweezer that functions as a bidentate ligand by using the two alkynyl functions to coordinate to a single cop-

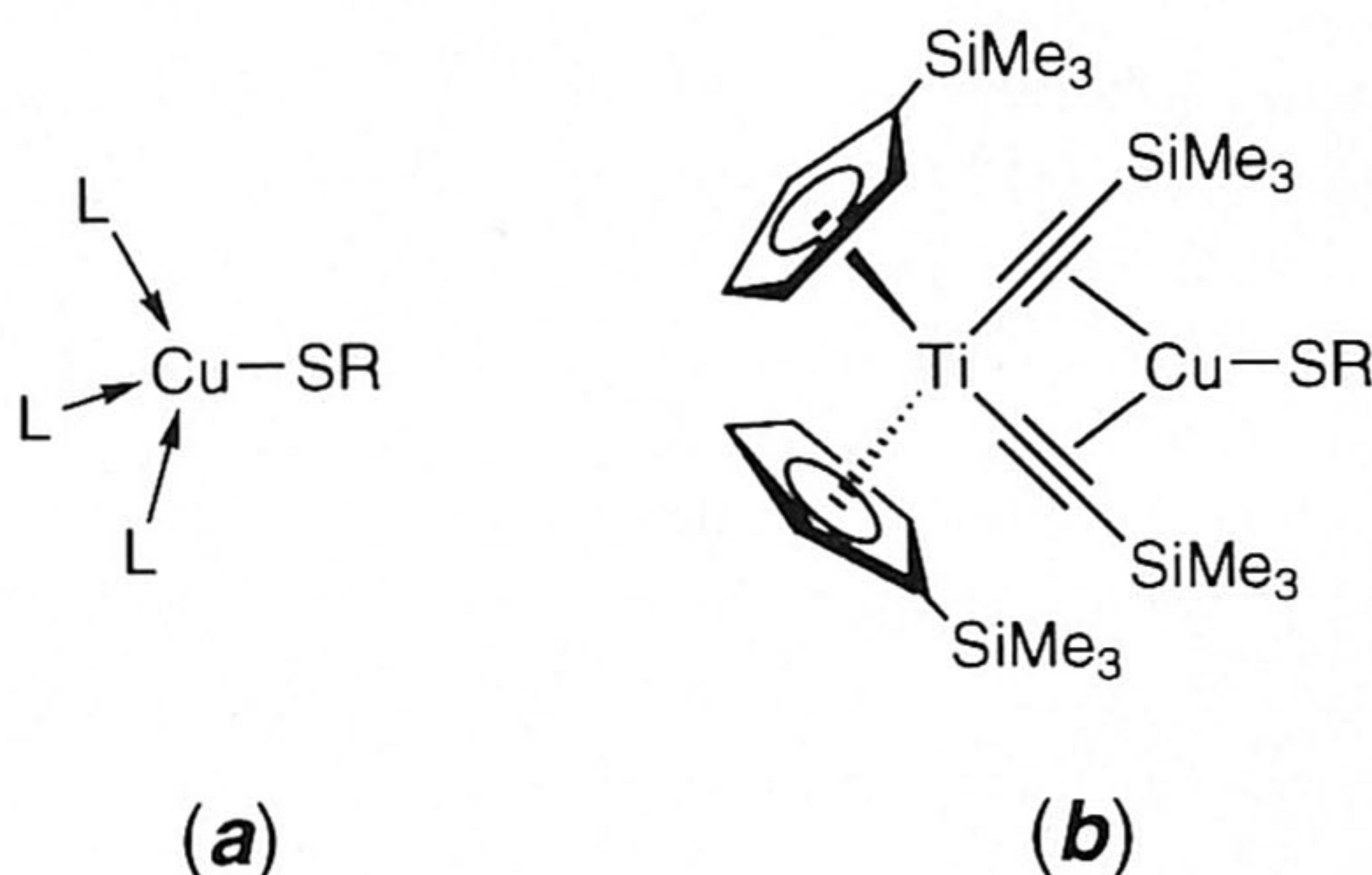


Figure 2. Monomeric copper(I) thiolates with auxiliary donor ligand coordination.

TABLE VI
 Geometrical Details of Monomeric Copper(I) Thiolate Complexes

Entry	Compound	L	Cu—S (Å)	Reference
<i>Four-Coordinate Cu</i>				
1	[Cu(SPh)(SO ₂)L ₃] ^a	PPh ₂ Me	2.404(2)	46
2	[Cu(SC(=NPh)(OAr))L ₂] ^b	PPh ₃	2.469(2)	106
3	[Cu(SC ₆ H ₄ NO ₂ -4)L]	HB(3,5-Me ₂ pz) ₃	2.19(1)	59
4	[Cu(SC ₆ F ₅)L]	HB(3,5- <i>i</i> -Pr ₂ pz) ₃	2.176(4)	96
5	[Cu(SCPh ₃)L]	HB(3,5- <i>i</i> -Pr ₂ pz) ₃	2.12(2)	96
<i>Three-Coordinate Cu</i>				
6	[Cu(SC ₆ H ₄ (CH ₂ NMe ₂)-2)L ₂]	TiC≡CSiMe ₃ ^c	2.237(3)	54b

^aThe SO₂ is bonded to the PhS⁻ ligand.

^bOAr = OC₆H₃Me₂-2,6; a four-membered Cu—S—C—N chelate ring is present.

^cL₂ = [(η⁵-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂].

per(I) center. In this way, there can be formed monomeric species [(η⁵-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂CuX] in which X is an η¹-bonded inorganic (54b) or organic (122) ligand. This class of species includes the arenethiolate complexes, where X is SC₆H₅, SC₆H₄NMe₂-2, SC₆H₄CH₂NMe₂-2, and S-1-C₁₀H₆NMe₂-8 (54b). The copper atom in these species has a trigonal geometry (Fig. 2b) (54b, 122).

2. Dimeric Complexes

Like monomeric copper(I) thiolates, all known dimeric thiolate species contain auxiliary coordinating donor ligands L. This class comprises complexes with two basic formulations, namely, [Cu₂(SR)₂L₄] and [Cu₂(SR)₂L₂], whose schematic structures are depicted in Figure 3. Reported examples of the former are [Cu₂(SPh)₂(PPh₃)₄] (27), [Cu₂(SC₆H₄Me-2)₂(phen)₂] (55), and [Cu₂(SC₅H₄NH)₆(X)₂] (X = Cl or Br) (100), while for the latter there is only one example, that is [Cu₂(SPh)₂(RC≡CR)₂] (RC≡CR = 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne) (99). A special example of the type [Cu₂(SR)₂L₂] is provided by the complex [Cu₂{SC(=NPh)(OC₆H₂-*t*-Bu₂-2,6-Me-4)}₂{P(OMe)₃}₂] (106), which is a dimer formed through intermolecular coordination between two monomeric units [Fig. 3(c)]. Some structural details of these complexes are listed in Table VII.

3. Trimeric Complexes

Most reported copper(I) thiolates in which there is intramolecular ligand coordination have aggregation states of three or higher, and to date three X-ray

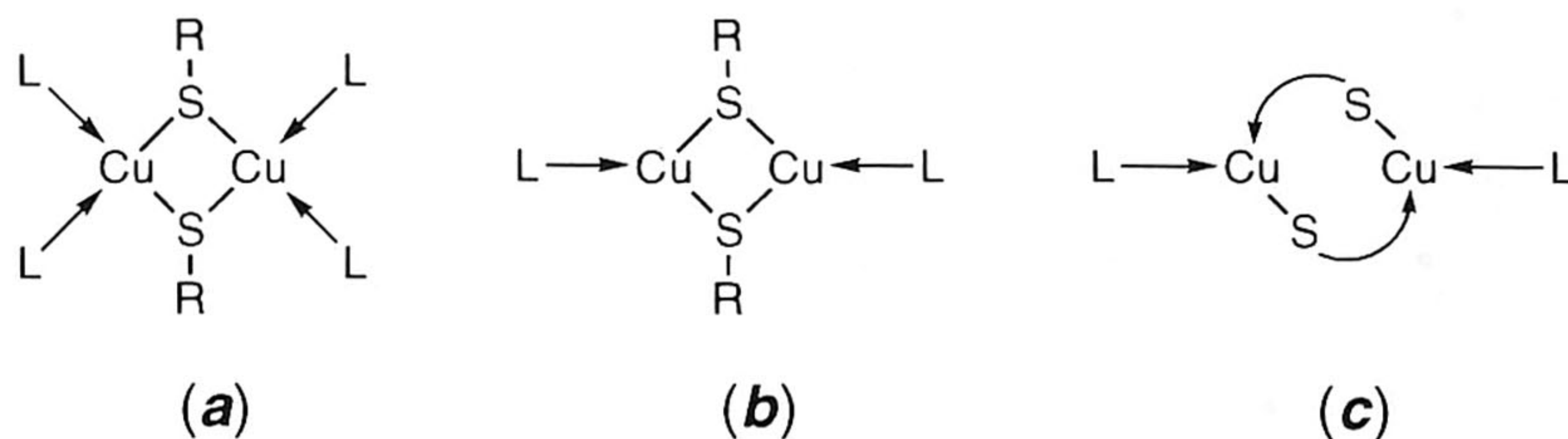


Figure 3. Schematic representation of copper(I) thiolate dimers: (a) $[\text{Cu}_2(\text{SR})_2\text{L}_4]$, (b) $[\text{Cu}_2(\text{SR})_2\text{L}_2]$, and (c) $[\text{Cu}_2(\text{SR})_2\text{L}_2]$ with additional intramolecular coordination.

structures of trimeric examples exist (Fig. 4). These three structures are: $[\text{Cu}_3(\text{SC}_6\text{H}_4\text{NMe}_2-2)_3]$ which contains a five-membered chelate ring (69), chiral $[\text{Cu}_3(\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2)-2)_3]$, which contains a six-membered chelate ring and which has some very interesting luminescence properties (50, 123), and a related species $[\text{Cu}_3(\text{SC}(\text{H})\text{Me}(\eta^5\text{-C}_5\text{H}_3\text{PPh}_2-2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5))_3]$, which is an alkylthiolato complex that not only has a six-membered chelate ring, but also a P-donor coordination (54a). The trinuclear structure of each of these complexes is characterized by the presence of a cyclohexane-like six-membered Cu_3S_3 heterocycle, which generally is in the chair conformation with the substituents on the thiolate sulfur atom occupying equatorial positions [Fig. 4(b)]. Geometrical details of some trimeric copper(I) thiolates are listed in Table VIII.

Apparently, it is the five- or six-membered chelate rings formed by intramolecular coordination that leads to species with the same aggregation state,

TABLE VII
Geometrical Details of Dimeric Copper(I) Thiolate Complexes

Entry	Compound	Cu—S (Å)	Cu—S—Cu (deg)	Reference
<i>Four-Coordinate Cu</i>				
1	$[\text{Cu}_2(\text{SPh})_2(\text{PPh}_3)_4]$	2.344(4), 2.415(4)	98.63(4), 102.75(4)	27
2	$[\text{Cu}_2(\text{SC}_6\text{H}_4\text{Me}-2)_2(\text{phen})_2]$	2.304(4), 2.379(5)	68.1(1), 67.8(1)	55
3	$[\text{Cu}_2(\text{SC}_5\text{H}_4\text{NH})_6]\text{Cl}_2^a$	2.308(2), 2.498(3)	74.3(1)	100a
4	$[\text{Cu}_2(\text{SC}_5\text{H}_4\text{NH})_6]\text{Cl}_2^a$	2.320(3), 2.538(4)	74.6(1)	100b
5	$[\text{Cu}_2(\text{SC}_5\text{H}_4\text{NH})_6]\text{Br}_2^a$	2.297(3), 2.534(3)	73.8(1)	100b
6	$[\text{Cu}_2(\text{SC}(=\text{NPh})(\text{OAr}))_2(\text{L})_2]^b$	2.258(2), 2.268(2)	^c	106
<i>Three-Coordinate Cu</i>				
7	$[\text{Cu}_2(\text{SPh})_2(\text{RC}\equiv\text{CR})_2]^d$	2.283(1)–2.295(1)	78.53(3), 78.95(4)	99

^aThione complex: the Cu—S distances of the terminal 2(1*H*)-pyridine-2-thione ligands are somewhat shorter: 2.274(3)–2.326(3) Å.

^bOAr = $\text{OC}_6\text{H}_2\text{-}t\text{-Bu}_2\text{-2,6-Me-4}$; L = $\text{P}(\text{OMe})_3$.

^cNot present: see text.

^d3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne = $\text{RC}\equiv\text{CR}$.

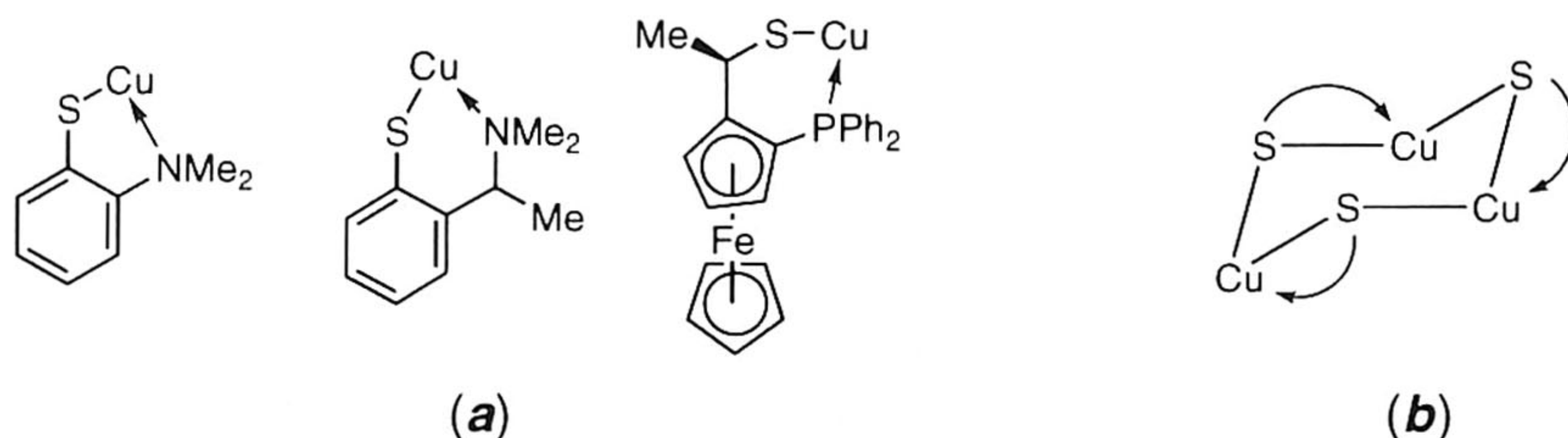


Figure 4. (a) Trimeric copper(I) thiolate complexes with intramolecular ortho-coordination. (b) The Cu₃S₃ heterocycle.

and the differences in either coordinating heteroatom (N vs. P) or the nature of the thiolate backbone (arenethiolate vs. alkylthiolate) do not seem to play an important role in determining the complex nuclearity. However, it must be noted that either a more rigid thiolate backbone or a smaller chelate ring size can affect both the aggregation state and the overall structure in a dramatic way (Sections II.C.5 and II.C.7).

The phosphine coordinated copper(I) thiophenolate [Cu₃(SPh)₃(PPh₃)₄] (28) has an analogous trimeric structure to those species with intramolecular coordination, although in this case the fourth extra phosphine ligand results in a distorted tetrahedral coordination of one of the copper atoms and a distortion of the Cu₃S₃ six-membered heterocycle (Fig. 5).

When no potentially coordinating ligands are present either as auxiliaries or as thiolate substituents, a trimeric aggregation state is unusual. To our knowl-

TABLE VIII
Geometrical Details of Trinuclear Copper(I) Thiolate Complexes

Entry	Compound	Cu—S (Å)	Cu—S—Cu (deg)	Reference
1	[Cu ₃ (SC ₆ H ₄ NMe ₂ -2) ₃]	2.198(1), 2.2219(9)	75.18(4)	69
2	[Cu ₃ (SC ₆ H ₄ (CH(Me)NMe ₂)-2) ₃]	2.186(2), 2.231(2)	79.63(7)	50
3	[Cu ₃ (SC(H)Me(Fc)PPh ₂ -2) ₃] ^a	2.178(6), 2.251(6)	92.3(2), 98.3(2)	54a
4	[Cu ₃ (SPh) ₃ (PPh ₃) ₄]	2.23–2.28 2.39–2.40 ^b	87 105, 124 ^b	28
5	[Cu ₃ (SCH ₂ CH ₂ S) ₃] ³⁻	2.208(2)–2.313(2) 2.245(2)–2.270(2) ^c	74.7(1)–78.4(1)	67
6	[Cu ₃ (SAr) ₂ (Mes)(PPh ₃) ₄] ^a	2.234(1), 2.246(1) 2.267(1), 2.280(1) ^d	75.13(4), 76.87(4)	20

^aSC(H)Me(Fc)PPh₂-2 = SC(H)Me(η⁵-C₅H₃PPh₂-2)Fe(η⁵-C₅H₅), SAr = SC₆H₄(CH₂NMe₂-2)(Cl-5).

^bInvolving the four-coordinate Cu atom.

^cContacts outside the Cu₃S₃ six-membered ring, See also Fig. 5.

^dInvolving the P-coordinated Cu atom.

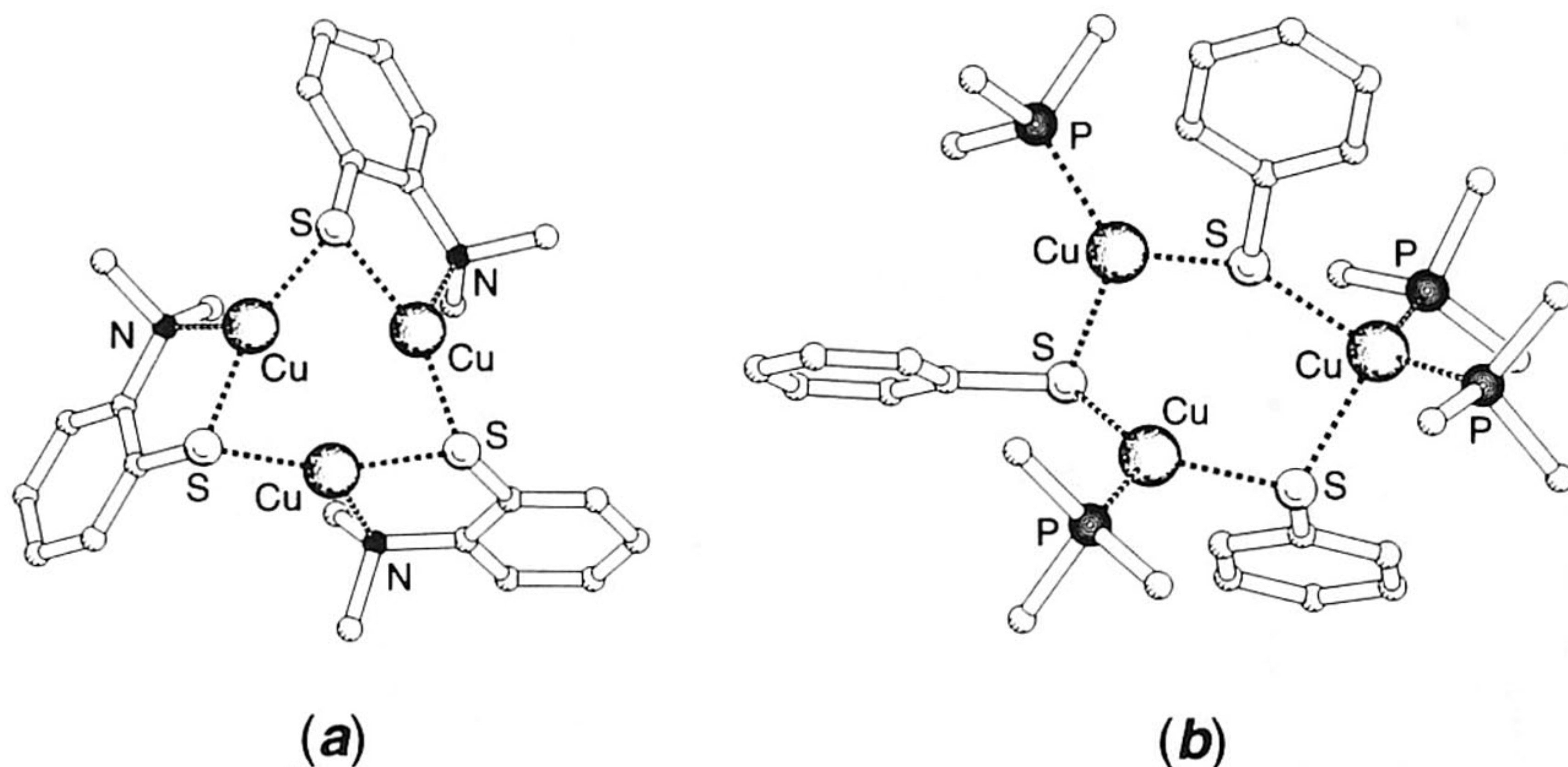


Figure 5. (a) Molecular structures of $[\text{Cu}_3(\text{SC}_6\text{H}_4\text{NMe}_2-2)_3]$ and (b) $[\text{Cu}_3(\text{SPh})_3(\text{PPh}_3)_4]$ (hydrogen atoms are omitted for clarity).

edge, the only trimeric structures with no further coordinating ligands are those of $[\text{Cu}_3\{\text{SC}(\text{SiMe}_3)_3\}_3]$ (76) and $[\text{Ag}_3\{\text{SC}(\text{SiMe}_2\text{Ph})_3\}_3]$ (33). The structure of the latter contains a slightly puckered almost planar Ag_3S_3 six-membered ring with an unusual coordination of two of the silver atoms; whereas silver(I) is usually almost linear, in this structure the $\text{S}-\text{Ag}-\text{S}$ angles are $149.9(1)^\circ$, $153.6(1)^\circ$, and $163.1(1)^\circ$. It has been proposed that these distortions arise from the steric bulk of the $\text{SC}(\text{SiMe}_2\text{Ph})_3$ ligand and from the constraints imposed by ring closure (33).

Interestingly, an anionic dithiolato copper(I) aggregate $[\text{Cu}_3(\text{SCH}_2\text{CH}_2\text{S})_3]^{3-}$ was also reported (67) and it possesses a structure, depicted in Figure 6, that is similar to that of trimeric copper(I) thiolates (Table VIII, entries 1–3). The sodium counterion in this complex has a tetrahedral geometry that results from coordination of the three sulfur atoms not involved in the Cu_3S_3 six-membered ring and the oxygen atom of a methanol molecule. Structural elements similar to that depicted in Figure 6 are also known for the copper(I) sulfido complexes $[\text{Cu}_3(\text{S}_4)_3]^{3-}$ and $[\text{Cu}_3(\text{S}_6)_3]^{3-}$ (118, 119), although aggregates based on other motives are also known (124).

A trinuclear mixed-organo(arenethiolato)copper(I) aggregate $[\text{Cu}_3\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)-2\text{-Cl-5}\}_2(\text{Mes})(\text{PPh}_3)]$ was also structurally characterized (20) and interestingly, like the trimeric copper(I) arenethiolates, it has a structure with a six-membered core. However, the puckering of the six-membered $\text{Cu}_3\text{S}_2\text{C}$ ring is of a boat type with the aryl ring of the arenethiolates bonded equatorially to the sulfur atoms in the ring and one of the three bridging atoms is the two-electron three-center (2e–3c) bonded mesityl C_{ipso} atom (20).

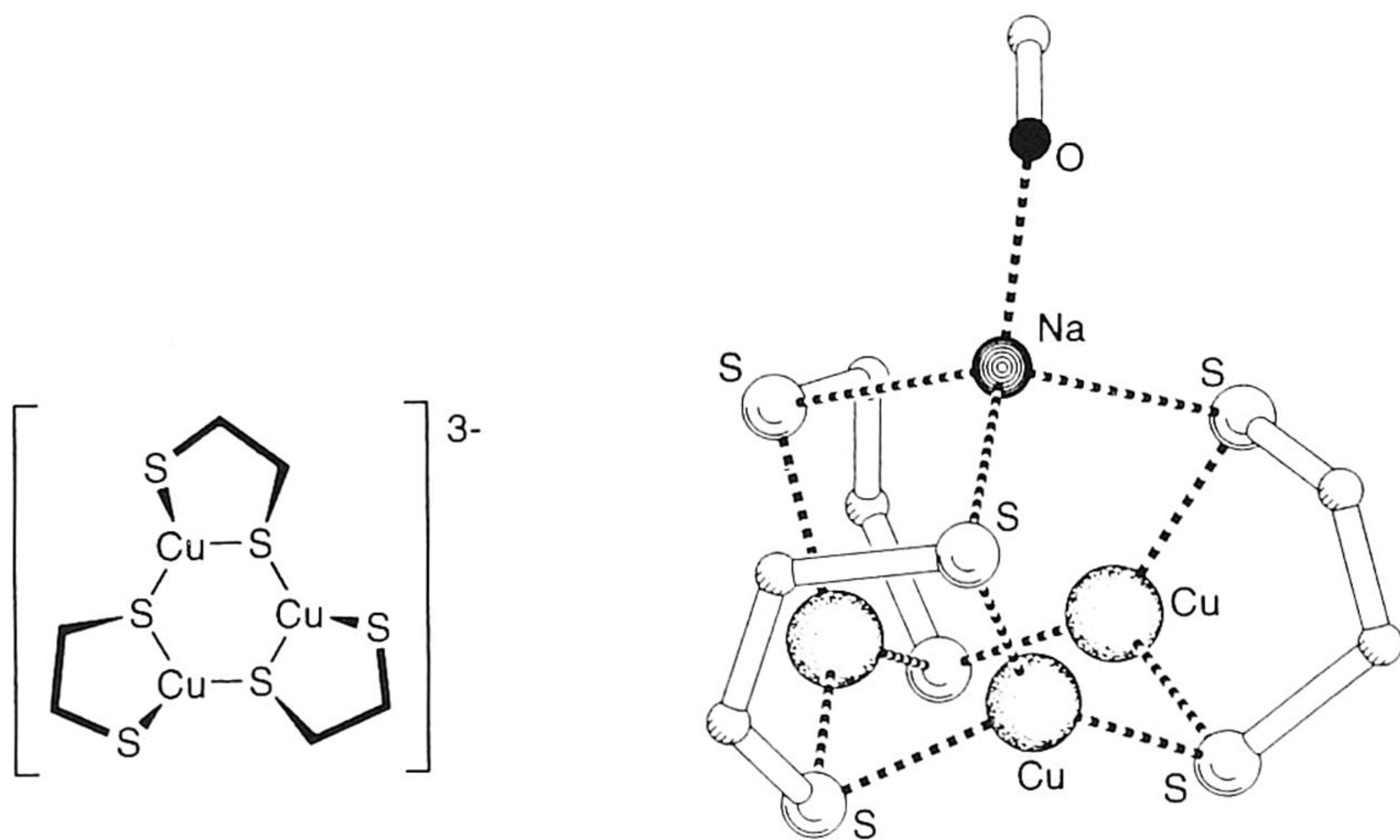


Figure 6. Schematic representation and molecular structure of $[\text{Cu}_3(\text{SCH}_2\text{CH}_2\text{S})_3]^{3-}$ (hydrogen atoms are omitted for clarity).

4. Tetrameric Complexes

Tetrameric copper(I) thiolate aggregates are common, not only with intramolecularly coordinating ligands and auxiliary donor ligands, but also without donor ligands of any type. In the complexes $[\text{Cu}_4\{\text{SC}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{OMe}-2)\}_4]$ (68), $[\text{Cu}_4(\text{S}-t\text{-Bu})_4(\text{PPh}_3)_2]$ (101), $[\text{Cu}_4(\text{SCMe}_2\text{Et})_4(\text{dppm})_2]$ (56), $[\text{Cu}_4(\text{SC}_6\text{H}_3(\text{SiMe}_3)_2-2,6)_4]$ (77), $[\text{Cu}_4(\text{SC}_6\text{H}_2-i\text{-Pr}_3-2,4,6)_4]$ (52b), $[\text{Cu}_4(\text{SSi}(\text{O}-t\text{-Bu})_3)_4]$ (78), $[\text{Ag}_4(\text{SC}(\text{SiMe}_3)_3)_4]$ (33), $[\text{Ag}_4(\text{SCH}(\text{SiMe}_3)_2)_4]$ (33), and $[\text{Ag}_4(\text{SC}_6\text{H}_4\text{SiMe}_3-2)_4]$ (40) the tetranuclear aggregate contains an open M_4S_4 ($\text{M} = \text{Cu}$ or Ag) eight-membered heterocycle (Type Ia, Fig. 7); this heterocycle can be based on Group 11 (IB) metal centers that are either solely two-coordinate, solely three-coordinate Group 11 (IB), or a mixture of two and three coordinate. In the mixed-organo(arenethiolato)copper(I) aggregate $[\text{Cu}_4\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)-2\text{-Cl-5}\}_2(\text{Mes})_2]$ one also finds an open tetranuclear structure, although in this case there are two types of bridging atoms leading to a central $\text{Cu}_4\text{S}_2\text{C}_2$ eight-membered heterocycle (Type 1b, Fig. 7) (20).

The Group 11 (IB) metal atoms in the structures of $[\text{Cu}_4(1\text{-methylimidazole-2-thionate})_4]$ (108), $[\text{Cu}_4(\text{SC}_3\text{H}_4\text{NS})_4(\text{py})]_\infty$ (109), $[\text{M}_2\text{M}'_2(\text{SC}_3\text{H}_4\text{NS})_4(\text{PPh}_3)_2]$ (109), ($\text{M} = \text{M}' = \text{Cu}$; $\text{M} = \text{M}' = \text{Ag}$; $\text{M} = \text{Cu}$, $\text{M}' = \text{Ag}$) and $[\text{Cu}_4\{\text{SC}(=\text{NPh})(\text{OC}_6\text{H}_3\text{Me}_2-2,6)\}_4]$ (106) are arranged in a tetrahedral form leading to a different structural format (Type II, Fig. 7).

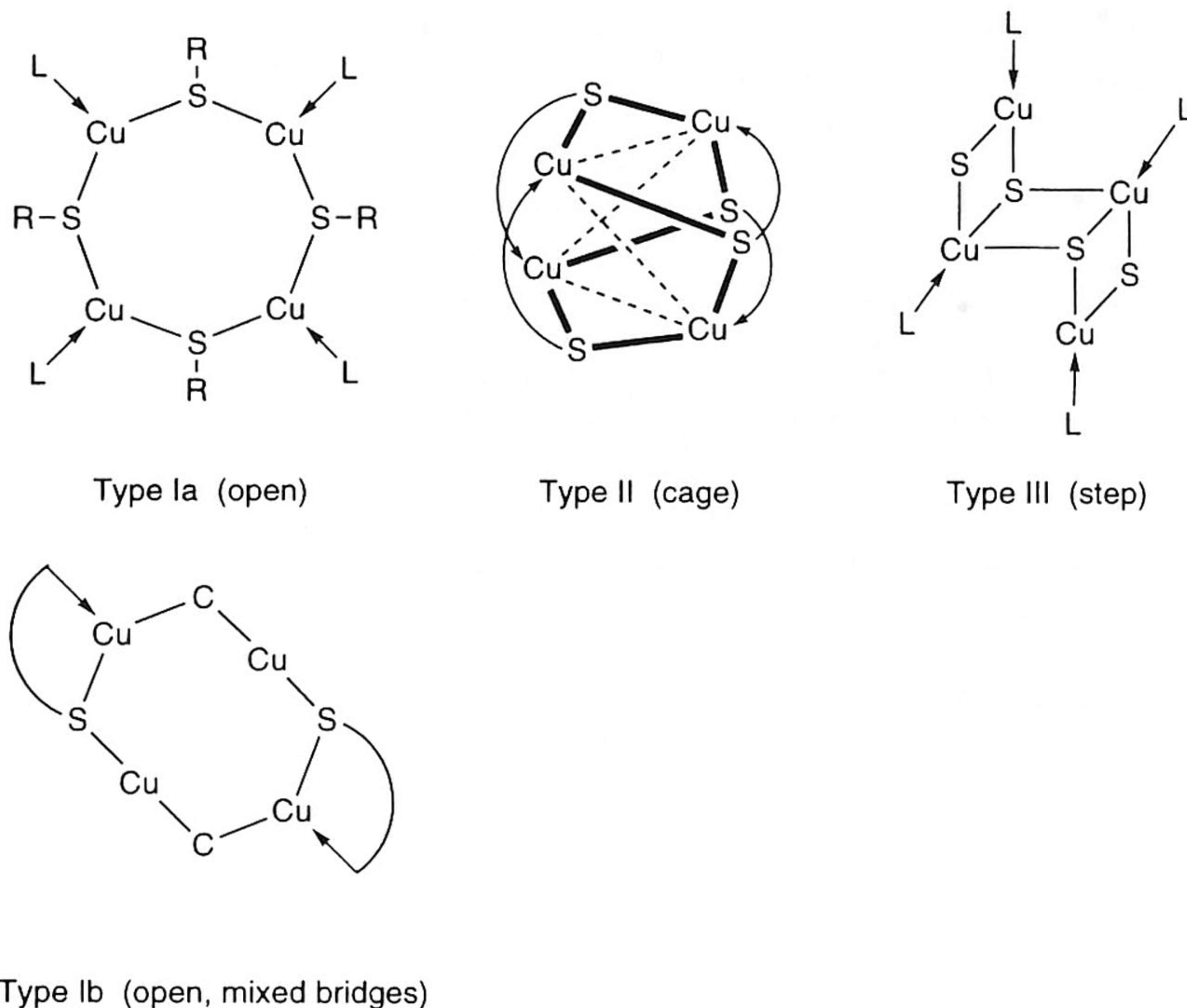


Figure 7. Tetrameric copper(I) thiolate aggregates.

Type II structural format is a cage structure derived from the Type Ia structure by folding of the eight-membered Cu_4S_4 ring. The reasons for this folding can be steric in origin but, as is evident in the structure of $[\text{Cu}_4(\text{1-methylimidazoline-2-thionate})_4]$ (108), can also arise from intramolecular coordination. Moreover, in the structure of $[\text{Cu}_4(\text{SPh})_4(\text{PPh}_3)_4]$ (29) the reduction of the Cu_8S_8 core size, resulting in a step structure (Type III, Fig. 7), was proposed to arise from steric factors. Some geometrical details of tetranuclear copper(I) thiolates are listed in Table IX.

5. Hexameric Complexes.

The next increase in aggregation state of Group 11 (IB) metal thiolates affords pentameric structures, but to the best of our knowledge a structurally characterized species of this type is unknown. In organocopper(I) chemistry, the only example is that of mesitylcopper $[\text{Cu}_5(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_5]$ (125), which has a structure based on an open Cu_5C_5 10-membered heterocycle.

TABLE IX
 Geometrical Details of Tetrameric Copper(I) Thiolate Complexes

Entry	Compound ^a	Cu—S (Å)	Cu—S—Cu (deg)	Reference
<i>Open Structures</i>				
1	[Cu ₄ (SAr) ₄]	2.1991(8)–2.2463(9)	74.12(2)–74.82(2)	68
2	[Cu ₄ (S- <i>t</i> -Bu) ₄ (PPh ₃) ₂]	2.145(2)–2.167(2) 2.245(2)–2.263(2) ^b	79.9(1)–89.9(1)	101
3	[Cu ₄ (SC(Me) ₂ Et) ₄ (dppm) ₂]	2.221(2)–2.268(2)	85.9(1)–98.5(1)	56
4	[Cu ₄ (SC ₆ H ₃ (SiMe ₃) ₂ -2,6) ₄]	2.134(8)–2.164(9)	82.9(3)–92.4(3)	77
5	[Cu ₄ (SSi(O- <i>t</i> -Bu) ₃) ₄]	2.161(2)–2.175(2)	82.1(1)	78
<i>Cage Structures</i>				
6	[Cu ₄ (Simid) ₄]	2.233(2)–2.307(2)	72.1(1), 96.5(2)	108
7	[Cu ₄ (SC ₃ H ₄ NS) ₄ (PPh ₃) ₂]	2.191(2), 2.265(2) 2.394(2), 2.424(2) ^b	77.5, 81.6	109
8	[Cu ₄ {SC(=NPh)(OAr)} ₄]	2.252(1)–2.319(2)	70.10(5)–73.01(6)	106
<i>Step Structure</i>				
9	[Cu ₄ (SPh) ₄ (PPh ₃) ₄]	2.277(2)–2.482(2)	70.8(1)–130.1(1)	29

^aSAr = SC₆H₄(CH₂N(Me)CH₂CH₂OMe)-2 and OAr = OC₆H₃Me₂-2,6.

^bInvolving P-coordinated Cu.

Hexameric structures are generally only found with thiolate ligands in which potentially intramolecularly coordinating substituents are present. The structures of hexameric copper(I) thiolate species [Cu(SR)]₆ can best be described as resulting from the alternate stacking of two trimeric units [Cu(SR)]₃, similar to the trimeric aggregates described in Section II.C.3, with coordination of a heteroatom (nitrogen) from a thiolate ligand in one trimeric unit to a copper atom in the opposite unit (Fig. 8). In this way, the thiolate ligand is *S* bonded

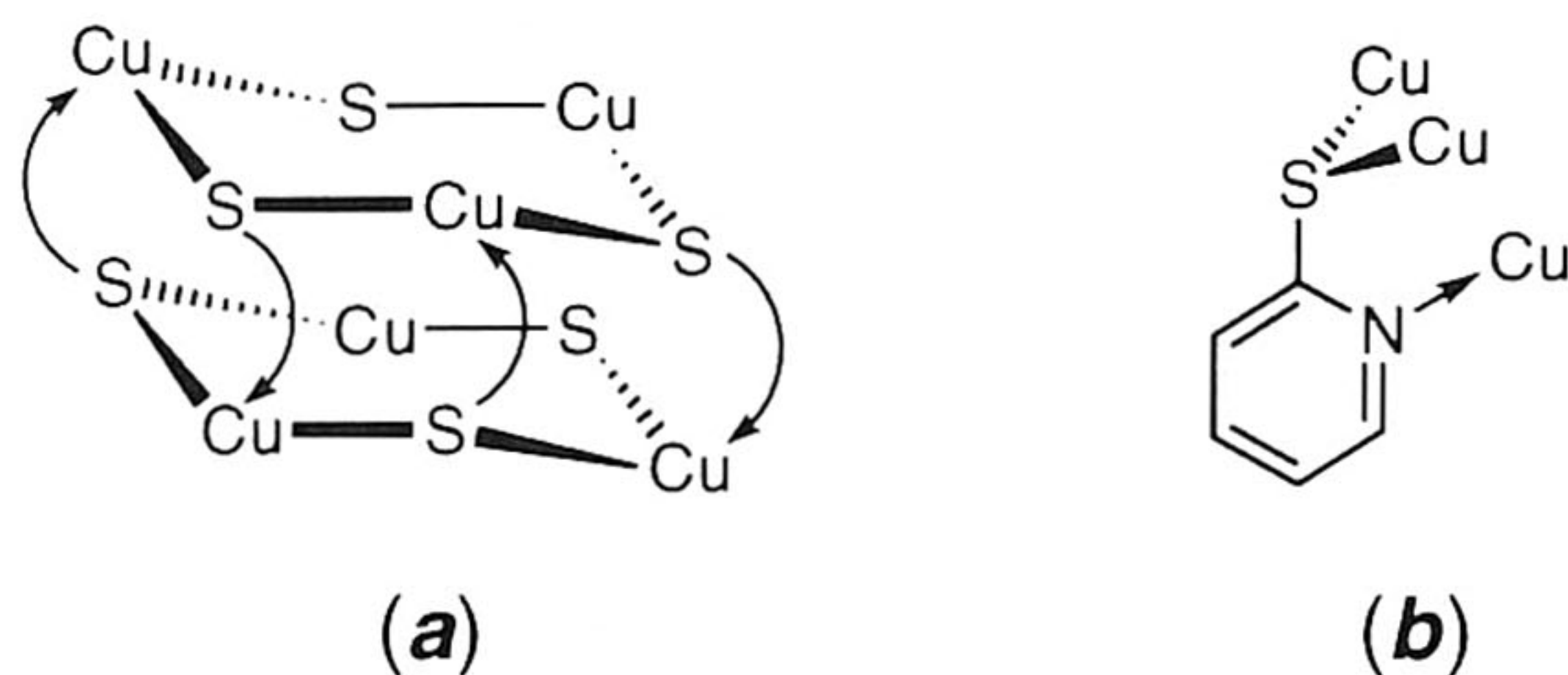


Figure 8. (a) Schematic structure of a hexameric copper(I) thiolate aggregates (ligands on the back of the structure omitted for clarity). (b) The bonding of the pyridine-2-thiolate to three copper atoms.

to two Cu atoms and *N* bonded to a third Cu atom [Fig. 8(b)]. When the alternate stacking of the two trimeric units of the structure is regular, the structure can also be described as an octahedral arrangement of six Cu atoms in which the thiolate ligands each bridge two Cu atoms.

Hexameric-type structures are found not only for the thionate complexes $[\text{Cu}_6(\text{SC}_5\text{H}_4\text{N})_6]$ (110), $[\text{Cu}_6(4,6\text{-dimethylpyrimidine-2-thionate})_6]$ (111), $[\text{Cu}_6(4\text{-hydroxy-6-methyl-pyrimidine-2-thionate})_6]$ (112), $[\text{Cu}_6(\text{SC}_5\text{H}_3\text{N}(\text{SiMe}_3)\text{-6})_6]$ (113), $[\text{Ag}_6(\text{SC}_5\text{H}_3\text{N}(\text{SiMe}_3)\text{-6})_6]$ (113), and $[\text{Cu}_6(\text{quinoline-2-thionate})_6]$ (114) but also for the *N,N*-diethylthiocarbamate complex $[\text{Cu}_6(\text{SC}(\text{O})\text{NEt}_2)_6]$ (115) and the *S*-butyldithiocarbamate species $[\text{Cu}_6(n\text{-BuSC}(\text{S})=\text{NPh})_6]$ (75). Interestingly, dipropyldithiocarbamate silver(I) also has a hexameric structure in which the dithiocarbamate ligands *S*-bridge two silver atoms and *S'*-coordinate to a third silver atom (116). The bonding nature of these *S,N*-chelating ligands resembles that of the *N,N*-chelating amido ligand in the amidocopper(I) species $[\text{Cu}_6(2\text{-N}(\text{SiMe}_3)\text{C}_5\text{H}_3\text{N-6-Me})_4\text{Cl}_2]$ (126).

The smallest possible chelate ring in these hexameric species is a Cu—S—C—N unit, and such a four-membered ring is present in $[\text{Cu}\{\text{SC}(\text{=NPh})(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})\}(\text{PPh}_3)_2]$ (106), though absent in its parent species $[\text{Cu}_4\{\text{SC}(\text{=NPh})(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})\}_4]$ (106). Finally, a rare example of a hexanuclear structure with auxiliary ligands is that of the silver thiolate triphenylphosphine complex $[\text{Ag}_6(\text{SC}_6\text{H}_4\text{Cl-4})_6(\text{PPh}_3)_5]$ (103). Selected data of hexameric copper(I) thiolates are given in Table X.

6. Octameric Complexes

As far as we can ascertain there are no heptanuclear Cu(I) thiolate aggregates known. Octanuclear aggregates with intramolecularly coordinating thiolate ligands have not been reported, although there are some examples either without

TABLE X
Geometrical Details of Hexameric Copper(I) Thiolate Complexes

Entry	Compound	Cu—S (Å)	Cu—S—Cu (deg)	Reference
1	$[\text{Cu}_6(\text{SC}_5\text{H}_4\text{N})_6]$	2.220(2)–2.257(2)	86.6 ^a	110
2	$[\text{Cu}_6(\text{dmpymt})_6]$	2.212(3)–2.279(3)	82.8, 92.4 ^a	111
3	$[\text{Cu}_6(\text{Me}(\text{OH})\text{pymt})_6]^b$	2.219(3)–2.272(4)	85.8(1)–99.8(1)	112
4	$[\text{Cu}_6(\text{SC}_5\text{H}_3\text{N}(\text{SiMe}_3)\text{-6})_6]$	2.236(2)–2.254(2)	82.6(1)–88.5(1)	113
5	$[\text{Cu}_6(\text{Squin})_6]$	2.243(3)–2.260(3)	87.97(9)–88.67(9)	114
6	$[\text{Cu}_6(\text{SC}(\text{O})\text{NEt}_2)_6]$	2.239(3)	78(1)	115b
7	$[\text{Cu}_6\{\text{SCS-}n\text{-Bu}=\text{NPh}\}_6]$	2.253(2)	79.39(6)	75

^aAverage from the Cambridge Crystallographic Structural Database.

^b4-hydroxy-6-methylpyrimidine-2-thionate = Me(OH)pymt.

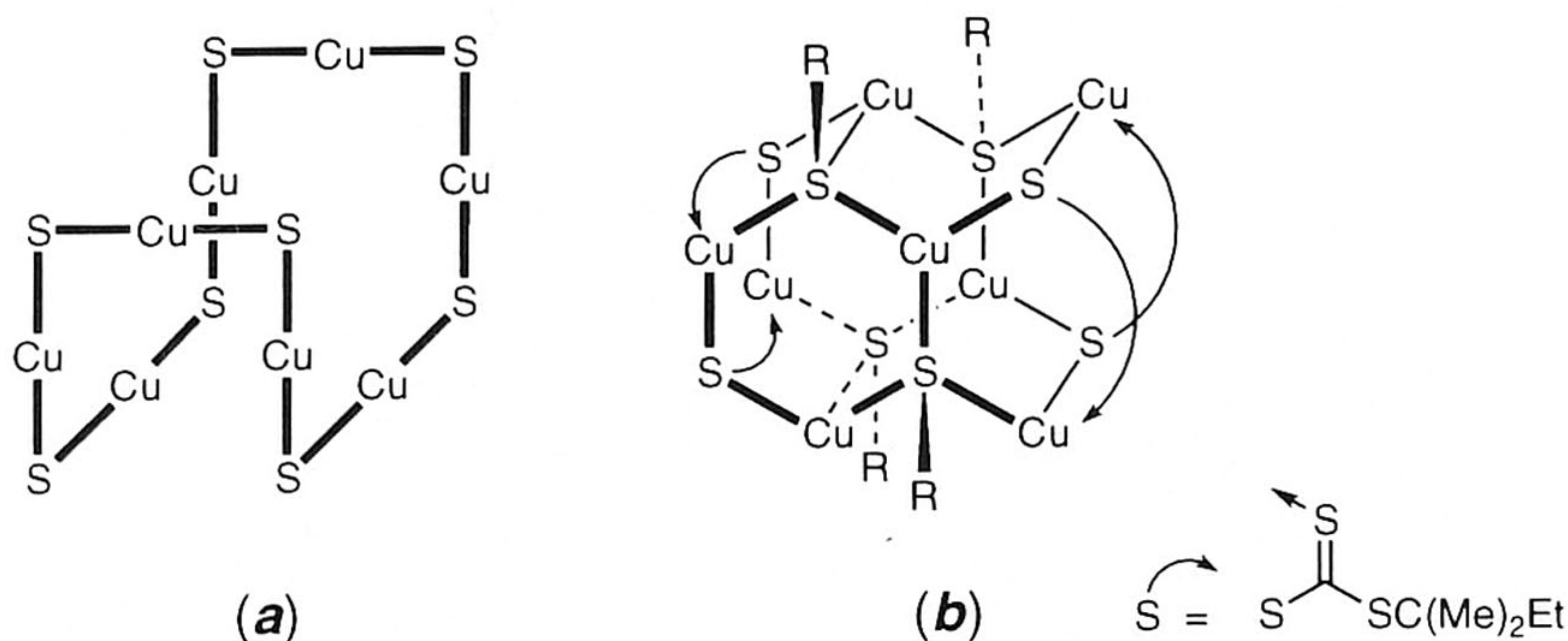


Figure 9. Octanuclear structural types: (a) open structure of $[\text{Cu}_8(\text{SC}_6\text{H}_2^i\text{Pr}_3\text{-2,4,6})_8]$ (b) cage structure of $[\text{Cu}_8(\text{SR})_4(\text{S}_2\text{CSR})_4]$ ($\text{R} = \text{C}(\text{Me})_2\text{Et}$).

coordinating ligands or with only auxiliary coordinating ligands. These octanuclear species can have an open Cu_8S_8 16-membered core that is folded to form a U-shaped structure in which the sulfur atoms are approximately at the corners of a cube. Moreover, some complicated cage structures are known. Examples representing complexes containing the former structural type are $[\text{Cu}_8(\text{SC}_6\text{H}_2\text{-}i\text{-Pr}_3\text{-2,4,6})_8]$ (52) and $[\text{Ag}_8(\text{SCMe}_2\text{Et})_8]$ [Fig. 9(a)] (82); a complex having a complicated cage structure is $[\text{Cu}_8(\text{SR})_4(\text{S}_2\text{CSR})_4]$ ($\text{R} = \text{CMe}_2\text{Et}$) [Fig. 9(b)] (117).

A different theme is met in the octanuclear structure of $[\text{Ag}_8(\text{SCMeEt}_2)_8(\text{PPh}_3)_2]$ (105), which is built from one tetranuclear Ag_4S_4 heterocycle, similar to that in $[\text{Cu}_4(\text{SC}_6\text{H}_3(\text{SiMe}_3)_2\text{-2,6})_4]$ (77), that does not contain auxiliary coordinating ligands and one Ag_4S_4 heterocycle that is similar to that in $[\text{Cu}_4(\text{S-}t\text{-Bu})_4(\text{PPh}_3)_2]$ (101) with two PPh_3 ligands coordinated to opposite Ag atoms. Close contacts between these tetranuclear units from silver in one unit to sulfur in the opposite unit and vice versa (range 2.86–2.97 Å) result in the formation of the overall octameric structure (105). Selected geometrical details of some octameric copper(I) arenethiolate aggregates have been collected in Table XI.

7. Higher Aggregation States

When one goes to highly aggregated species one finds that intramolecular coordination plays a less dominant but still important role. For example, in the nonameric aggregate $[\text{Cu}_9(\text{S-1-C}_{10}\text{H}_6\text{NMe}_2\text{-8})_9]$ (69), only six of the nine amine donor groups are involved in intramolecular coordination, in the decanuclear aggregate $[\text{Cu}_{10}(\text{SCF}_3)_{10}(\text{MeCN})_8]$ (58), auxiliary coordination occurs from eight MeCN ligands, and in dodecanuclear aggregates $[\text{Cu}_{12}(\text{SC}_6\text{H}_4\text{SiMe}_3\text{-2})_{12}]$

TABLE XI
Geometrical Details of Octameric Copper(I) Thiolate Complexes

Entry	Compound	Cu—S (Å)	Cu—S—Cu (deg)	Reference
1	[Cu ₈ (SC ₆ H ₂ - <i>i</i> -Pr ₃ -2,4,6) ₈]	2.162 ^a	77.2–92.5	52
2	[Cu ₈ (SR) ₄ (S ₂ CSR) ₄] ^b	2.237(5)–2.301(5)	119.7–120.4 ^c 86.7–89.7 ^c 71.5–75.1 ^c	117
		2.263(5)–2.292(5) ^d	74.2–77.8 ^c	

^aAverage.

^bR = C(Me)₂Et; formed by insertion of CS₂ into the Cu—S bond of [Cu(SR)]_n; the Cu—S—C(S) unit can formally be interpreted as a four-membered chelate ring.

^cObtained from the Cambridge Crystallographic Structural Database.

^dThe Cu—S (alkyl trithiocarbonate).

(40, 84) and [Ag₁₂(S-*c*-Hex)₁₂] (85), donor coordination is totally absent. The core structures and the subsequent cage expansion of the nonamer, the decamer, and the dodecamer, are depicted in Figure 10.

In these highly aggregated species, one can easily recognize one or more six-membered Cu₃S₃ subunits, and such rings seem very stable structural units in most of the structurally characterized copper(I) thiolates.

The highest Group 11 (IB) metal thiolate aggregate that does not have a polymeric structure is tetradecanuclear [Ag₁₄(S-*t*-Bu)₁₄(PPh₃)₄] (105). The structure of this aggregate has a central open 28-membered Ag₁₄S₁₄ heterocycle with only four PPh₃ ligands.

The structure of polymeric [Cu(SMe)]_∞ was determined by means of a Rietveld refinement of powder diffraction data and is depicted in Figure 11 (127). The determined structure can be described as two strings of fused Cu₃S₃ six-membered rings that are interconnected by bonding from a copper atom in one string to a sulfur atom in the opposite string. In this way, a structure is formed that contains Cu₃S₃ rings, which occur in both the chair and boat conformations. The copper atoms have a close to ideal trigonal planar coordination, whereas the sulfur atoms have a distorted tetrahedral geometry. In this structure of [Cu(SMe)]_∞, there are two acute Cu—S—Cu angles of 83.4(6)° and one wide Cu—S—Cu angle of 128.1(9)°, though a possible explanation for these different angles was not proposed in the original report (127).

D. Mixed-Organo(arenethiolato)copper and Mixed-Arenethiolatocopper Copper Halide Aggregates

Besides the pure copper thiolate aggregates [Cu(SR)]_n, there are several reported examples of mixed-organo(arenethiolato)copper(I) aggregates in which

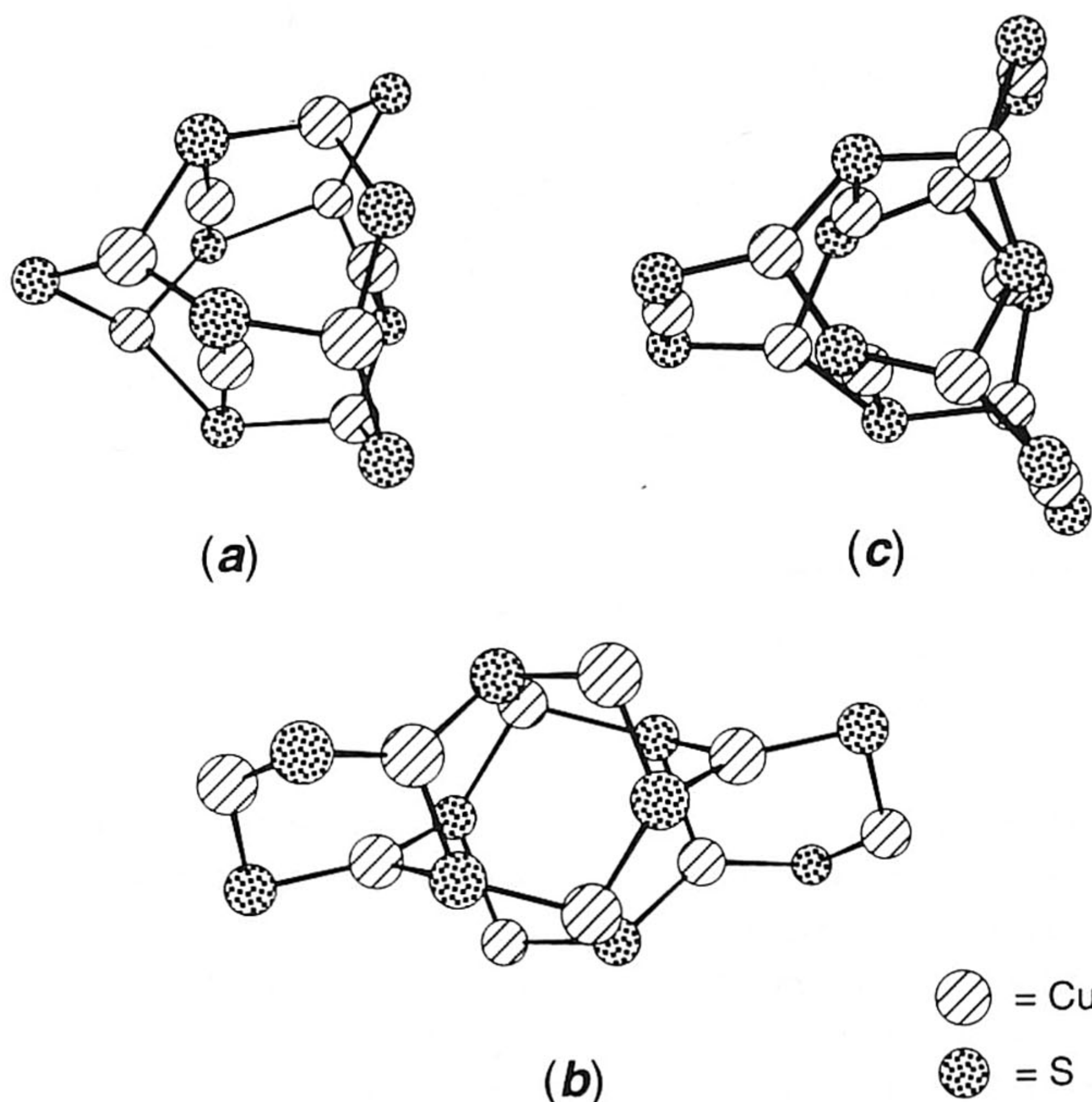


Figure 10. Cage structures of higher aggregates: (a) nonamer, (b) decamer, and (c) dodecamer.

intramolecularly coordinating arenethiolate ligands are present. Such complexes are a topic of major interest because of their possible occurrence in catalyzed organic reactions. Mixed-organo(arenethiolato) copper(I) aggregates can generally be prepared by reacting a pure copper(I) arenethiolate, $[\text{Cu}(\text{SAr})]_n$, with either an organolithium or an organocopper reagent (e.g., $\text{LiC}\equiv\text{C}-t\text{-Bu}$, $\text{CuC}\equiv\text{C}-t\text{-Bu}$, or CuMe_3).

It is important to note that all known examples of mixed-organo(arenethiolato)copper(I) aggregates possess additional coordination from a donor substituent. A typical example is trinuclear $[\text{Cu}_3\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)-2\text{-Cl}$

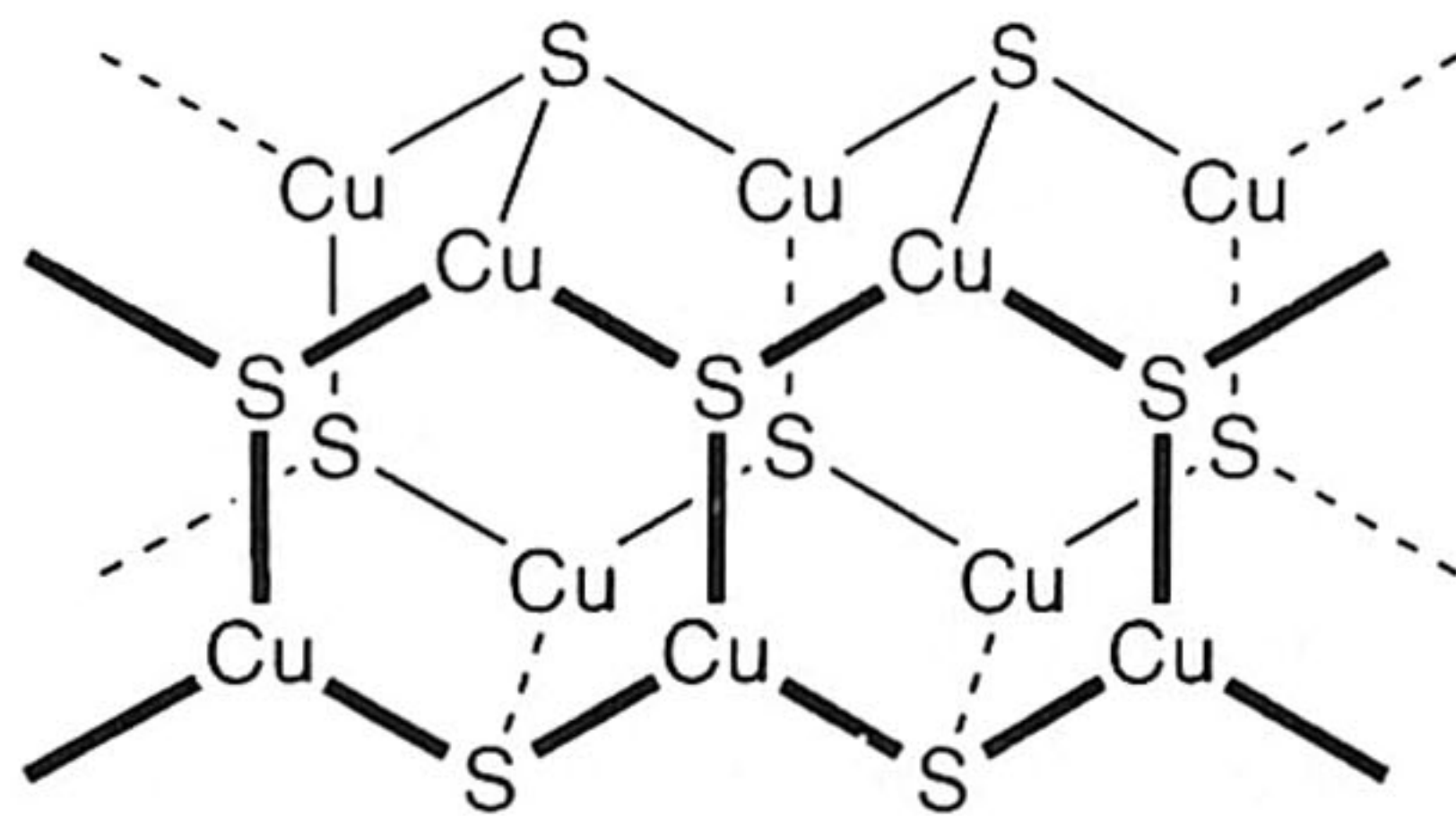


Figure 11. Part of the structure of polymeric $[\text{Cu}(\text{SMe})]_\infty$ (Me groups are omitted for clarity).

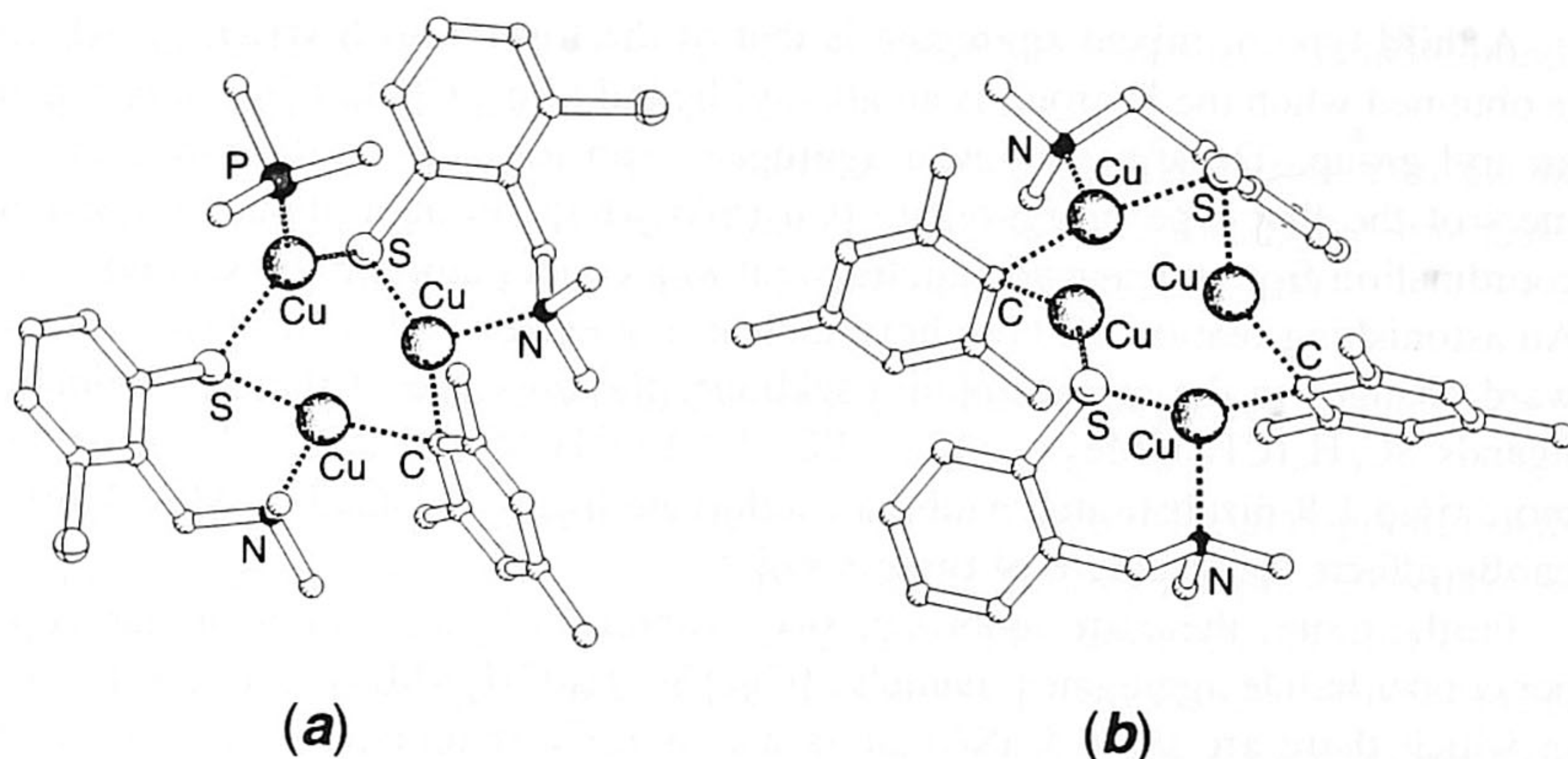
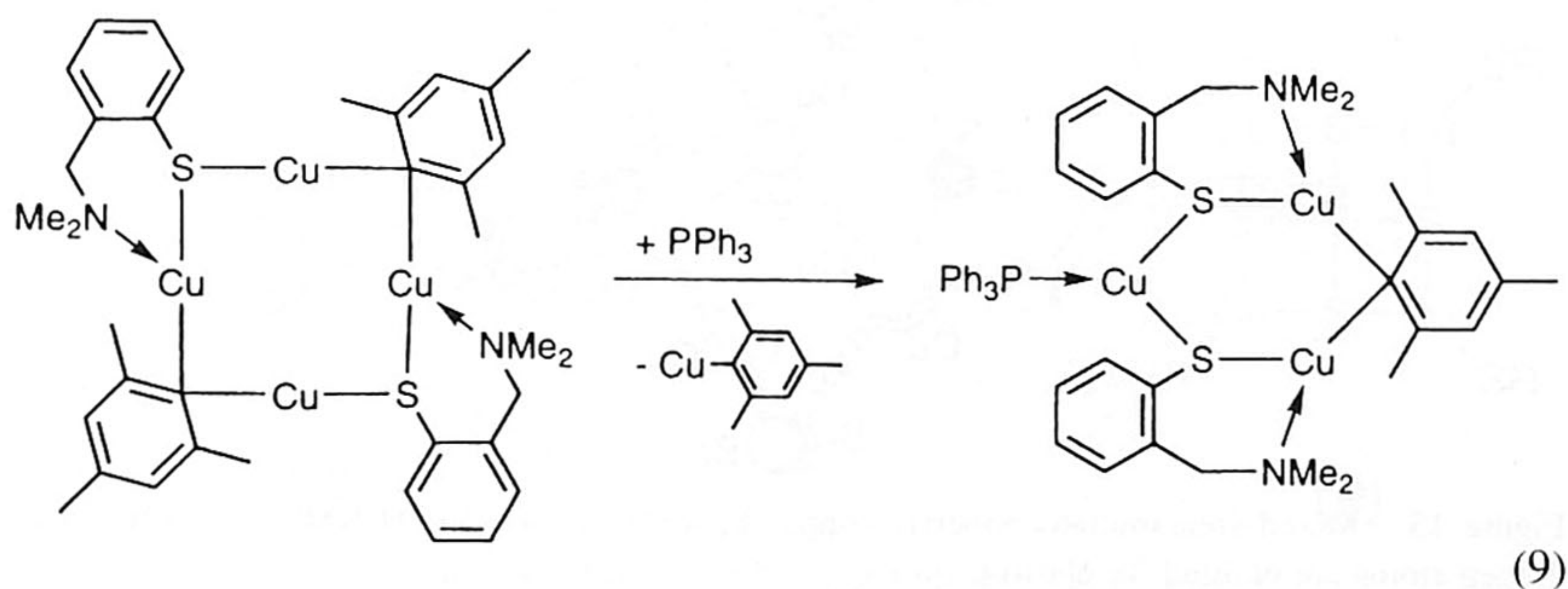


Figure 12. Mixed organo(arenethiolato)copper(I) aggregates $[\text{Cu}_3(\text{SAr})_2(\text{R})(\text{PPh}_3)]$ (a) and $[\text{Cu}_4(\text{SAr})_2(\text{R})_2]$ (b) (Ph groups of PPh_3 and hydrogen atoms are omitted for clarity).

$5\}_{2}(\text{Mes})(\text{PPh}_3)]$ (20), which is an aggregate of the type $[\text{Cu}_3(\text{SAr})_2(\text{R})(\text{L})]$ [Fig. 12(a)], comprising two arenethiolate entities: one organic (mesityl) group and one auxiliary coordinating donor ligand L that completes the coordination of the third copper atom. The structure of this aggregate contains a central $\text{Cu}_3\text{S}_2\text{C}$ ring that has a boat conformation; a feature that is seldom encountered in structures of pure copper(I) arenethiolates.

Other examples include aggregates of the type $[\text{Cu}_4(\text{SAr})_2(\text{R})_2]$ [$\text{R} = \text{Mes}$; $\text{SAr} = \text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2-Cl-5}$ (20), $\text{S-1-C}_{10}\text{H}_6\text{NMe}_2\text{-8}$ (69)] in which the formal ratio CuSAr/CuR is 1:1 [Fig. 12(b)]. A general structural feature in these aggregates is a central $\text{Cu}_4\text{S}_2\text{C}_2$ ring with the sulfur (and carbon) atoms on mutually opposite sides of the ring. Interestingly, these aggregates react with triphenylphosphine to afford the corresponding trinuclear aggregates $[\text{Cu}_3(\text{SAr})_2(\text{R})(\text{L})]$ which coexist in solution with free pentameric mesitylcopper(I) (Eq. 9).



(9)

A third type of mixed aggregate is that of the form $[\text{Cu}_6(\text{SAr})_4(\text{R})_2]$, which is obtained when the R group is an alkynyl ligand (e.g., $\text{C}\equiv\text{C}-t\text{-Bu}$) rather than an aryl group. These hexanuclear aggregates can formally be described as dimers of the first type of aggregate $[\text{Cu}_3(\text{SAr})_2(\text{R})]$, brought about by alkynyl coordination from one such trinuclear unit to a copper atom in the second unit. An astonishing feature of these hexanuclear aggregates is their insensitivity toward changes in the arenethiolate backbone: the presence of the arenethiolate ligands $\text{SC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2}$ (122), $\text{SC}_6\text{H}_4((S)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}$ (122), or the more rigid 1,8-disubstituted naphthalenethiolate ligand $\text{S-1-C}_{10}\text{H}_6\text{NMe}_2\text{-8}$ (69), hardly affects the structure of these species.

Furthermore, there are reports of two examples of mixed-arenethiolatocopper copper halide aggregates, namely, $[\text{Cu}_8\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2,6}\}_3\text{Br}_5]$ (60), in which there are three CuSAr units and five CuBr units, and a species of overall composition $[\text{Cu}_3(\text{S-oxazoline})_3]_4[\text{CuI}]_4$ (61), which comprises four trimeric copper arenethiolate entities connected to a central Cu_4I unit. It should be noted that in both structures the copper halide units do not occur as separate parts of the structure, but form part of an intimate assembly that produces one well-defined mixed aggregate.

From the structure of these mixed aggregates it is quite clear that, as regards its structural and bonding properties, an arenethiolate ligand is quite similar to a halide ligand. In fact, in the structure of $[\text{Cu}_8\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2,6}\}_3\text{Br}_5]$ (60) (see Fig. 13) one can distinguish not only different bridging modes of an

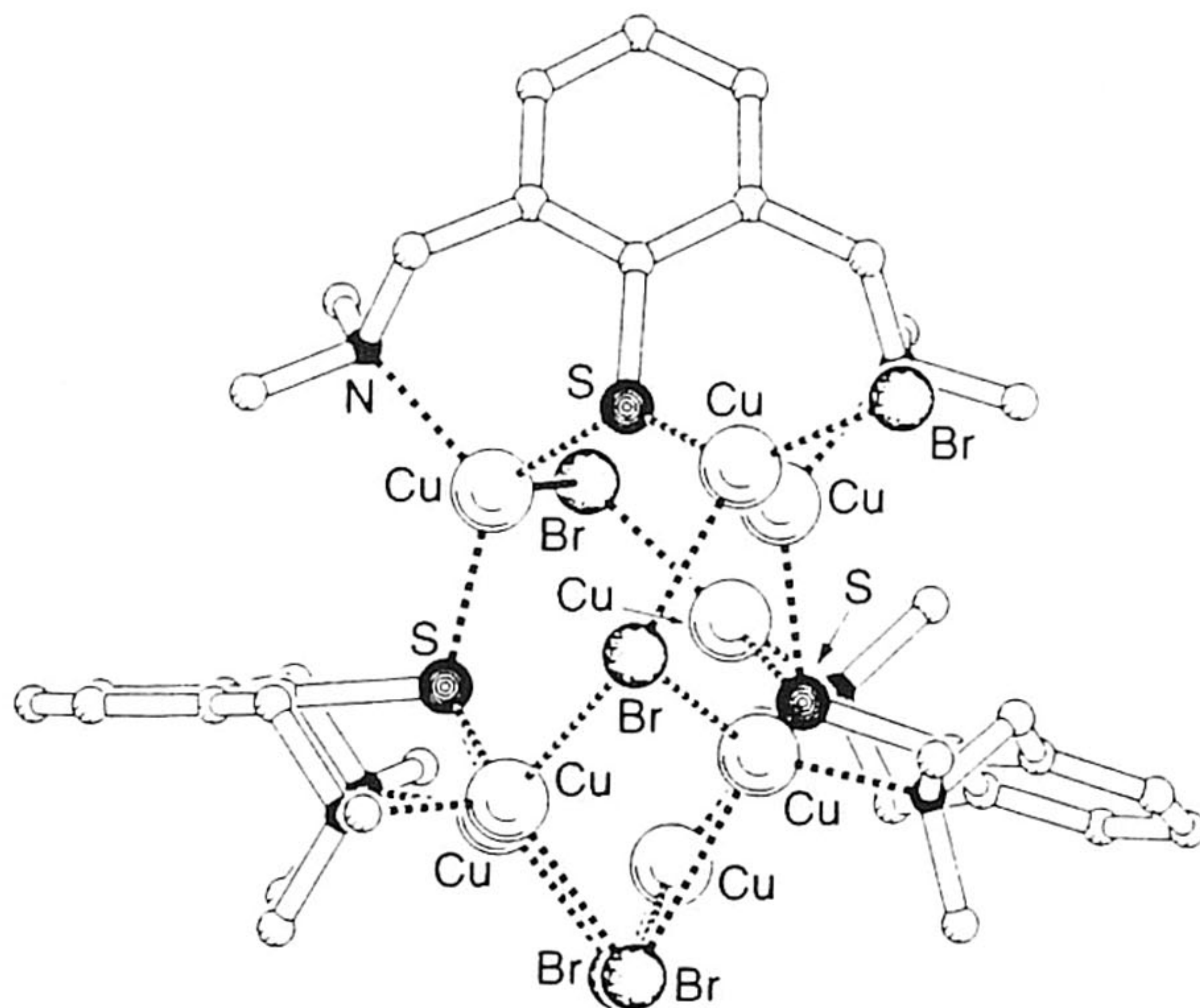


Figure 13. Mixed-arenethiolatocopper(I) copper halide $[\text{Cu}_8(\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2,6})_3\text{Br}_5]$ (hydrogen atoms are omitted for clarity).

arenethiolate ligand (i.e., μ^3 -S and μ^4 -S), but also different ways of halide bonding (i.e., η^1 -Br, μ^2 -Br, and μ^3 -Br).

The latter mixed aggregate is so thermodynamically stable that even in the presence of excess of lithium arenethiolate, which is used during the synthesis, one does not obtain a pure copper(I) arenethiolate $[\text{Cu}(\text{SAr})]_n$ (60).

E. Mixed-Metal Copper Thiolate Complexes

Interestingly, several examples were reported of mixed-metal copper thiolate complexes in which one or more copper thiolate entities are present within an aggregate that also contains another metal (Fig. 14, Table XII) (128–135).

For example, the structures of the complexes $[(\text{S}_2\text{MoS}_2)\text{Cu}(\text{SPh})]^{2+}$ (128) and $[(\text{PhS})\text{Cu}(\text{S}_2\text{MoS}_2)\text{Cu}(\text{SPh})]^{2+}$ (128) can be described as comprising a tetrathiomolybdate coordinating to one or two copper thiolate entities, respectively [Fig. 14(a), entries 1 and 2 in Table XII]. This structural description is furthermore validated by the absence of direct Cu—Mo bonding.

In other cases, the thiolate ligand is an intimate part of the mixed-metal assembly, and examples of these structural frameworks are complexes in which two thiolate ligands bridge the metal atoms, namely, $[\text{Cp}_2\text{Ti}(\text{SEt})_2\text{Cu}(\text{PR}_3)]^+$

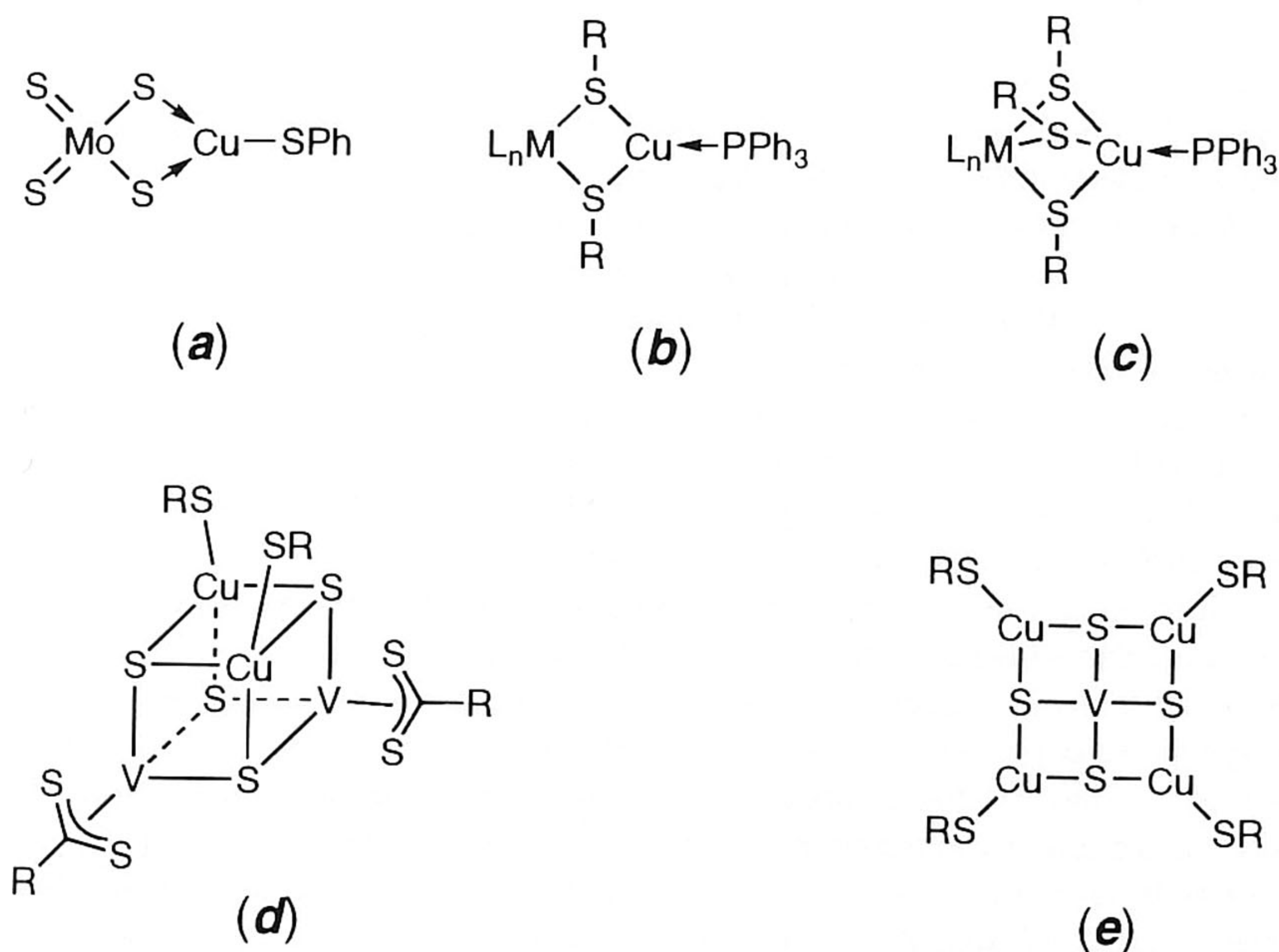


Figure 14. Mixed-metal copper thiolate complexes.

TABLE XII
Structurally Characterized Mixed-Metal Copper Thiolates

Entry	Compound	Reference
1	$[(S_2MoS_2)Cu(SPh)]^{2+} (N-n-Pr_4)_2^{+a}$	128
2	$[(PhS)Cu(S_2MoS_2)Cu(SPh)]^{2+} (N-n-Pr_4)_2^{+b}$	128
3	$[Cp_2Ti(SEt)_2Cu(PR_3)]^+ (PF_6)^- c$	129
4	$[(RS)_2In(SR)_2Cu(PPh_3)_2]^d$	130
5	$[(Ph_3P)Cu(ArS)_3Mo(SAr)_3Cu(PPh_3)]^e$	131
6	$[(Ph_3P)Cu(ArS)_3W(SAr)_3Cu(PPh_3)]^e$	132
7	$[V_2Cu_2S_4(SPh)_2(S_2CR)_2]^{2-} (NEt_4)_2^{+f}$	133
8	$[V_2Ag_2S_4(SPh)_2(S_2CR)_2]^{2-} (NEt_4)_2^{+f}$	133
9	$[VCu_4S_4(SPh)_4]^{3-} (NEt_4)_3^+$	134
10	$[VCu_4S_4(SPh)_3(S_2CR)]^{3-} (NEt_4)_3^{+f}$	134
11	$[VCu_4S_4(SPh)_2(S_2CR)_2]^{3-} (NEt_4)_3^{+f}$	134
12	$[Cu_6In_3(SEt)_{16}]^- (PPh_4)^+$	135

^aThe S_2MoS_2 unit acts once as a bidentate ligand.

^bThe S_2MoS_2 unit acts twice as a bidentate ligand.

^cR = Ph or *c*-Hex.

^dR = Et or *sec*-Bu.

^eThe $(SAr)_6$ unit (M = Mo or W) acts as two tridentate ligands, where $SAr = SC_6H_4Me-4$.

^fR = NC_4H_8O .

(R = Ph or *c*-Hex) (129) [Fig. 14(b)] and related $[(RS)_2In(SR)_2Cu(PPh_3)_2]$ having a tetrahedrally coordinated copper atom (130).

A variation of this structural type is one in which three thiolates bridge the two metals [Fig. 14(c)], examples being $[(Ph_3P)Cu(ArS)_3Mo(SAr)_3Cu(PPh_3)]$ (131) and $[(Ph_3P)Cu(ArS)_3W(SAr)_3Cu(PPh_3)]$ (132), which are of interest as model complexes for nitrogenase proteins. Theoretical calculations on these latter species show that the major bonding component between the $M(SR)_6$ and the $Cu(PPh_3)$ groups is electrostatic in character, though there is evidence for a weak direct M—Cu bonding interaction. The latter interaction has been substantiated by electrochemical investigations (131).

More complicated aggregate structures are found in the vanadium–copper and vanadium–silver species $[V_2M_2S_4(SPh)_2(S_2CR)_2]^{2-}$ (M = Cu or Ag) (133), in which the metal sulfido core is in the shape of a cube [Fig. 14(d)]; bulk magnetic susceptibility measurements have shown that there is probably a direct V—V bond within these species. These and related complexes are of interest since a vanadium-containing nitrogenase has been discovered (136).

As we have already seen, tetrathiometalates can act as bidentate ligands (entries 1 and 2 in Table XII) and tetrathiovanadate has even been found to coordinate to four $Cu(SPh)$ groups thus leading to aggregates such as $[VCu_4S_4(SPh)_4]^{3-}$ [Fig. 14(e)] (134). The thiophenolate groups in this aggre-

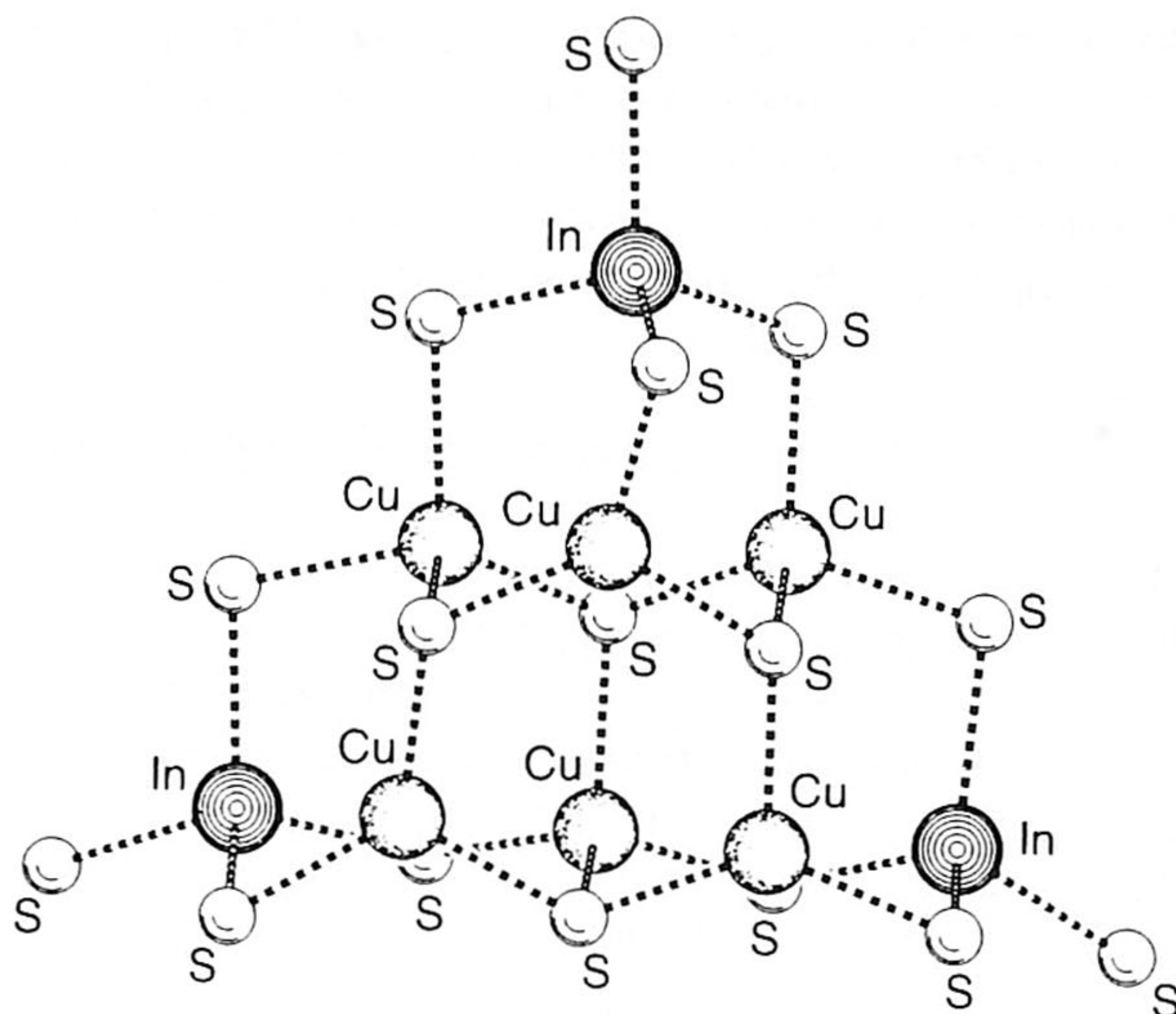


Figure 15. The indium copper thiolate aggregate $[\text{Cu}_6\text{In}_3(\text{SEt})_{16}]^-$ (Et groups are omitted for clarity).

gate can also be replaced by a dithiocarbamate grouping and a series of complexes $[\text{VCu}_4\text{S}_4(\text{SPh})_{4-n}(\text{S}_2\text{CR})_n]^{3-}$ ($n = 0, 1, \text{ or } 2$) has been subject to X-ray crystallographic techniques (134). From X-ray photoelectron spectroscopy it was concluded that the copper atoms in these species are monovalent Cu^I (134).

The nonanuclear complex $[\text{Cu}_6\text{In}_3(\text{SEt})_{16}]^-$ (Fig. 15) (135) cannot be easily placed into one of the frameworks above, and is unique in that it combines several structural features from pure copper thiolate species with those from indium salts. In the adamantoidal framework structure of $[\text{Cu}_6\text{In}_3(\text{SEt})_{16}]^-$ (135), it is possible to recognize several structural features that are present in the single adamantoidal aggregates $[\text{Cu}_4(\text{SR})_6]^{2-}$ (consisting of four fused six-membered Cu_3S_3 rings with alternating copper and sulfur atoms as in pure trimeric copper thiolates; Section II.C.3), where R is either Me (89b, 90), Et (91), or Ph (52, 48b, 89) and in the related tris-dithiolate aggregates (64, 66) shown in Table II. In this respect, $[\text{Cu}_6\text{In}_3(\text{SEt})_{16}]^-$ (135) can be seen as a polymeric adamantoidal framework structure that is terminated by three $\text{In}(\text{SEt})_n$ units.

Complexes of copper thiolates and indium were mainly studied as single source precursors for CuInS_2 , which can be used in thin-film solar cells, and the thermal decomposition of $[(\text{RS})_2\text{In}(\text{SR})_2\text{Cu}(\text{PPh}_3)_2]$ (130) indeed leads to the selective formation of CuInS_2 . However, this material has a much lower photovoltaic performance than the corresponding selenide CuInSe_2 . Based on the structure of nonanuclear $[\text{Cu}_6\text{In}_3(\text{SEt})_{16}]^-$ (135), which is reminiscent of the chalcopyrite structure of CuInS_2 (also constructed of fused adamantane units), a proposal has been made for the lower photovoltaic performance of CuInS_2 .

In this proposal, the $[\text{Cu}_4(\text{SEt})_6]$ clusters in $[\text{Cu}_6\text{In}_3(\text{SEt})_{16}]^-$ that may also occur in CuInS_2 , generate "dark-conducting" paths that short the photovoltaic device. The copper atoms in CuInSe_2 have larger $\text{Cu} \cdots \text{Cu}$ distances than in CuInS_2 and, therefore, there is a lower tendency for diffusion of the copper atoms, thus leading to a better photovoltaic performance.

F. The Coordination Geometry of Copper Atoms

The crystallographically found geometries of the copper atoms in copper arenethiolate structures are, at first sight, different to what one might expect for two- and three-coordinate copper atoms. However, when the copper atoms participate in 2e-3c bonds, the direction of the copper orbital involved with the bridging ligand is not directly clear from the molecular structure (Fig. 16). The 2e-3c description of the $\text{Cu}-\text{X}-\text{Cu}$ system is an alternative for a bonding scheme involving a direct $\text{Cu}-\text{Cu}$ interaction (137) and can provide a good explanation for the $\text{Cu}-\text{S}-\text{Cu}$ angles often found in the structures of copper(I) thiolate complexes. In these bridged systems, $\text{Cu}-\text{X}-\text{Cu}$, the bonding orbital on Cu that binds to the bridging ligand is generally positioned between the neighboring copper atom and the bridging ligand X rather than along the $\text{Cu}-\text{X}$ or $\text{Cu}-\text{Cu}$ vectors.

Knotter et al. (20) developed a trigonometric method to determine the position of this orbital from X-ray crystallographic data, using a model system (Fig. 16) that has a metal atom Cu_c that is surrounded by a neighboring metal atom, Cu_n , a 2e-2c bonded auxiliary or intramolecularly coordinating ligand L, and a ligand X, which is bridging Cu_c and Cu_n in a 2e-3c bond. Furthermore, one assumes: (1) that the vector of the bonding orbital of the bridging ligand is

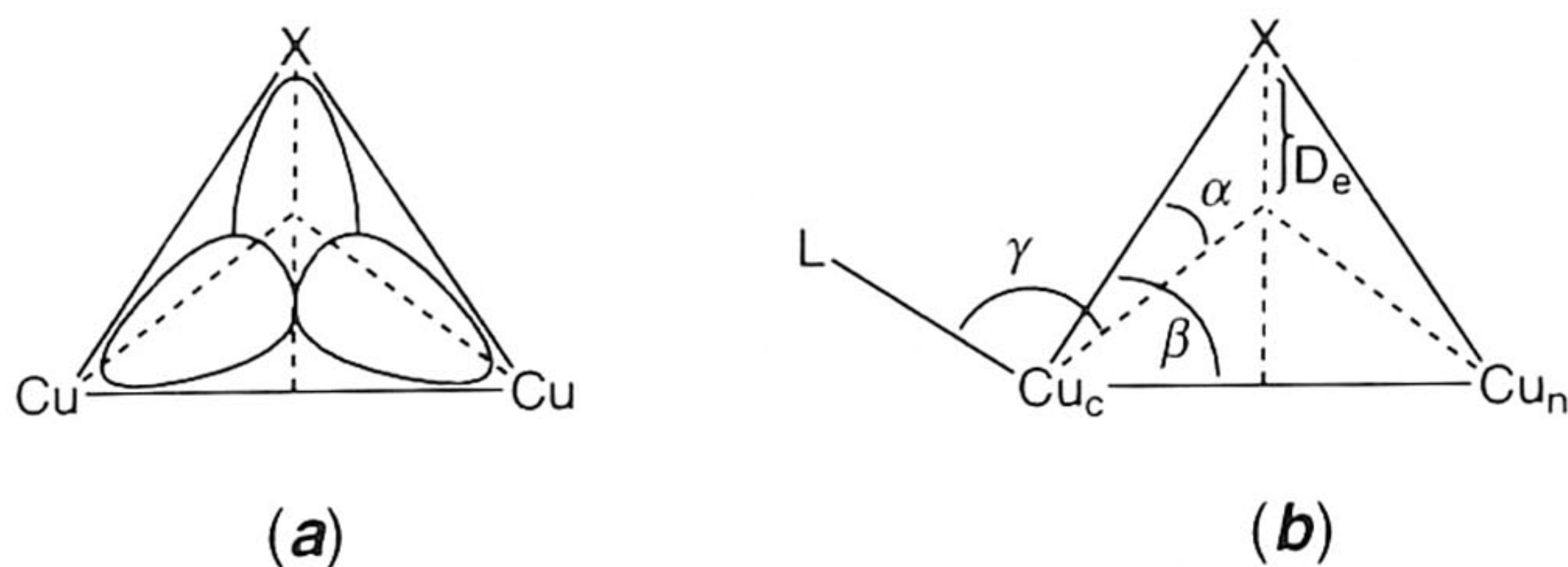


Figure 16. Two-electron three-center bonds. (a) Bonding model in which the solid lines are the connections between the atoms found crystallographically, while the dotted lines are the direction of the orbitals, which are indicative for the real geometry around the metal atoms. (b) A model for the calculation of the geometry around the metal center Cu_c . The angle γ between the two orbitals on Cu_c , which are responsible for bonding to ligand L and the bridging ligand X, is the summation of the angles α and $\text{X}-\text{Cu}_c-\text{L}$.

perpendicular to the $\text{Cu}_c \cdots \text{Cu}_n$ vector and is thus in the plane defined by the atoms Cu_c , X, and Cu_n , and (2) that the metal orbitals are directed toward the point of the highest electron density of the bridging ligand orbital.

The position of this orbital on the copper involved in the bridging multicenter interaction is defined as making an angle α with the $\text{Cu}_c\text{-X}$ bond; this angle is a fraction of the crystallographically determined $\text{Cu}_n\text{-Cu}_c\text{-X}$ angle β . If the point of the highest electron density is at a distance D_e away from the bridging atom X, then the angle α is given by Eq. 10.

$$\alpha = \beta - \text{arc tan} \left[\frac{d(\text{Cu}_c\text{-X}) \sin \beta - D_e}{d(\text{Cu}_c\text{-X}) \cos \beta} \right] \quad (10)$$

This equation can be solved by estimating D_e as one-half the bond distance either of a C=C bond if an sp^2 carbon is bridging ($D_e = 0.669 \text{ \AA}$), or of S_2 if an sp^2 sulfur atom is bridging ($D_e = 0.994 \text{ \AA}$). The calculated values of α when added to the angle $\text{L-Cu}_c\text{-X}$ provide an estimate for the interorbital angle γ which reflects the coordination geometry of copper.

The viability of this method has been illustrated by the results obtained from mixed-organo(arenethiolato)copper(I) aggregates $[\text{Cu}_3\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2-Cl-5}\}_2(\text{Mes})(\text{PPh}_3)]$, $[\text{Cu}_4\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2-Cl-5}\}_2(\text{Mes})_2]$, $[\text{Cu}_6\{\text{SC}_6\text{-H}_4(\text{CH}_2\text{NMe}_2)\text{-2}\}_4(\text{C}\equiv\text{C-}t\text{-Bu})_2]$ and $[\text{Cu}_6\{\text{SC}_6\text{H}_4((S)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}\}_4(\text{C}\equiv\text{C-}t\text{-Bu})_2]$, which show that the copper atoms in these species have an almost perfect trigonal or linear arrangement of their bonding orbitals, that is, sp^2 or sp hybridization. In those instances, where large deviations from 120° (or 180°) occur, the explanation can be found in steric strain caused by one or two of the ligands (20).

III. LITHIUM AND MAGNESIUM THIOLATE COMPLEXES

A. Lithium and Magnesium Thiolates in Perspective

Reports that thermolysis of metal chalcogenolate complexes offers a low-temperature route to the synthesis of novel solid state materials (32) is also stimulating research in this area. As is the case with copper(I) thiolates, lithium thiolates are often aggregated species (Section III.C) and from the few magnesium thiolate structures known (Section III.D) one sees a preference for monomeric and dimeric formulations when bulky substituents are present.

Whereas studies of the structures of transition metal thiolate complexes are quite numerous, analogous studies with complexes of the more electropositive

elements (e.g., alkali, alkaline earths, and the *f*-block elements) are less common. Of these latter elements the metals lithium and magnesium are unique from a structural and bonding perspective, as well as providing the most useful reagents in synthetic chemistry (138, 139).

B. Synthesis of Lithium and Magnesium Thiolates

1. Synthesis via Deprotonation of Thiols

The preparation of lithium and magnesium thiolates commonly comprises the reaction of a suitable lithium or magnesium base with the corresponding thiol at low temperature (Eq. 11).

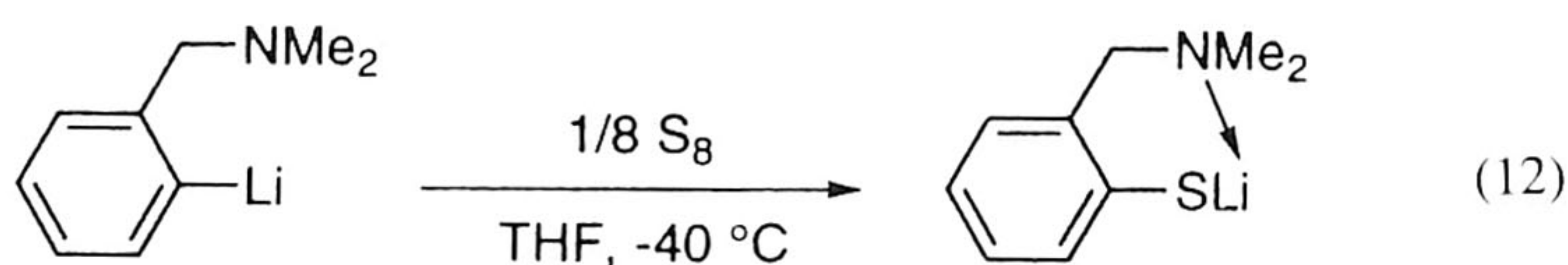


The commonly used bases in this reaction are commercially available solutions of *n*-BuLi (in hexane) (140–146), or *n*-Bu₂Mg (in heptane) (144); freshly prepared lithium amide LiNH₂ has also been used for the synthesis of lithium methylthiolate (147). Similarly, several bulky arenethiols (e.g., HSC₆H₂Ph₃-2,4,6) have been successfully deprotonated with either a 1:1 mixture of *n*-Bu₂Mg and *sec*-Bu₂Mg in heptane or Mg{N(SiMe₃)₂}₂ in toluene (148). A major shortcoming of this procedure is that thiols that are not commercially available have to be prepared via metal thiolate species—clearly a roundabout approach.

This type of deprotonation procedure can also be applied to prepare lithium or magnesium areneselenolates (143, 148) and sterically hindered silyltelluroate derivatives of the Group I (IA) metals Li, Na, and K (149). An alternative procedure based on the reduction of a diselenide (RSeSeR) with [LiHBEt₃] in THF can also afford the desired lithium areneselenolate (32).

2. Synthesis via Sulfur Insertion into Metal–Carbon Bonds

An alternative synthetic procedure to lithium arenethiolates is the insertion reaction of elemental sulfur (S₈) into the lithium–carbon bond of a suitable organolithium reagent in THF at low temperature (Eq. 12).



The insertion of sulfur into a reactive metal-carbon bond has been known in organic chemistry for some time, but was mainly used to prepare arenethiols (150). However, this method has only recently found its use in the synthesis of pure lithium arenethiolate complexes, which contain potentially intramolecularly coordinating heteroatom donor functions (50, 151). It has since then been reported that this method is also applicable for the preparation of lithium areneseelenolates and arenetellurolates (152). This route has also been used for the synthesis of bis(arenethiolato)magnesium complexes with intramolecular coordination (153).

C. Structures of Lithium Thiulates

1. Monomeric, Dimeric, and Trimeric Complexes

Structurally characterized monomeric species with a general formulation $[\text{Li}(\text{SAr})\text{L}_3]$ (Fig. 17) are included in Table XIII. These species have auxiliary donor ligands that are usually thf (141, 142) or py (140).

However, situations where more weakly coordinating ligands such as Et_2O (144) are present or where less than stoichiometric amounts (3 equiv) of thf are used (146), already lead to the formation of dimeric aggregates of the type $[\text{Li}(\text{SAr})\text{L}]_2$ (Fig. 18). Similarly, polynuclear lithium areneseelenolates $[\text{Li}(\text{SeAr})]_n$ react with bpy to afford dimeric aggregates $[\text{Li}(\text{SeAr})(\text{bpy})]_2$ (32). A trimeric structure, for which details were not reported, has very recently been found for the thiolato mono thf complex $[\text{Li}(\text{thf})(\text{SC}_6\text{H}_2-t\text{-Bu}_3-2,4,6)]_3$ (154); the structure of the analogous selenolato complex is also trimeric (155).

Interestingly, we have characterized the first representative of dinuclear mixed-arenethiolatolithium lithium halide aggregates, namely, $[\text{Li}_2\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}\text{I}(\text{thf})_2]$ (151). In this complex, the two lithium atoms are essentially symmetrically bridged by the sulfur atom of the arenethiolate ligand and the iodide anion. The tetrahedral coordination geometry of the lithium atoms is completed by intramolecular coordination of the dimethylamino groups and auxiliary coordination of two molecules of thf (Fig. 19).

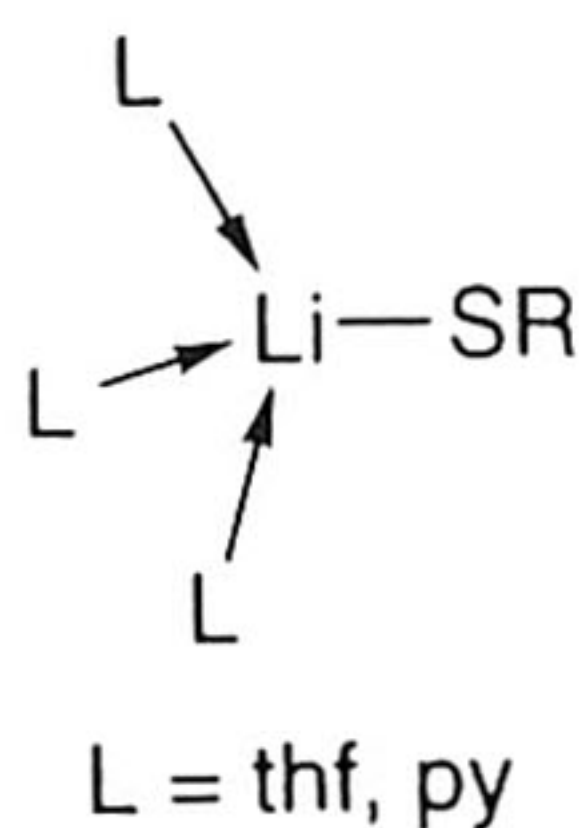


Figure 17. Monomeric lithium arenethiolates $[\text{Li}(\text{SAr})\text{L}_3]$.

TABLE XIII
Structurally Characterized Lithium Thiolate, Selenolate, and Tellurolate Species

Entry	Compound	Reference
1	$[\text{Li}(\text{SMe})]_n^a$	147
<i>Complexes with Auxiliary Donor Ligands</i>		
2	$[\text{Li}(\text{SC}_6\text{H}_4\text{Me-2})(\text{py})_3]$	140
3	$[\text{Li}(\text{SC}_6\text{H}_2\text{Ph}_3\text{-2,4,6})(\text{thf})_3]$	141
4	$[\text{Li}(\text{SC}_6\text{H}_2\text{-}t\text{-Bu}_3\text{-2,4,6})(\text{thf})_3]$	142
5	$[\text{Li}(\text{SeC}_6\text{H}_2\text{-}t\text{-Bu}_3\text{-2,4,6})(\text{thf})_3]$	143
6	$[\text{Li}_2(\text{SC}_6\text{H}_3\text{Mes}_2\text{-2,6})_2(\text{Et}_2\text{O})_2]$	144
7	$[\text{Li}_2(\text{SePh})_2(\text{bipy})_2]$	32
8	$[\text{Li}_2(\text{SeC}_5\text{H}_4\text{N})_2(\text{bipy})_2]$	32
9	$[\text{Li}_2(\text{SC}(\text{O})\text{Ph})_2(\text{tmeda})_2]$	145
10	$[\text{Li}_2(\text{SC}(\text{SiMe}_3)_3)_2(\text{thf})_{3,5}]$	146
11	$[\text{Li}_2(\text{SCH}(\text{SiMe}_3)_2)_2(\text{thf})_4]$	146
12	$[\text{Li}_2(\text{SC}(\text{NHPh})\text{C}(\text{NR}_2)\text{CO}_2\text{Et})_2(\text{Et}_2\text{O})_2^b]$	156
13	$[\text{Li}_3(\text{SeC}_6\text{H}_2\text{-}t\text{-Bu}_3\text{-2,4,6})_3(\text{thf})_3]$	155
14	$[\text{Li}(\mu^2\text{-SPh})(\text{py})_2]_\infty$	140
15	$[\text{Li}(\mu^3\text{-SCH}_2\text{Ph})(\text{py})]_\infty$	140
<i>Complexes with Intramolecular Coordination</i>		
16	$[\text{Li}\{\text{Te}(\eta^5\text{-C}_5\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{dme})]$	152
17	$[\text{Li}_2(\text{SC}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{OMe})\text{-2})_2]$	151
18	$[\text{Li}_2(\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6})\text{I}(\text{thf})_2]$	151
19	$[\text{Li}_6(\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2})_6]$	151
20	$[\text{Li}_6(\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6})_6]$	151

^aPowder diffraction.

^b $\text{R}_2 = \text{Me}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2$.

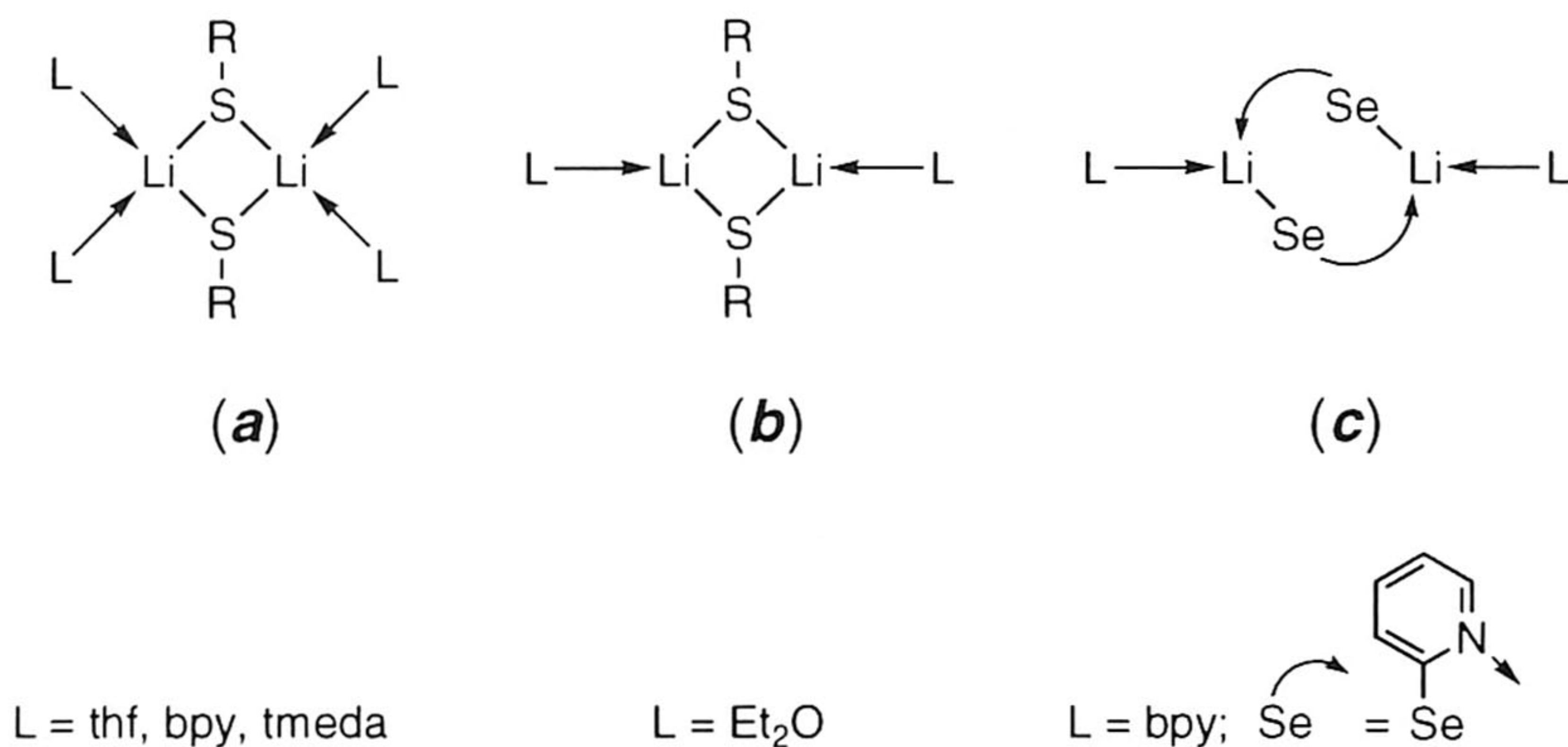


Figure 18. Dimeric lithium arenethiolates.

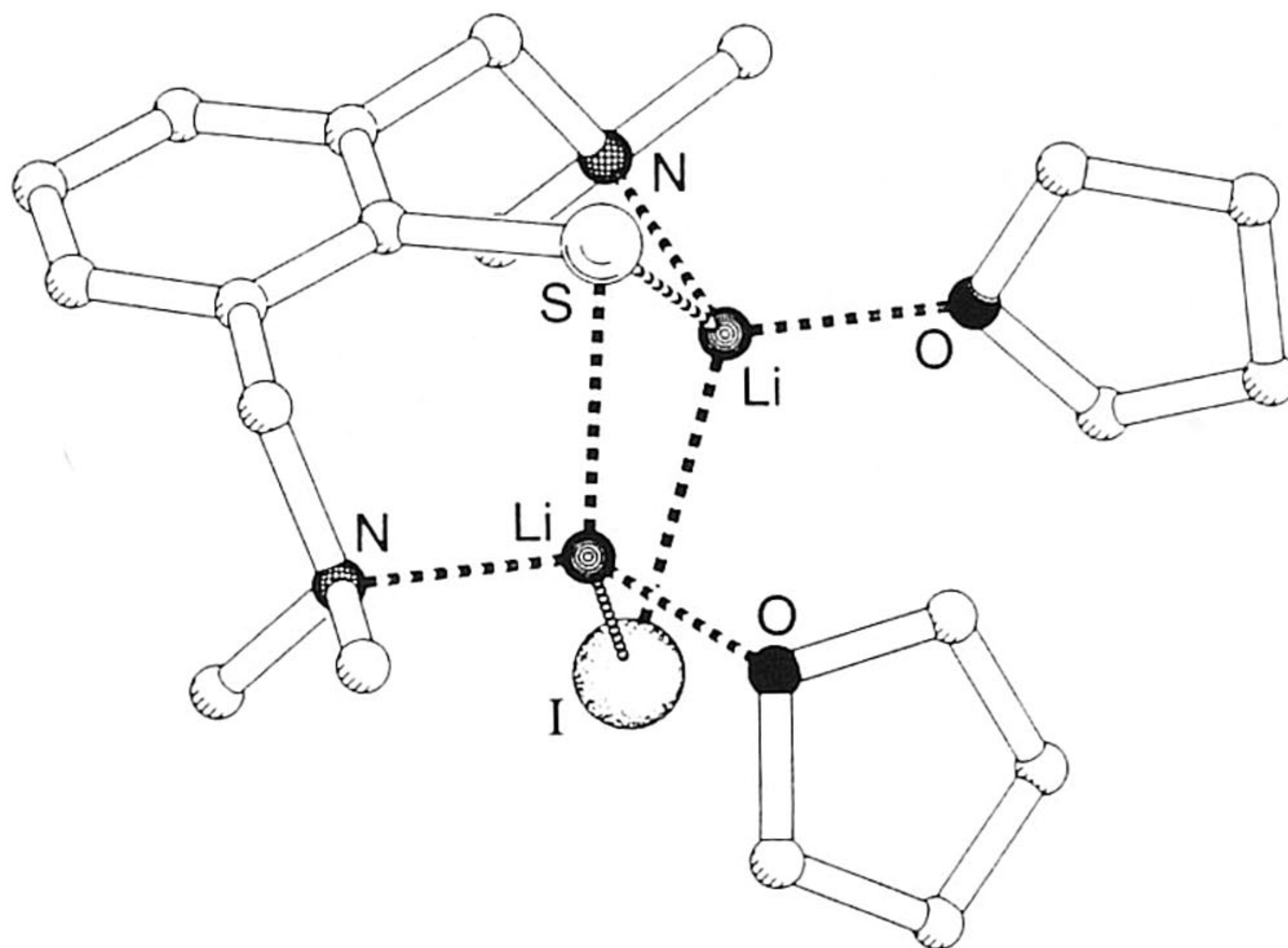


Figure 19. Mixed-arenethiolatolithium lithium halide species $[\text{Li}_2\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}\text{I}(\text{thf})_2]$ (hydrogen atoms are omitted for clarity).

It should be noted that, as is the case with the mixed-arenethiolatocopper copper halide aggregates, the metal halide unit forms part of an intimate assembly that produces one well-defined mixed aggregate.

2. Hexameric Complexes

There are no reported structures of lithium thiolate complexes with a tetrameric aggregation state. This situation contrasts sharply with the copper(I) thiolates where such aggregation states are well exemplified; pentameric lithium thiolate species are also unknown. However, hexameric structures are possible and can be formed when there is intramolecular coordination by the nitrogen donor functions in the arenethiolate ligand (151). This hexameric formulation has two structural appearances, namely, a flat 12-membered Li_6S_6 ring in $[\text{Li}\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}]_6$, which looks like a regular hexagon due to the T-shaped geometry of sulfur [Figs. 20(a) and 21] and, alternatively, a Li_6S_6 cage structure in $[\text{Li}\{\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}\}]_6$ in which two Li_3S_3 six-membered rings are connected by $\mu^3\text{-S}$ bonded arenethiolate ligands [Fig. 20(b)]. In both structural types, intramolecular coordination completes the tetrahedral coordination of the lithium atoms.

The latter hexanuclear structural type [Fig. 20(b)] is different from the copper(I) arenethiolate hexamers (Section II.C.5), since in these copper structures only $\mu^2\text{-S}$ bonded arenethiolate ligands are present, that is, the hexanuclear

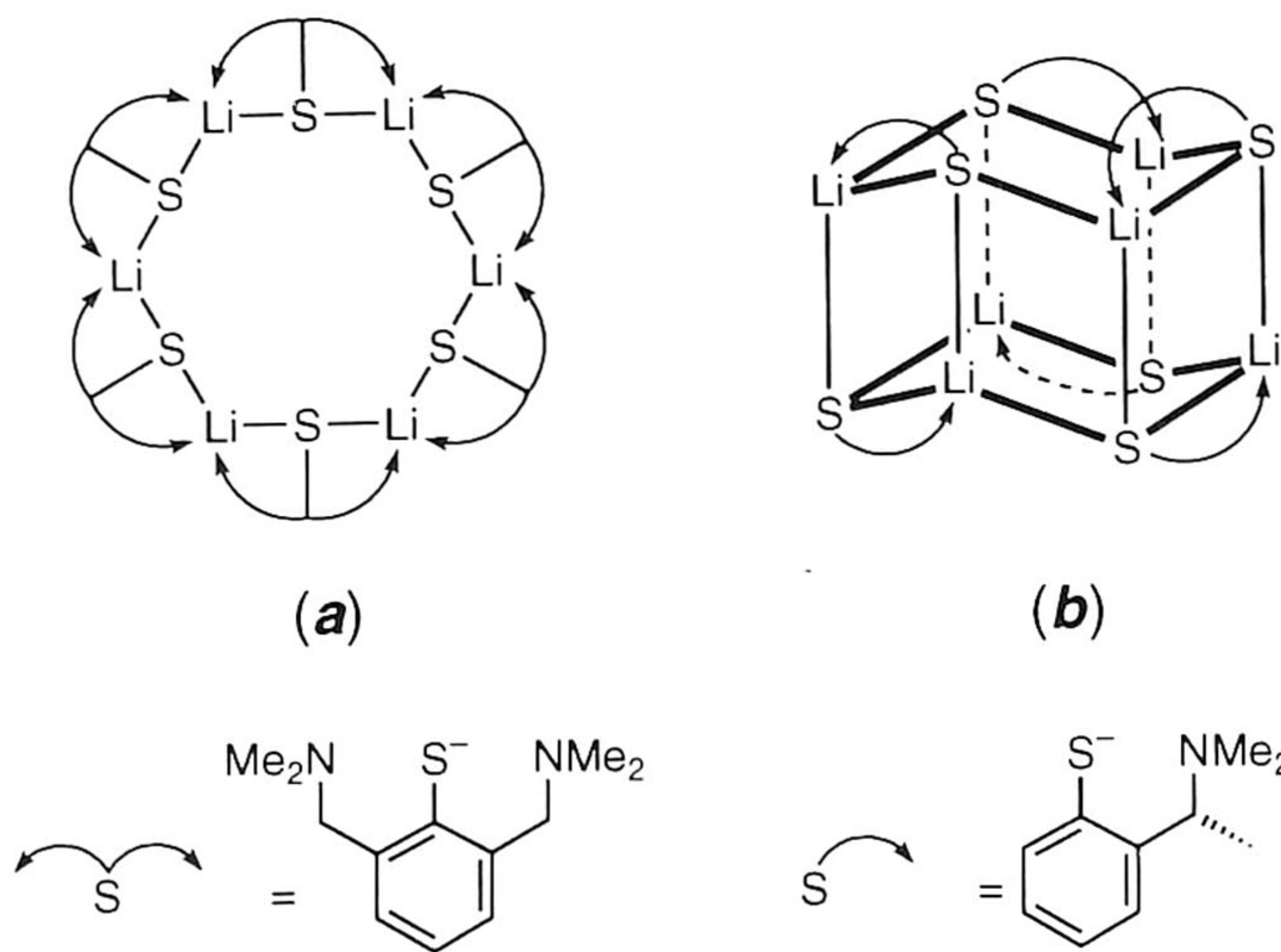


Figure 20. Hexameric lithium arenethiolates. (a) Planar Li_6S_6 12-membered ring structure. (b) Li_6S_6 cage structure.

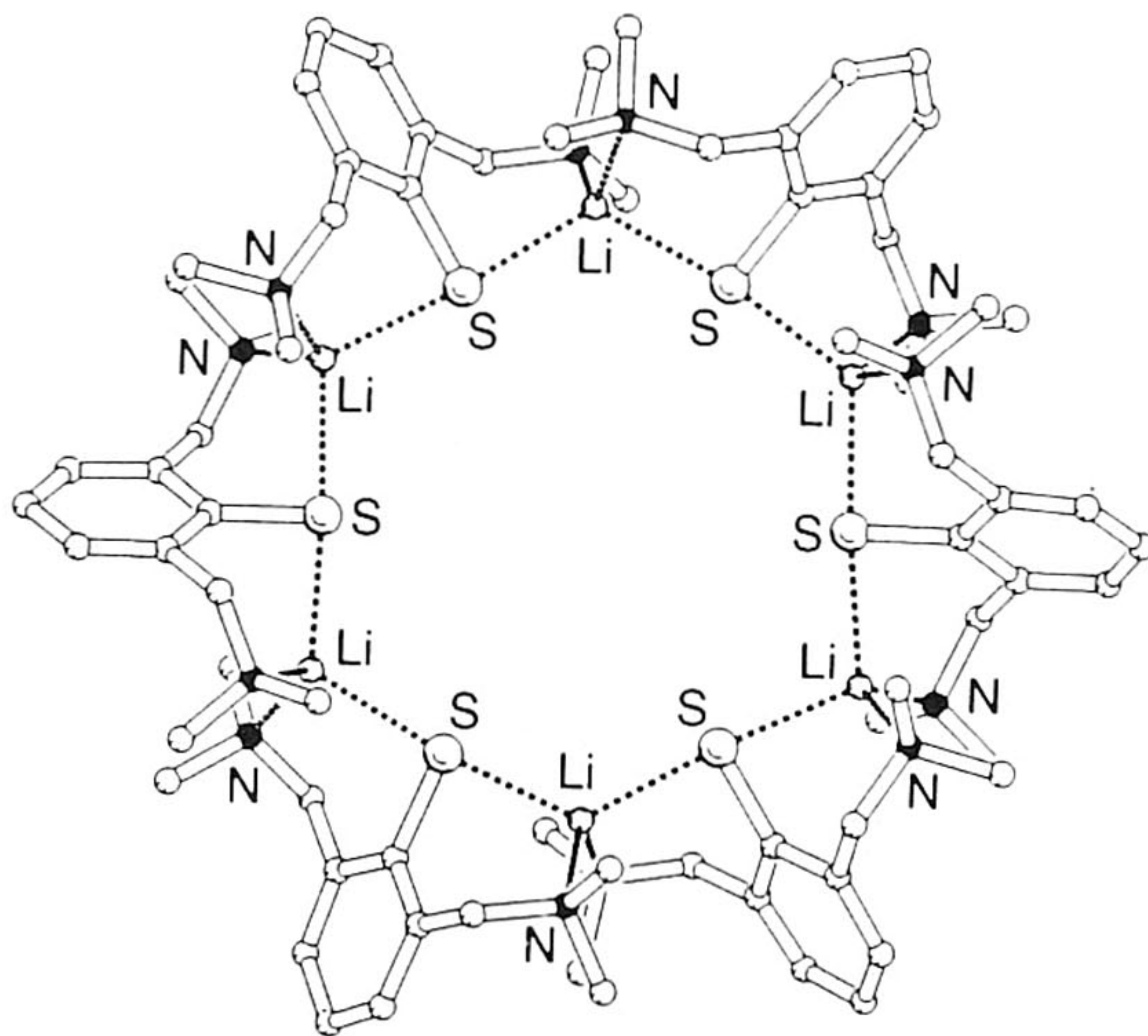


Figure 21. Molecular structure of planar hexanuclear $[\text{Li}_6\{\text{SC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}_6]$ (hydrogen atoms are omitted for clarity).

structure is brought about through intramolecular coordination from one Cu_3S_3 layer to the other.

The bonding mode of the sulfur atoms in lithium thiolate complexes is often not easily identifiable from the coordination geometry of these atoms (156). Ab initio calculations on the bonding in complexes $[\text{MSH}]$ (M = alkali and alkaline earth metal) indicate that this bonding is highly ionic (157).

3. Polymeric Complexes

As well as well-defined aggregates, there is ample evidence for polymeric lithium thiolate structures, and species that have been studied by X-ray diffraction techniques include $[\text{Li}(\text{SMe})]_n$, $[\text{Li}(\text{SPh})(\text{py})_2]_\infty$, and $[\text{Li}(\text{SCH}_2\text{Ph})(\text{py})]_\infty$ (see Table XIII). The latter two polynuclear structures are similar, but in the former structure, with two py ligands, the thiolate sulfur atoms bridge the lithium atoms in a μ^2 -fashion, whereas in the latter structure, with only one py, the sulfur atoms are involved in μ^3 -S bridges (Fig. 22). It is very striking that the structures resulting from coordination of two py ligands (i.e., polymeric ones) are very different from those obtained with two molecules of diethyl ether (i.e., dimeric ones). This result cannot be explained only by the Lewis-base strength of these ligands.

4. Mixed-Metal Lithium Thiolate Complexes

Interestingly, four examples exist of mixed-metal thiolate complexes in which one or more lithium thiolate moieties are present within an aggregate that also contains a lanthanide or actinide metal thiolate unit (Table XIV). These species

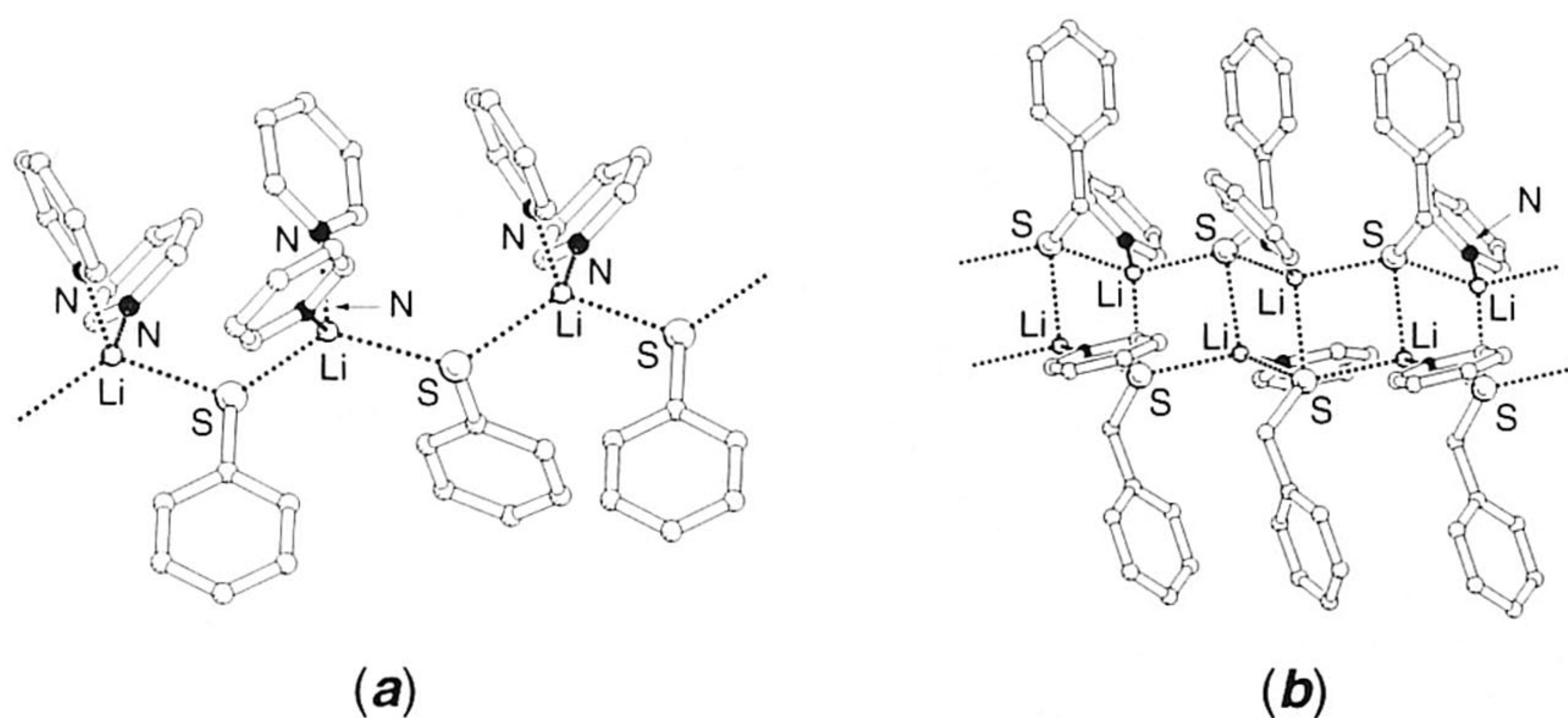


Figure 22. Molecular structures of $[\text{Li}(\mu^2\text{-SPh})(\text{py})_2]_\infty$ (a) and $[\text{Li}(\mu^3\text{-SCH}_2\text{Ph})(\text{py})]_\infty$ (b) (hydrogen atoms are omitted for clarity).

TABLE XIV
Structurally Characterized Mixed-Metal Lithium Thiolates

Entry	Compound	Reference
1	$[\text{Li}(\text{S}-t\text{-Bu})_2\text{Lu}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$	158
2	$[\text{Li}_3(\text{S}-t\text{-Bu})_6\text{Yb}(\text{tmeda})_3]$	159
3	$[\text{Li}_3(\text{S}-t\text{-Bu})_6\text{Sm}(\text{tmeda})_3]$	159
4	$[\text{Li}_4(\text{SCH}_2\text{CH}_2\text{S})_4\text{U}(\text{dme})_4]$	160

can be seen as lutetium, ytterbium, samarium, and uranium -ate complexes that are stabilized by lithium cations.

One should note that in these neutral monomeric complexes $[\text{Li}(\text{S}-t\text{-Bu})_2\text{Lu}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$ (158) (Fig. 23), $[\text{Li}_3(\text{S}-t\text{-Bu})_6\text{M}(\text{tmeda})_3]$ (M = Yb or Sm) (159), and $[\text{Li}_4(\text{SCH}_2\text{CH}_2\text{S})_4\text{U}(\text{dme})_4]$ (160) the Li atoms are still bonded to the thiolate ligands with corresponding Li—S distances of 2.44, 2.38, and 2.42 Å (average), respectively. In this area of *f*-block chemistry, the analogy between thiolates and halides does not hold well. For example, the incorporation of metal salts (e.g., NaCl) in lanthanum phenoxide complexes was reported and has a large influence on the overall structure of these species (161). In contrast, lithium arenethiolates $[\text{Li}(\text{SAr})]$, containing intramolecularly coordinating nitrogen-donor atoms, have been reported to react with YbCl_3 to form complexes $[\text{Yb}(\text{SAr})_2\text{Cl}]$ and $[\text{Yb}(\text{SAr})_3]$, where incorporation of lithium salts does not occur (162).

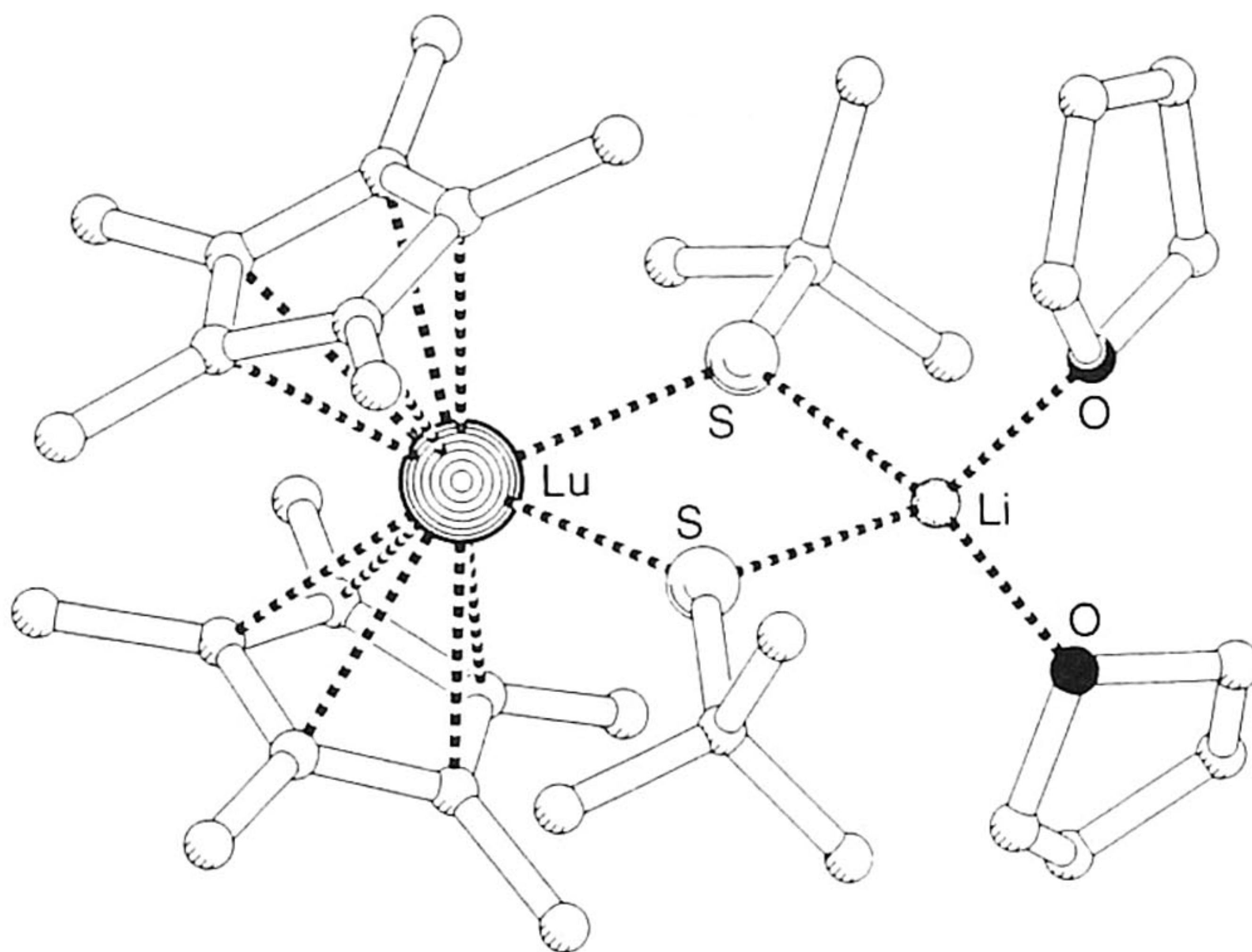


Figure 23. Molecular structure of $[\text{Li}(\text{S}-t\text{-Bu})_2\text{Lu}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$ (hydrogen atoms are omitted for clarity).

D. Structures of Magnesium Thiolates

Although magnesium arenethiolates, $\text{Mg}(\text{SAr})_2$, have long been known to be intermediates in the preparation of arenethiols by insertion of S_8 into the $\text{Mg}-\text{C}$ bond of diorganomagnesium reagents (150), it is only very recently that a few structures of these and related materials have appeared in the literature (Fig. 24). The first of these reports in 1992 was of the unprecedented aggregate $[\text{Mg}_2\{\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}\}_4\text{Cu}_4(\text{Mes})_4]$ formed by reaction of the copper(I) arenethiolate and mesitylcopper [see Fig. 24(d)] (20). Table XV lists the few structurally characterized magnesium thiolate complexes that are known.

In the presence of Lewis bases (e.g., thf or Et_2O), magnesium arenethiolate complexes are encountered as monomeric species $[\text{Mg}(\text{SR})_2\text{L}_2]$ [Fig. 24(a)] in which the coordination geometry of magnesium is tetrahedral. However, there is only one example of a magnesium arenethiolate in which there are no additional neutral donor ligands, and this complex, $[\text{Mg}_2(\text{SC}_6\text{H}_2\text{Ph}_3\text{-2,4,6})_4]$, has a dimeric structure [Fig. 24(b)], which was described as having three-coordinate

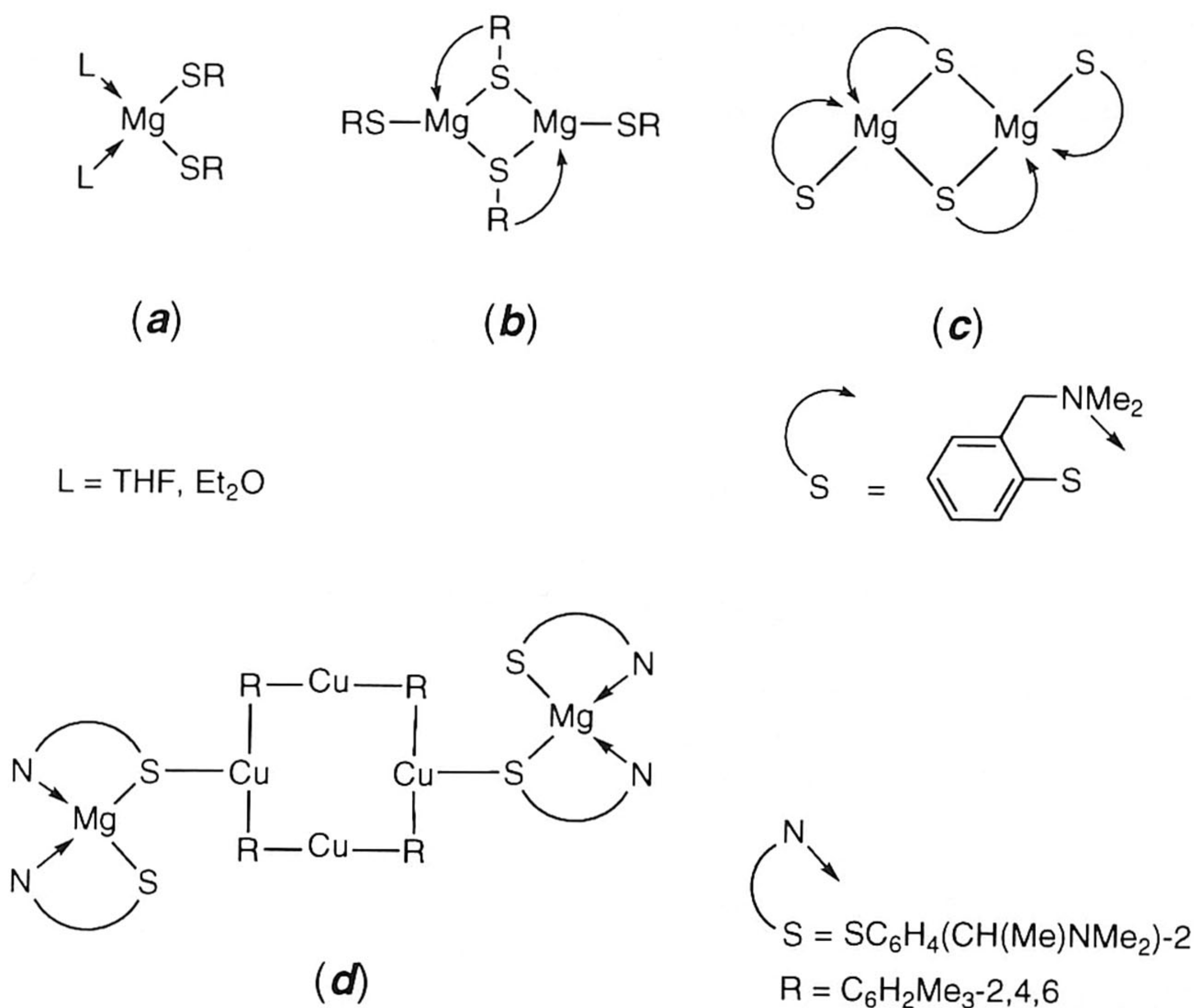


Figure 24. General structures of magnesium arenethiolates.

TABLE XV
Structurally Characterized Magnesium Thiolates and Selenolates

Entry	Compound	Reference
1	$[\text{Mg}(\text{SC}_6\text{H}_2\text{-}i\text{-Bu}_3\text{-2,4,6})_2(\text{Et}_2\text{O})_2]$	147
2	$[\text{Mg}(\text{SeC}_6\text{H}_2\text{-}i\text{-Bu}_3\text{-2,4,6})_2(\text{thf})_2]$	147
3	$[\text{Mg}_2(\text{SC}_6\text{H}_2\text{Ph}_3\text{-2,4,6})_4]$	147
4	$[\text{Mg}_2(\text{SC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2})_4]$	153
5	$[\text{Mg}_2\{\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2\text{-2})\}_4\text{Cu}_4(\text{Mes})_4]$	20

magnesium centers (148). However, since there is an additional intramolecular interaction between magnesium and one of the ortho phenyl substituents, we feel that this species is better described as having a distorted pseudotetrahedral (four-coordinate) geometry.

Interestingly, the magnesium bis(arenethiolate) complex based on the [2-(dimethylamino)methyl]phenylthiolate ligand that contains N-donor ortho-substituents, is not a monomer, but is instead a dimer $[\text{Mg}_2(\text{SC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2})_4]$ [Figs. 24(c) and 25] in which the magnesium atoms are five coordinate in the solid state (153). However, from variable temperature ^1H NMR experiments as well as from cryoscopic molecular weight determinations it was concluded that the latter species is a monomer in solution, that is, the magnesium atoms are now four coordinate (153).

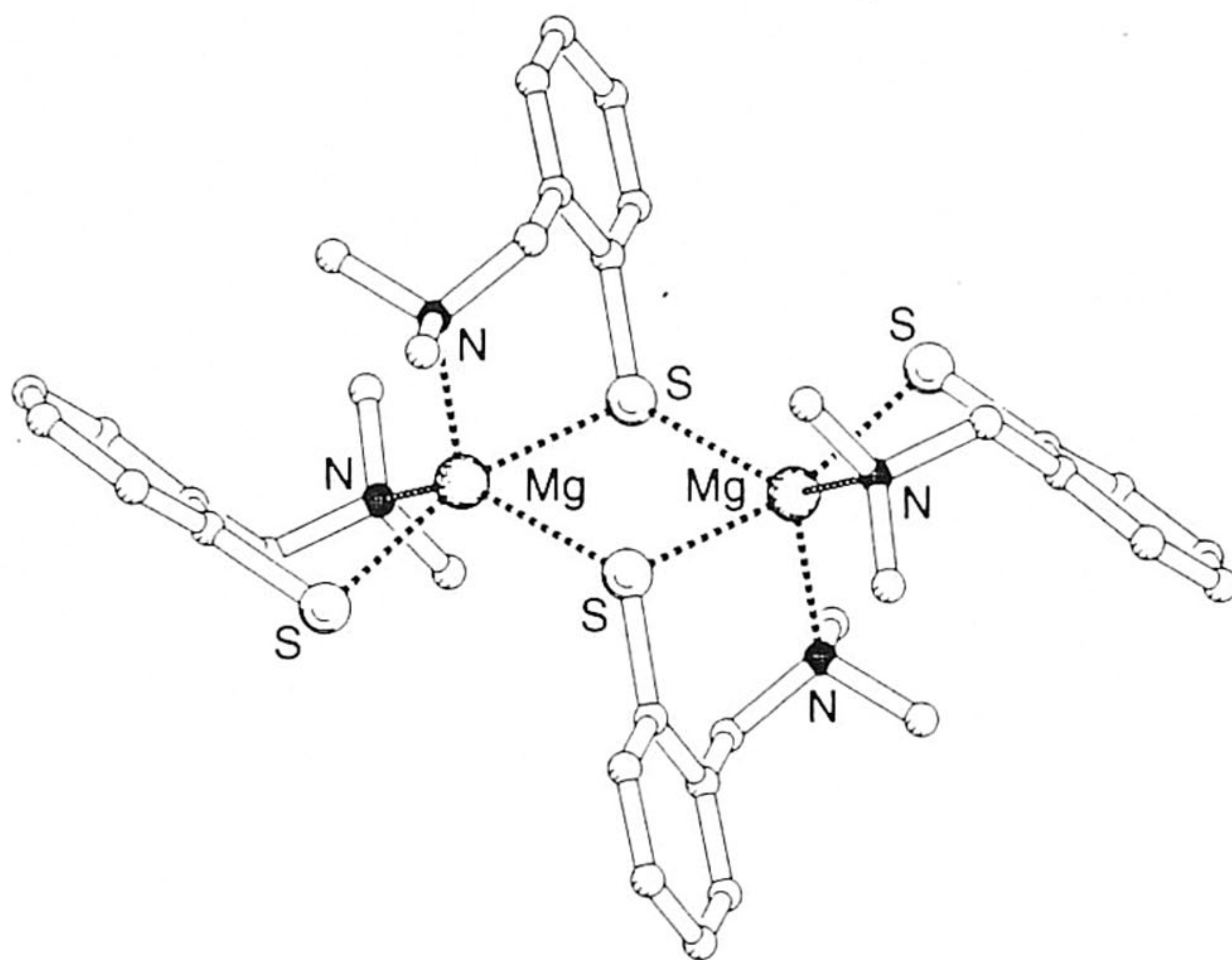


Figure 25. Molecular structure of $[\text{Mg}_2(\text{SC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2})_4]$ (hydrogen atoms are omitted for clarity).

IV. CONCLUSIONS

This chapter has clearly shown that the structures of copper(I), lithium, and magnesium thiolate complexes and, more especially, the aggregation state of these species are highly dependent on the nature of the thiolate ligand used. In particular, the use of thiolate ligands with potential for intramolecular coordination seems to be especially advantageous since this leads to a corresponding complex with a well-defined solid state and solution structure. Furthermore, the organic backbone, connecting the sulfur atom to the coordinating donor atom, plays an important role in the aggregate (self-)assembling process. This process is exemplified by the structures of trimeric $[\text{Cu}\{\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}\}]_3$ and nonameric $[\text{Cu}(\text{S-1-C}_{10}\text{H}_6\text{NMe}_2\text{-8})]_9$, where the more rigid naphthalene backbone leads to the formation of a higher aggregate. In the latter aggregate, the potential for coordination of the dimethylamino groups seems less important as only six of the nine available nitrogen atoms coordinate to copper. Higher aggregates are thus less influenced by intramolecularly or auxiliary coordinating ligands: in the largest reported aggregate, that is, $[\text{Cu}(\text{SC}_6\text{H}_4\text{SiMe}_3\text{-2})]_{12}$, coordinating ligands are even completely absent.

As far as the mixed-organo(arenethiolato)copper(I) aggregates are concerned, it seems that there are two basic building blocks, namely, a trinuclear $[\text{Cu}_3(\text{SAr})_2(\text{R})]$ and a tetranuclear $[\text{Cu}_4(\text{SAr})_2(\text{R})_2]$ entity, which are hardly influenced by the nature of the thiolate ligand. These species are more dependent on the nature of the organic grouping R (alkyl vs. aryl) and are thus best classified as organocopper copper (pseudo)halide aggregates (26b).

In the area of mixed-arenethiolatocopper copper halide aggregates, there is still much exploration to be done since so far only two species are known. However, these species have structures that combine several features of both copper arenethiolates and copper halides and may therefore become interesting model compounds in the near future.

The most evident characteristic of thiolate ligands, not only in the structure of the copper(I) thiolates, but also in those of lithium and magnesium thiolates, is that they are, through the variable hybridization of sulfur, ideally suited for bridging both equivalent and nonequivalent metal centers. This ability of sulfur to adapt to the further ligand environment of a metal center means that resulting aggregate structures and the (self-)assembling process are influenced primarily by steric factors (e.g., ligand rigidity) and the presence of other potentially coordinating groupings. The latter can be either thiolate substituents, where chelate ring size also plays a role, or auxiliary donor ligands.

These characteristics of thiolate ligands means they are ideally suited for applications where two or more metal centers are to be brought together in a well-defined way. Such is the case in a number of metal complex catalyzed organic reactions where organometallic reagents are employed for C—C cou-

pling reactions (2, 5–25). The successful use of arenethiolates for copper(I) catalyzed reactions, mentioned in the introduction, provides a specific example that illustrates the validity of this conclusion. Arenethiolates would seem to be particularly useful in that the aryl nucleus can be easily substituted to provide not only specific donor-atom containing groups with correctly chosen properties, but also chiral information. An example of this is $\text{SC}_6\text{H}_4((R)\text{-CH}(\text{Me})\text{NMe}_2)\text{-2}$, which has been used, among others, as a nontransferable group in enantioselective conjugate 1,4-addition reactions of Grignard reagents to benzylidene acetone and in regio- and enantioselective allylic substitution reactions (2, 20–25).

Based on the structural characteristics of thiolate ligands, as summarized in this chapter, we were able to make a reasonable postulate for the structure of the key intermediate in the latter catalytic system as one where the thiolate ligand bridges a heterodinuclear (Cu or Mg) unit (163). Molecular modeling shows that this postulated system is realistic and that the spatial orientation of the $\text{CH}(\text{Me})\text{NMe}_2$ ortho substituent is important in determining the aggregate stereochemistry that is important for relaying the information of the chiral center, so that *re*- and *si*-coordination of the enone substrate is well discriminated (163). Support for this type of structural postulate (Fig. 26) was also obtained from EXAFS measurements on cuprates derived from a copper(I) arenethiolate $[\text{Cu}(\text{SAr})]$ and an organometallic reagent (LiR or RMgI) (164). These measurements indicate that in the key intermediate the nitrogen coordination is to magnesium rather than to copper and that a magnesium atom is in close proximity to copper (164).

It is apparent that thiolate chemistry of Cu, Li, and Mg is a field of significant current interest and that structural studies in this area are very relevant to the development of new and better catalytic systems. We hope that this chapter, in bringing the most important structural elements to light, will be of use in stimulating further research in this area.

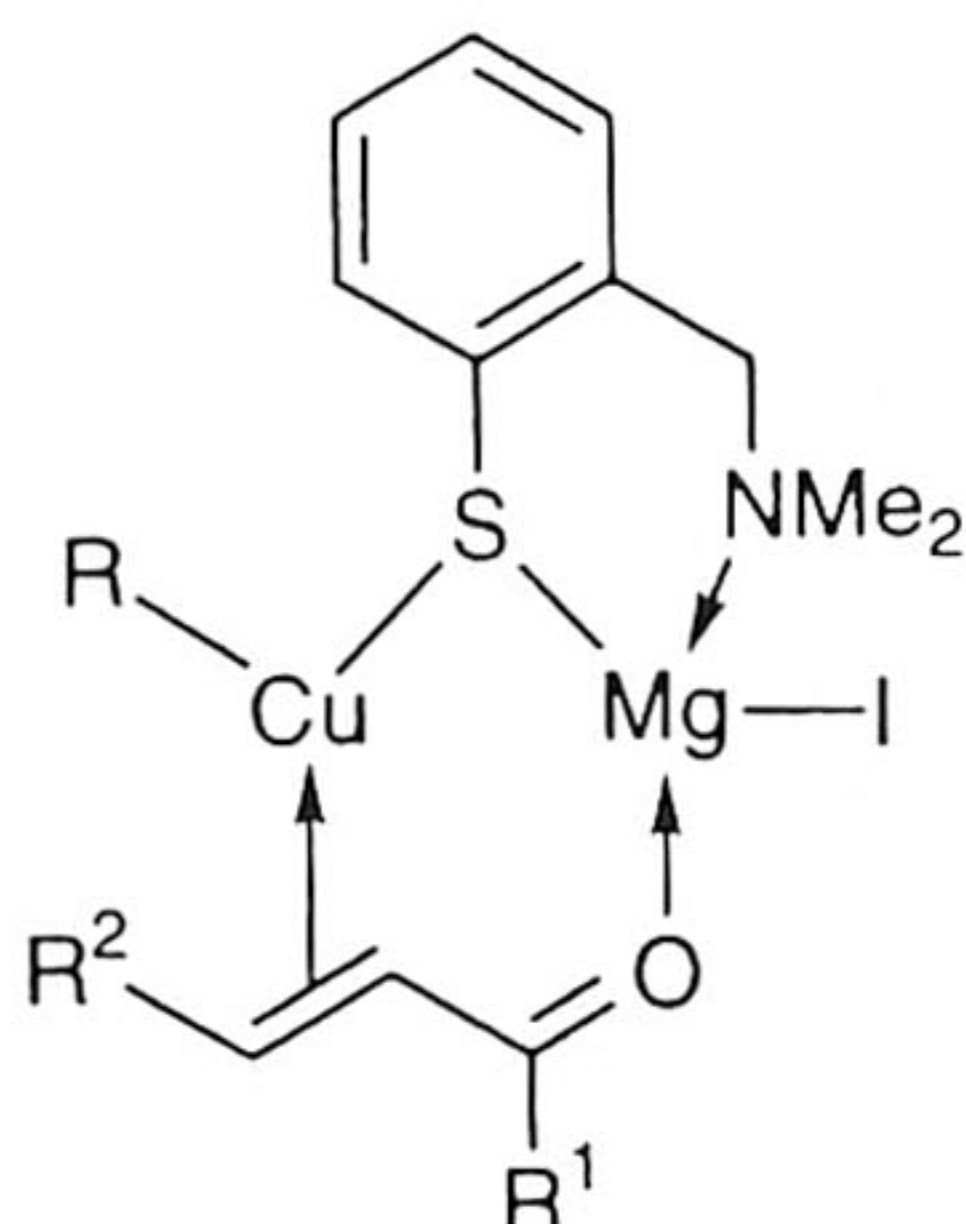


Figure 26. Proposed key-intermediate in copper(I) arenethiolate catalyzed reactions.

NOTE ADDED IN PROOF

After preparation of this manuscript, the following structure was brought to our attention: The complex $[\text{Cu}_4(\text{SCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{-2-C}_5\text{H}_4\text{N})_4]$ contains a flattened Cu_4 tetrahedron with bridging sulfur atoms and with the secondary amine nitrogen atoms coordinating to copper (Fig. 7). Interestingly, the 2-pyridyl groups participate in a hydrogen-bonding network with the metal-bound secondary amine groups (165).

ABBREVIATIONS

bpy	2,2'-Bipyridine
DED	1,1-Dicarboethoxy-2,2-ethylenedithiolate
dme	1,2-Dimethoxyethane
dmit	4,5-Dimercapto-1,3-dithiole-2-thionato-2
dmpymt	4,6-Dimethylpyrimidine-2-thionate
dppm	Bis(diphenylphosphino)methane, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$
DTS	Dithiosquarate
EXAFS	Extended X-ray absorption fine structure
^1H NMR	Proton nuclear magnetic resonance
Me(OH)pymt	4-Hydroxy-6-methylpyrimidine-2-thionate
Me_2phen	2,9-Dimethyl-1,10-phenanthroline
Mes	Mesityl = 2,4,6-trimethylphenyl = $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$
mimt	1-Methylimidazoline-2-thionate
phen	1,10-Phenanthroline
py	Pyridine
Simid	1-Methylimidazoline-2-thionate
Squin	Quinoline-2-thionate
thf	Tetrahydrofuran (ligand)
THF	Tetrahydrofuran (solvent)
tht	Tetrahydrothiophene
tmeda	N,N,N',N'-Tetramethylethylenediamine

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