Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 252 (2008) 2026–2049

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Synthetic and structural chemistry of groups 11 and 12 metal complexes of the zwitterionic ammonium thiolate ligands

Xiao-Yan Tang[a], Hong-Xi Li[a], Jin-Xiang Chen[a], Zhi-Gang Ren[a], Jian-Ping Lang[a,b,*]

[a] *School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, PR China*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China*

Received 27 August 2007; accepted 4 November 2007
Available online 21 February 2008

Contents

Abbreviations: 2-abSH, 2-aminobenzenethiol; damp, 2-(*N*,*N*-dimethylaminomethyl)phenyl; DMF, *N*,*N*′-dimethylformamide; DMSO, dimethylsulfoxide; dtdp, 4,4′-dithiodipyridine; Et_3N, triethylamine; Hdamp, 2-(*N*,*N*-dimethylammonium)methylphenyl; 2-mepSH, 1-methyl-2(2-mercaptoethyl)piperidine; 3-mmpSH, 1-methyl-3(mercaptomethyl)piperidine; 4-mpSH, 4-mercapto-1-methylpiperidine; PPh_3, triphenylphosphine; ptp, 1-(4-pyridyl)-4-thiopyridium; 4-pySH, pyridine-4-thiol; 2-SabH, 2-ammoniobenzonethiolate; 2-SmepH, 1-methylpiperidium-2(2-ethylthiolate); 3-SmmpH, 1-methylpiperidium-3-methylthiolate; 4-SmpH, 1-methylpiperidium-4-thiolate; 4-Spy, pyridine-4-thiolate; 4-SpyH, pyridium-4-thiolate; SthiazH, 1,3-thiazolium-2-thiolate; 2-StpmH, 3,4,5,6-tetrahydropyrimidium-2-thiolate; Tab, 4-(trimethylammonio)benzenethiolate; TabH, 4-(trimethylammonio)benzenethiol; tde, 2,2′-thiodiethanol; thiazSH, 2-mercapto-1,3-thiazoline; tht, tetrahydrothiophene; tmt, tetramethylthiourea; tmtat, 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate; 2-tpmSH, 2-mercapto-3,4,5,6-tetrahydropyrimidine.

* Corresponding author at: School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, PR China. Tel.: +86 512 65882865; fax: +86 512 65880089.

E-mail address: jplang@suda.edu.cn (J.-P. Lang).

doi:10.1016/j.ccr.2007.11.001

Abstract

The chemistry of metal complexes of the zwitterionic ammonium thiolates has expanded dramatically in the recent years. This review is intended to summarize the synthesis and crystal structures of groups 11 and 12 metal zwitterionic ammonium thiolate complexes. Seven methods for the synthesis of these metal complexes of the zwitterionic ammonium thiolates are outlined: proton transfer reaction, precursor reaction, ligand exchange reaction, oxidation–reduction reaction, solid-state reaction, electrochemical reaction and hydro(solvo)thermal reaction. These metal complexes of the zwitterionic ammonium thiolates are classified according to the number of metal atoms; their specific structures are briefly discussed.

Keywords: Zwitterionic ammonium thiolate; Synthesis; Structure; Group 11 metal complex; Group 12 metal complex

1. Introduction

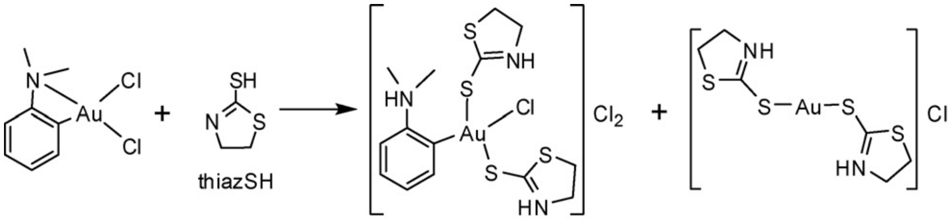
Interest in metal thiolates continues to be motivated by their remarkable structural diversity [1–7], their potential applications as precursors for advanced materials [8–16] and as structural and functional models for bioinorganic medicines [17–25] and active sites of some metalloproteins and metalloenzymes [26–37]. A large number of metal complexes with alkyl- or aryl-thiolates have so far been synthesized. Several excellent reviews covering the synthetic and structural aspects and important applications of these complexes have been published [38–48]. Another family of metal complexes of N-donor-containing thiolates has also received significant attention, namely, those that can act as ambidentate ligands capable of coordinating at metal centers *via* either sulfur or nitrogen or both atoms [49–55]. However, when the N atom of such a ligand is protonated or alkylated, it can be converted into a so-called zwitterionic ammonium thiolate carrying $-NH_3^+$, $-NR_2H^+$, or $-NR_3^+$ group, which is to some extent similar to cysteine, a well-known zwitterionic ammonium thiolate. Existing in various metalloproteins and metalloenzymes [56–58], cysteine is found to combine with different metal ions to form many intriguing metal active sites, which activate many chemists to employ different organic zwitterionic ammonium thiolates to mimic them [59–62]. In fact, many encouraging results in this respect have been reported in various journals over the years. However, to the best of our knowledge, there is no review covering the synthetic techniques and crystal structures of metal zwitterionic ammonium thiolate complexes. Therefore, this present review will summarize synthetic and structural aspects of the zwitterionic ammonium thiolate complexes containing metals of groups 11 and 12 (Cu(I), Ag(I), Au(I), Zn(II), Cd(II), Hg(II)). In the past decades, some synthetic approaches to metal complexes of zwitterionic ammonium thiolates have been developed. They are (i) proton transfer reaction of metal salts with N-donor-containing thiols [63–80] or the similar reaction in the presence of bases [81–89] or acids [90–98], (ii) precursor reaction [69,82,83], (iii) ligand exchange reaction [99–101], (iv) oxidation–reduction reaction [102], (v) solid-state reaction of metal acetate with thiols [103], (vi) electrochemical reaction of metal with thiols [98], and (vii) hydro(solvo)thermal reaction [104–107]. A great number of mono-, di-, tri-, tetra-, penta-, hexa-, high-nuclearity complexes, and polymeric metal complexes with various zwitterionic ammonium thiolates have been isolated based on the aforementioned methods. Therefore, we outline general methods to groups 11 and 12 metal zwitterionic ammonium thiolates and describe their pertinent structural characteristics based on the data searched from 2007's Cambridge Structural Database (CSD). Some heterocyclic aminothiols exist in the thione form, not as zwitterionic ammonium thiolate form, and they bind to metal centers *via* S atom of thione [108,109]. These metal complexes are not included taking the scope and length of this review into account.

2. Methods of preparation

There are seven typical methods for the synthesis of metal complexes of zwitterionic ammonium thiolates: proton transfer reaction, precursor reaction, ligand exchange reaction, oxidation–reduction reaction, solid-state reaction, electrochemical reaction, and hydro(solvo)thermal reaction. In the following subsections, we briefly describe the characteristics for each method.

2.1. Proton transfer reaction

The proton transfer reaction of metal salts with aminothiols is employed to synthesize metal complexes of zwitterionic ammonium thiolates. In fact, some of these thiols exist in solution as



Scheme 1.

an equilibrium mixture with the non-ionized thione and zwitterionic thiolate resonance forms. The aminothiol or the ammonium thiolate or the thione form depends very much upon the phase, i.e. solid state or solution and in the latter case also on the type of solvent. The proton transfer reaction is involved in the cleavage of the sulfydryl (S–H) followed by transferring its proton to N-donor site. Thus, the thiol with the deprotonated sulfydryl and the resulting ammonium group appears zwitterionic. According to the reaction media conditions, proton transfer reaction may be sub-classified into three groups: direct reaction of metal salts with thiols, reaction of metal salts with thiols under the presence of bases or acids.

2.1.1. *Direct reaction of metal salts with thiols*

As indicated by Eq. (1), several dinuclear complexes containing zwitterionic ammonium thiolate 4-SpyH ligand, $[CuX(PPh_3)(4\text{-SpyH})]_2$ (X = Cl, Br, I) [63] were readily isolated from reactions of $[Cu(PPh_3)X]_4$ with 4-pySH:

$$[Cu(PPh_3)X]_4 + 4(4\text{-pySH}) \rightarrow 2[CuX(PPh_3)(4\text{-SpyH})]_2 \quad (X = Cl, Br, I) \qquad (1)$$

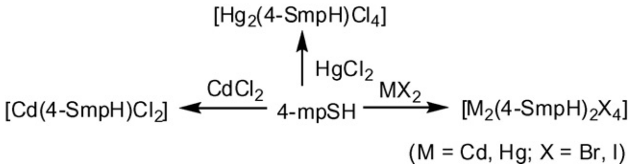
In the case of gold, protonolysis reactions of $[Au(damp\text{-}C^1,N)Cl_2]$ with thiazSH gave rise to a mixture of $[Au(Hdamp\text{-}C^1)(SthiazH)_2Cl]Cl_2$ and $[Au(SthiazH)_2]Cl$ (Scheme 1) [64]. During the reaction, one chlorine atom was preferably displaced together with the cleavage of Au–N bond and protonation of the dimethylamino group.

For group 12 metals, a number of mononuclear complexes $[M(4\text{-SpyH})_4](ClO_4)_2$ (M = Zn, Cd, Hg) and $[M(4\text{-Spy})_2(4\text{-SpyH})_2]$ (M = Cd, Hg) were obtained from reactions of $M(ClO_4)_2{\cdot}nH_2O$ (M = Zn, n = 4; M = Cd, Hg, n = 6) with 4-pySH (Eqs. (2) and (3)) [65]:

$$M(ClO_4)_2 \cdot nH_2O + 4(4\text{-pySH}) \xrightarrow{MeOH} [M(4\text{-SpyH})_4](ClO_4)_2 + nH_2O \quad (M = Zn, n = 4; M = Cd, Hg, n = 6) \qquad (2)$$

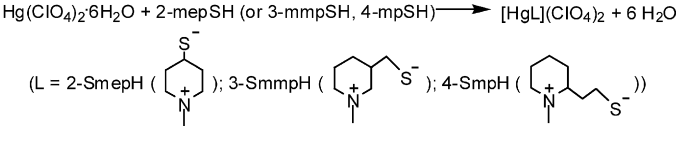
$$M(ClO_4)_2 \cdot 6H_2O + 4(4\text{-pySH}) \xrightarrow{DMSO/MeOH} [M(4\text{-SpyH})_2(4\text{-Spy})_2] + 6H_2O \quad (M = Cd, Hg) \qquad (3)$$

Mononuclear complexes $[HgL](ClO_4)_2$ (L = 2-SmepH, 3-SmmpH, 4-SmpH) could be prepared from stoichiometric reactions of $Hg(ClO_4)_2{\cdot}6H_2O$ with the corresponding thiols (2-mepSH, 3-mmpSH and 4-mpSH) (Eq. (4)) [66]. Treatment of ZnX_2 (X = Cl, Br, I) with a solution of $[4\text{-mpSH}]{\cdot}HCl$ in



Scheme 2.

H_2O produced $[Zn_2(4\text{-SmpH})_2X_4]$ (Eq. (5)) [67,68]. In addition, a family of $[M_2(4\text{-SmpH})_2X_4]$ (M = Cd, Hg; X = Br, I), $[Hg_2(4\text{-SmpH})Cl_4]$, and $[Cd(4\text{-SmpH})Cl_2]$ were prepared by the addition of MX_2 to the solution of the stoichiometric amount of 4-mpSH in MeOH (Scheme 2). In the case of HgI_2, slight excess NaI was employed to make HgI_2 soluble, forming $[Hg_2(4\text{-SmpH})_2I_4]$ [68].



(4)

$$2ZnX_2 + 2[4\text{-mpSH}] \cdot HCl \xrightarrow{H_2O} [Zn_2(4\text{-SmpH})_2X_4] + 2HCl \quad (X = Cl, Br, I) \qquad (5)$$

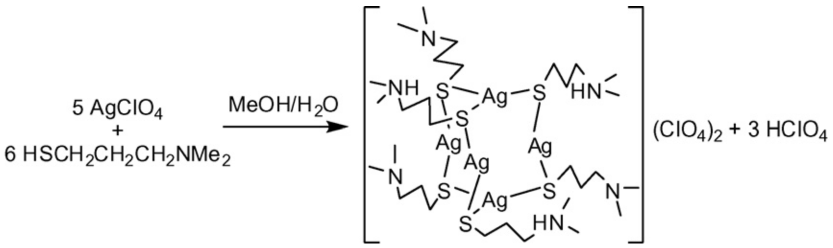
The complex $[Hg(Tab)_2](PF_6)_2$ was isolated in an almost quantitative yield by mixing $Hg(OAc)_2$ with $TabHPF_6$ (Eq. (6)) [69], whereas the analogous reactions of $HgCl_2$ with 2-abSH yielded $[HgCl(\mu\text{-}Cl)(2\text{-SabH})]_2$ [70] (Eq. (7)):

$$Hg(OAc)_2 + 2TabHPF_6 \rightarrow [Hg(Tab)_2](PF_6)_2 + 2HOAc \qquad (6)$$

$$2HgCl_2 + 2(2\text{-abSH}) \rightarrow [HgCl(\mu\text{-}Cl)(2\text{-SabH})]_2 \qquad (7)$$

For penicillamine, the polymeric complex $\{[CdBr(SCMe_2CH(NH_3)COO)H_2O]{\cdot}2H_2O\}_n$ was isolated from reactions of $CdBr_2{\cdot}4H_2O$ with excess D,L-penicillamine in aqueous ethanol (Eq. (8)) [71], while the trinuclear complex $[(\mu_3\text{-}Cl)\{HgSCMe_2CH(NH_3)COO\}_3]_2(\mu\text{-}Cl)_3{\cdot}(H_2O)_2{\cdot}(H_2O{\cdot}Cl)_3$ was prepared from reactions of $HgCl_2$ with equimolar D-penicillamine in EtOH/H_2O (Eq. (9)) [72]. Similar reactions using D,L-penicillamine yielded crystals giving the same X-ray diffraction pattern, indicating that identical or enantiomorphous crystals were obtained:

$$CdBr_2 \cdot 4H_2O + \text{D, L-pencilliamine} \xrightarrow{EtOH/H_2O} \{[CdBr(SCMe_2CH(NH_3)COO)H_2O] \cdot 2H_2O\}_n \qquad (8)$$



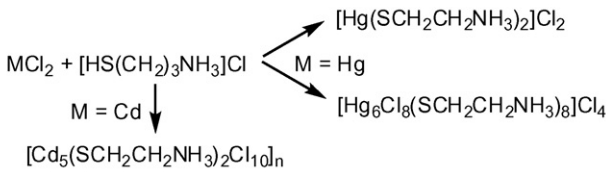
Scheme 3.

$$\mathrm{HgCl_2} + \text{D-pencilliamine} \xrightarrow{\mathrm{MeOH/H_2O}} [(\mu_3\text{-Cl})\{\mathrm{HgSCMe_2CH(NH_3)COO}\}_3]_2 \times (\mu\text{-Cl})_3 \cdot (\mathrm{H_2O})_2 \cdot (\mathrm{H_2OCl})_3 \tag{9}$$

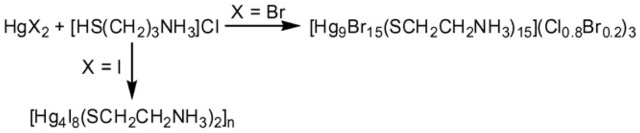
Polymeric complexes $[MX_2\{S(CH_2)_3NHMe_2\}]_n$ (M = Zn, Cd, Hg; X = Cl, Br) could be produced by reactions of stoichiometric amounts of MX_2 (M = Zn, Cd, Hg; X = Cl, Br) with $HS(CH_2)_3NMe_2$ (Eq. (10)) [73–75]. However, reactions of $AgClO_4$ with $HSCH_2CH_2CH_2NMe_2$ in a molar ratio of 1:2–3 in $MeOH/H_2O$ produced a pentanuclear complex $\{Ag_5[S(CH_2)_3NHMe_2]_3[S(CH_2)_3NMe_2]_3\}(ClO_4)_2$ (Scheme 3) [76]:

$$\mathrm{MX_2 + HS(CH_2)_3NMe_2 \rightarrow [MX_2\{S(CH_2)_3NHMe_2\}]_n}$$
$$(\mathrm{M = Zn, Cd, Hg; X = Cl, Br}) \tag{10}$$

Finally, a family of metal zwitterionic thiolate complexes could be synthesized by the reactions of metal salts with cysteamine hydrochloride. For instance, treatment of $CdCl_2$ with 2 equiv. of cysteamine hydrochloride in H_2O gave rise to a polymeric complex $[Cd_5(SCH_2CH_2NH_3)_2Cl_{10}]_n$ (Scheme 4) [77]. However, analogous reactions of $HgCl_2$ with cysteamine hydrochloride in water produced either a mononuclear complex $[Hg(SCH_2CH_2NH_3)_2]Cl_2$ [78] or a hexanuclear complex $[Hg_6Cl_8(SCH_2CH_2NH_3)_8]Cl_4$ [79] (Scheme 4). In the case of HgX_2 (X = Br, I), a nonanuclear complex $[Hg_9Br_{15}(SCH_2CH_2NH_3)_{15}](Cl_{0.8}Br_{0.2})_3$ [79] and a polymeric complex $[Hg_4I_8(SCH_2CH_2NH_3)_2]_n$ [80] were separated, respectively (Scheme 5).



Scheme 4.



Scheme 5.

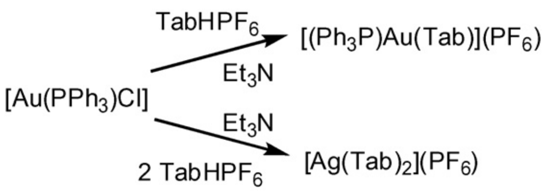
2.1.2. *Reaction of metal salts with thiols under the presence of bases*

In some reactions, the zwitterionic thiolate ligands were initially formed from the reactions of corresponding thiols with certain inorganic or organic bases and then reacted with metal salts. In these reactions Et_3N was preferably used. For example, the reactions of $[Au(PPh_3)Cl]$ with 1 or 2 equiv. of $TabHPF_6$ in the presence of excess Et_3N formed different mononuclear complexes $[Au(Ph_3P)(Tab)](PF_6)$ [81] and $[Ag(Tab)_2](PF_6)$ [82] (Scheme 6). Similar reactions of AuI with $TabHPF_6$ in DMF/MeOH afforded a dinuclear complex $[Au(Tab)_2]_2I_2$ (Eq. (11)) [83]. Polymeric complexes $[Ag_6Br_6(2\text{-}StpmH)_6]_n$ and $\{[Ag_4(2\text{-}StpmH)_6](NO_3)_4\}_n$ were obtained *via* reactions of AgBr (or $AgNO_3$) with tpmSH in DMSO under the presence of excess Et_3N (Scheme 7) [84]:

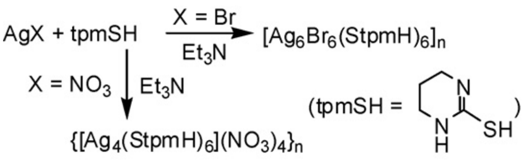
$$\mathrm{2AuI + 2TabHPF_6 \xrightarrow{Et_3N} [Au(Tab)_2]_2I_2} \tag{11}$$

Sodium hydroxide was also employed in the reactions of metal salts with thiols. For instance, reactions of $M(OAc)_2$ (M = Zn, Cd) with $[HS(CH_2)_3NMe_3](PF_6)$ in the presence of NaOH produced $[M\{S(CH_2)_3NMe_3\}_2](PF_6)_2$, while those of $[HS(CH_2)_3NMe_3](PF_6)$ with $Hg(OAc)_2$ afforded $\{[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2{\cdot}0.5[S(CH_2)_3NMe_3]\}_n$ and $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ (Scheme 8) [85]. However, the reactions of HgI_2 with the zwitterion, $^{-}SCH_2CH_2NH_3{}^{+}$ (prepared *in situ* from $[HSCH_2CH_2NH_3]Cl$ and NaOH), in $EtOH/H_2O$ yielded a tetranuclear complex $[Hg_4I_6(SCH_2CH_2NH_2)_2(SCH_2CH_2NH_3)_2]$ (Scheme 9) [86].

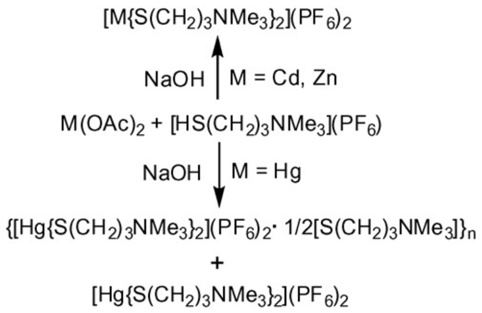
In addition, organometallic complexes [MeHgL] (L = D,L-penicillamine, L-cysteine) could be prepared either from



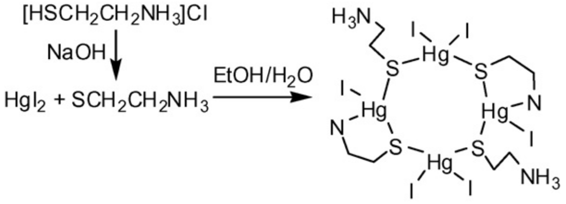
Scheme 6.



Scheme 7.



Scheme 8.



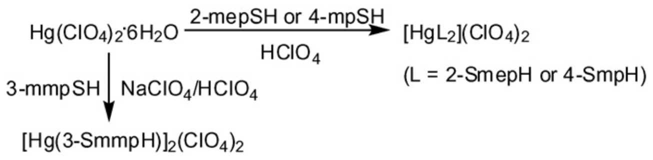
Scheme 9.

MeHgCl, D,L-penicillamine and NaOH in EtOH/H$_2$O [87] or from MeHgOH with L (L = D,L-penicillamine, L-cysteine) in aqueous ethanol [88,89] (Scheme 10). In the latter cases, MeHgOH works as a basic source.

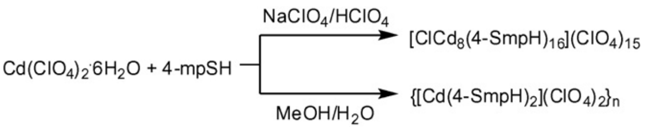
2.1.3. *Reaction of metal salts with thiols under the presence of acids*

There are some zwitterionic thiolate complexes that could be formed under the presence of acids. For instance, complexes $[HgL_2](ClO_4)_2$ (L = 2-SmepH, 4-SmpH) were formed by the reactions of 2-mepSH or 4-mpSH with $Hg(ClO_4)_2·6H_2O$ in $HClO_4$ solution (Scheme 11) [66]. In these cases, $HClO_4$ was used to adjust the pH value of the basic solution of the amine thiol ligands (2-mepSH, 4-mpSH) to form zwitterionic ligands (2-SmepH, 4-SmpH). Complex $[Hg(3\text{-SmmpH})_2](ClO_4)_2$ was isolated from the reactions of $Hg(ClO_4)_2·6H_2O$ with 3-mmpSH in an aqueous solution containing $NaClO_4$ and $HClO_4$ (Scheme 11) [66].

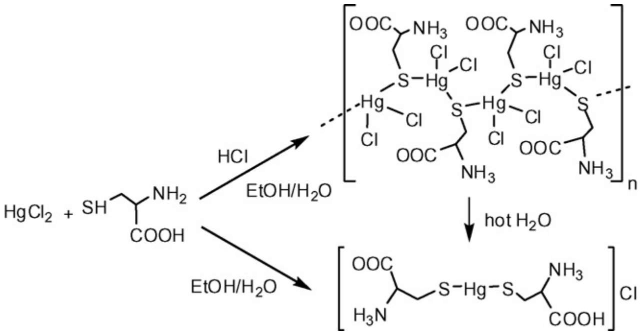
When the pH of the solution was fixed to 8.3 by 4 M $HClO_4$, the reactions of $Cd(ClO_4)_2·6H_2O$ with 5 equiv. of 4-mpSH under the presence of 10 M $NaClO_4$ afforded an octanuclear complex $[ClCd_8(4\text{-SmpH})_{16}](ClO_4)_{15}$ [90]. The central chlorine in this complex, confirmed by XPS and ^{113}Cd NMR results, may have originated from the decomposition of part of the ClO_4^- anions during the reactions. However, without acidification of 4-mpSH, the analogous reactions with same components in 1:2 molar ratio in MeOH/H$_2$O only formed a polymeric complex $\{[Cd(4\text{-SmpH})_2](ClO_4)_2\}_n$ (Scheme 12) [91]. The polymeric complex $\{[Ag_{13}(4\text{-SmpH})_{16}](ClO_4)_{13}\}_n$ could be prepared *via* the reactions of 4-mpSH with an aqueous solution of $AgNO_3$ containing $NaClO_4/HClO_4$ at pH 8.5 (Eq. (12)) [98]. In the cases mentioned above, it seems to be much more the concentration of the ClO_4^- counterion than that of the oxonium ion which plays the decisive role with respect to the question which complex is the most abundant or the least soluble:



Scheme 11.



Scheme 12.

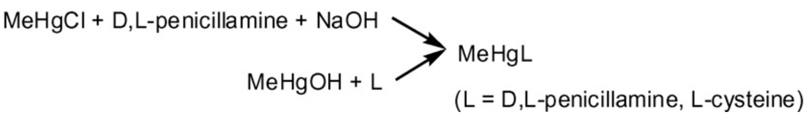


Scheme 13.

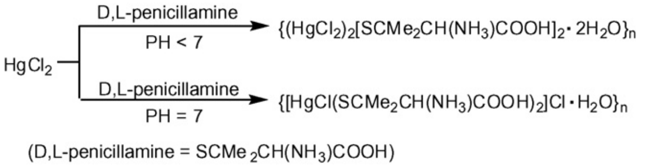
$$13AgNO_3 + 16(4\text{-mpSH}) + 13ClO_4^- \xrightarrow{NaClO_4/HClO_4} \{[Ag_{13}(4\text{-SmpH})_{16}](ClO_4)_{13}\}_n + 13NO_3^- \qquad (12)$$

As shown in Scheme 13, the reactions of $HgCl_2$ with L-cysteine in EtOH/H$_2$O in the presence of a minimum amount of HCl yielded a polymeric complex $[HgCl_2\{SCH_2CH(NH_3)COOH\}]_n$, which could be converted into a mononuclear complex $[Hg\{SCH_2CH(NH_3)COO\}\{SCH_2CH(NH_3)COOH\}]Cl$ in hot water. The latter product was also prepared *via* the reactions of $HgCl_2$ with 2 equiv. of L-cysteine in EtOH/H$_2$O. The bromide analogue of $[HgBr_2\{SCH_2CH(NH_3)COOH\}]_n$ could be prepared in similar manners from $HgBr_2$ [92].

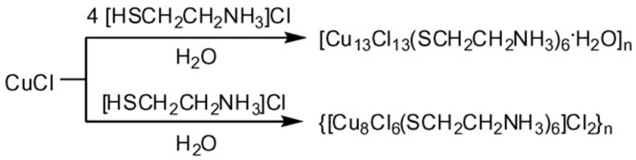
In addition, reactions of $HgCl_2$ with D,L-penicillamine in slightly acidic aqueous solution produced one polymeric complex $\{(HgCl_2)_2[SCMe_2CH(NH_3)COOH]\}_n$. However, in neu-



Scheme 10.



Scheme 14.



Scheme 15.

tral aqueous solution, the same reaction yielded the other polymeric complex $\{[HgCl(SCMe_2CH(NH_3)COOH)_2]Cl{\cdot}H_2O\}_n$ (Scheme 14) [93].

Reactions of MX (M = Cu, Ag) with cysteamine hydrochloride umder different conditions produced a series of cluster compounds of high nuclearity. As shown in Scheme 15, $[Cu_{13}Cl_{13}(SCH_2CH_2NH_3)_6{\cdot}H_2O]_n$ was obtained in a good yield by adding CuCl into the aqueous solution of $[HSCH_2CH_2NH_3]Cl$ at 1:4 molar ratio [94]. In this reaction, addition of equimolar CuCl into the cysteamine hydrochloride solution liberated equimolar HCl, and the pH value of the solution decreased from 4.7 to 1.9. Thus, the thiolate group was deprotonated, forming the zwitterion $^{-}SCH_2CH_2NH_3{}^{+}$, which presumably binds to copper atoms. When the molar ratio of CuCl and $[HSCH_2CH_2NH_3]Cl$ was dropped down to 1:1, the analogous reactions produced a polymeric complex $\{[Cu_8Cl_6(SCH_2CH_2NH_3)_6]Cl_2\}_n$ [95]. It seems not reasonable that a complex resulting from a 1:1 reaction between CuCl and cysteamine hydrochloride, has a smaller Cu:L ratio (i.e. 8:6) than that resulting from a 1:4 reaction (Cu:L = 13:6). However, this inconsistency may be due to the fact that the chloride also took part in the reactions and occupied more coordination sites of copper(I) than L ($SCH_2CH_2NH_3$) in both complexes. However, reactions of CuBr with 1.6 equiv. of $[HSCH_2CH_2NH_3]Cl$ in dilute HBr aqueous solution with a final pH of 1.52 afforded $[Cu_{13}Br_{13}(SCH_2CH_2NH_3)_6]_n$ (Eq. (13)) [96]. Complex $[Cu_{17}Cl_{17}(SCH_2CH_2NHMe_2)_6]_n$ was isolated by reactions of CuCl with $[HSCH_2CH_2NHMe_2]Cl$ (Eq. (14)) [96]. In addition, reactions of AgCl with $[HSCH_2CH_2NH_3]Cl$ and Et_4NCl in DMF afforded $[Ag_8(SCH_2CH_2NH_3)_6Cl_6]_n$ (Eq. (15)) [97]:

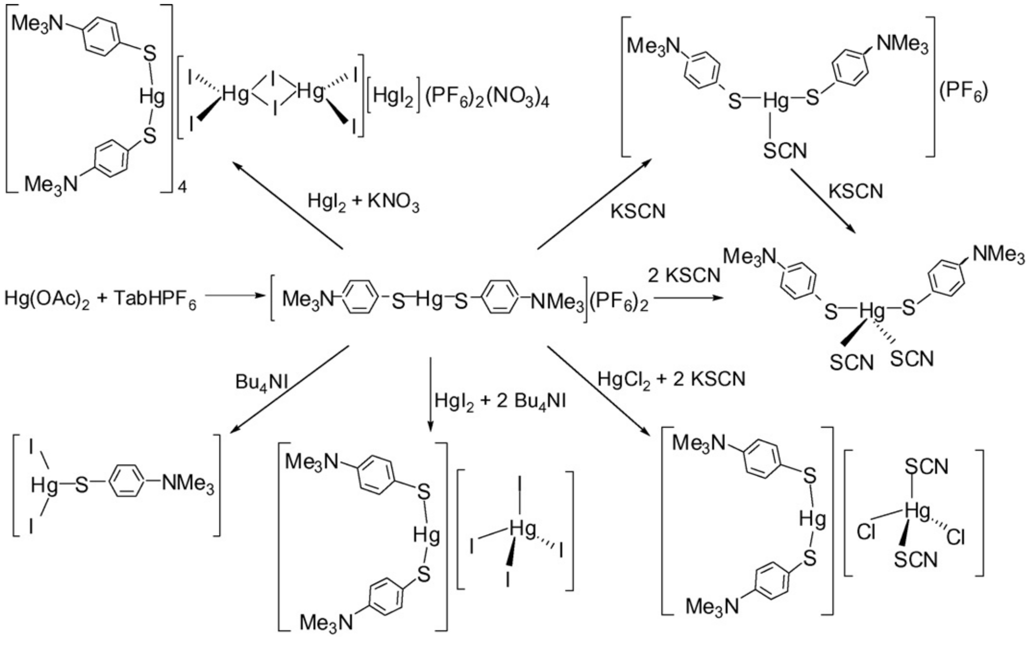
$$13CuBr + 6[HSCH_2CH_2NH_3]Cl \xrightarrow{H_2O/HBr} [Cu_{13}Br_{13}(SCH_2CH_2NH_3)_6]_n + 6HCl \qquad (13)$$

$$17CuCl + 6[HSCH_2CH_2NMe_2] \xrightarrow{H_2O} [Cu_{17}Cl_{17}(SCH_2CH_2NHMe_2)6]_n \qquad (14)$$

$$8AgCl + 6[HSCH_2CH_2NH_3]Cl \xrightarrow{DMF/Et_4NCl} \{[Ag_8(SCH_2CH_2NH_3)_6Cl_6]Cl_2\}_n \qquad (15)$$

2.2. *Precursor reaction*

Some metal complexes of the zwitterionic ammonium thiolates have the following two structural characteristics: (i) the coordination of the metal center is unsaturated and could be further completed through the coordination of additional donor ligands; (ii) the S atoms of the thiolate ligands have the ability to further bind to additional metal atoms. Therefore, these complexes could be employed as precursors to react with additional donor ligands or metal salts to form new metal zwitterionic ammonium thiolate complexes.



Scheme 16.

Mononuclear complexes $[M(Tab)_2](PF_6)_n$ (M = Ag, $n = 1$; M = Hg, $n = 2$) [69,82] could also be used as precursors for the preparation of new metal/Tab complexes. Besides the aforementioned two structural characteristics, they possess the third one that the linear configuration with two $C_6H_4NMe_3$ groups in *trans* positions may be broken up and rearranged into new complexes with two $C_6H_4NMe_3$ groups in *cis* positions.

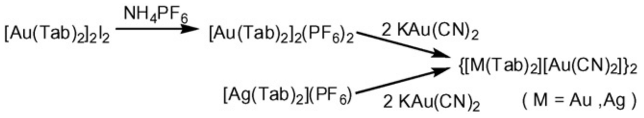
For example, reactions of $[Hg(Tab)_2](PF_6)_2$ with different ligands or metal salts afforded a family of new Hg/Tab complexes (Scheme 16) [69]. Reactions of $[Hg(Tab)_2](PF_6)_2$ and KSCN in 1:1–2 molar ratio gave rise to the corresponding stoichiometric products $[Hg(Tab)_2(SCN)](PF_6)$ and $[Hg(Tab)_2(SCN)_2]$, respectively. The latter complex could also be formed in a quantitative yield from the reactions of $[Hg(Tab)_2(SCN)](PF_6)$ with one or more equiv. of KSCN. When it was mixed with Bu_4NI or HgI_2/Bu_4NI or $HgCl_2/KSCN$, neutral complex $[Hg(Tab)I_2]$ or ionic complexes $[Hg(Tab)_2][HgI_4]$ or $[Hg(Tab)_2][HgCl_2(SCN)_2]$ were produced. Intriguingly, when it reacted with equimolar HgI_2 followed by dissolving the resulting yellow solid in hot DMF/H_2O solution containing KNO_3, an unexpected complex $[Hg(Tab)_2][Hg_2I_6][HgI_2](PF_6)(NO_3)_4$ was formed.

When the silver(I) complex $[Ag(Tab)_2](PF_6)$ was treated with Na_2S, a polymeric complex $\{[Ag_3(Tab)_4](PF_6)_3{\cdot}2DMF\}_n$ along with a minor product $[Ag_{14}(\mu_6\text{-}S)(Tab)_{12}(PPh_3)_8](PF_6)_{12}$ [82] were obtained (Eq. (16)). During the reactions, the linear structure was broken up and the remaining Ag atoms and Tab moieties were re-arranged into the structure of $\{[Ag_3(Tab)_4](PF_6)_3{\cdot}2DMF\}_n$. The formation of tetradecanuclear cluster may be ascribed to the existence of a very small amount of PPh_3 in the bulky sample of $[Ag(Tab)_2](PF_6)$:

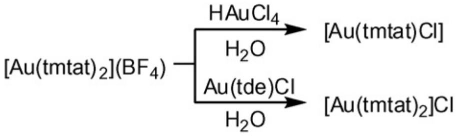
$$\begin{aligned}&[Ag(Tab)_2](PF_6) + Na_2S\\ &\quad\rightarrow \{[Ag_3(Tab)_4](PF_6)_3{\cdot}2DMF\}_n\\ &\qquad + [Ag_{14}(\mu_6\text{-}S)(Tab)_{12}(PPh_3)_8](PF_6)_{12}\end{aligned} \tag{16}$$

In the case of gold(I), two dimeric complexes $[Au(Tab)_2]_2L_2$ (L = I, PF_6) [83] consist of two $[Au(Tab)_2]^+$ cations linked by one aurophilic interaction, which assume the similar structure to those of the silver and mercury analogues. Complex $[Au(Tab)_2]_2(PF_6)_2$ was obtained from anion exchange reaction of $[Au(Tab)_2]_2I_2$ with NH_4PF_6 in DMF. Treatment of $[Au(Tab)_2]_2(PF_6)_2$ or $[Ag(Tab)_2](PF_6)$ with $K[Au(CN)_2]$ produced tetranuclear complexes $\{[M(Tab)_2][Au(CN)_2]\}_2$ (M = Au, Ag) (Scheme 17). Analogous reactions of $[Hg(Tab)_2](PF_6)_2$ with $K[Au(CN)_2]$ yielded $[Hg(Tab)_2][Au(CN)_2]_2$ (Eq. (17)):

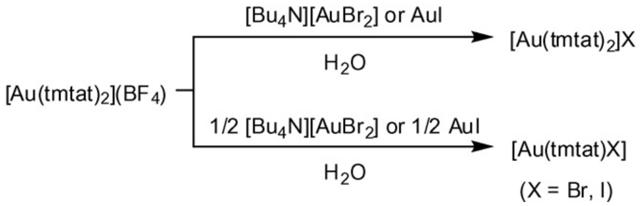
$$\begin{aligned}&[Hg(Tab)_2](PF_6)_2 + 2K[Au(CN)_2]\\ &\quad\rightarrow [Hg(Tab)_2][Au(CN)_2]_2 + 2KPF_6\end{aligned} \tag{17}$$



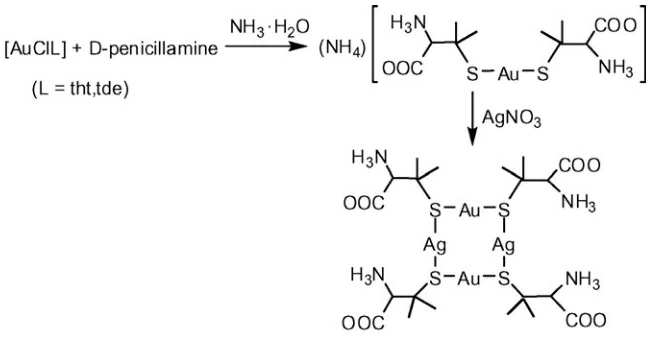
Scheme 17.



Scheme 18.



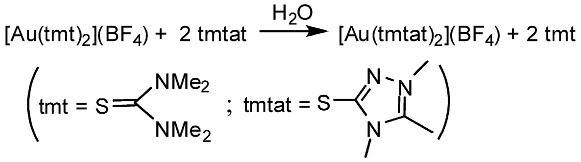
Scheme 19.



Scheme 20.

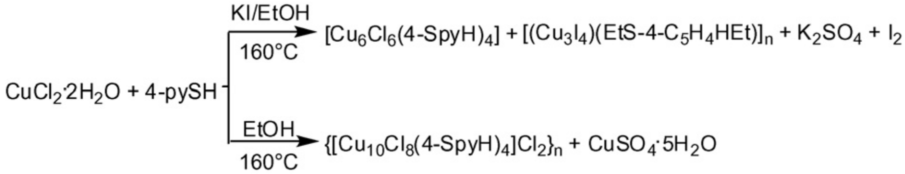
2.3. Ligand exchange reaction

Some metal zwitterionic ammonium thiolate complexes could also be prepared from the following three types of the ligand exchange reactions: those between some preformed complexes and zwitterionic ammonium thiolates; those between metal zwitterionic ammonium thiolate complexes with other donor ligands, and those between the counterions. For instance, the tmt ligands in $[Au(tmt)_2](BF_4)$ are weakly bonded and can be readily exchanged by a zwitterionic ammonium thiolate, tmtat, forming $[Au(tmtat)_2](BF_4)$ (Eq. (18)) [99]. When $[Au(tmtat)_2](BF_4)$ was treated with $HAuCl_4$ in H_2O, a neutral complex [Au(tmtat)Cl] was obtained, while reactions of $[Au(tmtat)_2](BF_4)$ with Au(tde)Cl in H_2O afforded an ionic complex $[Au(tmtat)_2]Cl$ (Scheme 18). Furthermore, the reactions of $[Au(tmtat)_2](BF_4)$ with $[Bu_4N][AuBr_2]$ or AuI afforded [Au(tmtat)X] (X = Br, I) and $[Au(tmtat)_2]X$ (X = Br, I), respectively (Scheme 19):

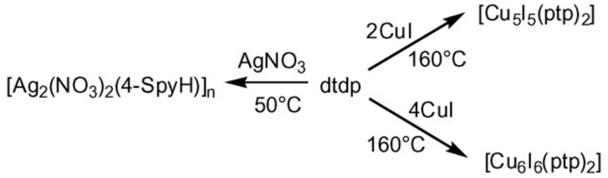


(18)

Complex $[NH_4][Au(SCMe_2CH(NH_3)COO)_2]$ could be obtained from reactions of [AuClL] (L = tht, tde) with D-penicillamine in $NH_3{\cdot}H_2O$ (Scheme 20) [100,101]. Addition of $AgNO_3$ into a solution of this complex gave rise to the



Scheme 21.



Scheme 22.

heterobimetallic complex $[AgAu(SCMe_2CH(NH_3)COO)_2]_2$ [101].

2.4. Oxidation–reduction reaction

Metal complexes of the zwitterionic ammonium thiolates could occasionally be prepared from the reactions of metal salts with reductive thiols. This approach sometimes suffers from the drawback of thiol-to-disulfide conversion, especially when the high valent metal salts or oxidizing agents are employed [69]. For example, when mononuclear complex $[Hg(Tab)_2](PF_6)_2$ was treated with a mixture of $HAuCl_4$ and excess Tab (prepared *in situ* from $TabHPF_6$ with excess Et_3N) in MeOH/MeCN, a binuclear complex $[Hg_2(Tab)_6]_3(PF_6)Cl_{11}$ along with two side-products, one reduced Au(I) complex $[Au(Tab)_2]_2(PF_6)_2$ and one oxidized species $[Tab–Tab](PF_6)_2$ were isolated (Eq. (19)):

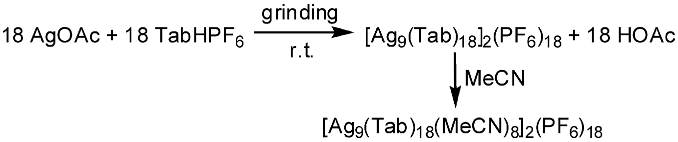
$$\begin{aligned}&[Hg(Tab)_2](PF_6)_2\\&\quad\xrightarrow{HAuCl_4/Tab}\{[Hg_2(Tab)_6]_3(PF_6)_{11}Cl+[Au(Tab)_2]_2(PF_6)_2\\&\qquad+(Tab–Tab)(PF_6)_2\end{aligned}\tag{19}$$

In addition, the disproportionation reaction of the Hg(I) complex could be used to prepare Hg(II)/zwitterionic ammonium thiolate complexes. For instance, treatment of Hg_2Cl_2 with 2-aminoethanethiol hydrochloride in H_2O afforded a Hg(II) thiolate complex $[\{Hg_3Cl_5(SCH_2CH_2NH_3)_3\}Cl]_n$ and elemental Hg (Eq. (20)) [102]:

$$\begin{aligned}&3Hg_2Cl_2+3[HSCH_2CH_2NH_3]Cl\\&\quad\xrightarrow{H_2O}\{[Hg_3Cl_5(SCH_2CH_2NH_3)_3]Cl\}_n+3Hg+3HCl\end{aligned}\tag{20}$$

2.5. Solid-state reaction

Only one example was reported for this type of reaction. Mixing argenteous silver acetate and white equimolar $TabHPF_6$ ligand and firmly grinding in an agate mortar at ambient temperature afforded $[Ag_9(Tab)_8]_2(PF_6)_{18}$, which was extracted with MeCN to form a solvent-ligated octadecanuclear cluster $[Ag_9(Tab)_8(MeCN)_8]_2(PF_6)_{18}$ in an almost quantitative yield (Eq. (21)) [103]. In this reaction, acetic acid vapor was observed to evolve from the solid mixture because of the bigger acidity of $TabHPF_6$ with respect to HOAc. The liberation of the volatile acetic acid vapor could be the driving force for the formation of this zwitterionic thiolate cluster:



$$\begin{tikzcd}18\,AgOAc+18\,TabHPF_6 \arrow[r, "grinding", "r.t."'] & {[Ag_9(Tab)_{18}]_2(PF_6)_{18}+18\,HOAc} \arrow[d, "MeCN"] \\ & {[Ag_9(Tab)_{18}(MeCN)_8]_2(PF_6)_{18}}\end{tikzcd}\tag{21}$$

2.6. Electrochemical reaction

Few examples are involved in the employment of electrochemical reactions for metal complexes of zwitterionic ammonium thiolates. For instance, the anodic oxidation of silver in a $NaNO_3$-saturated MeCN solution containing $[4\text{-}mpSH]\cdot HNO_3$ and PPh_3 in a 1:2 molar ratio led to the formation of $\{[Ag_{13}(4\text{-}SmpH)_{16}](NO_3)_{13}\}_n$ (Eq. (22)) [98]. In this reaction, the silver electrodes are oxidized into metal ions while the thiols are involved in the deprotonation and subsequent coordination at silver centers. The reactions in the cell could be described as the following:

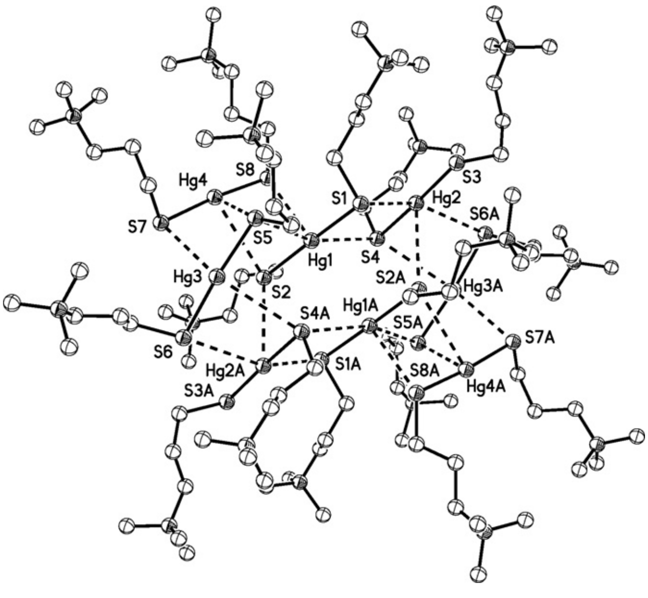


Fig. 1. View of the loosely bound octameric cation of $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ showing Hg···S secondary interactions in dashed lines. (From [85], with permission of © 1991 Elsevier Science Ltd.)

Table 1
Structural parameters of metal complexes of zwitterionic thiolate ligands

Compound	c.n.[a]	Bond type	Bond length (Å)	Ref.
Copper(I) complexes				
$[Cu_5I_5(ptp)_2]_n$	3	$Cu{-}\mu{-}S$	2.262 (2)	[106]
	4	$Cu{-}\mu{-}S$	2.276 (2) average	
$[Cu_6I_6(ptp)_2]_n$	4	$Cu{-}\mu{-}S$	2.391 (2) average	[106]
$[Cu_6(4\text{-}SpyH)_4Cl_6]$	4	$Cu{-}S$	2.252 (4) average	[104]
$\{[Cu_8Cl_6(SCH_2CH_2NH_3)_6]Cl_2\}_n$	3	$Cu{-}\mu_3{-}S$	2.248 average	[95]
	3	$Cu{-}\mu_4{-}S$	2.390 average	
	4	$Cu{-}\mu_3{-}S$	2.344 average	
$\{[Cu_{10}Cl_8(SpyH)_4]Cl_2\}_n$	4	$Cu{-}\mu_3{-}S$	2.278 average	[105]
$[Cu_{13}Br_{13}(SCH_2CH_2NH_3)_6]_n$	3	$Cu{-}\mu_4{-}S$	2.255 average	[96]
	4	$Cu{-}\mu_4{-}S$	2.267 average	
$[Cu_{13}Cl_{13}(SCH_2CH_2NH_3)_6\ H_2O]_n$	3	$Cu{-}\mu_4{-}S$	2.247 average	[94]
	4	$Cu{-}\mu_4{-}S$	2.257 (6) average	
$[Cu_{17}Cl_{17}(SCH_2CH_2NHMe_2)_6]_n$	3	$Cu{-}\mu_4{-}S$	2.244 average	[96]
	4	$Cu{-}\mu_4{-}S$	2.301 average	
Silver(I) complexes				
$[Ag(Tab)_2](PF_6)$	2	$Ag{-}S$	2.385 average	[82]
$[Ag_2(4\text{-}SpyH)(NO_3)_2]_n$	4	$Ag{-}\mu_4{-}S$	2.628 average	[107]
$\{[Ag(Tab)_2][Au(CN)_2]\}_2$,	2	$Ag{-}S$	2.3788 (16)	[83]
$\{[Ag_3(Tab)_4](PF_6)_3{\cdot}2DMF\}_n$	3	$Ag{-}\mu{-}S$	2.520 average	[82]
	3	$Ag{-}\mu_3{-}S$	2.561 (4) average	
$\{[Ag_4(StpmtH_2)_6](NO_3)_4\}_n$	4	$Ag{-}\mu{-}S$	2.574 average	[84]
$\{Ag_5[S(CH_2)_3NHMe_2]_3[S(CH_2)_3NMe_2]_3\}(ClO_4)_2$	3	$Ag{-}\mu{-}S$	2.399 average	[76]
$[Ag_6Br_6(StpmtH_2)_6]_n$	4	$Ag{-}\mu{-}S$	2.519 average	[84]
	4	$Ag{-}\mu_3{-}S$	2.721 average	
$[Ag_8(SCH_2CH_2NH_3)_6Cl_6]_n$	3	$Ag{-}\mu_4{-}S$	2.607 average	[97]
	4	$Ag{-}\mu_4{-}S$	2.649 average	
$\{[Ag_{13}(4\text{-}SmpH)_{16}]X_{13}\}_n$ ($X = NO_3, ClO_4$)	2	$Ag{-}\mu_3{-}S$	2.406 average	[98]
	2	$Ag{-}\mu_4{-}S$	2.375 average	
	3	$Ag{-}\mu{-}S$	2.435 average	
	3	$Ag{-}\mu_3{-}S$	2.518 average	
	3	$Ag{-}\mu_4{-}S$	2.6115 average	
	4	$Ag{-}\mu{-}S$	2.569 average	
	4	$Ag{-}\mu_3{-}S$	2.663 average	
$[Ag_{14}(\mu_6\text{-}S)(Tab)_{12}(PPh_3)_8](PF_6)_{12}$	3	$Ag{-}\mu_3{-}S$	2.423 average	[82]
	4	$Ag{-}\mu_3{-}S$	2.663 average	
$[Ag_9(Tab)_8(MeCN)_8]_2(PF_6)_{18}$	3	$Ag{-}\mu{-}S$	2.467 average	[103]
	3	$Ag{-}\mu_3{-}S$	2.478 average	
	4	$Ag{-}\mu_3{-}S$	2.567 average	
Gold(I) complexes				
$[Au(Tab)(PPh_3)](PF_6)$	2	$Au{-}S$	2.293 (3)	[81]
$[NH_4][Au(SCMe_2CH(NH_3)COO)_2]$	2	$Au{-}S$	2.2900 (13)	[100]
$[Au(tmtat)_2](BF_4)$	2	$Au{-}S$	2.272 (4) average	[99]
$[Au(Tab)_2]_2I_2$	2	$Au{-}S$	2.300 average	[83]
$[Au(Tab)_2]_2(PF_6)_2$	2	$Au{-}S$	2.304 average	[83]
$\{[Au(Tab)_2][Au(CN)_2]\}_2$	2	$Au{-}S$	2.314 average	[83]
Gold(III) complexes				
$[Au(SthiazH)_2(Hdamp\text{-}C^1)Cl]Cl_2$	4	$Au{-}S$	2.328 average	[64]
Zinc(II) complexes				
$[Zn_2(4\text{-}SmpH)_2Cl_4]$	4	$Zn{-}\mu{-}S$	2.371 average	[67]
$[Zn(4\text{-}SpyH)_4](ClO_4)_2$	4	$Zn{-}S$	2.349 average	[65]

Table 1 (*Continued*)

Compound	c.n.[a]	Bond type	Bond length (Å)	Ref.
Cadmium(II) complexes				
$[Cd(4\text{-}SpyH)_4](ClO_4)_2$	4	Cd—S	2.544 average	[65]
$[Cd(4\text{-}Spy)_2(4\text{-}SpyH)_2]$	4	Cd—S	2.540 average	[65]
$[Cd(SCH_2CH_2CH_2NHMe_2)_2Cl_2]_n$	4	Cd—μ—S	2.5135 average	[74]
$[Cd(SCH_2CH_2CH_2NHMe_2)_2Br_2]_n$	4	Cd—μ—S	2.5175 average	[75]
$[Cd(4\text{-}SmpH)(ClO_4)_2\ 2H_2O]_n$	4	Cd—S	2.548 (9) average	[91]
$[CdBr(SCMe_2CH(NH_3)COO)H_2O]_n$	6	Cd—S	2.444 (2)	[71]
$[Cd_5Cl_{10}(SCH_2CH_2NH_3)_2]_n$	6	Cd—S	2.531 average	[77]
$[ClCd_8(4\text{-}SmpH)_{16}](ClO_4)_{15}$	4	Cd—S	2.470 average	[90]
	4	Cd—μ—S	2.536 average	
Mercury(II) complexes				
$[Hg(Tab)_2](PF_6)_2$	2	Hg—S	2.331 (3) average	[69]
$[Hg(Tab)_2][Au(CN)_2]_2$	2	Hg—S	2.3369 (15)	[83]
$[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$	2	Hg—S	2.336 average	[85]
$[Hg(SCH_2CH_2NH_3)_2]Cl_2$	2	Hg—S	2.3355 average	[78]
$[Hg(4\text{-}SmpH)_2](ClO_4)_2$	2	Hg—S	2.329 average	[66]
$Hg[SCH_2CH(NH_3)COO][SCH_2CH(NH_3)COOH]Cl\ 0.5H_2O$	2	Hg—S	2.342 (4) average	[92]
$[MeHg(SCH_2CH(NH_3)COO)]$	2	Hg—S	2.352 (12)	[89]
$[MeHg\{SCMe_2CH(NH_3)COO\}]$	2	Hg—S	2.381	[87]
$\{[Hg(Tab)_2]_4[HgI_2][Hg_2I_6]\}(PF_6)_2(NO_3)_4$	2	Hg—S	2.328 average	[69]
$[Hg(Tab)_2][HgCl_2(SCN)_2]$	2	Hg—S(Tab)	2.3219 (14)	[69]
	2	Hg—S(SCN)	2.5144 (13)	
$[Hg(Tab)_2][HgI_4]$	2	Hg—S	2.383 (7)	[69]
$[Hg(Tab)I_2]$	3	Hg—S	2.432 (2)	[69]
$[Hg(Tab)_2(SCN)](PF_6)$	3	Hg—S(Tab)	2.338 average	[69]
	3	Hg—S(SCN)	2.801 (8) average	
$\{(HgCl)[SCMe_2CH(NH_3)COOH]_2Cl\cdot H_2O\}_n$	3	Hg—S	2.346 average	[93]
$\{[Hg_3Cl_5(SCH_2CH_2NH_3)_3]Cl\}_n$	3	Hg—μ—S	2.390 average	[102]
	4	Hg—μ—S	2.540 average	
$[Hg(4\text{-}SpyH)_4](ClO_4)_2$	4	Hg—S	2.540 average	[65]
$[Hg(4\text{-}Spy)_2(4\text{-}SpyH)_2]$	4	Hg—S	2.549 average	[65]
$[Hg(Tab)_2(SCN)_2]$	4	Hg—S(Tab)	2.3715 (11)	[69]
	4	Hg—S(SCN)	2.9281 (12)	
$\{(HgCl_2)[SCH_2CH(NH_3)COOH]\}_n$	4	Hg—S	2.472 average	[92]
$[HgCl_2\{S(CH_2)_3NHMe_2\}]_n$	4	Hg—μ—S	2.464 (6)	[73]
$\{[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot 0.5[S(CH_2)_3NMe_3]\}_n$	4	Hg—μ—S	2.566 average	[85]
$[Hg_2(Tab)_6](PF_6)_4$	4	Hg—S	2.424 average	[69]
	4	Hg—μ—S	2.690 average	
$[Hg_2(Tab)_6]_3(PF_6)Cl_{11}$	4	Hg—S	2.431 average	[69]
	4	Hg—μ—S	2.695 average	
$\{(HgCl_2)_2[SCMe_2CH(NH_3)COOH]_2\cdot 2H_2O\}_n$	4	Hg—μ—S	2.589 average	[93]
$[HgCl(\mu\text{-}Cl)(2\text{-}SabH)]_2$	4	Hg—S	2.340 (2) average	[70]
$[(\mu_3\text{-}Cl)\{HgSCMe_2CH(NH_3)COO\}_3]_2\cdot(\mu_2\text{-}Cl)_3\cdot(H_2O)_2\cdot(H_2O\cdot Cl)_3$	4	Hg—μ—S	2.32 (2)	[72]
$[Hg_4I_8(SCH_2CH_2NH_3)_2]_n$	4	Hg—μ—S	2.478 average	[80]
$[Hg_4I_6(SCH_2CH_2NH_3)_2(SCH_2CH_2NH_2)_2]$	4	Hg—μ—S	2.493 average	[86]
$[Hg_6Cl_8(SCH_2CH_2NH_3)_8]Cl_4$	4	Hg—μ—S	2.385 average	[79]
	5	Hg—μ—S	2.550 average	
$[Hg_9Br_{15}(SCH_2CH_2NH_3)_9](Cl_{0.8}Br_{0.2})_3$	4	Hg—μ—S	2.511 average	[79]

[a] c.n.: coordination number.

- cathode: $H^+ + e = 1/2H_2$
- anode: $Ag - e = Ag^+$

$$Ag^+ + 4\text{-mpSH} + NO_3^- = \{[Ag_{13}(1\text{-SmpH})_{16}](NO_3)\}_n$$

$$13Ag^+ + 16\,[4\text{-mpSH}]\cdot HNO_3 + 13NO_3^- \xrightarrow[PPh_3]{MeCN} \{[Ag_{13}(4\text{-SmpH})_{16}](NO_3)_{13}\}_n + 16HNO_3 \quad (22)$$

2.7. Hydro(solvo)thermal reaction

Several metal complexes of zwitterionic ammonium thiolates have recently been prepared from the hydro(solvo)thermal reactions. For example, solvothermal reaction of $CuCl_2{\cdot}2H_2O$, KI, 4-pySH and EtOH in a molar ratio of 1:1:1:500 at 160 °C for 60 h gave rise to $[Cu_6Cl_6(4\text{-SpyH})_4]$ and $[(Cu_3I_4)(EtS\text{-}4\text{-}C_5H_4NEt)]_n$ along with K_2SO_4 and I_2 as byproducts [104] (Scheme 21). It is suggested that the desulfurization process was followed by the reduction of Cu^{2+} to Cu^+ and the oxidation of S^{2-} to S^{6+} during the reaction. On the other hand, the analogous reactions without KI afforded a polymeric complex $\{[Cu_{10}Cl_8(SpyH)_4]Cl_2\}_n$ along with the byproduct $CuSO_4{\cdot}5H_2O$ (Scheme 21) [105].

The dtdp ligand was known to coordinate readily with metal ions through the N donor without S–S bond cleavage at room temperature [110,111]. However, the solvothermal reactions of dtdp with CuI at different molar ratios in MeCN at 160 °C for 80 h gave rise to two unexpected complexes containing a new ptp ligand $[Cu_5I_5(ptp)_2]_n$ and $[Cu_6I_6(ptp)_2]_n$ (Scheme 22) [106]. The ptp ligand may be produced by the *in situ* cleavage of the S–S and S–C(sp^2) bonds of the dtdp ligand and rearrangement reactions. In addition, a polymeric complex $[Ag_2(NO_3)_2(4\text{-SpyH})]_n$ was formed by the reactions of $AgNO_3$ with dtdp in $EtOH/H_2O$ at 50 °C [107].

3. Structural aspects

Based on the number of metal ions in metal zwitterionic ammonium thiolate complexes, they are classified into the eleven categories: mono-, di-, tri-, tetra-, penta-, hexa-, octa-, nona-, tetradeca-, and octadeca-nuclear, and polymeric compounds. Some important structural parameters for complexes of groups 11 and 12 metals are listed in Table 1. In the following subsections, we briefly describe the pertinent structural features of complexes in each category.

3.1. Mononuclear complexes

3.1.1. Two-coordinate

Two-coordinated metal complexes of zwitterionic ammonium thiolate are common and usually linear about the metal atoms. Examples include $[Hg(4\text{-SmpH})_2](ClO_4)_2$ [66], $[Hg(SCH_2CH_2NH_3)_2]Cl_2$ [78], $[Hg(Tab)_2](PF_6)_2$ [69], $[Ag(Tab)_2](PF_6)$ [82], $[Au(tmtat)_2](BF_4)$ [99], and $[NH_4][Au(SCMe_2CH(NH_3)COO)_2]$ [100]. In these complexes, each metal atom is in a linear MS_2 coordination geometry with two S atoms from two zwitterionic thiolates such as Tab, 4-SmpH, $^-SCH_2CH_2NH_3^+$, tmtat, and $^-SCMe_2CH(NH_3^+)COO^-$. In $[Hg(SCH_2CH_2NH_3)_2]Cl_2$ [78], the ammonium portions of $^-SCH_2CH_2NH_3^+$ ligands form short hydrogen bonding interactions with the S and Cl atoms. In the case of $[NH_4][Au(SCMe_2CH(NH_3)COO)_2]$ [100], the amine functional groups of the $^-SCMe_2CH(NH_3^+)COO^-$ ligands, the NH_4^+ ions and solvated water molecules are involved in hydrogen bonds with each other or with the portions of the neighboring ligands. For complex $[Au(tmtat)_2](BF_4)$ [99], the C–S bond lengths (1.73 and 1.76 Å) are close to the carbon-sulfur single bond, which, together with the short C–N bond lengths (1.26 and 1.30 Å), suggest that the tmtat ligand is in the zwitterionic form.

For complexes $[Au(Tab)(PPh_3)](PF_6)$ [81], $[MeHg\{SCMe_2CH(NH_3)COO\}]{\cdot}H_2O$ [87,88], $[MeHg\{SCH_2CH(NH_3)COO\}]{\cdot}H_2O$ [89], and $[Hg\{SCH_2CH(NH_3)COO\}\{SCH_2CH(NH_3)COOH\}]Cl{\cdot}0.5H_2O$ [92], each Hg center also adopts an approximately linear coordination geometry. In later three complexes, the aminoacid presents in the zwitterionic form $^-SCH_2CH(NH_3^+)COO^-$ or $^-SCMe_2CH(NH_3^+)COO^-$ bound to Hg atom *via* a deprotonated sulfydryl group.

Complex $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ [85] consists of four crystallographically independent $[Hg\{S(CH_2)_3NMe_3\}_2]^{2+}$ dications, which differ in the conformations of the aminothiolate chains. These dications are linked together by weak Hg···S secondary interactions (2.98(3)–3.598(3) Å), forming loosely bound octameric units (Fig. 1). Each Hg atom forms either two or three Hg···S secondary interactions, which lie approximately at right angles to the primary linear S–Hg–S groups.

For complex $[Hg(Tab)_2][HgI_4]$ [69], the linear $[Hg(Tab)_2]^{2+}$ dications and the tetrahedral $[HgI_4]^{2-}$ dianions are linked together by the Hg···I (3.223(2)–3.7294(6) Å) secondary interactions between Hg and I atoms, forming a zigzag chain structure. In contrast to $[Hg(Tab)_2][HgI_4]$, the secondary interactions in $[Hg(Tab)_2][HgCl_2(SCN)_2]$ [69] between the Hg atom in the linear $[Hg(Tab)_2]^{2+}$ dications and the N atoms of the SCN^- groups (Hg···N = 2.970(1) Å) afford another zigzag chain. Taking the Hg···I or Hg···N secondary interactions into account, the Hg atom of the $[Hg(Tab)_2]^{2+}$ dication in $[Hg(Tab)_2][HgI_4]$ has a *pseudo*-seesaw-shaped coordination geometry while that in $[Hg(Tab)_2][HgCl_2(SCN)_2]$ adopts a *pseudo*-square-planar coordination fashion.

In $\{[Hg(Tab)_2]_4[HgI_2][Hg_2I_6]\}(PF_6)_2(NO_3)_4$ [69], the secondary interactions work in a much more complicated way. As shown in Fig. 2, the $[Hg_2I_6]^{2-}$ dianions and the bent HgI_2 molecules are interconnected *via* weak I1···Hg5A (3.5284(5) Å) and Hg5···I3 (3.9567(5) Å) interactions, forming a $\{[Hg_2I_6{\cdot}HgI_2]^{2-}\}_n$ chain structure. Along this chain backbone, the HgI_2 molecules and the $[Hg_2I_6]^{2-}$ anions alternatively coordinate to the Hg atoms of the $[Hg(Tab)_2]^{2+}$ dications *via* Hg1···I4B (3.8210(6) Å) and Hg2···I2 (4.0858(7) Å) interactions. These weak interactions make it a 1D scolopendra-like structure. In addition, each NO_3^- anion is arranged between the two $[Hg(Tab)_2]^{2+}$ dications and interacts as a tridentate ligand with Hg1 and Hg2 (Hg···O = 2.987(5) Å) to form a wave-like chain structure.

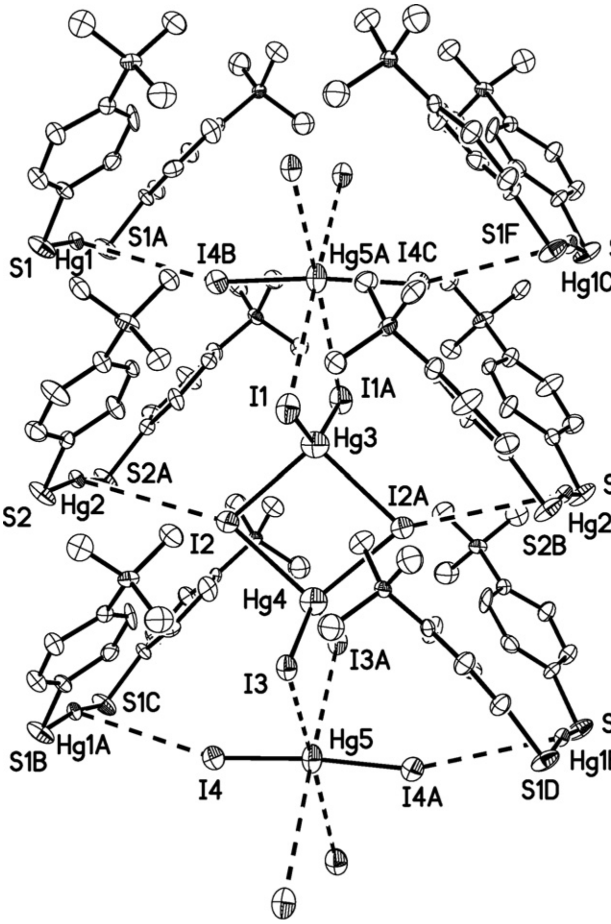


Fig. 2. View of a section of the 1D scolopendra-like structure formed by Hg···I secondary interactions among $[Hg(Tab)_2]^{2+}$, $[Hg_2I_6]^{2-}$, and HgI_2 in $\{[Hg(Tab)_2]_4[HgI_2][Hg_2I_6]\}(PF_6)_2(NO_3)_4$. (From [69], with permission of © 2006 American Chemical Society.)

3.1.2. Three-coordinate

The Hg atom in $[Hg(Tab)I_2]$ [69] has a typical trigonal planar geometry with one S atom and two I atoms. The $[Hg(Tab)I_2]$ molecules in the crystal are held together by secondary Hg···S (3.126(2) Å) and Hg···I (3.617(3) Å) interactions to give a chain structure.

For $[Hg(Tab)_2(SCN)](PF_6)$ [69], each Hg atom in $[Hg(Tab)_2(SCN)]^+$ cations is coordinated strongly by two S atoms from two Tab ligands and weakly by one S atom from SCN^-, forming an uncommon T-shaped coordination geometry. Each cation is further interconnected in an up-and-down way *via* long Hg···S secondary interaction (3.6148(4)–3.9237(4) Å), forming a zigzag chain (Fig. 3).

3.1.3. Four-coordinate

Four-coordinated metal complexes of the zwitterionic ammonium thiolates are mostly encountered: $[Au(SthiazH)_2(Hdamp\text{-}C^1)Cl]Cl_2$ [64], $[M(4\text{-}SpyH)_4](ClO_4)_2$ (M = Zn, Cd, Hg), $[M(4\text{-}Spy)_2(4\text{-}SpyH)_2]$ (M = Cd, Hg) [65], and $[Hg(Tab)_2(SCN)_2]$ [69].

The Au atom in $[Au(SthiazH)_2(Hdamp\text{-}C^1)Cl]Cl_2$ possesses a slightly distorted square-planar coordination sphere with the Cl atom *trans* to the σ-bonded phenyl ligand. The Au atom is out-of-plane by 0.15 Å. The C–S bond lengths (about 1.71 Å) vary between carbon–sulfur single and double bonds. However, the C–N distances (1.294 and 1.275 Å) and the Au–S–C angles (107° and 110°) clearly confirm the thiolate-type zwitterionic coordination of the ligands.

Complexes $[M(4\text{-}SpyH)_4](ClO_4)_2$ (M = Zn, Cd, Hg) [65] are isomorphous and isostructural, and they hold crystallographic twofold symmetry at Cd or Hg atoms. The M center possesses a distorted tetrahedral geometry, coordinated by four S atoms from four 4-SpyH ligands. For the other two isostructural complexes $[M(4\text{-}Spy)_2(4\text{-}SpyH)_2]$ (M = Cd, Hg) [65], each possesses a twofold crystallographic symmetry and its metal atom is tetrahedrally coordinated by two S atoms from 4-Spy and two S atoms from 4-SpyH ligands.

For $[Hg(Tab)_2(SCN)_2]$ [69], the central Hg atom lies at a crystallographic inversion center, and is strongly coordinated by two S atoms of the two Tab ligands and loosely coordinated by two S atoms of the two SCN^- anions, forming a unique seesaw-shaped coordination geometry.

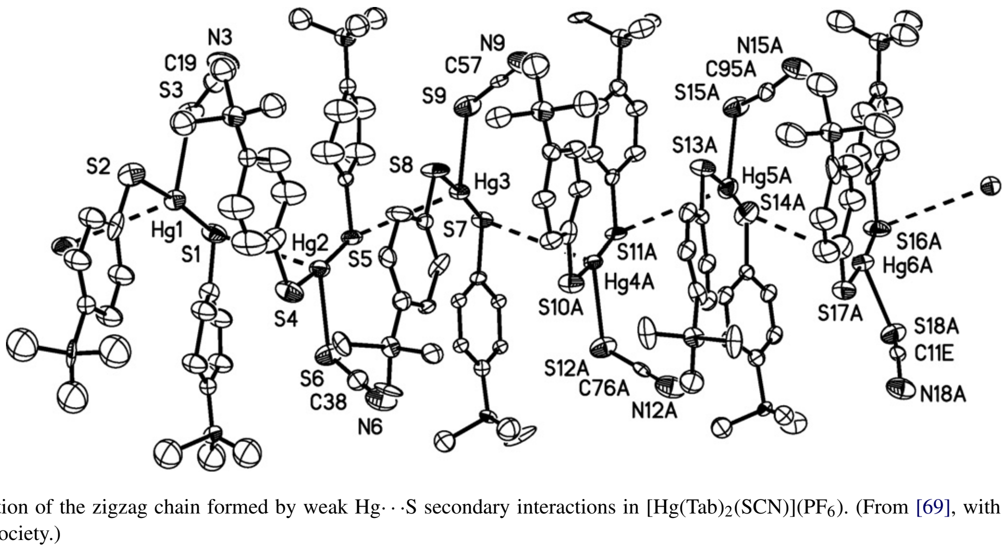


Fig. 3. View of a portion of the zigzag chain formed by weak Hg···S secondary interactions in $[Hg(Tab)_2(SCN)](PF_6)$. (From [69], with permission of © 2006 American Chemical Society.)

3.2. Dinuclear complexes

In this group are included six complexes: [HgCl(μ-Cl)(2-SabH)]$_2$ [70], [Zn_2(4-SmpH)$_2$$Cl_4$] [67], [$Hg_2(Tab)_6$]($PF_6$)$_4$, [$Hg_2(Tab)_6$]$_3$($PF_6$)$Cl_{11}$ [69], and [Au(Tab)$_2$]$_2$$X_2$ (X = I, PF_6) [83].

Complex [HgCl(μ-Cl)(2-SabH)]$_2$ [70] possesses a centrosymmetric dimeric structure in which two Hg atoms are linked by two μ-Cl atoms. The tetrahedral geometry of each Hg atom is completed by one terminal Cl and one S atom of the 2-SabH ligand. The molecules in the crystal are interconnected by four hydrogen bonding interactions between the terminal Cl atoms and the NH_3^+ groups, forming a 2D network.

Complex [Zn_2(4-SmpH)$_2$$Cl_4$] [67] consists of a Zn_2(4-SmpH)$_2$ dimeric core in which the tetrahedral coordination sphere of the Zn atom is completed by two bridging S atoms and two terminal Cl atoms. The crystallographic mirror plane passing through the Zn and Cl atoms imposes a C_s symmetry on the molecule.

Complexes [Hg_2(Tab)$_6$](PF_6)$_4$ and [Hg_2(Tab)$_6$]$_3$(PF_6)Cl_{11} [69] contain similar [Hg_2(Tab)$_6$]$^{4+}$ tetracations, which consists of a Hg_2S_2 parallelogram (Fig. 4). Each Hg atom is coordinated by four S atoms from Tab ligands, forming a strongly distorted tetrahedral coordination geometry. In the unit cell of [Hg_2(Tab)$_6$]$_3$(PF_6)Cl_{11}, the PF_6^- anion, working as an anionic template, is surrounded by six symmetry-related quaternary ammonium ions to form a ball-like structure.

Complexes [Au(Tab)$_2$]$_2$$X_2$ (X = I, PF_6) [83] have a linear [Au(Tab)$_2$]$_2^{2+}$ dication in which two linear [Au(Tab)$_2$]$^+$ cations are linked *via* one unsupported aurophilic Au···Au interaction (3.0184(4) Å for X = I; 3.0146(3) Å for X = PF_6) (Fig. 5). There is an inversion center lying on the midpoint of the Au···Au line and a crystallographic twofold axis running along the line of the Au atoms.

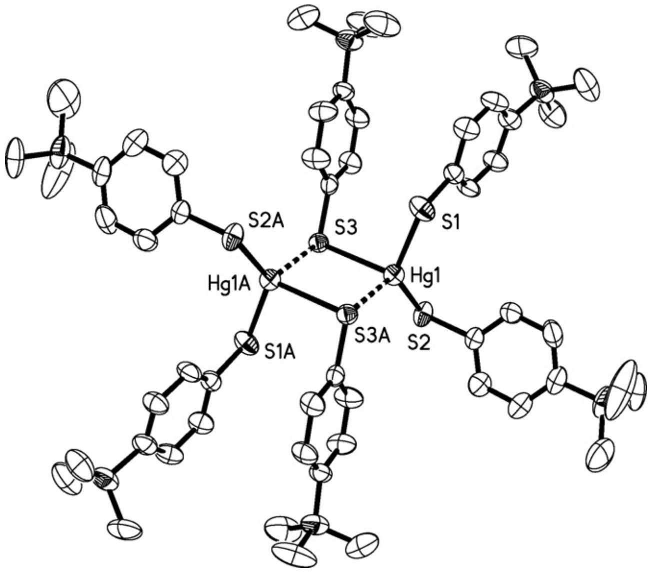


Fig. 4. View of the tetracation [Hg_2(Tab)$_6$]$^{4+}$ in [Hg_2(Tab)$_6$](PF_6)$_4$ or [Hg_2(Tab)$_6$]$_3$(PF_6)Cl_{11}. (From [69], with permission of © 2006 American Chemical Society.)

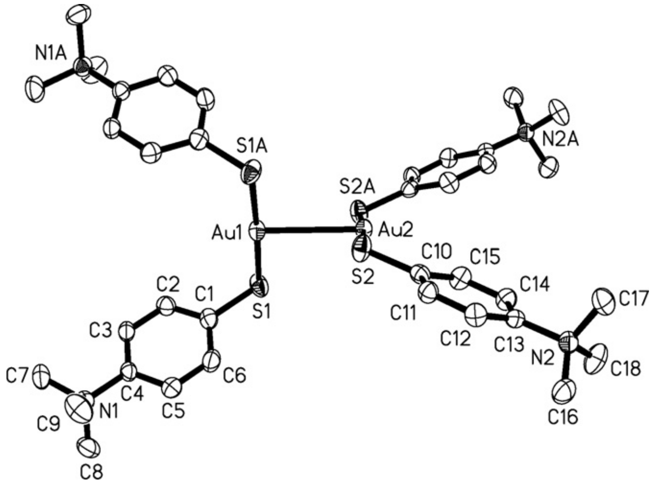


Fig. 5. Perspective view of the structure of the dication of [Au(Tab)$_2$]$_2$(PF_6)$_2$. (From [83], with permission of © 2006 American Chemical Society.)

3.3. Trinuclear complexes

Only one homoleptic complex [(μ_3-Cl){HgSCMe$_2$CH(NH_3)COO}$_3$]$_2$(μ-Cl)$_3$·(H_2O)$_2$·(H_2O·Cl)$_3$ [72], and one heterobimetallic complex [Hg(Tab)$_2$][Au(CN)$_2$]$_2$ [83] belong to this category.

Complex [(μ_3-Cl){HgSCMe$_2$CH(NH_3)COO}$_3$]$_2$(μ-Cl)$_3$·(H_2O)$_2$·(H_2O·Cl)$_3$ consists of a pyramidal trinuclear [(μ_3-Cl){HgSCMe$_2$CH(NH_3)COO}$_3$]$^{2+}$ unit in which three equivalent {HgSCMe$_2$CH(NH_3)COO}$^+$ units that are symmetrically linked by a μ_3-Cl atom. In contrast to the Cd(II) penicillamine complex {[CdBr(SCMe$_2$CH(NH_3)COO)H_2O]·2H_2O}$_n$ [71], the carboxylate groups in this Hg(II) complex fail to bind to Hg atoms but are strongly linked with the neighboring ones *via* O–H···O hydrogen bonds. Each trinuclear unit is further interconnected with adjacent ones by secondary Hg···Cl interactions (3.06(2) Å), affording a 3D network.

The heterobimetallic complex [Hg(Tab)$_2$][Au(CN)$_2$]$_2$ [83] is composed of the linear [Hg(Tab)$_2$]$^{2+}$ dications and [Au(CN)$_2$]$_2^{2-}$ dianions that are held together through secondary interactions between the Hg atom and two N atoms from the cyanides of the two neighboring dianions, forming a chain structure extending along the [1 0 1] plane (Fig. 6). There is an inversion centre on the Hg atom and a crystallographic twofold axis running through it. Each Hg center may be viewed as having a *pseudo*-square-planar coordination geometry. The dications are parallel to each other and each dianion is positioned between the dications. The Au···Au contact in [Au(CN)$_2$]$_2^{2-}$ dianion is 3.0140(5) Å.

3.4. Tetranuclear complexes

Complexes belonging to this group include: {[M(Tab)$_2$][Au(CN)$_2$]}$_2$ (M = Au, Ag) [83], and [Hg_4I_6($SCH_2CH_2NH_3$)$_2$($SCH_2CH_2NH_2$)$_2$] [86].

The two complexes {[M(Tab)$_2$][Au(CN)$_2$]}$_2$ (M = Au, Ag) [83] are isostructural and only the molecular structure of the

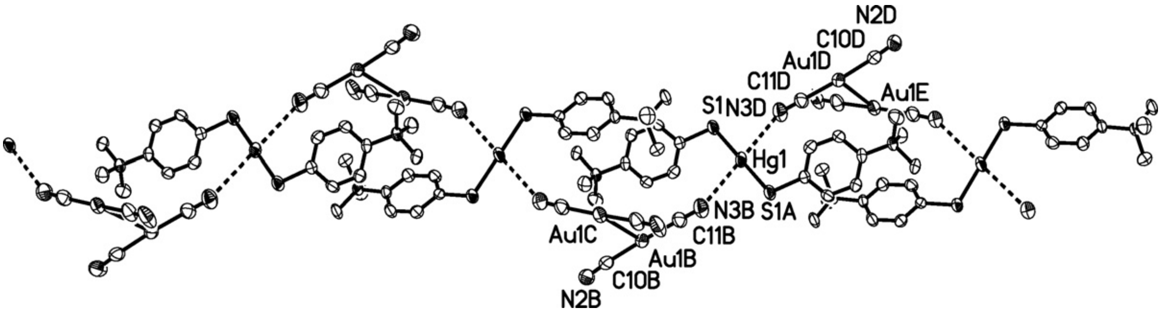


Fig. 6. View of a section of the chain formed *via* Hg···N secondary interactions in $[Hg(Tab)_2][Au(CN)_2]_2$. (From [83], with permission of © 2006 American Chemical Society.)

gold(I) complex is illustrated in Fig. 7. In both complexes, each pair of the $[M(Tab)_2]^+$ cation and the $[Au(CN)_2]^-$ anion are held together *via* ionic interaction to form a $\{[M(Tab)_2][Au(CN)_2]\}$ species. Two such species are further connected by one Au···Au aurophilic bonding interaction to form a Au_4 or Ag_2Au_2 string structure with three ligand-unassisted Au···Au or Ag···Au bonds. There is a crystallographic twofold axis running along the metal string. The length of the Au_4 or Ag_2Au_2 string is 9.124 or 8.892 Å.

Complex $[Hg_4I_6(SCH_2CH_2NH_3)_2(SCH_2CH_2NH_2)_2]$ [86] consists of a centrosymmetric non-planar octagonal ring with alternating Hg and S atoms, with the I atoms and S/N chelate emerged on the opposite sides of the mean plane. In this complex, the protonated $^-SCH_2CH_2NH_3^+$ and unprotonated $^-SCH_2CH_2NH_2$ ligands coexist. Two independent Hg atoms adopt distorted HgI_2S_2 or $HgIS_2N$ tetrahedral coordination geometries.

3.5. Pentanuclear complexes

Only one complex $\{Ag_5[S(CH_2)_3NHMe_2]_3[S(CH_2)_3NMe_2]_3\}(ClO_4)_2$ [76] was reported. Complex $\{Ag_5[S(CH_2)_3NHMe_2]_3[S(CH_2)_3NMe_2]_3\}(ClO_4)_2$ [76] contains a Ag_5S_6 core in which the Ag_5 polyhedron is a trigonal bipyramid and the S_6 polyhedron a trigonal prism. It has six doubly bridging thiolate ligands, leading to a trigonal planar coordination for Ag atoms that are related by a C_2 axis and a diagonal linear coordination for the other three Ag atoms that are related by one C_3 axis. Both protonated and unprotonated amine groups coexist in this complex.

3.6. Hexanuclear complexes

Two hexanuclear complexes $[Hg_6Cl_8(SCH_2CH_2NH_3)_8]Cl_4$ [79], and $[Cu_6(4\text{-}SpyH)_4Cl_6]$ [104] were structurally determined.

The cationic complex $[Hg_6Cl_8(SCH_2CH_2NH_3)_8]Cl_4$ [79] contains two equivalent trimeric $[Hg_3Cl_4(SCH_2CH_2NH_3)_3]^{2+}$ fragments linked by a pair of bridging $^-SCH_2CH_2NH_3^+$ ligands (Fig. 8). A μ_3-Cl atom links the three Hg atoms in each fragment at similar distances (average 2.924(3) Å). The geometries around Hg1 and Hg2 are distorted tetrahedral, namely HgS_2Cl_2, while that around Hg3 is distorted square pyramidal, namely HgS_3Cl_2. These $[Hg_6Cl_8(SCH_2CH_2NH_3)_8]^{4+}$ cations are held together *via* intermolecular hydrogen bonding involving the terminal NH_3^+ moiety and bridging S atoms, free chlorides, and water molecules, forming a 3D hydrogen-bonded network.

Complex $[Cu_6(4\text{-}SpyH)_4Cl_6]$ [104] may be viewed as having an octahedral core structure, in which six 'CuCl' units are bridged by four μ_3-4-SpyH ligands. Each Cu has an approximately trigonal planar coordination geometry.

3.7. Octanuclear complexes

Only one octanuclear cluster was reported: $[ClCd_8(4\text{-}SmpH)_{16}](ClO_4)_{15}$ [90]. Complex $[ClCd_8(4\text{-}SmpH)_{16}](ClO_4)_{15}$ contains a cationic $[ClCd_8(4\text{-}SmpH)_{16}]^{15+}$ species that consists of two Cd_4S_4 rings linked by a central Cl atom and four additional S atoms of 4-SmpH ligands that bridge the Cd atoms in the two rings (Fig. 9). The central Cl atom is surrounded by two pairs of Cd atoms in a nearly tetra-

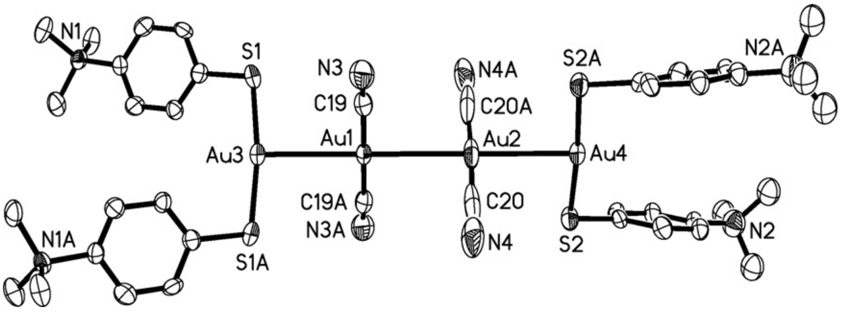


Fig. 7. Molecular structure of $\{[Au(Tab)_2][Au(CN)_2]\}_2$. (From [83], with permission of © 2006 American Chemical Society.)

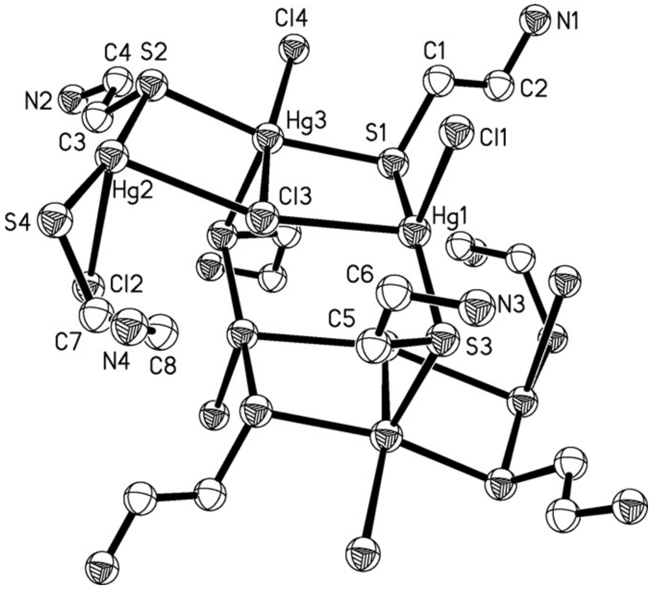


Fig. 8. Perspective view of the structure of the tetracation of $[\mathrm{Hg_6Cl_8(SCH_2CH_2NH_3)_8}]\mathrm{Cl_4}$. (From [79], with permission of © 2005 American Chemical Society.)

hedral geometry, and each pair belongs to a different $\mathrm{Cd_4S_4}$ ring, which contains two crystallographically independent Cd atoms. Each Cd atom is in a tetrahedral coordination: four are coordinated by two S atoms of their respective rings, the central Cl and an additional S of a mercaptoamine ligand, while the other four Cd atoms accomplish the tetrahedral coordination by two S atoms of their own ring, one of the bridging S atoms, and a terminal S atom from aminothiolate ligand. There are some structural correspondences between the $[\mathrm{ClCd_4(\mu\text{-}4\text{-}SmpH)_4(4\text{-}SmpH)_6}]$ fragment in $[\mathrm{ClCd_8(4\text{-}SmpH)_{16}}]^{15+}$ and the $\mathrm{Cd_4(S\text{-}Cys)_{11}}$ cluster in the α domain of the metallothionein (rat liver $\mathrm{Cd_5,Zn_2}$-MT) [112–116] both being formed by two fused six-membered cycles.

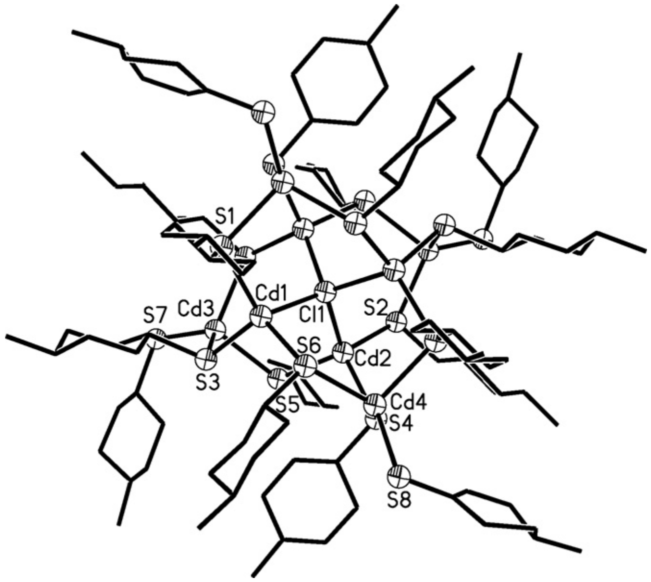


Fig. 9. View of the structure of the $[\mathrm{ClCd_8(4\text{-}mp)_{16}}]^{15+}$ cation looking along the crystallographic C_2 axis through the central Cl atom. All H atoms and the minor disorder components are omitted. (From [90], with permission of © 1998 American Chemical Society.)

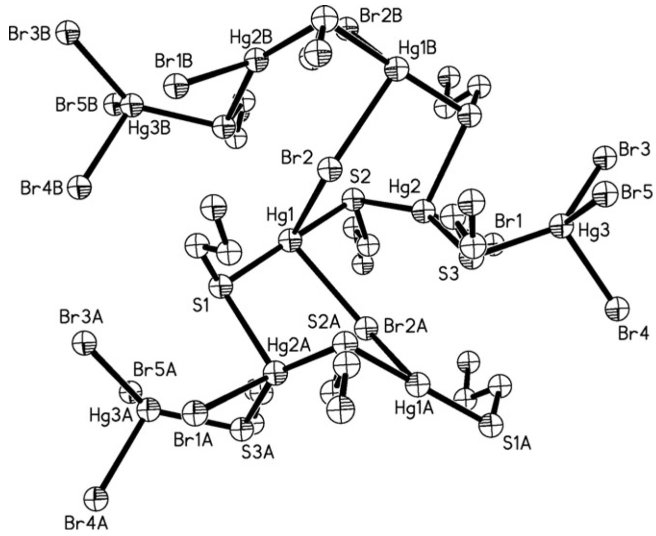


Fig. 10. View of the cation structure of $[\mathrm{Hg_9Br_{15}(SCH_2CH_2NH_3)_9}](\mathrm{Cl_{0.8}Br_{0.2}})_3$. (From [79], with permission of © 2005 American Chemical Society.)

3.8. *Nonanuclear complexes*

Complex $[\mathrm{Hg_9Br_{15}(SCH_2CH_2NH_3)_9}](\mathrm{Cl_{0.8}Br_{0.2}})_3$ [79] consists of three trinuclear $[\mathrm{Hg_3Br_5(SCH_2CH_2NH_3)_3}]^+$ units with bridging S and Br atoms (Fig. 10). In the whole molecule, three different types of coordination environments are observed for the Hg atoms, namely, $\mathrm{HgSBr_3}$, $\mathrm{HgS_2Br_2}$, and $\mathrm{HgS_3Br}$. The trimeric units are further interconnected *via* intermolecular hydrogen bondings between the terminal $\mathrm{NH_3}^+$ moiety and free halide, forming a 3D hydrogen-bonded network.

3.9. *Tetradecanuclear complexes*

Complex $[\mathrm{Ag_{14}(\mu_6\text{-}S)(Tab)_{12}(PPh_3)_8}](\mathrm{PF_6})_{12}$ [82] contains a $[\mathrm{Ag_{14}(\mu_6\text{-}S)(Tab)_{12}(PPh_3)_8}]^{12+}$ dodecacation which can be viewed as a distorted rock salt type, with the Ag atoms on the corners and the face centres and the S atoms on the edges and in the centre of the cube (Fig. 11). Each Ag atom on the cores adopts a distorted tetrahedral geometry while that on the face centres has a trigonal geometry.

3.10. *Octadecanuclear complexes*

The only octadecanuclear complex $[\mathrm{Ag_9(Tab)_8(MeCN)_8}]_2(\mathrm{PF_6})_{18}$ [103] contains an unprecedented long tubular motif in which one central saddle-shaped $\mathrm{Ag_6S_6}$ fragment and two identical $\mathrm{Ag_5S_6}$ fragments are interconnected by a pair of Ag atoms and four Ag–S bonds (Fig. 12). The $\mathrm{Ag_6S_6}$ fragment has two six-membered $\mathrm{Ag_3S_3}$ rings and each $\mathrm{Ag_5S_6}$ fragment is composed of one six-membered ring and one eight-membered ring, sharing a group of Ag and S atoms. The coordination geometry of the Ag atoms can be classified into three groups: distorted tetrahedral, pyramidalised Y-shape and trigonal planar.

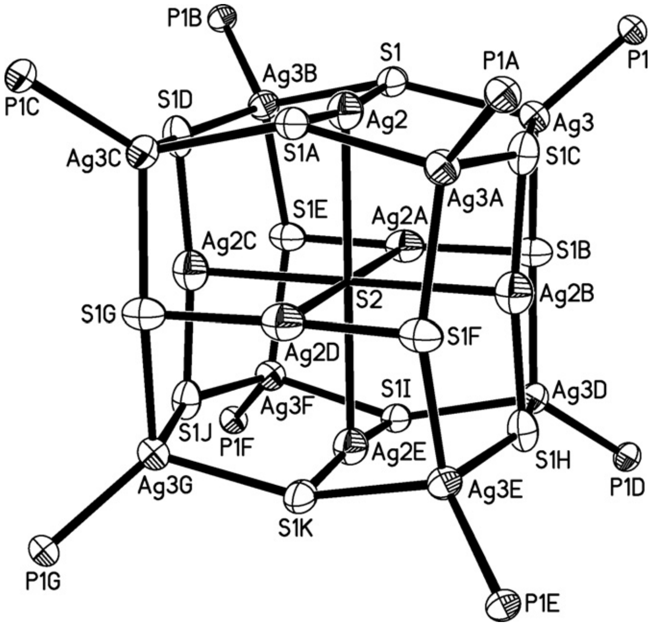


Fig. 11. Perspective view of the dodecacation of $[Ag_{14}(\mu_6\text{-}S)(Tab)_{12}(PPh_3)_8](PF_6)_{12}$. The $C_6H_4NMe_3$ and phenyl groups are omitted for clarity. (From [82], with permission of © 2004 Elsevier Science Ltd.)

3.11. Polymeric complexes

3.11.1. Copper(I) complexes

Complex $[Cu_5I_5(ptp)_2]_n$ [106] possesses a 3D network of twofold interpenetration formed by linking inorganic chains with ptp spacers (Fig. 13). The inorganic chains are constructed by alternately bridging the Cu_8I_8 and Cu_2I_2 cluster units with the μ-S atoms from ptp spacers. In the asymmetric unit three Cu(I) atoms adopt slightly distorted tetrahedral coordination geometries (CuI_2S_2, CuI_3N, CuI_2NS), while the other two adopt trigonal coordination geometries (CuI_3, CuI_2S) (Fig. 14). The Cu···Cu contacts are in the range of 2.538(3)–2.928(3) Å.

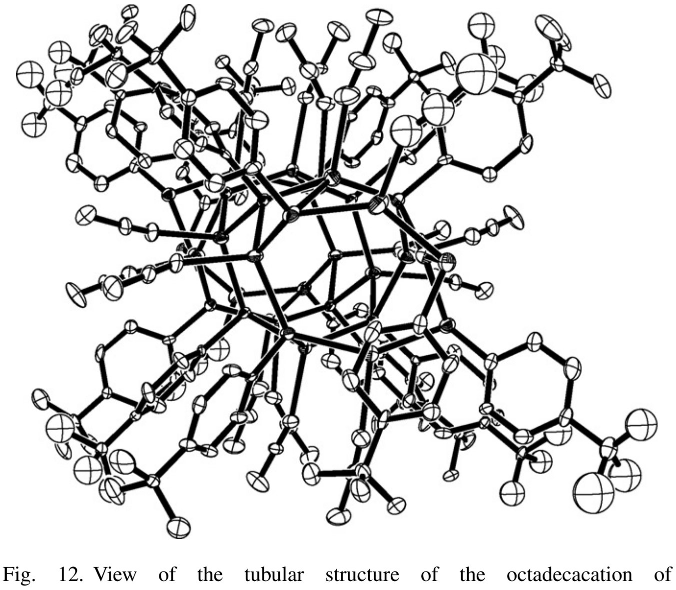


Fig. 12. View of the tubular structure of the octadecacation of $[Ag_9(Tab)_8(MeCN)_8]_2(PF_6)_{18}$, looking along the c axis. All H atoms are omitted for clarity. (From [103], with permission of © Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.)

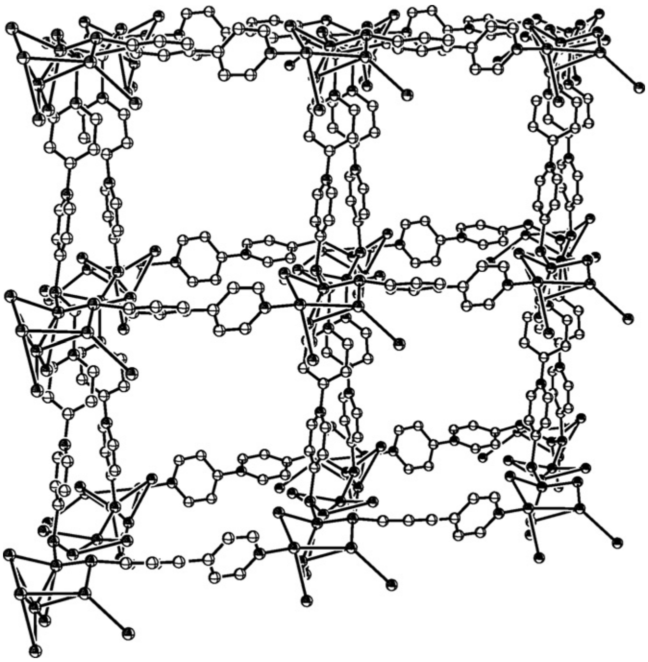


Fig. 13. View of a single 3D network of twofold interpenetrating nets in $[Cu_5I_5(ptp)_2]_n$. (From [106], with permission of © 2007 American Chemical Society.)

The other Cu(I)/ptp complex $[Cu_6I_6(ptp)_2]_n$ [106] has a non-interpenetrating 3D coordination network made up of 2D inorganic $(Cu_2I_2)_n$ layers and the ptp spacers (Fig. 15). There exists unique 20-membered $(CuI)_{10}$ circular units in the 2D $(Cu_2I_2)_n$ layers. Each layer of the (4,4) topology consists of three types of Cu_2I_2 dimeric units: the four-connected Cu_2I_2 unit, the two-connected Cu_2I_2 unit *via* the two I atoms as connectors, and the two-connected Cu_2I_2 unit *via* the two copper as connectors. Each Cu(I) atom completes a tetrahedral coordination environment with other two positions occupied by one I and one S from one ptp or by one S atom and one N atom from two ptp ligands.

Complex $\{[Cu_8Cl_6(SCH_2CH_2NH_3)_6]Cl_2\}_n$ [95] has a complicated polymeric ribbon structure in which the repeating

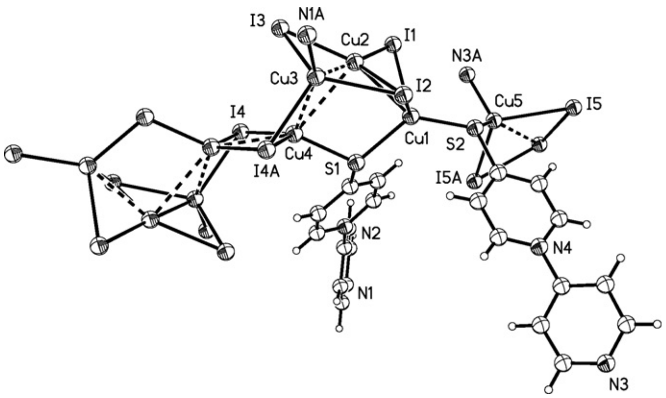


Fig. 14. View of a section of the inorganic chain in $[Cu_5I_5(ptp)_2]_n$. (From [106], with permission of © 2007 American Chemical Society.)

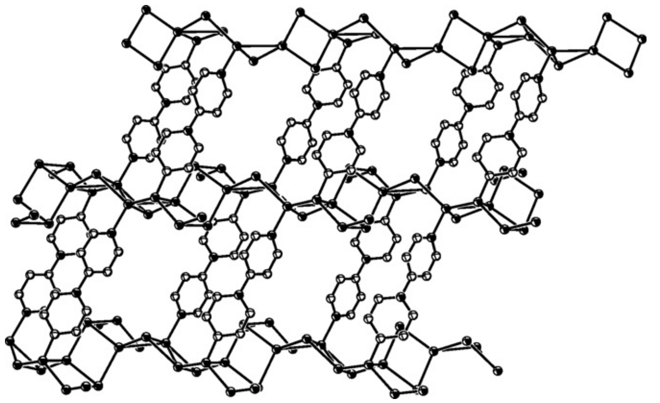


Fig. 15. View of the 3D network in $[Cu_6I_6(ptp)_2]_n$. (From [106], with permission of © 2007 American Chemical Society.)

$[Cu_{16}Cl_{12}(SCH_2CH_2NH_3)_{12}]^{4+}$ unit interconnects with its neighboring ones through two pairs of Cu–S bonds (Fig. 16). This tubular unit is composed of a centrosymmetric saddle-shaped Cu_6S_6 fragment and a centrosymmetric $Cu_{10}S_6$ fragment connected by Cu4–S1 and Cu5–S2 bonds. The Cu_6S_6 fragment contains two six-membered rings [Cu3–S1–Cu1–S2–Cu2–S3] and [Cu3A–S1A–Cu1A–S2A–Cu2A–S3A] linked by Cu1–S3A and Cu1A–S3 bonds. The $Cu_{10}S_6$ fragment contains two Cu_5S_3 sub-fragments held together by sharing two pairs of Cu–S bonds. Each sub-fragment may be viewed as a distorted Cu_5 square pyramid with a μ_4-S5 atom capping over its basal plane and two μ_3-S4 (or S6) atoms symmetrically capping over its two faces. Some Cu(I) atoms show trigonal planar coordination geometries ($CuClS_2$, CuS_3), while the other three adopt tetrahedral coordination geometries ($CuClS_3$). Most S atoms are in approximately tetrahedral geometries with three Cu atoms, but S5 atom is in the unique five-coordinated geometry that bridges four Cu atoms.

In the structure of $\{[Cu_{10}Cl_8(SpyH)_4]Cl_2\}_n$ [105], a 3D non-interpenetrating diamondoid network is formed by four-connecting a $Cu_{10}Cl_8$ unit to other equivalent units *via* four μ_4-Cl atoms. In the $Cu_{10}Cl_8$ unit, six Cu atoms form an octahedron and the other four Cu atoms are located at the capping sites of the four faces of the octahedron as a tetrahedral array (Fig. 17). Each Cu has a tetrahedral coordination while each S atom from 4-SpyH ligand acts as a μ_3-bridge. It is worth noting that each of the four μ_4-Cl atoms displays a square-planar coordination geometry.

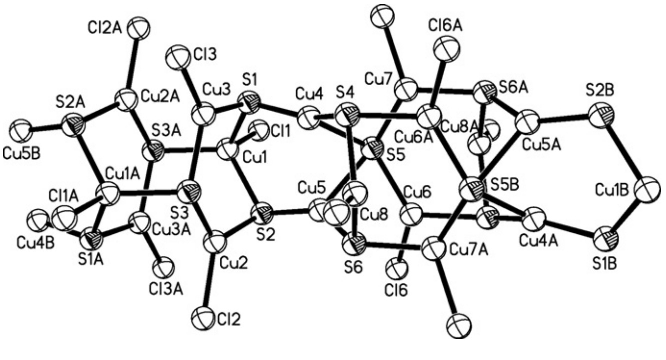


Fig. 16. View of a section of the chain in $\{[Cu_8Cl_6(SCH_2CH_2NH_3)_6]Cl_2\}_n$. The ethylammonium side chains of the $^-SCH_2CH_2NH_3^+$ ligand are omitted for clarity. (From [95], with permission of © The Royal Society of Chemistry 1997.)

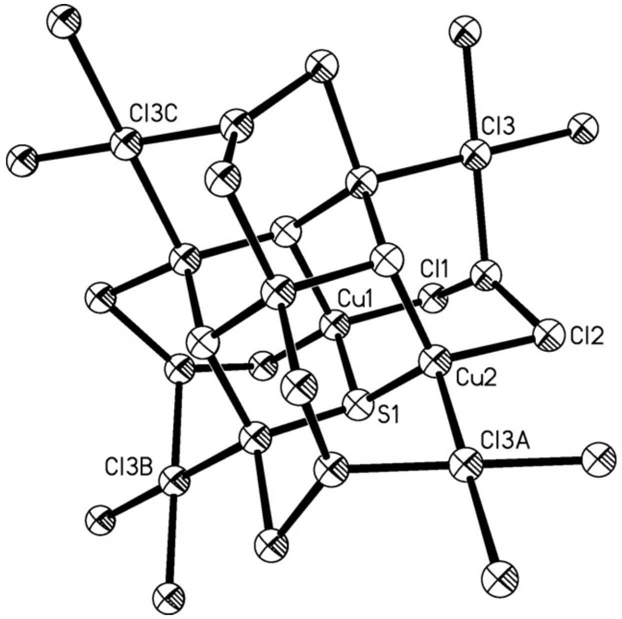


Fig. 17. Perspective view of the repeating unit of $\{[Cu_{10}Cl_8(SpyH)_4]Cl_2\}_n$. All pyridyl rings are omitted for clarity. (From [105], with permission of © 2005 American Chemical Society.)

The structure of $[Cu_{13}Cl_{13}(SCH_2CH_2NH_3)_6{\cdot}H_2O]_n$ [94] resembles that of $[Cu_{13}Br_{13}(SCH_2CH_2NH_3)_6]_n$ [96], and each of them contains an “Atlas-sphere” $Cu_{12}S_6$ core structure (Fig. 18). Each core has a regular octahedron of S atoms with each edge bridged by a CuCl unit. Alternatively, there are three mutually perpendicular, planar eight-membered $[CuCl(SCH_2CH_2NH_3)]_4$ rings that intersect gimbal-like “Atlas-sphere” at the μ_4-S atoms. All the thiolate S atoms are in the unique five-coordinated geometries with four equiva-

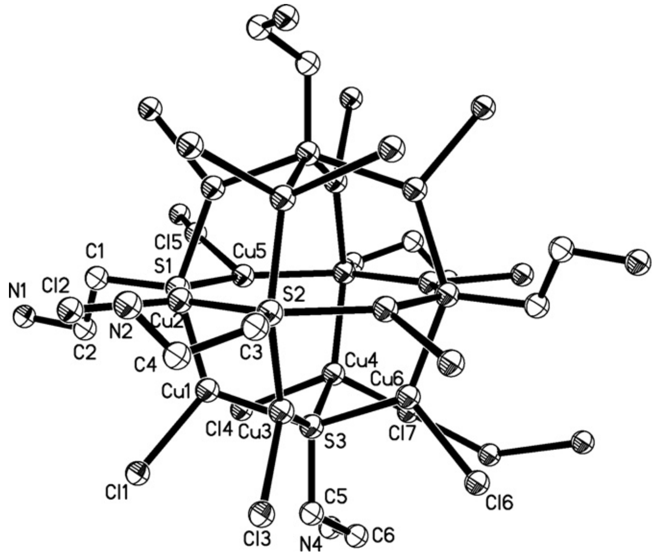


Fig. 18. Perspective view of the repeating unit of $[Cu_{13}Cl_{13}(SCH_2CH_2NH_3)_6{\cdot}H_2O]_n$. (From [94], with permission of © VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1997.)

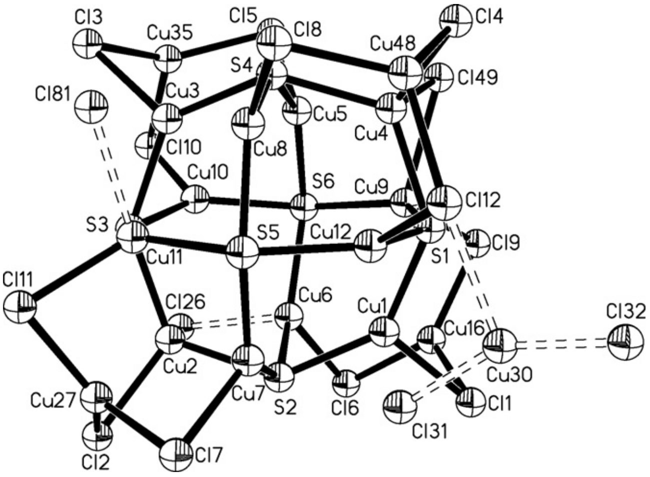


Fig. 19. Molecular structure of $[Cu_{17}Cl_{17}(SCH_2CH_2NHMe_2)_6]_n$. The $CH_2CH_2NHMe_2$ groups are omitted for clarity. (From [96], with permission of © The Royal Society of Chemistry 1999.)

lent copper atoms in addition to the ethylammonium group and each S atom is common to two eight-membered rings. The $Cu_{12}S_6$ cores in both complexes are linked by bridging halogen and Cu atoms, forming a 2D layer network. In the case of $[Cu_{13}Cl_{13}(SCH_2CH_2NH_3)_6{\cdot}H_2O]_n$ [94], one Cl atom links two Cu atoms of different clusters, forming a chain structure. Perpendicular to this direction, one Cu connects two Cl atoms of adjacent Atlas-spheres. Whereas in $[Cu_{13}Br_{13}(SCH_2CH_2NH_3)_6]_n$ [96], the second bridge is formed by a single Cu atom, which is disordered over four sites with unequal occupations.

Complex $[Cu_{17}Cl_{17}(SCH_2CH_2NHMe_2)_6]_n$ [96] holds a similar geometry and dimension to the two $Cu/SCH_2CH_2NH_3$ complexes [94,96]. Contrast to these two complexes, four alternate faces of the $Cu_{12}S_6$ octahedron in this complex are capped by additional four copper atoms, each of which is bonded to the Cl atoms of three separate CuCl units in the Atlas-sphere (Fig. 19). Four additional Cl atoms are located close to the remaining four faces of the $Cu_{12}S_6$ octahedron, being 2.5–2.6 Å from the two Cu atoms and 2.7 Å from a third Cu atom. Thus the third Cu(I) atom has a trigonal planar coordination geometry while the other copper atoms are four-coordinated. Atom Cl31 is bonded more closely (2.20 Å) to the 17th CuCl unit forming a $CuCl_2^-$ anion that is weakly (2.56 Å) connected to Cl12. The $Cu_{17}Cl_{17}S_6$ units are weakly linked by pairs of long bonds between two of the capping Cu atoms and Cl atoms of adjacent clusters, leading to a zigzag chain (across a glide plane).

3.11.2. *Silver(I) complexes*

Complex $[Ag_2(4\text{-SpyH})(NO_3)_2]_n$ [107] has a 2D lamella structure in which each Ag atom is tetrahedrally coordinated by two S atoms from two 4-SpyH ligands and two O atoms from two nitrate groups. Each 4-SpyH ligand acts as a μ_4-bridge linking four Ag atoms while the nitrate groups bridge two Ag atoms either with two O atoms or with one O atom.

Complex $\{[Ag_3(Tab)_4](PF_6)_3{\cdot}2DMF\}_n$ [82] contains a cationic chain in which the repeating $[Ag_6(Tab)_8]^{6+}$ units are linked by four Ag–S bonds (Fig. 20). Each $[Ag_6(Tab)_8]^{6+}$ has a saddle-shaped Ag_6S_6 core that involves two eight-membered Ag_4S_4 boat-like rings sharing the same boat-bottom plane. In the Ag_6S_6 core, Ag1 (or Ag1A) atom is coordinated by a μ_3-S and two μ-S atoms, forming an unique pyramidalised Y-shape coordination geometry.

Complex $\{[Ag_4(2\text{-StpmH})_6](NO_3)_4\}_n$ [84] has a cationic chain structure in which two infinite $[Ag(2\text{-StpmH})]_n^{n+}$ chains are connected by bridging 2-StpmH ligands (Fig. 21). A mirror plane parallel to the *bc* plane of the unit cell pass through atoms S1, C1, and C4. Each Ag atom has a trigonal planar geometry, coordinated by three S atoms from zwitterionic 2-StpmH ligands. Although the C–S bond length (1.724 Å) indicates a partial double-bond character, the C–N bond lengths as well as the C–N–C and N–C–S bond angles (123° and 120°) indicate that the ligand coordinates to the silver ion through its zwitterionic form.

In $[Ag_6Br_6(2\text{-StpmH})_6]_n$ [84], two cyclic $Ag_3(2\text{-StpmH})_3$ fragments are linked by two pair of bridging Br and 2-StpmH ligands and three Ag···Ag interactions (Ag2···Ag3B, Ag2···Ag3B; Ag3···Ag2B). The resulting dimeric $[Ag_3(2\text{-StpmH})_3(\mu\text{-Br})]_2$ species is further connected to the neighboring $Ag_3(2\text{-StpmH})_3$ *via* pairs of μ-Br atoms, forming a 1D ribbon structure (Fig. 22). Each Ag atom in $Ag_3(2\text{-StpmH})_3$ rings is tetrahedrally coordinated by two S atoms from 2-StpmH ligands and two Br atoms.

Complex $\{[Ag_8(SCH_2CH_2NH_3)_6Cl_6]Cl_2\}_n$ [97] consists of a cationic chain in which octanuclear $[Ag_8(SCH_2CH_2NH_3)_6Cl_6]^{2+}$ units are linked by Ag–S and Ag···Ag interactions (2.976(2)–3.046(3) Å) (Fig. 23). In the octanuclear unit, there is a crystallographic mirror plane going through Ag1, Ag3 and S2. Eight Ag centers display two types of coordination modes: AgS_3Cl and AgS_3. Each zwitterion $^-SCH_2CH_2NH_3^+$ acts as

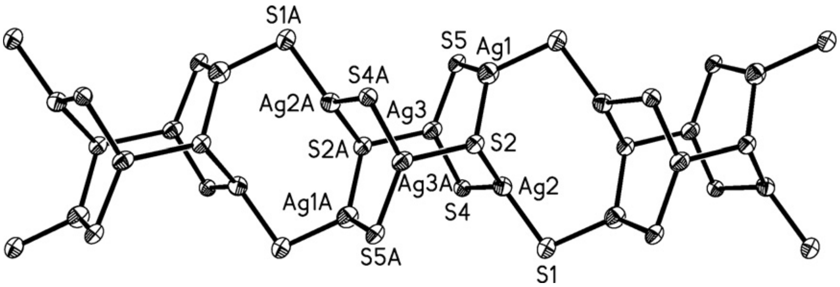


Fig. 20. Perspective view of a part of the cationic chain in $\{[Ag_3(Tab)_4](PF_6)_3{\cdot}2DMF\}_n$. The $C_6H_4NMe_3$ groups are omitted for clarity. (From [82], with permission of © 2004 Elsevier Science Ltd.)

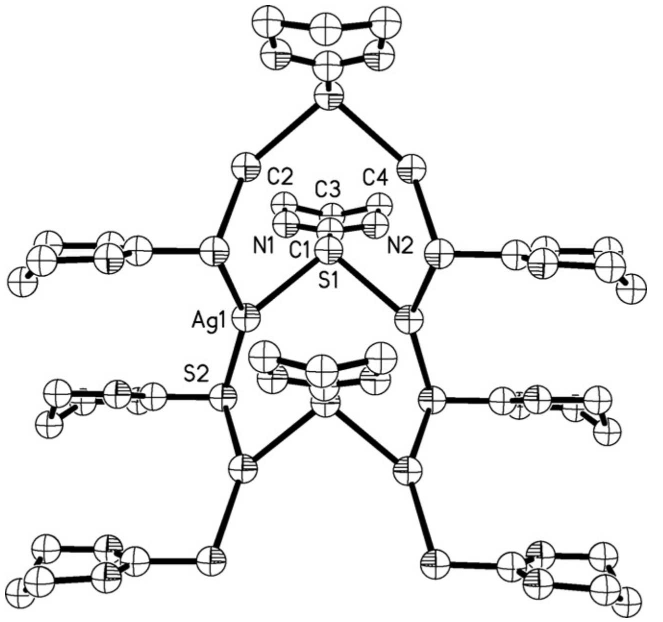


Fig. 21. View of a section of the cationic chain in $\{[Ag_4(StpmH_2)_6](NO_3)_4\}_n$. All H atoms are omitted for clarity. (From [84], with permission of © Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.)

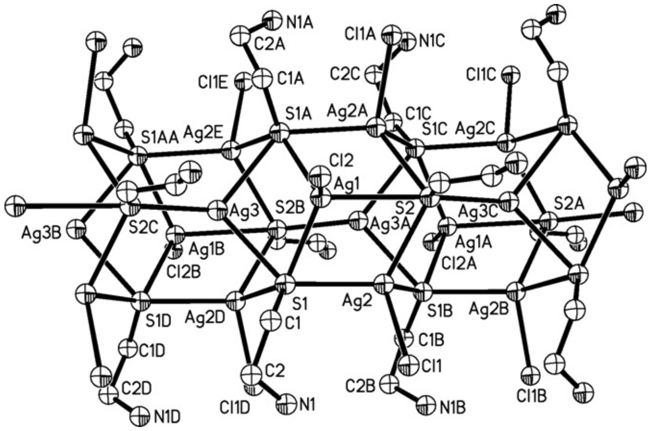


Fig. 23. View of a section of the cationic chain structure of $\{[Ag_8(SCH_2CH_2NH_3)_6Cl_6]Cl_2\}_n$. (From [97], with permission of © The Royal Society of Chemistry 1998.)

a μ_4-bridge linking four Ag atoms and is in a highly distorted square pyramidal geometry of $SCAg_4$ unit with one carbon atom at the apex and four Ag atoms in the equatorial plane.

Two silver(I) complexes with a common chemical formula $\{[Ag_{13}(4\text{-}SmpH)_{16}]X_{13}\}_n$ ($X = NO_3$, ClO_4) [98] are isostructural. Both consist of a cationic $\{[Ag_{13}(4\text{-}SmpH)_{16}]^{13+}\}_n$ chain formed *via* connecting $Ag_{10}(4\text{-}SmpH)_{16}$ fragments by three diagonally coordinated Ag atoms (Fig. 24). Each fragment is composed of a central $Ag_6(4\text{-}SmpH)_6$ core and two $Ag_4(4\text{-}SmpH)_4$ rings. The $Ag_6(4\text{-}SmpH)_6$ core can be further viewed as being built of four fused $Ag_3(4\text{-}SmpH)_3$ cycles in a boat fashion. Two eight-membered cycles of alternating Ag and S atoms emerge from the central Ag_6S_6 core. The 4-SmpH ligands serve as a doubly or triply bridging ligand and the silver centers adopt diagonal, trigonal and tetrahedral coordination geometries.

3.11.3. Cadmium(II) complexes

Complex $\{[CdBr(SCMe_2CH(NH_3)COO)H_2O]\cdot 2H_2O\}_n$ [71] contains a 1D ribbon structure in which two $[Cd(SCMe_2CH(NH_3)COO)H_2O]^+$ chains are linked by pairs of Br bridges (Fig. 25). These ribbons are further connected *via* hydrogen bonds between aminoacid moieties and water molecules trapped between the ribbons. Each Cd atom is in an octahedral fashion with one S atom from one penicillamine molecule, two Br atoms, two O atoms of the carboxylate group of a second aminoacid, and one O atom of a water molecule. Each penicillamine molecule acts as a tridentate bridge using a deprotonated sulfhydryl group and two O atoms of the carboxylate group to bind different Cd atoms.

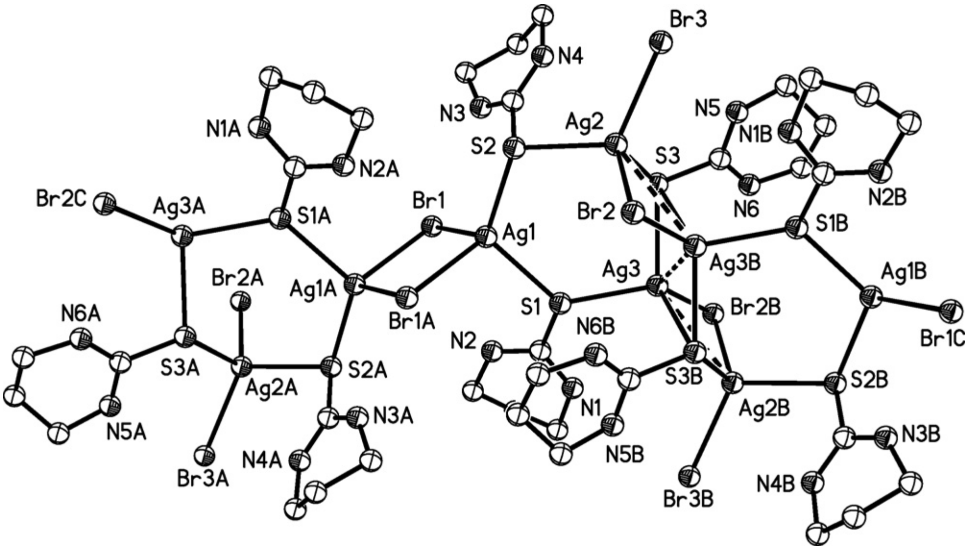


Fig. 22. View of a section of the 1D ribbon structure of $[Ag_6Br_6(StpmH_2)_6]_n$. (From [84], with permission of © Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.)

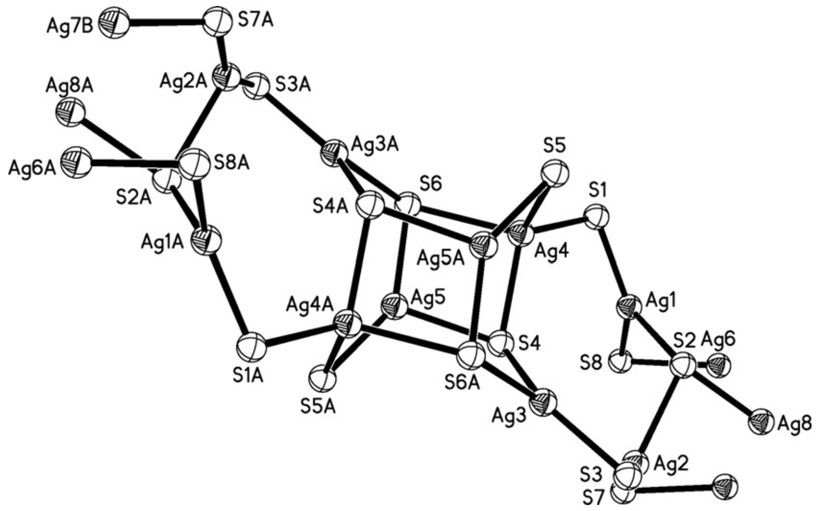


Fig. 24. View of the Ag_{10}(4-SmpH)$_6$ unit in $\{[Ag_{13}(4\text{-}SmpH)_{16}](ClO_4)_{13}\}_n$. All ligand atoms, except for S atoms are omitted for clarity. (From [98], with permission of © 1990 Elsevier Science Ltd.)

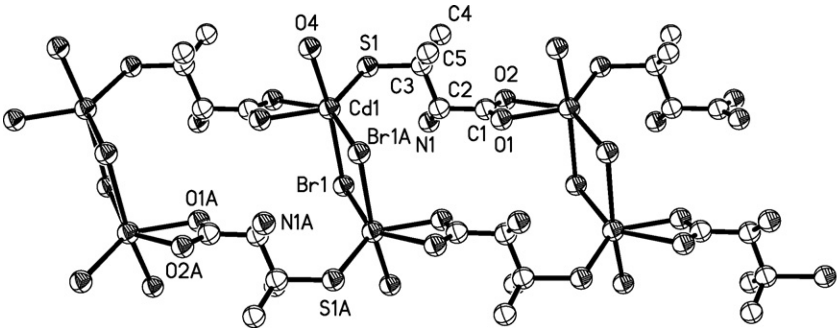


Fig. 25. View of a section of the ribbon structure in $\{[CdBr(SCMe_2CH(NH_3)COO)H_2O]\cdot 2H_2O\}_n$. (From [71], with permission of © 1977 American Chemical Society.)

$[\{Cd(4\text{-}SmpH)_2\}(ClO_4)_2\cdot 2H_2O]_n$ [91] consists of a cationic chain in which $[Cd_2(4\text{-}SmpH)_2]^{2+}$ fragments are linked with pairs of μ-4-SmpH ligands. Each Cd atom is tetrahedrally coordinated by μ-S atoms of 4-SmpH ligands and is spaced equidistantly along the *c* axis (Fig. 26).

Complex $[Cd_5Cl_{10}(SCH_2CH_2NH_3)_2]_n$ [77] has a 3D structure in which $[Cd_6Cl_6(SCH_2CH_2NH_3)_4]_n$ chains (extending along the a axis) are held together by three pairs of μ-Cl bridges along the *bc* plane. The chain is built from $[Cd_6Cl_6(SCH_2CH_2NH_3)_4]$ units *via* sharing two Cd atoms. Each $[Cd_6Cl_4(SCH_2CH_2NH_3)_4]$ unit contains two double incomplete cubane-like $[Cd_4Cl_4S_2]$ fragments fused by sharing one Cd_2Cl_2 ring (Fig. 27). The double incomplete cubane-like fragment is made of two opposite open cubane $[Cd_3Cl_3S]$ units sharing one Cd_2Cl_2 ring. The Cd atom is in an octahedral $CdSCl_5$ or CdS_2Cl_4 coordination geometry.

3.11.4. Mercury(II) complexes

In $\{[HgCl(SCMe_2CH(NH_3)COOH)_2]Cl\cdot H_2O\}_n$ [93], two S atoms of the two $SCMe_2CH(NH_3)COOH$ ligands coordinate to Hg atom in an approximately linear fashion. One Cl atom further binds to Hg(II) to form a T-shaped coordination geometry. The $[HgCl(SCMe_2CH(NH_3)COOH)_2]^+$ cations are linked

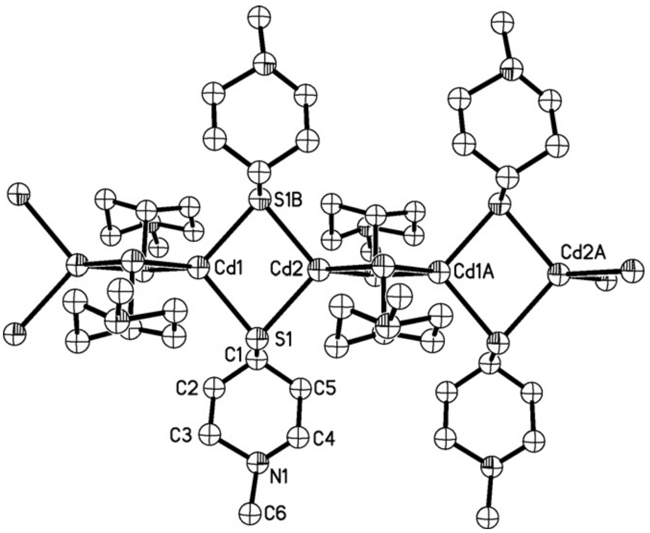


Fig. 26. View of a section of the chain in $[\{Cd(4\text{-}SmpH)\}(ClO_4)_2\cdot 2H_2O]_n$. (From [91], with permission of © 1979 American Chemical Society.)

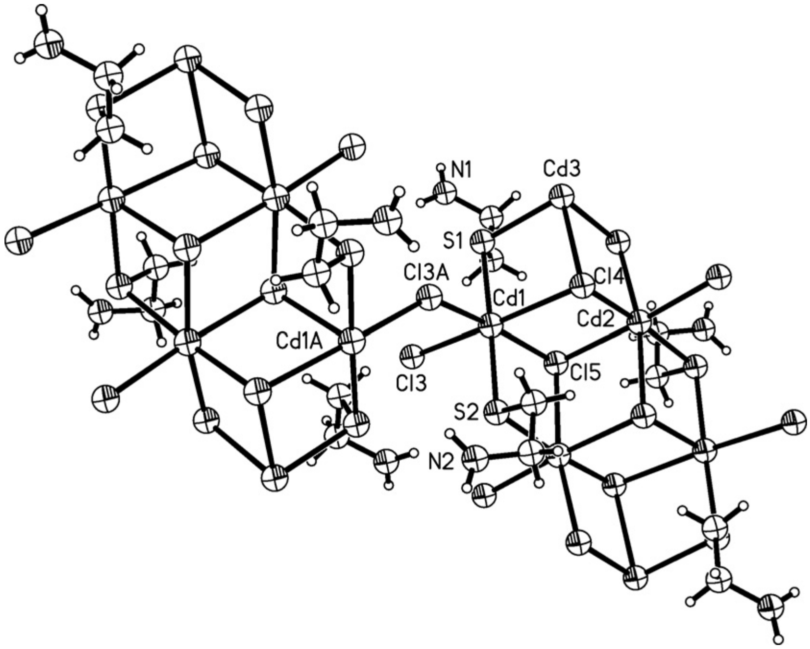


Fig. 27. View of the unique repeating unit of $[Cd_5Cl_{10}(SCH_2CH_2NH_3)_2]_n$. (From [77], with permission of © 2005 Elsevier Science Ltd.)

into a spiral cationic chain by Hg···Cl secondary interaction (3.323(5) Å).

Complex $\{[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot 0.5[S(CH_2)_3NMe_3]\}_n$ [85] contains a similar cationic chain to that of $[\{Cd(4\text{-}SmpH)_2\}(ClO_4)_2\cdot 2H_2O]_n$, in which Hg atoms are connected through pairs of two doubly bridging $S(CH_2)_3NMe_3$ ligands. Each Hg atom is tetrahedrally coordinated by four μ-S atoms of four $S(CH_2)_3NMe_3$ ligands. The surplus positive charge of this cationic chain is compensated by PF_6^- anions, which are located in-between the cation chains. Additional zwitterionic $S(CH_2)_3NMe_3$ molecules apparently lie in the wide channels running parallel to the *c* axis and to the cationic chains.

Complexes $[MX_2\{S(CH_2)_3NHMe_2\}]_n$ (M = Cd, X = Cl, Br; M = Hg, X = Cl) [73–75], and $[HgCl_2\{SCH_2CH(NH_3)COOH\}]_n$ are isostructural. In these structures, MX_2 units are connected by $^-S(CH_2)_3NHMe_2^+$ or $^-SCH_2CH(NH_3^+)COOH$ ligands to form a spiral chain. Each M atom is tetrahedrally coordinated by two bridging S atoms and two terminal halogen atoms, and the M and S atoms within a chain are coplanar.

Complex $\{(HgCl_2)_2[SCMe_2CH(NH_3)COOH]_2\cdot 2H_2O\}_n$ [93] consists of $[HgCl_3]^-$ anions and $[ClHgSCMe_2CH(NH_3)COOH]^+$ cations linked by secondary Hg···Cl and Hg···S interactions, forming a 1D ribbon structure. The penicillamine ligand strongly binds to one Hg atom (2.356(5) Å) and loosely interacted with the other Hg (2.822(5) Å) by the deprotonated sulfydryl group.

Complex $\{[Hg_3Cl_5(SCH_2CH_2NH_3)_3]Cl\}_n$ [102] has an infinite chain of alternative Hg and S atoms with three independent types of Hg atoms, namely HgS_2Cl (slightly distorted 'T' shaped), HgS_3Cl and $HgSCl_3$ (distorted tetrahedral) (Fig. 28). The amine protons are involved in intermolecular hydrogen bonding with Cl atoms of a second chain to acquire a 3D hydrogen-bonded structure.

Complex $[Hg_4I_8(SCH_2CH_2NH_3)_2]_n$ has a chain structure in which the tetranuclear repeating unit consists of three independent distorted tetrahedrally coordinated Hg centers, namely HgI_3S, HgI_2S_2, and HgI_4, and is connected through μ-S atoms (Fig. 29).

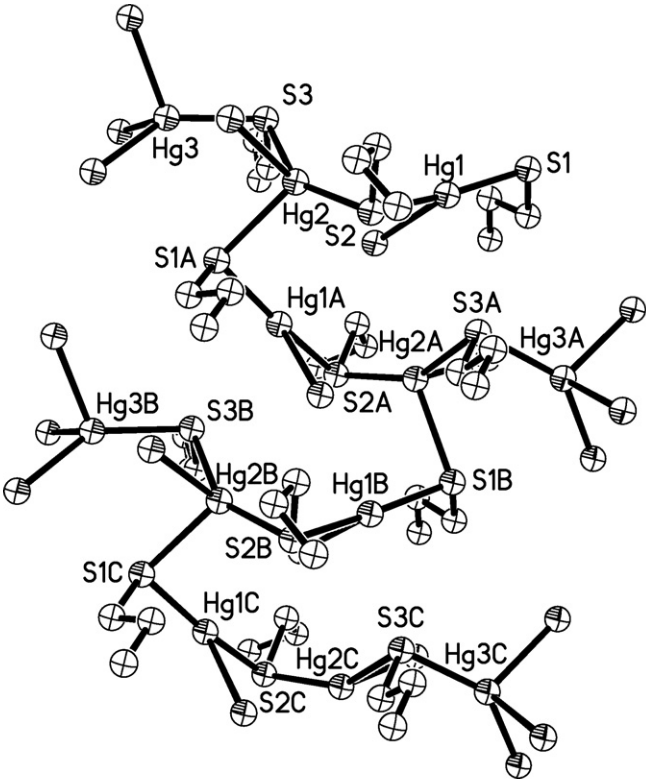


Fig. 28. View of a section of the chain structure of $\{[Hg_3Cl_5(SCH_2CH_2NH_3)_3]Cl\}_n$. The hydrogen and free Cl atoms are omitted for clarity. (From [102], with permission of © The Royal Society of Chemistry 2005.)

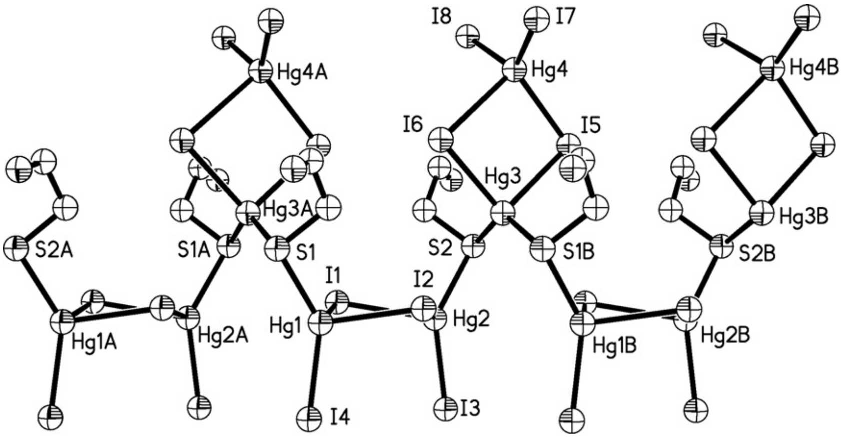


Fig. 29. View of a section of the chain in $[Hg_4I_8(SCH_2CH_2NH_3)_2]_n$. (From [80], with permission of © 2006 American Chemical Society.)

4. Conclusions

This review surveyed seven typical synthetic methods for the groups 11 and 12 metal complexes of the zwitterionic ammonium thiolates. About 70 metal complexes of zwitterionic ammonium thiolate complexes were collected and classified according to the number of metal atoms and their specific structures were briefly described. The general structural characteristics for these complexes are summarized as follows.

(1) Zwitterionic ammonium thiolates possess variable coordination modes and work as unidentate, doubly, triply, and quadruply bridged ligands. The alkyl zwitterionic thiolates (e.g. $^-SCH_2CH_2NH_3^+$) have more tendency to form high-nuclearity metal complexes than the heterocyclic and aromatic zwitterionic thiolates.

(2) The chemistry of copper(I) and silver(I) and mercury(II) complexes is more complicated than those of the gold(I), zinc(II), and cadmium(II) complexes. Copper(I) and silver(I) complexes are of high nuclearity (e.g. tetradeca- and octadeca-nuclear). Zn(II) and Cd(II) complexes seem less explored relative to those of group 11 metals and mercury(II).

(3) Copper(I), silver(I), and mercury(II) complexes usually show coordination numbers from 2 to 4. Whereas two-coordination prevails in the chemistry of Au(I), four- or six-coordination prevails in the chemistry of Zn(II) and Cd(II). However, some Au(I) complexes possess evident Au···Au aurophilic interactions in their structures [83], while some Hg(II) complexes have secondary interactions between Hg and S (or Cl, Br, I, O, N) atoms. These weak interactions play an important role in the formation of various intriguing low-dimensional structures [69,85,95].

(4) As shown in Table 1, there is a trend for the M–S bond distance to increase with increasing coordination number. For example, the terminal Hg–S distances vary from about 2.33 Å (two-coordinate) to 2.55 Å (four-coordinate). The triply bridging Ag-μ_3-S lengths range from 2.406 Å (two-coordinate) to 2.561 Å (three-coordinate) to 2.721 Å (four-coordinate). There are some exceptions, especially for the bridging M–S bond lengths which cover a wide range of values.

Although the synthetic and structural chemistry of the groups 11 and 12 metals complexes with zwitterionic ammonium thiolates are the theme in many reports, their potential applications in biological systems and advanced materials also appear in some literatures. For instance, some of these complexes might provide insights into the nature of the coordination of metal ions to the proteins and enzymes in living systems [69,90]. In $[ClCd_8(4\text{-SmpH})_{16}](ClO_4)_{15}$ [90], the $Cd_4(4\text{-SmpH})_{11}$ fragment shows similar structural features to the $Cd_4(S\text{-Cys})_{11}$ cluster found in the α domain of rat liver Cd_5,Zn_2-MT [112–116]. Furthermore, unique luminescent properties have been found for several metal complexes of zwitterionic thiolates [82,83,105,106]. Some silver(I) and gold(I) complexes could be used as preformed luminescent precursors to prepare emissive materials with optional performances [101,103]. Some silver(I)/StmpH complexes were investigated for their cytostatic activity against murine leukemia and human T lymphocyte cells and for their antiviral activity against a wide variety of viruses [84]. Some gold(I) complexes may be used as anti-arthritic drug models and have potential applications as anti-arthritic agents [100], substrates for self-assembled monolayers (SAMs) [117] and gold sensitizers for photographic silver halide dispersions [99]. Studies on these respects are anticipated to be very challenging but very important and promising topics in the future.

Acknowledgements

This work was supported by the Distinguished Young Scholar Fund of NNSF to J.P. Lang (No. 20525101), the NSF of Jiangsu Province (No. BK2004205), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20050285004), the State Key Laboratory of Organometallic Chemistry of Shanghai Institute of Organic Chemistry (06-26), and the Qin-Lan Project of Jiangsu Province in China. We highly appreciate the helpful comments of the editor and reviewers.

References

[1] R.D. Adams, S.B. Falloon, Chem. Rev. 95 (1995) 2587.
[2] B. Krebs, G. Henkel, Angew. Chem. Int. Ed. 30 (1991) 769.
[3] I.G. Dance, A. Choy, M.L. Scudder, J. Am. Chem. Soc. 106 (1984) 6285.
[4] I.J. Pickering, G.N. George, C.T. Dameron, B. Kurz, D.R. Winge, I.G. Dance, J. Am. Chem. Soc. 115 (1993) 9498.
[5] F. Nief, Coord. Chem. Rev. 178–180 (1998) 13.
[6] P.A. Perez-Lourido, J.A. Garcia-Vazquez, J. Romero, M.S. Louro, A. Sousa, Q. Chen, Y. Chang, J. Zubieta, J. Chem. Soc., Dalton Trans. (1996) 2047.
[7] Z.Q. Yang, A.B. Smetana, C.M. Sorensen, K.J. Klabunde, Inorg. Chem. 46 (2007) 2427.
[8] C.J. Murphy, J. Cluster Sci. 7 (1996) 341.
[9] S.H. Chen, T. Ida, K. Kimura, J. Phys. Chem. B 102 (1998) 6169.
[10] M. Liang, N. Lackey, S. Carter, M.L. Norton, J. Electrochem. Soc. 143 (1996) 3117.
[11] J. Rodriguez-Castro, P. Dale, M.F. Mahon, K.C. Molloy, L.M. Peter, Chem. Mater. 19 (2007) 3219.
[12] H. Gronbeck, H. Hakkinen, J. Phys. Chem. B. 111 (2007) 3325.
[13] V.W.W. Yam, C.L. Chan, C.K. Li, K.M.C. Wong, Coord. Chem. Rev. 216–217 (2001) 173.
[14] X.L. Jin, X.J. Xie, H. Qian, K.L. Tang, C.L. Liu, X. Wang, Q.H. Gong, Chem. Commun. (2002) 600.
[15] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Chem. Rev. 105 (2005) 1103.
[16] M.K. Corbierre, R.B. Lennox, Chem. Mater. 17 (2005) 5691.
[17] M.T. Coffer, C.F. Shaw, M.K. Eidsness, J.W. Watkins, R.C. Elder, Inorg. Chem. 25 (1986) 333.
[18] P.J. Sadler, Adv. Inorg. Chem. 36 (1991) 1.
[19] W. Kim, K.S. Gates, Chem. Res. Toxicol. 10 (1997) 296.
[20] M.J. McKeage, L. Maharaj, S.J. Berners-Price, Coord. Chem. Rev. 232 (2002) 127.
[21] K. Sorasaenee, J.R. Galan-Mascaro, K.R. Dunbar, Inorg. Chem. 41 (2002) 433.
[22] H.B. Kaatz, N. Metzler-Nolte (Eds.), Concepts and Models in Bioinorganic Chemistry, Wiley–VCH, Weinheim, 2006.
[23] M. Wruble, J. Am. Pharm. Assoc. Sci. Ed. 32 (1943) 80.
[24] K. Nomiya, S. Takahashi, R. Noguchi, J. Chem. Soc., Dalton Trans. (2000) 2091.
[25] K.C. Dash, H. Schmidbaur, in: H. Sigel (Ed.), Metal Ions in Biological Systems, 14, Marcel Dekker, New York, 1982, p. 179.
[26] J. Chan, Z.Y. Huang, M.E. Merrifield, M.T. Salgado, M.J. Stillman, Coord. Chem. Rev. 233–234 (2002) 319.
[27] A.J. Zelazowski, M.J. Stillman, Inorg. Chem. 31 (1992) 3363.
[28] M.D. Curtis, Appl. Organomet. Chem. 6 (1992) 429.
[29] C. Gourlay, D.J. Nielsen, J.M. White, S.Z. Knottenbelt, M.L. Kirk, C.G. Young, J. Am. Chem. Soc. 128 (2006) 2164.
[30] S. Akine, T. Nabeshima, Inorg. Chem. 44 (2005) 1205.
[31] C.A. Blindauer, P.J. Sadler, Acc. Chem. Res. 38 (2005) 62.
[32] G. Henkel, B. Krebs, Chem. Rev. 104 (2004) 801.
[33] J.M. Boyd, S.A. Ensign, Biochemistry 44 (2005) 13151.
[34] O. Einsle, S.L.A. Andrade, H. Dobbek, J. Meyer, D.C. Rees, J. Am. Chem. Soc. 129 (2007) 2210.
[35] A. Dey, S.P. Jeffrey, M. Darensbourg, K.O. Hodgson, B. Hedman, E.I. Solomon, Inorg. Chem. 46 (2007) 4989.
[36] D. Volkmer, B. Hommerich, K. Griesar, W. Haase, B. Krebs, Inorg. Chem. 35 (1996) 3792.
[37] J. Conradie, J.C. Swarts, A. Ghosh, J. Phys. Chem. B 108 (2004) 452.
[38] I.G. Dance, Polyhedron 5 (1986) 1037.
[39] J.A. Garcia-Vazquez, J. Romero, A. Sousa, Coord. Chem. Rev. 193 (1999) 691.
[40] M.J. Stillman, Coord. Chem. Rev. 144 (1995) 461.
[41] B.S. Kang, Z.N. Chen, Z.Y. Zhou, H.Q. Liu, H.R. Gao, B.M. Wu, T.C.W. Mak, Y.B. Cai, Y.J. Xu, Z.T. Xu, J. Cluster Sci. 7 (1996) 317.
[42] I. Dance, K. Fisher, Prog. Inorg. Chem. 41 (1994) 637.
[43] H.X. Li, Y.J. Zhu, M.L. Cheng, Z.G. Ren, J.P. Lang, Q. Shen, Coord. Chem. Rev. 250 (2006) 2059.
[44] D. Coucouvanis, Acc. Chem. Res. 24 (1991) 1.
[45] R.H. Holm, S. Ciurli, H.A. Weigel, Prog. Inorg. Chem. 38 (1990) 1.
[46] M.J. Stillman, D. Thomas, C. Trevithick, X. Guo, M. Siu, J. Inorg. Biochem. 79 (2000) 11.
[47] K. Tang, Y. Tang, Heteroatom Chem. 2 (1990) 345.
[48] P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121.
[49] E.S. Raper, Coord. Chem. Rev. 61 (1985) 115.
[50] E.S. Raper, Coord. Chem. Rev. 129 (1994) 91.
[51] E.S. Raper, Coord. Chem. Rev. 153 (1996) 199.
[52] E.S. Raper, Coord. Chem. Rev. 165 (1997) 475.
[53] H. Fleischer, Coord. Chem. Rev. 249 (2005) 799.
[54] P.D. Akrivos, Coord. Chem. Rev. 213 (2001) 181.
[55] M.A. Ali, S.E. Livingstone, Coord. Chem. Rev. 13 (1974) 101.
[56] R. Krishnan, J.K. Voo, C.G. Riordan, L. Zahkarov, A.L. Rheingold, J. Am. Chem. Soc. 125 (2003) 4422.
[57] Y.M. Yang, H.F. Ji, T. Thundat, J. Am. Chem. Soc. 125 (2003) 1124.
[58] L.R. Olsen, B. Huang, M.W. Vetting, S.L. Roderick, Biochemistry 43 (2004) 6013.
[59] G.G. Briand, N. Burford, T.S. Cameron, W. Kwiatkowski, J. Am. Chem. Soc. 120 (1998) 11374.
[60] C.Y. Zhou, J.W. Raebiger, B.M. Segal, R.H. Holm, Inorg. Chim. Acta 300–302 (2000) 892.
[61] H. Fleischer, D. Schollmeyer, Inorg. Chem. 43 (2004) 5529.
[62] G.G. Briand, N. Burford, T.S. Cameron, J. Chem. Soc., Chem. Commun. (1997) 2365.
[63] P. Karagiannidis, P. Aslanidis, D.P. Kessissoglou, B. Krebs, M. Dartmann, Inorg. Chim. Acta 156 (1989) 47.
[64] U. Abram, J. Mack, K. Ortner, M. Müller, J. Chem. Soc., Dalton Trans. (1998) 1011.
[65] K.S. Anjali, J.J. Vittal, P.A.W. Dean, Inorg. Chim. Acta 351 (2003) 79.
[66] H. Barrera, J.C. Bayon, P. Gonzalez-Duarte, J. Sola, J.M. Vinas, J.L. Brianso, M.C. Brianso, X. Solans, Polyhedron 1 (1982) 647.
[67] M.C. Brianso, J.L. Brianso, W. Gaete, J. Ros, C. Suner, J. Chem. Soc., Dalton Trans. (1981) 852.
[68] J.C. Bayon, I. Casals, W. Gaete, P. Gonzalez-Duarte, J. Ros, Polyhedron 1 (1982) 157.
[69] J.X. Chen, W.H. Zhang, X.Y. Tang, Z.G. Ren, Y. Zhang, J.P. Lang, Inorg. Chem. 45 (2006) 2568.
[70] N. Davidovic, D. Matkovic-Calogovic, Z. Popovic, I. Vedrina-Dragojevic, Acta Crystallogr. C 54 (1998) 574.
[71] A.J. Carty, N.J. Taylor, Inorg. Chem. 16 (1977) 177.
[72] L. Book, T.C.W. Mak, Inorg. Chim. Acta 92 (1984) 265.
[73] I. Casal, P. Gonzalez-Duarte, J. Sola, C. Miravitlles, E. Molins, Polyhedron 24 (1988) 2509.
[74] I. Casals, P. Gonzalez-Duarte, J. Sola, M. Font-Bardia, J. Solans, X. Solans, J. Chem. Soc., Dalton Trans. (1987) 2391.
[75] W. Clegg, I. Casals, P. Gonzalez-Duarte, Acta Crystallogr. C 49 (1993) 129.
[76] P. Gonzalez-Duarte, J. Sola, J. Vives, X. Solans, J. Chem. Soc., Chem. Commun. (1987) 1641.
[77] M.S. Bharara, C.H. Kim, S. Parkin, D.A. Atwood, Polyhedron 24 (2005) 865.
[78] C.H. Kim, S. Parkin, M. Bharara, D.A. Atwood, Polyhedron 21 (2002) 225.
[79] M.S. Bharara, T.H. Bui, S. Parkin, D.A. Atwood, Inorg. Chem. 44 (2005) 5753.
[80] M.S. Bharara, S. Parkin, D.A. Atwood, Inorg. Chem. 45 (2006) 2112.
[81] L.S. Ahmed, W. Clegg, D.A. Davies, J.R. Dilworth, M.R.J. Elsegood, D.V. Griffiths, L. Horsburgh, J.R. Miller, N. Wheatley, Polyhedron 18 (1998) 593.
[82] J.X. Chen, Q.F. Xu, Y. Zhang, Z.N. Chen, J.P. Lang, J. Organomet. Chem. 689 (2004) 1071.
[83] J.X. Chen, W.H. Zhang, X.Y. Tang, Z.G. Ren, H.X. Li, Y. Zhang, J.P. Lang, Inorg. Chem. 45 (2006) 7671.
[84] P.C. Zachariadis, S.K. Hadjikakou, N. Hadjiliadis, S. Skoulika, A. Michaelides, J. Balzarini, E.D. Clercq, Eur. J. Inorg. Chem. (2004) 1420.
[85] I. Casals, P. Gonzalez-Duarte, W. Clegg, Inorg. Chim. Acta 184 (1991) 167.

[86] M.S. Bharara, S. Parkin, D.A. Atwood, Inorg. Chem. 45 (2006) 7261.

[87] Y.S. Wong, P.C. Chieh, A.J. Carty, J. Chem. Soc., Chem. Commun. (1973) 741.

[88] Y.S. Wong, A.J. Carty, C. Chieh, J. Chem. Soc., Dalton Trans. (1977) 1801.

[89] N.J. Taylor, Y.S. Wong, P.C. Chieh, A.J. Carty, J. Chem. Soc., Dalton Trans. (1975) 438.

[90] P. Gonzalez-Duarte, W. Clegg, I. Casals, J. Sola, J. Rius, J. Am. Chem. Soc. 120 (1998) 1260.

[91] J.C. Bayon, M.C. Brianso, J.L. Brianso, P. Gonzalez-Duarte, Inorg. Chem. 18 (1979) 3478.

[92] N.J. Taylor, A.J. Carty, J. Am. Chem. Soc. 99 (1977) 6143.

[93] A.J. Carty, N.J. Taylor, J. Chem. Soc., Chem. Commun. (1976) 214.

[94] R.V. Parish, Z. Salehi, R.G. Pritchard, Angew. Chem. Int. Ed. Engl. 36 (1997) 251.

[95] Z. Salehi, R.V. Parish, R.G. Pritchard, J. Chem. Soc., Dalton Trans. (1997) 4241.

[96] R.G. Prichard, R.V. Parish, Z. Salehi, J. Chem. Soc., Dalton Trans. (1999) 243.

[97] W.P. Su, R. Cao, M.C. Hong, J.T. Chen, J.X. Lu, J. Chem. Soc., Chem. Commun. (1998) 1389.

[98] I. Casals, P. Gonzalez-Duarte, J. Sola, J. Vives, M. Font-Bardia, X. Solans, Polyhedron 9 (1990) 769.

[99] J.C. Deaton, H.R. Luss, J. Chem. Soc., Dalton Trans. (1999) 3163.

[100] D.J. Leblanc, J.F. Britten, Z.X. Wang, H.E. Howard-Lock, C.J.L. Lock, Acta Crystallogr. C 53 (1997) 1763.

[101] A. Toyota, T. Yamaguchi, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, Angew. Chem. Int. Ed. 44 (2005) 1088.

[102] M.S. Bharara, T.H. Bui, S. Parkin, D.A. Atwood, J. Chem. Soc., Dalton Trans. (2005) 3874.

[103] J.X. Chen, Q.F. Xu, Y. Xu, Y. Zhang, Z.N. Chen, J.P. Lang, Eur. J. Inorg. Chem. (2004) 4247.

[104] J.K. Cheng, Y.G. Yao, J. Zhang, Z.J. Li, Z.W. Cai, X.Y. Zhang, Z.N. Chen, Y.B. Chen, Y. Kang, Y.Y. Qin, Y.H. Wen, J. Am. Chem. Soc. 126 (2004) 7796.

[105] J.K. Cheng, Y.B. Chen, L. Wu, J. Zhang, Y.H. Wen, Z.J. Li, Y.G. Yao, Inorg. Chem. 44 (2005) 3386.

[106] J. Wang, S.L. Zheng, S. Hu, Y.H. Zhang, M.L. Tong, Inorg. Chem. 46 (2007) 795.

[107] Y.B. Chen, Y. Kang, Y.Y. Qin, Z.J. Li, J.K. Cheng, Y.G. Yao, Acta Crystallogr. C 60 (2004) 263.

[108] P. Aslanidis, P. Karagiannidis, P.D. Akrivos, B. Krebs, M. Lage, Inorg. Chim. Acta 254 (1997) 277.

[109] P. Aslanidis, P.J. Cox, S. Divanidis, A.C. Tsipis, Inorg. Chem. 41 (2002) 6875.

[110] J.P. Lang, Q.F. Xu, W.H. Zhang, H.X. Li, Z.G. Ren, J.X. Chen, Y. Zhang, Inorg. Chem. 45 (2006) 10487.

[111] F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang, J. Am. Chem. Soc. 123 (2001) 7740.

[112] W.F. Furey, A.H. Robbins, L.L. Clancy, D.R. Winge, B.C. Wang, C.D. Stout, Science 231 (1986) 704.

[113] A.H. Robbins, D.E. McRee, S.A. Williamson, S.A. Collett, N.H. Xuong, W.F. Furey, B.C. Wang, C.D. Stout, J. Mol. Biol. 221 (1991) 1269.

[114] P. Schultze, E. Worgotter, W. Braun, G. Wagner, M. Vasak, J.H.R. Kagi, K. Wuthrich, J. Mol. Biol. 201 (1988) 251.

[115] A. Arseniev, P. Schultze, E. Worgotter, W. Bruan, G. Wagner, M. Vasak, J.H.R. Kagi, K. Wuthrich, J. Mol. Biol. 201 (1988) 637.

[116] B.A. Messerle, A. Schaffer, M. Vasak, J.H.R. Kagi, K. Wuthrich, J. Mol. Biol. 214 (1990) 765.

[117] M.T. Ra1isa1nen, M. Kemell, M. Leskela1, T. Repo, Inorg. Chem. 46 (2007) 3251.