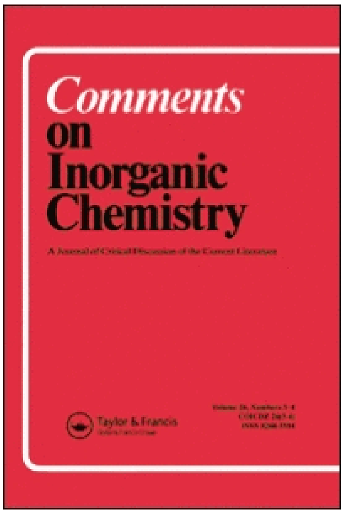

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DITHIOPHOSPHONATES AND RELATED P/S-TYPE LIGANDS OF GROUP 11 METALS

Werner E. Van Zyl[a]
[a] School of Chemistry, University of KwaZulu-Natal, Westville Campus, Durban, South Africa

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DITHIOPHOSPHONATES AND RELATED P/S-TYPE LIGANDS OF GROUP 11 METALS

WERNER E. VAN ZYL

School of Chemistry, University of KwaZulu-Natal,
Westville Campus, Durban, South Africa

Within the phosphor-1,1,-dithiolate class of compounds, the dithiophosphonato ligand $[S_2PAr(OR')]^-$ (typically Ar = aryl or ferrocenyl; R′ = alkyl) has emerged as an interesting choice for the preparation of a variety of new metal complexes. This review focuses on the dithiophosphonates and certain related thio species of the group 11 coinage metals, copper, silver and gold, with particular emphasis on structure and coordination modes. Amongst these three metals a rich coordination and structural chemistry had been developed and reported. For copper, a number of new complexes ranging from a single metal center, to di-, tetra-, and Cu_{14} clusters had been prepared. For silver, the number of reported complexes is not yet abundant but range in nuclearity from Ag_2 to Ag_{28}, which gives an indication of the potential scope. For gold, the majority of complexes are dinuclear gold(I) of the type $[AuS_2PR(OR')]_2$ where the variety of R′ can be enormous. A few silver and gold complexes with the title ligand had also been subjected to theoretical studies. New coordination modes have also been observed, particularly in cases where previously isolated complexes have been subjected to further reaction with phosphines. Copper and silver complexes have not yet shown the rich luminescent properties as gold, and developments of the latter are described also.

Keywords: copper, dithiophosphonate, gold, group 11 metals, Lawesson's Reagent, luminescence, silver, trithiophosphonate, Woollins Reagent

Address correspondence to Werner E. Van Zyl, School of Chemistry, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa. E-mail: vanzylw@ukzn.ac.za

Abbreviations of Chemicals**:** Ar, 4-anisyl (4-C_6H_4OMe); LR, Lawesson's Reagent; FcLR, Ferrocenyl Lawesson's Reagent; WR, Woollins Reagent; DME, 1,2 dimethoxyether; tht, tetrahydrothiophene; dppa, bis-(diphenylphosphino)amine; dppm, bis-(diphenylphosphino) methane; dppe, bis-(diphenylphosphino)ethane; dppp, bis-(diphenylphosphino)propane; dppb, bis-(diphenylphosphino)butane

DITHIOPHOSPHONATE AS LIGAND

As a single class of ligand, phosphines perhaps exceed all others in its utility and scope in both organic and inorganic chemistry.[1] However, it is the 4-coordinate phosphorus(V) species that hold the dubious distinction of being present in systems not only essential to the sustainability of life (DNA, RNA, bone, etc.) but also as a constituent of the most toxic man-made materials known (nerve gases). Not surprisingly, the increased air and moisture stability of metal phosphonates[2] well preceded the isolation and characterization of the heavier metal dithiophosphonates. Indeed, the inherent oxophilic nature of phosphorus proved of key importance to introduce effective strategies for the synthesis of dithiophosphonates because it essentially relies on replacement of a P-S bond by a P-O bond through facile nucleophilic attack of RO^- (see below). In recent years, synthetic routes to heavier chalcogenides in di*seleno*phosphonates have been developed, in large part due to the discovery and commercial availability of Woollins Reagent,[3] $(PhPSe_2)_2$. Copper(I) and silver(I) diselenophosphate clusters have thus been actively pursued.[4] Transition-metal di*telluro*phosphonate complexes as yet appear absent.

The phosphor-1,1dithiolate class of compounds are varied and include, amongst others, the dithiophos*pha*tes, dithiophos*phi*nates, and dithiophos*pho*nates as shown in Chart 1.

The dithiophosphates have been extensively studied and complexed to virtually all metals, presumably due to the comparative ease of ligand preparation.[5] The dithiophosphinates have been studied less frequently, although complexes of copper and silver[6] and gold[7] are known. Until the late 1990s, however, the literature showed a distinct scarcity of any metal dithiophosphonate complexes.[8]

The dithiophosphonato ligand, **C**, may be described as a *hybrid* of **A** and **B** and represents the major ligand type that is the subject of this

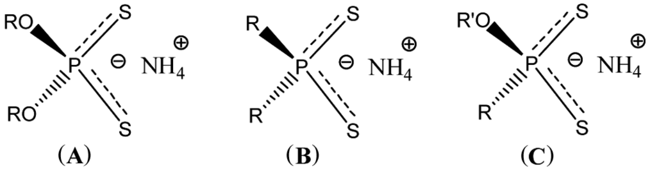
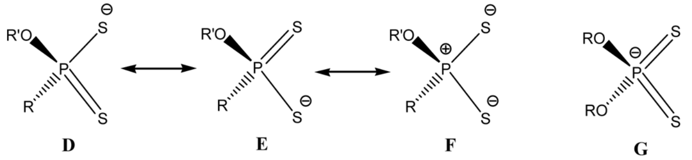


Chart 1. Comparison of three major classes of phosphor-1,1-dithiolates as ammonium salts: dithiophosphates (A), dithiophosphinates (B), and dithiophosphonates (C).

review. The dithiophosphonato ligand, $[S_2PR(OR')]^-$, is of interest for the following reasons: i) it can still be considered rare in the chemical literature and indeed for the majority of main- and transition metals simply non-existent; ii) from the reaction between a common precursor (usually Lawesson's Reagent or a derivative thereof), and any compound that contains a 1° or 2° alcohol functionality, a tremendous number of new and varied derivatives can be obtained in a facile manner; iii) the synthetic methodology allows for control in the design of the ligand (with respect to solubility and materials properties, and steric effects, etc.) to perform reactions and yield new products in both organic (and potentially aqueous) phases; iv) the asymmetric nature of the ligand allows for an additional challenge in that complex isomers can be formed, a feature not possible for the symmetrical dithiophosphinates, $[S_2PR_2]^-$, or dithiophosphates, $[S_2P(OR)_2]^-$; and v) solution and solid state $^{31}P\{^1H\}$ NMR spectroscopy is a valuable tool to obtain mechanistic and structural information.

If the closely related dithiophosphates established any precedent, then the dithiophosphonates can coordinate to virtually all main group and transition metals, giving rise to a wide variety of coordination patterns.[5] Using the deprotonated dithiophosphonate acid as an example, the dithiophosphonate contributions can be described by the resonance structures shown in Chart 2.

Depending on the metal type and its oxidation state, any of these resonance structures can predominate upon complexation, and have indeed all been observed. Resonance structures **D** and **E** have been observed for complexes where the ligand bind in a μ_1-fashion with a dangling sulfur atom. Resonance structure **F** predominates, for example, in the dinuclear gold(I) complexes reported here, and evidence thereof can be best provided by the two equal P-S bond



D **E** **F** **G**

Chart 2. Contributing resonance structures for the monoanionic dithiophosphonate species. An unusual dithiophosphate resonance structure is also shown.

lengths in the solid state. Structure **G** is shown separately; it was reported by Drew and co-workers in a study where a comparison in donor strength between dithio*phosphates* and dithiocarbamates was made,[9] but certainly the electronic contribution for a corresponding dithio*phosphonate* can also be considered and a similar resonance structure envisioned (alongside **D**, **E**, and **F**). The slow development of dithiophosphonates as a complexing agent is likely due to its commercial unavailability and sensitivity toward hydrolysis.

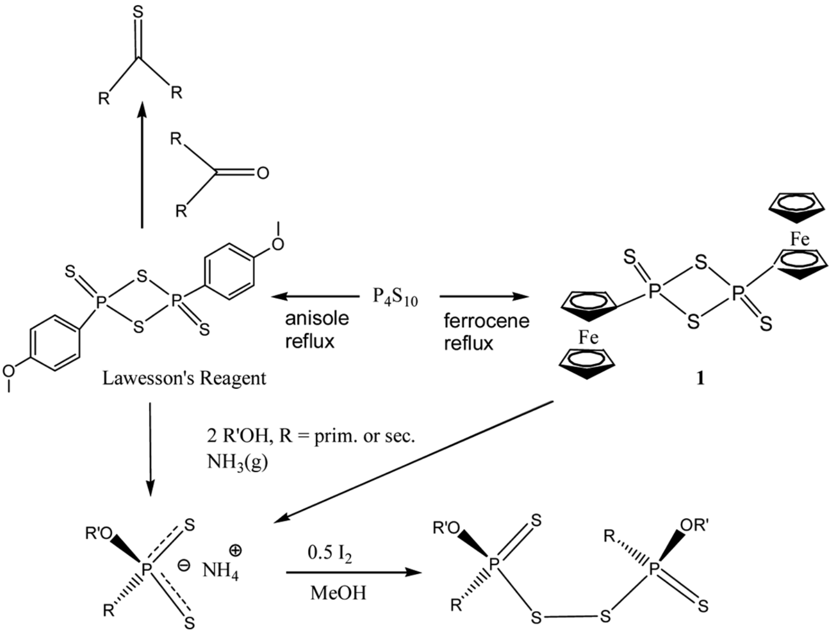
In terms of application, this class of ligand has demonstrated use in a variety of technological areas such as oligonucleotide synthesis,[10] agricultural insecticides[11] and pesticides,[12] derivatives of metal ore extraction reagents[13] and antioxidant additives in the oil and petroleum industry.[14] Indeed, the S-S coupling of the ligand salts with mild oxidants such as iodine[15] is amongst the simplest procedures to generate a host of interesting compounds.[16] In future, advances of these ligands and their complexes will undoubtedly be forthcoming in areas such as materials and medicinal chemistry.

This review covers all of the Group 11 coinage metal (copper, silver and gold) dithiophosphonate complexes, with particular emphasis on those reports where X-ray structural determinations were made to support the investigations. Where appropriate, the related thio ligands of the types $[ArS_2P{-}O{-}PS_2Ar]^{2-}$, $[ArPS_3]^{2-}$ and $[ArP(O)S_2]^{2-}$ are also pointed out.

Finally, a note on the systematic naming of the ligand. The nomenclature is not consistent within the literature and the ligand is randomly referred to as phosphonodithioate or organodithiophosphonate or dithiophosphonate. In this review the last terminology will be used throughout, or as dithiophosphonato when referring to the free monoanion.

SYNTHESIS METHODS

General and convenient methods to dithiophosphonate salt derivatives have been reported.[15] The method relies on the reaction of $[RP(S)S]_2$ type dimers and their reaction with alcohols, silanols, and trialkylsilanols. The cumbersome $[PhPS(S)]_2$ dimer synthesis was overcome by the discovery of the facile synthesis of $[(4\text{-}C_6H_4OMe)PS(S)]_2$, which became known as Lawesson's Reagent (LR). LR was initially used for the purpose of a sulfur transfer reagent, especially to convert ketones to thiones,[17] but was later used to form dithiophosphonic acids as well. LR is formed through the reaction between P_4S_{10} and anisole. Recognizing anisole to be an electron-rich aromatic, Woollins and co-workers skillfully introduced ferrocene, which performs similar electrophilic substitution type chemistry to afford the ferrocenyl derivative **1** as shown in Scheme 1.[18] This chemistry has been extended further by forming interesting ferrocenyl-type heterocycles.[19]



R = p-C_6H_4OMe or ferrocenyl (Fc)

Scheme 1. Starting with P_4S_{10}, the variety of synthesis routes that can form new P/S based derivatives are shown.

The ^{31}P NMR spectra of the ammonium salts of dithiophosphonates all resonate with a singlet peak in the approximate range 90–112 ppm.[15]

COPPER DITHIOPHOSPHONATE COMPLEXES

The simplest copper(I) dithiophosphonate complexes are monomeric four-coordinate chelates containing a bidentate dithiophosphonato ligand, as in the copper(I) complex $[Cu\{S_2P(4\text{-}C_6H_4OEt)(OMe)\}\{PPh_3\}_2]$, **2**, shown in Figure 1.[20]

Complex **2** was prepared through the reaction between $[(Ph_3P)_2CuNO_3]$ and $H[S_2P(4\text{-}C_6H_4OEt)(OMe)]$ (obtained *in situ* by dissolving the dimeric sulfide in methanol) in nitrobenzene. A related complex $[Cu\{S_2P(4\text{-}C_6H_4OMe)(OMe)\}\{PPh_3\}_2]$, **3**, was obtained[21] by reaction of $[Cu(CH_3CN)_4][PF_6]$ with PPh_3 (molar ratio 1:2) and $[NH_4][S_2P(4\text{-}C_6H_4OMe)(OMe)]$ in acetonitrile solution. Complexes **2** and **3** are colorless powders and form a distorted tetrahedral geometry

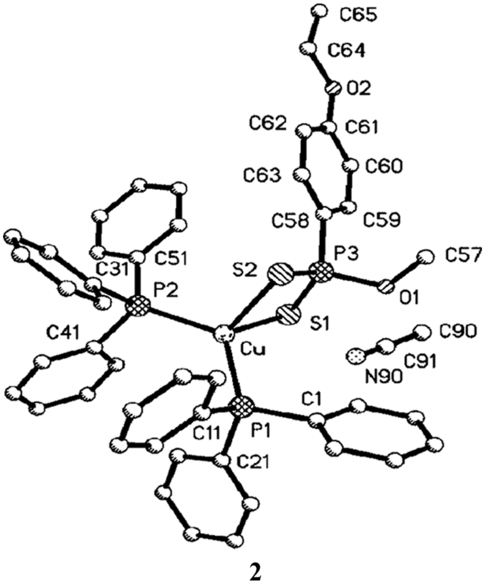


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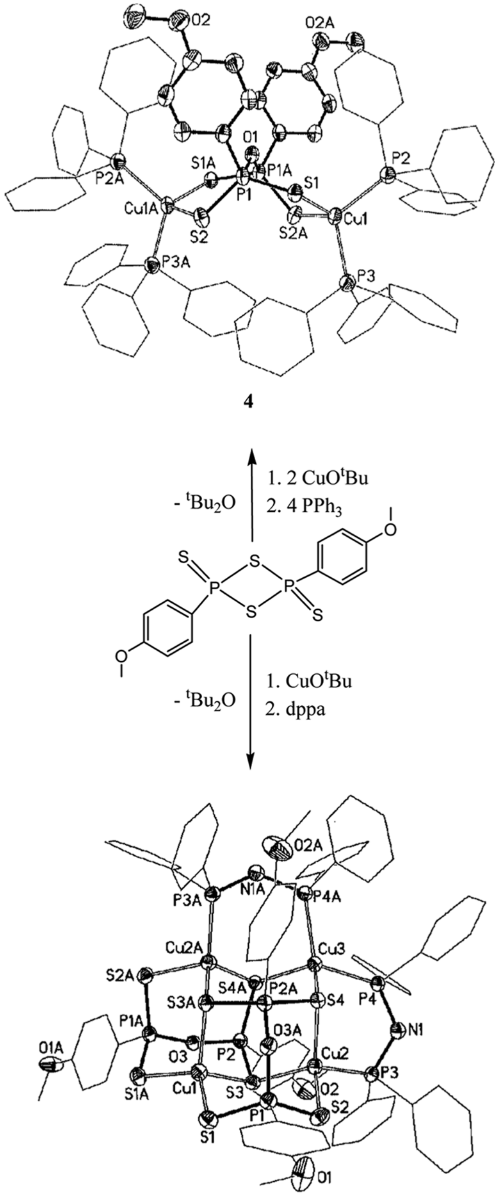
Figure 1. Molecular structure of mononuclear complex $[Cu\{S_2P(4\text{-}C_6H_4OEt)(OMe)\}\{PPh_3\}_2]$, **2**, derived from phenetole. Reprinted with permission from Haiduc et al.,[20] Copyright 2006: Wiley-VCH Verlag GmbH & Co. KGaA.

around the Cu atom due to the small S-Cu-S bite angle of 84°; both complexes have P-S bond lengths of 1.99 Å.

An impressive number of new copper and silver complexes (and clusters) have been developed in only the past five years by the so-called "anhydride route" as a synthetic protocol developed by Rothenberger and co-workers to introduce a range of unusual Group 15/16 ligands in oligomeric and polymeric environments.[22] Commercially available neutral precursor molecules such as LR and WR and metal salts are commonly used. Much of the Cu and Ag chemistry that follows were derived from this synthetic methodology. The copper(I) dithiophosphonate complex $[Cu_2(\mu_2ArS_2P–O–PS_2Ar)(PPh_3)_4]$, **4**, ($Ar = 4\text{-}C_6H_4OMe$) represents the only dinuclear Cu "dimeric" dithiophosphonate (two S_2ArP species bridged by an O atom) reported to date and was obtained through a synthesis route shown in Scheme 2.[23] LR was heated with 2 equivalents of Cu-O^{t}Bu in toluene, which formed a yellow precipitate and dissolved upon addition of 4 equivalents PPh_3. Complex **4** consists of two puckered annulated six-membered $[CuS_2P_2O]$ rings. The $^{31}P\{^1H\}$ NMR spectrum of **4** (in $CDCl_3$) shows resonances at $\delta = 91.5$ ppm for the generated $[ArS_2P-O-PS_2Ar]^{2-}$ dianion and at $\delta = -3.6$ ppm for coordinated PPh_3 ligand. The IR spectrum showed a strong band for $(P-O-P) = 841\ cm^{-1}$. The mechanism of complex formation for this reaction remains difficult to confirm. In a related experiment, addition of dppa (dppa = $Ph_2PNHPPh_2$) afforded the tetranuclear complex $[Cu_4\{Ar(\mu_2\text{-}S)_2P-O-P\text{-}(\mu_2\text{-}S)_2Ar\}_2(dppa)_2]$, **5** (Scheme 2). In both complexes **4** and **5** the Cu atoms exhibit a distorted tetrahedral geometry. These two complexes were the first to show that the reaction between Cu(I) alkoxides and LR in toluene forms new copper(I) complexes in high yield. Investigations in this area are extended to different LR-type reagents, metal alkoxides, and phosphane ligands. A variety of coordination modes can be expected.

Two other unique copper(I) clusters were reported by slight modification of the synthesis procedure used for **4** and **5** above; in particular, a simple change to ethereal solvents gives rise to completely different complexes.[24] The reaction of LR, Cu^{t}OBu, and PPh_3 (molar ratios 2:4:4) in 1,2-dimethoxyethane (DME) at reflux (4 hrs) led to the asymmetric cleavage of LR and the Cu_4 cluster $[Cu_2(\mu_4\text{-}ArPS_3)(PPh_3)_2]_2$, **6**, as product (Figure 2). The bond lengths and angles within the tetranuclear cage complex **6** are similar to those observed in the related



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Scheme 2. A synthesis route using LR, CuO^{t}Bu, and phosphines to form the Cu$_2$ (**4**) and Cu$_4$ (**5**) species. Reprinted with permission from Shi and Rothenberger,[23] Copyright 2005: Wiley-VCH Verlag GmbH & Co. KGaA.

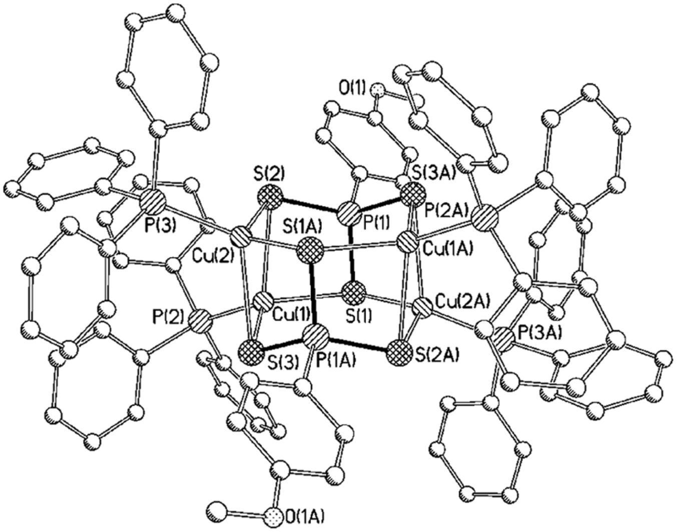

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Figure 2. Molecular structure of $[Cu_2(\mu_4\text{-}ArPS_3)(PPh_3)_2]_2$, **6**. Reprinted with permission from Shi et al.,[24] Copyright 2005: Royal Society of Chemistry.

trithiophosphonate complex $[Cu_4(PhPS_3)_2(PMe_3)_5]$.[25] The study of the nucleophilic ring-opening of LR with CuO^{t}Bu under different conditions showed that Cu(I) complexes containing the new dianionic ligands $[ArS_2P{-}O{-}PS_2Ar]^{2-}$ or $[ArPS_3]^{2-}$ can be produced selectively by careful selection of the reaction conditions. When the same reaction as for **6** is performed at room temperature, a larger Cu cluster $[Cu_{14}(\mu_6\text{-}ArP(O)S_2)_6(\mu_3\text{-}ArP(O)(OAc)S)_2(PPh_3)_6]$, **7**, was isolated in good yield (Figure 3).

Complex **6** is a trithiophosphonate but nevertheless incorporated in the discussion to point out how subtle manipulation of the reaction conditions (solvent type, temperature, stoichiometry), can form different nuclearities with different anions, i.e., $[ArP(O)S_2]^{2-}$ vs. $[ArPS_3]^{2-}$, etc. The same argument applies to the direct reaction of P_4S_{10} with CuO^{t}Bu leading to interesting trinuclear trithiophosphonate copper(I) species.[26] Due to poor solubility, NMR investigations of **7** were precluded but the compound could be unambiguously characterized by IR spectroscopy in combination with X-ray and elemental analysis. The formation of **7** could be rationalized by the nucleophilic addition of four equivalents

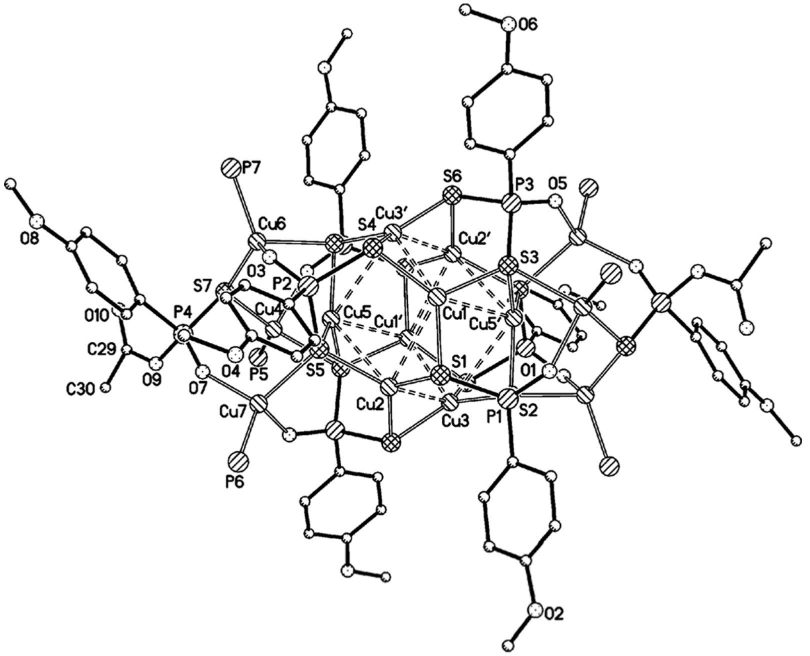

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Figure 3. Molecular structure of $[Cu_{14}(\mu_6\text{-}ArP(O)S_2)_6(\mu_3\text{-}ArP(O)(OAc)S)_2(PPh_3)_6]$, 7. Reprinted with permission from Shi et al.,[24] Copyright 2005: Royal Society of Chemistry.

of CuOAc to LR, followed by the elimination of acetic anhydride and copper(I) thioacetate $[CuSOCCH_3]$. In the solid state, 7 consists of a centrosymmetric arrangement of fourteen Cu^+ ions, six $[ArP(O)S_2]^{2-}$, two $[ArP(O)(OAc)S]^-$ anions and six PPh_3 ligands. Above the six faces of the central distorted cubic arrangement, six $[ArP(O)S_2]^{2-}$ anions are located. The S atoms of each $[ArP(O)S_2]^{2-}$ ligand coordinate four Cu atoms of one of the cubic faces in μ_2-mode. A remarkable feature of 7 is the formation of the $[ArP(O)(OAc)S]^-$ (Ac = acetyl) anion. It is likely the first example of such a substitution pattern observed for P atoms in an anionic fragment. The long P(4)–O(9) distance of 1.64 Å is typical for P–O(carboxylate) bonds and indicates the lability of this bond. Other P–O distances in 7 are considerably shorter (*ca.* 1.5 Å).

Note that no Cu(II) dithiophosphonate species had thus far been reported with regard to synthesis and X-ray analyses, but spectroscopic and magnetic measurements had been performed on some [Cu{S_2P(4-

$C_6H_4OEt\}(OR)\}_2]$ (R = Me, Et) type complexes from which the structure could be alluded.[27] The valence vibrations of the PS_2 group show that it coordinates isobidentate. Three absorption bands were observed ($^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$). The electronic spectra display two weak bands at 15 200 and 18 500 cm^{-1}, and show a strong band at 23 000 cm^{-1} (Ligand-to-Metal Charge Transfer, LMCT). The powder EPR spectra of Cu(II) complexes are typical for square-planar (idealized D_{4h} symmetry) monomeric species and present hyperfine and superhyperfine structure. In another study the transport of Cu(II) ions through a bulk liquid membrane was examined.[28]

SILVER DITHIOPHOSPHONATE COMPLEXES

Unlike copper and gold, no mononuclear silver(I) dithiophosphonate complexes have been structurally characterized to date; the simplest silver(I) complex is the dinuclear complex $[Ag\{S_2P(OMe)(4\text{-}C_6H_4OEt\}\{PPh_2\}]_2$, **8**, which is a centrosymmetric dimer based upon an eight-membered $Ag_2S_4P_2$ ring formed *via* bridging coordination of the ligands.[20] The silver atoms are trigonally coordinated and the Ag-S bond lengths differ slightly, Ag-S(2) = 2.68 Å and Ag-S(1) = 2.53 Å, as well as the P-S bonds, P(2)-S(1) = 2.019 Å and P(2)-S(1) = 1.989 Å, suggesting that one of the P-S bonds retains some double bond character. The structure is shown in Figure 4.

Reactions of metal alkoxides and carboxylates with LR produce metal complexes containing interesting P/S anions. Continuing with their earlier work,[22] Rothenberger and co-workers used this method in an attempt to synthesize larger cluster complexes *via* the fragmentation of P–S bonds in sulfur-analogs to phosphorus or phosphonous acid anhydrides. Metal salts with oxygen-containing anions such as carboxylates or alkoxides proved particularly useful due to the strong P–O bond vs. the weaker P–S bond as a thermodynamic driving force. This idea was illustrated by the following two reaction types.[29] The reaction between AgOAc and LR was investigated and produced a grey precipitate in THF. The intractable solid residue dissolved upon addition of the tertiary phosphine dppm. Slow diffusion of chilled (0°C) diethyl ether into the filtered reaction mixture produced crystals of the tetranuclear Ag(I) cluster $[Ag_4\{\mu_4\text{-}ArP(O)S_2\}_2(dppm)_4]$, **9**. The solid state structure exists as a dimer of $[Ag_2\{ArP(O)S_2\}(dppm)_2]$ units. Both $[ArP(O)S_2]^{2-}$ anions in **9** are coordinated to four Ag atoms

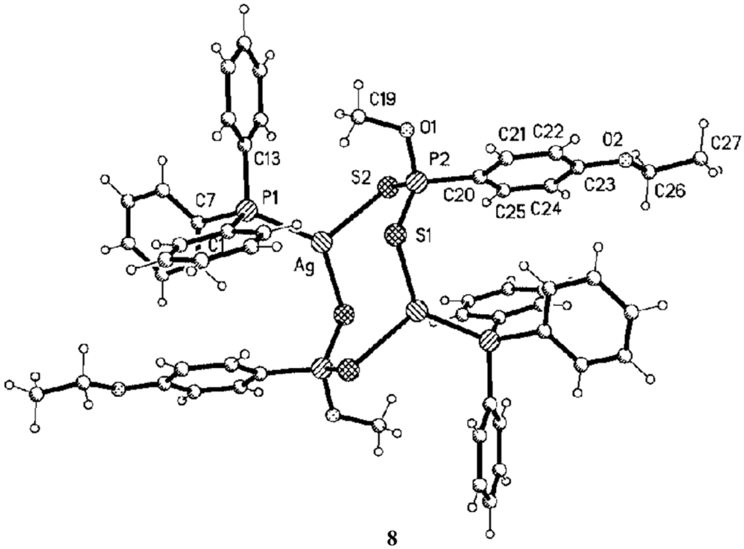

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Figure 4. Molecular structure of the dinuclear silver(I) dithiophosphinate complex, **8**. Reprinted with permission from Haiduc et al.,[20] Copyright 2006: Wiley-VCH Verlag GmbH & Co. KGaA.

forming an adamantane-like core of P, S and Ag atoms in which the remaining coordination sites at Ag atoms are occupied by dppm ligands (Figure 5).

In a separate experiment,[29] monodentate PPh_3 (instead of dppm) was used to dissolve the precipitate also obtained from the reaction between LR and AgOAc. X-ray analysis of the orange product of this reaction resulted in the spectacular cluster $[Ag_{28}(\mu_6\text{-}S)_2\{ArP(O)S_2\}_{12}\text{-}(PPh_3)_{12}]$ **10**. The X-ray structure is shown in Figure 6. The key structural features of **10** are the two central μ_6-S atoms with Ag–S(1) distances of 2.47–2.76 Å, coordinating the 10 inner Ag atoms. This arrangement is surrounded by an outer layer of 12 $[ArP(O)S_2]^{2-}$ ligands and the remaining 18 Ag atoms. A closer look at the structure of **10** reveals a variety of coordination modes of the $[ArP(O)S_2]^{2-}$ ligands, which coordinate Ag^+ ions either *via* S- and O-donor centers or solely *via* S atoms. Whilst tripodal $[ArP(O)S_2]^{2-}$ ligands tend to form cage complexes, sulfido ligands tend to form large, three-dimensional arrangements with Ag^+ ions, e.g., $[Ag_{344}S_{124}(S^tBu)_{96}]$.[30] The longest nonbonding distances between symmetry-related Ag atoms in the core of **10** are 1.3 nm.

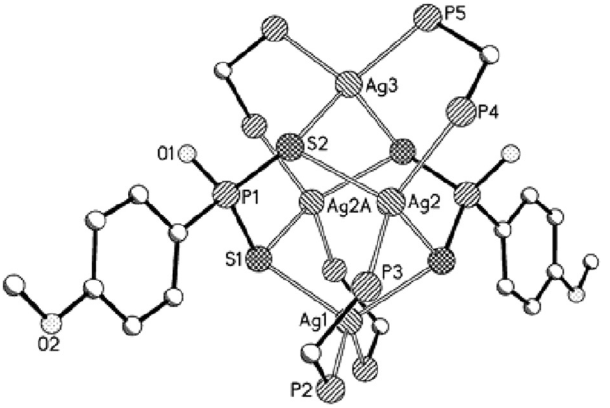

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Figure 5. Molecular structure of the tetranuclear Ag(I) cluster $[Ag_4\{\mu_4\text{-}ArP(O)S_2\}_2(dppm)_4]$, **9**. Reprinted with permission from Shi et al.,[29] Copyright 2005: Royal Society of Chemistry.

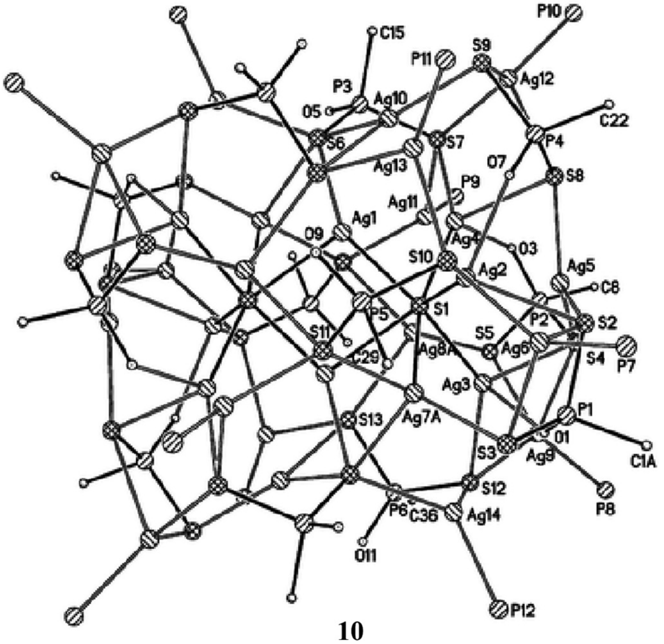

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Figure 6. Molecular structure of the silver(I) cluster $[Ag_{28}(\mu_6\text{-}S)_2\{ArP(O)S_2\}_{12}(PPh_3)_{12}]$ **10**. Reprinted with permission from Shi et al.,[29] Copyright 2005: Royal Society of Chemistry.

Cluster **10** had also been subjected to detailed theoretical studies.[31] In particular, density functional theory (DFT) modeling of disorder and mobility in this semiconductor cluster had been investigated. The ligand-stabilized cluster **10**, with a total of 666 atoms, displays in its X-ray structure highly localized disorder at two core silver atoms. DFT methods to its internal structure and flexibility had been applied to explore the nature of the disorder. The pseudo-S_6 symmetry of the cluster provides six equivalent pockets to place the pair of silver atoms, and with the exception of populating neighboring sites, all permutations relax to structures with similar cores. The barrier to concerted motion of the central silver atoms from one set of pockets to the next is estimated to be less than 26 kJ mol^{-1}. Cluster **10** can be considered a model for bulk phase cation mobility.

GOLD DITHIOPHOSPHONATE COMPLEXES

After more than two decades, the complex $[Au(S_2P(OH)Ph)_2]Cl$, **11**, remains the first and to date only structurally characterized mononuclear gold(III) dithiophosphonate complex.[32] The compound was prepared from the reaction between ClAu(tht) (tht = tetrahydrothiophene) and a large excess of $NaS_2P(OH)Ph$. Remarkably, its crystal structure consists of a co-crystallized mixture of the cis and trans isomers (relative orientation to phenyl rings) in a 2:1 ratio. The S−Au−S angles formed by the chelating ligand are 83°. For this 4-coordinate d^8 system, it is believed Cl coordination to the gold center, forming a 5-coordinate intermediate, could play a role in explaining the cis/trans isomerization. Note the gold(I) starting material became oxidized to the square planar gold(III) product during the reaction, but it is not clear which chemical species is simultaneously reduced in the process.

Mononuclear gold(I) dithiophosphonate complexes are as rare as their gold(III) counterparts. For the former, the first resulted from a straightforward reaction between $ClAuPPh_3$ and $[NH_4][S_2P(OMe)(p\text{-}C_6H_4OEt)]$ in acetone, following removal of NH_4Cl by filtration, the product $[Au\{S_2P(OMe)(p\text{-}C_6H_4OEt\}\{PPh_3\}]$, **12**, was evaporated to dryness.[20] The structure is shown in Figure 7.

The second type of mononuclear gold(I) complex was obtained through the reaction between the dinuclear complex $[AuS_2P(4\text{-}C_6H_4OMe)(OC_5H_9)]_2$, **13**, and PPh_3 (molar ration 1:4) in CH_2Cl_2 solution

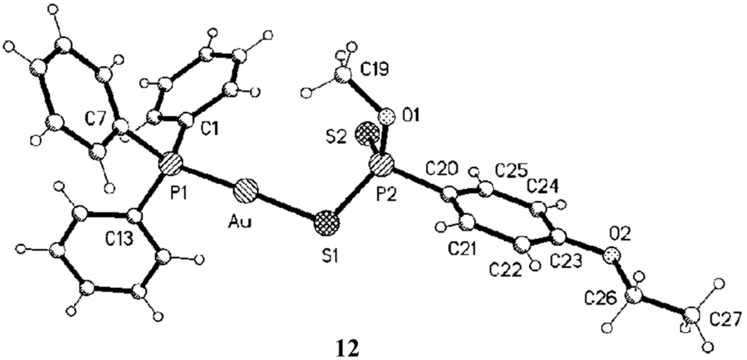

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Figure 7. Molecular structure of the mononuclear gold(I) complex $[Au\{S_2P(OMe)(4\text{-}C_6H_4OEt\}\{PPh_3\}]$, **12**. Reprinted with permission from Haiduc et al.,[20] Copyright 2006: Wiley-VCH Verlag GmbH & Co. KGaA.

leading to the stable 4-coordinate complex $[Au\{S_2P(4\text{-}C_6H_4OMe)(OC_5H_9)\}\{PPh_3\}_2]$, **14**, as shown in Figure 8.[33] The geometry is distorted tetrahedral around the gold center.

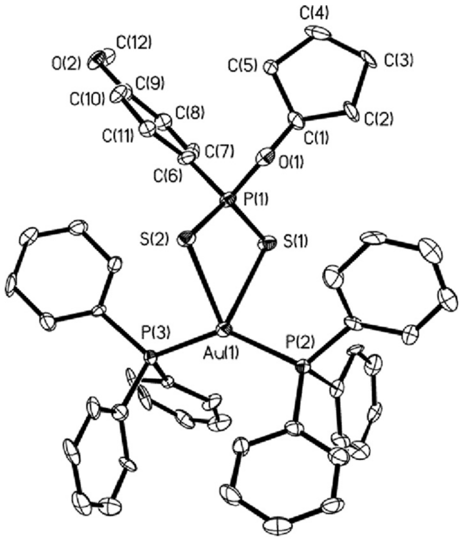

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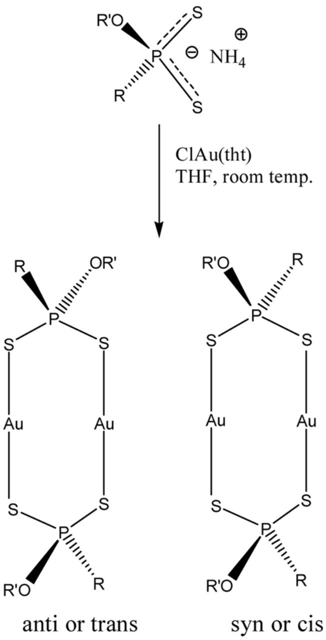
Figure 8. Molecular structure of mononuclear gold(I) complex $[Au\{S_2P(4\text{-}C_6H_4OMe)(OC_5H_9)\}\{PPh_3\}_2]$, **14**. Reprinted with permission from Maspero et al.,[33] Copyright 2003: American Chemical Society.

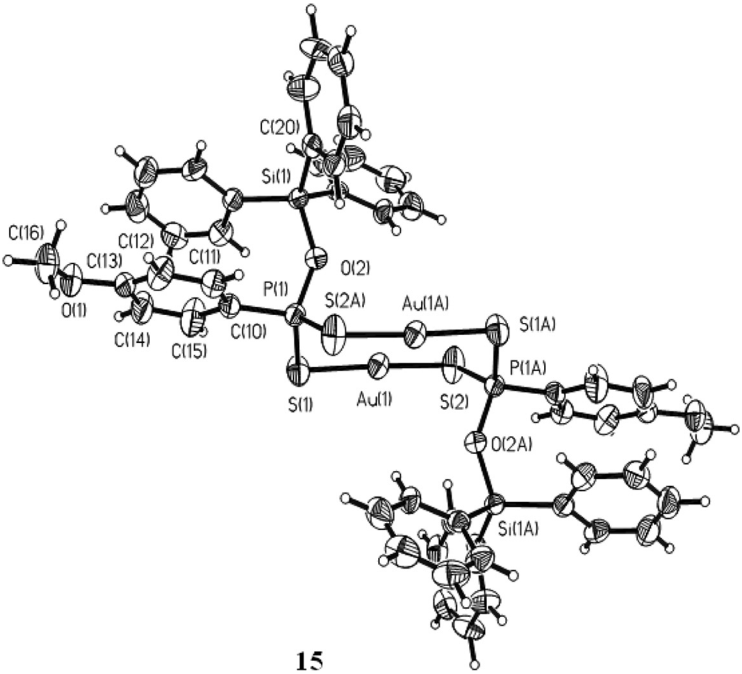
Characterized dinuclear gold(I) dithiophosphonate complexes of the type shown in Scheme 3 are by far the most studied in terms of *nuclearity* and *oxidation state* for this class of ligand. Indeed, only nickel(II) dithiophosphonate complexes surpass gold(I) complexes amongst *all metals* reported with the title ligand.[24,34] However, the high nuclearity clusters achieved for copper and especially silver are yet to be achieved for gold. Dinuclear gold(I) complexes have received considerable study because they provide an effective framework for the study of weak inter- and intramolecular interactions between closed-shell gold(I) atoms.[35]

All the dinuclear gold(I) dithiophosphonate complexes investigated thus far show the trans (or anti) configuration in the solid state exclusively. Solid-state magic-angle-spinning (MAS) ^{31}P NMR also confirms the trans isomer to be the sole product in bulk form. Solution ^{31}P NMR, however, clearly indicates both trans and cis forms exist in solution with a small isomerization energy involved. This area of research is clearly ripe for solution-based theoretical and/or physical-inorganic



Scheme 3. A typical synthesis method to form dinuclear gold(I) dithiophosphonate complexes.

studies for determining *inter alia* isomerization kinetics, and to perform detailed mechanistic studies. The exclusive trans isomer formation can be related to simple crystallographic arguments: this isomer contains an inversion center in the center of each molecule and this feature apparently contributes to a lowering of crystal packing forces. This operator of inversion (*i*) would have to be removed for a cis isomer to be formed. This could perhaps be achieved through unusual and/or extended hydrogen bonding assembly, or the presence of solvent molecule on a crystallographically relevant coordinate. An inversion center *between* two adjacent molecules could give rise to a cis isomer. The first reported gold(I) dithiophosphonate prepared in the manner described[36] was $[AuS_2P(4\text{-}C_6H_4OMe)(OSiPh_3)]_2$, **15**, as shown in Figure 9. The complex had no intermolecular Au $\cdots$ Au interactions. The importance of **15** is to demonstrate a different product forms when silicon replaces carbon in

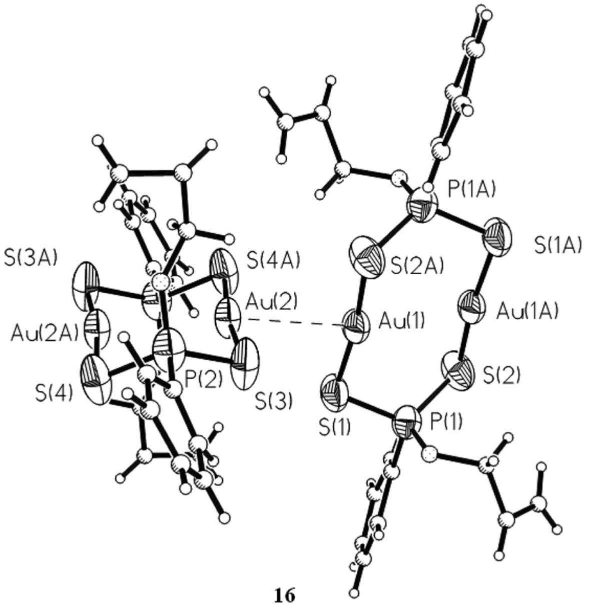


15

Figure 9. First reported example of a dinuclear gold(I) dithiophosphonate complex $[AuS_2P(4\text{-}C_6H_4OMe)(OSiPh_3)]_2$, **15**. Reprinted with permission from Van Zyl et al.,[36] Copyright 1998: Elsevier.

the precursor material. That is, dithiophosphonates can be prepared from reaction between LR and either primary or secondary alcohols, but tertiary alcohols lead to elimination reactions. For example, tert. butanol eliminates isobutene. Yet Ph_3SiOH, which can be considered a silicon analogue of a tertiary alcohol, afforded no elimination products. Complex **15** shows a rare, if not the sole example of a complex that contains the M–S–P–O–Si–C heteroatom chain (M = transition metal). The O–Si–C moiety is known to react with KF in MeOH to cleave the Si–O bond. Another feature of the complex is that it can open new research avenues to pursue through reactions between incompletely condensed polyhedral oligosilsesquioxane (POSS) materials (which can contain up to three hydroxy moieties) and LR or FcLR, forming new dithiophosphonate salts.

The dinuclear gold(I) complex $[AuS_2PPh(OCH_2CH{=}CH_2)]_2$, **16**, introduced unsaturation into the ligand with an allyl moiety.[37] The complex also has short intermolecular Au···Au interactions as shown in Figure 10. Complex **16** was furthermore subjected to a detailed

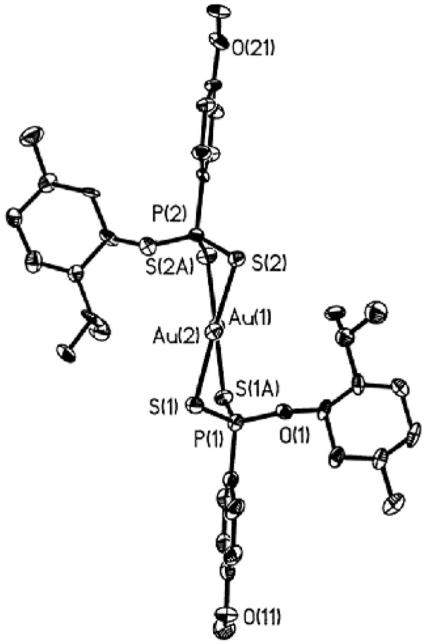


16

Figure 10. The dinuclear gold(I) complex $[AuS_2PPh(OCH_2CH{=}CH_2)]_2$, **16**, introducing unsaturation into the molecule, and containing an intermolecular Au···Au interaction. Reprinted with permission from Van Zyl et al.,[37] Copyright 2000: Elsevier.

theoretical study to gain better insight into its intra- and intermolecular bonding and luminescence properties.[38]

Fully optimized geometries were obtained by three computational methods: DFT/B3LYP, MPW1B95, and MP2. An Au(I)$\cdots$Au(I) *intra*-molecular bond was found in the ground state, at the three levels of theory, exhibiting an aurophilic interaction. The molecule has C_i ground state symmetry. Two crystallographic adjacent molecules of the complex were optimized using DFT/B3LYP in order to analyze the *inter*molecular interaction between them. The resulting analysis revealed that intermolecular bonding distance between the two adjacent gold atoms on each molecule is 3.16 Å, indicating a strong aurophilic attraction. Time-dependent calculations indicate that the first excited state with nonzero oscillator strength is a singlet, with an excitation energy equal to 3.16 eV. This should correspond to the absorption band seen experimentally at 3.10 eV. The lowest energy emission of **16** was obtained

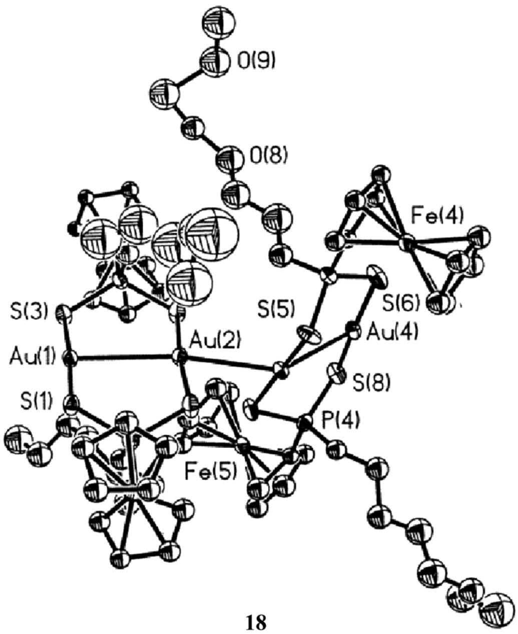


17

Figure 11. Molecular structure of dinuclear gold(I) complex $[AuS_2P(4\text{-}C_6H_4OMe)(O\text{-menthyl})]_2$, **17**, showing significant "cross-over." Reprinted with permission from Van Zyl et al.,[39] Copyright 2002: American Chemical Society.

at 2.73 eV, which corresponds to the emission peak resulting from phosphorescence and located at 2.53 eV. This transition comes from an excited electron on the p orbitals of the ligands that is transferred to the d orbitals of the gold atoms on the HOMO, or better formulated as low-lying SOMO. This interaction was attributed to a Ligand-to-Ligand–Metal Charge-Transfer (LL–MCT) absorption, with the corresponding emission derived from the same LMCT states. Complex **16** has a dangling allyl moiety and it would be of interest to investigate whether it can undergo facile metathesis reactions with a Grubbs catalyst through alkene coupling of adjacent molecules. If successful, such new materials could form large macrocycles, and through structural changes would certainly perturb the current luminescent properties of the complex.

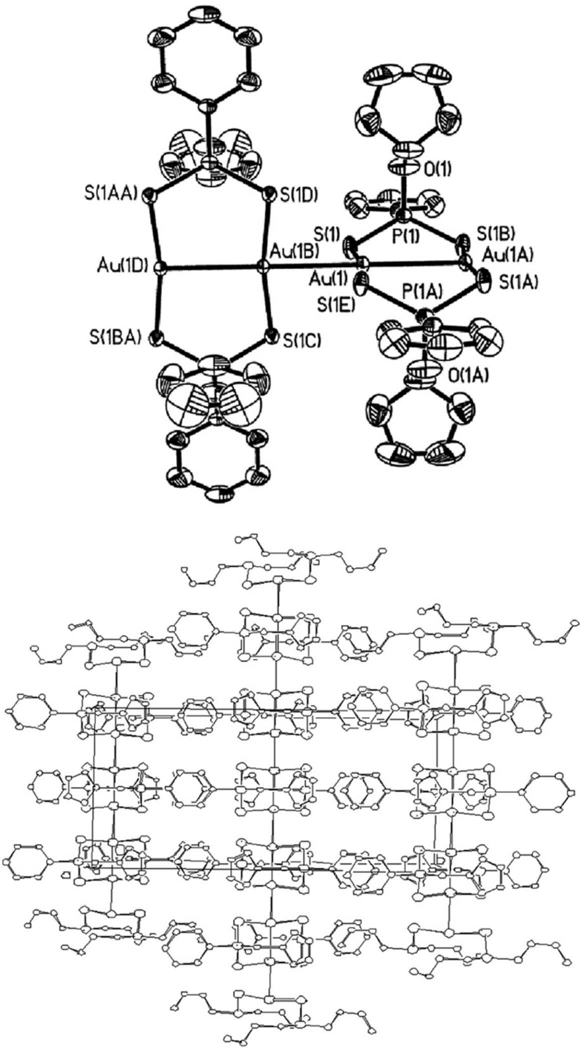
Menthol, a chiral compound containing an alcohol functionality, was utilized in forming the dinuclear complex $[AuS_2P(4\text{-}C_6H_4OMe)(O\text{-menthyl})]_2$, (menthyl = deprotonated menthol) **17**.[39] Complex **17**



18

Figure 12. The complex $[AuS_2PFc(O(CH_2)_2O(CH_2)_2OMe)]_2$, **18** containing the FcLR moiety. Reprinted with permission from Van Zyl et al.,[39] Copyright 2002: American Chemical Society.

satisfies a crucial requirement for obtaining a non-linear optical (NLO) response, namely its crystallization in a non-centrosymmetric space group, $P2_1$, presumably induced by the chiral ligand. Complex **17**



19

Figure 13. The molecular structure (top) of the dinuclear gold complex $[AuS_2PPh(OC_5H_9)]_2$, **19**, shows very strong inter- and intramolecular Au···Au interactions; and a portion of its crystal structure (bottom). Reprinted with permission from Van Zyl et al.,[39] Copyright 2002: American Chemical Society.

contains no intermolecular Au···Au interactions. The two S-Au-S linkages in the molecule are not “parallel” to each other, but instead a significant “cross-over” is present (Figure 11). The latter feature is common in open-ended dinuclear complexes but has not previously been observed in gold(I) metallocycles with S–P–S bridging ligands.

LR can also be prepared as a ferrocenyl analogue, FcLR (Figure 12).[39] The complex $[AuS_2PFc(O(CH_2)_2O(CH_2)_2OMe)]_2$, **18**, represents the first example where a ferrocenyl derivative was utilized to form part of a dithio-phosphorus ligand, which is subsequently complexed to a transition-metal center. The ether linkages may be utilized to coordinate to additional metal centers such as $PdCl_2$. The cyclopentadienyl rings on both ferrocenyl groups are in the eclipsed conformation. The chemistry utilizing FcLR was further developed for a host of other transition metals.[40]

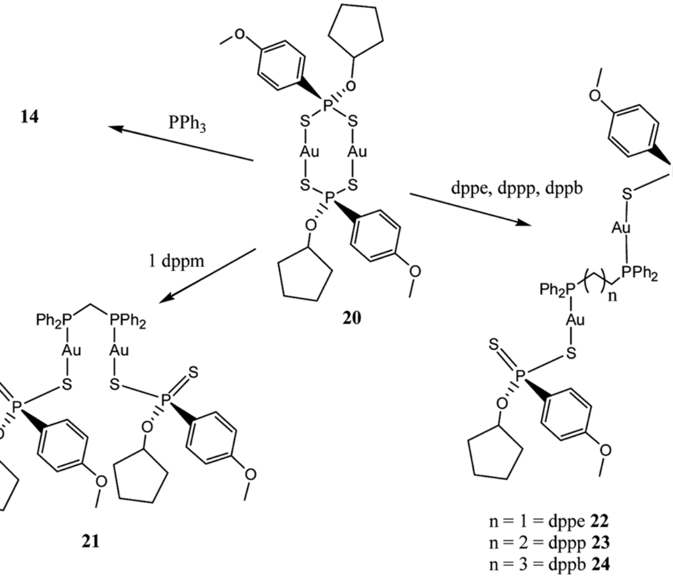
The dinuclear gold complex $[AuS_2PPh(OC_5H_9)]_2$, **19**, shows very strong inter- and intramolecular Au···Au interactions and represents the first structurally characterized dinuclear gold(I) complex with a S–P–S bridge where the gold contacts shorten to well below 3 Å, namely 2.92 Å (intra) and 2.95 Å (inter).[39] The compound strongly luminesces at room temperature and at 77 K under UV excitation. The complex has interesting layered crystal packing as shown in Figure 13. In photochemical studies, it was demonstrated that the luminescence of **19** is quenched when dissolved in $CHCl_3$. Small organic molecules may disrupt the close packing network in solution and quench the luminescence.

Finally, dithiophosphonate derivatives were synthesized and the electrochemical reduction mechanism investigated by cyclic voltammetry (CV), square wave voltammetry (SWV), and chronoamperometry (CA) in $[NBu_4][BF_4]$ in acetonitrile at platinum and gold electrodes.[41]

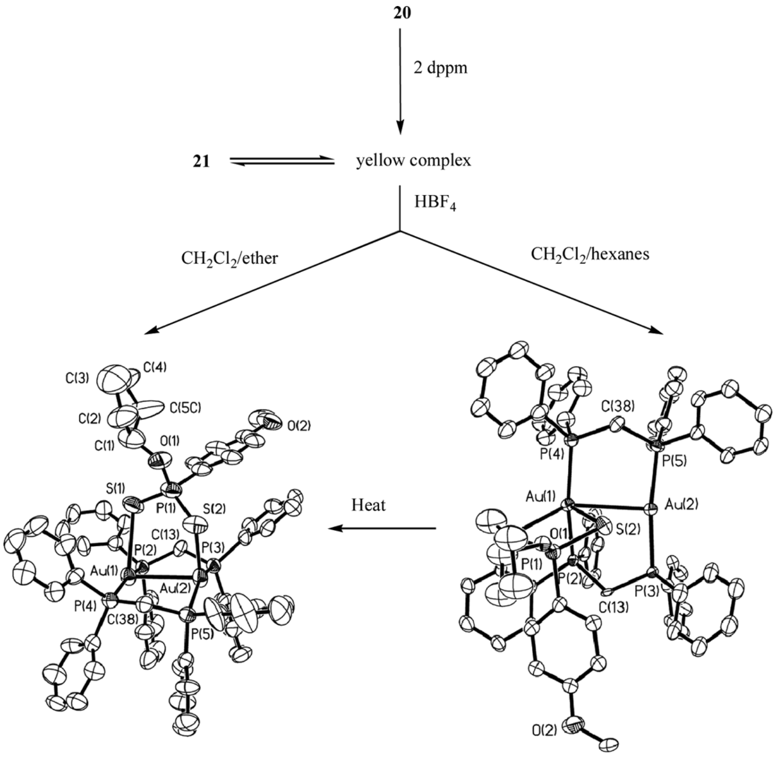
REACTIVITY STUDIES OF GOLD(I) COMPLEXES

Unlike copper and silver dithiophosphonate complexes, which to date concern only studies on synthesis and characterization, the gold complexes have proved a fertile testing ground toward the reactivity of some previously isolated complexes. For example, complex **19** described above was also prepared from LR yielding the related complex $[AuS_2P(4\text{-}C_6H_4OMe)(OC_5H_9)]_2$, **20**, and its reactivity with mono- PPh_3 and bis-phosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1 - 4$) studied.[33] Reaction of **20** with bis-phosphines (molar ratio 1:1) lead to dinuclear ring-opening complexes as shown in Scheme 4. The crystal structures of **20** and its reaction products with dppm show short intramolecular Au · · · Au aurophilic bonding interactions of 2.95 – 3.10 Å while no intermolecular interactions are discernible. However, reaction products of **20** with longer-chain $Ph_2P(CH_2)_nPPh_2$ ligands, $n = 2 - 4$, exhibit structures that lack both intra- and intermolecular Au · · · Au interactions.

The reaction with dppm is stoichiometry-dependent. Thus, when **20** reacts with 1 equivalent of dppm, it leads to the neutral dinuclear white complex **21**. When **20** reacts with >2 equivalents of dppm, the yellow ionic complex $[Au_2(dppm)_2\{S_2P(4\text{-}C_6H_4OMe)(OC_5H_9)\}]^+$ forms, and the counteranion can be exchanged with HBF_4 to yield $[Au_2(dppm)_2\{S_2P(4\text{-}C_6H_4OMe)(OC_5H_9)\}]BF_4$, the crystallization of which afforded two interconvertible isomers, yellow-**25** and white-**26**, as shown in Figure 14. These isomers are critically dependent on the choice of solvent in making up the solution. As already discussed, when the reaction of **20** is carried out with 4 equivalents PPh_3 the tetracoordinate mononuclear complex **14** is formed. The X-ray data show that the dithiophosphonate ligand in the isomer **25** is coordinated as a bridge



Scheme 4. The possible interconversions that can be achieved from **20** with a variety of mono- and bis-phosphines. Reprinted with permission from Maspero et al.,[33] Copyright 2003: American Chemical Society.



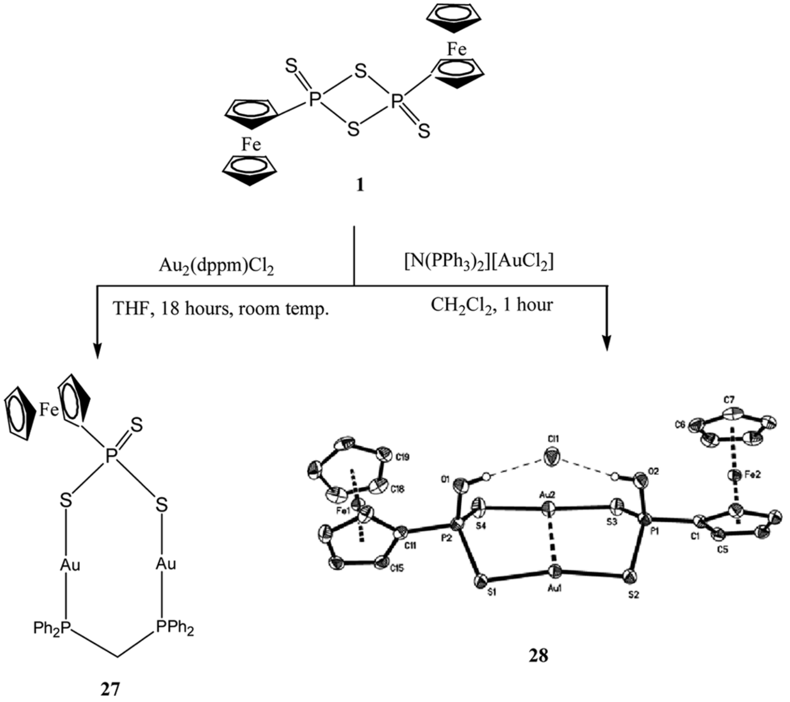
yellow, **25** white, **26**

Figure 14. Interconversion of **20** through reaction with dppm and solvent dependency. Reprinted with permission from Maspero et al.,[33] Copyright 2003: American Chemical Society.

with each of the two sulfur atoms bonded to a different gold(I) center. In contrast, the colorless crystals of isomer **26** have the dithiophosphonate ligand coordinated as a chelate with both sulfur atoms bonded to only one gold(I) atom. The structures are also consistent with the NMR data. Furthermore, heating the white powder of **26** converts it to the bright yellow powder of **25**. While the two isomers **25** and **26** are distinguishable in the solid state, solutions of both isomers in $CDCl_3$ give essentially identical $^{31}P\{^{1}H\}$ NMR spectra. Compound **26** rearranges to **25** in solvents such as acetone, THF, dichloromethane, ethanol, DMSO, acetonitrile, and chloroform.[33]

The characterized gold complexes **14**, **20-26** are diverse in their coordination types about the gold(I) centers such as tetrahedral, distorted trigonal (T-shape), in addition to the known linear coordination. Some of the isolated complexes show strong orange, yellow, and green luminescence at room temperature and at 77 K. It appears that details of the luminescence for compounds related to this work are yet to be published.

The second aspect of reactivity trends that deserves attention is direct reaction of FcLR with $[Au_2Cl_2(dppm)]$, in THF forming a trithiophosphonate, **27**,[36] and the recently reported reaction with $ClAuPPh_3$ forming mononuclear chelating complexes of the type $[Au\{S_2P(OH)Fc\}(PPh_3)]$, or reaction with $[PPN][AuCl_2]$ forming dinuclear complexes of the type $[Au_2\{S_2P(OH)Fc\}_2][N(PPh_3)_2]Cl$, **28**.[42] These reactions are summarized in Scheme 5. The source of the OH moiety is not entirely clear; presumably the phosphorus compound had been subjected to partial hydrolysis. The dinuclear complex **28** crystallizes as an adduct with PPNCl. The structure involves a central eight-membered ring with a rare boat conformation, in such a manner that



Scheme 5. Reactions of FcLR with gold(I) precursors. Structure of complex **28** reprinted with permission from Barranco et al.,[42] Copyright 2008: American Chemical Society.

the molecule acts as anion receptor toward the chloride anion via strong hydrogen bonds in a OH $\cdots$ Cl $\cdots$ HO system. In the course of this work, it was also observed that the anion $[S_2P(OH)Fc]^-$ can couple through condensation, eliminating H_2O, and forming the dianion $[FcArS_2P{-}O{-}PS_2Fc]^{2-}$; the ligand is not entirely unprecedented as claimed, but rather simply the ferrocenyl analogue of the same dianion previously reported for LR with copper(I) complexes.[22–24] Nevertheless, it would appear the time is ripe for numerous exciting yet challenging metal complexes in this area of research to be discovered.

LUMINESCENCE STUDIES

Luminescence studies on the copper and silver dithiophosphonate complexes are yet to be appreciably investigated. In contrast, the related gold(I) dithiophosphonate complexes reported to date demonstrate a rich but complex photochemistry and -physics. Aspects of closed-shell d^{10} systems in general have been reviewed.[43] Aurophilic interactions undoubtedly influence the optical properties of the formed compounds in the solid state, but in addition to the gold atom, other factors such as ligand type and coordination number, temperature, and M-M distance also play important roles with regards to type of emission energy observed. Investigations to find a relationship between the observation of emission and the presence of weak intermolecular bonding interactions between neighboring gold atoms have been addressed previously[44] but a conclusive answer that applies to gold-sulfur compounds in general has not yet been obtained. In particular, the photochemistry of dinuclear gold(I) dithiolate systems has been well studied, and they show an emission that arises from a S-Au charge transfer transition with contribution from the metal-metal bond formed in the excited state giving rise to a ligand-to-metal-metal-charge-transfer (LMMCT). When substituents on the sulfur ligands do not give rise to significant electronic changes, the emanating emission bands have to be strongly influenced by intermetallic distances.

Dinuclear gold(I) dithiophosphonates proved to be ideal candidates to test and find a clear correlation between the emission profiles and the presence of weak intermolecular Au $\cdots$ Au interactions. They represent a group of compounds of which: i) many of them have been structurally characterized; ii) all contain S-P-S bridging ligands; and iii) are a distribution of structures with and without intermolecular interactions in the solid state. This allows for direct comparisons to be made and the development of a more coherent understanding of the luminescence properties these complexes possess. Additionally, the S-P-S bridging ligands have been chosen to see if a comparison can be made, not only to predict the presence or absence of Au···Au interactions, but also to estimate the distances between these gold centers in cases where the emission bands have similar energies. With the title ligands and gold(I), a significant contribution occurred when it was demonstrated that the emission profile alone is a useful predictor of the presence of intermolecular Au···Au interactions.[37,39] This comparison would only be reliable if the S-P-S moiety is retained for different R and OR groups attached to the phosphorus atom. The relevant data is collected in Table 1. All the complexes are neutral eight-membered metallocycles in an elongated chair conformation with short transannular gold-gold interactions. Similar work, where the emission energy was correlated with the gold-gold distance, had later been performed on $[Au(SCN)_2]^-$ salts.[45] A major contribution in the assignment of the excited states responsible for emission was made by Eisenberg and co-workers in their study of related gold(I) dithiophosphates; a number of their comments correlated well with the earlier studies described above.[46] The Au(I) dimers $Au_2\{S_2P(OR)_2\}_2$ for R = Me, Et, were found to exhibit a structure in which aurophilic interactions yield one-dimensional Au···Au chains with intermolecular contacts (3.09 – 3.16 Å) similar to the Au···Au distances within the dimers (3.10 – 3.18 Å). The dimers are luminescent in the solid state and become brilliantly emissive at low temperatures. At 77 K, $Au_2\{S_2P(OMe)_2\}_2$ shows multiple emission bands, the two higher energy bands at 415 and 456 nm are assigned to ^{1}MC and ^{3}MC on the

Table 1. Solid state luminescence data for dinuclear gold(I) dithiophosphonate complexes. Adapted from Van Zyl et al.[37]

Complex	298 K emission (nm)	77 K emission (nm)	*d*(Au-Au)
$[AuS_2PPh(OC_3H_5)]_2$	443	445, 491	3.10, 3.12
$[AuS_2PPh(OEt)]_2$	447	453, 496	3.10, 3.12
$[AuS_2P(4\text{-}C_6H_4OMe)(OEt)]_2$	467	453, 494	No structure
$[AuS_2PPh(OC_5H_9)]_2$	487	491, 530	2.93, 2.95
$[AuS_2P(4\text{-}C_6H_4OMe)(OSiPh_3)]_2$	–	417	3.14
$[AuS_2P(4\text{-}C_6H_4OMe)(O\text{-menthyl})]_2$	–	447	3.04

basis of lifetime measurements (20 ns and 2.16 μs, respectively) and concentration-related effects, while the lower energy band at 560 nm is attributed to a LMCT excited state.

SUMMARY AND OUTLOOK

The chemistry of the dithiophosphonates and their metal complexes is by no means a mature field of research and many more exciting findings with this and related ligands can be expected. The scope shown here with only three metals makes it clear that a sound platform has been set for more discoveries to be made. Modification of the ligand toward water soluble/stable analogues has not yet been reported, nor mixed P/S/Se/Te analogues, and their respective chalcogen-chalcogen oxidized coupling reactions. Development of reactivity trends of especially copper and silver can be expected, and luminescent gold(I) complexes embedded within, for example, polymeric gels can be considered. The FcLR derivative proved useful in extending this chemistry. Can other metallocenes or organometallics in general be considered to perform the same function? The area of gold(III) dithiophosphonate complexes also seems to be completely unexplored. Moving toward nanomaterials, one feature that had been well demonstrated by proof-of-concept is clever design principles of the related dithiocarbamates and their attachment to Au nanoparticle (AuNP) surfaces.[47] There is no reason why this feature cannot also be exploited by the dithiophosphonates in the near future.

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