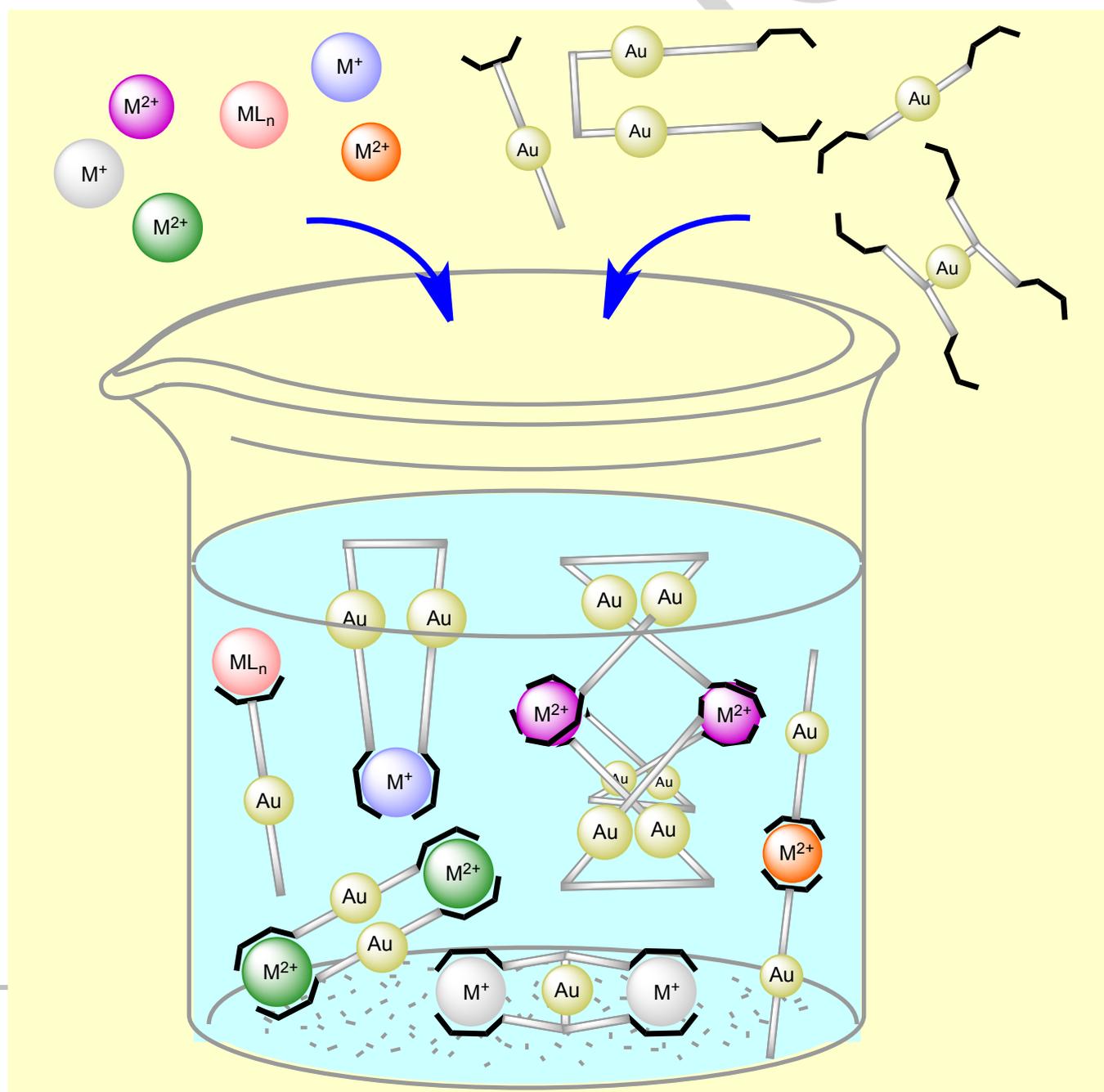


The Coordination and Supramolecular Chemistry of Gold Metalloligands

Juan Gil-Rubio^{[a]*} and José Vicente^[a]

This article is dedicated to Prof. Juan Forniés on the occasion of his retirement.



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Abstract: This review article deals with the use of gold metalloligands as building blocks for the assembly of heterometallic complexes. Several families of gold complexes decorated with crown-ether, amide, pyridine, bipyridine, terpyridine, carboxylato, aminoacid or π -alkyne binding sites have been reported. Adducts of these metalloligands with alkaline or transition metal cations, or with transition metal or lanthanide complexes, have been isolated and structurally characterized. The reported heterometallic species range from simple dinuclear complexes to self-assembled supramolecules, coordination polymers or solids. New structural motifs have been found in these complexes. Most of these metalloligands and complexes are photoluminescent and some of them show switchable emissions based on the formation and rupture of metallophilic contacts. Potential applications as sensors, sensitizers, *in vivo* imaging agents and anticancer drugs are envisaged.

1. Introduction

1.1. General Considerations

Owing to its strength, well-defined geometry and reversible character, the coordinative bond has become one of the most powerful tools for the assembly of supramolecular species with controllable architecture.^[1] The assembly of structurally complex species containing different types of metal ions is challenging, and requires the use of preformed building blocks containing one or several metal centers and binding sites.^[2] These building blocks are frequently referred to as metalloligands.^[2b, 3] In this context, a metalloligand can be defined as a coordination or organometallic complex containing one or several binding groups through which it can bind ions or molecules. The binding sites can be Lewis basic groups or hydrogen bond donors, which are suitably placed in the molecule in order to promote the selective self-assembly of the desired structure. In addition, metalloligands can be endowed with properties such as lipophilicity, luminescence, chirality or magnetism by introducing appropriate functional groups in its structure. Undesired metal-exchange reactions between the metalloligands and the target metal ions must be avoided. This can be achieved by introducing a hard/soft mismatch between the intra- and intermolecular metal-ligand interactions (Figure 1).^[2, 3c] Thus, a metalloligand containing a soft metal center and a free hard donor group will coordinate selectively to hard metal ions while maintaining its integrity.

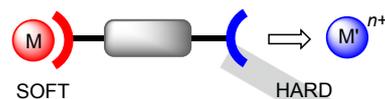


Figure 1. Schematic representation of a metalloligand containing a soft metal ion bound to a soft donor group and a free hard donor group.

1.2. Gold Metalloligands

As a prototypical soft metal center, Au^I binds weakly to hard Lewis bases such as amines, pyridine, alkoxides or carboxylates, whereas it forms stable complexes with C-, P-, or S-donor ligands, typically aryls, alkynyls, carbenes, isonitriles, phosphines, or thiolates.^[4] Thus, ditopic ligands containing both soft and hard donor groups will coordinate to the Au^I center through the soft groups, leaving the hard ones available to coordinate to another metal ion.

From the structural point of view, Au^I complexes show a linear geometry which, in combination with rigid ligands, such as alkynyls or isonitriles, has been used in the assembly of organometallic rigid-rod oligomers, polymers or catenanes.^[5]

Another important structural feature of Au^I complexes is its marked tendency to establish Au...Au interactions, called Aurophilicity.^[6] These interactions can be of similar strength to hydrogen bonds, and are originated by relativistic effects. Intra- or intermolecular aurophilic interactions are commonly observed in the solid state structures of Au^I complexes and, as we will see in the following, they can have a significant structural influence, in particular when they cooperate with other weak interactions, such as hydrogen bonds or π - π interactions.

Photoluminescence from both metal- or ligand-based excited states has been reported in many Au^I complexes.^[7] Triplet emissions from mainly ligand-based excited states are enabled by the strong heavy-atom effect of Au.^[8] In addition, the presence of aurophilic interactions has a marked influence on the energy and intensity of the emitted light.^[9]

These chemical, structural and physical properties make Au^I metalloligands useful building blocks for the assembly of complex supramolecular entities combining different types of interactions (metal-ligand, hydrogen bond and/or aurophilic interactions).^[5a, 9a] Moreover, as we will see along this article, the possibility of modulating the luminescence through the aurophilic interactions opens the way to interesting applications in the design of stimuli-sensitive light-emitting molecules.

This review article covers those reports in which previously prepared Au complexes were used as metalloligands to build heteronuclear complexes by coordination to other metal species. In some cases, the gold metalloligands were *in situ* generated and reacted with metal salts to assemble heteronuclear

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complexes (see for example the synthesis of complexes **22** and **106**, Figure 6 and Scheme 6). Complexes prepared by attaching gold fragments to existing metal complexes were not included.

José Vicente received his Ph.D. in Chemistry from the University of Zaragoza in 1973 under the supervision of Profs. Rafael Usón and Victor Riera. He was a postdoctoral fellow at Bristol University (1976-7) with Prof. F. Gordon A. Stone. He was appointed as a Lecturer in Zaragoza (1978), a Reader (1980) in the University of Murcia, later (1981) a Full Professor, and currently he is an Emeritus Professor. He was awarded in 2001 with the Gold Medal of the Real Sociedad Española de Química. He has supervised 40 PhD Theses. His past and current research focused on the syntheses, structural characterization and applications of Au, Ag, Pd, Pt, Rh, Hg, Tl, and Sn complexes.



Juan Gil-Rubio obtained his PhD in 1995, at the University of Murcia, under the supervision of Profs. J. Vicente and J. A. Abad. After a postdoctoral stay in the group of Prof. H. Werner. He was awarded with a Ramón y Cajal grant, and in 2010 he became Lecturer at the University of Murcia. His main research interests include the study of fluorinated organometallic complexes of the platinum-group metals and gold, and the study of self-assembly processes involving organometallic and coordination complexes.



2. Metalloligands containing oligoether or urea binding sites

The design of synthetic ionophores is important in supramolecular, analytical, environmental, and biological chemistry.^[10] Oligoethers are among the most popular ligands for alkaline and alkaline earth metal cations,^[11] whereas the strong hydrogen bond between ureas and anions has been exploited to design anion sensors.^[12] These binding units have been covalently attached to Au^I centers to create photoresponsive receptors for cation and anions. In some of the reported examples, modulation of the intermolecular aurophilic interactions during the complexation event produced abrupt changes in the optical response of the ionophore.

Yam and co-workers have reported a number of Au^I complexes containing cyclic oligoethers (Figure 2). The simplest examples contain a single benzocrown ether unit decorated with one,^[13] two, or four AuL groups (**1–3**).^[14] Calixcrown ethers functionalized with two AuL groups (**4**) were also reported.^[15] Complexation of these metalloligands with Na⁺ or K⁺ cations has been studied using UV-vis absorption and emission

spectroscopy, being the former more sensitive to changes in the cation concentration. Metalloligands **4** shows a remarkably high K⁺/Na⁺ selectivity factor.^[15a]

The group of Espinet reported similar metalloligands (**1b**, **1c**) which behave as liquid crystals. However, their mesogenic behavior disappeared upon coordination to a Na⁺ cation.^[16]

Metallocrown complexes (**5**) have been reported by Puddephatt and co-workers. Their alkali cation adducts were detected by ESI-MS.^[17]

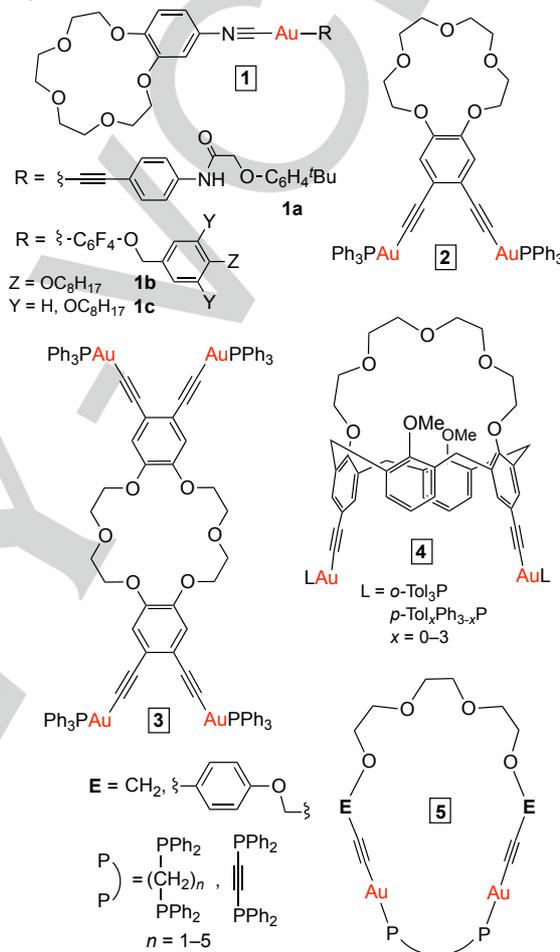


Figure 2. Gold metalloligands containing a crown or calixcrown ether unit.

Complexes containing two Au-Benzo-[15]-crown-5 moieties connected by a flexible bridging ligand were reported by Yam and co-workers (Figure 3).^[13, 18] Spectroscopic evidences suggest that these metalloligands form sandwich-type adducts with K⁺ cations. Interestingly, the approach of both Au atoms upon cation binding enables the aurophilic interaction between them, giving rise to a low-energy emission band which is not observed in the emission spectra of solutions of the pure metalloligands. The crystal structure of one of these adducts (**6f**) was determined.^[18d] Metalloligands **6a**, **6b** and **6g** showed a similar behavior in the presence of Cs⁺ cations.^[13, 18d]

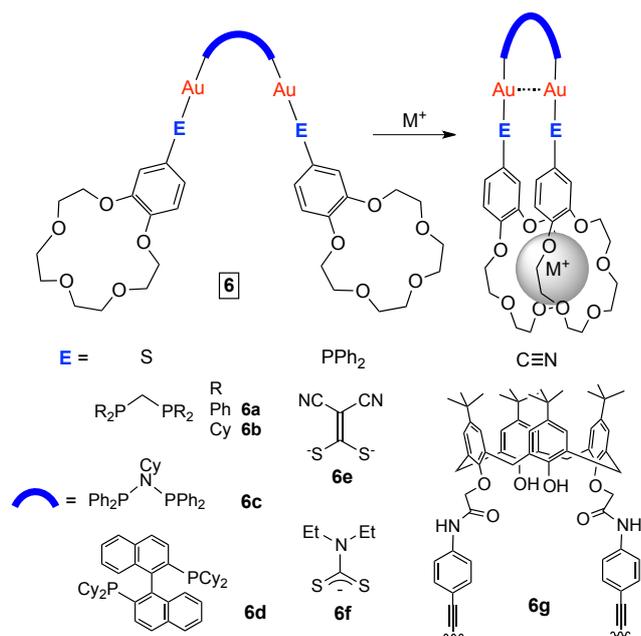


Figure 3. Metalloligands containing two benzo-[15]-crown-3 units. Schematic diagram showing the proposed sandwich structure of their alkali metal cation adducts.

The tripodal oligoether **7** (Figure 4) selectively binds to Mg^{2+} over Ca^{2+} , Ba^{2+} , Li^+ , Na^+ and K^+ . As for metalloligands of the type **6**, the complexation event switches on the low-energy emission of the Au-alkynyl luminophores.^[19]

A strongly luminescent Au_6Cu_2 cluster containing six alkynyl units and three diphosphine ligands has been functionalized with oligoether or urea units (**8**, Figure 4). The benzocrown and urea metalloligands **8a** and **8b** function as luminescent receptors of alkaline cations or anions (F^- , Cl^- , H_2PO_4^-), respectively.^[20]

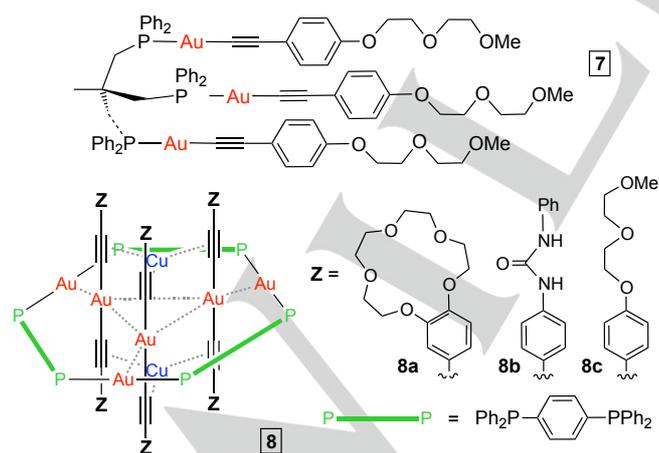


Figure 4. Au_3 and Au_6 luminescent metalloligands.

Other luminescent urea-functionalized Au complexes have been synthesized and tested as anion receptors by the groups of Zhou (**9**)^[21] and Yam (**10**) (Figure 5).^[22] The latter group also reported a ditopic metalloligand containing both a benzocrown and a urea moiety (**11**). The cooperative effect of both binding units is able to solubilize NaCl or NaI in CHCl_3 .^[23]

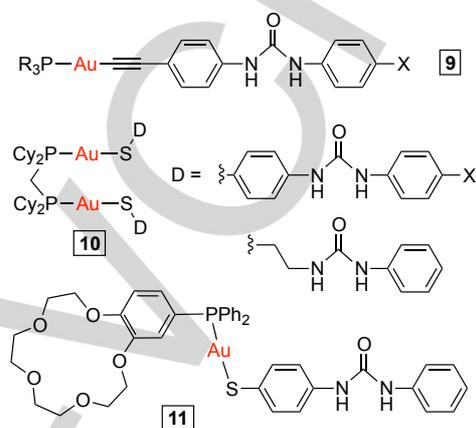
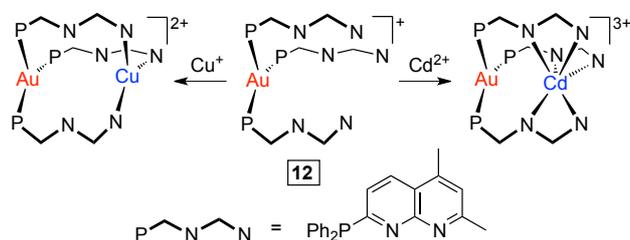


Figure 5. Anion-binding metalloligands containing urea moieties.

3. Metalloligands containing pyridine binding sites

Pyridine and polypyridines are among the most versatile ligands in transition metal coordination chemistry. They form stable complexes with most transition metal cations and have been used as binding units in the coordination-driven self-assembly of many types of supramolecular entities.^[24] The relatively low affinity of Au^I for pyridine offers the opportunity to design metalloligands containing one or several free pyridine groups which, upon coordination to metal cations, give rise to interesting self-assembly processes.

The first metalloligand of this type was reported by Che and co-workers by using 2-diphenylphosphinonaphthyridine (Scheme 1). This ditopic ligand coordinates selectively to Au^I through the PPh_2 groups to give complex **12**, where the naphthyridine atoms are available to bind other metal cations.^[25]



Scheme 1. Tripodal gold naphthyridine metalloligands.

Laguna, Gimeno and co-workers studied the coordination of metalloligands **13–18** to Cu^+ , Ag^+ , MCl_2 ($\text{M} = \text{Pd}, \text{Pt}$), and $\text{MCl}(\text{COD})$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{COD} = 1,5\text{-cyclooctadiene}$) (Figure 6). The heterometallic complexes of **13** and **15** show short $\text{M}\cdots\text{Au}$ interactions, supported by the (2-pyridyl)phosphine ligands, as illustrated by complexes **19–21**.^[26] An analogue of **19**, containing a 3,5-dichloro-2,4,6-trifluorophenyl group instead of the chloro group, has been similarly prepared by López de Luzuriaga, Catalano and co-workers.^[27] Laguna, Eisenberg and co-workers reported the self-assembly of tetranuclear complexes of the type **22** when **13** was reacted with Ag_2O and NaBF_4 ($\text{E} = \text{O}$), or with $[\text{Au}_2(\mu\text{-E})(\text{PPh}_2\text{py})_2]$ and AgBF_4 ($\text{E} = \text{S}, \text{Se}$).^[28] The presence of the thiolato ligand in **16–18** makes the coordination chemistry of these metalloligands more complex, because of the subtle interplay of M-S , Au-S and $\text{M}\cdots\text{Au}$ interactions, as illustrated by complex **23**.^[29] The absorption and luminescence spectra of the metalloligands and their complexes were studied.

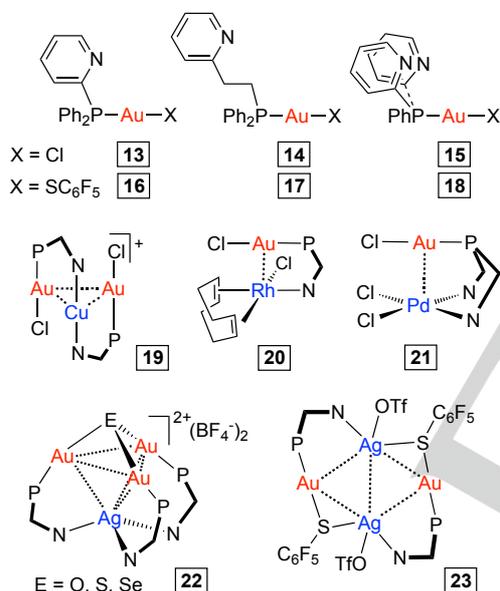


Figure 6. Metalloligands and heterometallic complexes containing a ditopic phosphine/pyridine ligand.

Catalano and co-workers obtained complex **25** by the reaction of **24** with $\text{Cu}(\text{NCMe})_4^+$ (Figure 7).^[30] Interestingly, when **25** is exposed to air the coordinated acetonitrile molecules are lost, producing a considerable shortening of the $\text{Au}\cdots\text{Cu}$ distance and a marked luminescent thermochromism in the resulting complex. López de Luzuriaga, Catalano and co-workers isolated complex **26** after the reaction of the corresponding digold metalloligand with $\text{Cu}(\text{NCMe})_4^+$ (Figure 7).^[27] Bodio and co-workers studied the anticancer activity of the heteronuclear Pt^{II} complexes (**27**) and their parent metalloligands.^[31] Very recently, Roesky and co-workers have prepared complex **28** and characterized two trinuclear MAuM derivatives ($\text{M} = \text{Cu}, \text{Ag}$), where both bipyridyl arms of each $\text{PPh}(\text{CH}_2\text{bpy})_2$ ligand coordinate to the same coinage metal cation.^[32]

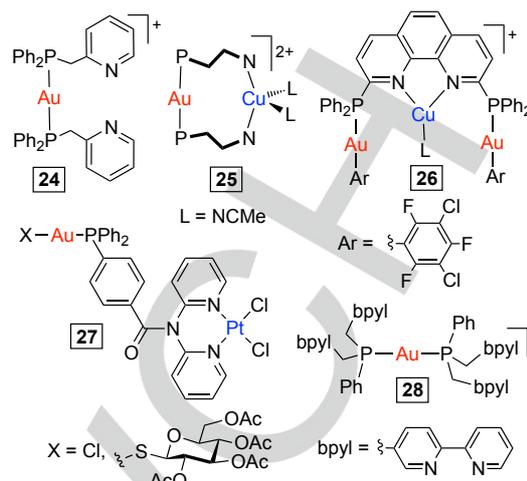
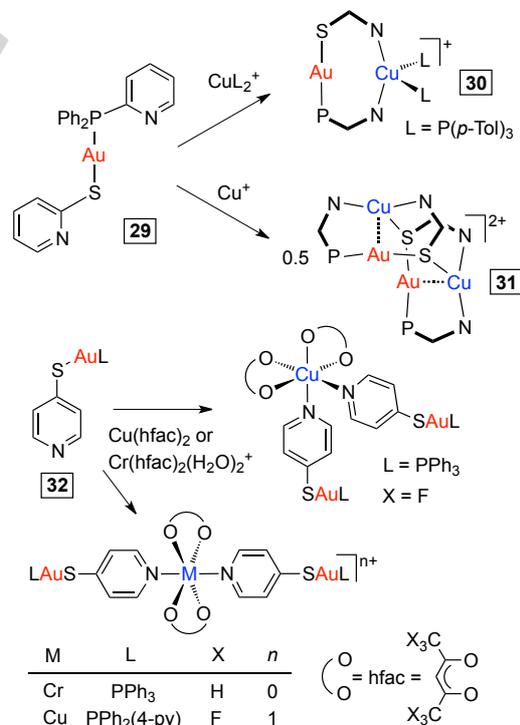


Figure 7. Metalloligands and heterometallic complexes containing pyridine, phenanthroline or bipyridine units.

Although many examples of Au^{I} thiolato complexes derived from pyridine thiols have been reported,^[33] only a few heteronuclear complexes resulting from coordination of the free pyridyl unit to another metal center have been prepared (Scheme 2). Eisenberg and co-workers studied the reactions of metalloligand **29** with different Cu^{I} precursors. Whereas the reaction with $\text{Cu}(\text{NO}_3)\{\text{P}(\textit{p}\text{-Tol})_3\}_2$ gave heterometallic complex (**30**), the reaction with $\text{Cu}(\text{NCMe})_4^+$ gave a dimer (**31**), where two heterometallic cycles are connected by two Cu-S bonds.^[34] By reaction of metalloligands of the type **32** with Cr^{III} or Cu^{I} diketonates, Onaka and co-workers have isolated Au_2Cr and Au_2Cu octahedral complexes (Scheme 2).^[35]



Scheme 2. Metalloligands and heterometallic complexes derived from mercaptopyrindines.

Complexes of the type $\text{LAuC}\equiv\text{Cpy}$ (**33**) have been synthesized by the groups of Ferrer,^[36] Yam^[37] and Gimeno,^[38] who also reported the imidazole **34** (Figure 8). The reactions of these metalloligands with a $\text{Re}(\text{CO})_3(\text{N}^*\text{N})^+$ (N^*N = 2,2'-bipyridine or 4,4'-bis(*t*-butyl)-2,2'-bipyridine) precursor gave heteronuclear complexes of the type **35**.^[37-38] Preliminary *in vivo* studies suggest that **35c**, **35d** and **35e** are potential candidates for applications in cell imaging and cancer therapy.^[38]

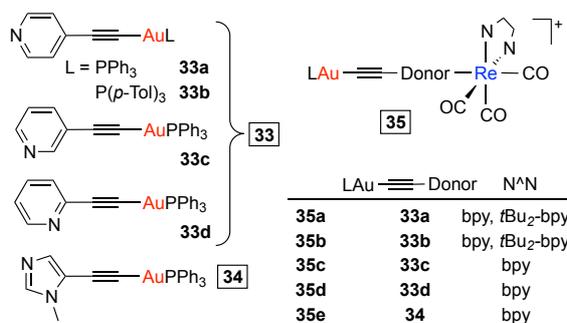


Figure 8. Metalloligands containing one ethynylpyridine or -imidazole unit and their Re^{I} complexes.

Pyridines decorated with two $\text{LAuC}\equiv\text{C}$ substituents **36** were reported by the groups of Vicente^[39] and Raithby (Figure 9).^[40] The former isolated Au^{I} (**37**) and Pt^{II} (**38**) complexes of metalloligand **36a**. Flexible metalloligands containing two (**39**) or three pyridine units (**40**),^[36] and rigid bis(pyridine)-complexes (**41**) were reported by Ferrer and co-workers.^[41]

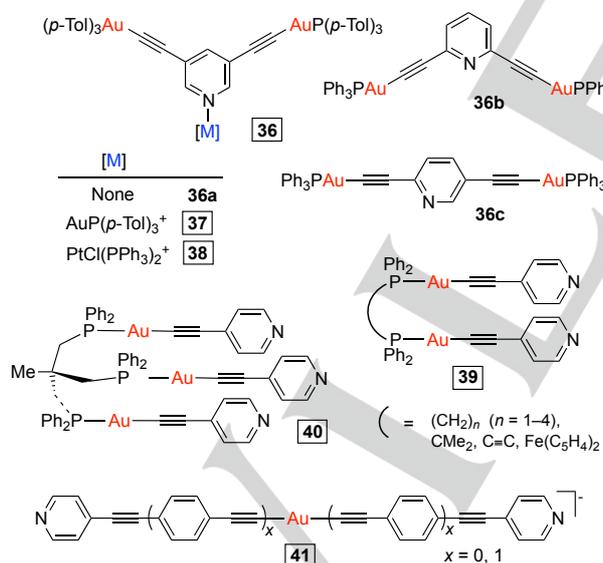


Figure 9. Metalloligands containing one, two or three pyridine units.

Ferrer, Rodríguez and co-workers have synthesized a series of metalloligands containing the 4-pyridyl-2,3,5,6-tetrafluorophenyl unit (tfppy).^[42] By reaction of $\text{Ph}_3\text{PAu}(\text{tfppy})$ with $[\text{M}(\text{OH})_2(\text{diphosphine})]^{2+}$ (diphosphine = dppp, dppf) (M = Pd, Pt) they isolated complexes of the type **42** (Figure 10).^[42a]

Analogously, macrocycles of the type **43** were formed by mixing metalloligands of the type $(\mu\text{-diphosphine})[\text{Au}(\text{tfppy})]_2$ with the precursors $[\text{M}(\text{OH})_2(\text{diphosphine})]^{2+}$. Depending on the combination of diphosphine, diphosphine' and M employed, complexes **43**, or mixtures of **43** with heterometallic assemblies of higher nuclearity were formed.^[42c] Finally, the self-assembly of two tripodal metalloligand containing three $\text{Au}(\text{tfppy})$ units and three Ag^+ cations gave the metallocage **44** (Figure 10), which is able to interact with aromatic guest such as naphthalene, methyl salicylate and 8-hydroxyquinoline.^[42b]

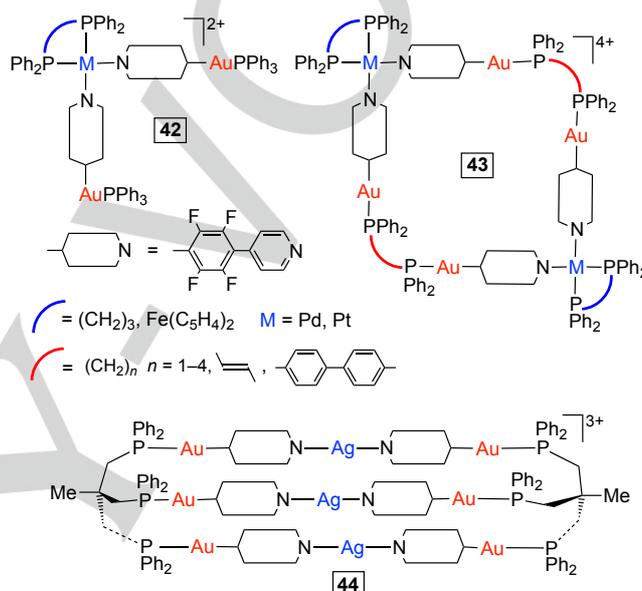
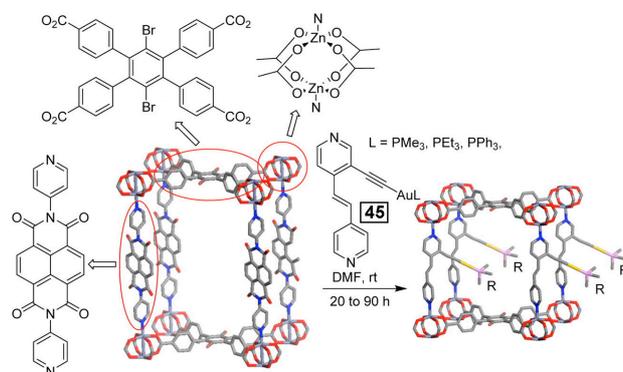


Figure 10. Heteronuclear complexes derived from Au^{I} metalloligands containing the 4-pyridyl-2,3,5,6-tetrafluorophenyl group.

A singular Metal Organic Framework (MOF) functionalized with $\text{C}\equiv\text{CAuPR}_3$ units has been obtained by Nguyen and co-workers by using metalloligand **45** (Scheme 3). To avoid decomposition of the gold complex under the hydrothermal conditions used to synthesize the MOF, the metalloligand was introduced in a previously prepared MOF by solvent-assisted linker exchange (SALE).^[43]



Scheme 3. Synthesis and structure of an organogold MOF. Adapted with permission from ref. [43]. Copyright 2014 American Chemical Society.

Catalano and co-workers have reported biscarbene-gold complexes containing pyridyl substituents (**46**, Figure 11). The reaction of these luminescent metalloligands with Cu^I or Ag^I salts gave a series of heteronuclear complexes with singular structures and interesting luminescent properties. Representative complexes are shown in Figure 11. For instance, the bis(pyridyl or quinolyl)-substituted metalloligands (**46a–c**) form adducts of the type **47**, where both binding units coordinate to the same Cu^+ or Ag^+ cation, or to each metal atom of a $\text{Cu}(\mu\text{-X})_2\text{Cu}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) fragment.^[44] In contrast, the coordination polymer **48** crystallized after the reaction of **46a** with AgBF_4 .^[45] The tetrapyridyl-substituted metalloligands (**46d–f**) give rise to AuM_2 complexes or coordination polymers.^[46] The AuCu_2 complex **49** reacts with MeOH to give complex **50**. This reaction also takes place when the solids are exposed to MeOH vapor and is reversible. A change in the photoluminescence maximum wavelength from blue (**49**) to green (**50**) takes place during the reaction, producing a marked vapochromism which can be used to detect volatile organic compounds, such as MeCN , MeOH , and Me_2CO .^[47] These abrupt changes in the emission energy are likely originated by switching on or off the $\text{Au}\cdots\text{Cu}$ metallophilic interactions.

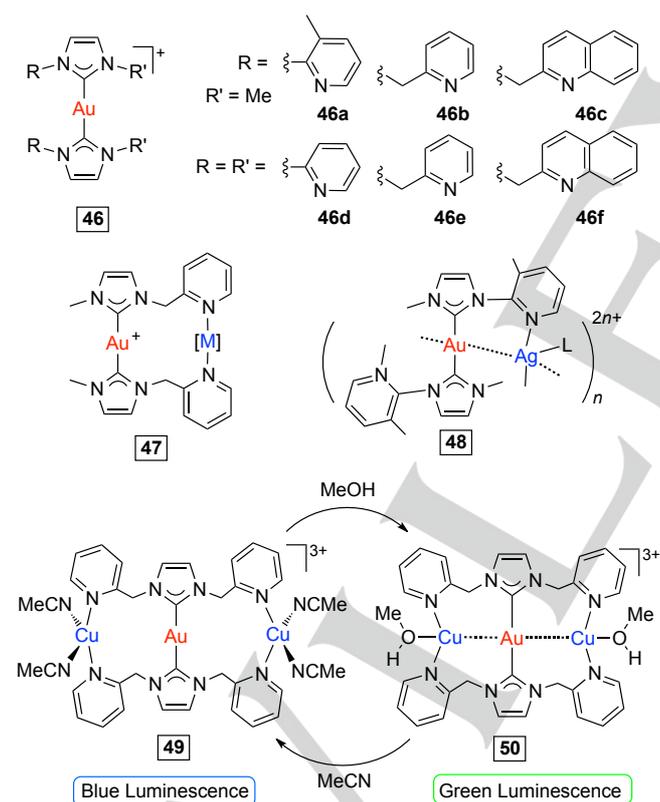


Figure 11. Metalloligands containing pyridyl-functionalized NHC carbenes and some representative complexes.

Metalloligands derived from mono- and bis(ethynyl)bipyridines were reported by our group^[48] (**51**), and the groups of Raithby^[40]

and Constable^[49] (**52**) (Figure 12). The analogous complexes derived from ethynylphenanthrolines were reported by Shiotsuka,^[50] Castellano^[51] and co-workers.

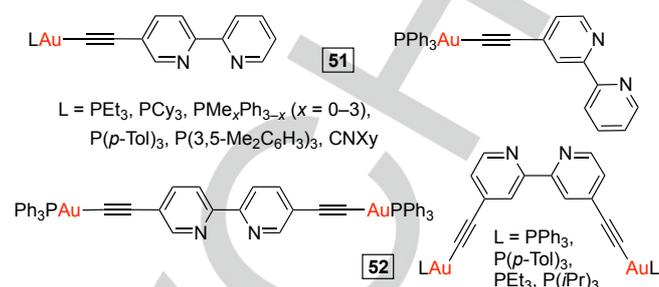


Figure 12. Metalloligands containing a bipyridine binding site.

Our group isolated Fe^{II} , Co^{II} or Zn^{II} complexes (**53**) containing metalloligands of the type **51** as mixtures of the facial (*fac*) and the meridional (*mer*) isomers, and complex **54**, containing three digold metalloligands of the type **52** (Figure 13).^[48b]

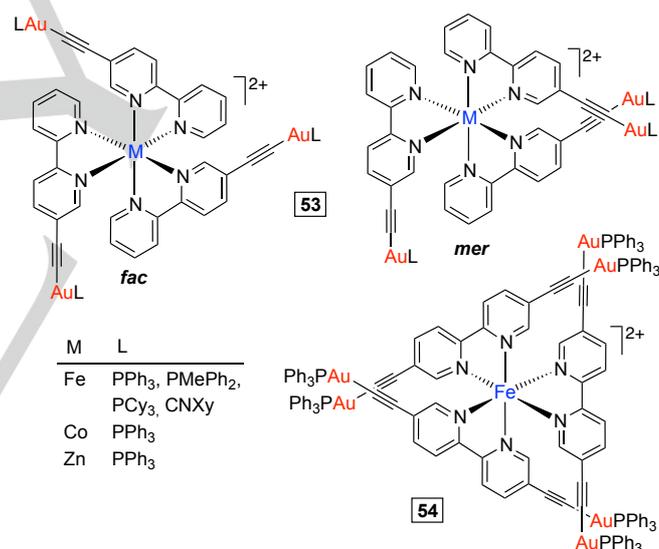
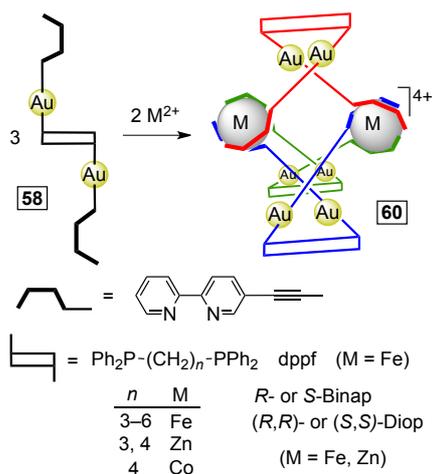


Figure 13. Fe^{II} , Co^{II} and Zn^{II} complexes of bipyridine metalloligands.

An unusual shift of the *fac-mer* equilibrium toward the *fac* isomer was observed when complexes of the type **53** containing PPh_3 ligands were dissolved in MeCN (Scheme 4). NMR, ESI-MS and X-ray diffraction studies suggested that this is originated by the self-assembly of two *fac* complexes, which mutually embrace to give a helical dimer. The X-ray structure of one of this dimers showed that they are stabilized by multiple weak interactions ($\text{Au}\cdots\text{Au}$, $\text{CH}\cdots\pi$ and $\pi\cdots\pi$). The dissociation of the dimers in less polar solvents (CH_2Cl_2 or C_6H_6) suggested that, in addition to these weak interactions, the dimer formation is driven by solvophobic effects.^[48b]



Scheme 5. Self-assembly of M_2Au_6 triple helicates.

Macrocyclic metalloligands containing two bipyridine donors (**61**) were reported by Li and co-workers (Figure 16). Their *in situ* formed complexes with $[Yb(hfac)_3]$ show an enhancement of the Yb^{III} NIR luminescence with respect to that of $[Yb(hfac)_3(H_2O)_2]$.^[56]

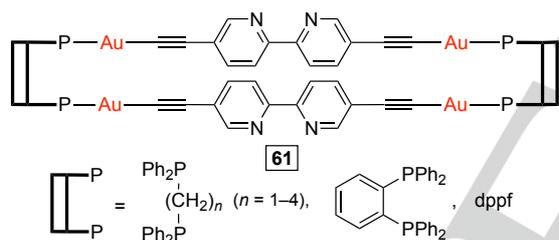


Figure 16. Macrocyclic Au_4 -metalloligands with two bipyridine binding units.

Heteronuclear complexes where a metalloligand of the type **62** coordinates to a $CuCl_2$ or $RuCl(1^6-cymene)$ metal fragment were synthesized by Bodio and co-workers (Figure 17). They show moderate anticancer activity.^[57]

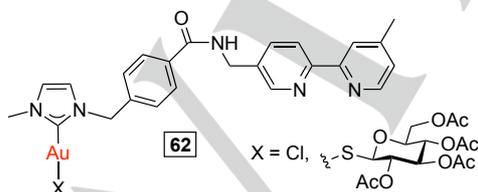


Figure 17. A bipyridyl-substituted NHC-Au complex.

Motivated by the excellent binding ability of terpyridine toward transition metal cations,^[24b, 58] we prepared metalloligands **63**, **64** ($n = 10$) and **65** from 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (Figure 18).^[48a] By using the same method, Chen and co-workers prepared a series of complexes of the type **64** with $n =$

2–6.^[59] We isolated and structurally characterized complexes (**66**) and coordination oligomers (**67**) by reaction of metalloligands **63** or **65** with Fe^{2+} , Co^{2+} or Zn^{2+} cations.^[60] The average size of these oligomers was estimated by diffusion NMR and Dynamic Light Scattering. Chen and co-workers used metalloligands **64** with $n = 2–6$ as sensitizers of lanthanide luminescence, but the *in situ* generated heteronuclear adducts were not structurally characterized.^[59] Constable and co-workers reported the synthesis of terpyridine metalloligands $Ph_3PAuC=C(CH_2O)_xTpy$ ($Tpy = 2,6':2',6''$ -terpyridine-4'-yl; $x = 0$ or 1), $(\mu-dppe)\{AuC=C(CH_2O)_xTpy\}_2$ ($dppe = Ph_2(CH_2)_2PPh_2$; $x = 0$ or 1) and $(^nBu_3PAuC=CCH_2OCH_2)_3CCH_2OTpy$.^[61]

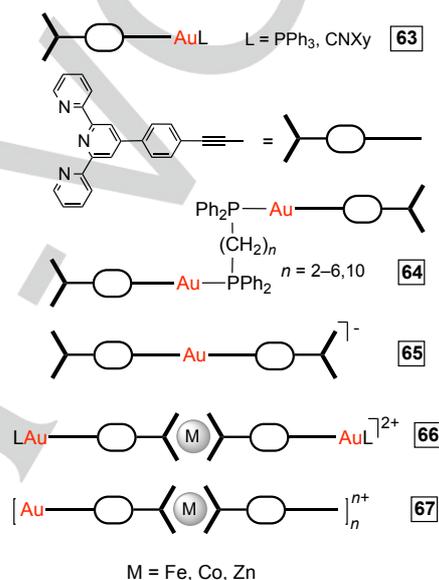


Figure 18. Terpyridine metalloligands and their Fe^{II} , Co^{II} or Zn^{II} complexes and coordination oligomers.

Yam and co-workers reported complex **68** (Figure 19), which is a selective ionophore for Cu^{2+} , as revealed by UV-visible absorption and luminescence studies.^[62]

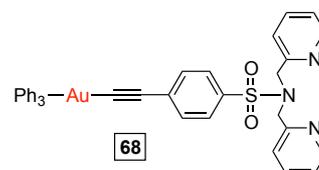


Figure 19. Organometallic Cu^{2+} -selective ionophore.

4. Metalloligands containing carboxylate binding sites

3- or 4-Mercaptobenzoic acids (MBA) present a rich coordination chemistry. They coordinate to soft metal ions, metallic particles or surfaces through the sulfur atom, while they can bind a hard metal center or form hydrogen bonds through the COOH group.^[63] A number of Au^I thiolato complexes derived from 4-MBA of the types $H[69]$, $H_2[70]$ and $H_2[71]$ have been reported

by Schmidbaur and co-workers (Figure 20).^[64] They show intra- or intermolecular auropilic and/or hydrogen bond interactions.

Espinet and co-workers have prepared liquid crystalline metallosupramolecular aggregates by hydrogen-bond-driven self assembly of complexes of the types H[69] (L = PPh₃, PCy₃) or H₂[70] (L = Binap) and tris(aryl amino)triazines.^[65]

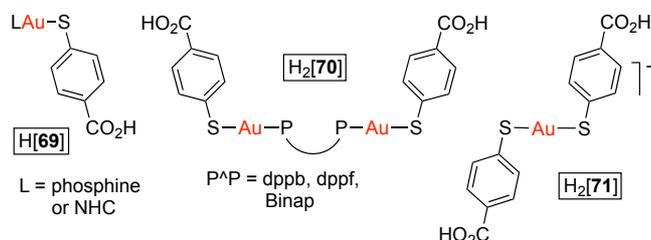


Figure 20. Metalloligands derived from 4-mercaptobenzoic acid.

The groups of Contel and Hey-Hawkins have synthesized gold-early transition metal complexes of the types 72^[66] and 73^[67] by reaction of metalloacids of the type H[69] with [M(η^5 -Cp)₂Me₂] (M = Ti, Zr) (Figure 21). The Au-Ti complexes (72) show a remarkable anticancer activity, being able to block renal cancer growth both *in vitro* and *in vivo*.^[66]

Sordo and co-workers have studied the anticancer activity of di- or tetranuclear complexes 75 and 76, obtained by coordination of metalloligands of the type [74] to LAg⁺ or LAu⁺ (L = PPh₃) fragments through both the carboxylate and thiolate groups (Figure 21).^[68]

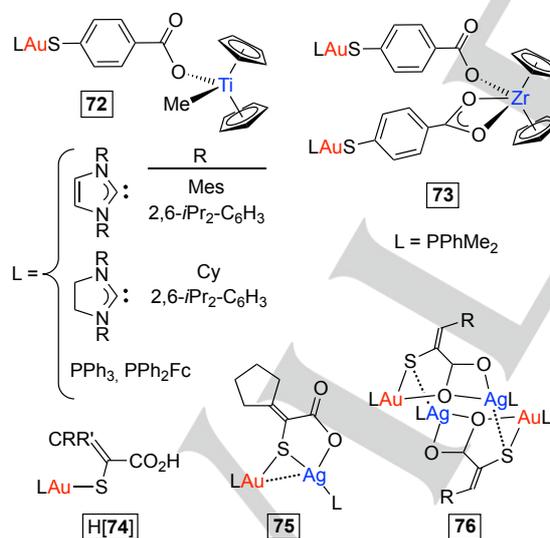


Figure 21. Heterometallic complexes of Au metalloligands containing carboxylate and thiolate binding sites.

Complex H₄[77] was prepared by Konno and co-workers from racemic thiomalic acid and [Au₂Cl₂(dppe)] (Figure 22). The outcome of its reaction with Ni²⁺ depended on the basicity of the

medium. Thus, in the presence of 4 equiv of NaOH the trinuclear complex 78 was formed, whereas in the presence of 2 equiv of NaOH, the salt Ni₃H₂[77]₂(MeOH)₃ was isolated. The crystal structure of this salt contains two octahedral Ni^{II} centers bridged by two units of [77]⁴⁻ and one of H₂[77]²⁻, and a Ni(MeOH)₃²⁺ fragment bound to three carboxylate oxygen atoms. Reversible interconversion between both species was accompanied of a change in the magnetic behavior from paramagnetic to ferromagnetic.^[69]

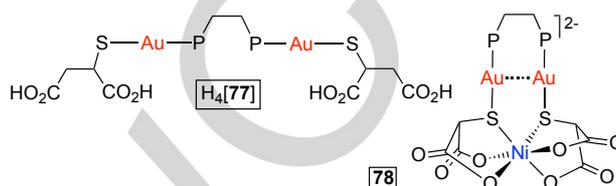


Figure 22. A gold metalloligand derived from racemic thiomalic acid and its Ni^{II} complex.

5. Metalloligands containing amino acid binding sites

Konno's group has extensively investigated the coordination chemistry of the Au^I thiolato complexes H[79], H₂[80] and H₂[81], containing one or two *D*-penicillaminato ligands, toward transition metal cations (Figure 23).^[70] Owing to the presence of the S, NH₂ and COO⁻ binding sites, these metalloligands are very versatile and their coordination behavior is markedly influenced by the pH of the reaction medium. In many cases the formed heteronuclear complexes undergo hierarchical self-assembly through intermolecular hydrogen bonds and/or coordination to added metal cations, giving rise to interesting supramolecular structures.

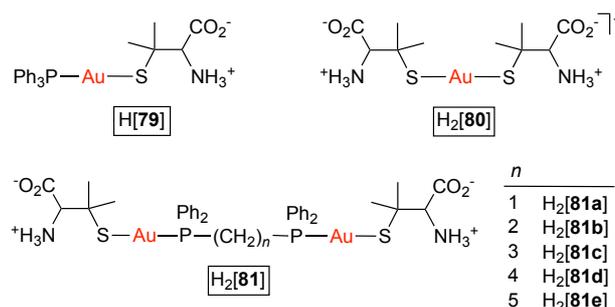


Figure 23. Gold metalloligands derived from *D*-penicillaminato.

The monotoxic metalloligand H[79] forms the Co^{III} complex 82, which contains two units of the deprotonated form of the metalloligand coordinated in a (S,N,O)-tridentate fashion (Figure 24).^[71]

Metalloligand H₂[80] is particularly suitable to act as a bridge between two metal cations. Thus, two of these metalloligands

coordinate to two Ag^+ cations through the S atoms to give metallocycle **83** (Figure 24). The reaction of **83** with CuCl_2 followed by crystallization gave rise to a salt containing the three coinage metal atoms, which is composed of large monocationic and monoanionic cages containing 20 and 21 metal atoms, respectively. These cages are arranged in a supramolecular ionic structure resembling that of the rock salt.^[72]

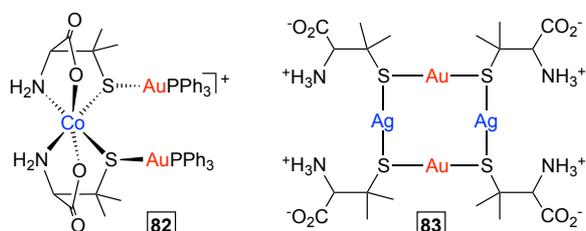


Figure 24. Co^{III} and Ag^{I} complexes derived from metalloligands H_2 (**73**) and H_2 (**74**).

Tetranuclear complexes containing two square-planar centers have been isolated by reaction of H_2 (**80**) with Ni^{II} ,^[73] Pd^{II} ^[74] or Pt^{II} ^[74] salts (Figure 25). The (*cis,cis*) or (*trans,trans*) forms of these complexes (**84** and **85**) have been isolated as potassium salts. The reaction of the (*trans,trans*) Au_2Pt_2 complex with $\text{Zn}(\text{NO}_3)_2$ gave coordination polymers, where the free carboxylate groups are bound to the Zn^{2+} cations. Depending on the pH, these polymers adopt a 3D framework or a 1D helical structure.^[75]

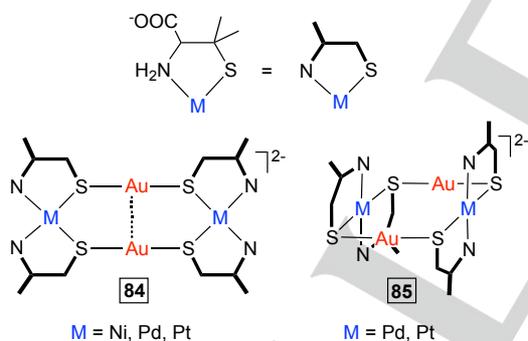


Figure 25. (*Cis,cis*) and (*trans,trans*) heteronuclear complexes of deprotonated H_2 (**80**) with square planar metal cations.

Ni^{II} complexes of the types **84**, **86**, **87** and **88** (Figures 25 and 26) have been isolated by reaction of H_2 (**80**) with $\text{Ni}(\text{NO}_3)_2$. Reversible interconversion between these complexes was observed as response to changes in the H_2 (**80**): Ni molar ratio, pH, solvent or temperature of the solution. The alterations in the Ni^{II} coordination environment produced in these equilibria are accompanied by marked changes in the color and magnetism of the complexes.^[73]

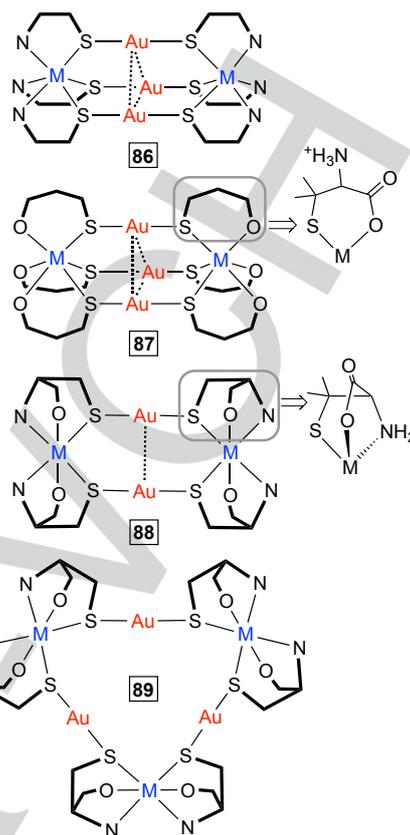


Figure 26. Heteronuclear complexes formed by coordination of deprotonated H_2 (**80**) to octahedral metal centers.

The reaction of H_2 (**80**) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ followed by oxidation with O_2 gave a mixture of a Co^{III} complex of the type **86** and the metallomacrocyclic complex **89** (Figure 26), which were separated by chromatography and characterized by single-crystal X-ray diffraction.^[76]

The deprotonated form of H_2 (**81a**) (Figure 23) coordinates to Ni^{2+} or Zn^{2+} cations to give trinuclear complexes of the type **90** (Figure 27). The presence of a $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligand places both Au atoms at a short distance, supporting the aurophilic interaction and the hexadentate coordination of the ligand.^[77] In contrast, metalloligand **81b** coordinates to two Co^{3+} ,^[78] Cr^{3+} ,^[78b] or Ni^{2+} ^[79] metal cations in a bridging mode to give complexes of the type **91** (Figure 27), which have been isolated and crystallographically characterized. Their crystal structures show interesting structural motifs originated by the self-assembly of the complexes through hydrogen bonding. Thus, six Co^{III} or Cr^{III} dipositively-charged complexes aggregate to build supramolecular octahedra, which closely pack in a FCC-type structure. The structures of the salts of these cations with different anions show an unusual feature. Instead of the commonly observed alternate distribution of cations and anions dictated by the Coulombic forces, they present separate aggregates containing only cations or anions. The authors attribute the stability of these structures to the presence of multiple non-Coulombic interactions, such as hydrogen bonds

and CH- π interactions, which balance the electrostatic repulsions between nearby ions of the same sign.^[70a, 78]

Coordination polymers of the type **92** (Figure 27) crystallize by slow evaporation, after mixing metalloligands H_2 (**81c**), H_2 (**81d**) or H_2 (**81e**) with Cu^{2+} ions. These polymers show different helical structures depending on the number of methylene units of the $Ph_2P(CH_2)_nPPh_2$ linker. Thus, for $n = 3$, a triple-stranded homochiral helix was formed, whereas for $n = 4$ a single-stranded *meso* helix was observed, and for $n = 5$ the polymer adopted a single-stranded helical structure.^[80]

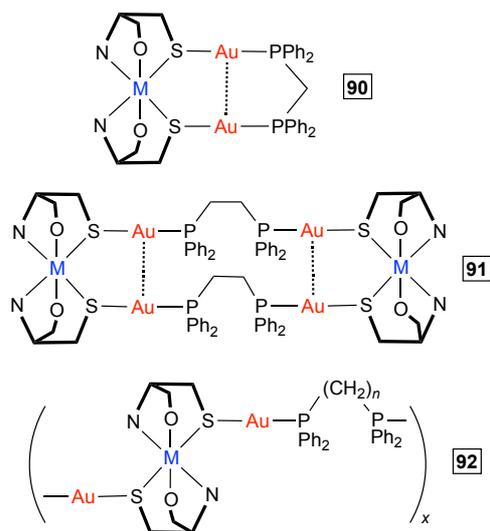


Figure 27. Different types of heteronuclear complex formed by metalloligands H_2 [**81**] and metal cations with an octahedral coordination geometry.

Tripodal metalloligand H_3 [**93**] forms complex **94** upon reaction with $K_3[Co(CO_3)_3]$ (Figure 28). An Au_6Co_3 cage (**95**) was obtained by reaction of the same metalloligand with $Co(OAc)_2$ in a 2:3 ratio. The three Co^{II} centers of this paramagnetic complex were oxidized to Co^{III} with the strong oxidant ceric ammonium nitrate to give a diamagnetic complex, whose X-ray structure was determined.^[81]

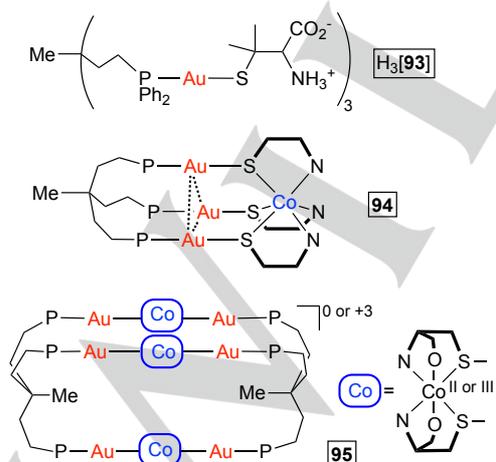


Figure 28. Co^{II} and Co^{III} complexes of tripodal metalloligand H_3 [**93**]. Complexes **94** or **95** (with Co^{II}) are formed depending on the molar ratio and the metal oxidation state.

6. Metalloligands containing η^2 -C=C binding sites

Heteronuclear clusters containing Au^I alkynyls and π -coordinated M^+ or ML^+ ($M = Cu, Ag$) cations have been studied since the pioneering reports of Abu-Salah and co-workers,^[82] due to their rich structural chemistry and intense photoluminescence.^[83] In most cases, they have been prepared by reacting Au^I alkynyls with Cu^I or Ag^I acetylides or salts, and free phosphines or Au^I phosphine complexes. In these reactions σ -alkynyl groups are transferred between different metal centers and $M-P$, $M-\pi(C\equiv C)$ and $M\cdots M'$ bonds are formed.^[83b, 84] In contrast, a relatively low number of compounds of this type have been prepared by coordination of well-defined Au -alkynyl metalloligands to other metal cations.

Simple Au^I alkynyl complexes form di-, tri- or tetranuclear complexes of the types **96**–**100** by coordination of the $C\equiv C$ bond to a coinage metal center (Figure 29).^[85] Complexes of the type **99** present an unsymmetrical coordination of the metal to the triple bond combined with a metallophilic contact.

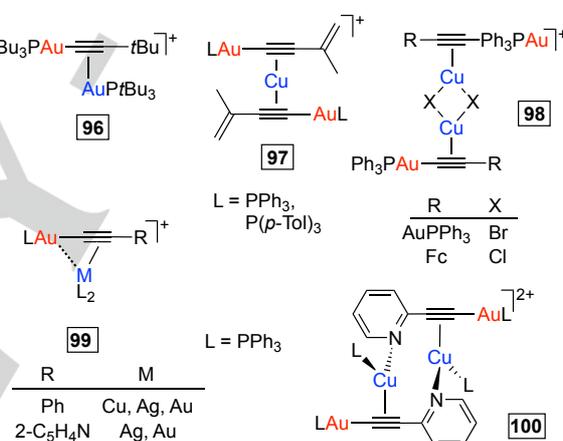


Figure 29. Heteronuclear complexes formed by η^2 -coordination of Au alkynyls to coinage metal fragments.

Eisenberg and co-workers isolated heteronuclear complexes by reaction of three different bis(alkynyl)aurates with Cu^+ (Figure 30). Compounds **101** or **102** were formed depending on the substituent of the ethynyl group and the stoichiometry of the reactants. Several polymorphic salts containing the anionic complexes **102** and the cation $[(Ph_3P)_2N]^+$ were structurally characterized. These polymorphs present subtle structural differences which have a strong influence in their emission energies.^[86]

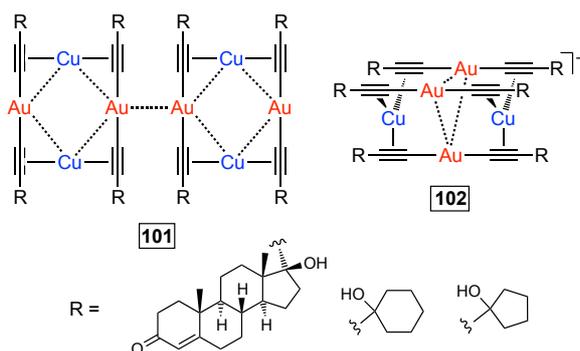


Figure 30. Two types of Au-Cu acetylides formed by reaction of dialkynylaurates with Cu^+ cations.

Yam and co-workers prepared complexes **103** by reaction of a bis-alkynyl metalloligand with Cu^+ or Ag^+ (Figure 31).^[85c] Whereas the free metalloligand is not luminescent in the solid state, the heteronuclear complexes are emissive. Lagunas and co-workers isolated complex **104** by reacting a bis(phenylethynylgold^I) complex containing a rigid diposphine linker with Cu^+ .^[87] Vicente and co-workers isolated complex **105**, where the Ag^+ cation presents an unsymmetrical coordination to the triple bonds and metallophilic contacts with the four surrounding Au atoms.^[19]

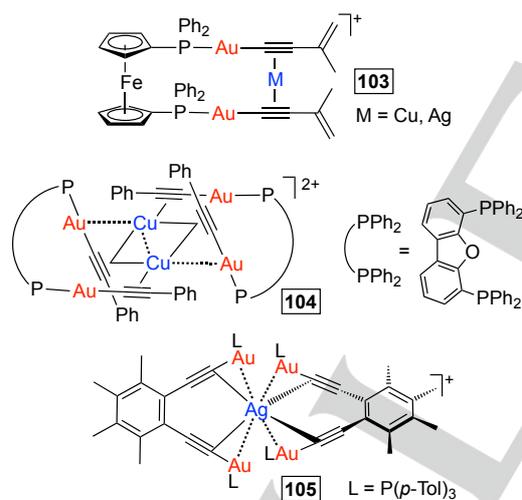
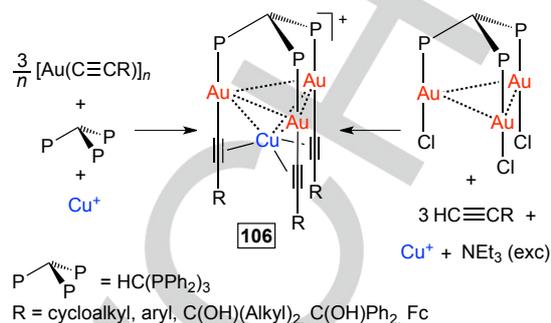


Figure 31. Heteronuclear complexes formed by coordination of metalloligands containing two Au-alkynyl units to Cu^+ or Ag^+ cations.

Tunik and co-workers reported an elegant synthesis of the tetranuclear complexes **106** (Scheme 6). The corresponding tripodal trialkynyl metalloligands were generated by two different methods and *in situ* reacted with Cu^+ .^[88] The reaction was highly selective and led to a family of complexes with different R substituents, as well as to Au_6Cu_2 complexes containing linear dialkynyl fragments (**107**).^[89] Some of these complexes present luminescent vapochromism.^[88c, 90] Similar tetranuclear

complexes were obtained by using $\text{PhP}\{(\text{CH}_2)_n\text{PPh}_2\}_2$ ($n = 1, 2$) instead of $\text{HC}(\text{PPh}_2)_3$.^[91]



Scheme 6. Self-assembly of tripodal Au_3Cu and Au_6Cu_2 complexes.

Photoswitchable metallomacrocycles **108** were prepared by Yam and co-workers (Figure 32).^[92] A reversible (*trans,trans*) to (*cis,trans*) isomerization of the macrocycle was observed upon irradiation with 360 nm or 485 nm light. Remarkably, in the presence of Ag^+ cations this photoisomerization was blocked. This was attributed to the coordination of the Ag^+ cations to the triple bonds of the (*trans,trans*) isomer, which was evidenced by vibrational spectroscopy, although the formed heteronuclear complex was not structurally characterized. Chao and co-workers reported that the tripodal Au^I alkynyl **109** selectively coordinates to a Ag^+ cation, giving rise to a strongly photoluminescent adduct.^[93]

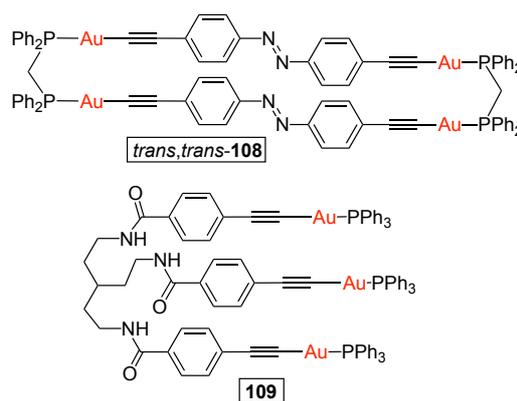
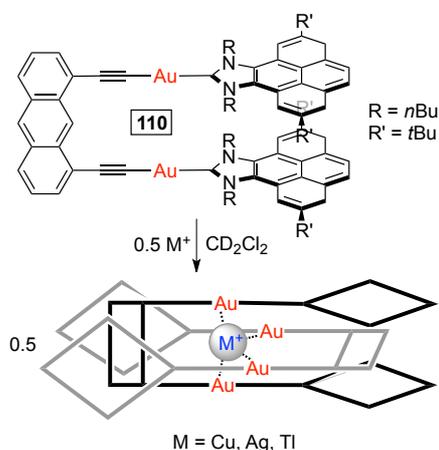


Figure 32. Ag^+ -sensitive photoswitchable metallomacrocycles *trans,trans*-**108** and Ag^+ -selective metalloligand **109**.

An interesting metallotweezer (**110**) has been reported by Peris and co-workers (Scheme 7).^[1c] When it is dissolved in benzene, **110** form dimers where two molecules are interpenetrated in

such a way that the two pyrene units of a molecule sandwich the anthracene unit of the other. Surprisingly, in dichloromethane the dimerization process is triggered by the presence of Cu^+ , Ag^+ or Ti^+ cations, which are enclosed inside the cavity of the dimer, giving rise to multiple metallophilic contacts with the surrounding four Au atoms (Scheme 7).



Scheme 7. Dimerization of metallotweezer **110** in the presence of metal cations.

7. Summary and Outlook

Gold^I complexes containing soft-hard multitopic organic ligands are able to bind metal cations or complexes through the hard binding sites while maintaining the integrity of the Au-soft donor bonds. By using this strategy, a large number of heterometallic gold complexes containing alkaline, transition, or lanthanide metal centers have been isolated and structurally characterized. Self-assembly processes leading to heteronuclear helicates, coordination polymers, or three-dimensional frameworks have been reported. Metallophilic interactions display a significant structural influence in these complexes, particularly when they act in cooperation with other secondary interactions, such as hydrogen bonds and π - π interactions.

These gold metalloligands are often photoluminescent and their emission energies and intensities are very sensitive to the Au coordination environment, in particular to the existence and the strength of metallophilic interactions. This phenomenon has been exploited to design switchable luminescent metalloligands. Potential applications as sensors, light-emitting materials and *in vivo* imaging agents have emerged. Since the application in cancer therapy of these heterometallic complexes has recently started to be studied with promising results, we believe that the biological chemistry and therapeutical applications of gold heterometallic complexes will be an active research field in the near future. Gold metalloligands can also play an important role in the synthesis of functional mixed-metal porous solids and soft materials. Finally, the study of the catalytic activity of gold-heterometallic complexes could lead to new developments in the field of gold catalysis.

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Keywords: Gold • metalloligands • organometallic complexes • heterometallic complexes • aurophilicity

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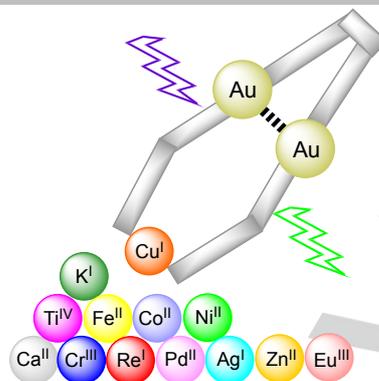
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Layout 1:

MINIREVIEW

Heterometallic complexes with unprecedented structures have been assembled by coordination of gold metalloligands to diverse metal ions or complexes. New types of helicates, coordination polymers, three-dimensional frameworks and stimuli-sensitive luminescent molecules are presented.

*Juan Gil-Rubio,* José Vicente****Page No. – Page No.****The Coordination and
Supramolecular Chemistry of Gold
Metalloligands**