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A New Dimension in Cyclic Coinage Metal Pyrazolates: Decoration with a Second Ring of Coinage Metals Supported by Inter-ring Metallophilic Interactions

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S *Supporting Information*

ABSTRACT: When pyrazolate ligands with thioether chelate arms are used in cyclic coinage metal pyrazolates $[Au(\mu\text{-pz})]_n$, the inner gold ring can be framed with an outer silver ring to give novel heterometallic double-crowned complexes $[AuAg(\mu\text{-L}^x)(BF_4)]_4$. They feature short intramolecular in-plane Ag−Au interactions, are stable as octanuclear species in solution, and show promising luminescence properties.

Pyrazoles are among the most popular building units in ligand design, and cyclic complexes of monovalent coinage metal ions represent benchmark systems in pyrazolate coordination chemistry.[1,2] These oligonuclear complexes may assume trimeric, tetrameric, or hexameric structures depending on the steric and electronic properties of the substituents on the pyrazole ring, with nine-membered macrocycles $[M(\mu\text{-pz})]_3$ being the most prominent and most common ones.[2,3] Such homoleptic pyrazolates of Cu(I), Ag(I), and Au(I) have attracted significant interest in recent years, not only because of their structural diversity but also because of their propensity to form tunable supramolecular aggregates and their interesting luminescence properties. Fluorinated pyrazolate ligands (e.g., with CF_3 groups in the 3- and 5-positions) have proven particularly valuable in this regard,[4] as they may form layered π-acid/π-base stacks with various arenes that give reversible luminescence responses.[5]

The photophysical properties of $[M(\mu\text{-pz})]_n$ metallacycles are strongly dependent on intramolecular and especially on intermolecular metallophilic d^{10}−d^{10} interactions.[6] The latter usually are encountered perpendicular to the metallacyclic plane, leading to face-to-face aggregates of the trinuclear units. This recently led to the targeted design of hexanuclear stacked pairs of $[M(\mu\text{-pz})]_3$ trimers based on linked bis(pyrazolato) ligands in either the staggered (**A**) or frontal (**B**) mode (Figure 1).[7] Here we introduce a new concept of extending the dimension of the cyclic coinage metal pyrazolates by surrounding the $[M(\mu\text{-pz})]_n$ core with a second peripheral ring of monovalent coinage metals *within* the metallacyclic plane. This is achieved through the synergetic effect of appropriate donor substituents appended at the 3- and 5-positions of the pyrazole heterocycle and in-plane metallophilic interactions.

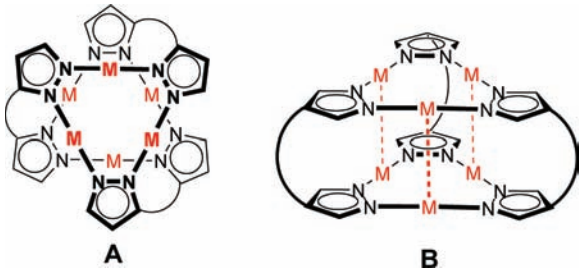

Figure 1. Stacked pyrazolate trimers in staggered (**A**) and frontal (**B**) modes based on linked bis(pyrazolato) ligands.

While multidentate compartmental pyrazole ligands featuring chelate arms are prominent scaffolds in biomimetic coordination chemistry and catalysis,[8] they have rarely been used for assembling cyclic Cu(I), Ag(I), and Au(I) complexes.[9−11] We reasoned that a single soft donor site such as a thioether provided within the R substituents (ligands HL^{a-c} in Figure 2) might bind additional monovalent coinage metal ions in the periphery of the metallacycle without disrupting the central $[M(\mu\text{-L}^x)]_n$ core.

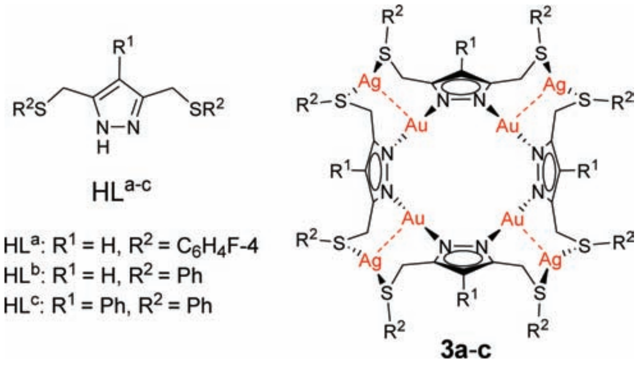

Figure 2. Pyrazolate ligands HL^{a-c} with appended thioether substituents and the new multinuclear coinage metal complexes **3a**−**c**.

The three ligands HL^{a-c} were chosen to evaluate the effect of different backbone substituents on either the pyrazole C^4 or the side-arm sulfur donor; they were synthesized in close analogy

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to previously reported procedures.[9,12] Treatment with an excess of Ag_2O cleanly gave the silver(I) complexes $[Ag(\mu\text{-}L^x)]_3$ (**1a**–**c**; Figure 3), and subsequent transmetalation of the isolated silver(I) complexes with $AuCl(SMe_2)$ led to the corresponding gold(I) species $[Au(\mu\text{-}L^x)]_3$ (**2a**–**c**; Figure 3). Single-crystal X-ray crystallography of **1a**, **1c**, **2a**, and **2c** revealed that all of these complexes adopt the common trinuclear pyrazolate-bridged motif $[M(\mu\text{-}L^x)]_3$ with the thioether side arms dangling [Figure 3 and Figures S10–S13 in the Supporting Information (SI)]. The central $[M(\mu\text{-}pz)]_3$ cores are almost planar, with Ag···Ag distances of 3.47–3.63 Å in **1a** and **1c** and Au···Au distances of 3.36–3.38 Å in **2a** and **2c**. Each of these values is longer than the sum of the van der Waals radii, and the intradimer d^{10}–d^{10} interactions are probably weak if present at all.[13,14] The NMR spectra of **2a**–**c** each showed a single set of signals typical for a planar $[Au(\mu\text{-}pz)]_3$ motif; in particular, only one narrow singlet at 4.01 ppm was observed for the hinge CH_2 groups. Furthermore, the H^{pz} singlet in **2a** and **2b** was shifted slightly downfield relative to the free ligand, while virtually no signal shifts were observed for the thioether side arms, confirming that they are not involved in metal coordination.

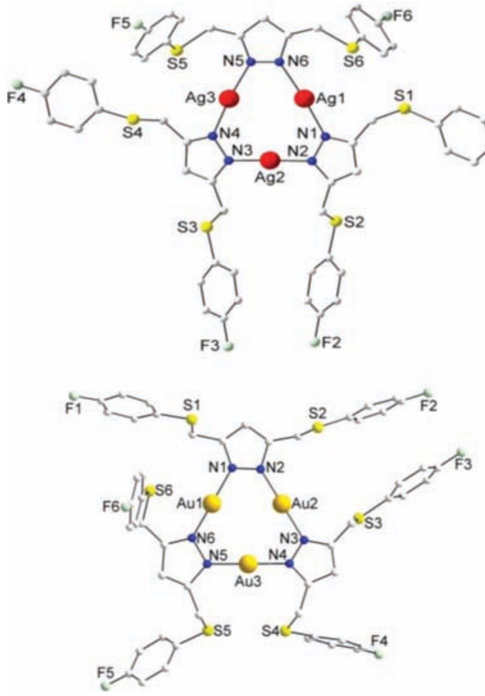

Figure 3. Molecular structures of (top) **1a** and (bottom) **2a**. H atoms have been omitted for clarity. For atom distances and bond angles, see the SI.

Pairs of dangling thioether substituents from adjacent pyrazolate ligands in **2a**–**c** appear to be well-positioned to bind additional coinage metal ions in close proximity to the inner gold(I) ions. Indeed, addition of stoichiometric amounts of $AgBF_4$ (3 equiv per $[Au(\mu\text{-}L^x)]_3$) in CH_2Cl_2 gave the sought-after heteromultimetallic complexes $[AuAg(\mu\text{-}L^x)(BF_4)]_n$ (**3a**–**c**). Single crystals could be obtained for all three derivatives, and X-ray crystallography in all cases revealed the formation of an oblate octanuclear species with a central $[Au(\mu\text{-}L^x)]_4$ core decorated by an outer ring of four silver(I) ions (Figure 4 and Figures S14–S16).

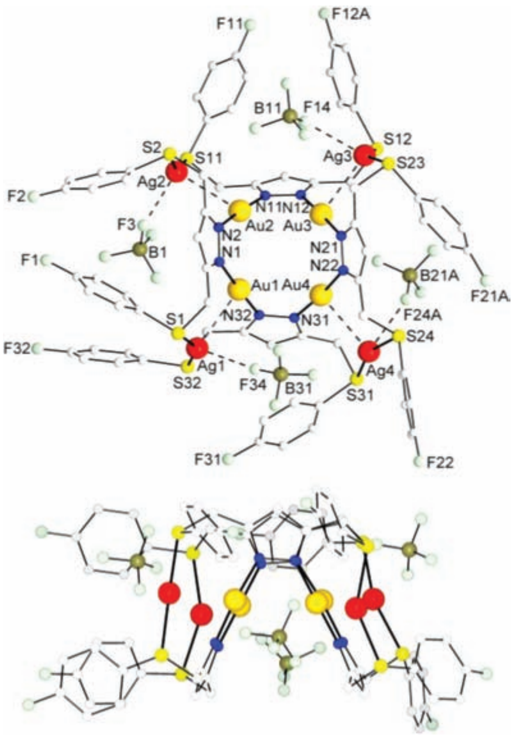

Figure 4. (top) Top view and (bottom) side view of the molecular structure of **3a**. H atoms have been omitted for clarity. For atom distances and bond angles, see the SI.

The four gold(I) ions in the inner circle are coordinated by two pyrazolate N atoms in the typical linear fashion; they are located in a square with Au···Au distances of 3.03–3.21 Å, which are slightly shorter than those in **2a**–**c** and in the range of weak intramolecular interactions.[13] In the saddlelike tetrameric structure, the pyrazolate groups are disposed alternately above and below the $\{Au_4\}$ square (see the bottom panel of Figure 4). Each silver(I) ion in the outer circle is held between the thioether functions of two adjacent pyrazole ligands, and all of the silver ions come to lie roughly within the $\{Au_4\}$ plane with short Ag···Au distances of 2.84–2.90 Å. These latter values are clearly shorter than the sum of the van der Waals radii[13] and indicate significant metallophilic d^{10}–d^{10} interactions.[14] The S–Ag–S angles in **3a**–**c** deviate from linearity and were found to be in the range 143.3–165.7°, since each silver atom is displaced toward one of the BF_4^- anions and also slightly displaced toward the gold atom. The anions are hosted between the flaps of the peripheral thioether substituents, alternately above and below the plane formed by the eight metal ions. The Ag–F distances of 2.48–2.67 Å suggest weak but non-negligible coordination in the solid state.

It is interesting to note that the present homometallic complexes $[Au(\mu\text{-}L^x)]_3$ all adopt trinuclear structures but transform to octametallic complexes with an inner tetrameric $[Au(\mu\text{-}L^x)]_4$ core upon addition of $AgBF_4$. Saddlelike tetrameric structures are less abundant than planar trimeric coinage metal pyrazolates but can be induced by large pyrazole substituents (e.g., *tert*-butyl).[2,3] The approximate (noncrystallographic) D_{2d} symmetry in **3a**–**c** is obviously imposed by symmetry constraints required for accommodation of the outer circle of metal ions: the alternate disposition of the thioether donors above and below that plane requires an even number of pyrazole ligands in the ring, since the S−Ag−S axes are roughly perpendicular to the metal plane.

A recent osmometry study of $[Ag(\mu\text{-}pz^{(CF_3)_2})]_3$ [$pz^{(CF_3)_2}$ = 3,5-bis(trifluoromethyl)pyrazolido] in toluene revealed the presence of monomeric, dimeric, trimeric, and hexameric species in a concentration-dependent dynamic equilibrium.[15] To characterize the identity of the new complexes **3a−c** in solution, some crystals were dissolved in dichloromethane-d_2 and investigated by NMR spectroscopy. Again, the ^{1}H NMR spectra of complexes **3a−c** at room temperature contained single sets of resonances, but here the side-arm signals were substantially shifted (Figure 5). As expected for a saddle-shaped tetrameric $[Au(\mu\text{-}L^x)]_4$ structure, the CH_2 groups yielded AB-type patterns.[11] One of the two diastereotopic protons appeared to be broad and at 0 °C split into an 8 Hz doublet, which could be assigned to $^3J_{H,Ag}$ coupling [see the SI for variable-temperature ^{1}H NMR and ^{109}Ag heteronuclear multiple bond correlation (HMBC) spectra]. The extraordinary large coupling constant may be explained by a H−C−S−Ag torsion angle that deviates on average only 10° from linearity.

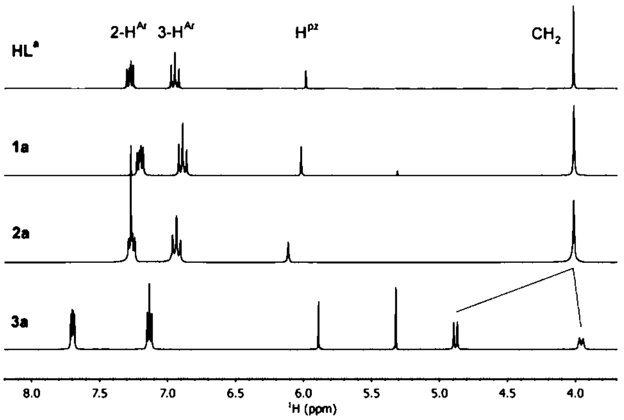

Figure 5. ^{1}H NMR spectra of HL^a, complexes **1a** and **2a** in chloroform-d and complex **3a** in dichloromethane-d_2.

Furthermore, the ^{19}F diffusion-ordered spectroscopy (DOSY) NMR spectrum of **3a** showed a decrease in the diffusion coefficient (5.5×10^{-10} m^2 s^{-1}) relative to **2a** (7.0×10^{-10} m^2 s^{-1}) (Figure S3), which is in agreement with the increase in molecular size. Both the Ar−F and BF_4^- signals displayed identical diffusion coefficients, indicating that the BF_4^- counterions are tightly bound in the complex. This was also confirmed by ^{1}H,^{19}F heteronuclear Overhauser effect spectroscopy (HOESY) (Figure S4), which yielded several short H···F distances that are in agreement with the crystal structure. The combined NMR data confirmed that the complexes $[AuAg(\mu\text{-}L^x)(BF_4)]_4$ (**3a−c**) remain intact in CD_2Cl_2 solution and retain the BF_4^- tightly associated with the octametallic core, explaining the good solubility in relatively nonpolar solvents.

The electrospray ionization (ESI) mass spectra of freshly prepared solutions of complexes **3a−c** in a 0.01:1 CH_2Cl_2/MeCN mixture showed peaks at m/z values corresponding to $[L_4Au_4Ag_xCl_{(x-1)}]^+$ (x = 2, 3);[16] Field-desorption (FD) mass spectrometry of **3a** showed a peak for $[L_4Au_4Ag_2(BF_4)]^+$. After some time, only signals for $[L_3Au_3]$ were discernible, indicating that the peripheral silver(I) ions are rather labile and tend to dissociate in coordinating solvents such as MeCN.[17]

With complexes **3a−c** in hand, preliminary investigations of the luminescence properties of these novel double-crowned coinage metal complexes were performed. First measurements were carried out in a frozen 2-methyl-THF glass matrix at 77 K. Under these experimental conditions, all of these complexes exhibited luminescence upon exposure to UV radiation (Figure 6 and Figures S5 and S6). The solid blue trace in Figure 6 is a representative (normalized) luminescence spectrum detected after excitation of compound **3b** at 280 nm. Vibrational fine structure with at least four members of a progression in an ~1600 cm^{-1} mode is easily discernible, and this observation appears to be consistent with coupling of the luminescence transition to breathing modes of the aromatic moieties present in the emissive complex.[18] Analogous vibrational progressions were observed for the other complexes investigated in this work, albeit in attenuated (i.e., spectrally less well resolved) form (Figures S5 and S6). Even though the exact nature of the electronic transition responsible for the luminescence is unclear at this point, the occurrence of the above-mentioned vibrational progression points toward a non-negligible contribution from ligand-localized excited states. Prior investigations of emissive cyclic coinage metal complexes are in line with this interpretation.[3,11c] The superposition of the excitation spectrum (dashed black line, detected at 415 nm) and the absorption spectrum (solid red line) of **3b** in the left part of Figure 6 strongly supports our notion that complex **3b** is indeed the emissive species in the glassy matrix.

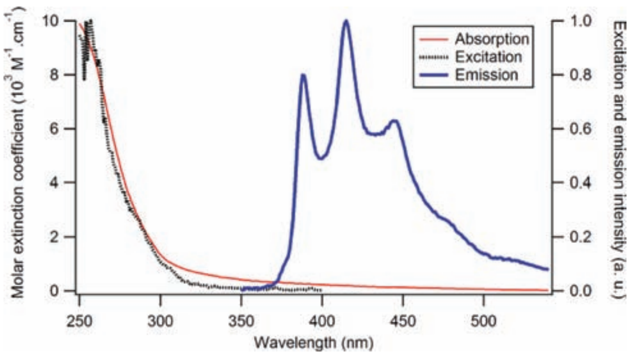

Figure 6. Photoluminescence spectra of **3b**. The emission spectrum (blue) was detected after excitation at 280 nm, while the excitation spectrum (dashed black) monitored the emission at 415 nm. The red line is the absorption spectrum of **3b** in 2-methyl-THF at room temperature.

In conclusion, the present work adds a new turn to coinage metal pyrazolate chemistry, since it demonstrates how the popular and common $[M(\mu\text{-}pz)]_n$ core can be framed by a further ring of coinage metal ions supported by in-plane closed-shell d^{10}−d^{10} interactions. It suggests further investigations to explore all of the homo- and heterometallic permutations of coinage metal ions (Cu$^+$, Ag$^+$, Au$^+$) in the inner and outer rings as well as the use of pyrazolate ligands that have multiple donor sites in their chelate arms for the targeted synthesis of high-nuclearity complexes. More detailed studies of the luminescence properties of the new complexes are on the way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and complete experimental details; selected NMR spectra; luminescence spectra of **3a**, **3c**, and the free ligands; and crystallographic details (CIF) and ORTEP plots for **1a**, **1c**, **2a**, **2c**, and **3a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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