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Structures and Photoluminescence of Coinage Metal(I) Phenylpyrazolato Trinuclear Complexes $[M(3,5\text{-}Et_2\text{-}4\text{-}Ph\text{-}pz)]_3$ and Arene Sandwich Complexes $\{[Ag(3,5\text{-}Et_2\text{-}4\text{-}Ph\text{-}pz)]_3\}_2(Ar)$ (Ar = Mesitylene and Toluene)

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The combination of 4-phenyl substituted pyrazolate ligand, **LEt(Ph)H** (4-phenyl-3,5-diethyl-1-pyrazole) with coinage metal(I) salts gave cyclic structures, **$[CuLEt(Ph)]_3$**, **$\{[AgLEt(Ph)]_3\}_2$**, and **$[AuLEt(Ph)]_3$**. Both **$[CuLEt(Ph)]_3$** and **$[AuLEt(Ph)]_3$** were trinuclear, while **$\{[AgLEt(Ph)]_3\}_2$** was hexanuclear with two intermolecular argentophilic interactions. **$\{[AgLEt(Ph)]_3\}_2$** formed arene-sandwiched, π acid/base complexes, **$\{[AgLEt(Ph)]_3\}_2$(mesitylene)** and **$\{[AgLEt(Ph)]_3\}_2$(toluene)**. Photoluminescent spectra of the Cu(I) and Ag(I) complexes were dominated by closed shell d^{10}-d^{10} M···M interactions, whereas those of the Au(I) complex exhibited ligand-based emissions.

Keywords: Coinage metal(I) complex | Pyrazole | π-acid/base

Cyclic trinuclear complexes of monovalent coinage metal ions are widely studied because of their propensity for metallophilic interactions,[1] supramolecular assembly,[2] metal(I)···metal(I) bonding interactions,[3] unique luminescent properties,[2a,2b,2d,3b,3f] chemosensing ability[4] and π-acid/base interactions.[5]

We have embarked on a systematic study of the steric and electronic factors that influence the coordination structures of pyrazolato d^{10} metal ions, *viz* $\{M(pz^*)\}_n$ (M = Cu(I), Ag(I), and Au(I); $n = 3$, 4, or 6). The aromatic pyrazole ligand with two adjacent nitrogen atoms can form a variety of coordination structures.[6] Tri- and tetranuclear complexes of metal(I) ions are obtained depending on the metal(I) ion and substituents on the pyrazolate ring.[7] We recently reported 4-aryl substituted pyrazolate ligands **L1(H)H** (= 3,5-iPr$_2$pzH = 3,5-diisopropyl-1-pyrazole), 4-phenyl-3,5-diisopropyl-1-pyrazole (**L1(Ph)H**) and 4-naphthyl-3,5-diisopropyl-1-pyrazole (**L1(Naph)H**) and their silver(I) and gold(I) complexes **$[AgL1(Ph)]_3$**, **$[AuL1(Ph)]_3$**, **$[AgL1(Naph)]_3$**, and **$[AuL1(Naph)]_3$**.[8] However, these aryl-substituted ligands were too bulky to permit solid-state metal···metal intermolecular interactions, and the photoluminescence that is often associated with argentophilic and aurophilic bonds. In the present work we have therefore reduced the bulkiness of the isopropyl substituents to ethyl groups at the 3- and 5-positions and investigated the spectroscopic properties of the corresponding coinage metal(I) complexes.

The same synthetic method[8] was employed to obtain this new phenyl substituted pyrazole. Suzuki-Miyaura coupling of **LEt(Br)Ts** and 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in DME/H_2O with $Pd(PPh_3)_4$ as the catalyst provided the desired compound in 36% yield (See supporting information).[9] Single crystal X-ray crystallography (Figure S1 and Table S1) revealed intermolecular hydrogen bonding interactions generating a zigzag type chain structure. The average dihedral angle between phenyl plane and pyrazole plane was 38.8 deg indicating significantly decreased steric hindrance relative to **L1(Ph)H** (61.14(5) deg).[8]

This ligand was reacted with coinage metal(I) sources to yield **$[CuLEt(Ph)]_3$**, **$\{[AgLEt(Ph)]_3\}_2$**, and **$[AuLEt(Ph)]_3$** (Scheme 1). Single crystal X-ray crystallography revealed cyclic polynuclear solid-state structures (Figures 1 and S2–S4, and Tables S1–S2). A comparison of the average intramolecular M···M interactions and average M–N bond distances (av. Cu···Cu, 3.2295(5) Å and av. Cu–N, 1.856(1) Å in **$[CuLEt(Ph)]_3$** (Figure 1 left and Figure S2), av. Ag···Ag, 3.4443(9) Å and av. Ag–N, 2.069(3) Å in **$\{[AgLEt(Ph)]_3\}_2$** (Figure 1 center and Figure S3), and av. Au···Au, 3.3677(5) Å and av. Au–N, 1.997(2) Å) in **$[AuLEt(Ph)]_3$** (Figure 1 right and Figure S4) indicated interesting trends in M···M interactions (Cu···Cu < Au···Au < Ag···Ag) and M–N distances (Cu–N < Au–N < Ag–N) resulting from

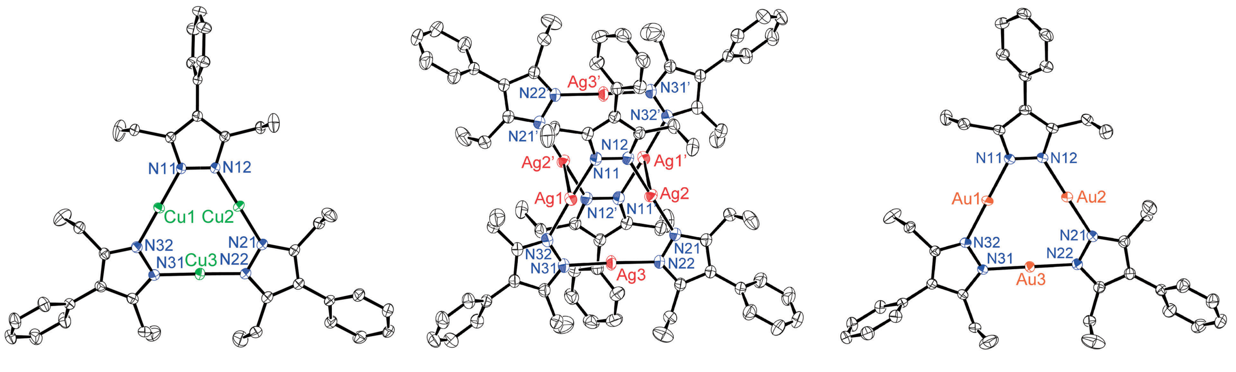

Figure 1. Molecular structures of **$[LEt(Ph)Cu]_3$** (left), **$\{[LEt(Ph)Ag]_3\}_2$** without solvent molecules (center), **$[LEt(Ph)Au]_3$** (right) showing 50% displacement ellipsoids and the atom labeling scheme for metal and N atoms. Hydrogen atoms are omitted for clarity.

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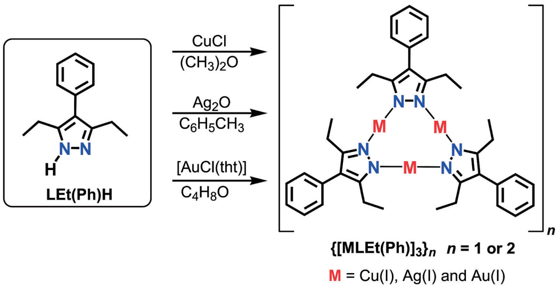

Scheme 1. Preparation of complexes.

relativistic effects.[10] These trends have been previously reported by Schmidbaur[11] and also by us.[7b,12] The related copper(I) complex, **[CuLMe(Ph)]$_3$**, where LMe(Ph)H = 4-phenyl-3,5-methyl-1-pyrazole, was structurally characterized as a trinuclear complex with relatively long Cu···Cu separations of 3.494(1) and 3.671(1) Å.[13]

The intramolecular M···M interactions were almost twice the Bondi van der Waals radius, Cu: 2.80 Å, Ag: 3.44 Å, and Au: 3.32 Å,[14] consistent with only very weak metallophilic intramolecular interactions. The bond angles of N–M–N were close to 180 deg, indicating little steric deformation of the almost linear coordination mode. Packing diagrams for **[MLEt(Ph)]** complexes are shown in Figures S2–S4. A pseudo dimeric structure was observed for **{[AgLEt(Ph)]$_3$}$_2$** with an Ag–Ag distance of 2.9690(6) Å clearly shorter than twice the Bondi's van der Waals radii for Ag of 3.44 Å.[14] By comparison, the shortest M···M distance in **[AgL1(Ph)]$_3$** is 6.0632(5) Å.[8] This difference is presumably due to the reduced bulkiness of the substituents, which also results in smaller dihedral angles between the phenyl and pyrazole planes of 45.8, 48.7, and 62.0 deg in **{[AgLEt(Ph)]$_3$}$_2$** compared to 56.5, 88.7, and 89.1 deg in **[AgL1(Ph)]$_3$**. The solid-state structures of the corresponding gold and copper complexes possessed intermolecular M···M distances greater than twice the Bondi's van der Waals radii.[14] The cyclic trinuclear structures in **[CuLEt(Ph)]** and **[AuLEt(Ph)]** were slipped relative to one another to give an overall stepwise structure, as was also observed for **[AgL1(Ph)]$_3$** and **[AuL1(Ph)]$_3$**.[8]

The ^{1}H- and ^{13}C NMR spectra of the polynuclear coinage(I) complexes were quite different from those of the ligand, indicating that the cyclic trinuclear coordination was retained in solution (Table S3). All electronic absorption bands measured in both solution (cyclohexane) and the solid-state (nujol) were very broad, mainly due to overlapping π-π* transition bands associated with the phenyl substituents and the pyrazolyl rings (Table S4 and Figure S5). Higher energy absorption bands due to metal to ligand charge transfer (MLCT) were observed on complexation in the order Cu (246.0 nm) < Au (223.5 nm) < Ag (206.0 nm). This trend was previously observed for other series of pyrazolato complexes.[7b,8]

Coordination of the ligand **LEt(Ph)H** to the metal caused a shift in the C=N IR stretching vibration from 1519 cm^{-1} to ~1542 cm^{-1} (Table S5). The far–IR and FT–Raman spectra of the pyrazole ligand and three complexes are shown in Figure S6. The M–N stretching vibrations would be expected in the 550 cm^{-1} to 450 cm^{-1} region[7,8,15] and were observed at ~483 cm^{-1} for **[CuLEt(Ph)]$_3$**, ~449 cm^{-1} for **{[AgLEt(Ph)]$_3$}$_2$** and ~459 cm^{-1} for **[AuLEt(Ph)]$_3$**, which is consistent with the M–N bond lengths discussed above: Cu–N < Au–N < Ag–N.

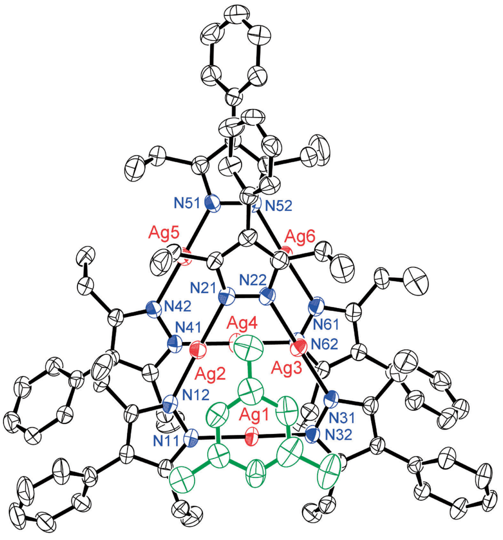

Figure 2. Molecular structure of **{[LEt(Ph)Ag]$_3$}$_2$(mesitylene)** showing 50% displacement ellipsoids and the atom labeling for Ag and N atoms. The incorporated mesitylene molecule is colored green. Hydrogen atoms are omitted for clarity.

Interestingly, when the recrystallization of **{[AgLEt(Ph)]$_3$}$_2$** was carried out in mixed solvents of CH_2Cl_2 and mesitylene or toluene, the arene-sandwiched complexes **{[AgLEt(Ph)]$_3$}$_2$(Ar)**, Ar = mesitylene and toluene were obtained (Figures 2, S7 and S8). Packing diagrams for both complexes **{[AgLEt(Ph)]$_3$}$_2$(Ar)** indicated slipped, stepwise structures different from the hexanuclear, irregular pattern of **{[AgLEt(Ph)]$_3$}$_2$**. Consequently, Ag···Ag interactions were longer at 3.2556(7) Å (Ag2···Ag4) in **{[AgLEt(Ph)]$_3$}$_2$(mesitylene)** and 3.2108(9) Å (Ag3···Ag4) in **{[AgLEt(Ph)]$_3$}$_2$(toluene)**. Silver(I) trinuclear pyrazolato complexes with incorporated organic molecules have been previously reported,[5a,5c,5d,5f–5g,5j] however, these examples generally had strongly electron deficient ligands to enhance the π-acid/base interaction. We propose that the phenyl substituted pyrazole ligand creates a nano-space, or nano-pocket, for the planar aromatic. Arene-sandwiched formation was only observed for **{[AgLEt(Ph)]$_3$}$_2$**, presumably due to appropriate dimensions of the micro-cavity and/or acidity for this complex. These arene guest molecules are tightly incorporated in the solid state and could not be removed by vacuum at room temperature (Figures S9–S10).

Photoluminescence spectra from the powdered samples of the ligand, three coinage metal(I) complexes and arene-sandwiched Ag(I) complexes are shown in Figures 3, S11–S16. Spectra were acquired at variable excitation wavelengths and at three different temperatures (83, 173, and 298 K). Phenyl group based emissions were observed for **LEt(Ph)H** (~320 nm at 280 nm excitation) and vibrational fine structure was observed at lower temperatures without any changes in intensity (Figure S11). Lower energy emissions at room temperature were observed at 684.5 nm (λ_{ex} 320 nm) for **[CuLEt(Ph)]$_3$**, at 699 nm (λ_{ex} 300 nm) for **{[AgLEt(Ph)]$_3$}$_2$**, and at 685.0 nm for **[AuLEt(Ph)]$_3$**. These lower energy emissions are attributed to metal-based phosphorescence arising from closed shell d^{10}-d^{10}

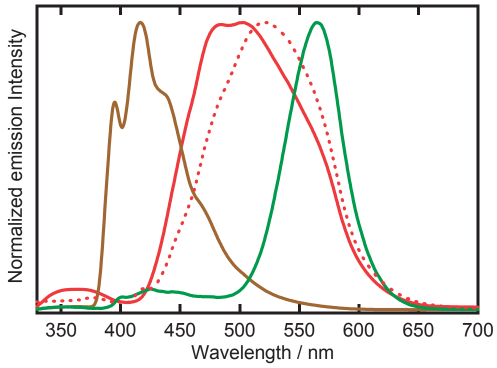

Figure 3. Solid-state photoluminescence spectra of **[CuLEt(Ph)]$_3$** (green, λ_{ex} 320 nm, **{[AgLEt(Ph)]$_3$}$_2$** (red, λ_{ex} 300 nm), **[AuLEt(Ph)]$_3$** (brown, λ_{ex} 300 nm), and **{[AgLEt(Ph)]$_3$}$_2$(mesitylene)** (red dotted, λ_{ex} 290 nm) at low temperature (83 K).

M···M interactions.[5c,7b,8,16] The same unstructured, broad emission for **[CuLMe(Ph)]$_3$** was observed at 630 nm with a life-time of 18.2 µs. On cooling **{[AgLEt(Ph)]$_3$}$_2$** to lower temperature, the intensity of emission become stronger with almost no change in wavelength. This behavior is different from that of **[AgL1(Ph)]$_3$** which does not possess solid-state intermolecular Ag···Ag interactions. On cooling **[AuLEt(Ph)]$_3$** to lower temperature, the maximum peak with vibrational fine-structure was more intense and shifted to higher energy, 417.0 nm. This is consistent with its overall stepwise structure, which was also observed for **[AgL1(Ph)]$_3$** and **[AuL1(Ph)]$_3$**.[8] By contrast, the emission spectrum of **[CuLEt(Ph)]$_3$**, which has the same stepwise structure, grew in intensity at lower temperatures, however there was no change in wavelength. This observation has been reported for CF_3 substituted pyrazolato Cu(I) complexes (Table S6). The emission spectra of arene-sandwiched **{[LEt(Ph)Ag]$_3$}$_2$(Ar)** complexes exhibited one broad band at 522.5 nm (mesitylene) and 529.0 nm (toluene), distinct from the two bands at 485.0 and 502.5 nm in **{[LEt(Ph)Ag]$_3$}$_2$**.

In summary, we have prepared a new 4-phenyl substituted pyrazole ligand and the corresponding coinage metal(I) complexes. Solid-state coordination environments were different from that of previously reported analogues **[ML1(Ph)]$_3$** (M = Ag and Au) and did possess intermetallic interactions for **{[AgLEt(Ph)]$_3$}$_2$**. Preliminary photoluminescent spectra obtained for the Cu(I) and Ag(I) complexes were dominated by closed shell d^{10}-d^{10} M···M interactions, whereas those of the Au(I) complex exhibited ligand-based emissions, as observed for **[ML1(Ph)]$_3$**. We are currently investigating the preparation of highly luminescent materials containing strong M···M intermolecular interactions and making use of the solid-state nano-pocket created by this phenyl substituted ligand.

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Dedicated to Professor Laurence Que, Jr. on the occasion of his 70th birthday.

Supporting Information is available on https://doi.org/10.1246/cl.200081.

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