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Toluene-Sandwiched Trinuclear Copper(I) and Silver(I) Triazolates and Phosphine Adducts of Dinuclear Copper(I) and Silver(I) Triazolates

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Cu^I and Ag^I complexes of the fluorinated triazolate ligand [3,5-(C$_3$F$_7$)$_2$Tz]$^-$ have been synthesized using the corresponding metal(I) oxides and the triazole. They form π-acid/base adducts with toluene, leading to **[Tol][M$_3$][Tol]** (**[Tol]** = toluene; **[M$_3$]** = {[3,5-(C$_3$F$_7$)$_2$Tz]Cu}$_3$ or {[3,5-(C$_3$F$_7$)$_2$Tz]Ag}$_3$) type structures. Packing diagrams show the presence of extended chains of the type **{[Tol][M$_3$][Tol]}$_\infty$**, but the intertoluene ring distances are too long for significant π-arene/π-arene contacts. These copper and silver triazolates react with PPh$_3$ (at a 1:1 metal ion/P molar ratio), leading to dinuclear {[3,5-(C$_3$F$_7$)$_2$Tz]Cu(PPh$_3$)}$_2$ and {[3,5-(C$_3$F$_7$)$_2$Tz]Ag(PPh$_3$)}$_2$. They feature a six-membered Cu(μ-N−N)$_2$Cu or Ag(μ-N−N)$_2$Ag core with a boat conformation.

Pyrazolate complexes of Cu^I and Ag^I have attracted considerable interest in recent years.[1] Depending on the reaction conditions and the pyrazolyl ring substituents, they form various pyrazolate ligand-bridged aggregates ranging from trimers (see Figure 1), tetramers, hexamers to polymers and supramolecular assemblies (e.g., dimer of trimers or chains of trimers resulting from unsupported metallophilic bonding between d^{10} metal atoms).[1–9] Closely related 1,2,4-triazolates also show interesting coordination chemistry.[10] However, there are key differences as well. For example, the third N atom of triazolate ligands often serves as a donor site, leading to more complicated metal triazolate aggregates and network structures.[10–14] Triazolyl ligands (due to the presence of an extra N atom in place of CH) are also somewhat weaker donors relative to the analogous pyrazolates.[15]

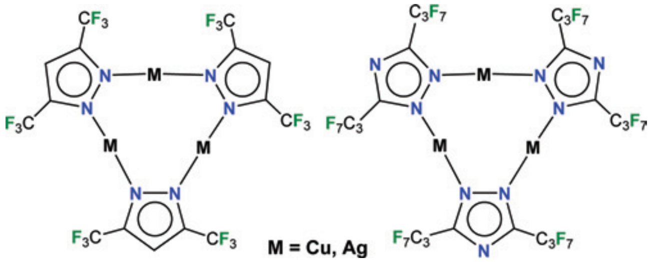

Figure 1. Copper and silver complexes of fluorinated pyrazolates and triazolates, {[3,5-(CF$_3$)$_2$Pz]M}$_3$ and {[3,5-(C$_3$F$_7$)$_2$Tz]M}$_3$ (M = Cu, Ag), showing the trinuclear structure.

Our work in this area primarily concerns the chemistry of coinage metal complexes supported by halogenated ligands like *fluorinated pyrazolates* and led to several interesting findings including supramolecular assemblies of {[3-(R),5-(R′)Pz]M}$_3$ (R, R′ = various alkyl, aryl groups; M = Cu, Ag) with metallophilic bonds,[4,6–8,16,17] tunable light emissions of {[3-(R),5-(R′)Pz]M}$_3$,[6,7,16] π-acid/base chemistry of {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$ and {[3,5-(CF$_3$)$_2$Pz]Au}$_3$ with

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arenes,[7,8,18] and the isolation of copper and silver pyrazolate based metallacycles with *para*-cyclophane skeletons.[19] These results and the interesting findings on coinage metal complexes of the nonfluorinated 1,2,4-triazolates swayed us to explore related triazolate systems bearing fluorinated substituents. Here we describe the synthesis of Cu^I and Ag^I complexes of the 3,5-bis(heptafluoropropyl)triazolate ligand, $[3,5\text{-}(C_3F_7)_2Tz]^-$ (Figure 1) and their π-acid/base adducts with toluene and reactivity with PPh_3. Recently, a metal−organic framework based on a fluorinated triazolate, $[Ag_2\{[3,5\text{-}(CF_3)_2Tz]_6Ag_4\}]_n$, appeared in the literature.[14] It is the only report that describes the isolation of a Cu^I, Ag^I, or Au^I complex involving *fluorinated triazolates* to our knowledge.

Copper(I) and silver(I) triazolato derivatives of $[3,5\text{-}(C_3F_7)_2Tz]^-$ are readily synthesized by the reaction of 3,5-bis(heptafluoropropyl)triazole with Cu_2O and Ag_2O, respectively, in toluene containing a small amount of acetonitrile. We have used a similar route quite successfully in the synthesis of a range of copper and silver pyrazolates.[4,6,8,17] X-ray analyses of the crystals obtained from toluene show the presence of two molecules of toluene (**[Tol]**) for each trinuclear $\{[3,5\text{-}(C_3F_7)_2Tz]Cu\}_3$ (**[Cu$_3$]**) and $\{[3,5\text{-}(C_3F_7)_2Tz]Ag\}_3$ (**[Ag$_3$]**) unit forming sandwiched molecules of the type **[Tol][M$_3$][Tol]** (Figure 2). The closest M···C(tol) distances to the toluenes on the opposite faces of **[M$_3$]** are at 2.87 and 2.91 Å for the copper adduct and 2.84 and 2.92 Å for the silver adduct. These distances are significantly smaller than the van der Waals contact distance of C and Cu (3.10 Å) or C and Ag (3.42 Å). The **[Cu$_3$]** and **[Tol]** centroids of **[Tol][Cu$_3$][Tol]** are separated by 3.27 and 3.42 Å, while the centroid-to-centroid distances observed in **[Tol][Ag$_3$][Tol]** are 3.20 and 3.34 Å. These closest M···C(tol) and **[Tol]** to **[M$_3$]** distances, taken together with a larger covalent radius of Ag^I, point to a much tighter π-acid/base interaction in the silver adduct.

Packing diagrams show that these **[Tol][M$_3$][Tol]** units crystallize, forming extended, somewhat slanted, chains of the general formula **{[Tol][M$_3$][Tol]}$_\infty$** (Figure 3), but closest C···C distance between adjacent toluenes is about 3.45 Å (for both systems), which is slightly longer than the van der Waals contact distance of two C atoms (3.40 Å). Several groups have reported the isolation of a variety of π-acid/base adducts using trinuclear d^{10} metal systems (mainly based on Hg^{II}, Au^I, and Ag^I).[8,18,20–24] A review of these structures shows that **[Ar][M′$_3$][Ar]** or **{[Ar][M′$_3$][Ar]}$_\infty$** type aggregates (**[Ar]** = arene) are quite rare while the **{[M′$_3$][Ar]}$_\infty$** pattern is the most common. The silver pyrazolate $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ (**[Ag″$_3$]**) is known to form **[Ar][Ag″$_3$][Ar]** type adducts with benzene and **{[Ar][Ag″$_3$][Ar]}$_\infty$** type aggregates with mesitylene.[18] Sandwiched systems like **[Tol][Cu$_3$][Tol]**, which involve *trinuclear copper* complexes, are unprecedented to our knowledge.

The formation of π-acid/base adduct **[Tol][Ag$_3$][Tol]** is a sign of the high π acidity of **[Ag$_3$]**, which is not surprising based on computational data[7,15] and our experience with the related pyrazolates.[8,18] However, the isolation of **[Tol][Cu$_3$][Tol]**, despite the presence of bulky C_3F_7 substituents on triazolates that could hinder good face-to-face contacts, is notable because **[Cu$_3$]** is less acidic compared to the

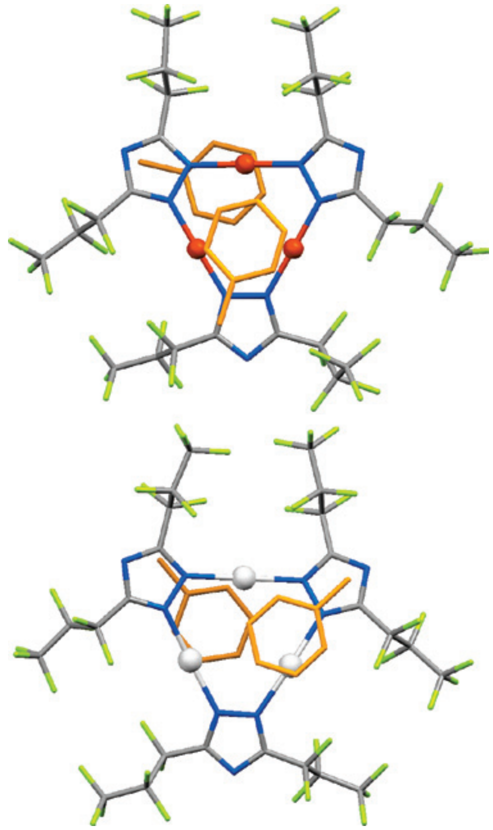

Figure 2. Molecular structures of $[(\text{toluene})\{[3,5\text{-}(C_3F_7)_2Tz]Cu\}_3(\text{toluene})]$, **[Tol][Cu$_3$][Tol]** (top), and $[(\text{toluene})\{[3,5\text{-}(C_3F_7)_2Tz]Ag\}_3(\text{toluene})]$, **[Tol][Ag$_3$][Tol]** (bottom). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg.): Cu1−N8 1.878(8), Cu1−N1 1.887(7), Cu2−N2 1.859(8), Cu2−N4 1.862(8), Cu3−N5 1.871(8), Cu3−N7 1.877(8), N8−Cu1−N1 163.5(3), N2−Cu2−N4 176.7(4), N5−Cu3−N7 173.2(4); Ag1−N8 2.130(3), Ag1−N1 2.139(3), Ag2−N4 2.102(3), Ag2−N2 2.110(3), Ag3−N7 2.116(3), Ag3−N5 2.117(3), N8−Ag1−N1 161.50(12), N4−Ag2−N2 173.23(12), N7−Ag3−N5 174.07(12).

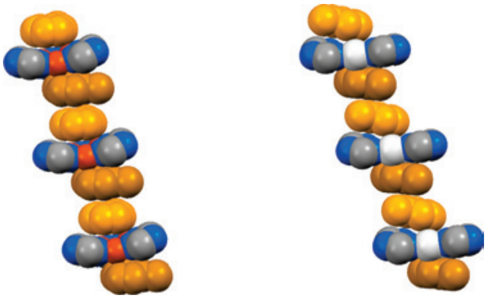

Figure 3. Extended structures of **[Tol][Cu$_3$][Tol** (left) and **[Tol][Ag$_3$][Tol]** (right). H atoms and C_3F_7 groups have been omitted for clarity.

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analogous **[Ag_3]**. Preliminary studies show that it is also possible to isolate compounds like **[Cu_3]**·2THF with Cu−THF bonds (see the Supporting Information).

The **[Cu_3]** and **[Ag_3]** units feature distorted, nonplanar M_3N_6 cores with N−Cu−N and N−Ag−N angles ranging from 163.5(3) to 176.7(7)° and from 161.50(12) to 174.07(12)°, respectively. The copper and silver centers with the smallest angles bend toward the toluene on one of the faces, leading to the closest Cu···C(tol) and Ag···C(tol) contacts. Thus, it appears that the distortions from M_3N_6 ring planarity are caused not only by the likely steric effects between C_3F_7 groups on adjacent triazolyl rings but also by M···arene attractions.

A few structurally characterized copper(I) (e.g., $\{[Tz]Cu\}_n$,[13] $\{[3,5\text{-}(CH_3)_2Tz]Cu\}_n$,[12] and $\{[3,5\text{-}(C_3H_7)_2Tz]Cu\}_n$[12]) and silver(I) triazolates (e.g., $\{[Tz]Ag\}]_n$,[13] ($[Ag_2\{[3,5\text{-}(CF_3)_2Tz]_6\text{-}Ag_4\}]_n$,[14] $[Ag_3\{[3,5\text{-}(Ph)_2Tz]_6Ag_5\}(BF_4)_2]_n$[11]) are in the literature. However, they have various types of network structures, primarily as a result of the involvement of the third triazolyl N atom in metal ion coordination. Thus, a comparison of metric parameters between trinuclear **[Cu_3]** and **[Ag_3]** and other triazolates in the literature is not that meaningful. For example, $\{[3,5\text{-}(C_3H_7)_2Tz]Cu\}_n$, which is the nonfluorinated relative of $\{[3,5\text{-}(C_3F_7)_2Tz]Cu\}_3$, forms a 4.12^2 net with three-coordinate copper sites.[12] The Cu−N bond distances of $\{[3,5\text{-}(C_3H_7)_2Tz]Cu\}_n$ [in the range 1.963(3)−1.973(3) Å] are closer to those seen for $\{[3,5\text{-}(C_3F_7)_2Tz]Cu(PPh_3)\}_2$ (see below) than those of $\{[3,5\text{-}(C_3F_7)_2Tz]Cu\}_3$.

We have also examined the chemistry between **[Cu_3]** and **[Ag_3]** with PPh_3. Treatment of **[Cu_3]** with triphenylphosphine at a 1:1 Cu/P molar ratio led to a dinuclear species, $\{[3,5\text{-}(C_3F_7)_2Tz]Cu(PPh_3)\}_2$, in excellent yield. The related silver adduct **[Ag_3]** also exhibits similar chemistry, forming $\{[3,5\text{-}(C_3F_7)_2Tz]Ag(PPh_3)\}_2$. X-ray data show that these complexes have trigonal-planar metal sites (Figure 4). Both adducts also feature a six-membered M(μ-N−N)$_2$M core with a boat conformation. The intramolecular Cu···Cu and Ag···Ag distances are 3.207 and 3.367 Å, respectively. The Ag···Ag distance is within the van der Waals contact distance of two Ag atoms (3.44 Å). The average Cu−P and Ag−P distances of $\{[3,5\text{-}(C_3F_7)_2Tz]Cu(PPh_3)\}_2$ [2.1802(11) Å] and $\{[3,5\text{-}(C_3F_7)_2Tz]Ag(PPh_3)\}_2$ [2.3502(13) Å] are slightly shorter than the corresponding distances in $[HB(3,5\text{-}(CF_3)_2Pz)_3]M(PPh_3)$ [2.219(1) Å for M = Cu and 2.376(1) Å for M = Ag].[25] This is not unusual because the latter features four-coordinate metal sites.

In summary, this paper describes the syntheses of trinuclear copper and silver complexes of fluorinated triazolyl ligands. They show interesting π-acid/base chemistry with π bases like toluene, leading to sandwich molecules. Dinuclear copper and silver adducts can be obtained using trinuclear precursors and PPh_3. We are currently investigating the effect of various substituents and different arenes on the π-acid/base adduct structures. Photophysical properties of coinage metal triazolates are also of interest.

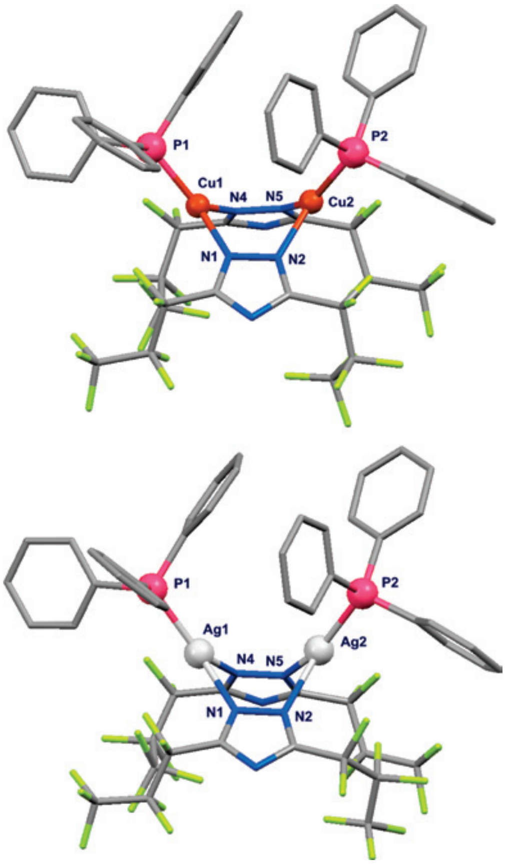

Figure 4. Molecular structures of $\{[3,5\text{-}(C_3F_7)_2Tz]Cu(PPh_3)\}_2$ (top) and $\{[3,5\text{-}(C_3F_7)_2Tz]Ag(PPh_3)\}_2$ (bottom). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg.): Cu1−N1 2.005(4), Cu1−N4 2.013(4), Cu1−P1 2.1765(11), Cu2−N5 1.982(4), Cu2−N2 2.046(4), Cu2−P2 2.1840(12), N1−Cu1−N4 100.63(15), N1−Cu1−P1 131.08(11), N4−Cu1−P1 126.63(12), N5−Cu2−N2 98.02(17), N5−Cu2−P2 141.21(13), N2−Cu2−P2 120.02(12); Ag1−N1 2.255(4), Ag1−N4 2.278(4), Ag1−P1 2.3502(13), Ag1···Ag2 3.3674(5), Ag2−N2 2.195(4), Ag2−P2 2.3503(13), Ag2−N5 2.402(5), N1−Ag1−N4 95.33(15), N1−Ag1−P1 134.22(12), N4−Ag1−P1 129.50(11), N2−Ag2−P2 152.08(12), N2−Ag2−N5 92.15(16), P2−Ag2−N5 115.23(12).

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Supporting Information Available: X-ray crystallographic data in CIF format for **[Tol][Cu_3][Tol]**, **[Tol][Ag_3][Tol]**, and $\{[3,5\text{-}(C_3F_7)_2Tz]M(PPh_3)\}_2$ (M = Cu, Ag) and experimental details for the synthesis of metal complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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