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Blue Phosphors of Dinuclear and Mononuclear Copper(I) and Silver(I) Complexes of 3,5-Bis(trifluoromethyl)pyrazolate and the Related Bis(pyrazolyl)borate

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The synthesis, structure, and photoluminescence properties are described for the three-coordinate mononuclear and dinuclear complexes $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]M(2,4,6\text{-collidine})$, $\mathbf{M_1}$, and $\{[3,5\text{-}(CF_3)_2Pz]M(2,4,6\text{-collidine})\}_2$, $\mathbf{M_2}$, respectively (M = Cu; Ag). The solids exhibit bright blue phosphorescence, at room temperature for the copper compounds and at 77 K for all compounds. $\mathbf{Ag_1}$, $\mathbf{Cu_1}$, and $\mathbf{Cu_2}$ exhibit blue pyrazole-based structured emissions with short phosphorescence lifetimes, 10^1–10^2 μs, due to an internal heavy-metal effect. Meanwhile, $\mathbf{Ag_2}$ exhibits curious multiple excitation-dependent emissions.

Pyrazolate ligands play an important role in coinage metal chemistry. They usually coordinate to metal ions like Cu(I), Ag(I), and Au(I) in *exo*-bidentate fashion to yield polynuclear complexes.[1] Depending on the reaction conditions and the substituents on the pyrazolyl moiety, these coinage metal pyrazolates adopt structures ranging from trimers, tetramers, hexamers, to polymers. The pyrazole ring also provides ligand assistance for closed-shell d^{10} metal centers to be in close proximity. Bonding metallophilic interactions[2] and photophysical properties[3] of such species are of significant current interest. Few luminescence studies of trinuclear Au(I) pyrazolates have appeared in the literature[4] while virtually nothing is known about the related dinuclear or mononuclear species, or the corresponding Cu and Ag analogues.

Our current efforts involve structural and spectroscopic studies of coinage metal complexes featuring fluorinated pyrazolyl ligands.[5] The first reported example of this type concerns the trinuclear Au(I) adduct $\{[3,5\text{-}(CF_3)_2Pz]Au\}_3$.[6] Syntheses of the related copper(I) and silver(I) complexes $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ were reported recently by Dias et al.[7] A mixed valent copper complex $[3,5\text{-}(CF_3)_2Pz]_5Cu(II)_2Cu(I)$ is also known.[8]

We have discovered that trinuclear, dinuclear, and mononuclear complexes of monovalent coinage metals with fluorinated pyrazolate ligands exhibit very interesting luminescence properties that render them attractive candidates for molecular light-emitting devices (MOLEDs)[9] and solvatochromic sensors.[10] The presence of a closed-shell transition metal may lead to enhanced metal-based[10] or ligand-based phosphorescence,[11] which is desired for MOLEDs.[12] Fluorination increases the volatility, thus facilitating thin-film fabrication, and leads to improved thermal and oxidative stability and reduced concentration quenching of the luminescence.[5,12b,13] Here we report the synthesis, structure, and photophysical properties of the dinuclear and mononuclear complexes $\{[3,5\text{-}(CF_3)_2Pz]M(2,4,6\text{-collidine})\}_2$, $\mathbf{M_2}$, and $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]M(2,4,6\text{-collidine})$, $\mathbf{M_1}$, where M = Cu or Ag.

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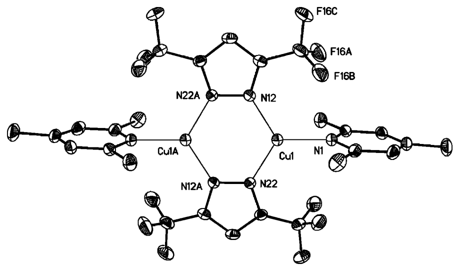

Figure 1. Molecular structure of **Cu$_2$** (only one of the two molecules in the unit cell is shown here). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−N(12) 1.974(2), Cu(1)−N(22) 1.983(2), Cu(1)−N(1) 2.002(2), N(12)−Cu(1)−N(22) 118.86(9), N(12)−Cu(1)−N(1) 121.66(10), N(22)−Cu(1)−N(1) 119.40(9).

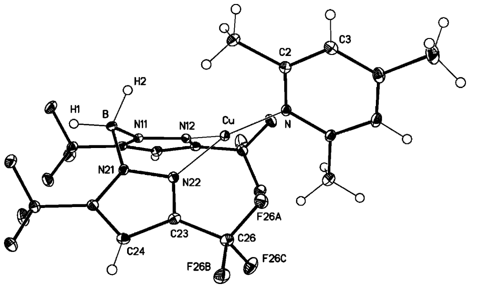

Figure 2. Molecular structures of **Cu$_1$**. Selected bond lengths (Å) and angles (deg): Cu−N 1.9400(17), Cu−N(12) 1.9734(16), Cu−N(22) 2.0830(15), N(11)−B 1.575(3), N(21)−B 1.569(3) N−Cu−N(12) 147.10(7), N−Cu−N(22) 117.95(6), N(12)−Cu−N(22) 94.88(7), N(21)−B−N(11) 107.69(16).

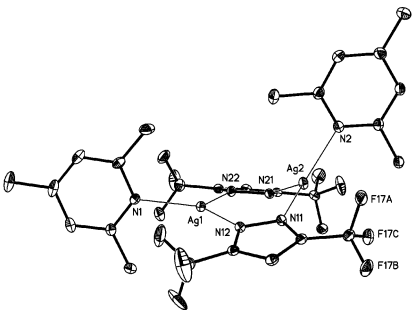

Figure 3. Molecular structure of **Ag$_2$**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−N(12) 2.2214(19), Ag(1)−N(1) 2.253(2), Ag(1)−N(22) 2.2733(19), Ag(2)−N(11) 2.2377(19), Ag(2)−N(21) 2.2532(19), Ag(2)−N(2) 2.253(2); N(12)−Ag(1)−N(1) 128.51(7), N(12)−Ag(1)−N(22) 116.67(7), N(1)−Ag(1)−N(22) 114.80(7), N(11)−Ag(2)−N(21) 112.74(7), N(11)−Ag(2)−N(2) 121.23(7), N(21)−Ag(2)−N(2) 121.70(7).

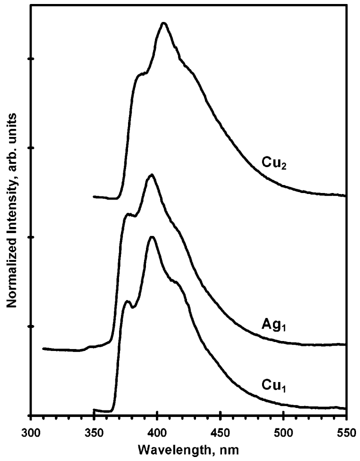

Figure 4. Photoluminescence spectra of crystals of **Cu$_1$**, **Ag$_1$**, and **Cu$_2$** at 77 K. **Cu$_1$** and **Cu$_2$** also emit strongly at room temperature.

The **Cu$_2$** dimer was prepared by treating {[3,5-(CF$_3$)$_2$Pz]-Cu}$_3$ with the appropriate amount of 2,4,6-collidine. The bis-(pyrazolyl)borate adduct **Cu$_1$** was synthesized from [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]K, CuOTf, and 2,4,6-collidine. The related silver adducts **Ag$_2$** and **Ag$_1$** were prepared using analogous procedures. All complexes were characterized by several methods, including X-ray crystallography.[14] Both **Cu$_2$** and **Cu$_1$** feature trigonal planar copper sites (Figures 1 and 2). **Cu$_2$** shows a planar six-membered ring consisting of the Cu(μ-N-N)$_2$Cu unit with an average intramolecular Cu···Cu separation of 3.3940(9) Å (Figure 1). The structure of **Cu$_1$** entails a six-membered ring consisting of the Cu(μ-N-N)$_2$B unit, but with a boat instead of planar conformation (Figure 2).

In contrast to **Cu$_2$**, **Ag$_2$** has a Ag(μ-N-N)$_2$Ag unit in a half-boat conformation (Figure 3). The intramolecular Ag···Ag distance is 3.5618(6) Å. We have also obtained crystals that feature **Ag$_2$** molecules with boat and flattened chair conformations (see Supporting Information).[15] This suggests that there is very little difference energetically between these conformations. The structure of the bis(pyrazolyl)boratosilver adduct **Ag$_1$** (see Supporting Information) is similar to that of **Cu$_1$**, but features a somewhat deeper boat. No close intermolecular M···M interactions were observed in these **M$_2$** and **M$_1$** adducts.

It should be noted that bis(pyrazolyl)borato complexes like **Ag$_1$** are particularly rare for Ag(I).[16] Such complexes usually decompose easily to silver metal. The relatively high thermal stability of **Ag$_1$** may be a direct result of the lowered reducing ability of the borohydride fragment due to the presence of the electron withdrawing trifluoromethylated pyrazolyl groups.

Photoluminescence emission spectra for crystals of **Cu$_1$**, **Ag$_1$**, and **Cu$_2$** are shown in Figure 4.[17] The **Cu$_2$** and **Cu$_1$** solids exhibit bright blue emissions even at ambient temperature with a similar structured profile and the same vibronic spacing in the resolved spectra at 77 K, but the **Cu$_2$** emission band is red-shifted relative to the **Cu$_1$** band. The **Ag$_1$** complex is luminescent only at cryogenic temperatures, and its spectrum at 77 K is essentially the same as that of the **Cu$_1$** complex. This observation suggests that the blue emission of the **Cu$_1$** and **Ag$_1$** samples is a ligand-based

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(14) Detailed synthetic, analytical, spectroscopic, and crystallographic data (CIF) have been deposited as Supporting Information.

(15) X-ray data for this **Ag$_2$** crystal form: triclinic, $P\bar{1}$, $a = 12.132(2)$ Å, $b = 12.283(2)$ Å, $c = 17.091(2)$ Å, $\alpha = 105.49(1)°$, $\beta = 94.82(1)°$, $\gamma = 100.56(1)°$, $V = 2388.9(6)$ Å^3, $T = 293$ K, $Z = 3$, R1 = 0.0387.

(16) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College: London, 1999.

(17) Steady-state photoluminescence spectra were acquired with a PTI QuantaMaster model QM-4 scanning spectrofluorometer equipped with a 75-W xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The spectra were corrected for the detector wavelength-dependent response. Lifetime data utilized a nitrogen laser interfaced with a tunable dye laser and a frequency doubler, as part of fluorescence and phosphorescence subsystem add-ons to the PTI instrument. The 337.1 nm line of the N$_2$ laser was used to pump a freshly-prepared 1×10^{-3} M solution of the organic continuum laser dye Coumarin-540A in ethanol, the output of which was tuned and frequency doubled to attain the 265 nm excitation used to generate the time-resolved data.

emission since altering the metal did not affect the emission energy. Further information was obtained from analysis of the vibronic structure and lifetime measurements. A vibronic progression with a constant spacing of 1270 cm^{-1} (±100) is observed in the emission spectra of **Cu_1** and **Ag_1**. The vibronic spacing is in the range of several heterocyclic ring vibrations of both ligands, i.e., the υ_{C-N} vibrations of 2,4,6-collidine and υ_{N-N} vibrations in 3,5-$(CF_3)_2$PzH (and other reported similar pyrazolates).[18] The lifetime data in the microsecond scale (vide infra) suggest that the emission is phosphorescence. Thus, we conclude that the blue emission of both **Cu_1** and **Ag_1** originates from a $^3\pi-\pi^*$ aromatic ligand excited state. This could be an intraligand transition localized on either the pyrazolate or 2,4,6-collidine ring, or an interligand charge transfer transition. We detected luminescence for 2,4,6-collidine at 77 K, but the emission occurred at a much higher energy in the UV region and with a different vibronic spacing compared to the emissions of **Cu_1** and **Ag_1** (see Supporting Information). Meanwhile, pyrazole is not known as a strongly luminescent species and we have failed to observe emission from 3,5-$(CF_3)_2$PzH even at cryogenic temperatures. Nevertheless, rare literature data are available for the somewhat related phenyl-substituted pyrazoles, which can exhibit detectable phosphorescence in rigid frozen solutions (77 K glasses) with similar energy and structured profile as the spectra in Figure 4.[19] Thus, it is reasonable to assign the emissions of **Cu_1** and **Ag_1** to phosphorescent transitions localized on the pyrazole ring. The fact that the blue but slightly red-shifted emission of **Cu_2** shows the same vibronic progression as in **Cu_1** suggests a common pyrazole-based HOMO for both **Cu_2** and **Cu_1**. The red shift for **Cu_2** is consistent with some significant copper contribution in the LUMO so that a triplet ligand-to-metal charge transfer (^{3}LMCT) excited state assignment is tempting. However, the small magnitude of the red shift suggests that the luminescent state may instead be a primarily ligand-based $^3\pi-\pi^*$ state that is slightly perturbed by interaction with copper. These results are in contrast to those reported by Sorrell and Borovik for other pyrazole complexes of Cu(I), which exhibited structureless emissions that were attributed to $^3(d-\pi^*)$ excited states.[20]

The emission properties of **Ag_2** are complicated and require further investigations to be fully understood. The emission spectrum is dependent on the excitation wavelength, and multiple emission bands are observed even for a homogeneous single crystal. For example, two blue emission bands with maxima at 405 and 455 nm are observed upon exciting with 260 nm while another UV emission is observed at ~280 nm upon exciting with very short wavelengths <250 nm. We also noticed a green emission band at ~500 nm in crystals for which the structure has two different Ag(μ-N-N)$_2$Ag conformations.

The work herein represents a strategy to enhance the phosphorescence of organic molecules via an *internal* heavy metal effect. The lifetime changes from 168 μs in **Cu_1** to shorter lifetimes on going to the heavier **Ag_1** (118 μs) or to the dinuclear **Cu_2** analogue (73 μs) in which the pyrazole ring is connected to two Cu atoms. The spin-forbidden $T_1 \rightarrow S_0$ radiative process of the organic part becomes allowed as evidenced by shortening the usually very long lifetimes (seconds in free organic molecules).[21] The reduction in lifetimes is more dramatic here (10^1-10^2 μs), where metals are directly σ-bonded to the organic moiety, than in cases where weak π-stacking interactions between the organic and metal components take place (~ms lifetimes).[11a] A recent example for an internal heavy atom effect by a d^{10} metal has been reported by Che et al., in which the phosphorescence of arylacetylide moieties is enhanced.[22] Finally, the ligand-based structured phosphorescent emissions in the 3-coordinate Ag(I) and Cu(I) monomers here are to be contrasted with the metal-based largely Stokes'-shifted structureless emissions of three-coordinate Au(I) monomers.[23]

In conclusion, the results here demonstrate interesting photophysical properties for dinuclear and mononuclear copper(I) and silver(I) complexes. All complexes exhibit ligand-based phosphorescent emissions owing to an internal heavy atom effect. We are specially encouraged by the copper complexes to be pursued as emitting materials for MOLEDs because of their bright emissions as solids at ambient temperature. Preliminary tests show that thin films of **Cu_2** coated on glass substrate (similar to films used in MOLEDs) show blue emission under UV irradiation. Further encouraging factors include the facts that these emissions (1) are phosphorescent and blue, which is the most sought-after emission color for MOLEDs; (2) have short lifetimes in the microsecond domain; and (3) occur in neutral fluorinated complexes that may be sublimed into thin films relatively easily.

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Supporting Information Available: X-ray data (CIF), complete synthetic and analytical data, further crystallographic views and conformations of **M_1** and **M_2**, and luminescence data for collidine (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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