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Isolable arene sandwiched copper(I) pyrazolates

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The π-acid/π-base adducts of {[3,5-$(CF_3)_2$Pz]Cu}$_3$ [Cu$_3$] and benzene [Bz], mesitylene [Mes] and naphthalene [Nap] have been isolated. They form columnar structures of the type {[Bz][Cu$_3$]$_2$}$_\infty$, {[Mes][Cu$_3$]}$_\infty$ and {[Nap][Cu$_3$]}$_\infty$ in the solid state, and are luminescent.

Copper(I) pyrzolates have attracted significant interest in recent years.[1-12] They show diverse structures, fascinating luminescent properties and are useful in catalysis and serve as excellent precursors for mixed ligand complexes of copper. For instance, [Cu(Pz)]$_n$ (**1**) (Pz = pyrazolate) is a polymer,[13] whereas {[3,5-$(Me)_2$Pz]Cu}$_3$ and {[3,5-(*i*-Pr)$_2$Pz]Cu}$_3$ adopt trinuclear structures[3] and {[3,5-(*t*-Bu)$_2$Pz]Cu}$_4$ is a tetramer.[14] Some copper(I) pyrazolates aggregate further, often through Cu•••Cu interactions, forming dimers of trimers or even extended chains of trimers.[3] Solid samples of {[3,5-(*i*-Pr)$_2$Pz]Cu}$_3$ emits orange light upon photo-excitation at room temperature, while the emitted color changes to green upon cooling to 77 K.[3] Aida *et al* has reported the development of rewritable media by exploiting the self-assembling process of trinuclear copper pyrazolate luminophors.[15]

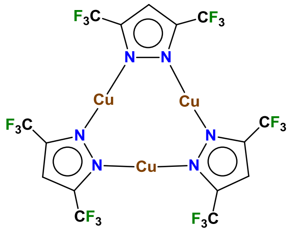

Figure 1. Trinuclear copper pyrazolate {[3,5-$(CF_3)_2$Pz]Cu}$_3$, **[Cu$_3$]**

An area of research focus in our laboratory concerns the chemistry of copper and related heavier coinage metal (Ag, Au) complexes featuring fluorinated pyrazolates.[3, 4, 16-18] The {[3,5-$(CF_3)_2$Pz]Cu}$_3$ (Figure 1) is a particularly interesting molecule.[16, 17] It forms chains of trimers in the solid state and exhibits bright luminescence in the solid state and glassy solutions upon irradiation with UV radiation that can be fine- and coarse-tuned to multiple bright visible colors by varying the solvent, concentration, temperature, and excitation wavelength. Here we demonstrate yet another aspect of {[3,5-$(CF_3)_2$Pz]Cu}$_3$; its π-acid character.[18] In particular, we report the isolation and structural characterization of π-acid/base sandwich adducts of copper(I) pyrazolate {[3,5-$(CF_3)_2$Pz]Cu}$_3$, **[Cu$_3$]** with simple hydrocarbon π-bases benzene, mesitylene and naphthalene.

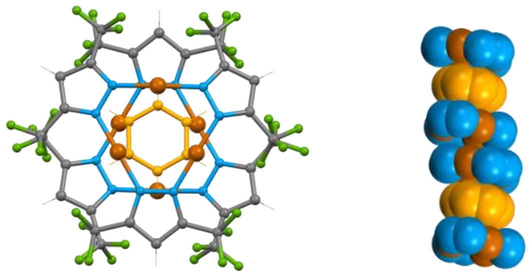

Figure 2. Left: molecular structure of {**[Bz][Cu$_3$]$_2$**}$_\infty$ showing the repeating unit **[Bz][Cu$_3$]$_2$** ({[3,5-$(CF_3)_2$Pz]Cu}$_3$ = **[Cu$_3$]** and benzene = **[Bz]).** Right: portion of the supramolecular chain of {**[Bz][Cu$_3$]$_2$**}$_\infty$ (carbon and fluorine atoms of the pyrazolyl moieties and hydrogen atoms have been omitted for clarity).

The benzene adduct of **[Cu$_3$]** was prepared by treating a chloroform solution of **[Cu$_3$]** with benzene. The mixture was kept at -20 ºC for several days to afford a colorless crystalline solid. X-ray analysis revealed that it is a π-acid/base sandwich adduct of the type {**[Bz][Cu$_3$]$_2$**}$_\infty$ consisting of alternating benzene **[Bz]** and **[Cu$_3$]$_2$** dimer of trimer units (Figure 2). Detailed analysis show that there are two crystallographically different {**[Bz][Cu$_3$]$_2$**}$_\infty$ chains in the crystal lattice resulting from minor differences in orientations of **[Bz]** and **[Cu$_3$]$_2$**. The

[Cu$_3$] units sandwich benzene rather symmetrically with benzene carbon centroid and Cu$_3$-core centroid distances of 3.16, 3.16 Å and 3.20, 3.20 Å for the two {**[Bz][Cu$_3$]$_2$**}$_\infty$ chains. The shortest Cu···C(benzene) distances are 3.17 and 3.22 Å. These distances are slightly longer than sum of the Bondi's van der Waals radii of copper and carbon 1.40+1.70 = 3.10 Å. However, more recent work from Alveraz[19] places van der Waals contact distance of copper and carbon at 4.15 Å implying noteworthy interactions between **[Bz]** and **[Cu$_3$]$_2$** in {**[Bz][Cu$_3$]$_2$**}$_\infty$. These Cu···C(benzene) distances, however are significantly longer than those observed for cationic Cu(I) arene adducts like [Cu(η^2-Me$_6$C$_6$)$_2$][PF$_6$] (2.092(2), 2.192(2) Å) or [Ph$_3$PCu(η^6-Me$_6$C$_6$)][PF$_6$] (2.284(5), 2.293(5) Å).[20]

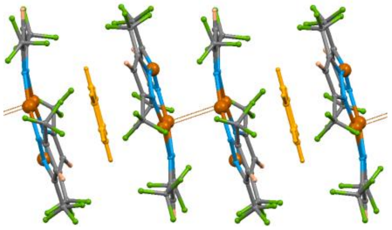

Figure 3. Portion of {**[Bz][Cu$_3$]$_2$**}$_\infty$ showing inter trimer Cu···Cu contacts

Each **[Cu$_3$]** dimer in {**[Bz][Cu$_3$]$_2$**}$_\infty$ also shows two close inter-trimer Cu···Cu contacts (Figure 3) at 3.031, 3.031 and 3.091, 3.091 Å (for two crystallographically different **[Cu$_3$]$_2$** units). The pyrazolyl moieties turn outward from the Cu$_3$N$_6$ core to facilitate this close approach of **[Cu$_3$]** units. The benzene free **[Cu$_3$]** crystallizes as zig-zag chains with much longer inter-trimer Cu···Cu separations (closest Cu···Cu distances of adjacent **[Cu$_3$]** trimers are at 3.813 and 3.987 Å at 100K).[3] This shows that the presence of benzene affects the cuprophilic interactions of **[Cu$_3$]**. It is probably one of the reasons for changes in **[Cu$_3$]** luminescence observed in its glassy solutions of benzene.[3]

The {**[Bz][Cu$_3$]$_2$**}$_\infty$ crystals lose benzene quite easily at room temperature upon air drying or under reduced pressure affording the **[Cu$_3$]**, as evident from NMR spectroscopic and elemental analysis data. This suggests that **[Bz]** and **[Cu$_3$]** interactions are rather weak. In contrast, {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$, **[Ag$_3$],** which is the strongest π-acid of the {[3,5-(CF$_3$)$_2$Pz]M}$_3$ series (M = Cu, Ag, Au)[18] and features the largest metal ion, forms isolable and more robust adducts with benzene and other arenes much easily.[21-23] Computational data show that **[Cu$_3$]** is a relatively weak π-acid.[18] **[Cu$_3$]** also has the smallest metal atom of group 11 series, and therefore more prone to adverse steric effects and weaker side-on (face-to-face) interactions. Thus obtaining isolable adducts of **[Cu$_3$]** with volatile arenes are particularly challenging and above observations are not surprising. For comparison, **[Ag$_3$]** is known to form **[Bz][Ag$_3$]$_2$[Bz]** type adducts with benzene.

Synthesis of **[Cu$_3$]-mesitylene** adduct was accomplished by mixing a chloroform solution of **[Cu$_3$]** with mesitylene **[Mes]**. This mixture was kept at -20 ºC for several days to obtain crystalline {**[Mes][Cu$_3$]**}$_\infty$ which has a columnar structure (Figure 4). It is a common stacking pattern for arene sandwiches of **[Ag$_3$],**[21, 24] and trinuclear Hg^{II}.[25, 26] The **[Ag$_3$]** for comparison, also forms π-acid/base adducts with mesitylene,

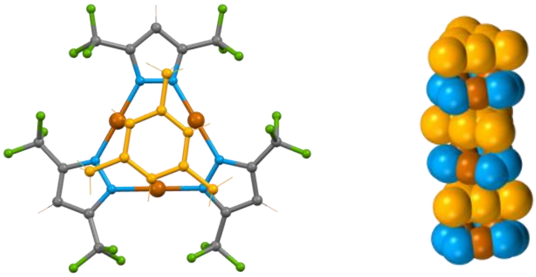

Figure 4. Left: Molecular structure of {**[Mes][Cu$_3$]**}$_\infty$ showing the repeating unit **[Mes][Cu$_3$]** (mesitylene = **[Mes]).** Right: Portion of the supramolecular chain of {**[Mes][Cu$_3$]**}$_\infty$ (carbon and fluorine atoms of the pyrazolyl moieties and hydrogen atoms have been omitted for clarity).

affording {**[Mes][Ag$_3$]**}$_\infty$ aggregates. The **[Cu$_3$][Mes]** unit in {**[Mes][Cu$_3$]**}$_\infty$ sits on a three-fold rotation axis. Two mesitylene ring carbon centroid and Cu$_3$-core centroid distances are 3.30 and 3.34 Å while the shortest Cu···C(mesitylene) distance is 3.34 Å. These distances are slightly longer than the corresponding distances observed for the {**[Bz][Cu$_3$]$_2$**}$_\infty$ adduct. It could be a result of having larger mesitylene because otherwise more electron rich π-base mesitylene should have closer interactions with **[Cu$_3$]**. The steric repulsions of methyl groups of mesitylene with CF$_3$-bearing pyrazolyl moieties of **[Cu$_3$]** lead to distortions as illustrated in Figure 5, which perhaps hinder the closer approach of a second **[Cu$_3$]** and formation of inter-trimer Cu···Cu interactions, as observed in {**[Bz][Cu$_3$]$_2$**}$_\infty$ (Figure 3).

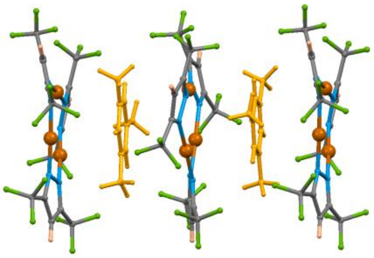

Figure 5. Portion of {**[Mes][Cu$_3$]**}$_\infty$ showing distortions of **[Cu$_3$]** moiety

The crystalline naphthalene adduct of **[Cu$_3$]** was isolated from a chloroform solution of **[Cu$_3$]** containing benzene and naphthalene at -20 ºC. It forms extended binary stacks of {**[Nap][Cu$_3$]**}$_\infty$ consisting of alternating **[Cu$_3$]** and naphthalene **[Nap]** moieties (Figure 6). In contrast to the benzene and mesitylene adducts of **[Cu$_3$]**, {**[Nap][Cu$_3$]**}$_\infty$ is more robust and does not lose the sandwiched arene easily even under reduced pressure. Also note that {**[Nap][Cu$_3$]**}$_\infty$ crystallized out from a solution containing benzene. The shortest Cu···C(naphthalene) distance in {**[Nap][Cu$_3$]**}$_\infty$ is 3.09 Å, which is shorter than those observed in the **[Cu$_3$]** benzene and mesitylene adducts. For comparison, the shortest Ag···C(naphthalene) distance in {**[Nap][Ag$_3$]**}$_\infty$ is 3.00 Å, which is slightly shorter than that observed in {**[Nap][Cu$_3$]**}$_\infty$ despite the larger atomic radius of silver. This points to the presence of relatively stronger π-acid/base interaction in the silver adduct.

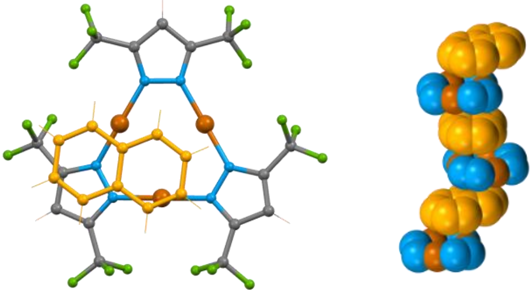

Figure 6. Left: Molecular structure of {**[Nap][Cu$_3$]**}$_\infty$ showing the repeating unit **[Nap][Cu$_3$]** (naphthalene = **[Nap])**. Right: Portion of the supramolecular chain of {**[Nap][Cu$_3$]**}$_\infty$ (carbon and fluorine atoms of the pyrazolyl moieties and hydrogen atoms have been omitted for clarity).

Room temperature ^{1}H NMR spectra of **[Cu$_3$]** containing sub-molar quantities of benzene, mesitylene or naphthalene taken in CDCl$_3$ show no notable chemical shift difference between the aromatic proton signals of adducts and the free components, **[Cu$_3$]** and arene. This suggests that these π-acid/base adducts are too weak to survive (i.e., they dissociate) in solution, or to influence the solution chemical shifts significantly. Similar observations were noted in adducts involving more π-acidic **[Ag$_3$]**.[21]

We have reported several types of arene adducts with **[Ag$_3$]** and the use of **[Ag$_3$]** to prepare a vapochromic sensor for benzene and its alkylated derivatives,[23] as well as strong sensitization of the triplet state of naphthalene.[24] This work shows that **[Cu$_3$]** may also serve as a viable option for such applications. At the room temperature, the arene free **[Cu$_3$]** adduct shows bright orange emissions centered at 645 nm. Although we could not study the photoluminescence of crystalline {**[Bz][Cu$_3$]$_2$**}$_\infty$ due to the easy loss of benzene, preliminary studies show that {**[Mes][Cu$_3$]**}$_\infty$ and {**[Nap][Cu$_3$]**}$_\infty$ display bright green photoluminescence (Figure 7). The emission maximum of {**[Mes][Cu$_3$]**}$_\infty$ was centered at 546 nm whereas the {**[Nap][Cu$_3$]**}$_\infty$ shows three bands at 497, 526, 564 (sh) nm at the room temperature pointing to significant blue shift relative to that of the arene free **[Cu$_3$]**. Removal of mesitylene from {**[Mes][Cu$_3$]**}$_\infty$ leads for the reappearance of **[Cu$_3$]** based emission signal.

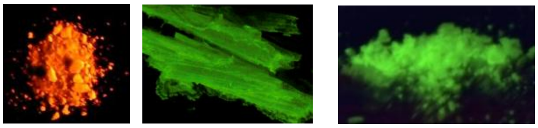

Figure 7. Photos (from left to right) showing the emission colors of **[Cu$_3$]**, {**[Mes][Cu$_3$]**}$_\infty$ and {**[Nap][Cu$_3$]**}$_\infty$

In summary, here we report the isolation of supramolecular stacks involving π-acidic **[Cu$_3$]** and electron rich aromatic π systems. They represent rare, isolable sandwich complexes of copper(I) pyrazolates and aromatic hydrocarbons. Recently, somewhat related **[Cu$_3$]** sandwiched ferrocene was reported.[27] We are currently expanding this π-acid/base chemistry of **[Cu$_3$]** and probing their photoluminescence properties and coinage metal family group trends in detail.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details on synthesis and characterization, photoluminescence spectra and additional figures of X-ray structures. The CCDC 1053391-1053393 contain the supplementary crystallographic data for this paper. See DOI: 10.1039/c000000x/

1. G. La Monica and G. A. Ardizzoia, *Prog. Inorg. Chem.*, 1997, **46**, 151-238.
2. J.-P. Zhang, Y.-B. Zhang, J.-B. Lin and X.-M. Chen, *Chem. Rev.*, 2012, **112**, 1001-1033.
3. H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 7489-7501.
4. C. V. Hettiarachchi, M. A. Rawashdeh-Omary, D. Korir, J. Kohistani, M. Yousufuddin and H. V. R. Dias, *Inorg. Chem.*, 2013, **52**, 13576-13583.
5. R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, 1988, **27**, 4179-4182.
6. F. Gong, Q. Wang, J. Chen, Z. Yang, M. Liu, S. Li, G. Yang, L. Bai, J. Liu and Y. Dong, *Inorg. Chem.*, 2010, **49**, 1658-1666.
7. L. Hou, W.-J. Shi, Y.-Y. Wang, H.-H. Wang, L. Cui, P.-X. Chen and Q.-Z. Shi, *Inorg. Chem.*, 2011, **50**, 261-270.
8. M. Veronelli, N. Kindermann, S. Dechert, S. Meyer and F. Meyer, *Inorg. Chem.*, 2014, **53**, 2333-2341.
9. Q. Xiao, J. Zheng, M. Li, S.-Z. Zhan, J.-H. Wang and D. Li, *Inorg. Chem.*, 2014, **53**, 11604-11615.
10. J.-P. Zhang and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 907-917.
11. S.-Z. Zhan, M. Li, X.-P. Zhou, J.-H. Wang, J.-R. Yang and D. Li, *Chem. Commun.*, 2011, **47**, 12441-12443.
12. J. He, Y.-G. Yin, T. Wu, D. Li and X.-C. Huang, *Chem. Commun.*, 2006, 2845-2847.
13. N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, *J. Am. Chem. Soc.*, 1994, **116**, 7668-7676.
14. K. Fujisawa, Y. Ishikawa, Y. Miyashita and K.-i. Okamoto, *Chem. Lett.*, 2004, **33**, 66-67.
15. A. Kishimura, T. Yamashita, K. Yamaguchi and T. Aida, *Nat. Mater.*, 2005, **4**, 546-549.
16. H. V. R. Dias, S. A. Polach and Z. Wang, *J. Fluorine Chem.*, 2000, **103**, 163-169.
17. H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman and M. A. Omary, *J. Am. Chem. Soc.*, 2003, **125**, 12072-12073.
18. M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage and H. V. R. Dias, *Inorg. Chem.*, 2005, **44**, 8200-8210.
19. S. Alvarez, *Dalton Trans.*, 2013, **42**, 8617-8636.
20. A. M. Wright, B. J. Irving, G. Wu, A. J. H. M. Meijer and T. W. Hayton, *Angew. Chem., Int. Ed.*, 2015, **54**, 3088-3091.
21. H. V. R. Dias and C. S. Palehepitiya Gamage, *Angew. Chem., Int. Ed.*, 2007, **46**, 2192-2194.
22. H. V. R. Dias, C. S. P. Gamage, J. Keltner, H. V. K. Diyabalanage, I. Omari, Y. Eyobo, N. R. Dias, N. Roehr, L. McKinney and T. Poth, *Inorg. Chem.*, 2007, **46**, 2979-2987.
23. M. A. Rawashdeh-Omary, M. D. Rashdan, S. Dharanipathi, O. Elbjeirami, P. Ramesh and H. V. R. Dias, *Chem. Commun.*, 2011, **47**, 1160-1162.
24. M. A. Omary, O. Elbjeirami, C. S. P. Gamage, K. M. Sherman and H. V. R. Dias, *Inorg. Chem.*, 2009, **48**, 1784-1786.
25. M. R. Haneline, J. B. King and F. P. Gabbai, *Dalton Trans.*, 2003, 2686-2690.
26. M. Tsunoda and F. P. Gabbaie, *J. Am. Chem. Soc.*, 2000, **122**, 8335-8336.
27. V. N. Tsupreva, A. A. Titov, O. A. Filippov, A. N. Bilyachenko, A. F. Smol'yakov, F. M. Dolgushin, D. V. Agapkin, I. A. Godovikov, L. M. Epstein and E. S. Shubina, *Inorg. Chem.*, 2011, **50**, 3325-3331.