For Table of Contents Entry Only
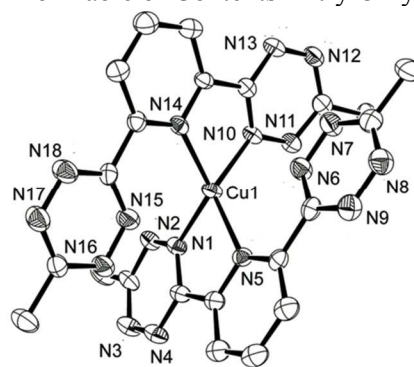
Electron transfer to ligand is the excited, not ground state when copper is surrounded by four tetrazines and two pyridines.

Journal Name

ARTICLE

In Search of Redox Noninnocence between a Tetrazine Pincer Ligand and Monovalent Copper

Alice K. Hui,[a] Richard L. Lord[b] and Kenneth G. Caulton[a*]

The synthesis and characterization of a "super-saturated" six-coordinate complex from monovalent copper (PF_6^- salt) and the potentially oxidizing pincer ligand 2,6, **b**is-(methyl **t**etra**z**inyl) **p**yridine, btzp, is described. This cation has a structure with the two pincers symmetry related, but each btzp having one short and one long Cu/N(tetrazine) bond; facile exchange is observed between short and long tetrazine donors. The structure shows no evidence for full electron transfer from Cu^+ to tetrazine, and DFT calculations not only confirm that conclusion, but also show that the lowest energy triplet state, an excited state relative to the singlet ground state, has MLCT character where the electron lost by copper now resides in *both* tetrazine rings of only *one* pincer ligand; the two pincers in this excited state are inequivalent, having charge $btzp^0$ and $btzp^{-1}$. The unusual orientation of the distinct tetrazines in the ground state structure of $Cu(btzp)_2^+$ is attributed to charge/dipole attraction unhindered by significant entropy cost.

Introduction

The new pincer ligand,[1] bis tetrazinyl pyridine, btzp, Scheme 1, complements the mandatory meridional structural feature of

Scheme 1:
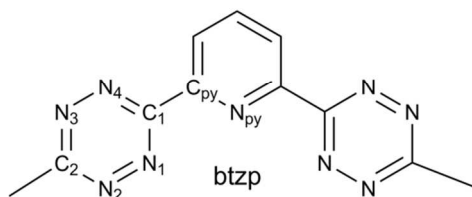
pincers[2] with the potential to be redox active. Tetrazines have such a heavy complement of sp^2 nitrogens that they are readily reduced, so the btzp ligand must be considered as a potential oxidizing agent when it is reacted with a metal source. Depending on the electron richness of the metal source, MX_n, the product may exist with no change of redox state from that in the reagents, or there might be electron transfer from metal to pincer, leading to a ground state with ligand-centered radical character and an oxidized metal. We consider here the case where the metal is copper, and in a reduced oxidation state, +1. To keep things structurally simple, we chose a relatively non-nucleophilic anion for copper, PF_6^-. As will be seen, the thermodynamics of this system dictate that two pincer ligands prefer to bind to copper here, giving a product of surprising formula $[Cu(btzp)_2]PF_6$, which seemingly has two oxidants bound to an initially reduced copper. What will be revealed in this report is the preferred oxidation level of components in this assembly, and the unusual outcome of how copper, with a traditionally maximum coordination number of four, accommodates two tridentate pincer ligands. Clearly one option for this higher coordination number is intramolecular oxidation of the metal, leading to Cu^{2+}, which readily accepts coordination number six. The reality, in this case, is considerably more complex.

Results

Synthesis and Characterization of $Cu(btzp)_2^+$ as its PF_6^- Salt

Reaction of $[Cu(NCMe)_4]PF_6$ with *equimolar* btzp occurs in time of mixing in MeCN and, followed by layering with Et_2O, gives dark black red crystals of product. The ^{1}H NMR spectrum of isolated compound dissolved in CD_3CN shows only three signals, consistent with a two-fold symmetric pincer ligand, and at different chemical shifts from those of free btzp. The salt is also soluble in THF and CH_2Cl_2, and is insoluble in benzene and pentane. The ESI(+) mass spectrum of this compound in MeCN showed both the ion $Cu(btzp)_2^+$ and the ligand displacement ion $Cu(btzp)(MeCN)^+$.

A single crystal X-ray structure determination shows (Figure 1) the compound to be the PF_6 salt of $Cu(btzp)_2^+$, with MeCN solvent filling lattice voids. The pincer thus binds to Cu^+ stronger than does MeCN. The cation has idealized C_2 symmetry, making the two pincer ligands chemically equivalent. Each pincer is planar, and the angle between the two CuN_2 planes is 86.4^o, hence nearly orthogonal. However, each pincer *deviates* from twofold symmetric κ^3 coordination,
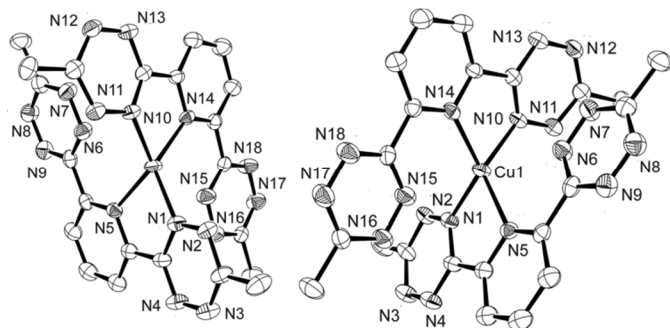
Figure 1. ORTEP drawing (50% probabilities) of the nonhydrogen atoms of the cation Cu(btzp)$_2$$^+$, showing selected atom labeling. Unlabeled atoms are carbons. Both figures are viewed down the idealized C$_2$ axis, one with two "pendant" tetrazines (involving N6 and N15) projecting towards the viewer (at right) and the other with those projecting away. Selected structural parameters: N1-Cu1, 1.994(3) Å; N5-Cu1, 2.123(3); N10-Cu1, 2.015(2); N14-Cu1, 2.090(3); N15-Cu1, 2.762(4); N6-Cu1, 2.728(4); N1-Cu1-N10, 126.52(11)$^\circ$; N1-Cu1-N14, 128.46(10); N10-Cu1-N14, 80.69(10); N1-Cu1-N5, 80.16(15); N10-Cu1-N5, 126.53(11); N14-Cu1-N5, 121.10(10).

since one tetrazine of each pincer has long (2.73 and 2.76 Å) Cu/N distances. While these distances are very long, the rotational conformation of the distant tetrazines, coplanar with neighboring pyridyl, is not what would be chosen to orient a nitrogen lone pair *away* from copper. It is also not what would be indicated by the 25 $^\circ$C ^{1}H NMR spectrum, unless the long and short Cu-N(tetrazine) groups rapidly exchange bonding roles. The ^{1}H NMR spectrum of this cation in d$_8$-THF at -60 $^\circ$C shows no decoalescence to more than the three signals observed at 25 $^\circ$C, indicating a low barrier to interconversion of long and short Cu/N(tetrazine) arms. The six-coordinate connectivity might be describes as "4+2." What remains to be understood is why the distances to the two distant tetrazines are shorter than the sum of the van der Waals radii (1.55 + 1.4 = 2.95 Å) but much longer than the sum of the covalent radii (0.71 + 1.32 = 2.03 Å).[3, 4]

Distances from copper to the pyridyl nitrogens are 2.09 - 2.12 Å, compared to those to the two more strongly bonded tetrazines (1.99 – 2.02 Å). The tetrazines are thus more strongly bonded to copper than are the pyridyls, an unusual situation which requires explanation. Angle N(pyridyl)-Cu-N(pyridyl) and N(tetrazine)-Cu-N(tetrazine) involving the closer tetrazines are 121 and 127°, respectively, showing that these four nitrogens adopt a flattened tetrahedral geometry around copper. The N/Cu/N angle between the two long Cu/N(tetrazine) centers is 109.1°, hence compressed. The pendant tetrazine conformation is clearly not influenced by any π stacking between the two pincers, since the two pincer planes are essentially orthogonal. We envisioned that the interaction of these two electron deficient tetrazines with copper might be charge transfer in nature. Two scenarios are possible. One has the pendant tetrazines (those with N6 and N15) collectively accepting charge from the electron rich and saturated Cu$^+$, thus

becoming incrementally anionic and attracted to be near copper. The other is that copper is incrementally oxidized by the *normally* bonded tetrazines, involving N1 and N10, so amide character *there* accounts for the observed shortening of those Cu/N distances compared to those to pyridyl nitrogens N5 and N14. The anionic character imparted to those tetrazines then benefits from delocalization throughout the entire pincer, favoring the pendant tetrazine being coplanar with the other linked rings, to conjugate with the reduced part of the ligand. In either case, the structure determination shows that, at most, fractional electron transfer is involved: analysis of the distances of atoms *within* the tetrazine rings shows no significant differences between the tightly bonded and the pendant tetrazines, so any electron transfer is too small to have structurally detectable impact on C/C and C/N distances, especially considering it occurs over several such electron deficient rings.

Any misdirection of the ring nitrogen lone pair bonding to copper can be judged by the angle (*para* atom)/(bonded N)/Cu. This angle is in the range 164.3 – 170.9° for the two pyridyls, and 164.6 and 170.6° for the tightly bonded tetrazines, hence comparable. For the two distant tetrazines, those angles are only slightly worse: 162.0 and 164.1°.

EPR spectroscopy of Cu(btzp)$_2$(PF$_6$) in MeCN at RT shows no signal, consistent with a singlet state and consistent with ^{1}H NMR chemical shifts in the diamagnetic region. After saturating the solution with air, EPR shows no change after 10 min of mixing, indicating the cation to be stable to oxidation by O$_2$. This unreactivity is rare for monovalent copper.[5]

Comparative Analysis of the Structure of Cu(btzp)$_2$$^+$.

The overwhelming number of structures of Cu(I) complexes show a maximum coordination number of four, and Cu/N(imine) distances in the range 1.99 – 2.09 Å. Cu(btzp)$_2$(PF$_6$) is thus very unusual. We also considered relevant comparison compounds; cuprous ion surrounded by two bipy ligands where the 6 and 6' sites (*ortho* to pyridyl N) of the bipy carry phenyl substituents show that all phenyl rings are orthogonal to their bipy planes, and show some face to face stacking of those phenyls to the bipy plane of the second chelate; the closest phenyl carbon to copper distance is 3.06 Å (nonbonding). There is thus no evidence for attractions between those *phenyls* and copper.[5]

Exceptions to coordination number four include five coordinate Cu(*bidentate imine*)$_2$Cl, where two Cu/N distances are 2.73 and 2.77 Å, thus as long as in Cu(btzp)$_2$$^+$.[6]

In contrast, five coordinate Cu(*o*-phenanthroline)$_2$Cl has Cu-N distances from 1.99 to 2.15 Å.[7]

Nevertheless, even based on van der Waals radii established by a new and sophisticated analysis[3] of the Cambridge Crystallographic Database, the longer Cu/N distances in Cu(btzp)$_2$$^+$ are far shorter than the sum of van der Waals radii, so indicate some attractive interaction, even with this copper center possessing no empty valence orbitals.
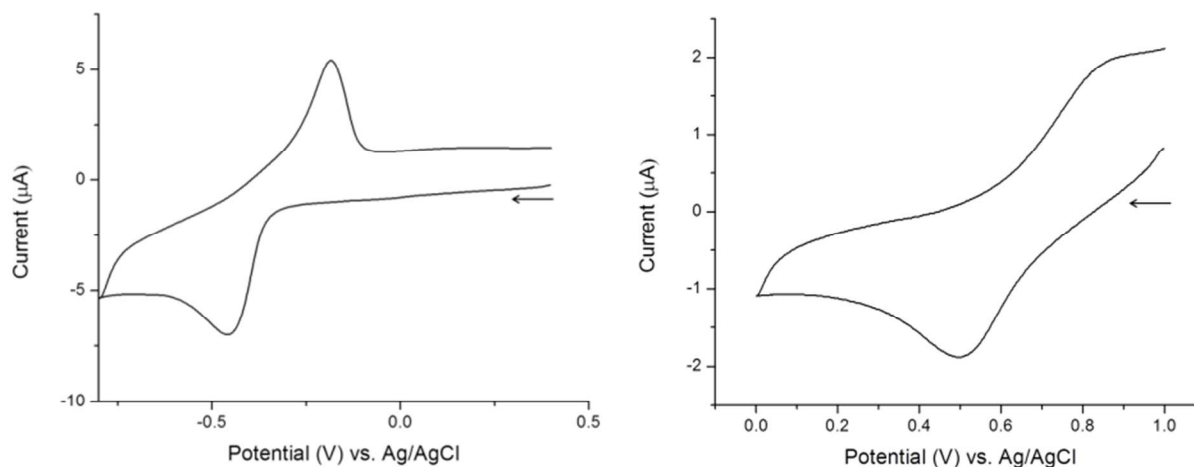
Figure 2. Cyclic voltammograms of Cu(btzp)$_2$(PF$_6$) (0.1 M in [Bu$_4$N][PF$_6$] and 250 mV/s). Left: Reductive scans. Right: scan at positive potentials. Analyte concentration: 1.0 x 10^{-3} M in MeCN.

Another relevant (isoelectronic) comparison compound is the d^{10} compound Zn(2,2'-terpyridyl)$_2$$^{2+}$ where the central pyridyl (2.068 Å) and the outer arm pyridyls (2.186 Å) have Zn/N bond lengths which differ by only 0.12 Å; the two pincer ligands are rigorously symmetry-related.[8]

A survey of the Cambridge Crystallographic Database for Cu(I) complexes with coordination number higher than four finds a limited number of examples, primarily with terpy and oligopyridines, as well as *ortho*-phenanthrolines, and all of these[9] show great (> 0.5 Å) lengthening of Cu/N distances beyond the first four "normal" ones at ~2.0 Å. None of these involve more than one electronegative nitrogen in the six-membered ring, so charge transfer (redox noninnocence) was not considered, and proximity at less than the sum of van der Waals radii was attributed to constraints of connectivity in the chelate backbone.

Cyclic Voltammetry

Cyclic voltammetry at a glassy carbon electrode in MeCN with TBAPF$_6$ was carried out (Figure 2) at 250 mVs^{-1} (all potentials measured vs. Ag/AgCl), cycling in the potential range -0.8 to +1.0 V. The copper complex shows one quasi-reversible process with E$_{pc}$ = -0.45 V, which we assign as reduction to form neutral Cu(btzp)$_2$; since there are no known zerovalent copper complexes, we assign this process to ligand centered reduction. Another chemically reversible process has E$_{pa}$ = +0.5 V, which we assign to oxidation to form Cu(btzp)$_2$$^{2+}$.

DFT Analysis of Electronic Structure

The goal here was to understand if any charge transfer occurs between Cu$^+$ and two potentially oxidizing btzp ligands in Cu(btzp)$_2$$^+$. If it occurs, then the question of overall species spin state also arises.

Singlet Cu(btzp)$_2$$^+$. DFT geometry optimization (see Supporting Information for computational details) of the singlet
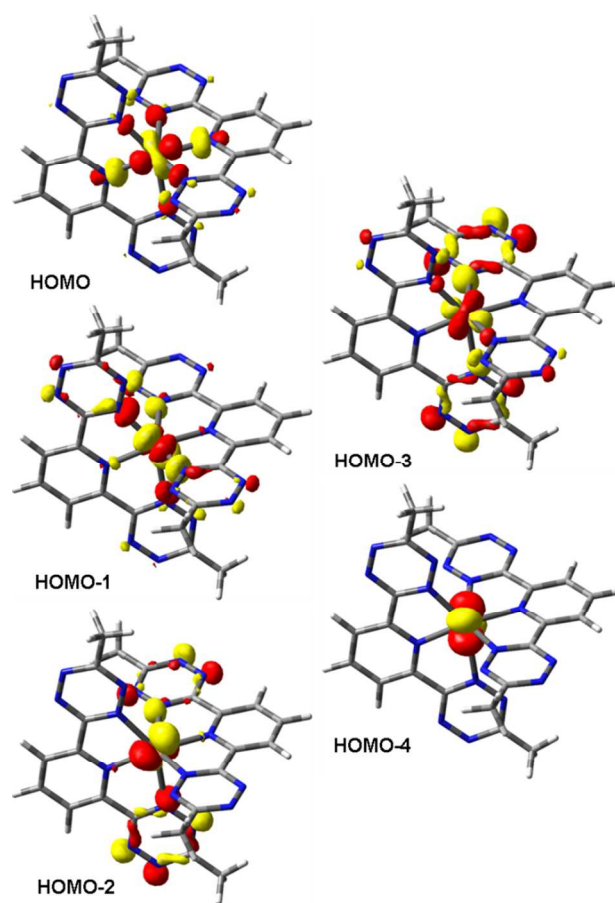
Figure 3. Highest occupied orbitals of singlet Cu(btzp)$_2$$^+$.

state of Cu(btzp)$_2$$^+$ yields a geometry in good agreement with the experimental parameters: the structure (Table 1) has an approximate C$_2$ axis relating the two pincer ligands and the two pincer planes are 90° from each other. The DFT model thus fully captures the unusually high copper coordination number. Each pincer has one tetrazine with a Cu/N distance shorter (by

0.06 Å) than that to pyridyl, and each pincer has one tetrazine with a long Cu/N distance of 2.66 Å. The five highest energy occupied orbitals (Figure 3) are heavily copper in character (hence approaching a d^{10} electronic configuration; note especially the purely metal HOMO-4). What ligand character there is all involves σ orbitals of the tetrazine nitrogens (with only a trace of pyridyl and tetrazine nitrogen lone pair in the HOMO). The HOMO-1 mostly involves the more strongly bound tetrazines, while the HOMO-2 and HOMO-3 involve the weakly bound tetrazines, in accord with the expected antibonding character based on the short and long Cu–N contacts, respectively. What ligand participation there is in these frontier orbitals involves the nitrogen lone pairs, so there is *no evidence* for charge transfer into tetrazine π* orbitals. Since the interactions shown in Figure 3 are Cu/N antibonding, these raise the energy of the d electrons and thus make this species *more* easily oxidized. Nevertheless, the electronic structure reveals the presence of conventional monovalent copper: five doubly occupied d orbitals. This left us wondering – how much energy would it take for Cu to give up one of its electrons to these ligands? We reasoned that the triplet state may involve metal-to-ligand charge transfer.

Triplet Cu(btzp)$_2$$^+$. At the level of theory we employed, this triplet is 20.0 kcal/mol higher in free energy than the singlet species. While the ground state singlet was best described as Cu^I with two neutral btzp ligands, this triplet state is Cu^{II} with one negative charge distributed elsewhere. Thus, the lowest energy triplet state of Cu(btzp)$_2$$^+$ is a metal-to-ligand charge transfer state as we hypothesized. Of exceptional interest is that the charge has been transferred to *one* pincer ligand and thus this triplet no longer has symmetry related pincers. The triplet state is $Cu^{II}(L^0)(L^{-1\bullet})^+$. This is evident from the spin density map in Figure 4 (left), where unpaired spin is only seen at one of the pincer ligands. A "corresponding orbital" analysis[10] shows that one SOMO is mainly sigma antibonding between one copper orbital and the nitrogens of the reduced ligand and the neutral pincer's pyridyl N (Figure 4, right), while the other SOMO is primarily tetrazine π* on the reduced ligand with only modest participation of that pyridyl *ortho* and *para* carbon π orbitals. This represents occupancy of the π*$_{NN}$ LUMO of free btzp.[1] What is also true is that there is still two-fold symmetry in this triplet state, but this relates two arms *within* each pincer, and not one pincer to the other; the triplet has C$_{2v}$ symmetry. Thus (Table 1), the two tetrazine arms in the singly reduced pincer are equidistant from copper (2.07 Å), and short compared to the singlet state, and the *two* arms in the unreduced pincer are *both* long (2.42 Å). The
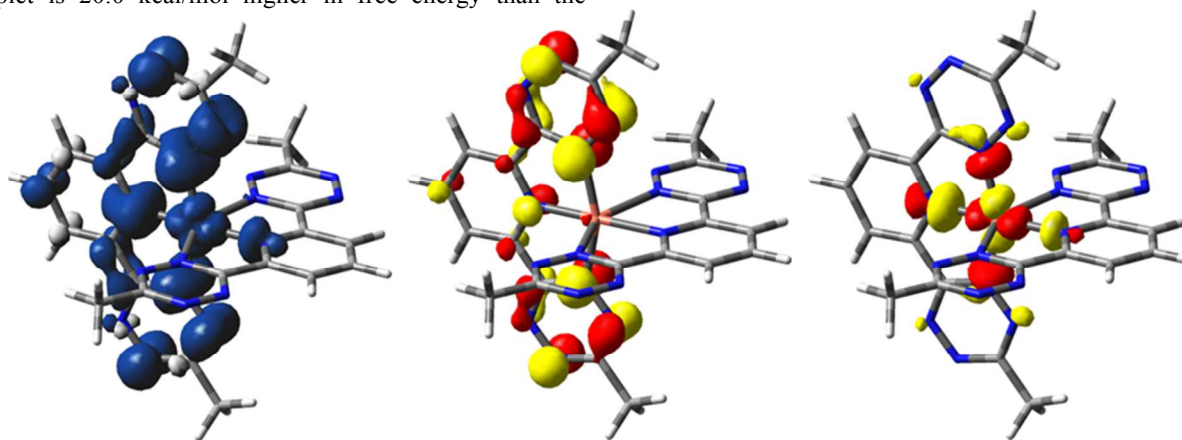
Figure 4. Isosurface plots for the spin density (left, 0.002 au) and SOMOs (middle and right, 0.05 au) of the $[Cu(L^-)(L^0)]^{1+}$ triplet species.

**Table 1.** Important bond length metrics (Å)[a].

	S=0 [Cu(bztp)$_2$]$^+$		*S*=1 [Cu(bztp)$_2$]$^+$	
	short	**long**	**L(1–)**	**L(0)**
Cu–N(tet)	2.130/2.131	2.663/2.660	2.068/2.070	2.420/2.422
Cu–N(py)	2.188/2.187		1.986	2.111
N(tet)–C(tet)	1.344	1.339	1.361	1.336
C(tet)–C(pyr)	1.480	1.485	1.462	1.483
C(pyr)–N(pyr)	1.343	1.342	1.346	1.346
trans N(pyr)–N(pyr)	4.171		4.097	
trans N(tet)–N(tet)	4.572/4.570		4.057	4.648
intra N(tet)–N(pyr)	2.692	2.730	2.570	2.731

a. In the approximately C$_2$ symmetric singlet molecule, two of the tetrazines are bound more closely to copper. Thus, the pincers are not internally symmetric. Their bond lengths and angles are labeled "short" and "long." The triplet MLCT state has structural differences *between* the ligands because one is reduced and one is neutral, but the two arms are symmetrical within each pincer.

Journal Name

ARTICLE

Cu/N(pyridyl) distance to the reduced pincer in the triplet is shorter (by 0.12 Å) than to the unreduced pincer in the triplet. Within the rings, the inter ring C(tet)-C(pyr) distance is slightly shorter (by 0.02 Å) in the reduced pincer. All these changes are consistent with the reduction (as illustrated for two-electron reduction in Scheme 2)[11] occurring in a given α–diimine four

Scheme 2:
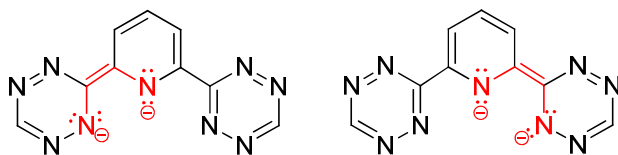
atom system in one pincer (illustrated in red in Scheme 2), just as it is in isolated α–diimines. This also explains the shorter bonds from pyridine nitrogen to copper since this nitrogen has taken on amide character. The difference here is that distances *within* the rings are changed less since the delocalization occurs over *both* tetrazines, as dictated by the C_2 symmetric structure. It bears mention that this asymmetric distribution of charge transfer was located in the DFT calculation starting from a symmetric structure (*i.e.* two symmetry equivalent pincers, the structure of the singlet ground state), so this charge segregation is not an artifact of a biased starting geometry during optimization.

Discussion and Conclusions

The fact that this 1:2 Cu:btzp species forms even when the global solution metal:pincer ratio is 1:1 and when there is abundant MeCN is probably a reflection of the noncomplementary *mer* geometry of one pincer and one MeCN in a hypothetical (btzp)Cu(NCMe)$^+$ species, since Cu(I) has an electronic preference for tetrahedral structure and a pincer (planar) cannot bind at tetrahedral sites. Repeating the synthesis with a 1:2 Cu:btzp ratio again gives this same species, in higher yield, but there is still the question of how the "extra" tetrazine in each pincer is accommodated structurally in the observed species. This same species is formed regardless of whether ligand is added to a solution of CuPF$_6$, or using the reverse direction of addition.

Given the collective lack of evidence for redox change away from Cu(I) in the ground state of Cu(btzp)$_2^+$, we are left to seek alternative explanations for the proximity to copper of two more distant tetrazines, one from each pincer. In other cases, terpyridyl becomes κ^2 in (aryl-terpy)Cu(PPh$_3$)$_2^{+}$,[12] where the third pyridine rotates to nearly perpendicular to the bidentate ring plane, leaving its Cu/N distance 3.07 Å. However the plasticity of Cu(I) is evident from the report that terpy

itself,[9] in (terpy)Cu(PPh$_3$)$_2^+$ is κ^3, and the arm pyridyls have Cu//N distances of 2.39 and 2.54 Å.

We propose that this originates from weak ion/dipole, or even ion/lone pair attractions, as a distant analog of a hydrogen bond. Indeed, here four-coordinate Cu$^+$ has spherical charge density from its filled d shell and its d orbitals lie at very deep energy here late in the transition series (many nuclear charges present), so the cationic copper warrants the description of a "fat proton." In addition, since the interaction is intramolecular (no entropy penalty), such a weak ion dipole interaction can appear and can influence structure; there *is* an energetic payoff for this orientation of the "pendant" tetrazine. Clearly, given this "prepared" orientation of the pendant tetrazine lone pair towards copper, the barrier to fluxionality, an intramolecular nucleophilic substitution reaction, will be small.

Experimental

General Methods. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a glovebox. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze-pump-thaw method twice prior to use. Glassware was oven-dried at 150 ^{o}C overnight. NMR spectra were recorded in various deuterated solvents at 25 ^{o}C on a Varian Inova-400 spectrometer (^{1}H: 400.11 MHz) Proton chemical shifts are reported in ppm versus SiMe$_4$. Mass spectrometry analyses were performed in an Agilent 6130 MSD (Agilent Technologies, Santa Clara, CA) quadrupole mass spectrometer equipped with a Multimode (ESI and APCI) source. All starting materials have been obtained from commercial sources and used as received without any further purification.

Cu(btzp)$_2$PF$_6$. btzp (6 mg, 22.45 μmol) was dissolved in 5 mL of MeCN, and added to a stirring solution of Cu(MeCN)$_4$PF$_6$ (8.37 mg, 22.45 μmol) in 5 mL of MeCN. The solution became dark red within seconds. The solvent was removed in vacuum to reveal a dark red solid. Dark red crystals were grown from layering Et$_2$O onto a concentrated solution. **^{1}H NMR (400MHz, CD$_3$CN):** 3.12 (s, 6H) 8.44 (t, 1H, C-H Ar) 8.91 (d, 2H, C-H Ar). **ESI(+) mass spectrum, in MeCN:** obs., 371.0532; calc. 371.0542 for (btzp)Cu(MeCN)$^+$ (C$_{13}$H$_{12}$N$_{10}$^{63}Cu); Obs., 597.1276, calc., 597.1258 for (btzp)$_2$Cu$^+$ (C$_{22}$H$_{18}$N$_{18}$^{63}Cu). In cyclic voltammetry studies, the peak-to-valley potential separations were somewhat larger than the 150 mV separation measured in our solvent medium for the Fc/Fc$^+$ couple. In addition scans out to -1.5 V showed one other irreversible process with E$_{pc}$ = -1.1 V.

Acknowledgements

Notes and references

[a] Indiana University, Department of Chemistry, 800 E. Kirkwood Ave., Bloomington, Indiana, 47405, USA. Fax: 812-855-8300, Tel: 812-855-4798, E-mail: Caulton@indiana.edu.

[b] Grand Valley State University, Department of Chemistry, Allendale, MI, USA.

1   C. R. Benson, A. K. Hui, K. Parimal, B. J. Cook, C.-H. Chen, R. L. Lord, A. H. Flood and K. G. Caulton, *Dalton Trans.,* 2014, **Accepted, DOI: 10.1039/C1034DT00341A**.

2   D. Morales-Morales, C. M. Jensen, *The Chemistry of Pincer Compounds*, First ed. *Oxford, Elsevier,* Amsterdam, 2007.

3   B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.,* 2008, 2832.

4   A. Bondi, *J. Phys. Chem.,* 1964, **68,** 441.

5   K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruna and C. Arana, *Inorg. Chem.,* 1993, **32,** 4450.

6   P. Kulkarni, S. Padhye, E. Sinn, C. E. Anson and A. K. Powell, *Inorg. Chim. Acta,* 2002, **332,** 167.

7   D. J. Awad, F. Conrad, A. Koch, U. Schilde, A. Pöppl and P. Strauch, *Inorg. Chim. Acta,* 2010, **363,** 1488.

8   M. A. Harvey, S. Baggio, A. Ibanez and R. Baggio, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 2004, **C60,** m375.

9   H. Feng, X.-P. Zhou, T. Wu, D. Li, Y.-G. Yin and S. W. Ng, *Inorg. Chim. Acta,* 2006, **359,** 4027.

10 F. Neese, *J. Phys. Chem. Solids,* 2004, **65,** 781.

11 To clarify predicted bond length changes, this shows results for two-electron reduction; changes for one-electron reduction are analogous.

12 M. I. J. Polson, G. S. Hanan and N. J. Taylor, *Acta Crystallographica, Section E: Structure Reports Online,* 2008, **E64,** m205/1.