The First Crystal Structure of a Metal-Stabilized Tetrazine Anion Radical: Formation of a Dicopper Complex through Self-Assembly in a Comproportionation Reaction

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The recently reported structural results on copper(I) and ruthenium(II) complexes of azo anion radicals[1,2] have shown that such generally interesting intermediates can be well stabilized for detailed characterization through metal coordination. The N−N bond lengths established in those systems lie right between the values of an azo double bond (N═N) and those of typical N−N single bonds, thus confirming the occupation of an antibonding π^* orbital by a *single* electron.[1,2]

A related[3] π acceptor function is the 1,2,4,5-tetrazine (tz) ring which formally contains two azo groups as part of an “aromatic” ring system. 1,2,4,5-Tetrazines are known to bind metal complex fragments in the aromatic[3,4] and semireduced states[4,5] and form structurally characterized 2e-reduced 1,4-dihydro species (H_2tz).[6] Using the established capacity of bis(triorganophosphane)copper(I) species to stabilize azo-containing radical anions,[1] we now describe the first structural characterization of a semireduced tz derivative, the radical anion of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) in metal-coordinated form, and compare the structural data with those of the free ligand[7] and of the 1,4-dihydro species (H_2bptz).[6c]

The stable compound $[(Ph_3P)_2Cu(\eta^4,\mu\text{-bptz})Cu(PPh_3)_2](BF_4)$ (**1**) is obtained most easily via a stoichiometrically controlled self-assembly comproportionation process (eq 1).[8a] Depending on the moisture content of the reaction mixture as introduced by the copper(II) salt, some H_2bptz is formed as side product.

$$3Cu + Cu(BF_4)_2 + 2bptz + 8PPh_3 \rightarrow 2[(Ph_3P)_2Cu(bptz)Cu(PPh_3)_2](BF_4) \quad (1)$$

The structure of **1** could be obtained from X-ray crystallography (Figure 1).[9]

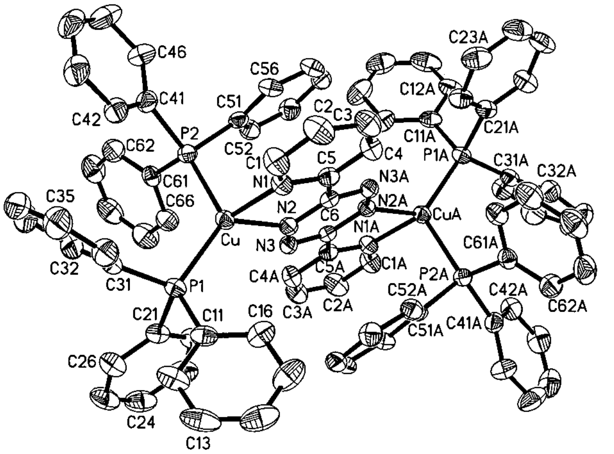

Figure 1. Molecular structure of the cation of **1** in the crystal. Selected bond lengths (Å): Cu−N1 2.084(4), Cu−N2 2.032(3), Cu−P1 2.2097(12), Cu−P2 2.2873(12), N2−N3 1.394(5), N2−C6 1.338(5), N3−C6 1.320(5), N1−C5 1.355(6), N1−C1 1.337(6). Selected angles (deg): N1−Cu−N2 79.54(14), P1−Cu−P2 119.80(5), N1−Cu−P1 120.90(11), N1−Cu−P2 105.44(11), N2−Cu−P1 124.64(11), N2−Cu−P2 98.20(11). Atoms A in $1 - x$, $2 - y$, $1 - z$; percentage of probability for the thermal ellipsoids: 50.

As previously recognized,[3−5] the bptz system acts as an essentially planar bis-bidentate ligand (5.8° angles between best pyridine and tetrazine planes), bridging two metal centers at a distance of 6.743 Å. The five-membered chelate rings adopt a slight envelope conformation with a 169.4° dihedral angle between

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(8) (a) A mixture containing 236 mg (1.0 mmol) of bptz,[8b] 90 mg (1.4 mmol) of activated copper powder, 164 mg (0.5 mmol) of $Cu(BF_4)_2 \cdot 5H_2O$, and 1049 mg (4 mmol) of PPh_3 was heated to reflux for 1 h in 75 mL of dried CH_2Cl_2 under dry air. The orange solution was then filtered warm to remove unreacted Cu, the filtrate was reduced to about $^1/_5$, and *n*-hexane was added until a precipitate formed. After 1 day at 5 °C the solid was collected by filtration, washed with *n*-hexane, and recrystallized from acetonitrile. Small amounts of orange H_2bptz may be removed by cooling a saturated solution in CH_2Cl_2 to 5 °C and filtering off this side product. Cooling to −10 °C of the remaining solution gave 480 mg (32%) of red, crystalline **1** suitable for X-ray diffraction. Anal. Calcd for $C_{84}H_{68}BCu_2F_4N_6P_4$: C, 67.29; H, 4.57; N, 5.61. Found: C, 67.47; H, 4.89; N, 5.13. UV−vis (CH_2Cl_2): $\lambda_{max} = 510, 427, 395$ (sh) nm. For EPR, see ref 4a. Cyclic voltammetry (CH_2Cl_2/0.1 M Bu_4NPF_6): $E_{1/2}(ox) = -0.35$ V vs $FeCp_2^{+/0}$. (b) Dallacker, F. *Monatsh. Chem.* **1960**, *91*, 294.

(9) (a) A Siemens P4 diffractometer equipped with a graphite monochromator and Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used to collect the data at −100 °C. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using all unique data and the SHELXTL program package.[9b,c] All non-hydrogen atoms were refined anisotropically with H atoms included in calculated positions (riding model). **1**: $C_{84}H_{68}BCu_2F_4N_6P_4$, monoclinic $P2_1/c$ (No. 14), $a = 15.597(1)$ Å, $b = 16.702(1)$ Å, $c = 15.573(1)$ Å, $\beta = 112.08(1)°$, $V = 3759.3(4)$ Å^3, $Z = 2$; R1 $= 0.062$, wR2 $= 0.165$ for 4986 reflections with $F > 4\sigma(F)$, $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. (b) Sheldrick, G. M. *SHELXTL-PLUS: An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1989. (c) Sheldrick, G. M. *SHELXL-93*, *Program for Crystal Structure Determination*; Universität Göttingen: Göttingen, Germany, 1993.

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the Cu/N1/N2 and N1/C5/C6/N2 planes. The coordination environment around the two copper(I) centers is not uncommon: There are two distinctly different bond lengths at 2.2097(12) Å ("equatorial" P1) and 2.2873(12) Å ("axial" P2) from the metal to the phosphorus atoms which confirm the frequently observed tendency away from a tetrahedral and toward a trigonal planar configuration.[10] The variation of N−Cu−P angles between 98° and 121° further reflects this distortion as does the sum $\Sigma = 648.52°$ of the six bond angles centered on copper; an ideal tetrahedron would have $\Sigma = 657°$ whereas $\Sigma = 630°$ for an ideal trigonal pyramid.[10b] The driving force for this distortion lies in a $\pi/\pi/\pi$ interaction between phenyl rings from PPh_3 coligands above and beneath the $bptz^{\bullet-}$ plane (Figure 1). The closest atom−atom contact at 3.224 Å (N2- -C51) lies in a range similar to the range of corresponding values in $[(Ph_3P)_2Cu(\eta^4,\mu\text{-bpym})Cu(PPh_3)_2](BF_4)_2$ (bpym = 2,2′-bipyrimidine), a diamagnetic "organic sandwich" complex.[10,a,b,f] At 2.084(4) Å the bond from copper(I) to the pyridine nitrogen atom is longer than that to the tetrazine N center (2.032(3) Å), revealing the propensity of Cu(I) to engage in π back-donation to the less basic but far better π accepting atom.[11]

The dimensions within the central tetrazine ring of bptz show significant variations, in agreement with the bond order changes as depicted in Scheme 1. Table 1 illustrates how compound **1** is indeed an intermediate between bptz and its two-electron reduced form H_2bptz with respect to bond order equilibration.

Scheme 1

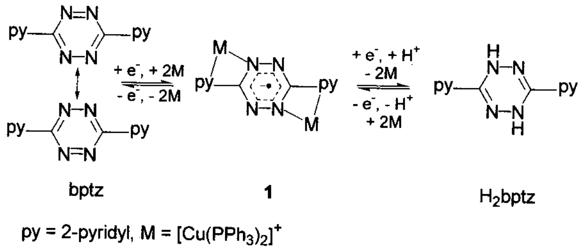

Table 1. Structural Parameters of the Tetrazine Ring in Three Oxidation States of bptz

	d(NN)[a]	d(NC)[b]	d(NCX)[c]	X	ref
bptz	1.3198(14)	1.3416(14)	1.3429(14)		7
1	1.394(5)	1.338(5)	1.320(5)	Cu	this work
H_2bptz	1.428(2)	1.281(2)	1.401(2)	H	6d
	1.431(2)	1.278(2)	1.401(2)		
H_2bptz	1.42(1)	1.28(1)	1.40(1)	H	6c
	1.43(1)	1.29(1)	1.40(1)		

[a] Distances $N^1{-}N^2$ and $N^4{-}N^5$. [b] Distances $N^2{-}C^3$ and $N^5{-}C^6$. [c] Distances $C^3{-}N^4$ and $C^6{-}N^1$.

Whereas the $N^2{-}C^3$ and $N^5{-}C^6$ bonds shorten in stepwise fashion on going from the "aromatic" state (bond order 1.5) to the C═N double bond in H_2tz and derivatives, the N−N bonds lengthen continuously (Table 1) due to the transition to a single bond. The C−NX bond lengths (X = n_N, H, or Cu, where n_N = N lone pair) should also increase, as they do on going from bptz to H_2bptz; however, the chelate coordination of the metal seems to distort the structure sufficiently to affect this parameter for compound **1**.

The structural effects thus illustrate and confirm directly the results obtained by EPR for bptz radical complexes[4,5,12] and related species,[13] indicating an almost complete localization of spin at the central tetrazine ring.

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Supporting Information Available: An X-ray crystallographic file in CIF format, including atomic coordinates, thermal parameters, complete listings of bond distances and angles, and three figures (packing, ORTEP, and non-ORTEP diagrams). This material is available free of charge via the Internet at http://pubs.acs.org.

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