The First Structural Characterization of an Azoaromatic Radical Anion Stabilized by Dicopper(I) Coordination**

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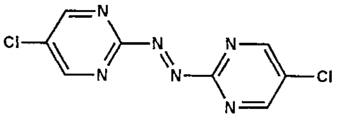
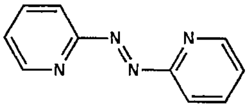
Dedicated to Professor Hans Bock
on the occasion of his 70th birthday

In contrast to the hyperoxide (superoxide) radical anion $O_2^{\cdot -}$, which has long been isolated in various forms and structurally characterized ($d_{O\text{-}O} = 1.26-1.36$ Å),[1] the related ($O \Leftrightarrow NR$) radical anions $RNNR^{\cdot -}$ of azo compounds have so far been detected only by EPR and other spectroscopic techniques.[2] This absence of structural information is all the more conspicuous as the occupation of the low-lying π^* orbital of azo compounds by one electron is also invoked in the excited-state formulation of the numerous azo-containing dyes.[3]

In the course of developing new bis-bidentate bridging ligands for molecule-mediated metal–metal communication,[4] we have recently synthesized the new compound 2,2′-azobis(5-chloropyrimidine) (abcp)[5a] and prepared its dinuclear bis(triphenylphosphane)copper complex by reaction with $[(Ph_3P)_4Cu](PF_6)$. Surprisingly, the main fraction of the isolated reaction mixture was the singly reduced compound $[(\mu\text{-abcp})\{Cu(PPh_3)_2\}_2](PF_6)$ (**1**-PF_6),[5b] which could be characterized by EPR and UV/Vis spectroscopy and X-ray crystal structure analysis.[6]



abcp



abpy

The cation $\mathbf{1}^+$ exhibits a familiar pattern of “S-frame” dimetal coordination ($d_{Cu\text{-}Cu} = 4.866(1)$ Å) as was similarly observed for $[(\mu\text{-abpy})\{Cu(PPh_3)_2\}_2](PF_6)_2$ (abpy = 2,2′-azobispyridine).[7] However, whereas the dicopper(I) complex dication in the latter compound exhibits an N=N bond length of 1.248(11) Å corresponding to a nonreduced azoaromatic ligand,[8] the monocation $\mathbf{1}^+$ displays a longer N–N bond length of 1.345(7) Å and shorter C–N(–N) bond lengths of 1.360(5) Å (Figure 1). On the other hand, the bonding parameters within the 5-chloropyrimidine rings are fairly normal (Figure 1), suggesting only minor participation of these π systems in the accommodation of the additional electron. The structural results strongly support the formulation of a bond order of 1.5 for the N–N bond, with the length of 1.345 Å lying between the values for HN=NH (calculated as 1.21 Å) and $H_2N{-}NH_2$ (1.45 Å).[9] Furthermore, this value coincides with the O–O bond distances found for MO_2 (M = Na, K).[1]

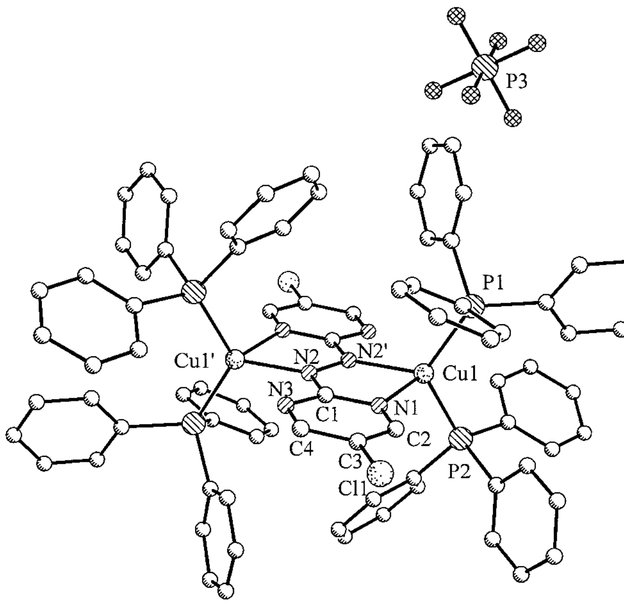


Figure 1. Molecular structure of **1**-PF_6 in the crystal. Selected bond lengths [Å] and angles [°]: Cu1–N2′ 2.045(3), Cu1–N1 2.098(3), Cu1–P2 2.2462(13), Cu1–P1 2.2636(12), N1–C2 1.337(5), N1–C1 1.360(5), N2–N2′ 1.345(7), N2–C1 1.363(5), N3–C4 1.322(6), N3–C1 1.344(5), C2–C3 1.379(6), C3–C4 1.402(6), C3–Cl1 1.720(4), Cu1–Cu1′ 4.866(1); N2′-Cu1-N1 76.58(14), N2′-Cu1-P2 113.05(10), N1-Cu1-P2 108.09(10), N2′-Cu1-P1 118.54(10), N1-Cu1-P1 103.40(10), P2-Cu1-P1 124.10(5), C1-N1-Cu1 112.2(3), N2′-N2-C1 113.6(4), N2-N2′-Cu1 117.8(4), N1-C1-N2 119.2(4).

EPR and UV/Vis spectroelectrochemical results support the formulation of a dicopper(I) complex containing an azaaromatic anion radical ligand: An EPR signal at $g = 2.0077$ with only insufficiently resolved hyperfine structure at 298 K (anisotropic line broadening[2a, g]) and a single feature at 110 K rule out any significant contribution from a formulation with copper-centered spin.[10] The long-wavelength absorptions at 700 and 560 nm for the radical species and at 930 nm for the electrogenerated dication $\mathbf{1}^{2+}$ are characteristic of metal-to-ligand charge-transfer transitions d(Cu) → π*(N=N).[10]

We attribute the unexpected formation and high stability of $\mathbf{1}^+$ mainly to the anodically shifted reduction potential of abcp (−1.01 V versus ferrocenium/ferrocene (Fc^+/Fc^0) in CH_3CN/0.1 M Bu_4NPF_6); the lowering of the π^* level in comparison to abpy ($E_{red} = -1.46$ V versus Fc^+/Fc^0 in CH_3CN/0.1 M Bu_4NPF_6) arises as a consequence of the introduction of chlorine substituents and of additional nitrogen functionalities. Furthermore, the twofold metal coordination[11] clearly facilitates the reduction of abcp; relative to the ligand, the reduction potential of the dicopper complex (+0.06 V versus Fc^+/Fc^0 in CH_2Cl_2/0.1 M Bu_4NPF_6) is shifted by more than 1 V to positive values. Finally, the metal complex fragments effectively protect the reduced azo functionality from attack by electrophiles such as H^+.[12]

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Keywords: azo compounds · bond order · copper · EPR spectroscopy · radical ions

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[5] a) Synthesis of abcp: A solution of lithium hypochlorite (50 g, 0.856 mol) in water (300 mL) was cooled until it began to solidify (external bath temperature $-30\,^{\circ}C$). A solution of 2-aminopyrimidine (5 g, 52.5 mmol) in H_2O (100 mL) was then added slowly and carefully. After completion, the orange-red reaction mixture was warmed to room temperature and extracted several times with dichloromethane. The organic phase was then purified by chromatography on silica gel (CH_2Cl_2/Et_2O, 2/1) to yield the separated red mono- and dichlorinated azo compounds. The ligand abcp was obtained in a yield of 1.20 g (18%). Correct C,H,N analysis; ^1H NMR (250 MHz, 300 K, $CDCl_3$): $\delta = 8.93$ (s). b) Synthesis of **1**-PF_6: The ligand abcp (51 mg, 0.20 mmol) and $[Cu(PPh_3)_4](PF_6)$ (503 mg, 0.40 mmol) were treated for two hours at $-70\,^{\circ}C$ in dichloromethane (10 mL). The addition of Et_2O after the mixture had warmed to room temperature precipitated the dark blue product, which was then redissolved in THF (10 mL). Careful addition of Et_2O (about 1 mL) produced a dark blue, partially crystalline material (178 mg, 54%). We attribute the reduction to the presence of excess PPh_3 (see J. W. Hershberger, R. J. Klingler, J. K. Kochi, *J. Am. Chem. Soc.* **1983**, *105*, 61). EPR (CH_2Cl_2, 298 K or 110 K): $g = 2.0077$; UV/Vis (CH_2Cl_2, 300 K): λ_{max} $(\varepsilon) = 700$ (1560), 560 (2350), 403 (6400), 373 (6270) nm ($\text{M}^{-1}\,cm^{-1}$); cyclic voltammetry (CH_2Cl_2/0.1 M Bu_4NPF_6): $E_{pa}(ox) = 1.42$ V, $E_{1/2}(red1) = 0.06$ V, $E_{1/2}(red2) = -0.75$ V versus Fc^+/Fc^0 at a scan rate of $100\,mV\,s^{-1}$.

[6] Crystal structure analysis of **1**-$(PF_6)\cdot 2\,THF$: $C_{80}H_{64}Cl_2Cu_2F_6N_6P_5\cdot 2\,C_4H_8O$, $M_r = 1720.50\,g\,mol^{-1}$, crystal size 0.4 × 0.3 × 0.6 mm, triclinic, space group $P\bar{1}$, $a = 11.5353(9)$, $b = 14.4228(10)$, $c = 14.8086(11)$ Å, $\alpha = 88.040(5)$, $\beta = 70.643(6)$, $\gamma = 66.855(5)^{\circ}$, $V = 2124.2(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.439\,g\,cm^{-3}$, $3.08^{\circ} < 2\theta < 50^{\circ}$; 8694 reflections (7472 independent; $h = -14$ to 14, $k = -17$ to 18, $l = -18$ to 19) were collected at $-90\,^{\circ}C$, 7198 reflections were used for the refinement. $R = 0.0578$ $[I > 2\sigma(I)]$, $wR_2 = 0.1748$; Siemens P4 diffractometer with graphite monochromator and $Mo_{K\alpha}$ radiation (0.71073 Å). The structure was solved by direct methods (Siemens SHELXS-86) and refined with full-matrix least-square methods (SHELXL-93). Two solvent molecules had to be included, one of which was disordered. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and refined freely (riding model). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101074. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] Note added in proof (July 24, 1998): The molecular structure of Ru complexes of azoaromatic radical anions will be reported by A. Chakravorty et al.

Highly Enantioselective Catalytic Hetero-Diels–Alder Reaction with Inverse Electron Demand[**]

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The hetero-Diels–Alder reaction of α,β-unsaturated carbonyl compounds with electron-rich alkenes gives excellent access to substituted 3,4-dihydro-2*H*-pyrans that are very useful precursors for the synthesis of carbohydrates and natural products.[1] The reaction is controlled by the LUMO of the α,β-unsaturated carbonyl compound and the HOMO of the dienophile; electron-withdrawing substituents on the former greatly enhances the reactivity.[1, 2]

Although the reaction usually is highly regioselective, Lewis acids can improve both regioselectivity and reaction rate.[1c] A variety of different achiral Lewis acids, such as $EtAlCl_2$,[3] Me_2AlCl,[3] $ZnCl_2$,[3] $TiCl_4$,[3] $Eu(fod)_3$,[4] $Yb(fod)_3$,[5] $LiClO_4$,[6] $Mg(ClO_4)_2$,[6] and $SnCl_4$[7] have been shown to catalyze inverse hetero-Diels–Alder reactions (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadiene).

Although much work has been devoted to the diastereoselective hetero-Diels–Alder reaction with inverse electron demand,[3a, b, 8] the enantioselective addition of electron-rich alkenes to α,β-unsaturated carbonyl compounds with chiral Lewis acids as catalysts is still a relatively unexplored field and only very few reactions have been reported. Examples include the intramolecular cycloaddition of an oxadiene with a diisopropylideneglucose–titanium complex as catalyst (33–88% *ee* for the tetracyclic product),[9] and a reaction catalyzed by *trans*-(4,5-dihydro-4,5-diphenyloxazole)–$Mg(ClO_4)_2$ which yields both ene and hetero-Diels–Alder products in a 89:11 ratio (89% *ee* for the ene product).[1c] Kanemasa has reported an intermolecular hetero-Diels–Alder reaction with inverse electron demand in which the enantioselective addition of (*E*)-oxo-phenylsulfonyl-3-alkenes to enol ethers

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