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A Coordination-Induced 1,4 → 1,2-Quinonediimine Isomerization**

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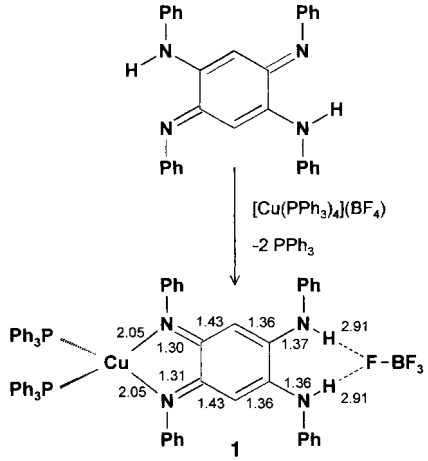
Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

Azophenine (2,5-diamino-1,4-benzoquinonediimine, ap) is a long known *para*-quinonoid compound, which can be obtained in various ways from aniline.[1] Although azophenine bears a close similarity to the increasingly used bis-chelate ligand family derived from 2,5-dihydroxy-1,4-benzoquinone[2] its coordination chemistry has hitherto remained unexplored.[3] This is all the more surprising since metal complexes of quinonoid compounds with O and N donor functionalities have been much studied recently for reasons of their unusual electronic structures (with sometimes ambiguous oxidation state formulations),[4] their potential uses in molecular biology,[5] and their possible occurrence in enzymes.[6] In particular, copper-dependent amine oxidases show an interaction between the redox-active metal center and a functionalized "topaquinone" ligand present as a modified tyrosine side chain.[7–9] Since this topaquinone ligand reacts with amine substrates to form quinoneimine intermediates,[6, 8, 9] we set out to treat copper compounds with the bifunctional azophenine ligand.

Treatment of azophenine with $[Cu(PPh_3)_4](BF_4)$ in acetone (or dichloromethane) results in the spontaneous formation of the copper(I) complex $[Cu(PPh_3)_2(ap)](BF_4)$ (**1**, Scheme 1).[10] The complex is highly soluble in acetone, dichloromethane, and alcohols, but insoluble in hydrocarbons. Any remaining azophenine could be removed by column chromatography. Treatment of ap with two equivalents of $[Cu(PPh_3)_4](BF_4)$ also yielded the mononuclear complex and not a dinuclear compound.

Single crystals of **1** were obtained from a solution of acetone/pentane and were analyzed by crystallography.[11] They were found to contain three equivalents of acetone as supported by elemental analysis and ^1H NMR spectroscopy. Refinement of the molecular structure (Figure 1) revealed two quite remarkable structural features of **1**:



Scheme 1. Synthesis of **1** from ap. The general bond pattern in **1** and selected bond lengths [Å] are shown.

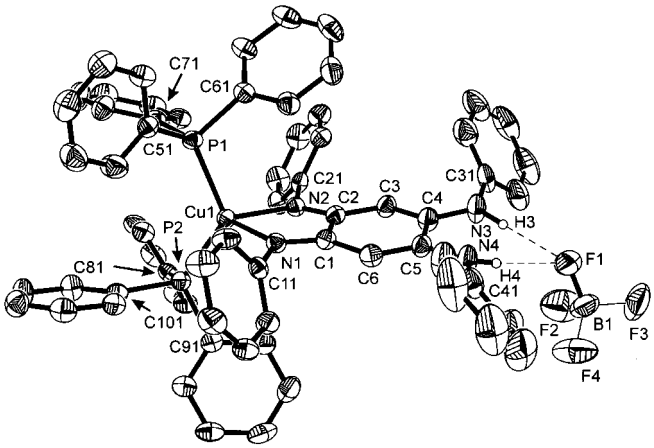


Figure 1. View of the structure of **1** in the crystal. Selected bond lengths [Å] and bond angles [°]: Cu1 – N1 2.052(4), Cu1 – N2 2.054(4), Cu1 – P2 2.2439(13), Cu1 – P1 2.2571(13), N1 – C1 1.307(5), N2 – C2 1.300(5), N3 – C4 1.368(6), N4 – C5 1.364(6), C1 – C6 1.430(6), C1 – C2 1.483(6), C2 – C3 1.426(6), C3 – C4 1.357(6), C4 – C5 1.486(6), C5 – C6 1.360(6); N1-Cu1-N2 79.18(14), N2-Cu1-P2 115.90(11), N2-Cu1-P1 104.88(11), C1-N1-Cu1 114.5(3), N1-Cu1-P2 111.57(11), N1-Cu1-P1 114.42(11), P2-Cu1-P1 122.62(5), C2-N2-Cu1 114.5(3).

1) The tetracoordinate copper(I) center is bound in a chelate fashion by two *o*-quinonediimine N-donor centers; the C=N bond lengths (standard deviation ≤ 0.006 Å) and the general bond pattern within the six-membered ring are summarized in Scheme 1. Clearly, there has been an isomerization from the usually more stable *para*-quinonediimine state[12] to the higher energy *ortho* form to allow the formation of a chelate complex between the π electron-rich metal and a strongly π-accepting[4b,c, 13] *o*-quinonediimine ligand.[14] This situation results in the occurrence of a metal-to-ligand charge transfer (MLCT) absorption of the complex at 525 nm (Figure 2); the long-wavelength intraquinone transition of the free ligand at 390 nm is slightly shifted to 395 nm in the complex.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagen Foundation, and the Fonds der Chemischen Industrie. We thank Dr. K.-W. Klinkhammer for helpful suggestions, and T. Sixt and T. Scheiring for assistance.

  1433-7851/98/3719-2681 $ 17.50+.50/0

2) The secondary amine functionalities in the 4,5-positions engage in N–H···F···H–N "chelate" hydrogen bonding[15] to one flourine center of the tetrafluoroborate anion (Scheme 1, Figure 1). The three remaining fluorine atoms are disordered.[11]

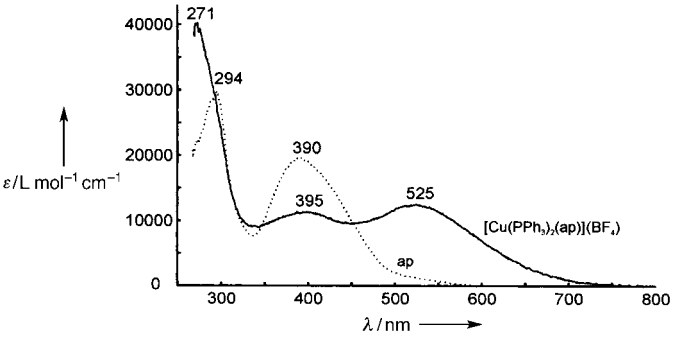

Figure 2. UV/Vis absorption spectrum of azophenine (ap) and **1** in dichloromethane.

Effects 1) and 2), therefore, both contribute to the stabilization of the *ortho*-quinonoid over the usually lower energy *para*-quinonoid form,[12] thus illustrating a further aspect to be considered in the intriguing coordination chemistry[2, 4, 13] of quinonoid ligands.

Received: May 4, 1998 [Z11808IE]
German version: *Angew. Chem.* **1998**, *110*, 2827–2829

Keywords: copper · hydrogen bonding · isomerizations · N ligands · quinones

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[10] Synthesis of **1**: A solution of $[Cu(PPh_3)_4](BF_4)$ (600 mg, 0.50 mmol) in acetone (10 mL) was added to a stirred suspension of azophenine[1d] (220 mg, 0.50 mmol) in acetone (20 mL). A rapid change from orange to deep purple was observed. After one hour the solution was filtered and subjected to column chomatography on silica gel. Elution with acetone/pentane (9/1) yielded first some azophenine and then the purple complex $[Cu(PPh_3)_2(ap)](BF_4)$ (**1**) (415 mg, 66%). Single crystals suitable for X-ray diffraction were grown at 4 °C from a solution of acetone/pentane (1/1) and were identified from crystallography as the solvate $[Cu(PPh_3)_2(ap)](BF_4)\cdot 3$ acetone. Correct C,H,N analysis; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 525$ (12500), 395 (11400 M^{-1} cm^{-1}) nm; ^1H NMR ($CDCl_3$): $\delta = 7.96$ (s, 2H, N-*H*), 6.7–7.4 (m, 50H, Ph), 6.21 (s, 2H, C3-*H*, C6-*H*), 2.15 (s, 18H, acetone solvate).

[11] a) Crystals of $[Cu(PPh_3)_2(ap)](BF_4)\cdot 3C_3H_6O$ were immersed in Nujol. One well-shaped crystal of dimensions $0.4 \times 0.3 \times 0.3$ mm^3 was transferred into a capillary and mounted on a Syntex P3 diffractometer. Data were collected at −90 °C with $Mo_{K\alpha}$ radiation (0.71069 Å, ω-scan): 12346 collected, 11541 unique, and 10929 observed reflections; 932 parameters and 84 restraints; $2\theta_{max} = 50°$. $C_{66}H_{54}BCuF_4N_2P_2\cdot 3C_3H_6O$, $M_r = 1289.66$ g mol^{-1}, monoclinic, space group $P2_1/c$ (No. 14), $a = 16.971(5)$, $b = 17.848(4)$, $c = 23.346(5)$ Å, $\beta = 107.36(2)°$, $V = 6749(3)$ $Å^3$, $Z = 4$, $\rho_{calcd} = 1.269$ g cm^{-3}, $\mu = 4.32$ cm^{-1}, $wR2 = 0.194$ ($R1 = 0.070$ based on 8244 reflections with $F_0 > 4\sigma(F_0)$). Largest difference peak/hole: +0.94/−0.59 e $Å^{-3}$. The structure was solved by direct methods by using the SHELXTL-PLUS package.[11b] Refinement was achieved with the same program employing full matrix least-squares methods on $|F^2|$. Except for the three disordered fluorine atoms and the solvent molecules, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined without geometrical constraints by adjusting their isotropic displacement parameters to 1.2 times the value for the corresponding carbon and nitrogen atoms. The BF_4^- ion showed disorder in terms of rotation around the B1–F1 axis in two orientations (50% occupation each). Acetone solvent molecules were found on three different sites in the asymmetric unit. 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-101396. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336–033; e-mail: deposit@ccdc.cam.ac.uk); b) G. M. Sheldrick, SHELXTL-PLUS An Integrated System for Solving, Refining and Displaying Structures from Diffraction Data, Rel. 5.03, Siemens Analytical X-Ray Instruments Inc., **1994**.

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