# Anion−π Interactions in a Carousel Copper(II)−Triazine Complex

Serhiy Demeshko, Sebastian Dechert, and Franc Meyer*

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany

Received January 30, 2004; E-mail: franc.meyer@chemie.uni-goettingen.de

Supramolecular interactions of aromatic systems have attracted considerable attention during the past few years.[1] While simple aromatics tend to associate via enthalpically preferred edge-to-face C−H···π contacts, the benzene−hexafluorobenzene complex shows favorable face-to-face stacking in its crystal structure.[2] This has been attributed to the large, permanent quadrupoles of the two molecules, which are similar in magnitude but of opposite sign. The ability of the π-cloud of aromatic compounds to interact with positively polarized or charged atoms is not limited to C−H···π interactions. One intuitively expects attractive forces between the π-system as a source of electron density and electron-deficient cations, and it is now well-known that noncovalent cation−π interactions are of great importance for many systems, including biological macromolecules.[3] In contrast, the concept of anion binding to aromatic rings is less intuitive and any interaction between electron donors and aromatic π-clouds is usually expected to be repulsive. The question of whether anion−π interactions exist has been raised in several recent publications. NMR studies have indicated association between neutral π-moieties and negatively charged groups,[4] and computational evidence indeed suggests that noncovalent electrostatic bonding between anions and π-electron-deficient aromatic rings such as hexafluorobenzene or 1,3,5-trinitrobenzene is energetically favorable.[5] The same is true for the synthetically more versatile π-deficient heteroaromatics 1,3,5-triazine and 1,2,4,5-tetrazine.[6,7,8] Mascal et al. have calculated an equilibrium distance of 3.2 Å between chloride and the aryl centroid in the Cl⁻···triazine complex 1, with the anion positioned on the C_3-axis above the ring.[6] While unambiguous crystallographic evidence for such anion−π bonding involving simple halide ions was still lacking, the theoretical prediction of an attractive anion−π interaction has already led to the proposal of heteroaromatics such as triazine and tetrazine as modules of new receptors for molecular anion recognition.[6,7]
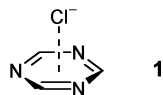
During our investigations of structural and magnetic properties of metal complexes with the hexakis(pyridin-2-yl)-[1,3,5]-triazine-2,4,6-triamine ligand (L), we have synthesized a copper(II) chloride complex that shows chloride−triazine binding with metric parameters almost exactly the same as those predicted theoretically for **1**.

Reaction of 3 equiv of copper(II) chloride with 1 equiv of L gives dark green crystals of [L₂(CuCl)₃][CuCl₄]Cl (**2**), which contain noncoordinating CH₂Cl₂ and CH₃OH solvent molecules in the crystal lattice.[9] The cationic moiety of **2** consists of two ligands L that are stacked in a parallel fashion and held together by three copper(II) ions in a [L₂(CuCl)₃]³⁺ carousel structure (Figure 1). Four pyridine-N and an apical chloride constitute a square-pyramidal coordination environment for each metal center. Cl atoms of CH₂Cl₂
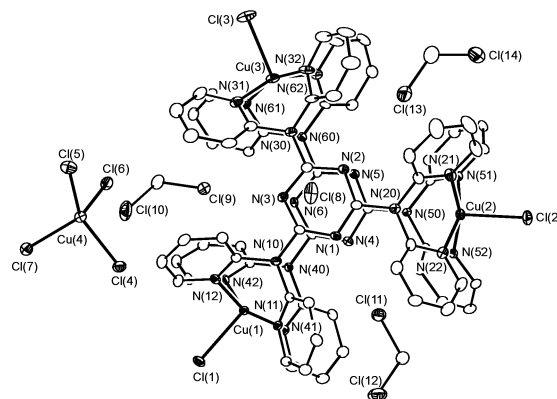

Figure 1. Structure of **2** (ORTEP; 30% probability thermal ellipsoids). All hydrogen atoms, two CH₂Cl₂, and CH₃OH are omitted for clarity. Selected bond lengths [Å]: Cu(n)−Cl(m), 2.382(1)−2.407(1) ($n = m = 1$−3), 2.238(1)−2.261(1) ($n = 4$, $m = 4$−7); Cu(n)−N, 2.025(4)−2.044(4) ($n = 1$), 2.022(4)−2.037(4) ($n = 2$), 2.016(4)−2.036(4) ($n = 3$).
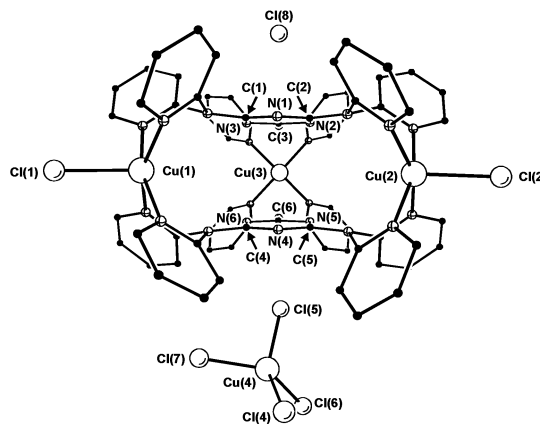

Figure 2. Emphasis of the position of the chlorine atoms Cl(8) and Cl(5) in relation to the cationic [L₂(CuCl)₃]³⁺ moiety of **2**. Distance from Cl(8) to [C(1)−N(3)] mean plane, 3.166(2) Å, and from Cl(8) to [C(1)−N(3)] ring centroid, 3.170(2) Å; ring-slippage, 0.163 Å. Angle of the Cl(8)−[C(1)−N(3)] centroid axis to the plane of the ring [C(1)−N(3)], 87.1(1)°. Distance from Cl(5) to [C(4)−N(6)] mean plane, 3.109(2) Å, and from Cl(5) to [C(4)−N(6)] ring centroid, 3.112(2) Å; ring-slippage, 0.118 Å. Angle of the Cl(5)−[C(4)−N(6)] centroid axis to the plane of the ring [C(4)−N(6)], 87.8(1)°.

solvent molecules are located between the paddle wheels of the (noncrystallographically) 3-fold symmetric [L₂(CuCl)₃]³⁺ complex. The [CuCl₄]²⁻ ion shows the expected strongly distorted tetrahedral geometry

Interestingly, both triazine rings in **2** are arranged in an almost perfect face-to-face arrangement (Figure 2) with the N atoms of one triazine ring located over the N atoms of the second ring. Although the distance between both triazine planes (3.78 Å) is somewhat larger than the distance usually found for aromatic stacking (3.5 Å), such enlargement is often observed for aromatic nitrogen-containing ligands.[1] It should be noted, however, that
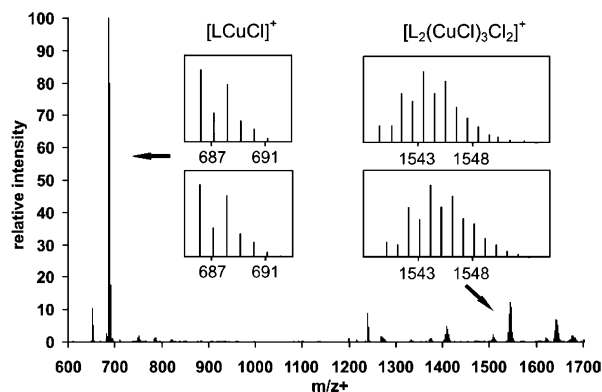
Figure 3. ESI mass spectrum of $[L_2(CuCl)_3][CuCl_4]Cl$ in methanol. Insets show the experimental (top) and simulated (below) data of characteristic fragments.

typically one ring is horizontally displaced by about 1.30 Å, in contrast to the situation in **2**. A similar face-to-face arrangement of two triazine rings has recently been found in $[\{(CO)_3Re(\mu\text{-}OC_4H_9)_2Re(CO)_3\}_3(\text{tri-2,4,6-pyridin-3-yl-1,3,5-triazine})_2]$, where the distance of the two ring centroids is 3.55 Å.[10] In contrast, the copper(I)−triazine complex $[(CuCl)_6(P(OPh))_6(1,3,5\text{-triazine})_2]$ features a face-to-face alignment with the triazine rings rotated by 60° with respect to each other, i.e., the N-atoms of one triazine ring are located over C-atoms of the second triazine ring.[11] This latter stacking arrangement should be electrostatically more favorable, and accordingly shorter ring−ring distances of 3.41/3.45 Å have been determined for that case.

Besides the unique and esthetically pleasing carousel structure of $[L_2(CuCl)_3]^{3+}$ itself, the most interesting feature of **2** concerns the position of the charge-compensating chloride and $[CuCl_4]^{2-}$ ions. Cl(8) resides above one of the triazine rings (Figure 2), where the distance between the centroid of this ring and the chlorine atom is 3.17 Å. The angle of the Cl⁻···centroid axis to the plane of the ring (87°) gives evidence that the chlorine atom is almost perfectly located on the C_3-axis above the ring.

Both values are in excellent agreement with values obtained from ab initio molecular orbital calculations for the parent chloride-1,3,5-triazine complex **1** (3.2 Å and 90°)[6] and also agree well with the equilibrium distance determined between C_6F_6 and Cl⁻ (3.155 Å, MP2/6-31++G** level).[5a] Hence, it is safe to state that a Cl⁻···triazine complex due to electrostatic anion−π interaction is present in **2**. The closest distance of Cl(8) to non-hydrogen atoms of the next neighboring $[L_2(CuCl)_3]^{3+}$ moiety and the adjacent CH_2Cl_2 is approximately 3.6 Å. Disordered solvent molecules are also present in close vicinity.

In a similar fashion, the opposite triazine face of the $[L_2\text{-}(CuCl)_3]^{3+}$ carousel is capped by the second counteranion of **2**, with an even shorter distance of 3.11 Å observed between the chlorine atom Cl(5) of the $[CuCl_4]^{2-}$ ion and the centroid of the [C(4)−N(6)] triazine ring (Figure 2). Again the chlorine atom is almost perfectly centered on the ring (angle to the Cl···centroid axis 88°). The O atom of an adjacent methanol is 3.206(5) Å away from Cl(5), suggesting the presence of hydrogen bonding between these atoms.[12] It should be noted that comparable distances between halogens and π systems have been observed for dihalogen π-donor complexes (e.g., Cl_2···Benzol 3.3 Å), even though the polarization is probably reversed in those cases.[13]

Interactions between chloride and $[L_2(CuCl)_3]^{3+}$ appear to be persistent also in solution and the gas phase. A stable $[L_2(CuCl)_3]Cl_2^+$

ion is detected as a prominent peak in the ESI mass spectrum of $[L_2(CuCl)_3][CuCl_4]Cl$ in methanol (Figure 3).

Comparison of the results from recent theoretical calculations and the crystallographic data obtained for the structure reported in this article clearly confirm the presence of anion−π interactions for the triazine rings in $[L_2(CuCl)_3][CuCl_4]Cl$. Checking the CSD for intra- or intermolecular contacts of halide atoms to 1,3,5-triazine rings reveals that halide contacts of less than 3.4 Å to the triazine centroid also occur in some melaminium salts of $Cu_2X_6^{2-}$ dimers.[14] Without usually being recognized as such, anion−π interactions are apparently quite versatile and should be of general importance for the solid-state structures and the supramolecular assembly of complexes with π-electron-deficient heteroaromatics.

Supporting Information Available: Synthetic procedure and analytical data for **2** (PDF) and crystallographic details for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885.
(2) (a) Williams, J. H.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem.* **1992**, *104*, 1666; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1655. (b) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593.
(3) (a) Schneider, H.-J. *Angew. Chem.* **1991**, *103*, 1419; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1417. (b) Schneider, H.-J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry;* Wiley & Sons: Chichester, 2000. (c) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem.* **2003**, *115*, 1244; *Angew. Chem., Int. Ed.* **2003**, *42*, 1210.
(4) Schneider, H.-J.; Werner, F.; Blatter, T. *J. Phys. Org. Chem.* **1993**, *6*, 590.
(5) (a) Quiñonero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *Angew. Chem.* **2002**, *114*, 3539; *Angew. Chem., Int. Ed.* **2002**, *41*, 3389. (b) Quiñonero, D.; Garau, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *Chem. Phys. Lett.* **2002**, *359*, 486.
(6) Mascal, M.; Armstrong, A.; Bartberger, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 6274.
(7) Garau, C.; Quiñonera, D.; Frontera, A.; Costa, A.; Ballester, P.; Deyà, P. M. *Chem. Phys. Lett.* **2003**, *370*, 7.
(8) Garau, C.; Frontera, A.; Quiñonero, D.; Ballester, P.; Costa, A.; Deyà, P. M. *Chemphyschem* **2003**, *4*, 1344.
(9) Crystal Data: $[C_{66}H_{48}Cl_3Cu_3N_{24}]^{3+}$, $[CuCl_4]^{2-}$, Cl⁻, $5CH_2Cl_2$, CH_3OH, $M = 2171.72$, $T = 133$ K, orthorhombic, $a = 15.7269(2)$, $b = 15.7630$-(2), $c = 38.0222(5)$ Å, $V = 9425.8(2)$ Å³, space group $P2_12_12_1$ (no. 19), $Z = 4$, $\rho_{calcd} = 1.53$ g/cm³, μ(Mo Kα) = 1.455 mm⁻¹, 144 364 reflections measured, 21 598 unique ($R_{int} = 0.073$), final R indices [$I > 2\sigma(I)$] $R1 = 0.0509$, w$R2 = 0.1241$, [all data] $R1 = 0.0566$, $wR2 = 0.1267$, Flack-parameter 0.042(9). Additionally, the unit cell contains disordered CH_2-Cl_2 and CH_3OH solvent molecules that occupy an area of 1270.5 Å³ (13.5%). No satisfactory model for the disorder could be found, and for further refinement the contribution of the missing solvent molecules (total electron count 332) was subtracted from the reflection data by the SQUEEZE[15] routine of the PLATON[16] program. An accurate determination of the stoichiometric quantity of solvent in the crystal was not possible, so no contribution from the solvent has been included in the calculations of molecular formula, $F(000)$ value, μ, and density.
(10) Manimaran, B.; Rajendran, T.; Lu, Y.-L.; Lee, G.-H.; Peng, S.-M.; Lu, K.-L. *Eur. J. Inorg. Chem.* **2001**, 633.
(11) Pike, R. D.; Borne, B. D.; Maeyer, J. T.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 631.
(12) Using the calculated position of the hydroxide H atom gives values of 140° for the O−H···Cl angle and 2.53 Å for the H···Cl distance.
(13) (a) Vasilyev, A. V.; Lindeman, S. V.; Kochi J. K. *New J. Chem.* **2002**, *26*, 582. (b) Legon, A. C. *Angew. Chem.* **1999**, *111*, 2850; *Angew. Chem., Int. Ed.* **1999**, *38*, 2686. (c) Ouvrard, C.; Le Questel, J.-Y.; Berthelot, M.; Laurence, C. *Acta Crystallogr.* **2003**, *B59*, 512.
(14) (a) Colombo, A.; Menabue, L.; Motori, A.; Pellacani, G. C.; Porzio, W.; Sandrolini, F.; Willett, R. D. *Inorg. Chem.* **1985**, *24*, 2900. (b) Scott, B.; Geiser, U.; Willett, R. D.; Patyal, B.; Landee, C. P.; Greeney, R. E.; Manfredini, T.; Pellacani, G. C.; Corradi, A. B.; Battaglia, L. P. *Inorg. Chem.* **1988**, *27*, 2454.
(15) Sluis, P.v.d.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.
(16) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

JA049458H