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Silver Corroles

Ligand Noninnocence in Silver Corroles: A XANES Investigation

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Abstract: Structural, optical spectroscopy, and DFT studies have recently suggested a remarkable electronic–structural switch between simple silver *meso*-triarylcorroles and silver β-octabromo-*meso*-triarylcorroles: the former were described as essentially innocent and the latter as substantially noninnocent. In a first X-ray absorption near-edge spectroscopic (XANES) study of ligand noninnocence in metallocorroles, Ag L_3-edge spectra have now provided direct experimental support for the variable electronic structure of silver corroles.

Introduction

Metallocorroles have provided many new examples of the phenomenon of ligand noninnocence in recent years, with the coinage metal corroles providing for an especially fascinating area of study.[1] Copper corroles are believed to be invariably noninnocent, with electronic structures best described as $\mathrm{Cu^{II}}$-corrole$^{\cdot 2-}$,[2–4] whereas gold corroles are innocent and best described as $\mathrm{Au^{III}}$-corrole^{3-}.[5] In a recent study, we concluded that silver corroles are poised on a knife-edge in this regard, adopting innocent or noninnocent electronic structures depending on the substitution pattern of the corrole.[6] Thus, simple silver *meso*-triarylcorroles were thought to be best formulated as $\mathrm{Ag^{III}}$-corrole^{3-}, whereas silver β-octabromo-*meso*-triarylcorroles appeared best formulated as $\mathrm{Ag^{II}}$-corrole$^{\cdot 2-}$.

The evidence for this electronic–structural switch in silver corroles comes from multiple sources. The X-ray structures of coinage metal corroles provide arguably the most compelling evidence for the above picture.[1] Thus, whereas copper corroles invariably exhibit strong saddling, which has been interpreted as indicative of antiferromagnetic coupling between a Cu $d_{x^2-y^2}$ electron and an "a_{2u}-type" corrole radical (using porphyrin nomenclature for the corrole HOMO, Figure 1),[2–4] gold corroles are at best only mildly saddled.[5] Simple silver triarylcorroles are also mildly saddled, but less so than analogous copper corroles.[5c,7,8] In contrast, the first crystal structure of a silver β-octabromo-*meso*-triarylcorrole revealed a strongly saddled macrocycle, with the degree of saddling essentially matching that observed for copper β-octabromo-*meso*-triarylcorroles.[6] Our tentative conclusion thus was that the silver octabromocorrole presumably had the same type of noninnocent electronic structure as its copper analogue.

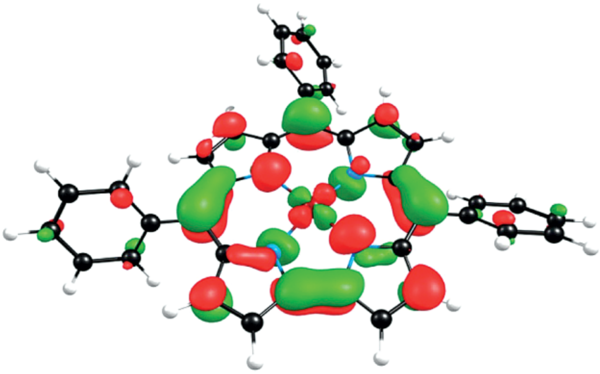

Figure 1. The Cu($d_{x^2-y^2}$)-corrole(π) orbital interaction thought to be responsible for the saddling of copper corroles.

Second, over a long series of studies, we found that the Soret maxima of noninnocent metallotriarylcorroles (M = Cu,[3,4a] FeCl,[9] FeNO,[10] MnCl,[11] Pt[12] etc.) shift markedly as a function of the electron-donating/withdrawing character of the *para* substituents on the *meso*-aryl groups. For innocent metallotriarylcorroles (M = Au,[5c] CrO/MoO,[13] OsN,[14] ReO,[15] etc.), the Soret maximum exhibits no such sensitivity to the nature of the *para* substituents. In the case of silver, simple silver triarylcorroles do not exhibit substituent-sensitive Soret bands,[5c] but the Soret maxima of the octabromo series exhibit quite significant shifts as a function of *meso*-aryl substituents,[6] which lends credence to the idea of a variable electronic structure for silver corroles. Third, DFT calculations also provided strong support for our ideas about the electronic structure of Ag corroles.[6]

Despite the multiple lines of evidence, there can be no denying that the above electronic–structural picture is unusual; we are not aware of any other set of complexes, where simple peripheral substitution of a porphyrin-type ligand results in an analogous electronic–structural switch. Under the circumstances, Ag L_3 X-ray absorption near-edge spectroscopy (XANES) appeared to provide the ideal tool for probing the metal oxid-

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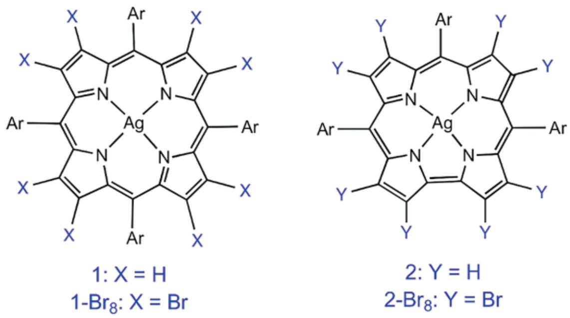
ation state (the Ag *K*-edge being too high in energy for accurate measurements of edge-shifts associated with oxidation state change).[16,17] Accordingly, we examined the four complexes shown in Figure 2. Gratifyingly, the results proved fully consistent with our idea of an electronic–structural switch between simple silver corroles and their β-octabromo counterparts, as described below.



1: X = H
1-Br$_8$: X = Br

2: Y = H
2-Br$_8$: Y = Br

Figure 2. Compounds examined by Ag L$_3$-edge XANES in this study.

Results and Discussion

Figure 3 presents the normalized Ag L-edge XANES data for **1**, **1-Br$_8$**, **2** and **2-Br$_8$**. The Ag L-edge spectrum reflects the electric dipole-allowed 2p→4d transition that splits into two peaks (L$_3$ and L$_2$) separated by $3/2\lambda_{LS}$ (λ_{LS} = spin-orbit coupling), with the L$_3$ edge reflecting the 2p$_{3/2}$ state. Previous Cu L-edge studies have shown that the L$_3$ pre-edge energy shifts to a higher value with an increase in the ligand-field strength (LF).[18,19] The same considerations are expected to apply to the present study as well. Furthermore, the integrated intensity of the L$_3$-edge spectrum should be directly correlated with the amount of Ag 4d-hole character in the ground-state wavefunction. These expectations are fully borne out in the Ag L$_3$-edge of the two bona fide Ag$^{\text{II}}$ complexes **1** and **1-Br$_8$**, which both occur at 3349.7 eV, with similar integrated areas (13 and 9 units), and in that of the supposed Ag$^{\text{III}}$ complex **2**, which occurs at 3352.1 eV with a significantly larger integrated area (24 units). These observations are consistent with the expected doubling in the number of d-holes in **2** relative to **1** and **1-Br$_8$**. On going from **2** to **2-Br$_8$**, the pre-edge position downshifts to 3351.4 eV, which is halfway between the supposed Ag$^{\text{II}}$ and Ag$^{\text{III}}$ species. The intensity and total area (21 units) also decrease. These observations indicate a decrease in the valence Ag 4d-hole character in **2-Br$_8$**, which in turn is consistent with significant Ag$^{\text{II}}$-corrole$^{\cdot 2-}$ character.[6]

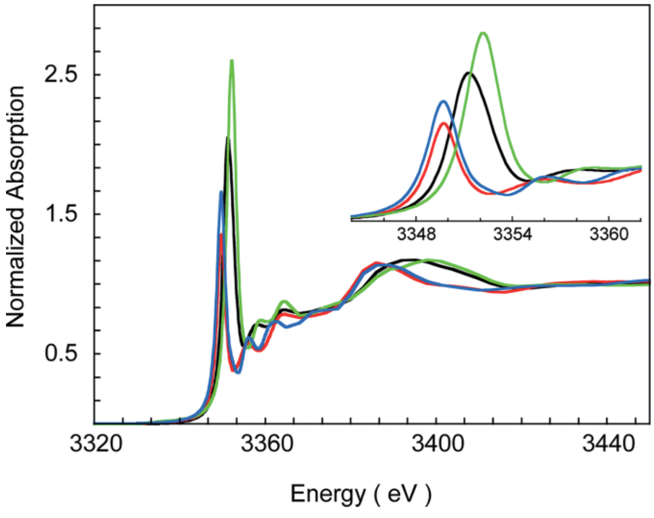


Figure 3. Normalized Ag L$_3$-edge XANES data for 1 (blue line), 1-Br$_8$ (red line), 2 (green line) and 2-Br$_8$ (black line). The inset shows the expanded 2p→4d pre-edge region.

Conclusion

To sum up, Ag L$_3$-edge XANES has provided direct experimental support for ligand noninnocence in the silver corrole **2-Br$_8$** and thereby also for the unique electronic–structural switch described above.[6] The present study is the first to apply XANES to probe the issue of ligand noninnocence in metallocorroles. Given the widespread occurrence of ligand noninnocence in metallocorroles, there can be little doubt that XANES will play an increasingly important role in the elucidation of many of the unique subtleties of metal-corrole bonding.

Experimental Section

Materials and Instrumentation: All reagents and solvents were used as purchased, except pyrrole, which was passed through basic aluminum oxide 60 (Activity I, 0.063–0.200 mm particle size, Merck Millipore) before use. Basic alumina 60 and silica gel 150 (35–70 µm particle size, Davisil) were used for flash chromatography. Complexes **1**,[20] **2**,[7b] and **2-Br$_8$**[6] were prepared as described previously in the literature. Although previously reported,[21] **1-Br$_8$** was prepared via a new protocol as described below. Spectroscopic data for all four complexes matched those reported in the literature. Ultraviolet-visible spectra were recorded on an HP 8453 spectrophotometer. Mass spectra were recorded on an LTQ Orbitrap XL spectrometer.

Synthesis of 1-Br$_8$: Silver(I) acetate (4 equiv., 27 mg, 0.16 mmol) was added to a hot (65 °C) solution of free-base 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (50 mg, 0.04 mmol) in THF (20 mL). Upon stirring at 65 °C, the mixture gradually changed from green to orange and subsequently to brown. TLC indicated completion of the reaction after 30 min. After evaporation of the solvent, the residue obtained was chromatographed on a basic alumina column with CHCl$_3$ as eluent. The product **1-Br$_8$** was obtained in 61 % (33 mg) yield upon removal of the solvent. UV/Vis (THF) λ_{max}, nm ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 384 (2.88), 454 (11.05), 527 (1.23), 572 (1.36), 609 (0.70). HRMS (ESI$^+$, major isotopomer): [M]$^+$ = 1350.4124 (expt), 1350.4132 (calcd).

The Ag L-edge X-ray absorption spectra of **1**, **1-Br$_8$**, **2** and **2-Br$_8$** were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) on the unfocused 20-pole 2 T wiggler side-station beamline 4–3 under standard ring conditions of 3 GeV and approximately 500 mA. Standard room temperature measurement protocols were employed,[22,23] including a He–sample chamber and a PIPS detector for measuring fluorescent photons. All complexes were measured as solids: the samples were ground with a mortar and pestle and applied on Kapton tape as a thin layer. Single-point internal energy calibration was accomplished by simultaneous measurement of the absorption of a silver metal foil placed between the two ionization chambers situated after the sample. The first inflection point of the foil L_3-edge spectrum was fixed at 3551 eV. All the samples were resistant to photoreduction/damage. The data presented here are 3-scan averages for all samples and were processed in the Demeter suite of programs.[24] The data were then renormalized in Kaleidagraph for comparison and quantification purposes.

Supporting Information (see footnote on the first page of this article): Ag *K*-edge EXAFS data for **1**, **1-Br$_8$**, **2** and **2-Br$_8$** (5 pages).

Acknowledgments

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Keywords: Silver · Corrole · Noninnocence · XANES · X-ray absorption

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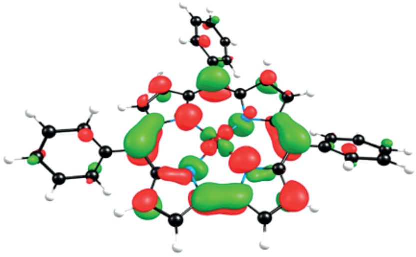

Silver L_3 X-ray absorption spectroscopy has provided direct experimental support for variable innocent/noninnocent electronic structures among silver corroles.

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