Can ternary surface complexes and surface hydroxy polymer coexist as sorbed species? A multiple spectroscopy approach

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The mobility of trace elements in surficial environments is, to a large extent, controlled by the interplay of two types of reaction. Adsorption onto solid particles leads to the immobilization of the trace element whereas complexation with dissolved ligands leads to their enhanced mobility. Metal ions and ligands can further be adsorbed together forming mixed complexes. Ligands and metal ions are immobilized at the water-mineral interface in this way. This phenomenon, referred to as a ternary surface complex formation, has been shown to play an important role not only in the migration of trace elements in soils and natural waters, but also in heterogeneous catalysis, mineral flotation and natural photocatalytic processes. In this paper we report on the model Cu^{2+}-bipyridine(bipy)–silica system. Together with wet chemical studies, three spectroscopic techniques have been used in this study: UV reflection, Electron Spin Resonance (ESR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopies.

Wet chemical data indicate the formation of >SiO-Cu-bipy and >SiO-Cu-$(bipy)_2$ from solutions of Cubipy complexes, depending on the speciation in solution. The symbol $>SiO^-$ refers to a deprotonated reactive surface site, a site which can be formed of one or two silanol groups (see Motschi, 1984). No assumption is made at this point regarding the molecular structure of the >SiO-Cu-$(bipy)_i$ complexes, corner or edge sharing between the copper distorted octahedron and the silica tetrahedra. Data could be adequately described within the constant capacitance complexation model framework, as done previously (Bourg and Schindler, 1978). Different formation constants for >SiO-Cu-bipy are however derived using this approach, depending on whether the complex is formed by >SiOH with previously formed Cu-bipy complex or >SiO-Cu with bipy. The thermodynamic circle is therefore not closed, and the true existence of assumed surface species has to be questioned.

The existence of isolated inner-sphere surface complex, such as $>SiO\text{-}Cu^+$, is at odds with the interpretation of the EXAFS Radial Distribution Functions (RDF). The observed Cu-O and Cu-Cu distances, and the corresponding number of atoms in each neighbour shell, in the sorbed sample are similar to those observed in copper hydroxy phases, and even closer to those observed in crystalline $Cu(OH)_2(s)$ than to those observed in amorphous $Cu(OH)_2(s)$. These results clearly contradict the model in which some Cu octahedra would share only one edge with silica tetrahedra, and others only one or two corners as such a model would result in a much lower number of Cu neighbours (Motshi, 1984). Instead they are fully consistent with the formation of linear edge sharing chains of Cu octahedra, i.e. $Cu(OH)_2(s)$. This phase forms in conditions and where surface coverage was equal to 1.0% and 6.3% and where local supersaturation in solution, i.e. homogeneous precipitation, was avoided as much as possible. Indeed the resemblance between the new phase and the crystalline copper hydroxy phase indicates that silica surface, although not detectable in the EXAFS spectra, acts as a template. The formation of Cu(II) hydrous clusters had been previously pointed out by Bleam and McBride (1986) in a pioneer study on titanium oxide and it has been further confirmed recently in a study on Cu adsorption on silica (Xia *et al.*, 1997). The presence of bipy in solution had little impact on the structure of the new surface phase. A slightly longer Cu-O distance (2.00 instead of 1.94 Å) and shorter Cu-Cu distances (2.9 Å instead of 2.94 Å, 3.20 Å instead of 3.31 Å) could only be noticed. Furthermore, the same structure was built whereas copper has been added first to the silica suspension or whether it has been added after bipy. All experiments were done at pH 6.0 in a 0.1 $NaClO_4$ ionic medium. The potential drift of the pH electrode was found to be < 1 mV h^{-1} after 2 h reaction time, a time hereafter chosen as reaction time.

The results obtained by ESR and UV-visible spectroscopy brought an apparent contradictory picture of the interface. In the absence of bipy a weak signal is observed in accordance with the results reported by Xia *et al.* (1997), corresponding to a few isolated sorbed copper atoms in a coordination sphere of axial symmetry. The presence of bipyridine leads to an increase of the signal and to the complexation of all surface copper ions observed by ESR by the organic ligand, within experimental error (± 5%). The type of ternary complex formed is not strongly influenced by the copper to bipyridine ratio in solution. With a 1:1 ratio, only one type of ternary surface complex is detected, presumably a 1:1:1 complex. The ESR and UV reflection spectra characteristics of this complex are the same, whereas copper has been added first to the silica suspension or has been added after bipy. It corresponds to the spectrum observed if the 1:1 complex is adsorbed from solution. With a 1:2 ratio, a mixture of 1:1:1 with traces of 1:1:2 complexes is formed on the silica surface (Kokorin *et al.*, 1997). Once the 1:1:1 (or 1:1) complex is formed, if further bipy is added to reach a 1:2 total concentration ratio, 1:1:2 complex formation is not observed either by ESR or by UV reflection spectroscopy. Clearly, only the 1:1:1 complex can be formed in this case. The distance between these complexes has been estimated on the basis of the individual uniform ESR line width to be 35 ± 4 Å and 14 ± 1 Å for the 1.0 % and 6.3 % surface coverage samples, respectively (Kokorin *et al.*, 1997). An equal distribution of the Cu-bipy complex on the silica surface would lead to 50 Å and 20 Å between them, respectively. Nonetheless, as opposed to EXAFS, ESR and UV reflection spectroscopic point out to the presence of individual ternary surface complexes spread out on the silica surface.

The contradictions between the EXAFS picture of the interface and the ESR one can be resolved as follows. The EXAFS technique averages over all structural environment in the sample and thus cannot reveal whether or how many distinct chemical environments exist. It just indicates that the major part of the Cu in the sample is present in a Cu hydroxy surface phase. In this phase, dipolar interactions provide a relaxation pathway for copper atoms, which result in a broaden, i.e. lost, ESR signal given by the hydoxy cluster atoms (Berger and Roth, 1967). Thus the ESR signal originates from a very minority of the total copper atoms present on the silica surface. In the absence of bipy this signal is estimated to originate from <1% of total unpaired electrons in the system according to Xia *et al.* (1997)! In the presence of bipy in a 1:1 ratio, the majority of copper ions would still form hydroxy clusters, and a minority would form the 1:1:1 ternary complexes. As bipy is further added to the system, no formation of a 1:1:2 complex is observed. This might be due to an inhibition of the rearrangement reaction. The thermodynamic equilibrium is not reached within the 2 h reaction time, which has been chosen on the basis of pH stability. It is known that the breakdown of Cu hydroxy clusters is a very slow process. The same might be true for the change from a 1:1:1 complex, in which bipy bridges two equatorial Cu coordination positions to a 1:1:2 configuration in which both bipy would bridge an equatorial and an axial copper coordination positions, may not have reached equilibrium. The slow reaction rate would account for the non-closed thermodynamic circle mentioned at the beginning.

The model system on which we have reported here has been chosen for convenience (paramagnetic cation, iron free mineral particles of high surface area, ligands with well known complexation constants and complex geometry). However it should be kept in mind that this model system is a tool to address a much wider problem, namely the interaction of metal ions and ionizable organic ligands with a mineral particle surface, and the sorption of heavy metal ions on e.g. the soil 'humic-clay complex'. The present study demonstrates that the presence of both metal hydroxy surface clusters, often referred to as polynuclear metal complex in the EXAFS literature, and 'true' ternary surface complexes is possible in such natural complex systems.

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