Gas-phase study of metal complexes with redox-active ligands

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ABSTRACT

Singly charged complexes of copper, silver, sodium, and zinc with redox-active ligands (catechol, maltol, and phenanthraquinone) were studied by mass spectrometry, infrared multiphoton dissociation (IRMPD) spectroscopy, and density functional theory calculations. The redox processes in copper complexes were evaluated based on a comparison with complexes bearing a non-redox active metal and by using the C—O stretching mode as a redox marker. We have detected changes in electron distribution in copper complexes with phenanthraquinone and maltol. It led to a partial reduction of the phenanthraquinone ligands on one hand and to the oxidation of maltol on the other.

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1. Introduction

Transition-metal complexes with redox active ligands represent an attractive research topic [1–4]. Both partners, the metal as well as the ligand, can provide or accept electrons and thus open a door to rich chemistry. The classical examples involving cascades of electron transfers are from biochemistry [5–7]. Organic molecules participating in the electron transfer processes are quite often based on phenol or quinone motifs, *e.g.* tyrosine or coenzyme Q [8,9]. Among other metals, copper is known to be present in a wide range of biochemical redox active systems [10,11]. As an example, we refer to galactose oxidase that combines a copper ion with redox-active ligands and thereby allows oxidation of an alcohol group to aldehyde [12].

Reversible redox changes are applied also in design of molecular switches [13]. In a molecular system formed from redox active molecules electronic changes can lead to *e.g.* valence-tautomeric structures with different physical properties. The observable change of a property can be used as a switch indicator [14].

Prototypical redox-active model ligands are based on *ortho*-benzoquinone skeleton (Scheme 1) [15,16]. One-electron reduction leads to the formation of semiquinone and two-electron reduction yields catecholate. Our work aims to spectroscopically study cop-

per complexes with model ligands for all three oxidation states and compare the results with other metal complexes bearing non-redox active metal center (Na, Ag, and Zn). To this end, we have generated a series of metal complexes with catechol (**1**), phenanthraquinone (**2**), and, maltol (**3**) [17]. We have expected a possibility of redox processes in copper (I) and copper(II) complexes with phenanthraquinone and maltol (Scheme 1b,c).

2. Experimental and theoretical details

Mass spectrometry experiments were carried out with Finnigan LCQ mass spectrometer coupled with electrospray ionization (ESI) source. The ions of interest were generated by electrospray ionization from a methanolic solution of the respective metal salt ($Cu(CF_3SO_3)$, $Cu(CF_3SO_3)_2$, $CuCl_2$, $ZnCl_2$, $AgSbF_6$ and $NaCl$) and the ligand. The electrospray voltage was 4.5 kV and the capillary was heated to 180–250 °C. The sheath gas, flow rate and voltages of capillary and lenses were optimized in order to obtain the maximum signal of the required ions. Collision induced dissociation (CID) experiments were performed for mass-selected ions with the excitation period of 30 ms and a trapping parameter $q_z = 0.25$. We are using the Schröder's method for calibration of the collision energy and determination of the appearance energies [18].

The infrared multiphoton dissociation spectra of mass-selected ions were performed using a Bruker Esquire 3000 ion trap mounted to a free electron laser at CLIO (Centre Laser Infrarouge Orsay, France) [19]. The laser was operated in the 40–45 MeV electron-

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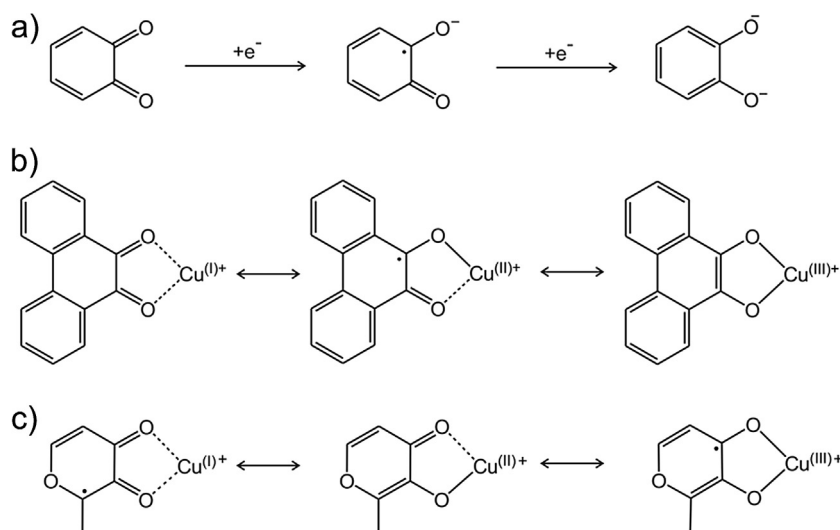
Scheme 1. (a) One-electron and two-electron reduction of *ortho*-benzoquinone. (b) Model system based on phenanthraquinone. (c) Model system based on maltol.

energy range and it provided light in a 1000–1800 cm^{-1} range. The ions were generated in an analogous way as above, stored in the ion trap, and irradiated by the tunable laser. The dependence of the fragmentation intensities on the wavelength of IR photons provided the IRMPD spectra of the investigated ions.

The geometry optimizations and thermochemistry calculations were performed using the density functional theory method B3LYP-D3 [20–22] as implemented in the Gaussian 09 package [23]. The basis set was combined from 6–31G* at C, H, O and Cl and LanL2TZ at Ag or 6–311+G* at Cu, Zn or Na. The optimized structures were characterized by harmonic frequency analysis. The reported theoretical harmonic IR spectra were scaled and the scaling factor can be found in the figure captions. Similar scaling factors gave a good agreement between experimental and theoretical IR absorption spectra for various gas phase molecular ions [24]. For the determination of the binding energies, the most stable structures were reoptimized with the TZVP basis set at all atoms and corrected for the basis set superposition error (BSSE) [25,26]. For each complex many possible structures were optimized. The energetically preferred structures are shown in the main document; all other isomers together with their theoretical IR spectra are shown in the Supporting information.

3. Results

3.1. Infrared spectroscopy in the gas phase

3.1.1. Catechol complexes

We have started with the investigation of complexes of catechol with copper(I) and silver(I). Hence both, the ligand as well as the metals, are in the reduced oxidation states. Comparison of the IRMPD spectra of [Cu(catechol)$_2$]$^+$ and [Ag(catechol)$_2$]$^+$ (Fig. 1a and d) suggests that both spectra contain peaks at similar positions and therefore a similar structure is expected. The metals can bind either to the π-electrons of the aromatic ring or to the oxygen atoms. None of the coordination modes is strongly energetically preferred. The DFT calculations slightly favor coordination to the ring [27]. The ring-coordinated structures are even more favored, if the correction for dispersion interactions is included to the calculations (cf. Fig. S1 in the Supporting information).

In the IR spectra we can identify bands that correspond to the C=C and C—O stretching vibrations and the C—O—H bending modes (cf. Fig. 1). The different coordination modes lead only to modifica-

tions of the band intensities, but there are no significant changes in band positions that would be detectable with our resolution of IRMPD spectra. Hence, we cannot give a definite answer to the question about the coordination modes in these complexes. It is highly probable that several isomers can be in equilibrium.

3.1.2. Phenanthraquinone complexes

Phenanthraquinone, a prototype of a fully oxidized ligand, forms complexes with copper(II) or zinc(II) with the stoichiometry of [CuCl(PQ)$_2$]$^+$ and [ZnCl(PQ)$_2$]$^+$, respectively (Fig. 2). The IRMPD spectra of both complexes are very similar. They are dominated by two intense, overlapping broad bands between (1560–1700 cm^{-1}) corresponding to the C=O stretches coupled with the C=C stretching modes. Minor bands representing the C—C—H bending modes and the C—C stretching modes of phenanthraquinone can be found at 1306, 1347, and 1450 cm^{-1} (the values were determined from the spectrum of [ZnCl(PQ)$_2$]$^+$). Theoretically, it is predicted that the zinc complex prefers a symmetrical coordination by all oxygen atoms of the ligands and chlorine in the apex. The zinc atom is not in the plane with the oxygen atoms but slightly above it.

The copper center prefers a square-planar coordination by three oxygen atoms and chlorine. The last oxygen atom is weakly coordinated in the apex of a distorted tetragonal pyramid. The C=O stretching mode of this carbonyl group is too weak to be detected (it should be located at 1691 cm^{-1} – see Fig. 2b). Nevertheless, it is predicted that the shape of the composite C=C/C=O stretching band of the copper complex should be narrower and with a relatively larger intensity at about 1600 cm^{-1} compared to the zinc complex. This is exactly, what we detect (cf. Fig. 2).

In the second step, we have combined phenanthraquinone ligand with copper(I) and its redox-inactive (or less active) analogs silver(I) and sodium(I). The IRMPD spectra are again fairly similar (Fig. 3). The C—C and C—C—H characteristics of the phenanthraquinone ligand are found at about the same positions as above (1300, 1340, and 1455 cm^{-1}). Positions of the C=O and C=C stretching bands depend on the central metal. Complexes of sodium and silver are similar to each other, but we can see a distinct difference in the spectrum of the copper complex. This change does not originate in a different geometry, because all complexes have analogous structure with a tetrahedral coordination of the ligands.

The analysis of the theoretical IR spectrum of [Na(PQ)$_2$]$^+$ suggests that the largest band at 1668 cm^{-1} corresponds to the C=O stretching, while the band at 1595 cm^{-1} represents the C=C stretching of the ligand. Analogous results are obtained for [Ag(PQ)$_2$]$^+$, but