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Redox reactions of copper(II) upon electrospray ionization in the presence of acridine ligands with an amide side chain

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The complexation of copper(II) to acridine derivatives has been studied by means of electrospray ionization (ESI) mass spectrometry. Under soft conditions of ionization, the ESI mass spectra of methanolic solutions of copper(II) chloride and the acridine ligands show abundant signals of the mononuclear complexes formed from the metal and ligand. Depending on the position of the *N*-benzoylamino substituent in the acridinic heterocycle, however, the copper atom involved in the complexation process adopts different oxidation states in the resulting cations. Hence, the metal is reduced to copper(I) in the monocationic complex with the compound substituted in position 2, whereas it keeps its divalent state in the monocation formed with the compound substituted in position 4. As a consequence, the regioisomers lead to monocations with different masses in the ESI spectra. In order to understand this unusual behavior of two isomeric compounds, additional experiments have been performed with quinoline as a model.

Keywords: acridine; copper; electrospray ionization; mass spectrometry; quinoline; redox reactions

INTRODUCTION

Transitional-metal ions play an important role in many chemical and biochemical processes, and it is therefore important to understand the specificity of the binding site(s) in complex organic molecules. Although most knowledge concerning transitional-metal chemistry is based upon solution and solid-state studies, gas-phase experiments allow to investigate the interactions of naked ions, thereby eliminating solvent stabilization of the metal ion – ligand interactions[1] and the effects of counterions which are necessarily present in the bulk. Structure determination of complexes formed with transitional metals presents unique challenges because the metal may have several stable oxidation states. In this respect, copper is particularly interesting due to its involvement in oxygen transport and electron transfer in proteins and enzymes.[2] Cu^{I} is considered as a soft Lewis acid whereas Cu^{II} is considered being at the borderline to hard Lewis acids. In solution, Cu^{I} preferentially coordinates sulfur- and phosphorous-containing ligands, whereas Cu^{II} is mostly involved in complexes of ligands with nitrogen and oxygen. In contrast, in the gas-phase chemistry of peptides,[3] it was observed that monovalent copper has a strong tendency to coordinate with amino acids possessing a nitrogen atom in the side chains (e.g., arginine, lysine, and hystidine) rather than residues containing sulfur (e.g., cysteine).[4,5] Likewise, interaction of uracil and thiouracil bases with copper(I)[6] and copper(II)[7] leads to monocationic species in both cases, that is, $[(uracil)Cu]^+$ for the former and $[(uracil—H)Cu]^+$ for the latter.[8,9]

Acridines are heterocyclic compounds based on the anthracene skeleton containing a nitrogen atom in the central ring, which we here consider as a model for the coordination of copper by nitrogen ligands with potential biological activity.[10,11] The presence of a benzoylamino substituent in different positions, that is, 4-(*N*-benzoylamino)-acridine (compound **A**, Scheme 1) and 2-(*N*-benzoylamino)-acridine (compound **B**), offers an additional coordination site which could change the complexation mode of copper as well as the stability of the redox states of copper. The present study investigates the gas-phase interactions of these compounds with copper using electrospray ionization (ESI) tandem mass spectrometry.

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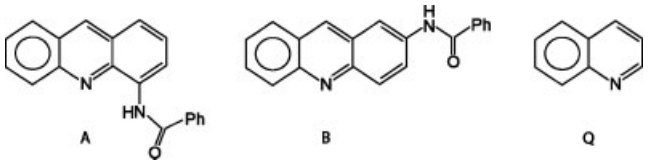


Scheme 1. Structures of the investigated compounds **A** and **B** as well as that of quinoline (**Q**); Ph stands for a phenyl group. The numbering used for acridine follows the convention known for anthracene

RESULTS AND DISCUSSION

In the presence of copper dichloride, $CuCl_2$, formation of different complexes was evidenced in ESI mass spectra of methanolic solutions of compounds **A** and **B**, depending on the acridine isomer considered. In both cases, these complexes were singly charged and characterized by a 1:2 stoichiometry between copper and the ligand. Based upon accurate mass measurements (measured *m/z* 658.1336, theoretical *m/z* 658.1425; *error*: −14 ppm) and the isotope pattern (Fig. 1a), the major copper complex involving compound **A** (substitution in 4-position) can be assigned to a monocation with the composition $[\mathbf{A}Cu(\mathbf{A}—H)]^+$ (refer structure in Scheme 2a). This stoichiometry agrees with a copper(II) complex, whose formation can tentatively be ascribed to a substitution of solvent molecules in the precursor species $[CuCl(CH_3OH)_m]^+$ present in solution and subsequent dehydrohalogenation (reactions 1 and 2), most probably involving the hydrogen atom of the benzoylamino side chain.

$$[CuCl(CH_3OH)_m]^+ + 2\mathbf{A} \rightarrow [\mathbf{A}_2CuCl]^+ + mCH_3OH \quad (1)$$

$$[\mathbf{A}_2CuCl]^+ \rightarrow [\mathbf{A}Cu(\mathbf{A}—H)]^+ + HCl \quad (2)$$

In marked contrast, copper occurs in the reduced oxidation state Cu^I in the complex formed with the ligand **B** (substitution in 2-position). Indeed, both accurate mass data (measured *m/z* 659.1514, theoretical *m/z* 659.1502; *error*: +2 ppm) and the isotope profile (Fig. 1b) indicate the formation of a $[\mathbf{B}_2Cu]^+$ complex, which structure is presented in Scheme 2b, and hence a copper(I) compound. In contrast, the signal due to the corresponding Cu^{II} complex $[\mathbf{B}Cu(\mathbf{B}—H)]^+$ (Scheme 2c) is smaller by an order of magnitude. ESI of divalent metal salts MX_2 in dipolar solvents (solv) usually leads to solvated mono- and dications of the type $[MX(solv)_m]^+$ and $[M(solv)_n]^{2+}$, respectively. In the presence of additional ligand molecules L with better complexation abilities than the solvent molecules, the latter are successively replaced by L to afford the corresponding ions $[MX(L)_m]^+$ and $[M(L)_n]^{2+}$.[12,13] Thus, the formation of the corresponding cations, with L = **A** or **B,** would be expected upon ESI of compounds such as **A** and **B** from $CuCl_2$ solution.[14] Even for redox-active metals such as vanadium,[15–17] iron,[18–21] or copper,[7,22–24] the valence state of the metal is usually not changed in ESI under soft ionization conditions;[25,26] note however, that the occurrence of intramolecular electron transfer from the ligand to copper(II) centers has recently been deduced from the infrared spectra of gaseous phenolato-copper(II) complexes.[27,28] This pronounced difference observed for the binding of copper to the two isomeric acridine ligands is obviously due to the position of the substituents relative to the nitrogen atom of the heterocycle. In our previous study, compounds **A** and **B** were already shown to behave very differently when protonated. In the case of compound **A**, hydrogen bonds formed between the acridinic nitrogen and heteroatoms in the substituent group were shown to promote specific fragmentation pathways, which allow the distinction of the isomers.[29] Thus, next to this possible differentiation of both isomers by the MS/MS experiment, already the source spectra of copper complexes of compounds **A** and **B** can serve for a distinction of both isomers; quantitative analysis of mixtures of **A** and **B** would however require a deconvolution of the overlapping isotope distributions.[30] Before returning to the unexpected different oxidation states of copper in its complexes with the acridine ligands **A** and **B**, the fragmentation behavior of the ions $[\mathbf{A}Cu(\mathbf{A}—H)]^+$ and $[\mathbf{B}_2Cu]^+$, respectively, is addressed in order to investigate if the differences are also maintained upon collision-induced dissociation (CID).

As illustrated in Fig. 2, CID of mass-selected $[\mathbf{A}Cu(\mathbf{A}—H)]^+$ (*m/z* 658) initially gives rise to the elimination of a neutral ligand **A** from the precursor ion to yield $[Cu(\mathbf{A}—H)]^+$ (*m/z* 360), which then undergoes loss of a CuO molecule to produce *m/z* 281. The assignment of these fragments is supported by accurate mass measurements and MS/MS experiments performed on precursors with different isotopic composition (i.e., *m/z* 659 and 660). While loss of a neutral metal fragment from a cationic transition-metal complex might appear surprising at the first sight, in extended aromatic ligands such a process can be supported by the formation of resonance-stabilized cations,[18] and a proposal for the formation of *m/z* 281 is sketched in Scheme 3 for the loss of CuO from $[Cu(\mathbf{A}—H)]^+$.

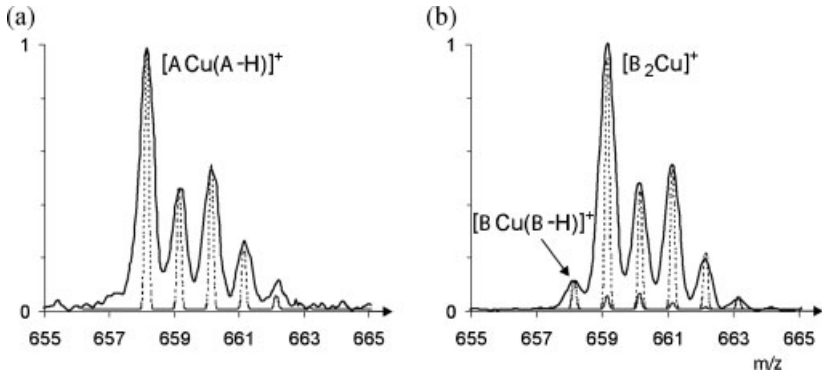
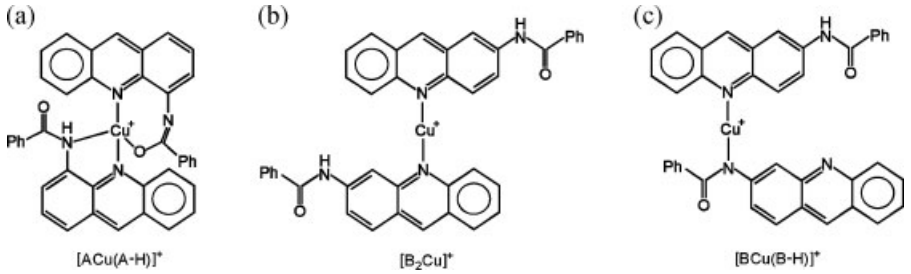


Figure 1. ESI mass spectra of the copper complexes formed with (a) compound **A**, that is, the Cu^{II} species $[\mathbf{A}Cu(\mathbf{A}–H)]^+$ with *m/z* 658 for the light isotopes and (b) **B**, that is, the Cu^I species $[\mathbf{B}_2Cu]^+$ with *m/z* 659 for the light isotopes. The thin, dashed lines represent the calculated isotope patterns for each of complexes. Note that in the case of compound **B**, about 10% of the corresponding Cu^{II} species $[\mathbf{B}Cu(\mathbf{B}–H)]^+$ is co-generated upon ESI



Scheme 2. Plausible structures suggested for the different Cu^{I} and Cu^{II} complexes of the acridines **A** and **B**. Note that no distinction between *N*- and *O*-coordination of copper to the amido ligand can be made on the basis of the experimental data

Fragmentation of $[\mathbf{B}_2Cu]^+$ (*m/z* 659) also first results in the elimination of a neutral acridine ligand **B** as indicated by a peak at *m/z* 361 (data not shown). At elevated collision energies, a daughter ion detected at *m/z* 281 can be accounted for by the release of a CuOH neutral from the copper(I) species $[\mathbf{B}Cu]^+$. By reference to the significantly larger proton affinity (PA) of the acridine N-atom in **B** ($PA_{N,acridine} = 1048\ kJ\ mol^{-1}$)[29] as compared to those of the heteroatoms of the amide sidechain ($PA_{N,amide} = 898\ kJ\ mol^{-1}$, $PA_{O,amide} = 958\ kJ\ mol^{-1}$)[29] and the general correlation of Cu^+ affinities and proton affinities,[31] we assume that the copper preferentially binds to the ring nitrogen. It seems, however, that at least due to the large internal energy imparted in the collisions, change of coordination site from the acridine N-atom to the amide unit in **B** can take place, which is then followed by the release of neutral CuOH.

In order to shed further light on the mechanism of the reduction from copper(II) to copper(I) during the ESI process, quinoline (**Q**) was taken as a model compound for the generation of the corresponding copper complexes. Upon ESI of a methanolic copper-dichloride solution containing quinoline, the aromatic nitrogen base shows a high propensity to form ionic complexes of the type $[Cu(\mathbf{Q})_n]^{2+}$ which upon slightly harder ESI conditions undergo charge reduction to the corresponding monocations $[Cu(\mathbf{Q})_m]^+$ $(m < n)$.[32]

Most interesting for the understanding of the formation of copper(I) species is the consideration of the chloro-copper(II) complex $[\mathbf{Q}_2CuCl]^+$. Indeed, instead of ligand loss, CID of mass-selected $[\mathbf{Q}_2CuCl]^+$ leads to the expulsion of a chlorine radical to afford the bisligated copper(I) cation $[\mathbf{Q}_2Cu]^+$ with *m/z* 321 for the ^{63}Cu isotope (Fig. 3a) and *m/z* 321/323 for the parent ion containing the heavier isotopes ^{65}Cu and ^{37}Cl, respectively (Fig. 3b). Because an open-shell species is released as a neutral, the occurrence of reaction (3) can explain the redox process taking place upon ESI.

$$[\mathbf{Q}_2CuCl]^+ \rightarrow [\mathbf{Q}_2Cu]^+ + Cl^{\bullet} \quad (3)$$

$$[\mathbf{Q}_2CuCl]^+ \rightarrow [\mathbf{Q}CuCl]^+ + \mathbf{Q} \quad (4)$$

Specifically, in $[\mathbf{Q}_2CuCl]^+$ the metal cation is still sufficiently stabilized to support the copper(II) oxidation state, but the loss of a quinoline ligand to afford $[\mathbf{Q}CuCl]^+$ according to reaction (4) is obviously much more energy-demanding compared to the redox process concomitant with loss of atomic chlorine in reaction (3). In other words, the bond dissociation energy $D(\mathbf{Q}_2Cu^+—Cl)$ of the covalent bond between copper and chlorine is significantly lower than $D(\mathbf{Q}CuCl^+—\mathbf{Q})$ of the coordinating quinoline ligand.[33]

In recursion to the isomeric acridines discussed above, the facile occurrence of reaction (3) can easily account for the reduction from Cu^{II} to Cu^{I} in the case of compound **B** to afford the bisligated species $[\mathbf{B}_2Cu]^+$, presumably with a coordination of copper to both acridinic nitrogen atoms (Scheme 2b), in which the metal can adopt the linear geometry preferred for many copper(I) complexes.[34] A similar behavior is hence to be expected for other aromatic nitrogen bases.[22,28,32,35–37] The exception is thus in fact the isomer **A**, in which the proximity of ring nitrogen atoms and the potentially acidic NH proton permits loss of HCl according to reaction (2), rather than expulsion of atomic chlorine concomitant with reduction to Cu^{I}. Hence, the chelating ligand environment itself serves for the stabilization of the copper(II) state in the case of compound **A**, as indicated by the tetracoordinated metal atom in the tentative structure of $[\mathbf{A}Cu(\mathbf{A}—H)]^+$ shown in Scheme 2a. Along this line of reasoning, the small amount of $[\mathbf{B}Cu(\mathbf{B}—H)]^+$ observed in Fig. 1b can accordingly be attributed to an initial coordination of copper to the amide moiety, enabling loss of HCl concomitant with the formation of an amido complex as indicated in Scheme 2c.

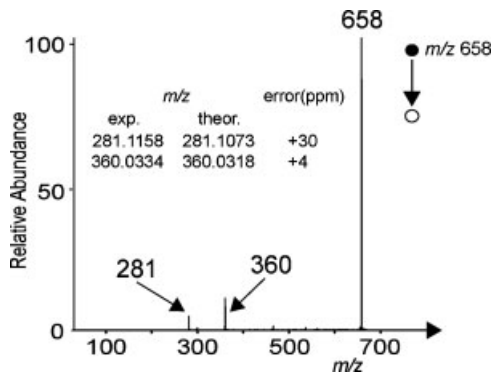
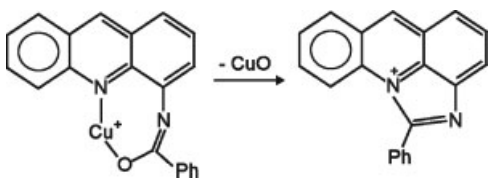


Figure 2. CID spectrum of mass-selected $[\mathbf{A}Cu(\mathbf{A}–H)]^+$, *m/z* 658, to afford fragments at *m/z* 360 and *m/z* 281. Experiments with different isotopes of $[\mathbf{A}Cu(\mathbf{A}–H)]^+$ reveal that *m/z* 281 does not contain copper anymore (In the insert, the accurate mass values are given.)



Scheme 3. Possible formation of a polycyclic acridinium ion upon loss of neutral CuO from $[Cu(\mathbf{A}–H)]^+$

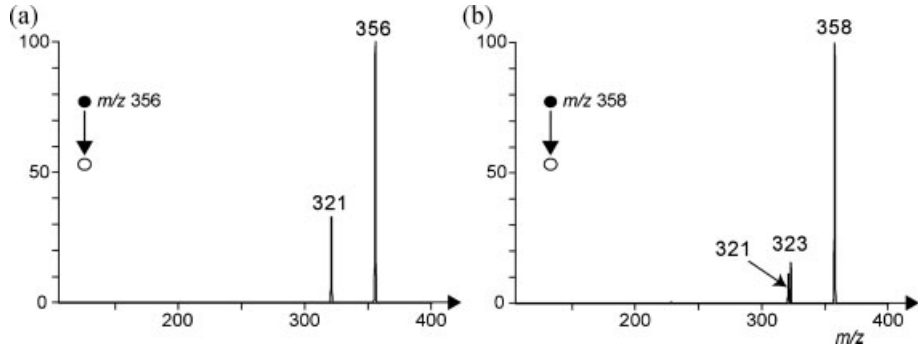


Figure 3. CID spectra of mass-selected $[\mathbf{Q}_2CuCl]^+$ for (a) the lighter $^{63}Cu^{35}Cl$ isotope with *m/z* 356 and (b) the heavier $^{63}Cu^{37}Cl$ and $^{65}Cu^{35}Cl$ isotopes with *m/z* 358 showing the loss of atomic chlorine according to reaction (3). Even at elevated collision energies, no traces of $[\mathbf{Q}CuCl]^+$ (*m/z* 227) due to loss of a quinoline ligands (reaction 4) are observed

CONCLUSIONS

In their coordination with copper, the acridines **A** and **B** serve as an example, how isomeric compounds not only can be distinguished by their fragmentation behavior in MS/MS experiments,[29] but also already by reference to the ions directly generated upon ESI. Thus, the acridine **B** with the benzoylamino substituent in the 4-position remote from the acridine nitrogen atom cannot sufficiently support the copper(II) oxidation state upon desolvation and hence leads to a reduction from Cu^{II} to Cu^{I} concomitant with the release of a radical. In contrast, the proximity of the benzoylamino substituent to the ring nitrogen in acridine **A** permits N—H bond activation and the formation of a chelate-stabilized Cu^{II} species. The present case is thus one of the presently still rare examples, where structurally similar isomeric compounds give ions of different mass-to-charge ratios in their ESI mass spectra.[25]

In a more general perspective, this case study also demonstrates the large effect of the formal valence state on the reactivity of gaseous ions. Thus, as far as bond activation is concerned, the monovalent Cu^+ cation is among the least reactive 3d transition-metal cations,[3,38,39] whereas copper(II) obviously is quite different in this respect,[6–9] and we will explore this particularly interesting aspect further.

EXPERIMENTAL DETAILS

Most experiments were performed with a Finnigan LCQ Classic ion-trap mass spectrometer as described elsewhere.[40] In brief, the LCQ bears a conventional ESI source consisting of the spray unit (flow rate set at 5 μl min^{-1} and spray voltage at 4.5 kV) with nitrogen as a sheath gas, followed by a heated transfer capillary (kept at 175 °C), a first set of lenses which determine the soft- or hardness of ionization by variation of the degree of collisional activation in the medium-pressure regime,[41–43] two transfer octopoles, and a Paul ion-trap for ion storage and manipulation[44] in the presence of *ca.* $2 \cdot 10^{-5}$ mbar helium as a trapping gas. For detection, the ions were ejected from the trap to an electron multiplier. Low-energy CID was performed by the application of an excitation AC voltage to the end caps of the trap to induce collisions of the isolated anions with the helium buffer gas for a period of 100 ms. While the CID energies can be varied continuously and also schemes for the conversion into threshold energies have been proposed,[45] we refrain from an exact quantification here and rather refer to them as a percentage of the 2.5 V excitation voltage applied. Xcalibur software version 1.3 was used for instrument control, data acquisition, and data processing.

Accurate mass determinations were performed with a QStar Elite mass spectrometer (Applied Biosystems SCIEX, Concord, ON, Canada) equipped with an electrospray source operated in positive ion mode. The capillary voltage was set at 5500 V and the declustering potential at 80 V. In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight mass analyzer. A quadrupole was used for selection of precursor ions to be further submitted to CID in MS/MS experiments. Nitrogen was used as the nebulizing gas (18 psi), the curtain gas (20 psi) as well as the collision gas. The collision energy was set for each species separately to afford a sufficient amount of fragmentation in the experiments. The Analyst software version 2.1 was used for instrument control, data acquisition, and data processing.

The acridine derivatives were synthesized as described previously.[16] All other chemicals and solvents were used as purchased (Sigma-Aldrich, St. Louis, MO, USA).

Acknowledgements

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