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Unimolecular dissociation characteristics of cationic complexes between nicotinic acid and Cu(II) and Ni(II)

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ABSTRACT

Cu^{2+} and Ni^{2+} form dimeric $ML(L-H)^+$ complexes with nicotinic acid (M = Cu, Ni; L = nicotinic acid) upon electrospray ionization. Quantum chemical calculations indicate thermochemical preference for coordination of the carboxylate groups rather than the ring nitrogens to the central metal ion in both cases. In analogy to the dimeric metal complexes of amino acids the primary dissociation reaction upon collisional activation of $ML(L-H)^+$ is the loss of CO_2 in both cases. Further dissociation of the decarboxylated species show preference for loss of a 3-pyridinyl radical for M = Cu and $NiCO_2$ for M = Ni. This can be understood in light of the redox properties of the two metals and from previous studies of similar complexes with amino acids. Loss of the pyridinyl radical bonded to the carboxylate group in these cationic entities does not lead to $M(\eta^2\text{-}O_2C)$ structures previously observed for similar anionic metal species.

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1. Introduction

Recently, a new bidentate structural binding motif of carbon dioxide to various metals and metal ions has been described [1–4]. Such tetragonal structures (Scheme 1) can be formed by electrospray ionization (ESI) of liquids containing suitable precursor compounds in combination with collisional activation and have very interesting chemical properties. For example $XMg(\eta^2\text{-}O_2C)^-$ (X = Cl, Br or OH) formed from mixtures of MgX_2 salts and oxalic acid has been shown to be a carbon nucleophile and may serve as a model system for carbon dioxide activation during organic and biological C—C bond formation reactions, for example during photosynthesis. Carboxylation reactions of this kind are of significant current interest as a promising method for CO_2 sequestration in industrial processes for combined combustion and chemical synthesis [5]. In this respect it is of great interest to investigate how chemical factors (the metal, the charge state, complexation and solvent) influence the stability of this binding motif. In our quest for suitable model systems of this kind we have chosen a simple

strategy, namely to mix a salt of the metal in question with carboxylic acids and study the collisionally induced decomposition of the ionic complexes formed in situ in the electrospray process. In the present context we chose to study the M(II) salts of nickel and copper, since they are among the most interesting metals both for industrial catalysis and in biological systems. On the other hand, copper and nickel have quite different redox properties. While copper normally displays oxidation state 0, I and II, oxidation state I is rare for nickel. The former metal is characterized for its flexibility in oxygen processing and radical initiated processes, the latter by its catalytic role in hydrogenation/dehydrogenation reactions (Raney nickel) and in C—C activation.

The simplest conceivable Cu^{2+} and Ni^{2+} complex structures formed with carboxylates are of the type $(R\text{-}CO_2)_2M$, providing a conceptual starting point for forming precursors that by direct loss of R may lead to structures of the type $(R\text{-}CO_2)M(\eta^2\text{-}O_2C)$ upon activation, see Scheme 1 (the $\eta^2\text{-}O_2C$ notation indicates that both oxygens are bonded to the metal). In order to form positively charged ions of such $(R\text{-}CO_2)_2M$ complexes by ESI it is necessary that the ligand in addition to a carboxylic acid residue also contains a sufficiently basic site, for example an amino group to pick up an extra proton. On the other hand, amino groups also have affinity for cationic transition metal ions so within the ligand there will be competition between metal complexation of the

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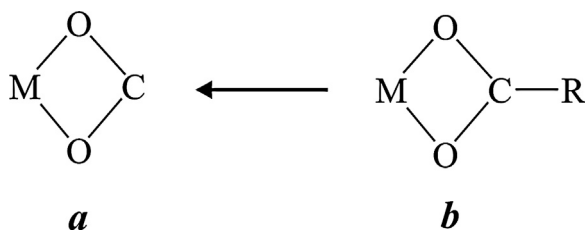
Scheme 1.

carboxylate and the amino groups, leading to structural complexity. This is a well-known situation for amino acids, which give rise to various monomeric, dimeric and trimeric complexes with both copper and nickel in ESI mass spectrometry, and the unimolecular dissociation of Cu(II) amino acid and carboxylic acid complexes has been particularly well studied by mass spectrometry due to the rich radical cation chemistry resulting from the open shell d^9 electronic configuration of Cu^{2+} [6–13]. On the other hand Ni^{2+} is d^8, an even electron species with lower tendency towards radical chemistry [14–16].

The structural flexibility of amino acids allows for strong interaction between the metal ion and several functional groups of the ligand. To overcome this issue we decided to investigate complexes of nicotinic acid since this ligand is both simpler and more rigid than amino acids, avoiding simultaneous binding to the nitrogen and the carboxylic acid/carboxylate group of the same ligand molecule to the metal. Different mass spectrometric approaches have been used in order to determine the binding patterns of the formed complexes as well as their dissociation behaviour. These efforts were complemented by density functional theory (DFT)-based calculations.

2. Methods

2.1. Experimental details

2.1.1. General

All chemicals have been purchased from Sigma–Aldrich (St. Quentin Fallavier, France) and used without further purification. 40 µM solutions of MCl_2 (M = Cu, Ni) and nicotinic acid were prepared in methanol. Working solutions were prepared by mixing these two solutions in a 5:1 ratio (v:v).

2.1.2. Ion trap

Experiments were in part performed on a quadrupole ion trap mass spectrometer (Esquire 3000, Bruker, Bremen, Germany) equipped with an orthogonal ESI source. Sample solutions were infused with a syringe pump model 74900 (Cole-Parmer, Vernon Hills, IL) at a flow rate of 160 µL h^{-1}. Nitrogen was used as nebulizing gas at a pressure of 6 psi, and as drying gas at a temperature of 250 °C and a flow rate of 4 L min^{-1}. Optimized source voltages were as follows: capillary at −3.5 kV, end plate offset at −500 V, capillary exit (CE) at +45 V, skimmer 1 at +15 V (providing a potential difference of 30 V with CE), and skimmer 2 at +6 V. These relatively soft source conditions were used in order to preserve the rather weakly complexed ions. The low mass cut-off (LMCO) was fixed at 28% of the m/z of the precursor ions and the analytical scan range for mass spectra was m/z 50–600. The scan rate was set at 13,000 m/z s^{-1} (standard mode). Ion accumulation time was automatically set with ion charge control (ICC) with a target of 10,000 to limit space charge effects. For low-energy sequential collisionally induced dissociation (CID) experiments, resonant excitation was used with an amplitude voltage of 0.70 V_{p-p} and an ion

isolation window of m/z 0.8 in order to obtain monoisotopic ion selection.

2.1.3. FT-ICR

A hybrid quadrupole Fourier transform ion cyclotron resonance (hQh-FT/ICR) mass spectrometer (Solarix, Bruker Daltonics, Bremen, Germany) equipped with an actively shielded 7 T magnet was used for accurate mass measurements. The samples were infused in the electrospray ion source at a flow rate of 120 µL h^{-1} with the assistance of N_2 nebulizing gas. Ionization was performed in the positive ion mode with an ESI high voltage of 4000 V. Voltage applied in the desolvation zone were: capillary exit 200 V, deflector 180 V, funnel 110 V, skimmer 50 V. Complexes of interest were first mass-selected with the quadrupole (m/z 5 window), accumulated for 0.5 s in a linear ion trap and then isolated in the ICR cell in order to obtain monoisotopic precursor ion selection (13% of frequency sweep amplitude). Activation of the ions was performed using sustained off-resonance irradiation collision-induced dissociations (SORI-CID) using argon as collision gas introduced through a pulse valve. The ions were excited using excitation amplitude of 0.5 V_{p-p} with a frequency offset of −500 Hz applied for 200 ms. A pumping delay of 2 s was used before the excitation/detection step.

All mass spectra and collision activation spectra were acquired with Solarix control (version 1.5. Bruker Daltonics) in broadband mode from m/z 21.5 to m/z 500. The image signal was amplified and digitized using 2 M data point resulting in the recording of a 0.4 s time domain which was transformed into the corresponding frequency domain by Fourier transform (one zero fill and apodization using the sinbell function).

The ESI mass spectra were internally calibrated from unambiguous signals (single point calibration). Typically the precursor ion was used as internal calibrant for CID spectra. Reported m/z ions were compared to the theoretical m/z and ions with an error higher than 5 ppm were not considered.

2.1.4. Ion mobility measurements

The ion mobility experiments were carried out using a Synapt G2 HDMS (Waters, Manchester, United Kingdom). This instrument is a hybrid quadrupole/time-of-flight mass spectrometer, which incorporates a travelling-wave ion mobility (TWIM) device, in which low-voltage waves push the ions through a gas filled cell [17]. The gas flow (N_2) was set at 90 mL min^{-1}, the travelling wave height and velocity were set to 40 V and 600 m s^{-1}, respectively. For comparison, theoretical collision cross section values were computed using the trajectory method (TM) method with the MOBCAL software [18,19]. The number of data points in the Monte Carlo integrations of impact parameter and orientation was set to 1000. IMS cell calibration was carried out with polyalanines at the concentration of 10 ng µL^{-1} using collision cross section (CCS) values used for calibration from the Clemmer lab database [20].

2.1.5. Computational procedure

Quantum chemical calculations were carried out using the program system GAUSSIAN 09 [21]. Geometry optimization and single point energies were obtained using the B3LYP method with the 6-31G(2df,p) basis set. All structures presented in this work were characterized either as minima or saddle points from vibrational analysis. Relative energies were corrected by including unscaled zero-point vibrational energies (ZPVE). The accuracy of the computational approach was probed by comparing calculated bond dissociation energies of selected copper and nickel complexes with experimental values found in the literature. The results show satisfying agreement and are presented in the Supplementary information.