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### Tweezer-like Complexes of Crown Ethers with Divalent Metals: Probing Cation-Size-Dependent Conformations by Vibrational Spectroscopy in the Gas Phase

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Crown ethers constitute central building blocks for the synthesis of molecular tweezers capable of trapping cationic species. In this study, isolated ternary complexes comprising two [18]crown-6 (18c6) ether molecules and one divalent cation of varying size ( $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ) are investigated by means of laser vibrational action spectroscopy and computations. In the ternary (18c6)<sub>2</sub>– $Cu^{2+}$  complex, one of the crown units folds tightly around the cation, while the second crown ether unit binds peripherally. Such asymmetrical binding manifests itself

#### Introduction

Molecular pincers or "tweezers" were introduced about three decades ago as synthetic molecular structures capable of trapping specific guest molecules, and nowadays play a key role in the development of novel supramolecular and nanotechnological materials.<sup>[1–7]</sup> Particular efforts have been devoted to the design of dynamical architectures providing molecular recognition and a clipping action that may be reversibly modulated by photon absorption or chemical additives.<sup>[3–7]</sup>

Crown ethers bind with remarkable selectivity monovalent and divalent metal cations, as well as molecular cations such as ammonium and protonated amines.<sup>[8-10]</sup> An important class of molecular pincers and related supramolecular assemblies is based on crown ether building blocks.<sup>[3, 11-21]</sup> The fundamental understanding of such complex structures demands for benchmark systems that capture the main driving forces of pincer action within a simplified molecular framework. The core of pincer activity can be considered to rely on the interaction of the guest species with the two capping molecular moieties that act as selective binders. Such interaction can be investigated in detail in isolated ternary complexes resembling the chemical and conformational features of the actual pincer molecule while being sufficiently small to be accessible to both experimental and computational techniques. The potential of this approach has been demonstrated in different gas phase investigations of binary crown-cation  $\mathsf{complexes}^{[21-25]}$  and of ternary tweezer-like complexes formed between one metal cation and two capping crown ether units.<sup>[18-21]</sup> Those investigations have probed relevant conformational and energetic aspects that control the stability and selectivity of the complexes. Specifically, the flexibility and orientational freedom of the crown ether units was shown to aid in providing an optimum balance between the crown-cation attractive forces and as a bimodal splitting of the vibrational bands measured for the complex. The size of the cation in the Ca<sup>2+</sup> and Ba<sup>2+</sup> complexes leads to a progressively more symmetrical coordination of the two crown ether molecules with the metal. In particular, in the spectrum of the (18c6)<sub>2</sub>–Ba<sup>2+</sup> complex, the two components of the vibrational bands are merged into single-maximum envelopes. This is consistent with a  $C_2$  arrangement predicted by the computation, in which the cation coordinates with the two crown ether units in a fully symmetrical way.

the mutual repulsive forces exerted by the crown ether backbones. Nevertheless, efforts devoted to characterize isolated ternary cationic complexes of crown ethers are scarce in comparison to their binary counterparts.

The ternary complexes formed between a pair of crown ether units and a cation are actually relevant by themselves for both fundamental and practical reasons. It has been shown that these complexes tend to dominate the thermodynamic equilibrium in diluted cation/crown ether solutions, at least for a range of guest-host pairs.<sup>[26]</sup> In addition, the ternary complexes display an enhancement of the selectivity of the complexation with respect to the crown-cation binary system.<sup>[12]</sup> Herein, we aim at providing novel insights into the conformational properties of the tweezer-like complexes formed by the common native [18]crown-6 crown ether with divalent metal cations (Cu<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>). The investigation employs laser-induced vibrational action spectroscopy of the cationic complexes isolated in an ion trap at room temperature. Density functional theory quantum computations are carried out to assign the recorded spectra to molecular conformations of the complexes. In addition to inspecting specific aspects of the in-

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dividual complexes, we address the issue of the constraints imposed by the relative size of the cation and the crown ether ring in determining the conformation and stability of the ternary system. The results are expected to aid in the design of optimal molecular tweezer architectures based on crown ethers for specific cation binding.

#### **Results and Discussion**

#### Cu<sup>2+</sup> complexes

The starting point of this investigation was the characterization of the binary and ternary complexes formed by the [18]crown-6 crown ether with the  $Cu^{2+}$  cation. On the one hand, we intended to determine what kind of coordination arrangement this open shell divalent cation would build with the oxygen atoms of the 18c6 ether ring. Furthermore, we were interested in describing how that coordination changes when a second ether molecule binds to the complex to form the  $(18c6)_2-Cu^{2+}$  ternary complex.

We focus first on the results for the  $18c6-Cu^{2+}$  complex. Figure 1 shows the gas phase infrared multiple photon dissociation (IRMPD) spectrum recorded for this system together with the computed IR spectrum corresponding to the lowest energy conformer predicted by the B3LYP/6-311 + +G(2d,2p) method. For the sake of discussion, the vibrational bands are labeled A through F in order of increasing wavenumber. The dominant types of nuclear motions of the vibrational modes associated with these bands are as follows: Band A is due to COC bending coupled with CH<sub>2</sub> torsion vibrations, bands B and C correspond to the C–C and C–O stretching modes, respec-



**Figure 1.** Top panel: experimental IRMPD spectrum (upper trace) of the  $18c6-Cu^{2+}$  binary complex, and corresponding computational B3LYP/6-311 + + G(2d,2p) IR spectrum (lower trace), obtained from the convolution of the transitions represented by the histograms with a broadening of  $15 \text{ cm}^{-1}$ . The vibrational bands are labeled A–F for discussion and the associated vibrational modes are indicated in the text. Bottom panel: representation of the lowest energy B3LYP conformer indicating the approximately square-planar coordination network built by the crown ether backbone around the cation.

tively, and bands D, E, and F are related to CH<sub>2</sub> torsions, wagging, and scissoring motions, respectively. It can be observed that the B3LYP spectrum reproduces quite accurately the experimental IRMPD spectrum, except for a slight shift of the bands of higher frequency associated with the CH<sub>2</sub> vibrations (bands D, E, and F).

The lower panel of Figure 1 depicts the molecular structure of the B3LYP lowest energy 18c6–Cu<sup>2+</sup> conformer and sketches the six-fold coordination of the cation involving all the oxygen atoms of the ring. It can be seen that this coordination arrangement demands that the 18c6 ring folds tightly around the cation. Such conformation is qualitatively similar to that displayed by the analogous complex of 18c6 with Mg<sup>2+</sup>,<sup>[23]</sup> a cation with an ionic radius similar to Cu<sup>2+</sup> (ca. 0.7 Å). However, whereas the lowest energy conformation of the 18c6–Mg<sup>2+</sup> complex was found to be of  $D_2$  symmetry,<sup>[23]</sup> for 18c6–Cu<sup>2+</sup> it is of  $C_1$  symmetry, with the  $D_2$  conformation lying higher in energy by about 2 kJ mol<sup>-1</sup> at the B3LYP/6-311++G(2d,2p) level of theory.

Such loss of symmetry appears to be related to the tendency of Cu<sup>2+</sup> to build a roughly square-planar coordination with four oxygen atoms of the ring, and a somewhat looser coordination with the other two oxygen atoms in normal directions. With the notation indicated in Figure 1, in the most stable  $C_1$  conformer the bond lengths take values  $a \approx b \approx 2.0$  Å and c = 2.3 Å. In the higher lying  $D_2$  conformer (not shown but visually similar), the bonds a and b are coplanar as in the  $C_1$  conformer but the bond lengths are a = 2.0 Å, b = c = 2.2 Å (hence, the bonds of equal length are not coplanar). In any case, the difference in energy between the  $C_1$  and  $D_2$  conformations is small and within the typical accuracy of the B3LYP computations, so that a contribution from both conformers in the present room temperature experiments can be expected. Our measurements cannot confirm nor rule out this possibility as the two structures are conformationally close and display similar IR spectra within the resolution of the present experiments.

Irrespective of the precise symmetry ( $C_1$  or  $D_2$ ) of the 18c6– Cu<sup>2+</sup> system, the folded cage-like arrangement of the crown ring around the cation makes the stability and structure of the (18c6)<sub>2</sub>–Cu<sup>2+</sup> ternary complex uncertain. It is a priori not clear to what extent the incorporation of the second ether unit would be able to disrupt the tight coordination of the cation with the first 18c6 molecule. The IRMPD spectrum measured for the  $(18c6)_2$ -Cu<sup>2+</sup> complex is shown in the top panel of Figure 2 together with the IRMPD spectrum of the 18c6–Cu<sup>2+</sup> binary complex. It can be appreciated that the vibrational bands of the ternary complex are split into two components with maxima at about 820 and 850 cm<sup>-1</sup> for band A, 930 and 950  $\text{cm}^{-1}$  for band B (unresolved), and 1040 and 1100  $\text{cm}^{-1}$  for band C. It is also noticeable that the IRMPD spectrum of the binary complex overlaps closely with the component of lower frequency within each of the bands. An intuitive interpretation of this finding readily emerges: in the  $(18c6)_2$ -Cu<sup>2+</sup> complex one of the crown ether units is coordinated tightly with the cation in a similar way as in the binary complex, while the second 18c6 molecule binds more peripherally to the 18c6-

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**Figure 2.** Comparison of the experimental IRMPD spectra of the  $(18c6)_2-M^{2+}$  ternary complexes (solid line traces, M = Cu, Ca, Ba) with the corresponding  $18c6-M^{2+}$  binary complexes (dashed line traces). The  $18c6-Ca^{2+}$  and  $18c6-Ba^{2+}$  spectra are from reference [23]. See text for a description of the vibrational modes associated with the bands labeled A–C. In the  $(18c6)_2-Cu^{2+}$  ternary complex, each band is split into two components (denoted "1" and "2"), one of which roughly coincides with the bands of the  $18c6-Cu^{2+}$  binary complex. The two components merge into a single band as the size of the cation increases in the Ca<sup>2+</sup> and Ba<sup>2+</sup> complexes. This is indicative of a transition from a marked asymmetry in the binding strength of the two crown ether molecules with the cation for  $(18c6)_2-Cu^{2+}$  to an even sharing of the coordination for  $(18c6)_2-Ba^{2+}$ , with the  $(18c6)_2-Ca^{2+}$  complex being an intermediate case (see text and Figure 4).

Cu<sup>2+</sup> moiety. That second, weakly bound 18c6 molecule would then be responsible for the blue-shifted component of the bands (denoted "2" in Figure 2). Such an interpretation is in fact supported by the present computations.

The IRMPD spectrum of the (18c6)<sub>2</sub>-Cu<sup>2+</sup> complex is shown in its full extent in the top panel of Figure 3, where it is compared with the IR spectrum of the most stable conformer predicted by the B3LYP/6-311 + + G(d,p) computation. The agreement between the B3LYP and the experimental spectra is remarkable. Figure 4 represents the molecular structure of the B3LYP conformer which is indeed characterized by the asymmetrical binding of the two crown ether units with the cation, as anticipated above. The inspection of the vibrational motions associated with each of the normal modes predicted by the computation corroborates the assignment of the two band components in the IR spectrum to the two differentiated 18c6 units of the complex. Notably, the peripheral "spectator" 18c6 molecule is bound due to an ensemble of short range (2.2-2.4 Å) CH-O hydrogen-bonding intermolecular interactions, in addition to the longer range (4–6 Å) charge-dipole interactions of the oxygen atoms with the  $Cu^{2+}$  cation.

It is of interest to mention that it was fairly straightforward to produce and store the  $(18c6)_2$ -Cu<sup>2+</sup> ternary complex in the ICR trap. In contrast, no trace of the  $(18c6)_2$ -Cu<sup>+</sup> complex could be found when the same experiment was performed with the monovalent Cu<sup>+</sup> cation (with CuCl as the precursor).



**Figure 3.** Full representation of the experimental IRMPD spectra recorded for the  $(18c6)_2-M^{2+}$  (M=Cu, Ca, Ba) ternary complexes (upper trace in each panel), and comparison with the respective computational B3LYP/6-311 + +G(d,p) IR spectra (lower race in each panel). The vibrational bands are labeled A–F for discussion and the associated vibrational modes are indicated in the text. The intense C–O stretching band C was measured independently with attenuated laser power in order to avoid saturation effects. The B3LYP spectra are obtained from the convolution of the transitions represented by the histograms with a broadening of  $15 \text{ cm}^{-1}$ . The lowest energy B3LYP conformers associated with the spectra are represented in Figure 4.



**Figure 4.** Representation of the computational lowest energy conformers of the  $18c6-M^{2+}$  binary (B3LYP/6-311 + +G(2d,2p)) and  $(18c6)_2-M^{2+}$  ternary (B3LYP/6-311 + +G(d,p)) complexes (M = Cu, Ca, Ba) associated with the IR spectra shown in Figures 1 and 3. The hydrogen atoms of the crown ether backbone have been removed for clarity, except those involved in CH- $\cdot$ O bonds (indicated with dashed lines) between the two ether rings in the ternary systems. The  $18c6-Ca^{2+}$  and  $18c6-Ba^{2+}$  conformers are from reference [23].

The binding energy of the "spectator" 18c6 molecule appears to be significantly decreased for the singly charged cations, so that the complex is unstable under the present operating conditions of the ion source and the preconcentration hexapole trap. This observation suggests that charge-dipole interactions

should be a key factor for the stability of this type of asymmetric ternary complex.

#### Ternary complexes of Ca<sup>2+</sup> and Ba<sup>2+</sup>

The second stage of the study was devoted to the evolution of the  $(18c6)_2-M^{2+}$  most stable conformation for progressively larger guest divalent cations. For this purpose, we considered as reference our previous study on the binary complexes formed by 18c6 with the cations of the alkaline-earth series.<sup>[23]</sup> The cations Ca<sup>2+</sup> and Ba<sup>2+</sup> (ionic radii of 1.00 and 1.35 Å, respectively) seemed appropriate choices to work out the transition from a folded conformation to a fully open one in the 18c6–M<sup>2+</sup> binary system. Figure 4 shows that indeed the 18c6–Ca<sup>2+</sup> complex displays a partly folded structure, while the 18c6–Ba<sup>2+</sup> complex is fully open and quasi-planar. In this study, we explore how the structure of the corresponding ternary complexes evolves with cation size.

The IRMPD spectra recorded for the  $(18c6)_2-Ca^{2+}$  and  $(18c6)_2-Ba^{2+}$  complexes are shown in Figures 2 and 3 in similar representations as the ones described above for the Cu<sup>2+</sup> complex. One of the most obvious changes in the spectra as the cation becomes larger is the merging of the two components of the vibrational bands. This is particularly apparent for the C–O stretching band  $(1000-1200 \text{ cm}^{-1})$ , which is dominant in the IRMPD spectra. The splitting between the two components of this band is only of about 25 cm<sup>-1</sup> for the Ca<sup>2+</sup> complex (i.e. more than a factor of two smaller than in the case of Cu<sup>2+</sup>), while both components are merged into a relatively narrow single-maximum envelope for the Ba<sup>2+</sup> complex. This trend is indicative of a progressively more symmetric participation of the two 18c6 molecules in the binding of the cation. The agreement with the B3LYP IR spectra is again very good.

Figure 2 also shows that the C–O stretching bands of the ternary complexes of  $Ca^{2+}$  and  $Ba^{2+}$  are appreciably blue-shifted with respect to the corresponding bands of the binary complexes. This finding can be attributed to an overall weakening of the interactions of each of the ether oxygen atoms with the cations owing to the sharing of the coordination between the two 18c6 molecules. Such a shift was not observed when comparing the spectra of the binary and ternary complexes of  $Cu^{2+}$  since in that case one of the 18c6 molecules essentially retains the same coordination arrangement with the cation in the two types of complexes. Note that the C–C stretching band does not shift from the binary to the ternary complex as it is not so directly affected by the coordination of the oxygen atoms with the cation.<sup>[23]</sup>

The most stable B3LYP conformations for the  $(18c6)_2$ -Ca<sup>2+</sup> and  $(18c6)_2$ -Ba<sup>2+</sup> complexes, depicted in Figure 4, are consistent with the above considerations. In the ternary Ca<sup>2+</sup> complex, the participation of the two 18c6 molecules is still uneven but the cation interacts directly with oxygen atoms of the two ether molecules. One 18c6 embraces the cation in a somewhat more open conformation than in the binary complex, while the second 18c6 molecule places two oxygen atoms in tight coordination with the cation. In this way, the Ca<sup>2+</sup> coordinates with eight ether oxygen atoms in a remarkable uniform way, at distances within 2.5–2.6 Å (in the binary complex all six cation–oxygen distances are 2.4 Å<sup>[23]</sup>). It can also be noted that this ternary complex is sustained in addition by two weak CH···O intermolecular hydrogen bonds (2.2 Å bond distance) between the two ether backbones.

The  $(18c6)_2$ -Ba<sup>2+</sup> complex stabilizes in a noticeable symmetric  $C_2$  arrangement in which the interaction with the cation is evenly balanced between the two 18c6 molecules. The partly folded conformation displayed by the two crown ether units is in marked contrast with the quasi-planar  $D_{3d}$  structure of the ether ring in the binary complex (see Figure 4). In this way, all twelve oxygen atoms coordinate with the Ba<sup>2+</sup> cation at distances within 3.0–3.3 Å (vs. 2.8 Å in the binary complex). Two CH--O weak intermolecular hydrogen bonds are also formed between the crown ethers in this complex with bond distances of about 2.4 Å.

Interestingly, the coordination of the  $Ca^{2+}$  and  $Ba^{2+}$  cations in the ternary complexes with eight and twelve ether oxygen atoms, respectively, is in line with previous hydration studies for the 18c6 complexes of these two cations.<sup>[26]</sup> Hydration numbers of two and six were determined for the 18c6–Ca<sup>2+</sup> and 18c6–Ba<sup>2+</sup> complexes, respectively. It turns out that the number of water molecules that each of the binary complexes can accommodate is coincident with the number of oxygen atoms from a second ether that it can bind tightly.

#### Conclusion

Infrared multiple photon dissociation vibrational spectroscopy in combination with quantum-chemical computations have been employed to provide insights into the conformational features of tweezer-like prototypes involving the [18]crown-6 ring molecule. The ternary complexes comprised of two [18]crown-6 molecules and one of the divalent metal cations  $Cu^{2+}$ ,  $Ca^{2+}$  or  $Ba^{2+}$  have been considered as benchmark systems to explore the dependence of the resulting structures on cation size.

The Cu<sup>2+</sup> cation induces a tightly folded arrangement of the crown ether backbone in the binary  $18c6-Cu^{2+}$  complex, in a qualitatively similar way as found previously for the  $18c6-Mg^{2+}$  complex.<sup>[23]</sup> As a consequence, the ternary  $(18c6)_2-Cu^{2+}$  complex displays a markedly asymmetric conformation for the two ether units. Whereas one 18c6 molecule coordinates with the cation in a folded conformation similar to that of the binary complex, the second 18c6 molecule binds peripherally through longer range electrostatic interactions with the cation and CH···O intermolecular bonds with the first 18c6 ring. This behavior leads to a pronounced splitting in some of the main vibrational bands of the complex into two components, namely a red-shifted component for the strongly bound crown ether backbone and a blue-shifted one associated with the more weakly bound "spectator" crown ether.

As the size of the cation becomes larger, represented here by the Ca<sup>2+</sup> and Ba<sup>2+</sup> complexes, the participation of the two 18c6 molecules becomes progressively greater. In the  $(18c6)_{2^{-}}$ Ca<sup>2+</sup> complex, one of the crown ether units still retains a resemblance of the coordination found in the  $18c6-Ca^{2+}$  binary

complex. Nevertheless, the cation manages to coordinate tightly with two of the oxygen atoms of the second 18c6 molecule, for a total cation–oxygen coordination number of eight. For the  $(18c6)_2$ –Ba<sup>2+</sup> complex, the appreciable size of the cation favors a symmetric coordination of the two ethers with the cation in a C<sub>2</sub> conformation in which all twelve ether oxygen atoms are involved. In accord with these trends, the experimental IRMPD spectrum shows a moderate splitting of the vibrational bands for  $(18c6)_2$ –Ca<sup>2+</sup> complex, while the two components are fully merged into single bands for the (18c6)<sub>2</sub>–Ba<sup>2+</sup> complex.

The present study has shown that the conformation adopted by the crown ethers in ternary  $(18c6)_2-M^{2+}$  complexes depends dramatically on the relative sizes of the ether ring and the cation. This general result indicates that the flexibility of the crown ether moiety in a molecular pincer should play a key role in the type of binding that it will achieve with a given cationic species. If the crown ethers have sufficient conformational freedom in the pincer architecture, the simultaneous participation of the two pincer arms will only be efficient for large cations while small cations will tend to coordinate with only one of the crown ether arms. The good agreement found between the experiments and the computations in this study indicate that the relatively inexpensive density functional theory approach can be employed to draw predictions in this field.

#### **Experimental Section**

#### ESI-FTICR IRMPD spectroscopy

Infrared multiple photon dissociation (IRMPD) spectra were recorded using a Fourier-Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer coupled to the free electron laser FELIX.<sup>[27]</sup> The binary 18c6–Cu<sup>2+</sup> and ternary (18c6)<sub>2</sub>–M<sup>2+</sup> (M = Cu, Ca, Ba) crownmetal complexes were produced at room temperature by electrospray of solutions of the crown ether and a metal salt (CuCl<sub>2</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub>, 1 mM) in a water/methanol (1:1) mixture. Ions are accumulated in a hexapole trap and then pulse injected into the ICR cell for isolation of the parent mass and subsequent irradiation with typically ten FELIX macro-pulses. Each macro-pulse is approximately 5  $\mu$ s long, has an energy of about 35 mJ, and consists of a train of micro-pulses with a repetition frequency of 1 GHz. The nominal spectral bandwidth of the radiation amounts to 0.5% of the central wavelength. Further description of typical experimental procedures can be found in reference [28].

If the infrared wavelength is in resonance with a vibrational mode of the complex, multiple photon absorption occurs leading to dissociation of the parent ion. The IRMPD spectrum is constructed by plotting the relative ionic fragment yield as a function of the wavenumber of the radiation. For the binary  $18c6-Cu^{2+}$  complex, two dominant fragmentation channels are observed, namely those associated with the cleavage of one or two  $OC_2H_4$  ether monomers from the crown ring. In all ternary complexes, a single dominant fragment was detected which corresponded to the loss of one of 18c6 molecules, hence leading to the binary complex  $18c6-M^{2+}$ . The laser pulse power was monitored and the recorded fragment ion signals were corrected in consonance with the linear laser power dependence of the noncoherent multiple photon dissociation yield characteristic of IRMPD.<sup>[28]</sup> The intense C–O stretching band (ca.  $1000-1200 \text{ cm}^{-1}$ ) was repeatedly probed with attenuated laser power to avoid saturation owing to depletion of complexes in the laser beam path.

#### Quantum chemistry calculations

Simulated annealing with the universal force field was employed to generate an ensemble of molecular structures. For the ternary complexes, the procedure was initiated from arrangements generated ad hoc, by incorporating a second 18c6 unit to the  $18c6-M^{2+}$ binary structures determined here for Cu<sup>2+</sup> and in a previous similar investigation for Ca<sup>2+</sup> and Ba<sup>2+</sup>.<sup>[23]</sup> The conformations of lowest energy resulting from the simulated annealing were optimized with density functional theory calculations at the B3LYP/6-31G(d,p) level. Finally, the overall most stable conformers were reoptimized with the larger basis set  $6\mathchar`-311\mathchar`+G(d,p).$  For the 18c6–Cu $^{2+}$ binary system the basis set was also extended to 6-311 + +G(2d,2p) for a better comparison with the previous studies on the analogous alkaline-earth complexes.<sup>[23]</sup> All energies reported here for the conformers are Gibbs free energies including vibrational zero-point corrections. The nonvalence electrons of Ba<sup>2+</sup> were treated with the Stuttgart/Dresden effective core potential.<sup>[29]</sup> For the Cu<sup>2+</sup> complexes, only the doublet ground electronic state of the cation was considered. Spin promotion owing to the ligand field, inducing the stabilization of spin states of higher multiplicity, was observed for lighter third-row transition-metal cations (e.g. Cr<sup>+</sup>).<sup>[30]</sup> A similar effect is not expected for the d<sup>9</sup> electronic configuration of Cu<sup>2+</sup>. The calculations were carried out with the Gaussian 09 code.<sup>[31]</sup>

The theoretical harmonic IR spectra shown in this work were calculated by convoluting the B3LYP lines with a Lorentzian broadening of 15 cm<sup>-1</sup> (full width at half maximum). The computed vibrational frequencies for all the complexes were scaled for comparison with experiment by a factor 0.982, which is in agreement with the scaling derived in previous studies for the level of theory presently employed.<sup>[32]</sup>

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