The Site of Cr⁺ Attachment to Gas-Phase Aniline from Infrared Spectroscopy

Jos Oomens,[†] David T. Moore,[†] Gert von Helden,[§,†] Gerard Meijer,[§,†] and Robert C. Dunbar*,[‡]

FOM Institute for Plasma Physics "Rijnhuizen", Postbus 1207, 3430 BE Nieuwegein, The Netherlands, and Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44118

Received October 3, 2003; E-mail: robert.dunbar@case.edu

There has been widespread interest in the structure, bonding, and reactivity of metal ion complexes in the gas phase.[1] When a gas-phase metal ion complex forms with a ligand offering more than one likely binding site, it is a difficult challenge for mass spectrometric techniques to establish which of the possible structures is favored. Information from experiments such as collision-induced dissociation,[2] namely the binding thermochemistry and the fragmentation pattern, is often uninformative or inconclusive. Potentially more structurally incisive fragmentation approaches such as Coulomb explosion imaging[3] are difficult to apply to larger ions. It is obvious that chemists would like to apply the power of spectroscopic molecular characterization techniques, in particular infrared spectroscopy, to such structural questions. The availability of powerful, full-spectrum infrared (IR) light sources, most notably the free electron laser (FEL), is opening new opportunities to achieve this goal. Combining the versatility of a mass spectrometric technique such as Fourier transform ion cyclotron resonance (FTICR)[4] for gas-phase synthesis of ions with the power of the FEL for IR spectroscopy yields a spectrometer that allows structural characterization of metal ion complexes of significant chemical complexity.

The complexes of Cr⁺ with aniline provide a particularly apt application of such IR-spectroscopic structure probing, because the calculated energies for the ring-bound and side-chain-bound structures are so close that a clear choice cannot be made from the computational results. We show here the particular effectiveness of broadband IR spectroscopy with the FEL for characterizing these structurally ambiguous complexes. In the Cr⁺/aniline systems the spectroscopy gives clear and graphic demonstrations of preference for the ring-bound structure for the monomer complex and the ring–ring structure for the dimer complex.

Broadband IR spectroscopy, using for instance the *free electron laser for infrared experiments* (FELIX) facility at the FOM Institute,[5] has been used to generate spectra of a number of gas-phase ionic species in ion traps and molecular beams, including polycyclic aromatics and metal ion–benzene complexes.[6] Recently, IR spectra of proton-bound ether complexes were reported, obtained using an FT-ICR instrument interfaced to FELIX.[6d] A similar setup at the FEL facility in Orsay has been used to obtain IR spectra of Fe⁺ complexes of unsaturated hydrocarbons.[6e] It should be noted that many of these studies (including the present work) operate via the mechanism of infrared multiple photon dissociation (IRMPD).[7] Although IRMPD is inherently a multiple-photon technique, the mechanism is incoherent, and thus it yields IR spectra that are comparable to those obtained via linear direct absorption methods. However, the relative intensities of the bands should be compared only qualitatively.[6b]

Table 1. Cr⁺(aniline) Binding Energetics from DFT Calculations Using Two Different Functionals, Comparing the Sites with Cr over the Ring and over the Side-Chain Nitrogen[a]

	ΔH_0		ΔG_{298}	
	ring	N	ring	N
MPW1PW91	188.1	178.2	154.4	147.4
B3LYP	177.1	181.4	143.4	150.6

[a] Binding enthalpy (ΔH_0) at 0 K and binding free energy (ΔG_{298}) at 298 K (kJ mol⁻¹).

The experimental apparatus consists of a laboratory-built 4.7-T FT-ICR spectrometer interfaced to FELIX; further details may be found elsewhere.[8] Cr⁺ ions are produced by laser ablation[9] and trapped in the ICR cell, where they undergo ion–molecule reactions with aniline vapor to produce the desired species, either Cr⁺(aniline) or Cr⁺(aniline)₂. Undesired species are ejected from the ICR cell, and the complex of interest is irradiated with several macropulses (~35 mJ/pulse) from FELIX. The photodissociation products and any remaining parent ion are then measured using a standard FT-ICR excite/detect sequence.[4] IRMPD spectra are generated by plotting the fragmentation yield as a function of the wavelength of FELIX.[10]

As mentioned above, a primary goal of this work is to use IR spectroscopy to resolve structural ambiguity in cases where computational results are inconclusive. Density functional theory (DFT) computations provide reasonable results for transition-metal-containing molecules of substantial size, but the results are somewhat subject to detailed choices of functional and basis sets. As shown in Table 1, the DFT binding energy results for the two Cr⁺(aniline) isomers actually show a reversal depending on functional.[11] The popular B3LYP functional favors the N-binding site, but the MPW1PW91 functional (which was considered to be better for ring vs side-chain comparison in a previous study of metal ion complexes of phenol[12]) favors the ring-binding site of aniline. Thus, within computational uncertainty, the two sites are not resolvable; this was also found to be true for the Cr⁺(aniline)₂ isomers. The IR spectra calculated using the different functionals were not significantly different, so only the MPW1PW91 results are explicitly considered here.

Figure 1 shows the IRMPD spectrum of the monomer complex along with the computed IR spectra[11] of the two isomers. The most diagnostic features from the calculations are the peak near 1070 cm⁻¹ for the N-bound structure and the peak near 1310 cm⁻¹ for the ring-bound structure. The experimental spectrum shows a strong feature at 1300 cm⁻¹, but nothing near 1070 cm⁻¹, clearly indicating a ring-bound geometry. Overall, the fit of the spectrum to the calculated ring-bound spectrum is very good.

The 1070 cm⁻¹ peak in the N-bound geometry is due to the frustrated inversion motion of the NH₂ group. It should be noted that the inversion mode in bare aniline has a double-well potential and is thus poorly represented by harmonic calculations.[6a] However,

† FOM Institute for Plasma Physics "Rijnhuizen".
‡ Case Western Reserve University.
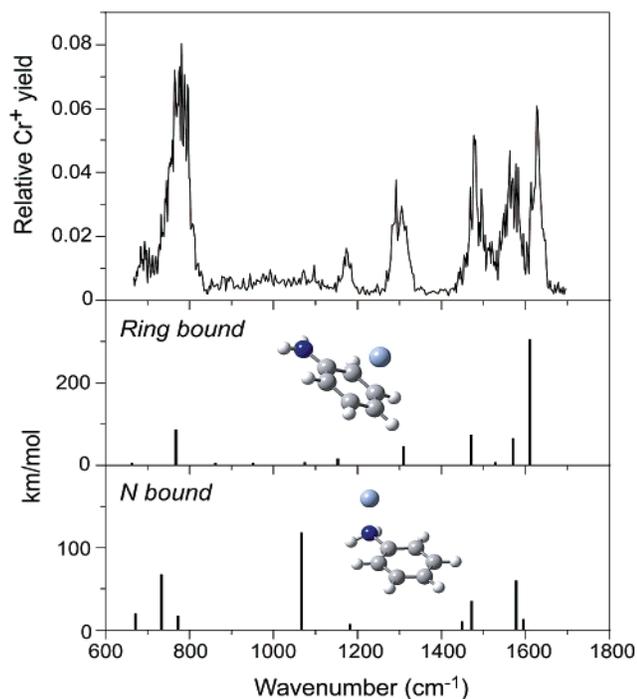§ Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany.

Figure 1. IRMPD spectrum of the Cr$^+$(aniline) complex, along with calculated IR absorption spectra of the two isomeric structures. The DFT frequencies are scaled down by a factor of 0.955 in Figures 1 and 2.
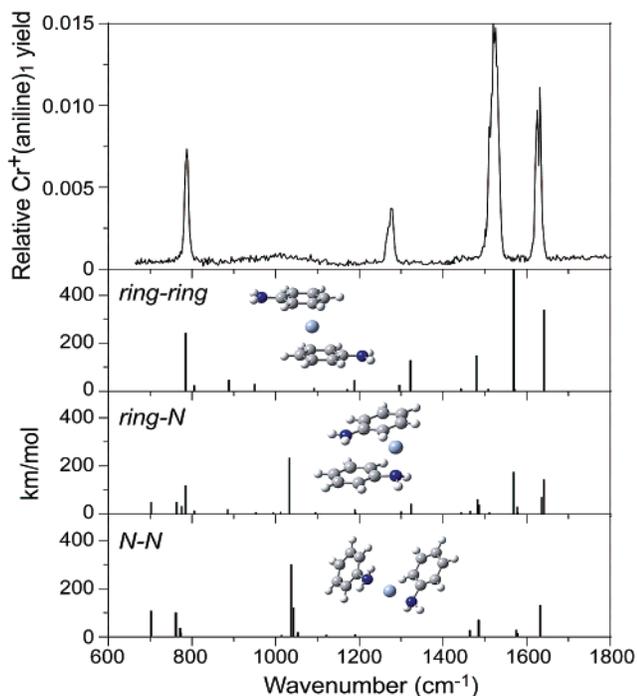

Figure 2. IRMPD spectrum of the Cr$^+$(aniline)$_2$ complex, along with calculated spectra for the ring−ring, ring−N and N−N isomers.

the presence of the Cr atom in the N-bound structure strongly destabilizes one of the wells; therefore, we expect this mode to be well represented by the methods used here. The 1310 cm^{-1} peak in the ring-bound spectrum is a mixed mode incorporating primarily CN stretching and in-plane CH bending motions, and is mildly blue-shifted from a similar mode in the calculated spectrum of bare aniline at 1266 cm^{-1}.

Figure 2 shows experimental and calculated spectra for the Cr$^+$(aniline)$_2$ dimer complex. The diagnostic features from the

computed spectra are quite analogous to the single aniline case above, with a feature near 1040 cm^{-1} if either of the aniline ligands is N-bound to the metal ion, while a peak near 1320 cm^{-1} is characteristic of a ring-bound ligand. The experimental spectrum indicates that the complex prefers a structure with two ring-bound ligands, since it has a peak near 1280 cm^{-1} (very similar to the monomer complex) and no peak near 1040 cm^{-1}. The overall agreement between the experimental and calculated spectra is not quite as good as for the monomer complex, and further refinement of this vibrational calculation seems called for in the future.

The observed IRMPD spectra of both the monomer and dimer complexes are in excellent agreement with the predictions for ring coordination of the Cr to aniline. The presence of as much as 10% of N-bound complexes seems unlikely based on the spectra. This indicates that the N-bound structures are less stable (with respect to free energy) than the ring-bound structures by at least ~5 kJ mol^{-1}, in accord with the computational results using the MPW1PW91 functional. This latter functional seems clearly superior to the B3LYP functional for calculating the binding energetics in this system. Future work will explore whether the close balance between the ring and the aromatic−nitrogen binding sites might be reversed by the presence of perturbing substituents or by choice of a different metal partner.

References

(1) (a) Leary, J. A., Armentrout, P. B., Eds. *Int. J. Mass. Spectrom.* **2001**, *204*, 1−299. (b) Armentrout, P. B., Rhyzhov, V., Eds. *Int. J. Mass. Spectrom.* **2003**, *227*, 1−216.
(2) Rodgers, M. T.; Armentrout, P. B. *Mass Spectrom. Rev.* **2000**, *19*, 215.
(3) Baer, A.; Grieser, M.; Knoll, L.; Levin, J.; Repnow, R.; Schwalm, D.; Vager, Z.; Wester, R.; Wolf, A.; Zajfman, D. *Phys. Rev. A* **1999**, *59*, 1865.
(4) Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. *Mass Spectrom. Rev.* **1998**, *17*, 1.
(5) Oepts, D.; van der Meer, A. F. G.; van Amersfoort, P. W. *Infrared Phys. Technol.* **1995**, *36*, 297.
(6) (a) Piest, H.; von Helden, G.; Meijer, G. *J. Chem. Phys.* **1999**, *110*, 2010. (b) Oomens, J.; Tielens, A. G. G. M.; Sartakov, B.; von Helden, G.; Meijer, G. *Astrophys. J.* **2003**, *591*, 968. (c) van Heijnsbergen, D.; von Helden, G.; Meijer, G.; Maitre, P.; Duncan, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1562. (d) Moore, D. T.; Oomens, J.; van der Meer, L.; von Helden, G.; Meijer, G.; Valle, J.; Marshall, A. G.; Eyler, J. R., submitted. (e) Lemaire, J.; Boissel, P.; Heninger, M.; Mauclaire, G.; Bellec, G.; Mestdagh, H.; Simon, A.; LeCaer, S.; Ortega, J. M.; Glotin, F.; Maitre, P. *Phys. Rev. Lett.* **2002**, *89*, art. no. 273002.
(7) The principles of resonant photofragmentation via IRMPD using a mechanism of sequential absorption of many IR photons have been discussed in detail elsewhere (see ref 6b).
(8) Valle, J.; Oomens, J.; Moore, D. T.; von Helden, G.; Hendrickson, C. L.; Blakney, G. T.; van der Meer, A. F. G.; Marshall, A. G.; Eyler, J. R., manuscript in preparation.
(9) The fundamental (1064 nm) of a Nd:YAG laser (~10 mJ/pulse) was used to ablate the chromium sputtering target (99.98%) located ~1 m from the ICR cell. The laser beam was lightly focused (1.5 m focal length).
(10) The fragment/parent channels for Cr$^+$(aniline) and Cr$^+$(aniline)$_2$ complexes were 52/145 and 145/238, respectively, corresponding to loss of a single aniline from each complex. A linear correction was also applied to account for power variations in FELIX (see ref 6b).
(11) Energy calculations used a 6-311+g(d,p) basis. Structure optimization and vibrational properties used a reduced basis with 6-311+g(d) on Cr and 6-31+g(d) on other elements. Reported energies have been corrected for zero-point and basis set superposition effects. A scale factor of 0.955, which gave the best fit to the neutral aniline spectrum, was applied to the calculated vibrational frequencies.
(12) Dunbar, R. C. *J. Phys. Chem. A* **2002**, *106*, 7328.

JA038867V