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Link to publication

Supplementary Information

Preparation of Labile Ni$^+$(cyclam) Cations in the Gas Phase Using Electron Transfer Reduction through Ion-Ion Recombination in an Ion Trap and Structural Characterization with Vibrational Spectroscopy

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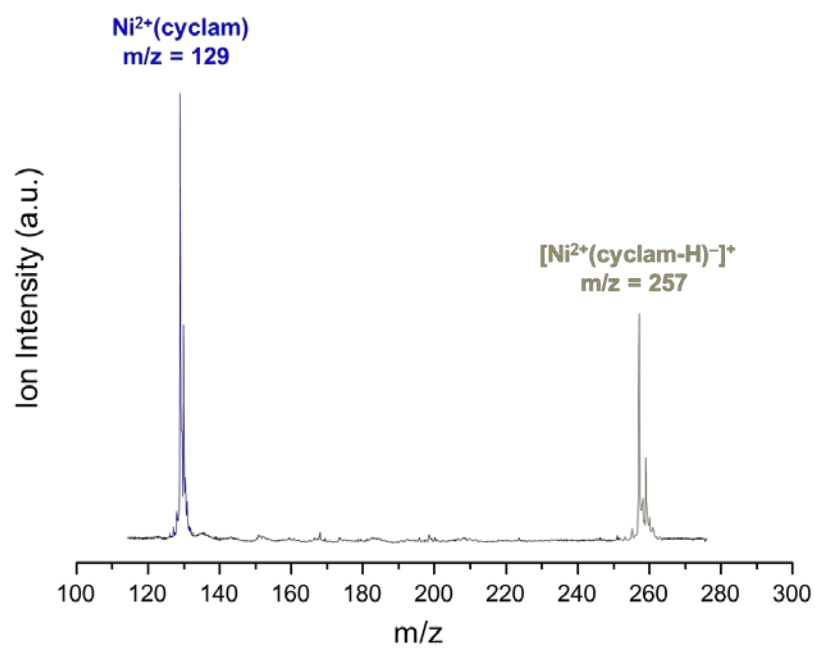
Figure S1. Mass spectrum of Ni^{2+}(cyclam) (blue) and $[Ni^{2+}(cyclam-H^-)]^+$ (gold) obtained on the Yale tandem time of flight photofragmentation mass spectrometer.
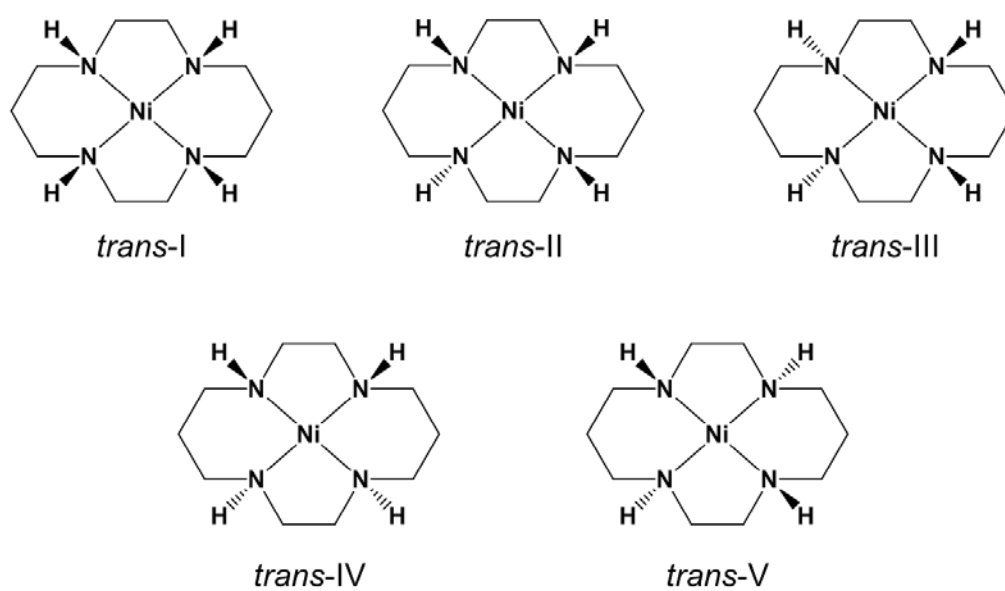
Figure S2. Structures of the five isomers of Ni^{2+}(cyclam).
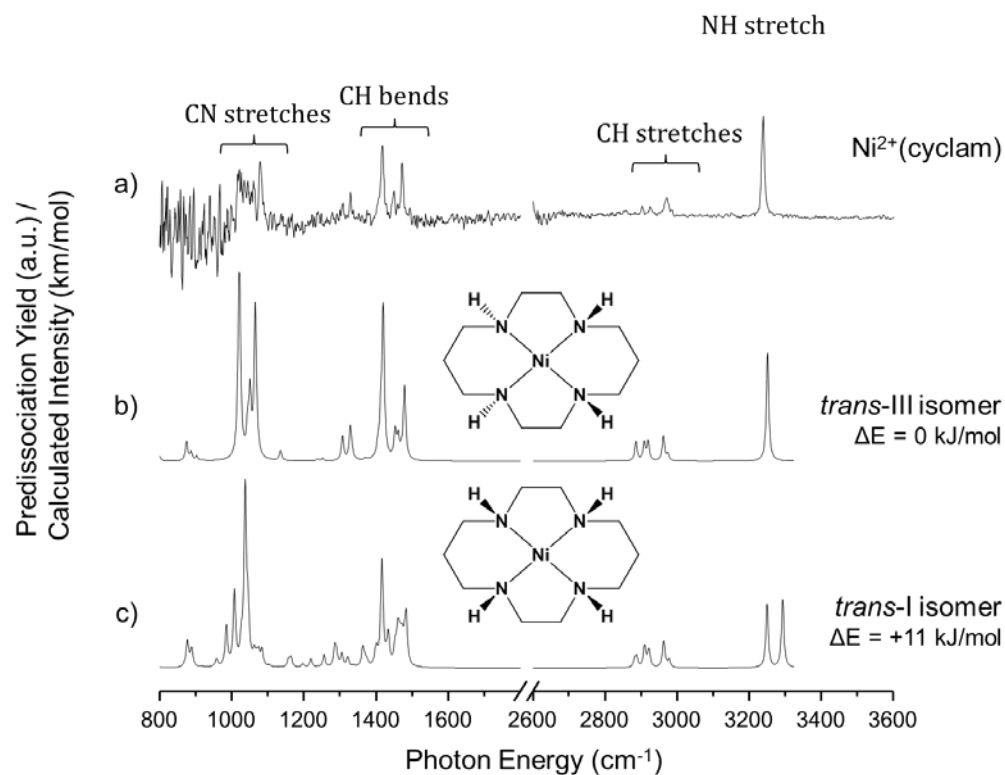
Figure S3. The vibrational predissociation spectrum of a) Ni^{2+}(cyclam) shows good agreement with the calculated vibrational spectrum of the lowest energy isomer, b) the *trans*-III isomer. The next lowest energy isomer, the *trans*-I isomer, is 11 kJ/mol higher in energy and c) its calculated vibrational spectrum shows less agreement, especially in the NH stretching region. All calculations were performed at the B3LYP/6-31++G(d,p) level of theory and scaled by 0.975 below 2200 cm^{-1} and by 0.95 above 2200 cm^{-1}.
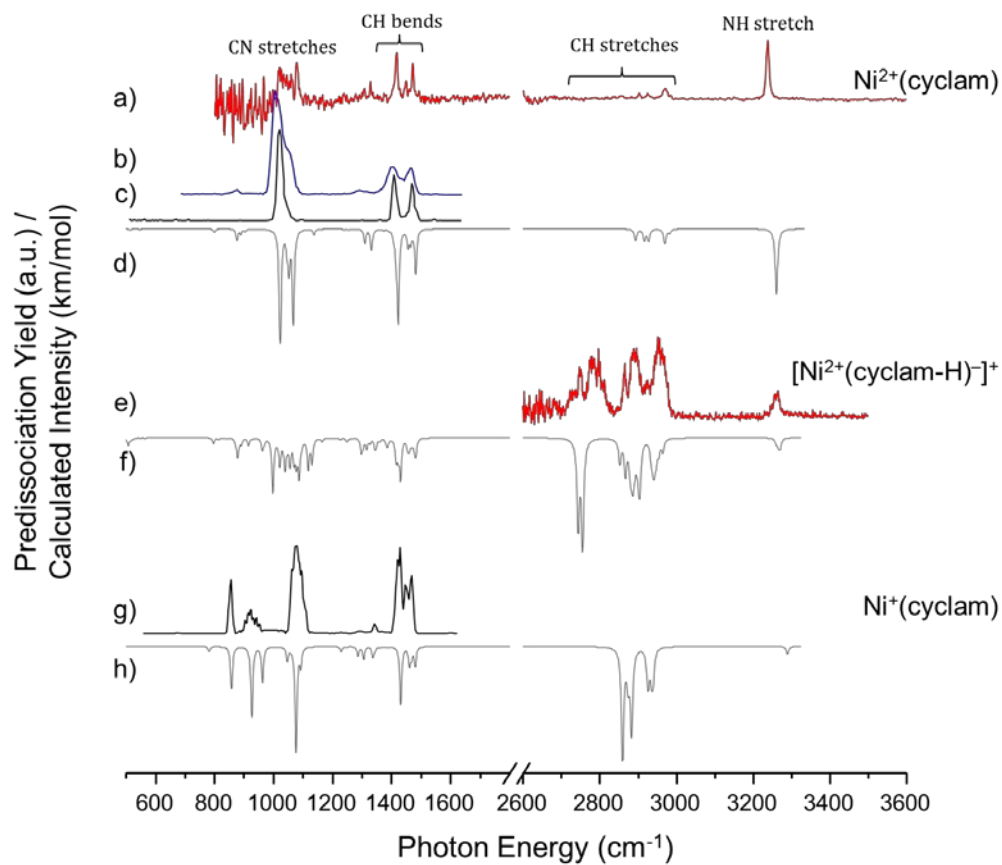
Figure S4. Vibrational spectra of a-c) Ni^{2+}(cyclam), e) [Ni^{2+}(cyclam-H)$^-$]$^+$, and g) Ni$^+$(cyclam). The red traces indicate N$_2$ predissociation spectra taken at 30 K, while the black traces indicate IRMPD spectra taken at 300 K. The blue trace (b) shows the IRMPD spectrum of Ni^{2+}(cyclam) recorded in the FTICR-MS at FELIX which recovers more spectral features than the IRMPD spectrum recorded in the QIT. Calculated vibrational spectra are included as the grey inverted traces for b) Ni^{2+}(cyclam), d) [Ni^{2+}(cyclam-H)$^-$]$^+$, and f) Ni$^+$(cyclam). All calculations were performed at the B3LYP/6-31++G(d,p) level of theory and scaled by 0.975 below 2200 cm^{-1} and by 0.95 above 2200 cm^{-1}.

Experimental and Computational Details

Mass Spectrometry

The FELIX experiments were carried out using a modified 3D quadrupole ion trap (Bruker, AmaZon Speed ETD, Bremen, Germany).[1] The Ni^{2+}(cyclam) ions (m/z = 129 for the ^{58}Ni isotope) were generated directly *via* electrospray ionization (ESI) from a solution containing 10^{-6} M cyclam and 10^{-5} M Ni(NO$_3$)$_2$ in 1:1 MeOH:H$_2$O. The ^{58}Ni^{2+}(cyclam) at m/z = 129 was then mass isolated, and singly charged ^{58}Ni$^+$(cyclam) (m/z = 258) ions were generated by charge reduction using the ETD option of the QIT MS. This involves the transfer of an electron from the reagent anion (fluoranthene radical anion) in an ion-ion reaction directly inside the ion trap[2]. A reaction time of 200-300 ms was found to give optimal conversion to the charge-reduced species. Mass spectra of the reactant ions as well as the products generated by ion-ion recombination are presented in Fig. 2 of the main text. In addition to simple charge reduction, substantial fragmentation of the reduced ions by sequential H-atom loss is also observed, a process that is well known from the more common application of ETD in protein sequencing[3]. In fact, the product ion resulting from H-atom abstraction from the charged reduced species (m/z = 257) was the dominant ion in the ETD mass spectrum, though a sufficient number of intact charge-reduced ions Ni$^+$(cyclam) (m/z = 258) remained for mass isolation and subsequent IRMPD measurements. Note that the removal of Ni isotopes other than ^{58}Ni prior to charge reduction allows us to uniquely mass-isolate the one-electron reduction product and distinguish it from potential H-loss fragments involving higher mass Ni isotopes.

In the FTICR MS, which has been described in detail previously[4-5], Ni^{2+}(cyclam) ions were produced from solutions containing approximately 10^{-3} M cyclam and 10^{-3}M Ni(II) in 1:1 MeOH:H$_2$O by ESI. As this MS has no possibility for charge reduction, only IRMPD spectra for Ni^{2+}(cyclam) ions were measured on this platform.

At Purdue, ETR was performed using a modified QTRAP 4001 (Sciex, Concord, ON, Canada). The instrument was run in mutual ion storage mode, which allowed simultaneous trapping of cations and anions in the q2 linear ion trap (LIT) by applying RF trapping potentials to the exit and entrance lenses as previously reported.[6] The cations were generated by ESI of Ni(cyclam)Cl$_2$, which was synthesized according to the procedure by Bosnich *et al*.[7] Azobenzene anions were generated by atmospheric pressure chemical ionization (APCI). As

previously described,[8] a solid azobenzene sample was attached inside the curtain plate of the Sciex ESI source for the counter-current N_2 so that the flowing gas sampled the headspace to volatilize the organic, which was ionized by a corona discharge on a platinum wire ($\approx$-2 kV) at atmospheric pressure. Both the azobenzene anion (m/z = 182) and Ni^{2+}(cyclam) (m/z = 129) were isolated by a transmission-mode RF/DC mass filter (q1) prior to 10 ms of mutual storage in q2. The products were analyzed by mass selective axial ejection (MSAE) in q3.[9]

IRMPD Spectroscopy

Trapped ions were irradiated for 1.5 (in the QIT) or 6 seconds (in the FTICR) by the tuneable infrared radiation of the FELIX free electron laser (FEL)[10-11] in the fingerprint region (600-1800 cm^{-1}). Operating at a repetition rate of 10 Hz, FELIX produces 6-10 µs long macropulses with energies up to 100 mJ per pulse. When the frequency of the FEL is resonant with a vibrational mode of the trapped ions, multiple photons are absorbed and the internal energy of the ions increases. Following statistical redistribution throughout the many background states of the ion, unimolecular dissociation occurs along the pathway with the lowest energy barrier. We generate IR spectra by relating the fraction of dissociation (yield=$\sum$(fragment ions)/$\sum$(precursor + fragment ions)) to the IR wavelength as the laser is scanned[10, 12]. The yield is linearly corrected for the wavelength dependence of the laser pulse energy and wavelength is calibrated (online) using a grating spectrometer.

Measurements in the FT-ICR MS proceed analogously as those in the QIT, though for this experiment the ions were additionally irradiated for 20 ms by the output of a continuous-wave CO_2-laser (10.6 µm, 30 W) directly after each FEL pulse or pulses from an optical parametric oscillator/amplifier (OPO/OPA) IR source (Laser Vision, USA) in order to enhance the extent of dissociation[13]. The OPO/OPA allows us to acces the H-stretching region in order to probe the N-H stretching vibrations.

N_2 Tagged Predissociation Spectroscopy

At Yale University, ions were generated from solution in acetonitrile using ESI and introduced into the custom Yale tandem time-of-flight photofragmentation mass spectrometer previously described[14-15]. After being guided through several regions of differential pumping, the ions were turned 90° by a quadrupole bender into a 3D Paul trap (Jordan), held at a temperature

of 30 K by a helium cryostat (Sumitomo). The ions are trapped for 90 ms where they are collisionally cooled by a helium buffer gas doped with 10% N_2 in order to promote N_2 tagging. The tagged ions are then extracted from the trap and enter the time-of-flight region of the mass spectrometer. The ions of interest are then mass selected and interrogated with an OPO/OPA laser (LaserVision) from 800-4000 cm^{-1} in order to induce the loss of the tag, thus forming a photofragment. The formation of this photofragment is measured as a function of photon energy in order to generate a vibrational spectrum.

Computational Details

DFT optimizations and vibrational spectrum calculations were performed at the B3LYP/6-31++G(d,p) level of theory with Gaussian09.[16] For Ni^{2+}(cyclam), both the singlet and triplet states were calculated, and the triplet state was found to be ~70 kJ/mol higher in energy. An overview of these calculations is given in Table S1. For Ni^{+}(cyclam) a multiplicity of 2 (doublet) was used. An overview of these calculations is given in Table S2. Natural population analysis (NPA)[17] was performed using the B3LYP/6-31++G(d,p) level of theory using Gaussian09 using the keyword "pop=npa".

Table S1. DFT derived energies (in kJ/mol) for the lowest energy structures for the five isomers of Ni^{2+}(cyclam) in the singlet spin state. All calculations were performed at the B3LYP/6-31++G(d,p) level of theory.

Ni^{2+}(cyclam)	
	ΔE (kJ/mol)
trans-I	10.96
trans-II	38.96
trans-III	0
trans-IV	56.58
trans-V	30.66

Table S2. DFT derived energies (in kJ/mol) for the lowest energy structures for the five isomers of Ni^{2+}(cyclam). All calculations were performed at the B3LYP/6-31++G(d,p) level of theory.

Ni^{+}(cyclam)	
	ΔE (kJ/mol)
trans-I	9.00
trans-II	40.34
trans-III	0
trans-IV	55.19
trans-V	31.49

Table S3. Charge state, multiplicity and XYZ coordinates for *trans*-III Ni^{2+}(cyclam) and *trans*-III Ni$^+$(cyclam). All coordinates are in Angstroms. All optimizations were performed at the B3LYP/6-31++G(d,p) level of theory.

	Ni^{2+}(cyclam)				Ni$^+$(cyclam)		
2	1			1	2		
Ni	0.000000	0.000027	-0.000018	Ni	-0.000001	0.000001	-0.000004
N	1.323099	-1.440642	-0.274931	N	1.383601	-1.547603	-0.302603
N	-1.322560	-1.441008	0.274789	N	-1.383579	-1.547615	0.302595
N	-1.323086	1.440695	0.274739	N	-1.383592	1.547611	0.302590
N	1.322647	1.441029	-0.274666	N	1.383590	1.547611	-0.302611
C	0.729472	-2.733520	0.198590	C	0.738988	-2.785539	0.197626
C	-0.728556	-2.733760	-0.198585	C	-0.738971	-2.785525	-0.197710
C	-2.718191	-1.271127	-0.250340	C	-2.734660	-1.302470	-0.259451
C	-3.382552	-0.000566	0.261752	C	-3.361143	-0.000008	0.256056
C	-2.718858	1.270495	-0.249934	C	-2.734665	1.302450	-0.259465
C	-0.729423	2.733421	-0.199177	C	-0.738989	2.785525	-0.197707
C	0.728502	2.733841	0.198354	C	0.738969	2.785540	0.197634
C	2.718048	1.271039	0.250981	C	2.734639	1.302467	0.259512
C	3.382588	0.000663	-0.261315	C	3.361156	0.000010	-0.255966
C	2.718844	-1.270608	0.249824	C	2.734653	-1.302456	0.259509
H	1.404678	-1.510911	-1.295160	H	1.483163	-1.636555	-1.315760
H	-1.404410	-1.511239	1.294998	H	-1.483098	-1.636617	1.315752
H	-1.404636	1.511260	1.294950	H	-1.483119	1.636606	1.315746
H	1.404846	1.511142	-1.294855	H	1.483166	1.636588	-1.315764
H	1.267633	-3.586771	-0.226871	H	1.232389	-3.692870	-0.177071
H	0.844559	-2.773314	1.286413	H	0.834555	-2.790401	1.289461
H	-0.843616	-2.773693	-1.286411	H	-0.834540	-2.790322	-1.289545
H	-1.266483	-3.587114	0.226949	H	-1.232375	-3.692876	0.176936
H	-2.659462	-1.265631	-1.343219	H	-2.634061	-1.260324	-1.349715
H	-3.302159	-2.150068	0.044893	H	-3.405767	-2.142822	-0.028358
H	-4.422696	-0.000782	-0.080413	H	-4.413851	-0.000013	-0.048506
H	-3.433430	-0.000758	1.359730	H	-3.374367	-0.000002	1.355939
H	-3.303034	2.149082	0.045929	H	-3.405780	2.142801	-0.028389
H	-2.660550	1.265525	-1.342838	H	-2.634057	1.260291	-1.349729
H	-0.844205	2.772700	-1.287055	H	-0.834555	2.790329	-1.289542
H	-1.267764	3.586826	0.225739	H	-1.232396	3.692873	0.176944
H	1.266517	3.587145	-0.227170	H	1.232370	3.692877	-0.177048
H	0.843293	2.773951	1.286205	H	0.834530	2.790386	1.289470
H	3.302128	2.150084	-0.043724	H	3.405759	2.142821	0.028462
H	2.658888	1.265180	1.343837	H	2.633977	1.260316	1.349771
H	4.422651	0.000784	0.081086	H	4.413845	0.000014	0.048660
H	3.433712	0.001206	-1.359283	H	3.374447	0.000011	-1.355847
H	2.660525	-1.266094	1.342730	H	2.634003	-1.260316	1.349769
H	3.303066	-2.149054	-0.046381	H	3.405776	-2.142803	0.028443

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