Electronic Supplementary Information for:

Halide Anion Discimination by a Tripodal Hydroxylamine Ligand in Gas and Condensed Phases

Thibault Cheisson,^{1,†} Jiwen Jian,^{2,4,†} Jing Su,^{3,†} Teresa M. Eaton,^{2,5} Michael R. Gau,¹ Patrick J. Carroll,¹ Enrique R. Batista,^{3,*} Ping Yang,^{3,*} John K. Gibson,^{2,*} Eric J. Schelter^{1,*}

[†] These authors contributed equally.

¹ P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 S 34th St., Philadelphia, Pennsylvania 19104

² Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

³ Theorical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

⁴ Present address: Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou, Zhejiang, China, 311231

⁵ Present address: Embry-Riddle Aeronautical University, Department of Natural Sciences, 3700 Willow Creek Road, Prescott, Arizona 86301

*Corresponding authors: erb@lanl.gov; pyang@lanl.gov; jkgibson@lbl.gov; schelter@sas.upenn.edu

Table of contents.

Gas-Phase Experimental Methods	S2
Density Function Theory	S10
Condensed-Phase Experimental Details	
Materials	
Synthesis and Characterization	
Titration Experiments	
X-ray Crystallography	
References	

Gas-Phase Experimental Methods. The gas phase experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer (OIT/MS).¹ The $[L(X)]^-$, $[L(HX_2)]^-$, and mixed halide $[L(HX_aX_b)]^ (X/X_a/X_b = Cl, Br, or I)$ anion complexes were produced by ESI of a solution of $\sim 100 \mu$ M ligand and $\sim 500 \mu$ M HX, or ~500 µM of both HX_a and HX_b in ethanol (<10% water). Particular difficulties handling HF precluded including fluoride in the gas-phase experiments. The employed ligand concentration and solution flow rate were empirically identified as providing sufficient abundances of ions of interest for isolation and manipulation in the ion trap. Adjustment of these parameters could certainly result in changes in relative abundances of reported species of interest. In particular, lower concentrations and/or flow rates generally diminish abuncances of complexes, including dimers. It should be reemphasized that the observed gas phase complexes may be largely, or even entirely, a result of ESI phenomena rather than directly reflecting solution speciation. The ions isolated inside the trap are at a temperature of ~ 300 K.² Ions with a specific mass-to-charge ratio (m/z, which is the mass for z = 1) can be isolated and subjected to collision induced dissociation (CID) whereby the ions are resonantly excited in the OIT, resulting in multiple energetic collisions with the helium bath gas, which essentially heats the ions to very high effective temperatures and ultimately results in fragmentation. The compositions of the one or more CID product ions are then determined by mass-selective ejection from the ion trap. The intensity distribution of ions in both the parent ESI and CID mass spectra are dependent on instrumental parameters. Negative ion mass spectra were acquired using the following instrumental parameters: solution flow rate, 60 µL min⁻¹; nebulizer gas pressure, 15 psi; capillary voltage, +3500 V; end plate voltage offset, -500 V; dry gas flow rate, 5 L min⁻¹; dry gas temperature, 325 °C; capillary exit, -136.0 V; skimmer, -40.0 V; octopole 1 and 2 dc, -12.0 and -1.74 V; octopole RF amplitude, 200.0 Vpp; lens 1 and 2, 5.0 and 60 V; trap drive, 74. The high-purity nitrogen gas for nebulization and drying in the ion transfer capillary was the boil off from a liquid nitrogen Dewar. The results reported here were obtained at CID energies of $\sim 0.3-0.5$ V, with the specific value selected depending primarily on the ease of fragmentation. It should be noted that the CID energy alone is an instrumental parameter that only provides an indication of relative ion excitation, not actual ion energetics.



Figure S1. CID mass spectrum (at 0.55 V) of $[L(H)]^+$. The dominant CID pathways are indicated, with the corresponding H₃TriNOx fragmentations identified by the red lines through the structure. The fragmentations are accompanied by H-atom transfer to yield the observed CID products



Figure S2. CID mass spectra of $[L(H^{37}Cl^{81}Br)]^-$ (at 0.30 V) and $[L(H^{81}Br^{127}I)]^-$ (at 0.35 V). The dominant CID pathways are identified.



Figure S3. CID mass spectra of $[L(HX_2)]^-$ with X = Cl (a), Br (b), and I (c). CID voltages: (a) V=0.30, (b) V=0.40, (c) V=0.50.



Figure S4. Same ESI mass spectra as in Figure 1, but showing data for a wider m/z range 200–1000 m/z.



Figure S5. Negative mode ESI mass spectrum of a solution of L and HBr using as solvent 70% CH_2Cl_2 and 30% ethanol. Asterisks denote where some of the non-observed CH_2Cl_2 adducts would have appeared ("S" = CH_2Cl_2).



Figure S6. Positive-ion ESI mass spectra of synthesized and isolated L(HX) in EtOH with X = Cl (top), Br (middle), and I (bottom).



Figure S7. Negative-ion ESI mass spectra of synthesized and isolated L(HX) in EtOH with X = Cl (top), Br (middle), and I (bottom).



Figure S8. Positive- and negative-ion ESI mass spectra of synthesized and isolated L(HBr) in EtOH before and after the addition of $[N^nBu_4]Br$ to form $[L(HBr_2)]N^nBu_4$.



Figure S9. CID mass spectrum of $[(L)_2(H_2Br_3)]^-$ using a nominal excitation energy of 0.25 V. The dominant pathway is elimination of L(HBr). A minor pathway corresponds to elimination of $[L(H_2Br_2)]$, or L(HBr) followed by HBr.

Density Functional Theory. Ground-state electronic structure calculations were performed on ESI species $[L(HX_2)]^-$, and the corresponding mixed halide compounds $[L(HX_aX_b)]^-$, and CID products $[L(X)]^-$ and HX, and [L(HX)] compounds (X = Cl, Br, I) using the hybrid functional B3LYP³ with Grimme's D3 dispersion correction⁴ and Becked-Johnson damping⁵ implemented in the Gaussian 16 package.⁶ All the geometries were optimized in the gas phase. Harmonic frequency calculations were performed to obtain the corresponding thermochemical corrections and to confirm that the optimized structures were stationary points on the potential energy surface. Isomers of the above compounds were constructed to include crytal structure and configurations that maximize hydrogen-bonding interactions based on the literature. Generally, isomers with more hydrogen bonds are expected to be lower in energy than those with less hydrogen bond. We applied the 6-311G** basis sets⁷ for all atoms. The optimized geometries are merged in an attached file appended to the supporting information.

Table S1. Relative energies (ΔE_0 in kcal mol⁻¹) of [L(HX₂)]⁻ isomers (X = Cl, Br, I). H-bonding interactions are shown in dashed line, other hydrogen atoms were omitted for clarity. The zero-point energy is included.

Structuro	Isomor -	X=Cl	X=Br	X=I
Structure	Isomer	ΔE_0	ΔE_0	ΔE_0
	1 _X	0	0	0
	2 _X	5.5	5.6	5.4
	3x	10.6	9.7	6.6



Table S2. Relative energies (ΔE_0 in kcal mol⁻¹) of $[L(HX_aX_b)]^-$ isomers ($X_a = Cl$, Br, I; $X_b = Cl$, Br, I; X_a (green) $\neq X_b$ (brown)). H-bonding interactions are shown in dashed line, other hydrogen atoms were omitted for clarity. The zero-point energy is included.^a

Structure	Isomer	X _a =Cl, X _b =Br	X _a =Cl, X _b =I	X _a =Br, X _b =I
	15011101	ΔE_0	ΔE_0	ΔE_0
	1a	0	0	0
	1b	0.6	1.3	0.7
	2a	2.2	2.1	2.2
	2b	2.8	3.2	3.4
	3 a	4.6	2.7	3.7



S13



^a The effort to get isomer **7b** failed for X_a =Cl/Br, X_b =I, and the geometry was finally optimized to the isomer **2b** with NH---X_a hydrogen bond but without NH---NOH hydrogen bond.

Structure	Isomer —	X=Cl	X=Br	X=I
Structure	Isomer	ΔE_0	ΔE_0	ΔE_0
	10 _X	0	0	1.4
	11 _x	0.5	2.3	6.4
	12 _X	1.0	1.6	3.1
	13 _X	1.6	1.1	0.0
	14 _X	2.8	3.4	4.6

Table S3. Relative energies (ΔE_0 in kcal mol⁻¹) of [L(X)]⁻ isomers (X = Cl, Br, I). Hbonding interactions are shown in dashed line, other hydrogen atoms were omitted for clarity. The zero-point energy is included.

15 _X	2.9	3.7	Optimized to 12 _X
16 _X	2.9	3.3	4.4
17 _X	4.6	4.1	3.0
18 _X	4.7	5.5	7.5
19 _X	5.6	6.0	7.6
20 _X	7.9	7.9	8.3

S16



Table S4. DFT/B3LYP calculated gas-phase reaction energies (ΔE_0) of $[L(X_a)]^- + HX_b \rightarrow [L(HX_aX_b)]^- (X_{a,b} = Cl, Br, I)$. The zero-point energy is included. $[L(X_a)]^-$ and $[L(HX_aX_b)]^-$ refer to the lowest energy isomers listed in Tables S1–S3.

Reactions	ΔE_0 (kcal mol ⁻¹)
$[LCl]^- + HCl \rightarrow [L(HClCl)]^-$	-37.6
$[LCl]^- + HBr \rightarrow [L(HClBr)]^-$	-41.5
$[\mathrm{LCl}]^- + \mathrm{HI} \to [\mathrm{L}(\mathrm{HClI})]^-$	-45.2
$[LBr]^- + HCl \rightarrow [L(HClBr)]^-$	-37.1
$[LBr]^- + HBr \rightarrow [L(HBrBr)]^-$	-40.5
$[LBr]^- + HI \rightarrow [L(HBrI)]^-$	-44.0
$[LI]^- + HCl \rightarrow [L(HClI)]^-$	-34.6
$[LI]^- + HBr \rightarrow [L(HBrI)]^-$	-37.9
$[LI]^- + HI \rightarrow [L(HII)]^-$	-40.6

Table S5. DFT/B3LYP calculated gas-phase dissociation reaction energies (ΔE_0) of $[L(HX_aX_b)]^- \rightarrow [LX_a]^- + HX_b$ ($X_{a,b} = Cl$, Br, I). The zero-point energy is included. $[L(X_a)]^-$ and $[L(HX_aX_b)]^-$ refer to the lowest energy isomers listed in Tables S1–S3.

Reactions	ΔE_0 (kcal mol ⁻¹)
$(1a) [L(HClBr)]^{-} \rightarrow [LBr]^{-} + HCl$	37.1
(1b) $[L(HClBr)]^{-} \rightarrow [LCl]^{-} + HBr$	41.5
$(2a) [L(HCII)]^{-} \rightarrow [LI]^{-} + HCI$	34.6
(2b) $[L(HCII)]^- \rightarrow [LCI]^- + HI$	45.2
$(3a) [L(HBrI)]^{-} \rightarrow [LI]^{-} + HBr$	37.9
(3b) $[L(HBrI)]^{-} \rightarrow [LBr]^{-} + HI$	44.0

Table S6. Derived energies for reaction (6)	5)	
---	----	--

Reactions	ΔE_0 (kcal mol ⁻¹)
(6a) $[L(HClBr)]^- \rightarrow [LBr]^- + H + Cl$	130
(6b) $[L(HClBr)]^- \rightarrow [LCl]^- + H + Br$	118
$(6c) [L(HCII)]^{-} \rightarrow [LI]^{-} + H + CI$	129
(6d) $[L(HCII)]^{-} \rightarrow [LCI]^{-} + H + I$	104
$(6e) [L(HBrI)]^{-} \rightarrow [LI]^{-} + H + Br$	115
(6f) $[L(HBrI)]^{-} \rightarrow [LBr]^{-} + H + I$	103

Table S7. Relative energies (ΔE_0 in kcal mol⁻¹) of [L(HX)] isomers (X = Cl, Br, I). H-bonding interactions are shown in dashed line, other hydrogen atoms were omitted for clarity. The zero-point energy is included.

Structure	Isomor -	X=Cl	X=Br	X=I
Structure	Isomer —	ΔE_0	ΔE_0	ΔE_0
	23 _X	0	0	3.4ª
	24 _X	3.5	3.0	2.3ª
	25 _X	4.8	3.8	2.3
	26 _X	5.0	2.8	0.0





^a No hydrogen bonding interaction between I⁻ and ammonium (NH⁺)

Table S8. DFT/B3LYP calculated gas-phase association reaction energies (ΔE_0) of $[L(HX)] + X^- \rightarrow [L(HX_2)]^-$ (X = Cl, Br, I). The zero-point energy is included. [L(HX)] and $[L(HX_2)]^-$ refer to the lowest energy isomers listed in Tables S7, S1 and S2, respectively.

Reactions	ΔE_0 (kcal mol ⁻¹)
(7a) $[L(HCl)] + Cl^{-} \rightarrow [L(HCl_2)]^{-}$	-43.8
(7b) $[L(HCl)] + Br^{-} \rightarrow [L(HClBr)]^{-}$	-43.2
(7b) $[L(HCl)] + I^{-} \rightarrow [L(HClI)]^{-}$	-35.8
$(8a) [L(HBr)] + Cl^{-} \rightarrow [L(HClBr)]^{-}$	-46.4
$(8b) [L(HBr)] + Br^{-} \rightarrow [L(HBr_{2})]^{-}$	-45.2
$(8c) [L(HBr)] + I^{-} \rightarrow [L(HBrI)]^{-}$	-37.7
$(9a) [L(HI)] + CI^{-} \rightarrow [L(HCII)]^{-}$	-50.4
$(9b) [L(HI)] + Br^{-} \rightarrow [L(HBrI)]^{-}$	-49.2
$(9c) [L(HI)] + I^{-} \rightarrow [L(HI_{2})]^{-}$	-40.8

Structure	Isomer	ΔE_0
	36a	0.0
	36b	3.0
JAC AC	36c	10.8
	36d	11.2
Ale Ale	36e	12.7

Table S9. Relative energies (ΔE_0 in kcal mol⁻¹) of L isomers. H-bonding interactions are shown in dashed line, other hydrogen atoms were omitted for clarity. The zero-point energy is included.

Table S10. DFT/B3LYP calculated gas-phase association reaction energies (ΔE_0) of $L + X^- \rightarrow [LX]^-$ (X = Cl, Br, I). The zero-point energy is included. L and $[LX]^-$ refer to the lowest energy isomers listed in Tables S3 and S9, respectively.

Reactions	ΔE_0 (kcal mol ⁻¹)	
(10a) $L + Cl^{-} \rightarrow [LCl]^{-}$	-23.6	
(10b) $L + Br^{-} \rightarrow [LBr]^{-}$	-23.6	
(10c) $L + I^- \rightarrow [LI]^-$	-18.6	

Condensed-Phase Experimental Details. All reactions were performed in the air without exclusion of oxygen and moisture. Manipulations involving hydrofluoric acid were performed with polypropylene (PP) containers and utensils. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker UNI-400 Fourier transform NMR spectrometer operating at 400 MHz for ¹H and 100.6 MHz for ¹³C. Characteristic solvent peaks were used as internal references for ¹H chemical shifts (in units of parts per million). The following abbreviations are used; b, broad; s, singlet; d, doublet; t, triplet. Resonances were attributed thanks to combined ¹H–¹³C HSQC (Heteronuclear Single Quantum Correlation) and ¹H–¹³C HMBC (Heteronuclear Multiple-Bond Correlation) experiments and labeled according to Scheme S1. Elemental analyses were performed on a Costech ECS 4010 Analyzer. Attenuated Total Reflectance Fourier-Transform Infrared (ATR FT-IR) spectra were obtained on a Perkin Elmer Spectrum Two spectrometer.



Scheme S1. Labeling scheme

Materials. Benzene, dichloromethane, dichloromethane- d_2 , ethanol were obtained from commercial sources and used without further purification. Deionized water was employed. HF_(aq) (49 wt%) and HCl_(aq) (37 wt%) were obtained from Fisher at the ACS Plus grade; HBr_(aq) (48 wt%) was obtained from Acros at the analysis grade; HI_(aq) (57 wt%) was obtained from Sigma-Aldrich (stabilizer-free, 99.99% trace metal basis). H₃TriNOx (L) was prepared as previously described.⁸

Caution! HF is an acute contact-poison that can result in deep burns or death; it must be handled by trained personnels wearing appropriate personal protection equipment in a well-aerated fume hood.

Synthesis and Characterization.

L(HF) ([H₄TriNOx]F). In a 50 mL PP centrifugation tube, L (380 mg, 0.69 mmol) was dissolved in EtOH (15 mL) at 50 °C with shaking. HF_(aq) (6 M, 4 mL, 35 equiv.) was added with a PP pipette, the centrifugation tube was closed, shaken and allowed to stand for 15 min. Water (25 mL) was carefully added, inducing the precipitation of a white solid. The tube was closed and centrifuged for 30 min at 4000 rpm. The supernatant was still cloudy but was separated from the white solid. The solid was suspended in water (40 mL) and centrifuged for 30 min at 4000 rpm. The cloudy supernatant was again separated from the white solid. The resulting solid was suspended in water (40 mL) and filtered on a fritted glass filter and finally dried under high vacuum to yield a white solid (201 mg, 0.35 mmol, 51 %). Attempts to grow crystals resulted in the formation of thin needles, which were not suitable for XRD analysis.



¹H NMR (CD₂Cl₂, 320 K) δ 9.12 (bs, v_{1/2} = 235 Hz, 3H, OH), 7.59 (t, ³*J*_{HH} = 8.2 Hz, 3H, H_c), 7.35 (m, 6H, H_{e+f}), 7.19 (t, ³*J*_{HH} = 7.5 Hz, 3H, H_d), 4.04 (bs, 6H, v_{1/2} = 70 Hz, H_a), 0.84 (s, 27H, H_i). Low solubility in CD₂Cl₂ prevented full ¹³C{¹H} NMR characterization, partial data were obtained by HSQC: ¹³C{¹H} NMR (CD₂Cl₂, 320 K) δ 131.95 (C_f), 128.68 (C_e), 127.72 (C_c), 125.28 (C_d), 25.83 (C_i); complete data were obtained in DMSO-d₆: ¹³C{¹H} NMR (DMSO-d₆, 300 K) δ 149.01 (C_g), 136.38 (C_f), 126.56, 126.02, 125.65, 125.44, 59.94 (C_h), 53.59 (C_a), 25.55 (C_i). Anal. Cald. for C₃₃H₄₉FN₄O₃: C, 69.69; H, 8.68; N, 9.85. Found: C, 69.88; H, 8.27; N, 9.76.



Figure S10. ¹H NMR (CD_2Cl_2 , 320 K) spectrum of L(HF).



Figure S11. ${}^{13}C{}^{1}H$ NMR (DMSO-d₆, 300 K) spectrum of L(HF).



Figure S12. HSQC spectrum (CD₂Cl₂, 320 K) of L(HF).



Figure S13. HMBC spectrum (CD₂Cl₂, 300 K) of L(HF).

L(HCl) ([H₄TriNOx]Cl). L (420 mg, 0.77 mmol) was dissolved in EtOH (25 mL) at 60 °C with stirring. $HCl_{(aq)}$ (6 M, 5 mL, 39 equiv.) was added and the mixture was stirred at room temperature for 30 min. Water (60 mL) was added inducing the precipitation of a white solid, the mixture was stirred for 15 min. and filtered, the solid was washed with water (2 × 15 mL) and finally dried under high vacuum to yield a white solid (303 mg, 0.52 mmol, 68 %). X-ray quality crystals were obtained by slow evaporation of a concentrated EtOH solution.



¹H NMR (CD₂Cl₂, 300 K) δ 8.95 (bs, $v_{1/2}$ = 47 Hz, 1H, NH), 8.39 (bs, $v_{1/2}$ = 18 Hz, 3H, OH), 7.57-7.52 (m, 6H, H_{c+f}), 7.41 (t, ³*J*_{HH} = 7.7 Hz, 3H, H_e), 7.20 (t, ³*J*_{HH} = 7.1 Hz, 3H, H_d), 4.34 (bs, $v_{1/2}$ = 85 Hz, 6H, H_a), 0.83 (s, 27H, H_i). ¹³C{¹H} NMR (CD₂Cl₂, 300 K) δ 151.14 (C_g), 133.46 (C_f), 130.24 (C_e), 128.75 (C_c), 126.05 (C_d), 125.61 (C_b), 61.69 (C_k), 53.84 (C_a), 26.11 (C_i). Anal. Cald. for C₃₃H₄₉ClN₄O₃: C, 67.73; H, 8.44; N, 9.57. Found: C, 67.89; H, 8.25; N, 9.26.



Figure S15. $^{13}C\{^{1}H\}$ NMR (CD₂Cl₂, 300 K) spectrum of L(HCl).



Figure S16. HSQC spectrum (CD₂Cl₂, 300 K) of L(HCl).



Figure S17. HMBC spectrum (CD_2Cl_2 , 300 K) of L(HCl).

L(HBr) ([H₄TriNOx]Br). L (470 mg, 0.86 mmol) was dissolved in EtOH (15 mL) at 60 °C with stirring. HBr_(aq) (6 M, 5 mL, 35 equiv.) was added and the mixture was stirred at room temperature for 30 min. Water (90 mL) was added inducing the precipitation of a white solid, the mixture was stirred for 15 min. and filtered, the solid was washed with water (2 × 15 mL) and finally dried under high vacuum to yield a white solid (311 mg, 0.49 mmol, 58 %).



X-ray quality crystals were obtained by slow evaporation of EtOH or after recrystallization in benzene.

¹H NMR (CD₂Cl₂, 300 K) δ 8.91 (bs, v_{1/2} = 87 Hz, 1H, NH), 7.68 (bd, 3H, H_f), 7.57 (bs, v_{1/2} ~ 30 Hz, 3H, OH), 7.56 (d, ³*J*_{HH} = 7.9 Hz, 3H, H_c), 7.41 (t, ³*J*_{HH} = 7.7 Hz, 3H, H_e), 7.20 (t, ³*J*_{HH} = 7.2 Hz, 3H, H_d), 4.43 (bs, v_{1/2} = 47 Hz, 6H, H_a), 0.86 (s, 27H, H_i); ¹³C{¹H} NMR (CD₂Cl₂, 300 K) δ 150.47 (C_g), 133.25 (C_f), 130.03 (C_e), 128.30 (C_c), 126.65 (C_d), 126.37 (C_b), 61.90 (C_k), 54.96 (C_a), 26.04 (C_i). Anal. Cald. for C₃₃H₄₉BrN₄O₃•C₆H₆: C, 66.18; H, 7.83; N, 7.92. Found: C, 65.90; H, 7.49; N, 8.03.



Figure S18. ¹H NMR (CD₂Cl₂, 300 K) spectrum of L(HBr).



Figure S20. HSQC spectrum (CD_2Cl_2 , 300 K) of L(HBr).



Figure S21. HMBC spectrum (CD₂Cl₂, 300 K) of L(HBr).

L(HI) ([H₄TriNOx]]). L (330 mg, 0.60 mmol) was dissolved in EtOH (15 mL) at 60 °C with stirring. $HI_{(aq)}$ (7.6 M, 2 mL, 25 equiv.) was added and the mixture was stirred at room temperature for 5 min. Water (150 mL) was added inducing the precipitation of a pale yellow solid, the mixture was stirred for 15 min. and filtered, the solid was washed with water (2 × 50 mL) and finally dried under high vacuum to yield a pale yellow solid (317 mg, 0.47 mmol, 78 %). The material could be recrystallized from minimal CH₂Cl₂ to yield off-white needles that were suitable for elemental analyses. X-ray quality crystals were obtained by slow evaporation of EtOH.



¹H NMR (CD₂Cl₂, 300 K) δ 8.61 (bs, v_{1/2} = 220 Hz, 1H, NH), 7.80 (d, 3H, ³*J*_{HH} = 7.5 Hz, H_f), 7.56 (t, ³*J*_{HH} = 8.1 Hz, 3H, H_c), 7.43 (t, ³*J*_{HH} = 7.7 Hz, 3H, H_e), 7.28 (t, ³*J*_{HH} = 7.4 Hz, 3H, H_d), 6.85 (bs, v_{1/2} = 90 Hz, 3H, OH), 4.57 (bs, v_{1/2} = 18 Hz, 6H, H_a), 0.88 (s, 27H, H_i); ¹³C{¹H} NMR (CDCl₃, 300 K) δ 149.94 (C_g), 133.30 (C_f), 130.26 (C_e), 128.22 (C_c), 127.14 (C_d), 126.37 (C_b), 62.10 (C_h), 53.93 (C_a), 26.09 (C_i). Anal. Cald. for C₃₃H₄₉IN₄O₃•CH₂Cl₂: C, 53.62; H, 6.75; N, 7.36. Found: C, 53.86; H, 6.30; N, 6.93.



Figure S23. ¹³C{¹H} NMR (CD₂Cl₂, 300 K) spectrum of L(HI).



Figure S24. HSQC spectrum (CD₂Cl₂, 300 K) of L(HI).



Figure S25. HMBC spectrum (CD₂Cl₂, 300 K) of L(HI).



Figure S26. Cyclic voltammogram of L(HCl), L(HBr), and L(HI) (~5 mM) collected in 0.1 M [$^{n}Pr_{4}N$][BAr^F₄] in CH₂Cl₂ against Fc^{0/+}.



Figure S27. Experimental ATR FT-IR of L(HF) (light green), L(Cl) (dark green), L(HBr) (orange), L(HI) (purple) and L (black); inset: magnification of the 2700-3700 cm⁻¹ region.



Figure S28. DFT-predicted IR spectra of isomers 1_X (Table S1) of $[L(HCl_2)]^-$ (dark green), $[L(HBr_2)]^-$ (orange), and $[L(HI_2)]^-$ (purple); inset: magnification of the 2800–3500 cm⁻¹ region. A scaling factor of 0.97 was applied on the DFT-predicted frequencies.



Figure S29. Variable-temperature ¹H NMR (CD₂Cl₂) of L(HCl).



Figure S30. Superposition of ¹H NMR (CD_2Cl_2 , ~15 mM) spectra of L(HX) (X = F, Cl, Br, I). Dashed lines highlight the evolution of selected resonances.

Titration Experiments.

Figure S31. ¹H NMR titration of L(HCl) by [*ⁿ*Bu₄N]Cl in CD₂Cl₂ at 298 K.

Figure S32. Binding isotherms for L(HCl) and $[^{n}Bu_{4}N]Cl$ and corresponding fit for a 1:1 model.

Figure S33. ¹H NMR titration of L(HBr) by [*ⁿ*Bu₄N]Br in CD₂Cl₂ at 298 K.

Figure S34. Binding isotherms for L(HBr) and $[{}^{n}Bu_{4}N]Br$ and corresponding fit for a 1:1 model.

Figure S35. ¹H NMR titration of L(HI) by ["Bu₄N]I in CD₂Cl₂ at 298 K.

Figure S36. Binding isotherms for L(HI) and [^{*n*}Bu₄N]I and corresponding fit for a 1:1 model.

X-ray Crystallography. X-ray intensity data were collected on a Bruker APEXII⁹ CCD area detector or a Bruker APEXIII¹⁰ D8QUEST CMOS area detector, both employing graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at 100(1) K. Rotation frames were integrated using SAINT,¹¹ producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXT program package¹² for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS or TWINABS.¹³ Refinement was performed by full-matrix least squares based on F^2 using SHELXL-2014.¹⁴ All of the reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Crystallographic parameters are summarized on Table S11.

Compounds	L(HCl)·EtOH	L(HCl)	L(HBr)·EtOH	$L(HBr) \cdot \frac{1}{2}(C_6H_6)$	L(HI)·½(EtOH)	L(HBr)·2(CHCl ₃)
Formula	C ₃₄ H ₅₅ ClN ₄ O ₄	C ₃₃ H ₄₉ ClN ₄ O ₃	$C_{34}H_{55}BrN_4O_4$	C ₃₆ H ₅₂ BrN ₄ O ₃	$C_{68}H_{104}I_2N_8O_7$	$C_{35}H_{51}BrCl_6N_4O_3$
$M_{ m r}$	631.28	585.21	824.12	668.72	1399.39	868.40
<i>a</i> [Å]	16.6055(10)	24.8659(6)	16.9397(8)	29.0180(11)	9.8928(4)	21.169(2)
<i>b</i> [Å]	19.9177(14)	15.3224(4)	19.8774(9)	15.6456(6)	34.9965(14)	12.0506(11)
<i>c</i> [Å]	21.7032(14)	20.1555(8)	21.6754(10)	19.7456(7)	20.5965(8)	16.8977(16)
α[°]	90	90	90	90	90	90
β [°]	90	119.3740(10)	90	129.4510(10)	90.4500(10)	97.492(6)
γ[°]	90	90	90	90	90	90
V[Å ³]	7178.2(8)	6692.1(4)	7298.5(6)	6922.2(5)	7130.6(5)	4273.7(7)
Ζ	8	8	8	8	4	4
Space group	Pbca	C2/c	Pbca	C2/c	$P2_{1}/c$	$P2_{1}/c$
$ ho_{ m calcd}$, [g cm ⁻³]	1.168	1.162	1.230	1.283	1.304	1.350
μ [mm ⁻¹]	0.147	0.151	1.167	1.228	0.936	1.374
2θ range [deg]	3.704-55.078	3.42-55.048	3.676-55.118	3.174-55.038	3.956-55.042	4.164-50.162
Data collected	80007	52559	45991	30306	57042	7537
No. unique data, R_{int}	8265, 0.0407	7666, 0.0417	8374, 0.0743	7927, 0.0268	16335, 0.0269	7537, 0.11
R_I (all data) ^[a]	0.0506	0.0951	0.0848	0.0536	0.0576	0.1065
wR_2 (all data) ^[b]	0.0944	0.1499	0.0887	0.1144	0.1243	0.2674
GoF ^[c]	1.017	1.032	1.002	1.035	1.072	1.067
No. of variables	407	431	411	410	812	492
peak/hole [e Å ⁻³]	0.30/-0.27	0.982/-0.642	0.481/-0.36	1.571/-0.47	2.315 /-0.654	0.81 /-1.12

 Table S11. Crystallographic data for reported compounds.

 $[a] R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|. [b] wR_2 = [\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2]]^{\frac{1}{2}}. [c] Goodness-of-Fit [\Sigma [w(F_0^2 - F_c^2)^2] / (N_{obs} - N_{params})]^{\frac{1}{2}}, based on all data.$

Figure S37. Illustration of the H-bonded polymer of L(HBr)·EtOH along the *a* axis. Heteroatoms are depicted by their thermal ellipsoids (50 %), relevant hydrogen atoms are depicted in black, ethanol molecules in light pink.

Figure S38. Illustration of the H-bonded polymer of L(HCl) along the b axis. Heteroatoms are depicted by their thermal ellipsoids (50 %), relevant hydrogen atoms are depicted in black.

Figure S39. Illustration of the H-bonded polymer of L(HI)·½EtOH along the *b* axis. Heteroatoms are depicted by their thermal ellipsoids (50 %), relevant hydrogen atoms are depicted in black, ethanol molecules in light pink.

References.

(1) Rios, D.; Rutkowski, P. X.; Shuh, D. K.; Bray, T. H.; Gibson, J. K.; Van Stipdonk, M. J. Electron transfer dissociation of dipositive uranyl and plutonyl coordination complexes, *J. Mass Spectrom.* **2011**, *46*, 1247-1254.

(2) Gronert, S. Estimation of effective ion temperatures in a quadrupole ion trap, J. Am. Soc. Mass. Spectrom. **1998**, *9*, 845-848.

(3) (a) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* **1988**, *38*, 3098-3100. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **1988**, *37*, 785–789.

(4) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* **2010**, *132*, 154104.

(5) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

(6) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.;

Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell,

A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.;
Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin,
A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.;
Voth, V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford, CT, 2009.

(7) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self - consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.* **1980**, *72*, 650-654. (b) McLean, A. D.; Chandler, G. S. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–

18, J. Chem. Phys. 1980, 72, 5639-5648. (c) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J. P.; Davis, N.

E.; Binning, R. C.; Radom, L. Extension of Gaussian - 2 theory to molecules containing third - row atoms Ga-Kr, J. Chem. Phys. **1995**, 103, 6104-6113.

(8) Bogart, J. A.; Lippincott, C. A.; Carroll, P. J.; Schelter, E. J. An Operationally Simple Method for Separating the Rare-Earth Elements Neodymium and Dysprosium, *Angew. Chem. Int. Ed.* **2015**, *54*, 8222-8225.

(9) Bruker APEX 2, v2014.11-0; Bruker AXS Inc.: Madison, Wisconsin, 2012.

(10) Bruker APEX 3, v2016.1-0; Bruker AXS Inc.: Madison, Wisconsin, 2015.

(11) Bruker SAINT, v8.37a; Bruker AXS Inc.: Madison, Wisconsin, 2012.

(12) Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination, *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2015**, *71*, 3–8.

(13) Bruker SADABS, v2014/5; Bruker AXS Inc.: Madison, Wisconsin, 2001.

(14) Sheldrick, G. M. Crystal structure refinement with *SHELXL*, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3–8.