Solid-State and Solution-Phase Characterization of Sm^{II}-Aza[2.2.2]Cryptate and Its Methylated Analogue

Sergely Steephen Bokouende,[a] Tyler C. Jenks,[a] Cassandra L. Ward,[b] Matthew J. Allen*,[a]

[a] Department of Chemistry, Wayne State University, 5101 Cass Ave., Detroit, MI 48202, USA
[b] Lumigen Instrument Center, Wayne State University, 5101 Cass Ave., Detroit, MI 48202, USA
*Email: mallen@chem.wayne.edu.

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Experimental Procedures

All manipulations were performed in dry gloveboxes filled with inert atmospheres of either N_2 or Ar. All reagents were purchased from commercial sources and used without purification unless otherwise noted. All glassware, stoppers, and magnetic stir bars were dried in an oven at 120 °C for 24 h and transferred into a dry glovebox while hot. Anhydrous acetonitrile, *N*,*N*-dimethylformamide (DMF), and tetrahydrofuran were purchased, degassed under reduced pressure, and stored over activated molecular sieves (3 Å) inside a dry glovebox prior to use. Isopropylamine was dried by passing through a column of activated molecular sieves (3 Å), then degassed under reduced pressure, and stored over activated molecular sieves (3 Å) at –35 °C in a dry glovebox freezer prior to use. 1,4,7,10,13,16,21,24-Octaazabicyclo[8.8.8]hexacosane (**1**) and 4,7,13,16,21,24-hexamethyl-1,4,7,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (**2**) were synthesized following reported procedures.[S1,S2]

UV–visible spectra were collected using a Jasco V–570 UV/VIS/NIR Spectrophotometer. Samples of Sm**1**I_2, [Sm**2**]I_2, and SmI_2 (0.95–1.3 mM) were prepared in an Ar-filled dry glovebox at ambient temperature in acetonitrile or DMF.

Cyclic voltammetry experiments were performed in triplicate with Sm^{II}-cryptates (5 mM) in DMF (11 or 22 mL) containing tetraethylammonium perchlorate (30 or 67 mM) as the electrolyte using a Pine Wavenow USB potentiostat and a three electrode system: Ag/AgCl (reference electrode), platinum wire (auxiliary electrode), and glassy carbon (working electrode). The system was kept under an inert atmosphere of Ar. Samples were prepared in a N_2-filled glovebox, and cyclic voltammograms were obtained in eight segments at a scanning rates of 100 mV s^{-1} with an initial potential of –2 V (rising) and upper and lower potentials of 0 and –2 V, respectively.

Table S1. Electrochemical potentials of SmI_2, [Sm**1**I]I, and [Sm**2**]I_2

Complex	Anodic Potential (V vs Ag/AgCl)	Cathodic Potential (V vs Ag/AgCl)	$E_{1/2}$ (V vs Ag/AgCl)
SmI_2	–1.87	–1.29	–1.58
[Sm**1**I]I	–1.47	–1.34	–1.41
[Sm**2**]I_2	–1.77	–1.47	–1.62

Elemental analysis (C, H, and N) was performed by Midwest MicroLab in Indianapolis, IN 46250, USA. All values are reported in percentages.

Synthesis of [Sm**1**I]I

To a chilled (–35 °C), colorless, and stirring solution of **1** (0.130 g, 0.351 mmol) in isopropylamine (0.010 L) in an Ar-filled glovebox was added SmI_2 (0.160 g, 0.396 mmol), and a red-brown precipitate immediately formed. The reaction mixture was allowed to warm at ambient temperature for 3 min before the mother liquor was decanted. The solids were washed with chilled (–35 °C) isopropylamine (2 × 3.0 mL). Residual isopropyl amine was removed under reduced pressure to yield 200 mg (73.5%) of a red–brown fine powder. Anal. Calcd for $C_{18}H_{42}I_2N_8Sm$: C, 27.91; H, 5.46; N, 14.46. Found: C, 27.35; H, 5.49; N, 14.20.

Synthesis of [Sm**2**]I_2

In a nitrogen-filled glovebox, a yellow solution of **2** (0.113 g, 0.248 mmol) in tetrahydrofuran (7.0 mL) was prepared. A separate dark-blue solution of SmI_2 (90.6 mg, 0.224 mmol) in tetrahydrofuran (0.010 L) was also prepared. The two solutions were mixed, resulting in the immediate precipitation of a green solid. Centrifugation, decanting, washing of the solids with tetrahydrofuran, and removal of residual tetrahydrofuran under reduced pressure yielded

162 mg (84%) of a green powder. Anal. Calcd for $C_{24}H_{54}I_2N_8Sm$: C, 33.56; H, 6.34; N, 13.05. Found: C, 33.92; H, 6.31; N, 13.10.

X-ray crystallography data for [Sm**1**I]I

A suitable red crystal (0.035 mm × 0.098 mm × 0.10 mm) of [Sm**1**I]I was mounted on a MicroMount (MiTeGen) with polyfluoroether oil (Fomblin YR-1800, Alfa Aesar) on a Bruker D8 Venture diffractometer with kappa geometry, an Incoatec IμS micro-focus source X-ray tube (Mo K_α radiation), and a multilayer mirror for monochromatization. The X-ray diffraction intensities were measured using a Photon III CPAD area detector at a distance of 45 mm and 0.5° image width. Data were acquired at 100 K with an Oxford 800 Cryostream low-temperature apparatus. The intensities were integrated using SAINT V8.38a. A multiscan absorption correction was applied with SADABS v2016/2 using APEX4 v2021.10-0. The crystal structure was solved using a dual-space approach as implemented in SHELXT[S3] and difference Fourier (ΔF) maps during least-squares refinement, as embedded in SHELXL-2018[S4] running under Olex2.[S5] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined isotropically using a riding model. At 100 K, [Sm**1**I]I was refined in the polar space group $Pca2_1$ with one metal-ligand complex (coordinating to one iodide) and one iodide counter ion in the asymmetric unit and Z=4.

Table S2. Crystal data and structure refinement of [Sm**1**I]I, CCDC 2162698

Empirical formula	$C_{18}H_{42}I_2N_8Sm$	
Formula weight	774.74	
Temperature	100 K	
Crystal system	orthorhombic	
Space group	*Pca*2_1	
Unit cell dimensions	a = 15.7551(9) Å	α = 90°
	b = 12.1307(7) Å	β = 90°
	c = 13.7979(8) Å	γ = 90°
Volume	2637.1(3) Å^3	
Z	4	
Density (calculated)	1.951 g cm^{-3}	
Absorption coefficient	4.588 mm^{-1}	
F(000)	1496.0	
Crystal size	0.1 × 0.098 × 0.035 mm^3	
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection	4.238 to 66.474°	
Index ranges	–24 ≤ h ≤ 24, –18 ≤ k ≤ 18, –20 ≤ l ≤ 21	
Reflections collected	51941	
Independent reflections	9830 [R_{int} = 0.0832, R_{sigma} = 0.0682]	
Data/restraints/parameters	9830/1/262	
Goodness-of-fit on F^2	1.052	
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0400, wR_2 = 0.0718	
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.0773	
Largest diff. peak/hole / e Å^{-3}	0.95/–0.98	
Flack parameter	–0.006(15)	

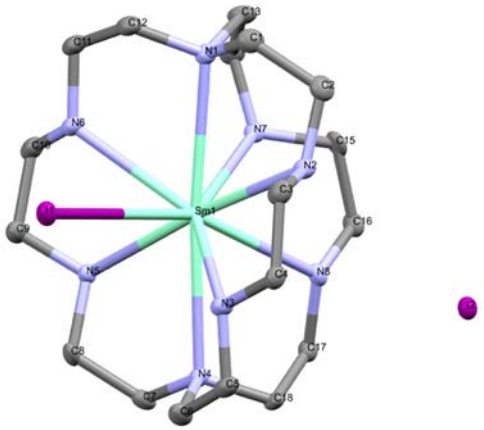

Figure S1. X-ray structure of [Sm**1**I]I with displacement ellipsoids drawn at 50% probability. Hydrogen atoms were omitted for clarity.

Table S3. Selected Bond Lengths of [Sm**1**I]I.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Sm1	I1	3.6397(5)	N7	C15	1.473(9)
Sm1	N5	2.747(8)	N7	C14	1.467(8)
Sm1	N4	2.934(6)	C5	N3	1.452(9)
Sm1	N8	2.780(5)	C5	C6	1.513(10)
Sm1	N6	2.767(6)	C8	C7	1.517(10)
Sm1	N7	2.710(5)	C1	N1	1.470(9)
Sm1	N1	2.904(6)	C1	C2	1.530(10)
Sm1	N3	2.802(6)	N1	C13	1.496(9)
Sm1	N2	2.782(8)	N1	C12	1.480(9)
N5	C8	1.485(9)	N3	C4	1.479(9)
N5	C9	1.465(9)	C18	C17	1.501(10)
N4	C18	1.476(9)	C3	N2	1.470(9)
N4	C6	1.479(9)	C3	C4	1.521(10)
N4	C7	1.480(9)	C11	C12	1.524(11)
N8	C17	1.464(9)	C9	C10	1.517(10)
N8	C16	1.468(9)	N2	C2	1.466(10)
N6	C11	1.454(9)	C15	C16	1.510(10)
N6	C10	1.468(10)	C13	C14	1.519(10)

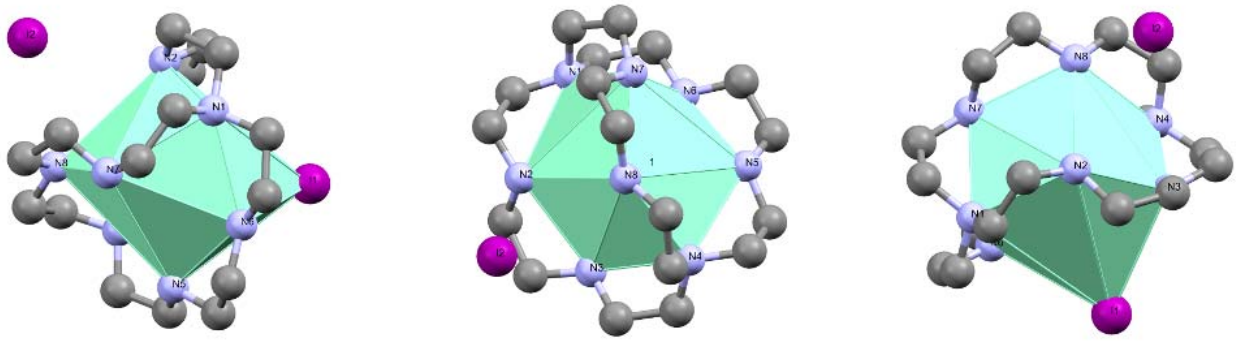

Figure S2. Solid state structure of [Sm**1**I]I viewed along the a, b, and c axes, from left to right.

X-ray crystallography data for [Sm**2**]I_2

A suitable dark-green crystal (0.13 mm × 0.20 mm × 0.42 mm) of Sm**2**I_2 was mounted on a MiTeGen MicroMount with paratone oil on a Bruker X8 APEX-II diffractometer with Mo radiation and a graphite monochromator. X-ray diffractions were measured using a Bruker APEX-II charge-coupled device detector. Data were acquired at 100 K with an Oxford 800 Cryostream low-temperature apparatus. The intensities were integrated using SAINT and a multi-scan absorption correction was applied using SADABS in the APEX3 software package. Using Olex2,[S5] the structure was solved by Intrinsic Phasing using the ShelXT structure solution program and refined with the ShelXL refinement package.[S3,S4] The structure was solved in the space group *Aea*2. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were positioned with idealized geometries and refined isotropically using a riding model.

Table S4. Crystal data and structure refinement of [Sm**2**]I_2, CCDC 2157499

Empirical formula	$C_{28}H_{60}I_2N_8Sm$	
Formula weight	941.01	
Temperature	100 K	
Crystal system	orthorhombic	
Space group	*Aea*2	
Unit cell dimensions	a = 19.4034(11) Å	α = 90°
	b = 18.0204(10) Å	β = 90°
	c = 10.3393(6) Å	γ = 90°
Volume	3615.2(4) $Å^3$	
Z	4	
Density (calculated)	1.729 g cm^{-3}	
Absorption coefficient	3.365 mm^{-1}	
F(000)	1864.0	
Crystal size	0.42 × 0.2 × 0.13 mm^3	
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection	4.198 to 52.898°	
Index ranges	–24 ≤ h ≤ 24, –22 ≤ k ≤ 20, –12 ≤ l ≤ 12	
Reflections collected	32079	
Independent reflections	3724 [R_{int} = 0.0563, R_{sigma} = 0.0337]	
Data/restraints/parameters	3724/1/190	
Goodness-of-fit on F^2	1.053	
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0229, wR_2 = 0.0444	
Final R indexes [all data]	R_1 = 0.0294, wR_2 = 0.0463	
Largest diff. peak/hole / e $Å^{-3}$	0.70/–0.50	
Flack parameter	0.004(10)	

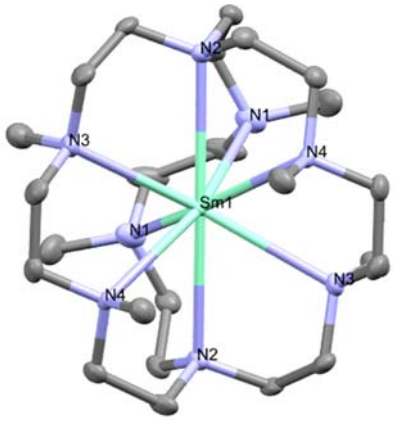

Figure S3. X-ray structure of [Sm**2**]I_2 with displacement ellipsoids drawn at 50% probability. Outer-sphere anions and non-coordinating solvent molecules were omitted for clarity.

Table S5. Selected Bond Lengths of [Sm**2**]I_2.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Sm1	N4	2.840(5)	N2	C7	1.483(6)
Sm1	N4[1]	2.840(5)	N2	C6	1.476(8)
Sm1	N1	2.859(5)	N2	C4	1.479(8)
Sm1	N1[1]	2.859(5)	C7	C8	1.495(9)
Sm1	N2	2.931(4)	C6	C5	1.502(10)
Sm1	N2[1]	2.931(4)	N3	C9	1.468(8)
Sm1	N3[1]	2.872(5)	N3	C8	1.474(8)
Sm1	N3	2.872(5)	N3	C10	1.459(8)
N4	C12	1.463(8)	C1S	C2S	1.452(10)
N4	C11	1.473(8)	N1S	C2S	1.136(8)
N4	C5[1]	1.495(8)	C3	C4	1.520(9)
N1	C3	1.487(8)	C11	C10	1.501(9)
N1	C2	1.472(9)	C1	C1[1]	1.523(16)
N1	C1	1.462(8)			

[1]1–X,1–Y,+Z

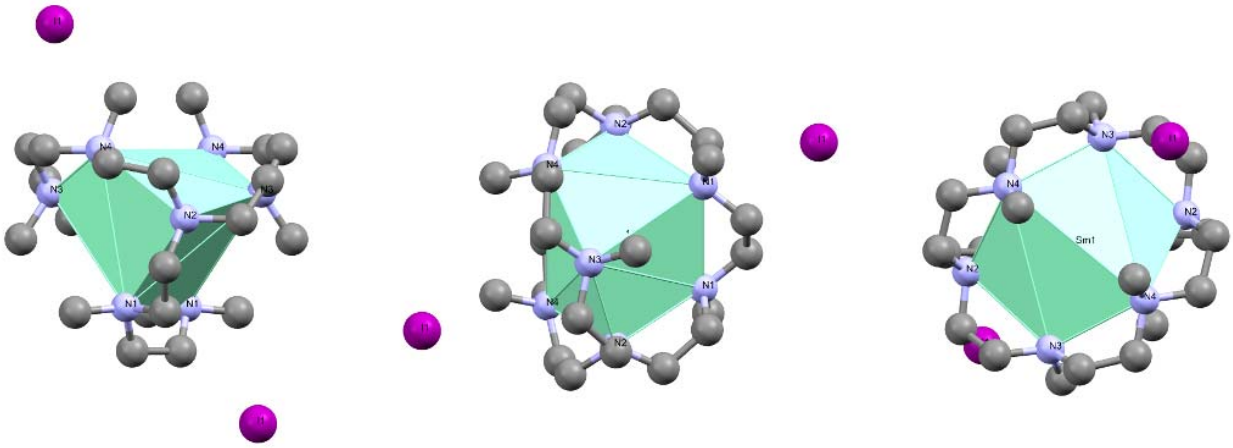

Figure S4. Solid state structure of [Sm**2**]I_2 viewed along the a, b, and c axes, from left to right

Table S5. Shape analysis of Sm^{II} in [Sm**1**I]I

Shape	Shape Code	Point Group	CShM
Enneagon	EP–9	D_{9h}	34.21786
Octagonal pyramid	OPY–9	C_{8v}	26.18684
Heptagonal bipyramid	HBPY–9	D_{7h}	11.84786
Triangular cupola (J3) = trivacant cuboctahedron	JTC–9	C_{3v}	12.95592
Capped cube (Elongated square pyramid, J8)	JCCU–9	C_{4v}	5.09742
Capped cube	CCU–9	C_{4v}	2.95595
Capped sq. antiprism (Gyroelongated square pyramid J10)	JCSAPR–9	C_{4v}	11.39496
Capped square antiprism	CSAPR–9	C_{4v}	10.07381
Tricapped trigonal prism (J51)	JTCTPR–9	D_{3h}	12.02288
Tricapped trigonal prism	TCTPR–9	D_{3h}	11.14889
Tridiminished icosahedron (J63)	JTDIC–9	C_{3v}	10.27630
Hula-hoop	HH–9	C_{2v}	4.62337
Muffin	MFF–9	C_s	8.29965

CShM values were computed using SHAPE analysis version 2.1.[S6]

Table S6. Shape analysis of Sm^{II} in [Sm**2**]I_2

Shape	Shape Code	Point Group	CShM
Octagon	OP–8	D_{8h}	32.16335
Heptagonal pyramid	HPY–8	C_{7v}	21.47681
Hexagonal bipyramid	HBPY–8	D_{6h}	9.04948
Cube	CU–8	O_h	4.33453
Square antiprism	SAPR–8	D_{4d}	12.46487
Triangular dodecahedron	TDD–8	D_{2d}	10.07503
Johnson-Gyrobifastigium (J26)	JGBF–8	D_{2h}	14.12007
Johnson-Elongated triangular bipyramid	JETBPY–8	D_{3h}	14.00683
Johnson-Biaugmented trigonal prism (J50)	JBTPR–8	C_{2v}	12.57694
Biaugmented trigonal prism	BTPR–8	C_{2v}	12.45903
Snub disphenoid (J84)	JSD–8	D_{2d}	13.47073
Triakis tetrahedron	TT–8	T_d	5.21177
Elongated trigonal bipyramid	ETBPY–8	D_{3h}	9.99170

CShM values were computed using SHAPE analysis version 2.1.[S6]

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