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Multi-electron reactivity of a cofacial di-tin(II) cryptand: partial reduction of sulfur and selenium and reversible generation of $S_3^{\cdot-}$ †

Julia M. Stauber,^a Peter Müller,^a Yizhe Dai,^c Gang Wu,^{*c} Daniel G. Nocera^{*b}
and Christopher C. Cummins^{*a}

Cofacial bimetallic tin(II) ($[Sn_2(mBDCA-5t)]^{2-}$, **1**) and lead(II) ($[Pb_2(mBDCA-5t)]^{2-}$, **2**) complexes have been prepared by hexadeprotonation of hexacarboxamide cryptand *mBDCA-5t-H₆* together with double Sn(II) or Pb(II) insertion. Reaction of **1** with elemental sulfur or selenium generates di-tin polychalcogenide complexes containing μ -E and bridging μ -E₂ ligands where E = S or Se, and the Sn(II) centers have both been oxidized to Sn(IV). Solution and solid-state UV-Vis spectra of $[(\mu-S_5)Sn_2(\mu-S)(mBDCA-5t)]^{2-}$ (**4**) indicate that the complex acts reversibly as a source of $S_3^{\cdot-}$ in DMF solution with a $K_{eq} = 0.012 \pm 0.002$. Reductive removal of all six chalcogen atoms is achieved through treatment of $[(\mu-E_5)Sn_2(\mu-E)(mBDCA-5t)]^{2-}$ with PR_3 (R = ^tBu, Ph, OⁱPr) to produce six equiv. of the corresponding EPR₃ compound with regeneration of di-tin(II) cryptand complex **1**.

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Introduction

Multi-electron transfer reactions are an area of intense interest due to their key role in both biological¹ and synthetic systems for the activation and transformation of small molecules germane to energy conversion. These systems have the ability to accommodate and deliver multiple electrons to reaction substrates at one time, and typically feature two or more redox active metal ions confined within a single structural unit. Synthetic organometallic complexes that undergo multi-electron redox processes have been extensively studied for their applications in electrocatalysis,² sensing,³ homogeneous,⁴ and heterogeneous⁵ catalysis. Many of these systems are based upon face-to-face diporphyrins, in which two metalloporphyrins are rigidly linked together in a cofacial arrangement.⁶ Complexes of this type have received considerable interest due to their ability to carry out multi-electron processes such as oxygen reduction,⁷ nitrogen reduction,⁸ and H₂O₂ disproportionation.⁹

We have shown previously that macro-bicyclic hexacarboxamide cryptand molecules,¹⁰ in hexa-deprotonated form, serve as excellent frameworks engendering cofacial transition-metal

bimetallic systems with a range of intermetal distances;^{10,11} these systems are distinguished from bis-porphyrin constructs in that the metal ion coordination environment is trigonal rather than tetragonal. While transition metal complexes that carry out multi-electron reactions have, and continue to receive attention, functional p-block metal analogues have been far less studied.¹² Recent work has shown that the chemistry of some heavy main group elements can resemble that of transition-metal complexes, and main-group metal systems have displayed small-molecule reactivity previously thought to be the exclusive domain of d-block elements.¹³

For the present work, in extending the approach we sought to access a pair of tin(II)/tin(IV) redox couples giving the potential for four-electron transformations within the capsular cryptand environment. We chose to investigate redox reactions involving the group 16 elements, the ensuing finding that clean and informative reactivity was observed for both sulfur and selenium forming the basis of the present work. We note that both the reduction of oxygen to peroxide dianion, and the reduction of sulfur to sulfide ion, are currently targets for the development of new battery chemistries;¹⁴ fundamental studies such as the present one have the potential to reveal how the reduction processes may become controlled and selective in response to the utilization of a pre-organized architecture.

Results and discussion

Double insertion of tin(II) or lead(II) into the cryptand proceeds upon treatment of *mBDCA-5t-H₆* (ref. 15) with KO^tBu in the presence of Sn[N(SiMe₃)₂]₂ or Pb[N(SiMe₃)₂]₂ (ref. 16) in THF. This procedure affords the $[K_2(THF)][Sn_2(mBDCA-5t)]$ ($[K_2(THF)]$)

^aDepartment of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139-4307, USA. E-mail: ccummins@mit.edu

^bDepartment of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138-2902, USA. E-mail: dnocera@fas.harvard.edu

^cDepartment of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6. E-mail: gang.wu@chem.queensu.ca

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Scheme 2 Reactivity of $[Sn_2(mBDCA-5t)]^{2-}$ (**1**) with elemental selenium and sulfur to generate $[(\mu-E)_5Sn_2(\mu-E)(mBDCA-5t)]^{2-}$ (E = Se, S, **3**, **4**).

the *mBDCA-5t* cryptand framework would direct the system into new assemblages of atoms otherwise inaccessible in the absence of such a supramolecular construct.

Treatment of **1** with elemental selenium (6 equiv.) in DMF solution was found to elicit a color change from colorless to deep red upon thorough mixing (Scheme 2). After workup, the selectively formed product of this reaction, $[(\mu-Se_5)Sn_2(\mu-Se)(mBDCA-5t)]^{2-}$ (**3**), was isolated in 71% yield as a brick red solid. The 1H NMR spectrum of **3** (Fig. S12[†]) features three distinct *tert*-butyl resonances, each with integrations of nine protons, and six aryl resonances with integrations of one and two protons in a 1 : 1 ratio. The ^{119}Sn NMR spectrum of **3** consists of one singlet ($\delta -876.5$ ppm, Fig. 5a, $^1J_{119Sn-77Se} = 3381$ Hz), and the ^{77}Se NMR spectrum contains four resonances that are attributed to the four distinct selenium environments of complex **3**. The resonances located at δ 537.2, and 884.4 ppm contain well-resolved satellite peaks corresponding to $^1J_{119Sn-77Se}$ coupling of 3371 and 785 Hz, respectively (Fig. 3).²⁸ While the 1H NMR spectrum revealed that the three arms of the cryptand are inequivalent, the ^{119}Sn NMR data indicate that **3** contains only one tin environment, indicating that a lowering of symmetry from C_{3h} to C_s has occurred through the reaction of **1** with selenium.

A solid-state structure established the identity of this species as $[K_2(DMF)_3][(\mu-Se_5)Sn_2(\mu-Se)(mBDCA-5t)]$ (**3**), and Fig. 4 shows a thermal ellipsoid plot of the dianion in this complex salt. X-ray



Fig. 3 Experimental ^{77}Se NMR spectrum of **3** (top, DMSO- d_6 , 76.3 MHz, 20 °C), and simulated spectrum (bottom) showing satellite peaks corresponding to the $J_{119Sn-77Se}$ coupling.

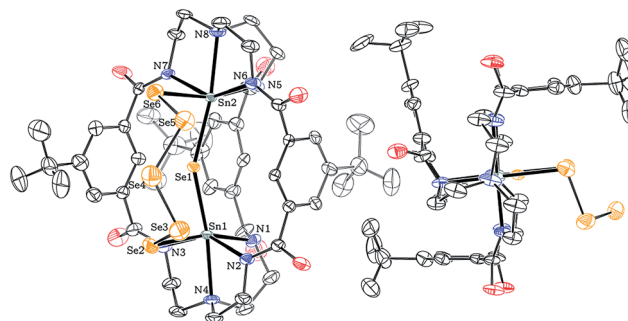


Fig. 4 Solid-state structure of $[(\mu-Se_5)Sn_2(\mu-Se)(mBDCA-5t)]^{2-}$ (**3**) with thermal ellipsoids (drawn using PLATON¹⁷) shown at the 50% probability level. K^+ cations, DMF solvent molecules, disorder, and H-atoms omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1–Sn2 4.932(1), Sn1–Se1 2.578(2), Sn2–Se1 2.605(2), Sn1–Se2 2.726(3), Sn2–Se6 2.710(3), Sn1–N2 2.243(16), Sn1–N3 2.235(16), Sn1–N4 2.354(14), Sn2–N5 2.241(18), Sn2–N6 2.251(16), Sn2–N7 2.248(17), Sn2–N8 2.343(14), Sn1–Se1–Sn2 144.20(8), N3–Sn1–N1 86.8(18), N2–Sn1–N1 90.3(17), N3–Sn1–Se2 88.8(15), N2–Sn1–Se2 86.0(15), N5–Sn2–N7 90.1(15), N5–Sn2–N6 95.8(13), N7–Sn2–Se6 87.0(12), N6–Sn2–Se6 80.5(10).

quality dark red crystals of $[K_2(DMF)_3][\mathbf{3}]$ were grown by vapor diffusion of diethyl ether into a saturated DMF solution of the salt over the course of 12 h at 23 °C. The solid-state molecular structure of **3** reveals that the two Sn(IV) ions reside in a distorted octahedral environment, each coordinated to the three carboxamide nitrogen atoms from the cryptand as well as one $\mu-Se^{2-}$ ligand and one selenium from the five membered Se_5Se pentaselenide chain that links the two tin(IV) centers. The observed molecular structure of dianion **3** provides the first glimpse of a conformation in which two cryptand arms are splayed apart in a manner that permits the pentaselenide chain to bridge the tin(IV) ions in between them, revealing a degree of flexibility we had not previously appreciated for this type of bimetallic hexacarboxamide ligand architecture. The selective formation of this product shows that elemental selenium reacts with complete consumption of all four reducing equivalents stored in the di-tin(II) reservoir of dianion **1**, while the level of reduction of the elemental selenium, to Se^{2-} and Se_5^{2-} , is such that only one-third of the complete oxidizing power of 6 Se^0 is quenched and four reducible Se–Se bonds remain.

The UV-Vis spectrum of **3** in DMF solution shows two major absorptions located at $\lambda_{max} = 452$ ($\epsilon = 4207$ $M^{-1} cm^{-1}$), and 585 ($\epsilon = 842$ $M^{-1} cm^{-1}$) nm (0.26 mM, Fig. S16[†]). Both observed bands are in good agreement with the literature reported absorption values for Se_6^{2-} of $\lambda_{max} = 440$ and 598 nm in DMA solution.²⁹

Similarly, the reactivity of **1** with elemental sulfur was investigated. Treatment of **1** with 3/4 eq. S_8 in DMF solution elicits a rapid color change from colorless to blue green. Addition of Et_2O to the crude reaction mixture results in the precipitation of the $[K_2(DMF)_3][(\mu-S_5)Sn_2(\mu-S)(mBDCA-5t)]$ complex (**4**, Scheme 2) as a bright yellow solid in 63% yield. Although suitable crystals were not obtained for an X-ray diffraction study, the structure of the sulfur-containing product



in agreement with the literature reported EPR signal of S_3^{2-} .³⁷ Therefore, the observed data suggest that in solution, the sulfur atoms of complex **4** undergo dissociation from the di-tin cryptand to release S_3^{2-} .

The presence of S_3^{2-} upon dissolution of **4** may be a result of initial release of S_6^{2-} followed by dissociation into two equivalents of S_3^{2-} . According to this overall stoichiometry, dissociation of two equivalents of S_3^{2-} from the dianionic complex **4** would require the concomitant formation of a neutral $[Sn_2-(mBDCA-5t)]$ species. Although this is perhaps the most straightforward explanation, we cannot definitively rule out S_5^{2-} or S_4^{2-} as the source of S_3^{2-} . While more work is required to substantiate this proposal, such a postulated neutral $[Sn_2-(mBDCA-5t)]$ species may exist as a Sn–Sn bonded hexaaminodistannane analogous to one which Gade *et al.* obtained upon oxidative coupling of a tin(II) triamidostannate and for which the Sn–Sn interatomic distance was reported to be 2.8204(4) Å.³⁸ The metal–metal single bond in such a species corresponds to the HOMO–1 of complex **1** (Fig. 2b).

In an effort to drive to full completion the level of sulfur/selenium reduction in this system, we probed the reaction of **3** and **4** with PR_3 reductants ($R = ^tBu, Ph, O^iPr$, Scheme 2). Proceeding accordingly, we found that treatment of either complex with PR_3 (6 equiv.) resulted in abstraction of all six chalcogen atoms and quantitative regeneration of di-tin(II) complex **1**! Incomplete conversion of **3** and **4** to **1** was the result when using <6 equiv. PR_3 , with no other species observed by 1H or ^{119}Sn NMR spectroscopy. Treatment of either **3** or **4** with $PMes_3$ (excess), however, led to no observed reaction, this being explicable in terms of steric effects. Dechalcogenation of transition³⁹ and group 14 (ref. 31 and 40) metal cyclic polychalcogenide complexes is commonly accomplished using tertiary phosphines or electron deficient alkenes and alkynes. These reactions, however, typically result in only partial reduction in the size of the chalcogen ring or conversion to the typical bis- μ -chalcogen thermodynamic product instead of complete dechalcogenation. The present polychalcogen/di-tin cryptand complexes are very unusual inasmuch as PR_3 compounds are capable of complete de-chalcogenation and reduction of tin back to the +2 oxidation state, suggesting in turn that the macrobicyclic nature of bimetallic complex **1** imbues the tin(II) oxidation state with comparatively greater stability than is typical sans such structural constraints.

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