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Functionalizing the surface of II–VI clusters: redox active centres on the adamantoid complex $[Cd_4Cl_4\{\mu\text{-}(SeC_5H_4)Fe(C_5H_5)\}_6]^{2-}$

Terry P. Lebold, Donald L. B. Stringle, Mark S. Workentin and John F. Corrigan*
Department of Chemistry, The University of Western Ontario, London N6A 5B7, Canada.
E-mail: corrigan@uwo.ca; Fax: 1-519-661-3022; Tel: 1-519-661-2111 ext. 86387

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Trimethylsilylselenoferrocene 1 has been prepared in good yield. The reactive silyl group on 1 is used as a driving force for the synthesis $[Cl_4Cd_4\{\mu_2\text{-}Se(C_5H_4)Fe(C_5H_5)\}_6]^{2-}$ 2, a Cd_4Se_6 adamantoid cluster with six surface ferrocenyl groups.

The chemistry of II–VI cluster complexes has burgeoned recently, as new synthetic strategies have led to controlled routes to structurally characterized cluster and nanocluster frameworks, and the utility of silylated selenium reagents ($RSeSiMe_3$, R = alkyl, aryl) in the formation of cadmium–selenolate clusters has been demonstrated.[1] The solubility of $RSeSiMe_3$ reagents in common organic solvents offers an advantage over using related alkali metal selenolates, as homogenous reaction solutions are important for the synthesis of nanometer sized metal–selenium clusters.[2] The ability to modify the chalcogen substituent "R", and thus the surfaces of the generated particles, clearly offers a powerful method for the purpose of enhancing emission properties of metal–selenide particles[3] or in introducing designed chemical functionality to metal–selenium polynuclear frames.[4] Furthermore, the presence of redox active ferrocenyl groups, intimately associated with the cluster *via* the Se linkage, may permit modulation of the rich photophysical properties of CdSe nanoclusters.[1] Herein we describe the synthesis and characterization of trimethylsilylselenoferrocene, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4SeSiMe_3)]$ **1** and its utility in polyferrocene complex formation with the structural determination of $[Cl_4Cd_4\{\mu_2\text{-}Se(C_5H_4)Fe(C_5H_5)\}_6]^{2-}$ **2**, which possesses an unprecedented arrangement of six ferrocenyl units about an adamantoid core. The assembly of multiferrocene complexes including nanoclusters[5] and redox-active anion recognition dendrons[6] has been the focus of much attention. Recent examples of structurally characterised multiferrocene assemblies include the report on the structure of an arrangement of six ferrocene units on a supercubane framework[7] and work detailing a hexaferrocene assembly on a Sn_6O_{12} cluster core.[8]

The new reagent trimethylsilylselenoferrocene, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4SeSiMe_3)]$ **1**, can be prepared readily in > 80% yield from $Na[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4Se)]$ and $ClSiMe_3$, the former generated from the sonochemical reduction of diferrocenyldiselenide[9,10] with sodium metal/Ph_2CO in THF solutions.† Complex **1** is crystallized as orange needles by cooling concentrated hexane solutions. A single crystal X-ray analysis confirmed the functionalization of the selenium centre on the monosubstituted ferrocene (Figure 1). The molecule resides on a crystallographic mirror plane, which bisects atoms Fe1, Se1, Si1, C1, C6 and C8. The cyclopentadienyl rings are virtually parallel (∠ = 0.9°), with the bond lengths and angles associated with Se1 (Se1–C1 = 1.924(4), Se1–Si1 = 2.299(1) Å; C1–Se1–Se1 = 94.5(1)°) similar to those observed in the related molecule $[Fe(\eta^5\text{-}C_5H_4SeSiMe_3)_2]$.[4]

When **1** is added to a solution of $(Pr_3P)_2CdCl_2$ in tetrahydrofuran, orange crystals of $[Cd_4Cl_4\{(SeC_5H_4)\text{-}Fe(C_5H_5)\}_6]^{2-}$ **2** (Fig. 2) form after layering with heptane in ~50% yield.† Cluster **2** is isolated as the $[Pr_3PH]^+$ salt, the latter generated from PPr_3, adventitious water and the $ClSiMe_3$ side product. The structure of **2** is based on a central Cd_4Se_6 core with an adamantane-like arrangement, typical of CdSe cluster complexes,[1,11] tetrahedral coordination about each cadmium completed with a terminal chloride ligand (Cd–Cl = 2.424(2)–2.475(2) Å). The selenium centres in **2** symmetrically bridge the cadmium atoms [2.615(1)–2.668(1) Å] and the six ferrocenyl units are spatially arranged to effectively shield the Cd_4Se_6 core. In the solid state structure, the ferrocenyl groups adopt both axial (*a*) and equatorial (*e*) dispositions relative to the six-membered Cd_3Se_3 rings.[12]

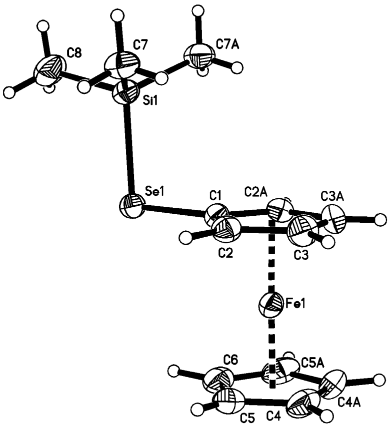

Fig. 1 The molecular structure of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4SeSiMe_3)]$ **1**. Selected bond lengths and angles are discussed in the text.

In CD_3CN solutions the ^1H NMR spectrum of **2** indicates a structure with all C_5H_4Se and C_5H_5 fragments rendered equivalent on the NMR timescale: three cyclopentadienyl resonances are observed at 4.34 (12H), 4.14 (30H) and 3.95 (12H) ppm. A single resonance is observed in the $^{77}Se\{^1H\}$ spectrum at $\delta = -199$ ppm, in the expected range for μ_2-selenolate ligands bridging Cd(II) centres.[11a] The UV-Vis spectrum of **2** displays a weak absorption at 435 nm (ε = 760

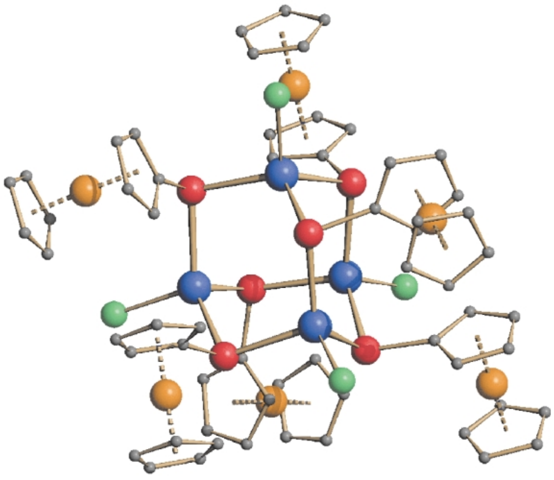

Fig. 2 The molecular structure of $[Cl_4Cd_4\{\mu_2\text{-}Se(C_5H_4)Fe(C_5H_5)\}_6]^{2-}$ **2** (Cd: blue; Cl: green; Se: red: Fe: orange; C; grey). Cd–Se = 2.615(1)–2.668(1); Cd–Cl = 2.424(2)–2.475(2) Å.

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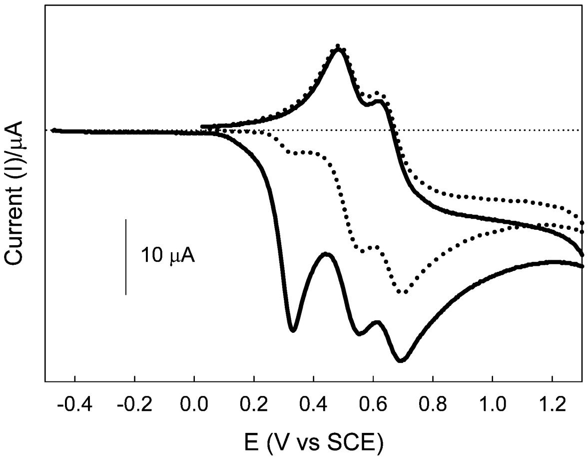

Fig. 3 Cyclic voltammogram of a 0.51 mM solution of **2** in 0.1M TBAP/MeCN. Solid line is the initial scan from −0.47 V to 1.33 V, dotted line shows the current response when rescanning through the 0.03 V to 1.33 V potential window.

L·mol^{-1}·cm^{-1}) assignable to the ferrocenyl chromophores with a more intense maximum at 325 nm (ε = ~6000 L·mol^{-1}·cm^{-1}) characteristic of $[X_4Cd_4(\mu_2\text{-}SeAr)_6]^{2-}$ clusters and assigned to the Se–Cd framework.[1] Cyclic voltammetry of **2** (0.51 mM) shows a single irreversible anodic oxidation wave at 0.33 V followed by two reversible oxidations with $E°$'s of 0.53 V and 0.67 V *versus* SCE, respectively (Fig. 3). The two reversible oxidations are due to the product from the first irreversible oxidation; this is evidenced by repetitive cycling through the oxidation (dashed line in Fig. 3). Constant potential electrolysis of a solution of **2** at the potential of the irreversible oxidation (0.35 V) requires approximately 6 electron equivalents to yield *ca.* three molar equivalents of diferrocenyldiselenide. The product was determined by work up and isolation of the electrolysis mixture and confirmed by comparing the reversible oxidation potentials observed in the electrochemistry to that of an authentic sample.[13] The potential of the irreversible oxidation of **2** is much more positive than those reported for similar chalcogenolate ligands in Cd(II) diimine complexes[14] and more typical of the potential region of ferrocene oxidation. It appears that oxidation of the ferrocenyl units in **2** initiates the oxidative cleavage of the ferrcenylselenolate leading to the formation of the diselenide. The nature of this electrochemical behaviour is currently being probed by investigating other ferrocenyl-CdSe and -CdS complexes.

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Notes and references

† *Synthesis of* **1***:* 1.00 g (1.9 mmol) of FcSeSeFc was dissolved in 35 mL of THF with ~2.2 equivalents of Na and a catalytic amount of Ph_2CO. The mixture was sonicated for 5 hours and the solvent removed *in vacuo* to yield crude Na[SeFc]. 40 mL of hexane was added to the residue to generate an orange suspension, which was cooled to −30 °C. An excess of $ClSiMe_3$(4 mmol) was added dropwise and the suspension was maintained at this temperature overnight. Solutions of **1** were filtered to remove NaCl and the filtrate was concentrated and cooled to −80 °C to afford golden orange crystals of **1**. Yield: 83% NMR $\delta(CDCl_3)$ ^{1}H: 4.20 (vt, 2H, J_{HH} = 2.0 Hz), 4.15 (s, 5H), 4.11 (vt, 2H, J_{HH} = 2.0 Hz), 0.27 (s, 9H); $^{13}C\{^1H\}$: 75.1 (CH, s), 69.7 (*C*H, s), 68.8 (*C*H, s), 67.5 (*C*–Se, s), 1.9 (*C*H$_3$, s); ^{77}Se: −54.1 (s); ^{29}Si: 14.6 (s) ppm. UV-Vis: λ_{max} = 436 nm (ε = 1 × 10^2 L·mol^{-1}·cm^{-1}). Anal calcd. (found): C, 46.31 (46.04); H, 5.38 (5.41)%.

Synthesis of **2***:* 0.056 g (0.30 mmol) of $CdCl_2$ was dissolved in 18 mL of THF with 0.70 mmol of PPr_3. To this solution was added 0.22 g (0.64 mmol) of **1** to yield a clear, orange solution. Layering with hexane (50 mL) yielded 0.097 g of orange crystals of **2** (48%). NMR $\delta(CD_3CN)$ ^{1}H: 5.99 (d sept, 2H, $^1J_{PH}$ = 479 Hz, $^3J_{HH}$ = 13 Hz), 4.34 (s, 12H), 4.14 (s, 30H), 3.95 (s, 12H), 2.16 (mult., 12H), 1.65 (mult., 12H), 1.06 (td, 18H, $^3J_{HH}$ = 7 Hz, $^4J_{PH}$ = 1 Hz); ^{77}Se: −199.0 (br s, $W_{1/2}$ = 80 Hz); $^{31}P\{^1H\}$: +11.1 (s) ppm. UV-Vis: λ_{max} = 436 (ε = 1 × 10^2), 325 nm (ε = 6000 L·mol^{-1}·cm^{-1}). Anal calcd. (found): C, 37.5 (37.3); H, 3.95 (4.35)%.

Crystal data for **1**: $C_{13}H_{18}FeSeSi$, M = 337.2, Orthorhombic, space group *Pnma*, a = 13.6164(6), b = 9.9392(4), c = 10.3578(4) Å, V = 1401.8(1) Å^3, at 200 K, Z = 4, μ = 3.730 mm^{-1}, $2\theta_{max}$ = 55.2, 3068 measured, 1707 independent reflections (R_{int} = 0.042) on an Enraf-Nonius Kappa-CCD diffractometer. R = 0.0347, wR_2 = 0.0663, GoF = 0.972. Crystal Data for **2**: $C_{78}H_{98}Cd_4Cl_4Fe_6Se_6P_2$·THF, M = 2569.1, triclinic, space group $P1$, a = 14.8446(2), b = 15.0614(2), c = 20.9175(3) Å, α = 84.0927(4), β = 83.5737(4), γ = 88.3638(5)°, V = 4622.0(1) Å^3, at 293 K, Z = 2, μ = 4.366 mm^{-1}, $2\theta_{max}$ = 50.8, 25898 measured, 16266 independent reflections (R_{int} = 0.038). R = 0.0525, wR_2 = 0.1350, GoF = 1.043. CCDC 205968 and 205969. See http://www.rsc.org/suppdata/cc/b3/b302829a/ for crystallographic data in .cif or other electronic format.

Electrochemical experiments utilized an E.G.&G PAR 283 potentiostat and were measured in an acetonitrile solution containing 0.1M tetrabutylammonium perchlorate using glassy carbon working electrodes at 25 °C. Potentials are reported against SCE. Constant potential electrolysis was performed using a glassy carbon rotating disk electrode.

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