Selective Insertion of Oxygen and Selenium into an Electron-Precise Paramagnetic Selenium−Manganese Carbonyl Cluster [Se₆Mn₆(CO)₁₈]⁴⁻

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O_2 activation by transition metal complexes is an attractive research topic from the standpoint of bioinorganic and synthetic chemistry.[1,2] Although the activation of O_2 by transition metal complexes is well-known, it is rare in the field of metal carbonyl complexes.[1−3] Chalcogenide derivatives of metal carbonyls characteristically exist as clusters, and this field has matured over the previous decades.[1b,4] The structures of these clusters, as well as their redox and substituted derivatives, can be predicted using simple electron-counting rules. While a relatively large number of manganese carbonyl clusters are known,[5] manganese carbonyl chalcogenide clusters are scarce, especially with regard to selenium−manganese carbonyl clusters.[6,7] In the present study, we describe a new family of manganese carbonyl selenide clusters, Mn−Se−CO anions, which deviate from well-established reactivity patterns. They exhibit unprecedented bonding properties, demonstrated by their magnetism, in which a novel electron-precise paramagnetic hexa-manganese carbonyl selenide cluster [Se₆Mn₆(CO)₁₈]⁴⁻ (**1**) exhibits contrasting reactivity toward O_2 and elemental selenium (Se₈) under mild conditions to afford the O- and Se-inserted clusters [Se₆Mn₆(CO)₁₈(O)]⁴⁻ (**2**) and [Se₁₀Mn₆(CO)₁₈]⁴⁻ (**3**), respectively.

When Se₈ was treated with Mn₂(CO)₁₀ at a molar ratio of 1:2.6 in concentrated KOH/MeOH solutions, the novel cluster [Se₆Mn₆(CO)₁₈]⁴⁻ (**1**) was formed in a moderate yield (Scheme 1). X-ray analysis showed that **1** was composed of two Se₂Mn₃(CO)₉ units that were linked by a μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$-Se₂²⁻ ligand, in which three Mn atoms were capped above and below by two μ_3-Se²⁻ atoms with an inversion center located at the midpoint of the Se−Se bond (Figure 1a). While one of three Mn atoms of the Se₂Mn₃(CO)₉ unit exhibited a distorted octahedral geometry, the other two Mn centers were seven-coordinated with a direct Mn−Mn interaction. Cluster **1** can be considered a result of the coupling reaction of two [Se₂Mn₃(CO)₉]⁻ units and one Se₂²⁻ unit, which was confirmed by the reaction of [Se₂Mn₃(CO)₉]⁻ [6h] with a 1/8 equiv of Se₈ in a concentrated KOH/MeOH solution. Conversely, cluster **1** could be reconverted back to [Se₂Mn₃(CO)₉]⁻ upon treatment with [Cu(MeCN)₄][BF₄] in MeCN.

Differential pulse voltammetry measurement indicated that [Et₄N]₄[**1**] underwent two quasi-reversible oxidations at ∼0.398 V ($W_{1/2}$ = 212 mV), suggesting that **1** could be oxidized by two electrons. As a consequence, the reactivity of cluster **1** toward O_2 was investigated. Interestingly, **1** was found to react readily with 0.5 equiv of O_2 (see Supporting Information) in MeCN to give the O-inserted cluster [Se₆Mn₆(CO)₁₈(O)]⁴⁻ (**2**). X-ray analysis revealed that **2** consisted of two Se₃Mn₃(CO)₉ units bridged by an O atom (Figure 1b). The average Se−O distance of **2** was 1.99(1) Å which can be considered a normal single

bond (the sum of the covalent radii for Se and O is 1.90 Å), and the Se−O−Se bond angle was 106.2(3)°, which is indicative of the tetrahedral geometry around the O center. Cluster **2** evidently resulted from the insertion of an O atom into the Se−Se bond of **1**, which served as a two-electron reductant toward O_2. The isomeric η^2-Se₂O was observed in [Ir(Se₂O)(dppe)₂]⁺ from [Ir(Se₂)(dppe)₂]⁺ with peracetic acid.[8] Although thiolates and polysulfido complexes have been shown to undergo S-oxidation with O_2,[9] and some dichalcogenido metal carbonyl complexes exhibited the oxidative addition of small organic molecules or metal fragments across the E−E bond,[6a,10] cluster **1** represents the first example of O_2 activation by the E−E bond (E = Se).

Scheme 1
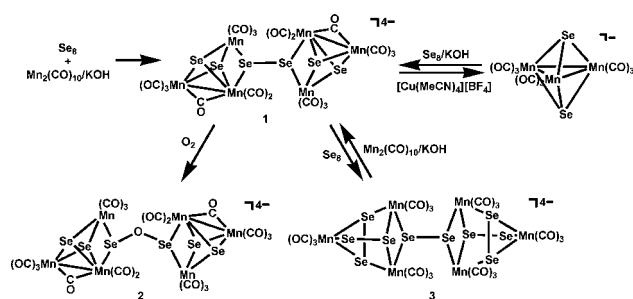

In place of oxygen, selenium was also found to oxidize **1**. Thus with either a 1/8 or a 1/2 equiv of Se₈ in MeCN, the Se-rich cluster [Se₁₀Mn₆(CO)₁₈]⁴⁻ (**3**) was produced (Scheme 1). As depicted in Figure 1c, cluster **3** possessed two (μ_3-Se₂)₂Mn₃(CO)₉ moieties that were bridged by a Se₂²⁻ unit with an inversion center located at the midpoint of the central Se−Se bond and gave a dumbbell-like conformation. The six Mn atoms in **3** were nonbonded (Mn···Mn, 3.665(3) to 4.244(3) Å) and held together by five Se₂²⁻ units to give rise to three different bonding modes: μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$-; μ_3-η^1,η^1,η^1-; and μ_3-η^1,η^1,η^2-Se₂²⁻. The formation of **3** can be described as involving the insertion of Se atoms into the Se−Mn and Mn−Mn bonds of the Se₂Mn₃(CO)₉ fragments of **1**, accompanied by the Se−Se bond formation. Cluster **3** could also be reconverted back to **1** by the addition of Mn₂(CO)₁₀ in concentrated KOH/MeOH solutions.

Clusters **1** and **2** are both 104-electron species and cluster **3** is a 108-electron species, which all obey the 18-electron rule. Surprisingly, the magnetic measurements showed that [Et₄N]₄[**1**], [Et₄N]₄[**2**], and [Et₄N]₄[**3**] had effective magnetic moments, μ_{eff} = 2.98, 2.47, and 2.79 μ_B at 300 K, respectively, which were close to the spin-only value (μ_{eff} = 2.83 μ_B) predicted for a simple $S = 1$ species (Figure S1). The slow decrease of μ_{eff} with the decreasing temperature was due to antiferromagnetic

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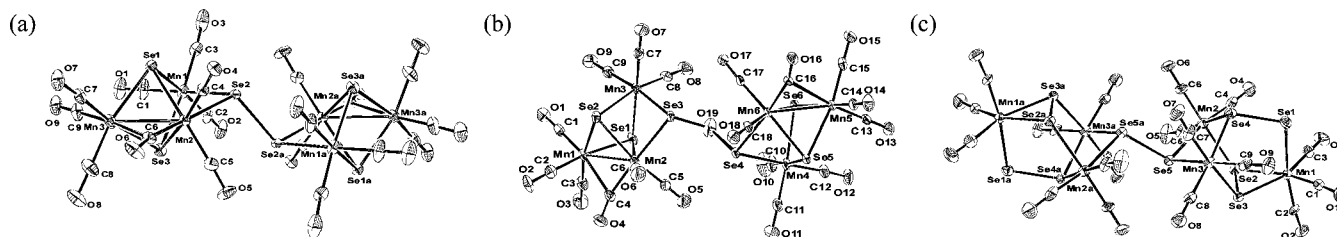
Figure 1. ORTEP diagram of anion **1**−**3**, showing 30% probability thermal ellipsoids.

interaction. Paramagnetic behavior of **1**−**3** was also shown by broadening of the ^{1}H NMR signals of their $[Et_4N]^+$ salt.[7b] Although electron-precise, clusters **1**−**3** are paramagnetic, a rare property for metal carbonyl clusters.[5c,7b,11,12] Clusters **1**−**3** represent the first examples of electron-precise paramagnetic main-group transition metal carbonyl clusters.

The formation of **2** can be related to the higher-energy SOMO of **1** (Figure S2a), which had a large component on the antibonding interaction of the *p* orbitals of the Se_2-linkage. It is suggested that this orbital interacts with the π^* orbitals of the O_2 molecule in its initial reaction with **1**. The insertion of the *p*-like orbital of one of two oxygen atoms into the Se−Se bond gave the O-bridged cluster **2**. On the other hand, the lower-energy SOMO of **1** received major contributions from the *s* and *d* orbitals of the Mn atoms and from the *p* orbital of the Se atoms of the two $Se_2Mn_3(CO)_9$ units, in which the overlaps between the terminal Mn atom and the two nearby Se or Mn atoms were not significant (Figure S2b). Hence, it is postulated that this orbital is a reactive site for the reaction of cluster **1** with Se_8 to give the Se-inserted cluster **3**. Since we had no evidence for the Se analogue of **2**, we calculated the relevant binding energies for **2** and its analogous Se-bridged cluster, which showed that the binding energy of **2** was stronger than its proposed Se-bridged cluster by more than 150 kcal/mol, which supports our experimental results. Furthermore, our calculations indicated that the unpaired electrons of **1** were significantly localized on both the terminal Mn and the central Se atoms. The central Se−O−Se fragment in **2** carried significant unpaired spin density (Figure S3).

In summary, an electron-precise, but paramagnetic, hexamanganese carbonyl selenide cluster $[Se_6Mn_6(CO)_{18}]^{4-}$ (**1**) was prepared, which afforded a versatile synthon for the activation of O_2 and Se_8 under mild conditions. The selectivity and their bonding properties are further elucidated by theoretical calculations.

Supporting Information Available: Experimental details for synthesis, characterization, and X-ray structure determinations (in CIF format) of $[Et_4N]_4[\mathbf{1}]$, $[Et_4N]_4[\mathbf{2}]$, and $[Et_4N]_4[\mathbf{3}]$. Computational details for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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