

Selective Insertion of Oxygen and Selenium into an Electron-Precise Paramagnetic Selenium–Manganese Carbonyl Cluster $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$

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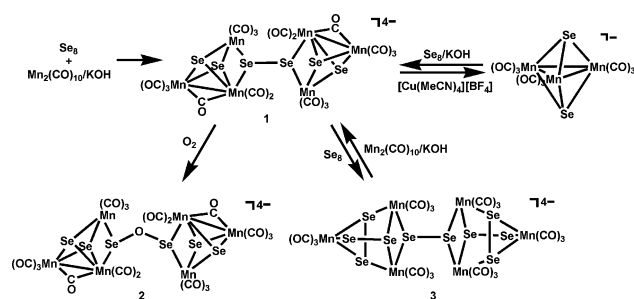
O_2 activation by transition metal complexes is an attractive research topic from the standpoint of bioinorganic and synthetic chemistry.^{1,2} Although the activation of O_2 by transition metal complexes is well-known, it is rare in the field of metal carbonyl complexes.^{1–3} Chalcogenide derivatives 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 hexamanganese carbonyl selenide cluster $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$ (**1**) exhibits contrasting reactivity toward O_2 and elemental selenium (Se_8) under mild conditions to afford the O- and Se-inserted clusters $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}(\text{O})]^{4-}$ (**2**) and $[\text{Se}_{10}\text{Mn}_6(\text{CO})_{18}]^{4-}$ (**3**), respectively.

When Se_8 was treated with $\text{Mn}_2(\text{CO})_{10}$ at a molar ratio of 1:2.6 in concentrated KOH/MeOH solutions, the novel cluster $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$ (**1**) was formed in a moderate yield (Scheme 1). X-ray analysis showed that **1** was composed of two $\text{Se}_2\text{Mn}_3(\text{CO})_9$ units that were linked by a $\mu_4\text{-}\eta^1, \eta^1, \eta^1, \eta^1\text{-Se}_2^{2-}$ ligand, in which three Mn atoms were capped above and below by two $\mu_3\text{-Se}^{2-}$ atoms with an inversion center located at the midpoint of the Se–Se bond (Figure 1a). While one of three Mn atoms of the $\text{Se}_2\text{Mn}_3(\text{CO})_9$ 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 $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^-$ units and one Se_2^{2-} unit, which was confirmed by the reaction of $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^-$ ^{6h} with a 1/8 equiv of Se_8 in a concentrated KOH/MeOH solution. Conversely, cluster **1** could be reconverted back to $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^-$ upon treatment with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ in MeCN.

Differential pulse voltammetry measurement indicated that $[\text{Et}_4\text{N}]_4[\mathbf{1}]$ 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 $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}(\text{O})]^{4-}$ (**2**). X-ray analysis revealed that **2** consisted of two $\text{Se}_3\text{Mn}_3(\text{CO})_9$ 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 $\eta^2\text{-Se}_2\text{O}$ was observed in $[\text{Ir}(\text{Se}_2\text{O})(\text{dppe})_2]^+$ from $[\text{Ir}(\text{Se}_2)(\text{dppe})_2]^+$ 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 Se_8 in MeCN, the Se-rich cluster $[\text{Se}_{10}\text{Mn}_6(\text{CO})_{18}]^{4-}$ (**3**) was produced (Scheme 1). As depicted in Figure 1c, cluster **3** possessed two $(\mu_3\text{-Se}_2)_2\text{Mn}_3(\text{CO})_9$ moieties that were bridged by a Se_2^{2-} 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 ($\text{Mn}\cdots\text{Mn}$, 3.665(3) to 4.244(3) Å) and held together by five Se_2^{2-} units to give rise to three different bonding modes: $\mu_4\text{-}\eta^1, \eta^1, \eta^1, \eta^1\text{-}$; $\mu_3\text{-}\eta^1, \eta^1, \eta^1\text{-}$; and $\mu_3\text{-}\eta^1, \eta^1, \eta^2\text{-Se}_2^{2-}$. The formation of **3** can be described as involving the insertion of Se atoms into the Se–Mn and Mn–Mn bonds of the $\text{Se}_2\text{Mn}_3(\text{CO})_9$ fragments of **1**, accompanied by the Se–Se bond formation. Cluster **3** could also be reconverted back to **1** by the addition of $\text{Mn}_2(\text{CO})_{10}$ 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 $[\text{Et}_4\text{N}]_4[\mathbf{1}]$, $[\text{Et}_4\text{N}]_4[\mathbf{2}]$, and $[\text{Et}_4\text{N}]_4[\mathbf{3}]$ had effective magnetic moments, $\mu_{\text{eff}} = 2.98$, 2.47, and 2.79 μ_B at 300 K, respectively, which were close to the spin-only value ($\mu_{\text{eff}} = 2.83$ 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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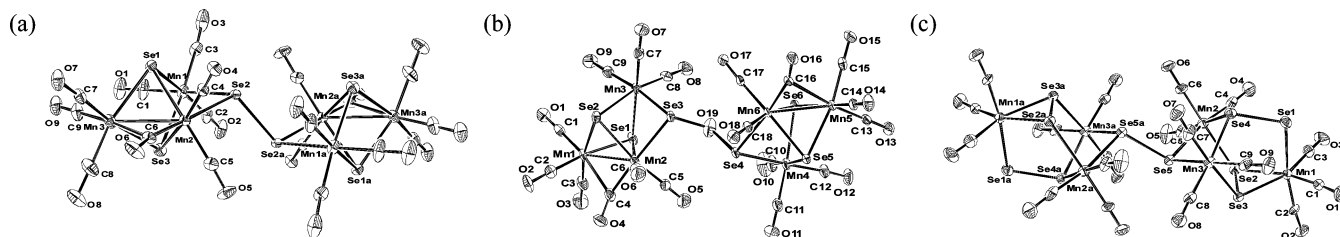


Figure 1. ORTEP diagram of anion 1–3, showing 30% probability thermal ellipsoids.

interaction. Paramagnetic behavior of 1–3 was also shown by broadening of the ^1H NMR signals of their $[\text{Et}_4\text{N}]^+$ 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 $\text{Se}_2\text{Mn}_3(\text{CO})_9$ 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 $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$ (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.

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

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