

in Table III. Additional experimental details are given in the supplementary material, along with tables of anisotropic thermal parameters, bond distances and angles, and observed and calculated structure factors.

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Supplementary Material Available: Tables of crystallographic data and refinement parameters, anisotropic thermal parameters, and bond distances and angles (7 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Clemson University, Clemson, South Carolina 29634

Oxidative Decarbonylation of Dimanganese Decacarbonyl by Polyselenide Anions: Molecular Structure of $[(C_6H_5)_4P]_2[Mn_2(Se_2)_2(CO)_6] \cdot C_4H_{10}O$, $[(C_6H_5)_4P]_2[Mn_2(Se_4)_2(CO)_6]$, and $[(C_6H_5)_4P]_2[Mn(Se_4)_2]$

S. C. O'Neal, W. T. Pennington, and J. W. Kolis*

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A series of three manganese polyselenide anions has been isolated and characterized. They are all derived from the reaction of $Mn_2(CO)_{10}$ and polyselenide anions in DMF solution. The reaction of $Mn_2(CO)_{10}$ with 1 equiv of K_2Se_3 in DMF generates $[Mn_2(Se_2)_2(CO)_6]^{2-}$ (Ia). Reaction of $Mn_2(CO)_{10}$ with 2 equiv of K_2Se_3 produces $[Mn_2(Se_4)_2(CO)_6]^{2-}$ (IIa), which can also be obtained by reaction of Ia with red selenium. Thermolysis of IIa in DMF leads to $[Mn(Se_4)_2]^{2-}$ (IIIa), which is the final product of oxidative decarbonylation. Thermolysis of Ia does not appear to lead to IIIa, suggesting that IIa is a necessary intermediate in the oxidative decarbonylation reaction. All three products have been structurally characterized as their $[(C_6H_5)_4P]^+$ salts (I-III). Structural data are as follows. For I: formula = $[(C_6H_5)_4P]_2[Mn_2(Se_2)_2(CO)_6] \cdot C_4H_{10}O$, space group $P1$, $Z = 1$, $a = 11.120$ (6) Å, $b = 11.319$ (5) Å, $c = 13.062$ (7) Å, $\alpha = 114.90$ (4)°, $\beta = 107.64$ (4)°, $\gamma = 90.57$ (4)°, $V = 1403$ (1) Å³, $R(F_o) = 0.0688$, $R_w(F_o) = 0.0684$. For II: formula = $[(C_6H_5)_4P]_2[Mn_2(Se_4)_2(CO)_6]$, space group $P2_1/n$, $Z = 2$, $a = 12.022$ (5) Å, $b = 14.542$ (7) Å, $c = 16.251$ (8) Å, $\beta = 98.46$ (4)°, $V = 2810$ (1) Å³, $R(F_o) = 0.0554$, $R_w(F_o) = 0.0580$. For III: formula = $[(C_6H_5)_4P]_2[Mn(Se_4)_2]$, space group $P2_1$, $Z = 4$, $a = 10.048$ (3) Å, $b = 13.394$ (4) Å, $c = 33.969$ (11) Å, $\beta = 92.11$ (2)°, $V = 4756$ (1) Å³, $R(F_o) = 0.0624$, $R_w(F_o) = 0.0613$. Both carbonyl containing anions, Ia and IIa, consist of two manganese tricarbonyl fragments chelated by a Se_n^{2-} chain ($n = 2, 4$). One of the terminal selenium atoms on each manganese also bridges to the second metal center, completing its 18-electron count. Thus each metal center is pseudooctahedrally coordinated by three Se atoms and three carbonyl ligands. The monomer IIIa has two Se_4^{2-} chains chelating to a manganese(II) center in a tetrahedral fashion.

Introduction

We have recently reported a series of reactions involving transition-metal carbonyls with polychalcogenides in polar aprotic solvents.¹⁻³ It turns out that the group 6 metal carbonyls undergo a remarkably diverse series of reactions with polychalcogenides. These reactions range from simple substitution with polytellurides¹ to oxidative decarbonylation of the metal center to form molybdenum and tungsten sulfides and selenides² and to oxidation of coordinated carbon monoxide to form chromium(III) trisulfidocarbonate.³

However, there has been very little work previously reported on the sulfides⁴ and selenides⁵ of group 7 metals. In general they do not enjoy the popularity of their group 6 neighbors. In fact, the only molecular binary sulfide of manganese reported to date is MnS_{11}^{2-} , which contains a disordered tetrahedron of two polysulfide rings coordinated to the metal center.^{4f} The tetrathio-rhenate ReS_4^- , has been prepared, along with several of its complexes,⁶ as well as $ReS_9^{-6b,7}$ and $Re_4S_{22}^{4-}$.⁸ In addition, there

have been several group 7 complexes reported that contain either selenide or diselenide as a ligand.⁹ However, the area is very underdeveloped.

Recently, we reported the formation of $[Re_2(Se_4)_2(CO)_6]^{2-}$ from $Re_2(CO)_{10}$ and polyselenide anions in DMF solution.¹⁰ In this paper, we describe the results of the investigation of the corresponding reactions of $Mn_2(CO)_{10}$ with polyselenide solution. We report the structure of a completely decarbonylated product $[Mn(Se_4)_2]^{2-}$, as well as the isolation and characterization of two possible precursors. Also, we provide more mechanistic information about the oxidative decarbonylation reaction.

Experimental Section

General Information. The compounds investigated in this report are air-sensitive, as is typical for d-block metal carbonyl anions. Thus, all reactions were performed in dried, degassed solvents under a purified argon atmosphere by using standard Schlenk techniques. All solids were stored and handled in an argon-filled glovebox. The selenide reagent, K_2Se_3 , was prepared by a previously reported procedure,² and all other reagents are commercially available and were used as received. Solvents were Aldrich Gold Label grade and stored over activated sieves and degassed. IR spectra were obtained as Nujol mulls between KBr plates or polyethylene bags, and analytical data were obtained from Atlantic Microlabs, Atlanta, GA.

Preparation of $[(C_6H_5)_4P]_2[Mn_2(Se_2)_2(CO)_6] \cdot C_4H_{10}O$ (I). In a typical reaction, 0.25 g (0.79 mmol) of K_2Se_3 , 0.30 g (0.76 mmol) of Mn_2CO_{10} , and 0.66 g (1.58 mmol) of $(C_6H_5)_4PBr$ were dissolved in 5 mL of DMF, and stirred at room temperature for 15 min. The red solution was then

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Table I. Crystallographic Information for Molecules I–III

(a) Crystal Data for $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mn}_2(\text{Se}_2)_2(\text{CO})_6] \cdot (\text{C}_2\text{H}_5)_2\text{O}$
 chemical formula: $\text{C}_{58}\text{H}_{50}\text{O}_7\text{P}_2\text{Mn}_2\text{Se}_4$
 fw = 1346.74
 unit cell dims: $a = 11.1105$ (46) Å, $b = 11.3084$ (41) Å, $c = 13.0518$ (52) Å, $\alpha = 114.829$ (29)°, $\beta = 107.639$ (33)°, $\gamma = 90.602$ (32)°
 $V = 1403$ (1) Å³
 $Z = 1$
 space group: $P\bar{1}$ (No. 2)
 $\lambda = 0.71073$ Å
 $T = 21$ °C
 $\rho_{\text{calc}} = 1.60$ g cm⁻³
 $\mu = 31.12$ cm⁻¹
 transm coeff = 0.63–1.00
 $R(F_o) = 0.0688$
 $R_w(F_o) = 0.0684$

(b) Crystal Data for $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]$
 chemical formula: $\text{C}_{54}\text{H}_{40}\text{O}_6\text{P}_2\text{Se}_8\text{Mn}_2$
 fw = 1588.44
 unit cell dims: $a = 12.0216$ (52) Å, $b = 14.5422$ (71) Å, $c = 16.2505$ (81) Å, $\beta = 98.460$ (37)°
 $V = 2810$ (2) Å³
 $Z = 2$
 space group: $P2_1/n$ (No. 14)
 $\lambda = 0.71073$ Å
 $T = 21$ °C
 $\rho_{\text{calc}} = 1.88$ g cm⁻³
 $\mu = 56.65$ cm⁻¹
 transm coeff = 0.57–1.00
 $R(F_o) = 0.0555$
 $R_w(F_o) = 0.0580$

(c) Crystal Data for $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mn}(\text{Se}_4)_2]$
 chemical formula: $\text{C}_{48}\text{H}_{40}\text{P}_2\text{MnSe}_8$
 fw = 1365.44
 unit cell dims: $a = 10.0491$ (32) Å, $b = 13.9449$ (45) Å, $c = 33.9690$ (120) Å, $\beta = 92.107$ (27)°
 $V = 4757$ (3) Å³
 $Z = 4$
 space group: $P2_1$ (No. 4)
 $\lambda = 0.71073$ Å
 $T = 21$ °C
 $\rho_{\text{calc}} = 1.91$ g cm⁻³
 $\mu = 64.27$ cm⁻¹
 transm coeff = 0.59–1.00
 $R(F_o) = 0.0623$
 $R_w(F_o) = 0.0613$

heated to 100 °C with stirring, for 30 min. The resulting red solution was filtered, layered with 3 mL of diethyl ether, and stored at 4 °C overnight. The solution was filtered to remove a white powder, which was deposited, and the volume of the solution was reduced by half under dynamic vacuum. Fresh diethyl ether, 3 mL, was added, and further storage at 4 °C overnight resulted in precipitation of orange needle crystals. Isolated yield, 15%. Anal. Calcd: C, 51.73; H, 3.75. Found: C, 49.91; H, 3.65. IR (cm⁻¹): 1942 (ms), 1836 (ms). (Note: It is difficult to obtain this compound in analytically pure form as it is often contaminated with trace amounts of II.)

Preparation of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]$ (II). Method A. A flask was charged with 0.25 g (0.79 mmol) of K_2Se_3 , 0.15 g of (0.38 mmol) $\text{Mn}_2\text{CO}_{10}$, and 0.66 g (1.58 mmol) of $(\text{C}_6\text{H}_5)_4\text{PBr}$. After addition of 5 mL of DMF, the reaction was stirred for 30 min at room temperature. The resulting green solution was heated to 100 °C for 2 h, and the red solution was filtered, layered with 3 mL of diethyl ether, and stored at 4 °C overnight. This produced red-orange crystals in 30% yield, which were isolated by filtration. Anal. Calcd: C, 40.81; H, 2.52. Found: C, 40.11; H, 2.58. IR (cm⁻¹): 1970 (ms), 1878 (ms).

Preparation of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]$ (II). Method B. A flask was charged with 0.25 (0.79 mmol) of K_2Se_3 , 0.30 g (0.76 mmol) of $\text{Mn}_2(\text{CO})_{10}$, and 0.66 g (1.58 mmol) of $(\text{C}_6\text{H}_5)_4\text{PBr}$, and 5 mL of DMF was added. After being stirred for 15 min at room temperature, the red solution was heated at 100 °C for 30 min. Then, 0.10 g (1.27 mmol) of red selenium was added and the mixture stirred at room temperature for 30 min, giving the solution a deeper red color. The solution was filtered and layered with 3 mL of diethyl ether and stored at 4 °C overnight. Large red crystals of II formed in 30% yield.

Preparation of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}(\text{Se}_4)_2]$ (III). A flask was charged with 0.25 g (0.79 mmol) of K_2Se_3 , 0.15 g (0.38 mmol) of $\text{Mn}_2(\text{CO})_{10}$, and 0.66

Table II. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mn}_2(\text{Se}_2)_2(\text{CO})_6] \cdot (\text{C}_2\text{H}_5)_2\text{O}$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) ^a |
|-------|------------|------------|------------|----------------------------|
| Se(1) | 935 (1) | 1102 (1) | -13 (1) | 50 (1) |
| Se(2) | 2406 (2) | 54 (2) | 859 (2) | 59 (1) |
| Mn(1) | -684 (2) | -841 (2) | -1704 (2) | 49 (1) |
| O(1) | -2523 (13) | -3145 (12) | -3624 (11) | 96 (7) |
| O(2) | 1405 (12) | -2280 (11) | -2254 (11) | 75 (7) |
| O(3) | -932 (13) | 325 (13) | -3356 (12) | 93 (8) |
| C(1) | -1816 (16) | -2268 (17) | -2860 (15) | 60 (8) |
| C(2) | 628 (16) | -1697 (16) | -2006 (14) | 60 (9) |
| C(3) | -869 (15) | -119 (15) | -2716 (14) | 59 (8) |

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) ^a |
|-------|------------|-----------|------------|----------------------------|
| Se(1) | 125 (2) | 93 (2) | 1043 (1) | 46 (1) |
| Se(2) | 1600 (2) | 1066 (2) | 1707 (1) | 70 (1) |
| Se(3) | 1163 (2) | 2489 (2) | 1045 (1) | 73 (1) |
| Se(4) | 527 (2) | 2018 (2) | -310 (1) | 63 (1) |
| Mn(1) | -1043 (2) | 970 (2) | -107 (2) | 43 (1) |
| O(1) | -2904 (12) | -271 (11) | 154 (9) | 78 (7) |
| O(2) | -2480 (11) | 1715 (10) | -1589 (8) | 67 (6) |
| O(3) | -1876 (13) | 2290 (10) | 1016 (8) | 70 (7) |
| C(1) | -2149 (18) | 190 (14) | 39 (11) | 45 (9) |
| C(2) | -1914 (14) | 1438 (12) | -1012 (12) | 41 (7) |
| C(3) | -1507 (16) | 1773 (15) | 575 (11) | 46 (9) |

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

g (1.58 mmol) of $(\text{C}_6\text{H}_5)_4\text{PBr}$. Addition of 5 mL of DMF and stirring of the reaction mixture at room temperature for 30 min produced a green solution, which was then heated to 100 °C for 4 h. The resulting red solution was filtered and layered with 3 mL of diethyl ether and stored at 4 °C overnight. Dark red crystals of III were isolated in 25% yield. Anal. Calcd: C, 42.19; H, 2.93. Found: C, 42.09; H, 3.01.

X-ray Crystallographic Investigations. The appropriate crystallographic data for all three molecules are summarized in Table I. In each case a suitable crystal was sealed in Duro Master Blend epoxy resin and mounted on a Nicolet R3/mv diffractometer. Photographs were taken to ascertain crystal quality and obtain preliminary space group information. Each unit cell determination was obtained from approximately 35 well-centered reflections in the range $15^\circ < 2\theta < 30^\circ$. Each cell was subjected to standard reduction programs to determine the highest symmetry cell. After unit cell determination, data was collected for each crystal in the range $2^\circ < 2\theta < 45^\circ$. Each structure was solved by direct methods using the SHELXTL program and refined by successive full-matrix least-squares cycles using the standard Nicolet package of programs. All non-hydrogen atoms were refined anisotropically, except for carbon atoms of the tetraphenylphosphonium molecules, which were refined isotropically. Hydrogen atoms were idealized. Absorption correction of the data was performed by the ψ -scan technique using six intense reflections at high χ angles. Positional and thermal parameters for compounds I–III are listed in Tables II–IV, respectively. Selected distances and angles for I–III are given in Tables V–VII, respectively. Complete listings of bond distances and angles, positional and thermal parameters, and observed and calculated structure factors have been deposited as supplementary material.

Results

Structure of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}_2(\text{Se}_2)_2(\text{CO})_6] \cdot \text{C}_4\text{H}_{10}\text{O}$. Compound I consists of two well-separated tetraphenylphosphonium cations and a disordered diethyl ether molecule in addition to the diselenide-bridged manganese dimer. The diethyl ether molecule has very high thermal parameters so the site is probably only partially occupied. This is also consistent with the elemental analyses, which are repeatedly low in carbon. An ORTEP view of the manganese selenide cluster of I is shown in Figure 1. The dianion consists of two manganese atoms, which are bridged to two diselenide groups, each of which is bridging through one selenium and bonded in a η^2 , or side-on fashion, to one of the manganese atoms. The molecule is symmetrical due to a crys-

Table IV. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{Mn}(\text{Se}_4)_2]$

| | x | y | z | $U(\text{eq})^a$ |
|--------|-----------|-----------|----------|------------------|
| Mn(1) | 222 (4) | 3096 | 3725 (1) | 45 (2) |
| Se(11) | -1369 (3) | 1801 (4) | 3477 (1) | 48 (1) |
| Se(12) | -580 (4) | 1989 (4) | 2850 (1) | 64 (1) |
| Se(13) | 1625 (3) | 1595 (4) | 2947 (1) | 60 (1) |
| Se(14) | 2384 (3) | 2734 (4) | 3391 (1) | 58 (1) |
| Se(15) | -497 (3) | 4836 (4) | 3634 (1) | 54 (1) |
| Se(16) | 1252 (3) | 5193 (4) | 4070 (1) | 62 (1) |
| Se(17) | 626 (3) | 4466 (4) | 4653 (1) | 54 (1) |
| Se(18) | 432 (3) | 2877 (4) | 4471 (1) | 52 (1) |
| Mn(2) | 7372 (5) | -1041 (4) | 1236 (1) | 47 (2) |
| Se(21) | 6399 (3) | -2684 (4) | 1119 (1) | 59 (1) |
| Se(22) | 7662 (4) | -3364 (4) | 1621 (1) | 80 (2) |
| Se(23) | 7318 (4) | -2404 (4) | 2168 (1) | 80 (2) |
| Se(24) | 7945 (4) | -885 (4) | 1974 (1) | 80 (2) |
| Se(25) | 5765 (3) | 141 (4) | 910 (1) | 57 (1) |
| Se(26) | 6632 (3) | -392 (4) | 323 (1) | 61 (1) |
| Se(27) | 8851 (3) | 75 (4) | 387 (1) | 53 (1) |
| Se(28) | 9622 (3) | -755 (4) | 937 (1) | 68 (1) |

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Distances (\AA) and Angles (deg) for $[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{Mn}_2(\text{Se}_2)_2(\text{CO})_6] \cdot (\text{C}_2\text{H}_5)_2\text{O}$

| | | | |
|--------------------|------------|---------------------|------------|
| Se(1)-Se(2) | 2.327 (3) | Se(1)-Mn(1) | 2.525 (2) |
| Se(1)-Mn(1A) | 2.474 (4) | Se(2)-Mn(1A) | 2.482 (3) |
| Mn(1)-C(1) | 1.796 (14) | Mn(1)-C(2) | 1.809 (18) |
| Mn(1)-C(3) | 1.789 (21) | O(1)-C(1) | 1.129 (17) |
| O(2)-C(2) | 1.135 (22) | O(3)-C(3) | 1.127 (28) |
| Se(2)-Se(1)-Mn(1) | 101.4 (1) | Se(2)-Se(1)-Mn(1A) | 62.2 (1) |
| Mn(1)-Se(1)-Mn(1A) | 99.0 (1) | Se(1)-Se(2)-Mn(1A) | 61.8 (1) |
| Se(1)-Mn(1)-Se(1A) | 81.0 (1) | Se(1)-Mn(1)-Se(2A) | 91.7 (1) |
| Se(1)-Mn(1)-C(1) | 177.1 (7) | Se(1)-Mn(1)-C(2) | 88.6 (4) |
| Se(1)-Mn(1)-C(3) | 92.3 (4) | Se(1A)-Mn(1)-Se(2A) | 56.0 (1) |
| C(1)-Mn(1)-C(2) | 90.5 (7) | C(1)-Mn(1)-C(3) | 90.6 (8) |
| C(2)-Mn(1)-C(3) | 97.6 (9) | C(1)-Mn(1)-Se(1A) | 96.5 (7) |
| C(2)-Mn(1)-Se(1A) | 105.1 (7) | C(3)-Mn(1)-Se(1A) | 156.1 (5) |
| C(1)-Mn(1)-Se(2A) | 88.2 (6) | C(2)-Mn(1)-Se(2A) | 160.7 (7) |
| C(3)-Mn(1)-Se(2A) | 101.7 (6) | Mn(1)-C(1)-O(1) | 176.8 (22) |
| Mn(1)-C(2)-O(2) | 176.3 (9) | Mn(1)-C(3)-O(3) | 176.9 (16) |

Table VI. Selected Distances (\AA) and Angles (deg) for $[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]$

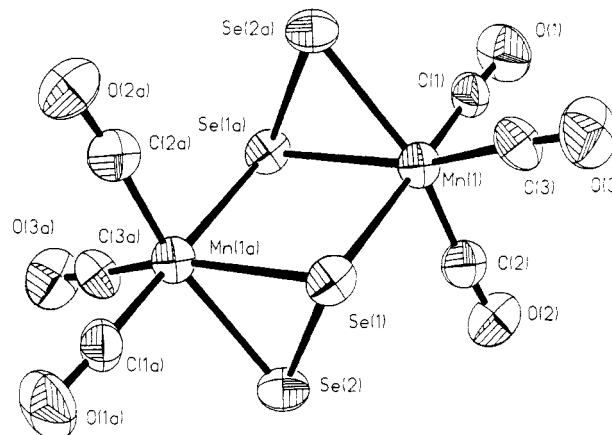
| | | | |
|--------------------|------------|--------------------|------------|
| Se(1)-Se(2) | 2.397 (3) | Se(1)-Mn(1) | 2.513 (3) |
| Se(1)-Mn(1A) | 2.533 (4) | Se(2)-Se(3) | 2.356 (4) |
| Se(3)-Se(4) | 2.326 (3) | Se(4)-Mn(1) | 2.485 (4) |
| Mn(1)-C(1) | 1.790 (22) | Mn(1)-C(2) | 1.808 (17) |
| Mn(1)-C(3) | 1.756 (20) | O(1)-C(1) | 1.165 (27) |
| O(2)-C(2) | 1.147 (21) | O(3)-C(3) | 1.169 (25) |
| Se(2)-Se(1)-Mn(1) | 109.3 (1) | Se(2)-Se(1)-Mn(1A) | 105.8 (1) |
| Mn(1)-Se(1)-Mn(1A) | 96.2 (1) | Se(1)-Se(2)-Se(3) | 102.3 (1) |
| Se(2)-Se(3)-Se(4) | 101.2 (1) | Se(3)-Se(4)-Mn(1) | 101.8 (1) |
| Se(1)-Mn(1)-Se(4) | 93.3 (1) | Se(1)-Mn(1)-C(1) | 85.7 (6) |
| Se(4)-Mn(1)-C(1) | 178.4 (7) | Se(1)-Mn(1)-C(2) | 171.5 (6) |
| Se(4)-Mn(1)-C(2) | 91.2 (6) | C(1)-Mn(1)-C(2) | 89.7 (8) |
| Se(1)-Mn(1)-C(3) | 93.6 (6) | Se(4)-Mn(1)-C(3) | 89.7 (7) |
| C(1)-Mn(1)-C(3) | 91.5 (9) | C(2)-Mn(1)-C(3) | 93.7 (8) |
| Se(1)-Mn(1)-Se(1A) | 83.8 (1) | Se(4)-Mn(1)-Se(1A) | 83.5 (1) |
| C(1)-Mn(1)-Se(1A) | 95.2 (7) | C(2)-Mn(1)-Se(1A) | 89.6 (6) |
| C(3)-Mn(1)-Se(1A) | 172.5 (6) | Mn(1)-C(1)-O(1) | 175.6 (19) |
| Mn(1)-C(2)-O(2) | 178.3 (13) | Mn(1)-C(3)-O(3) | 176.2 (16) |

tallographically imposed inversion center. The overall geometry is a chair with the transition metals trans to each other.

This mode of bonding has been observed previously for a variety of transition-metal disulfide complexes,^{4a,11,12} including a related manganese cluster.¹³ This coordination type has recently been reported for bridging diselenides for the first time in a cationic

Table VII. Selected Distances (\AA) and Angles (deg) for $[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{Mn}(\text{Se}_4)_2]$

| | | | |
|----------------------|-----------|----------------------|-----------|
| Mn(1)-Se(11) | 2.537 (5) | Mn(1)-Se(14) | 2.540 (6) |
| Mn(1)-Se(15) | 2.547 (5) | Mn(1)-Se(18) | 2.553 (5) |
| Se(11)-Se(12) | 2.315 (5) | Se(12)-Se(13) | 2.295 (5) |
| Se(13)-Se(14) | 2.301 (6) | Se(15)-Se(16) | 2.311 (5) |
| Se(16)-Se(17) | 2.334 (6) | Se(17)-Se(18) | 2.307 (7) |
| Mn(2)-Se(21) | 2.517 (8) | Mn(2)-Se(24) | 2.560 (6) |
| Mn(2)-Se(25) | 2.535 (7) | Mn(2)-Se(28) | 2.544 (6) |
| Se(21)-Se(22) | 2.292 (6) | Se(22)-Se(23) | 2.328 (7) |
| Se(23)-Se(24) | 2.314 (8) | Se(25)-Se(26) | 2.327 (5) |
| Se(26)-Se(27) | 2.325 (5) | Se(27)-Se(28) | 2.308 (6) |
| Se(11)-Mn(1)-Se(14) | 104.4 (2) | Se(11)-Mn(1)-Se(15) | 117.7 (2) |
| Se(14)-Mn(1)-Se(15) | 112.3 (2) | Se(11)-Mn(1)-Se(18) | 105.8 (2) |
| Se(14)-Mn(1)-Se(18) | 112.3 (2) | Se(15)-Mn(1)-Se(18) | 104.4 (2) |
| Mn(1)-Se(11)-Se(12) | 89.6 (2) | Se(11)-Se(12)-Se(13) | 101.7 (2) |
| Se(12)-Se(13)-Se(14) | 103.0 (2) | Mn(1)-Se(14)-Se(18) | 99.3 (2) |
| Mn(1)-Se(15)-Se(16) | 85.5 (2) | Se(15)-Se(16)-Se(17) | 103.2 (2) |
| Se(16)-Se(17)-Se(18) | 102.3 (2) | Mn(1)-Se(18)-Se(17) | 98.9 (2) |
| Se(21)-Mn(2)-Se(24) | 107.7 (2) | Se(21)-Mn(2)-Se(25) | 106.6 (2) |
| Se(24)-Mn(2)-Se(25) | 119.3 (3) | Se(21)-Mn(2)-Se(28) | 115.2 (3) |
| Se(24)-Mn(2)-Se(28) | 101.9 (2) | Se(25)-Mn(2)-Se(28) | 106.5 (2) |
| Mn(2)-Se(21)-Se(22) | 93.3 (2) | Se(21)-Se(22)-Se(23) | 105.2 (3) |
| Se(22)-Se(23)-Se(24) | 104.4 (2) | Mn(2)-Se(24)-Se(23) | 98.5 (2) |
| Mn(2)-Se(25)-Se(26) | 85.1 (2) | Se(25)-Se(26)-Se(27) | 102.6 (2) |
| Se(26)-Se(27)-Se(28) | 103.1 (2) | Mn(2)-Se(28)-Se(27) | 97.2 (2) |

**Figure 1.** ORTEP view of the anionic fragment $[\text{Mn}_2(\text{Se}_2)_2(\text{CO})_6]^{2-}$ (1a), with thermal ellipsoids at 35% probability level.

rhodium dimer $[(\text{triphos})\text{Rh}(\mu\text{-Se}_2)\text{Rh}(\text{triphos})]^{2+}$,¹⁴ as well as a cobalt complex that has not been structurally characterized.¹⁵ An interesting iron complex has been described that contains two disulfide groups which are bonded side by side.¹⁶

The Se-Se bond distance is 2.327 (3) \AA (see Table V), which is slightly longer than the distance in the rhodium complex, which contains an identical metal geometry (2.298 \AA). This may be due to the greater electron density in the manganese anion, which presumably results in increased back-bonding to the diselenide ligand. The Mn-Se distances are nearly identical for the side-bonded distances (Mn(1)-Se(1A) = 2.474 (4) \AA and Mn(1)-Se(2) = 2.482 (3) \AA), but slightly longer for the bridging Mn(1)-Se(1) (2.525 (2) \AA). This may be taken as sign of a dative interaction (vide infra). There have been few molecular metal selenides characterized structurally, but these Mn-Se distances are not unreasonable. The overall geometry around each metal is a distorted octahedron, with the three carbonyls in an almost ideal facile environment. The only appreciable distortion involves the diselenide, which is distorted about 20° from ideal due to the Se-Se bond. The Mn-Mn distance is greater than 3.7 \AA , which is too long to be considered bonding.

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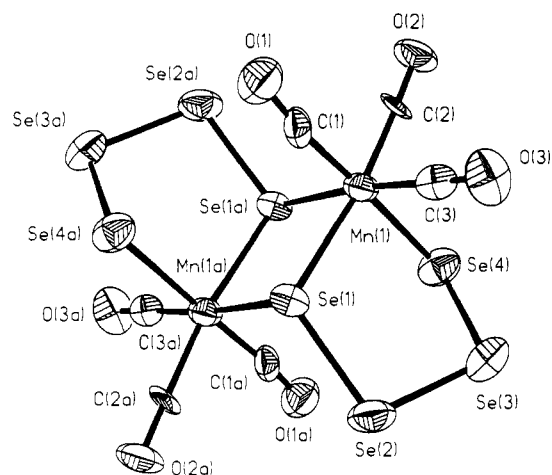


Figure 2. ORTEP view of the $[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]^{2-}$ dimer (IIa), with thermal ellipsoids at the 35% probability level.

Structure of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]^{2-}$ (II). An ORTEP view of compound II is given in Figure 2. It consists of a dianionic manganese dimer that is bridged by two Se_4^{2-} groups. It also contains a crystallographically imposed inversion center. The overall geometry is similar to that of I, but contains tetraselenide rather than diselenide bridging groups. Again, the Mn–Mn distance is greater than 3.7 Å and clearly nonbonding. The Mn–Se distances are almost identical with those in I (See Table VI). The Se–Se distances are slightly longer than in I, ranging from 2.326 to 2.397 Å. However, they do not display the alternating bond lengths characteristic of chalcogen rings.^{4c} One significant difference in II is that the geometry around each metal atom is much closer to an ideal facial-substituted octahedron. This is presumably due to the fact that the four-membered chain is more flexible than the Se_2^{2-} fragment.

Molecule II is isomorphous and isostructural with the corresponding rhenium analogue,¹⁰ but this structural type is not very common for transition-metal complexes of four-membered chalcogen rings. It has been observed in a linear chromium selenide trimer¹⁷ and a linear silver chain,¹⁸ as well as copper and silver sulfide compounds.¹⁹ However, in general it is much more common for metal organodithiolate complexes.²⁰

Structure of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mn}(\text{Se}_4)_2]^{2-}$ (III). Molecule III has two tetraselenide chains chelated to a Mn(II) center with tetrahedral coordination around the metal. The cell also contains two well-separated tetraphenylphosphonium counterions. An ORTEP view of the dianion is shown in Figure 3. Molecule III is chiral, and both enantiomers are present in the unit cell.

Each molecule contains a slightly distorted tetrahedral coordination environment around the metal center. The Se–Mn–Se angles for selenium atoms in the same chain are approximately 104.5°, whereas the Se–Mn–Se angles involving Se atoms in different chains is greater (about 112°) (see Table VII). The overall geometry is not dissimilar to that of the previously reported binary sulfide anion MnS_4^{2-} , which contains a disordered molecule with a pentasulfide and a hexasulfide ring each chelated to a Mn(II) center, creating a tetrahedral coordination sphere around the metal.^{4f} This coordination environment is well-known for group 12 clusters.^{4f,21}

The Mn–Se distances average 2.545 Å, which is slightly longer than the longest distances in either of the carbonyl complexes

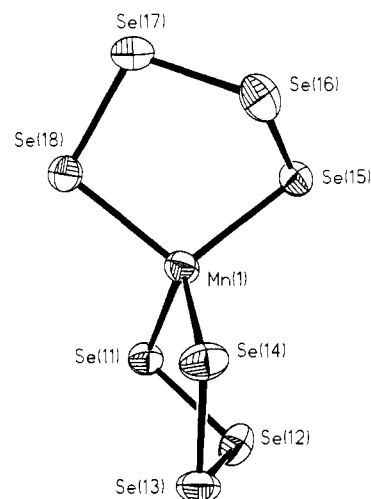


Figure 3. ORTEP view of one of the enantiomers of $[\text{Mn}(\text{Se}_4)_2]^{2-}$ (IIIa), with ellipsoids at the 35% probability level.

described above. This is somewhat surprising in view of the higher oxidation state of the metal and the uncrowded metal environment. The Se–Se distances range from 2.292 to 2.327 Å, which are comparable to the other polyselenide distances.

Discussion

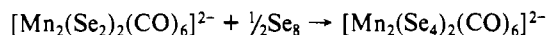
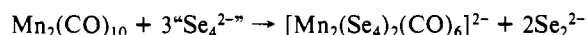
Dimanganese decacarbonyl reacts readily with polyselenide solution in DMF to form several manganese selenide carbonyl dimers (I and II). Even though the molecules are anions, the metal center has been formally oxidized from Mn(0) to Mn(I), breaking the metal–metal bond. The oxidant in each case is presumably a polyselenide anion, which results in reductive cleavage of a Se–Se bond.

The IR spectra of the metal carbonyl polyselenides I and II reveal two stretches in the CO region. This is expected in view of the localized C_{3v} symmetry at the metal center. The stretching frequencies for I are slightly lower than those for II, in keeping with the greater negative charge density on the smaller I.

The use of polychalcogenide anions to affect oxidation of low-valent metal carbonyls has proven to be an extremely versatile entry to metal chalcogenide complexes. The use of a 1:1 ratio of K_2Se_3 to metal dimer leads predominantly to formation of $[\text{Mn}(\text{Se}_2)_2(\text{CO})_6]^{2-}$ (Ia).



The infrared spectrum of the carbonyl region in situ consists predominantly of the two peaks assignable to I. This suggests that it is the major carbonyl-containing product in solution, despite its low isolated yield. Use of an increased ratio of K_2Se_3 to metal dimer (>2:1) leads to formation of $[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]^{2-}$ (IIa) as the only isolatable product. Compound II can also be prepared in good yield by reaction of I with red selenium in DMF solution. Possible balanced equations are



At this point it is not known whether I is a necessary intermediate between $\text{Mn}_2(\text{CO})_{10}$ and II, or if is merely a side product that can be easily converted to II in situ. It should be noted that the polyselenide solution contains a series of complex equilibria between the various polyselenide chains, and the redox chemistry is complex.^{4a,e,22} Thus, any balanced equations are speculative at best.

In the case of both carbonyl dimers, the distances between the manganese atoms and the bridging selenide is slightly asymmetric. The distances of the selenide to the chelated metal are shorter

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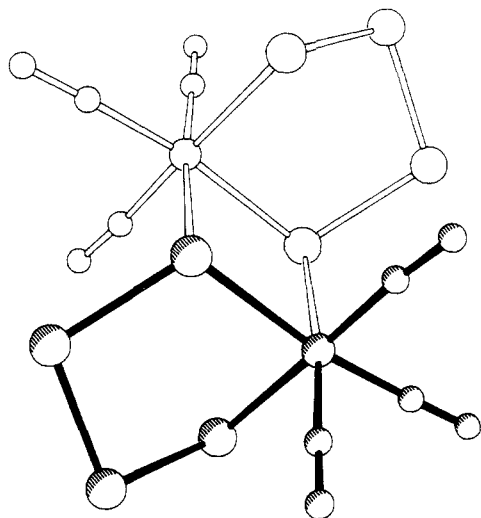
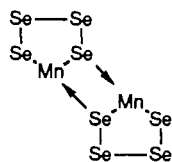
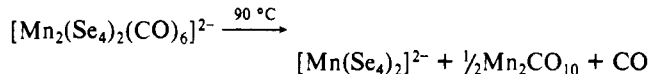


Figure 4. View of $[\text{Mn}_2(\text{Se}_4)_2(\text{CO})_6]^{2-}$, highlighting the coordination environment around one of the metal atoms, suggesting a possible intermediate in the oxidative decarbonylation reaction.

by approximately 0.025 Å, leading to the suggestion that there is some dative bonding holding the two metal centers together. A simplified valence bonding picture is shown below. This is also observed with the corresponding rhenium complex.¹⁰



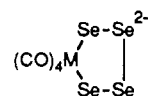
Heating a solution of II in DMF at 90 °C leads to complete decarbonylation of the metal center and production of $[\text{Mn}(\text{Se}_4)_2]^{2-}$ (IIIa). Again, the simplicity of the solution IR spectrum in the CO region suggests that II is the predominant metal carbonyl in solution. A possible balanced equation is



It would appear that thermal activation is required for this reaction

to proceed, as prolonged stirring of II does not lead to III. In addition, heating or stirring of I does not lead to any observable formation of III. It is fairly certain that II is a direct intermediate in the formation of III, as we have performed the thermolytic conversion by using an analytically pure crystalline sample of II and obtained analytically pure III in similar yield to the one-pot reaction.

It should also be noted that the thermolysis of the rhenium analogue of II has not yet led to production of any binary rhenium selenides. Instead, only decomposition to insoluble gray powder is observed. We have no details of the mechanism of conversion of II to the final product III. It may be inter- or intramolecular migration of a tetraselenide chain along with further oxidation. However, Figure 4 highlights a view of half of molecule II, which bears a strong resemblance to the previously proposed intermediate in the oxidative decarbonylation of molybdenum and tungsten carbonyls.³



Summary

In this paper, we report the stepwise synthesis and structural characterization of a series of manganese selenide complexes. These have all been derived from the reaction of $\text{Mn}_2(\text{CO})_{10}$ and soluble polyselenides in DMF solution. The stepwise nature of the reaction, from the parent carbonyl, through several polyselenide-chelated metal carbonyl anions, to a completely decarbonylated Mn(II) polyselenide, suggests that the isolated products I and II, are possible intermediates in the general oxidative decarbonylation reaction. These types of intermediates have been previously proposed in the oxidative decarbonylation of group 6 carbonyls. We are currently investigating extensions of this general reaction.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-8802217.

Supplementary Material Available: Complete listings of crystallographic information, bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms for I-III, an ORTEP diagram of a $[(\text{C}_6\text{H}_5)_4\text{P}]^+$ cation, and tables of positional parameters of $[(\text{C}_6\text{H}_5)_4\text{P}]^+$ for I-III (25 pages); tables of observed and calculated structure factors for I-III (52 pages). Ordering information is given on any current masthead page.