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Syntheses and X-ray Structures of a Series of Chalcogen-Containing Manganese Carbonylates $[E_2Mn_3(CO)_9]^-$, $[E_8C_2Mn_2(CO)_6]^{2-}$, and $[E_2Mn_4(CO)_{12}]^{2-}$ (E = Se, S)

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The reaction of SeO_2 with $Mn_2(CO)_{10}$/KOH in methanol solution forms a trigonal bipyramid cluster anion $[Se_2Mn_3(CO)_9]^-$ (**Ia**). Cluster **Ia** can also be synthesized from the treatment of Se powder with $Mn_2(CO)_{10}$/KOH in 2:1 molar ratio in methanol solution. If Se is reacted with $Mn_2(CO)_{10}$/KOH in a molar ratio of 8:1, the deoxygenation occurs to produce a novel cluster $[Se_8C_2Mn_2(CO)_6]^{2-}$ (**IIa**). Cluster **IIa** can readily transform into a new octahedral cluster $[Se_2Mn_4(CO)_{12}]^{2-}$ (**IIIa**) by further treatment with $Mn_2(CO)_{10}$/KOH in CH_2Cl_2/MeOH solutions, and the use of a molar ratio of 1:1 of Se powder to $Mn_2(CO)_{10}$/KOH in methanol also can yield complex **IIIa**. In the sulfur−manganese system, the synthesis of the analogous complexes $[S_2Mn_3(CO)_9]^-$ (**Ib**), $[S_8C_2Mn_2(CO)_6]^{2-}$ (**IIb**), and $[S_2Mn_4(CO)_{12}]^{2-}$ (**IIIb**) also can be accomplished from the reactions of S powder with $Mn_2(CO)_{10}$/KOH in similar fashions. Clusters **Ia**−**IIIa** and **Ib**−**IIIb** are fully characterized by spectroscopic methods or/and X-ray analyses. The novel clusters $[E_8C_2Mn_2(CO)_6]^{2-}$ (E = Se, **IIa**; E = S, **IIb**) each consist of two separate $Mn(CO)_3$ groups which are doubly bridged by two CE_4 fragments. Clusters **Ia** and **Ib** each display a trigonal bipyramid framework with two chalcogen atoms in the axial positions, while clusters **IIIa** and **IIIb** each exhibit an octahedral metal skeleton.

Introduction

Chalcogen-containing transition metal carbonyl complexes attract much attention recently due to their versatile bonding modes and reactivities.[1] With our recent interest in the syntheses and reactivity studies of the iron−chalcogen carbonyl complexes,[2] we believe that the chalcogen-containing transition metal system represents a very exciting area of research. To extend the understanding of other chalcogen-containing transition metal complexes, we explored the selenium− and sulfur−manganese carbonyl systems. Surprisingly, there has been very little work previously reported concerning the selenium− and sulfur−manganese carbonyl clusters. The selenium−manganese cluster anions $[Mn_2(Se_2)_2(CO)_6]^{2-}$ and $[Mn_2(Se_4)_2(CO)_6]^{2-}$ have been reported from the reactions of soluble polyselenide anions with $Mn_2(CO)_{10}$,[3] and the sulfur−manganese cluster $[S_2Mn_3(CO)_9]^-$ was isolated from the reaction between $[Mn(CO)_5]^-$ and 5-substituted 1,3,4-oxathiazol-2-one.[4] Some organomanganese complexes such as $[Mn(CO)_4SeR]_2$,[5] $[\{\eta^5\text{-}MeC_5H_4)(CO)_2Mn\}_2SeMes]^+$,[6] $[MnSR(CO)_3]_4$,[7] and $[Mn_2(\mu\text{-}pyS)_2(CO)_6]$[8] are also reported. Very recently, a paramagnetic cluster $[Se_2Mn_3(CO)_9]^{2-}$ has been isolated from the reaction of $Mn_2(CO)_{10}$ with Se^{2-}.[9] It also has been shown that the chalcogen elements and their oxides can be employed as convenient sources for the preparation of mixed-metal clusters with transition metal anions under suitable conditions.[2,10] In this paper, we modify these synthetic routes and wish to report the syntheses of a series of chalcogen-containing manganese carbonylates $[E_2Mn_3(CO)_9]^-$, $[E_8C_2Mn_2(CO)_6]^{2-}$, and $[E_2Mn_4(CO)_{12}]^{2-}$ (E = Se, S). Also, we provide some information of transformations and reactivities of these cluster anions.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[11] Solvents were purified, dried, and distilled under nitrogen prior to use. $Mn_2(CO)_{10}$ (Strem), S powder (Strem), Se powder (Strem), bis(triphenylphosphine)nitrogen(1+) chloride, (PPN)Cl (Aldrich), and benzyltrimethylammonium chloride, (TMBA)Cl (Aldrich), were used as received. Infrared spectra were recorded on a Jasco 5300 IR spectrometer as solutions in CaF_2 cells. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University,

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Taipei, Taiwan. ESI mass spectra were obtained on a JMS D-300 mass spectrometer.

Synthesis of $[Et_4N][Se_2Mn_3(CO)_9]$ ($[Et_4N]$[Ia]). Method 1. To a mixture of 0.50 g (1.28 mmol) of $Mn_2(CO)_{10}$ and 1.00 g (17.8 mmol) of KOH was added 20 mL of MeOH. The mixed solution was stirred for 10 min to give a red solution. To this solution was added 0.20 g (1.80 mmol) of SeO_2, and the reaction solution turned to brown and was allowed to stir overnight. The resulting solution was filtered and concentrated, and an aqueous solution of 1.0 g (4.76 mmol) of $[Et_4N]Br$ was added dropwise, precipitating the solid. The solid was washed with deionized water several times and then extracted into 60 mL of Et_2O. The Et_2O extract was then recrystallized with CH_2Cl_2/hexanes to give 0.186 g (0.26 mmol) of $[Et_4N][Se_2Mn_3(CO)_9]$ (30% based on Mn). IR (ν_{CO}, CH_2Cl_2): 1975 vs, 1927 m, br cm^{-1}. Anal. Calcd for $[Et_4N][Se_2Mn_3(CO)_9]$: C, 28.96; H, 2.86; N, 1.99. Found: C, 29.07; H, 2.50; N, 1.79. The crystals suitable for X-ray analysis were grown from CH_2Cl_2/hexanes solution.

Method 2. To 0.304 g (0.780 mmol) of $Mn_2(CO)_{10}$ and 0.756 g (13.5 mmol) of KOH was added 25 mL of MeOH. The solution was stirred in an ice/water bath for 10 min, and 0.123 g (1.56 mmol) of Se powder was added into the solution. The reaction solution turned to brown and was allowed to stir for 8 h. The resulting solution was filtered and concentrated, and an H_2O solution of 0.804 g (4.33 mmol) of (TMBA)Cl was added dropwise, precipitating the solid. The solid was washed with deionized water several times and then extracted into CH_2Cl_2 to give 0.308 g (0.424 mmol) of $[TMBA][Se_2Mn_3(CO)_9]$ (82% based on $Mn_2(CO)_{10}$). IR (ν_{CO}, CH_2Cl_2): 1977 vs, 1925 m, br cm^{-1}.

Synthesis of $[PPN]_2[Se_8C_2Mn_2(CO)_6]$ ($[PPN]_2$[IIa]). Method 1. To 0.40 g (1.03 mmol) of $Mn_2(CO)_{10}$ and 1.00 g (17.8 mmol) of KOH was added 30 mL of MeOH. The solution was stirred for 10 min, and 0.650 g (8.23 mmol) of Se powder was added into the solution. The reaction solution turned to brown and was allowed to stir for 14 h. The resulting solution was filtered and concentrated, and a CH_2Cl_2 solution of 1.20 g (2.09 mmol) of (PPN)Cl was added dropwise, precipitating the solid. The solid was washed with deionized water several times and then extracted into CH_2Cl_2 to give 1.80 g (0.895 mmol) of brick-red $[PPN]_2[Se_8C_2Mn_2(CO)_6]$ (87% based on Se). IR (ν_{CO}, CH_2Cl_2): 2064 w, 1988 vs, 1909 s cm^{-1}. ESI-MS for negative ion: $m/2e$ 470.5. Anal. Calcd for $[PPN]_2[Se_8C_2Mn_2(CO)_6]$: C, 47.79; H, 3.01; N, 1.39. Found: C, 47.57; H, 3.04; N, 1.28. Crystals suitable for X-ray analysis were grown from a CH_2Cl_2 solution.

Method 2. To 0.250 g (0.344 mmol) of [TMBA][**Ia**] in 25 mL of MeOH was added 0.196 g (2.48 mmol) of Se powder in 0.256 g (4.56 mmol) of KOH. The solution was stirred for 24 h to give an orange-red solution which was filtered and concentrated, and a 10 mL CH_2Cl_2 solution of 0.697 g (1.21 mmol) of (PPN)Cl was added dropwise. The mixed solution was stirred overnight and dried under vacuum. The residue was washed with 60 mL × 4 deionized H_2O and then dried under vacuum. The solid was extracted with CH_2Cl_2 to give 0.302 g (0.150 mmol) of $[PPN]_2[Se_8C_2Mn_2(CO)_6]$ (44% based on [TMBA][**Ia**]).

Synthesis of $[PPN]_2[Se_2Mn_4(CO)_{12}]$ ($[PPN]_2$[IIIa]). Method 1. To 0.600 g (1.54 mmol) of $Mn_2(CO)_{10}$ and 1.504 g (26.8 mmol) of KOH was added 30 mL of MeOH. The solution was stirred for 10 min, and 0.120 g (1.52 mmol) of Se powder was added into the solution. The reaction solution turned to reddish-brown and was allowed to stir for 24 h, and 20 mL of CH_2Cl_2 was added. The solution was allowed to stir for another 57 h. The resulting solution was filtered and concentrated, and a CH_2Cl_2 solution of 1.042 g (1.82 mmol) of (PPN)Cl was added dropwise, precipitating the solid. The solid was washed with deionized water several times and then extracted into CH_2Cl_2 to give 0.320 g (0.179 mmol) of purple $[PPN]_2[Se_2Mn_4(CO)_{12}]$ (24% based on Se). IR (ν_{CO}, CH_2Cl_2): 1985 w, 1944 s, 1890 m, 1842 vw cm^{-1}. ESI-MS for negative ion: $m/2e$ 357.9. Crystals suitable for X-ray analysis were grown from a MeOH/THF solution. Anal. Calcd for $[PPN]_2[Se_2Mn_4(CO)_{12}]$: C, 56.33; H, 3.38; N, 1.56. Found: C, 56.09; H, 3.08; N, 1.57. The MeOH extract was shown to be an unidentified complex. IR (ν_{CO}, MeOH): 1975 m, 1942 w, 1901 s cm^{-1}.

Method 2. To 0.4000 g (1.03 mmol) of $Mn_2(CO)_{10}$ and 0.434 g (0.216 mmol) of $[PPN]_2$[**IIa**] was added 20 mL of CH_2Cl_2. The solution was stirred for 3 days, and then 1.00 g (17.9 mmol) of KOH in 10 mL of MeOH was added into the solution. The reaction solution was allowed to stir at room temperature for 21 h. The resulting solution was filtered and then extracted into CH_2Cl_2 to give 0.200 g (0.112 mmol) of $[PPN]_2[Se_2Mn_4(CO)_{12}]$ (52% based on $[PPN]_2$[**IIa**]).

Method 3. To 0.360 g (0.495 mmol) of [TMBA][**Ia**] in 25 mL of MeOH was added 0.103 g (0.264 mmol) of $Mn_2(CO)_{10}$ and 20 mL of CH_2Cl_2. The solution was stirred for 22 h, and 0.069 g (1.18 mmol) of $Mn_2(CO)_{10}$ with 0.45 g (8.02 mmol) of KOH was added. The mixed solution was allowed to stir for 3 days and was then filtered, and a 10 mL of CH_2Cl_2 solution of 0.778 g (1.36 mmol) of (PPN)Cl was then added. The mixed solution was stirred, dried under vacuum, and then washed with deionized H_2O. The residue was extracted with CH_2Cl_2 to give 0.142 g (0.0793 mmol) of $[PPN]_2[Se_2Mn_4(CO)_{12}]$ (16% based on [TMBA][**Ia**]).

Synthesis of $[TMBA][S_2Mn_3(CO)_9]$ ([TMBA][Ib]). To a mixture of 0.400 g (1.03 mmol) of $Mn_2(CO)_{10}$ and 1.003 g (17.9 mmol) of KOH was added 20 mL of MeOH. The mixed solution was stirred for 10 min to give a red solution. To this solution was added 0.064 g (2.00 mmol) of S powder, and the reaction solution turned to reddish-brown and was allowed to stir 6 h. The resulting solution was filtered and concentrated, and an aqueous solution of 0.562 g (3.03 mmol) of (TMBA)Cl was added dropwise, precipitating the solid. The solid was washed with deionized water several times, dried under vacuum overnight, and then extracted into 60 mL of Et_2O to give 0.120 g (0.190 mmol) of $[TMBA][S_2Mn_3(CO)_9]$ (28% based on Mn). IR (ν_{CO}, Et_2O): 1983 s, 1942 m, 1917 sh cm^{-1}. An unidentified complex is soluble in CH_2Cl_2. IR (ν_{CO}, CH_2Cl_2): 1979 s, 1954 vs, 1888 s, 1871 sh cm^{-1}.

Synthesis of $[PPN]_2[S_8C_2Mn_2(CO)_6]$ ($[PPN]_2$[IIb]). Method 1. To 0.60 g (1.54 mmol) of $Mn_2(CO)_{10}$ and 1.040 g (18.5 mmol) of KOH was added 30 mL of MeOH. The solution was stirred for 10 min, and 0.384 g (12.0 mmol) of S powder was added into the solution. The reaction solution turned to brown and was allowed to stir for 16 h. The resulting solution was filtered and concentrated, and a CH_2Cl_2 solution of 1.20 g (2.10 mmol) of (PPN)Cl was added dropwise, precipitating the solid. The solid was washed with deionized water several times and then extracted into CH_2Cl_2 to give 1.48 g (0.905 mmol) of brick-red $[PPN]_2[S_8C_2Mn_2(CO)_6]$ (60% based on S). IR (ν_{CO}, CH_2Cl_2): 2000 vs, 1917 s cm^{-1}. Anal. Calcd for $[TMBA]_2[S_8C_2Mn_2(CO)_6]$: C, 39.15; H, 3.76; N, 3.26. Found: C, 39.14; H, 3.38; N, 3.14. Crystals suitable for X-ray analysis were grown from a CH_2Cl_2 solution.

Method 2. To 0.351 g (0.556 mmol) of [TMBA][**Ib**] in 25 mL of MeOH was added 0.125 g (3.90 mmol) of S powder. The solution was stirred for 23 h to give an orange-red solution which was filtered and concentrated, and a 10 mL CH_2Cl_2 solution of 0.697 g (1.21 mmol) of (PPN)Cl was added dropwise. The mixed solution was stirred overnight and dried under vacuum. The residue was washed with 60 mL × 3 deionized H_2O and then dried under vacuum. The residue was extracted with CH_2Cl_2, and 0.366 g (0.638 mmol) of (PPN)Cl was added to precipitate the solid which was extracted with CH_2Cl_2 to give 0.158 g (0.097 mmol) of $[PPN]_2[S_8C_2Mn_2(CO)_6]$ (17% based on [TMBA][**Ib**]).

Synthesis of $[PPN]_2[S_2Mn_4(CO)_{12}]$ ($[PPN]_2$[IIIb]). Method 1. To 0.601 g (1.54 mmol) of $Mn_2(CO)_{10}$ and 1.508 g (26.9 mmol) of KOH was added 20 mL of MeOH. The solution was stirred for 10 min, and 0.049 g (1.53 mmol) of S powder was added into the solution. The reaction solution turned to reddish-brown, and 15 mL of CH_2Cl_2 was added which was allowed to stir for 3 days. The resulting solution was filtered and concentrated, and a CH_2Cl_2 solution of 0.987 g (1.72 mmol) of (PPN)Cl was added dropwise; the mixture was concentrated to precipitate the solid. The solid was washed with deionized water and MeOH several times and then extracted into CH_2Cl_2 to give 0.320 g (0.189 mmol) of purple $[PPN]_2[S_2Mn_4(CO)_{12}]$ (25% based on S). IR (ν_{CO}, CH_2Cl_2): 1990 w, 1946 s, 1894 m, 1826 vw cm^{-1}. ESI-MS for negative ion: $m/2e$ 310. Anal. Calcd for $[PPN]_2[S_2Mn_4(CO)_{12}]$: C, 59.45; H, 3.56; N, 1.65. Found: C, 59.0; H, 3.67; N, 1.68. The structure of $[PPN]_2[S_2Mn_4(CO)_{12}]$ was further confirmed by single-crystal X-ray analysis.

Method 2. To 0.343 g (0.400 mmol) of $[TMBA]_2$[**IIb**] and 1.13 g of $Mn_2(CO)_{10}$ (2.90 mmol) in 2.92 g (51.9 mmol) of KOH was added 20 mL of MeOH and 20 mL of CH_2Cl_2. The solution was stirred for 6 days, and the resulting solution was filtered and concentrated. A CH_2Cl_2 solution of 0.854 g (1.49 mmol) of (PPN)Cl was added into the solution and stirred for 4 h. The resulting solution was dried under vacuum to give the oily solid which was then washed with deionized H_2O several times and dried under vacuum. The residue was extracted

Table 1. Crystallographic Data for $[Et_4N][Se_2Mn_3(CO)_9]$ ($[Et_4N]$[**Ia**]), $[PPN]_2[Se_8C_2Mn_2(CO)_6]$ ($[PPN]_2$[**IIa**]), $[PPN]_2[Se_2Mn_4(CO)_{12}]$ ($[PPN]_2$[**IIIa**]), and $[PPN]_2[S_8C_2Mn_2(CO)_6]$ ($[PPN]_2$[**IIb**])

	$[Et_4N]$[**Ia**]	$[PPN]_2$[**IIa**]	$[PPN]_2$[**IIIa**]	$[PPN]_2$[**IIb**]
empirical formula	$C_{17}H_{20}Mn_3NO_9Se_2$	$C_{80}H_{60}Mn_2N_2O_6P_4Se_8$	$C_{84}H_{60}Mn_4N_2O_{12}P_4Se_2$	$C_{80}H_{60}Mn_2N_2O_6P_4S_8$
fw	705.08	2010.79	1790.95	1635.6
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P\bar{1}$
a, Å	9.185(3)	12.191(3)	24.399(3)	12.140(6)
b, Å	11.902(4)	12.428(3)	18.194(2)	12.392(5)
c, Å	12.494(2)	14.078(4)	17.791(2)	13.811(7)
α, deg	103.55(2)	72.25(2)		72.57(4)
β, deg	95.85(2)	86.66(2)		87.07(4)
γ, deg	108.36(3)	78.89(2)		79.28(4)
V, $Å^3$	1237.2(7)	1993.5(9)	7898(2)	1948(2)
Z	2	1	4	1
ρ(calc), g cm^{-3}	1.893	1.675	1.506	1.394
μ, cm^{-1}	44.055	13.617	16.525	11.579
radiation, λ (Å)	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107
temp, °C	25	25	25	25
residues: R,[a] R_w[a]	0.056, 0.055	0.045, 0.043	0.051, 0.044	0.066,0.079

[a] The functions minimized during least-squares cycles were $R = \sum|F_o - F_c|/\sum F_o$ and $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N][Se_2Mn_3(CO)_9]$ ($[Et_4N]$[**Ia**])

(A) Distances			
Se(1)−Mn(1)	2.374(2)	Se(1)−Mn(2)	2.377(3)
Se(1)−Mn(3)	2.366(3)	Se(2)−Mn(1)	2.352(2)
Se(2)−Mn(2)	2.334(2)	Se(2)−Mn(3)	2.351(2)
Mn(1)−Mn(2)	2.813(3)	Mn(1)−Mn(3)	2.858(3)
Mn(2)−Mn(3)	2.832(3)		
(B) Angles			
Mn(1)−Se(1)−Mn(2)	72.61(8)	Mn(1)−Se(1)−Mn(3)	74.16(8)
Mn(2)−Se(1)−Mn(3)	73.31(8)	Mn(1)−Se(2)−Mn(2)	73.78(8)
Mn(1)−Se(2)−Mn(3)	74.84(8)	Mn(2)−Se(2)−Mn(3)	74.37(8)
Mn(2)−Mn(1)−Mn(3)	59.91(7)	Mn(1)−Mn(3)−Mn(2)	59.26(7)
Mn(1)−Mn(2)−Mn(3)	60.83(7)		

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[PPN]_2[Se_8C_2Mn_2(CO)_6]$ ($[PPN]_2$[**IIa**])

(A) Distances			
Se(1)−Se(2)	2.357(2)	Se(1)−Mn	2.495(2)
Se(1)−Mn′	2.478(2)	Se(2)−C(4)	1.861(9)
Se(3)−Mn	2.485(2)	Se(3)−C(4)′	1.852(9)
Se(4)−C(4)	1.816(9)	C(4)−Se(3)′	1.852(9)
(B) Angles			
Se(2)−Se(1)−Mn	109.72(6)	Se(2)−Se(1)−Mn′	100.73(5)
Mn−Se(1)−Mn′	96.34(6)	Se(1)−Se(2)−C(4)	105.4(3)
Mn−Se(3)−C(4)′	108.0(3)	Se(1)−Mn−Se(1)′	83.66(6)
Se(1)−Mn−Se(3)	82.56(6)	Se(1)′−Mn−Se(3)	92.35(6)
Se(2)−C(4)−Se(3)′	122.6(5)	Se(2)−C(4)−Se(4)	114.2(5)
Se(3)′−C(4)−Se(4)	123.2(5)		

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[PPN]_2[Se_2Mn_4(CO)_{12}]$ ($[PPN]_2$[**IIIa**])

(A) Distances			
Se−Mn(1)	2.478(2)	Se−Mn(1)′	2.473(2)
Se−Mn(2)	2.473(2)	Se−Mn(2)′	2.476(2)
Mn(1)−Se′	2.473(2)	Mn(1)−Mn(2)	2.712(2)
Mn(1)−Mn(2)′	2.698(2)	Mn(2)−Se′	2.476(2)
Mn(2)−Mn(1)′	2.698(2)		
(B) Angles			
Mn(1)−Se−Mn(1)′	101.22(5)	Mn(1)−Se−Mn(2)	66.43(5)
Mn(1)−Se−Mn(2)′	65.99(5)	Mn(1)′−Se−Mn(2)	66.11(5)
Mn(1)′−Se−Mn(2)′	66.44(5)	Mn(2)−Se−Mn(2)′	101.19(5)
Mn(2)−Mn(1)−Mn(2)′	89.96(6)	Mn(1)−Mn(2)−Mn(1)′	90.04(5)

into THF to give 0.545 g (0.321 mmol) of purple $[PPN]_2[S_2Mn_4(CO)_{12}]$ (20% based on $[TMBA]_2$[**IIb**]).

Method 3. To 0.280 g (0.275 mmol) of [PPN][**Ib**] in 10 mL of MeOH and 15 mL of CH_2Cl_2 was added 0.091 g (0.233 mmol) of $Mn_2(CO)_{10}$ and 0.178 g (3.17 mmol) of KOH. The mixed solution was allowed to stir for 22 h and was then filtered, and a CH_2Cl_2 solution of 0.117 g (0.204 mmol) of (PPN)Cl was added into the solution and stirred for 1 h. The solution was dried under vacuum which was washed with deionized H_2O and dried under vacuum. The residue was extracted with CH_2Cl_2 to give 0.140 g (0.0825 mmol) of $[PPN]_2[S_2Mn_4(CO)_{12}]$ (30% based on [PPN][**Ib**]).

X-ray Structural Characterization of Complexes $[Et_4N]$[Ia], $[PPN]_2$[IIa], $[PPN]_2$[IIIa], and $[PPN]_2$[IIb]. A summary of selected crystallographic data for $[Et_4N]$[**Ia**], $[PPN]_2$[**IIa**], $[PPN]_2$[**IIIa**], and $[PPN]_2$[**IIb**] is given in Table 1. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation at 25 °C employing the $\theta/2\theta$ scan mode. A φ scan absorption correction was made.[12] All crystals were mounted on glass fibers with Epoxy cement. Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages,[13] and atomic scattering factors were taken from ref 14.

Structures of $[Et_4N]$[Ia], $[PPN]_2$[IIa], $[PPN]_2$[IIIa], and $[PPN]_2$[IIb]. The crystal of $[Et_4N]$[**Ia**] chosen for diffraction measurement was ca. 0.05 × 0.13 × 0.50 mm, the crystal of $[PPN]_2$[**IIa**] had dimensions 0.02 × 0.30 × 0.55 mm, and the crystal of $[PPN]_2$[**IIIa**] had dimension 0.15 × 0.40 × 0.60 mm, and the crystal of $[PPN]_2$[**IIb**] had dimension 0.30 × 0.40 × 0.45 mm. Cell parameters were obtained from 25 reflections with 2θ angle in the range 19.00−26.50° for $[Et_4N]$[**Ia**], $14.90° < 2\theta < 24.40°$ for $[PPN]_2$[**IIa**], $18.00° < 2\theta < 24.80°$ for $[PPN]_2$[**IIIa**], and $17.00° < 2\theta < 24.90°$ for $[PPN]_2$[**IIb**]. A total of 2168 reflections with $I > 2.0\sigma(I)$ for $[Et_4N]$[**Ia**] (3491 reflections with $I > 2.0\sigma(I)$ for $[PPN]_2$[**IIa**], 3023 reflections with $I > 2.0\sigma(I)$ for $[PPN]_2$[**IIIa**], and 3599 reflections with $I > 2.0\sigma(I)$ for $[PPN]_2$[**IIb**]) were refined by least-squares cycles. All the non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least-squares refinement led to convergence with $R = 5.6\%$ and $R_w = 5.5\%$ for $[Et_4N]$[**Ia**], with $R = 4.5\%$ and $R_w = 4.3\%$ for $[PPN]_2$[**IIa**], with $R = 5.1\%$ and $R_w = 4.4\%$ for $[PPN]_2$[**IIIa**], and with $R = 6.6\%$ and $R_w = 7.9\%$ for $[PPN]_2$[**IIb**].

The selected bond distances and angles for $[Et_4N]$[**Ia**], $[PPN]_2$[**IIa**], $[PPN]_2$[**IIIa**], and $[PPN]_2$[**IIb**] are presented in Tables 2−5, respectively. Additional crystallographic data are available as Supporting Material.

Results and Discussion

Syntheses of Ia, IIa, IIIa, Ib, IIb, and IIIb. Dimanganese decacarbonyl in basic solution reacts readily with Se or S powder in various ratios to give a series of mixed-metal carbonylates. The species of $Mn_2(CO)_{10}$ in saturated KOH solution were reported to be $[Mn_3(CO)_{11}]^{3-}/[HMn_3(CO)_{11}]^{2-}$,[15] which were considered to act as reducing agents to react with Se or Se powder. Different ratios of chalcogen to $Mn_2(CO)_{10}$/KOH were

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Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $[PPN]_2[S_8C_2Mn_2(CO)_6]$ ($[PPN]_2$[**IIb**])

(A) Distances			
Mn−S(1)	2.395(3)	Mn−S(1)′	2.355(3)
Mn−S(2)	2.372(3)	S(1)−S(3)	2.074(4)
S(2)−C(4)	1.69(1)	S(3)−C(4)′	1.76(1)
S(4)−C(4)	1.67(1)	C(4)−S(3)′	1.76(1)
(B) Angles			
S(1)−Mn−S(1)′	82.8(1)	S(1)−Mn−S(2)	84.6(1)
S(1)′−Mn−S(2)	88.8(1)	Mn−S(1)−Mn′	97.3(1)
Mn−S(1)−S(3)	111.5(2)	Mn′−S(1)−S(3)	102.8(1)
Mn−S(2)−C(4)	109.0(4)	S(1)−S(3)−C(4)′	107.5(4)
S(2)−C(4)−S(3)′	120.9(6)	S(2)−C(4)−S(4)	125.8(6)
S(3)′−C(4)−S(4)	113.3(5)		

found to affect the reactions drastically. When chalcogen (E = Se, S) was treated with $Mn_2(CO)_{10}$/KOH in a molar ratio of 2:1, the trigonal bipyramid clusters $[E_2Mn_3(CO)_9]^-$ (E = Se, **Ia**; E = S, **Ib**) were produced, respectively. Cluster **Ia** can be alternatively obtained from the reaction of SeO_2 with $Mn_2(CO)_{10}$/KOH in methanol solution. Clusters **Ia** and **Ib** are anionic species with lone pair electrons on the chalcogen atoms; however, they were found to be quite inert toward electrophililes such as MeI or HCl.

On the other hand, the use of a 8:1 molar ratio of chalcogen to $Mn_2(CO)_{10}$/KOH in CH_2Cl_2/MeOH led to the formation of novel clusters $[C_2E_8Mn_2(CO)_6]^{2-}$ (E = Se, **IIa**; E = S, **IIb**), respectively. These clusters are isomorphous and each can be described as two CE_4^{2-} fragments bridging two Mn(I) carbonyl groups in the μ_2-η^2 fashion. It is apparent that deoxygenation of manganese carbonyls in basic solution occurs upon the addition of chalcogen atoms. To our best knowledge, this type of deoxygenation is rare in metal carbonyl clusters and may be somewhat related to the reduction of CO to carbide atom in the iron clusters.[16] However, the detailed mechanism is not clear and further investigation is under progress. Furthermore, when the molar ratio of 1:1 (E: $Mn_2(CO)_{10}$) was employed, the new octahedral clusters $[E_2Mn_4(CO)_{12}]^{2-}$ (E = Se, **IIIa**; E = S, **IIIb**) were afforded.

Transformations of Ia, IIa, IIIa, Ib, IIb, and IIIb. Since the ratios of chalcogen to dimanganese affected the outcomes of these reactions, it was wondered if structural transformations of these chalcogen−manganese carbonylates could be achieved. We, therefore, conducted some reactions by tuning the ratios of chalcogen to dimanganese and found some interesting cluster transformations in these two systems (Scheme 1). It has been found that clusters **Ia** or **Ib** can react with appropriate amounts of chalcogen (E = Se, S) in basic solution to form clusters **IIa** or **IIb** in each case. Further, cluster **IIa** or **IIb** would slowly convert to clusters **IIIa** or **IIIb**, respectively, by treatment with $Mn_2(CO)_{10}$/KOH in CH_2Cl_2/MeOH solutions. One would propose that the transformation of **IIa** into **IIIa** (**IIb** into **IIIb**) is occurring via the elimination of CE_3^{2-}. In the sulfur case, we did not detect the formation of $BaCS_3$ in the reaction solution upon addition of Ba^{2+}.[17] Hence, this transformation may involve more complicated bond breakage/formation processes. By the similar methodology, cluster **IIIa** or **IIIb** could be formed directly from cluster **Ia** or **Ib** when **Ia** or **Ib** reacted with $Mn_2(CO)_{10}$/KOH in CH_2Cl_2/MeOH solutions. These results suggest that clusters $[C_2E_8Mn_2(CO)_6]^{2-}$ (E = Se, **IIa**; E = S, **IIb**) may represent the intermediate states for the transformations of the trigonal bipyramidal clusters $[E_2Mn_3(CO)_9]^-$ (E = Se, **Ia**; E = S, **Ib**) to the octahedral complexes $[E_2Mn_4(CO)_{12}]^{2-}$ (E = Se, **IIIa**; E = S, **IIIb**). The structural transformations are shown in Scheme 1.

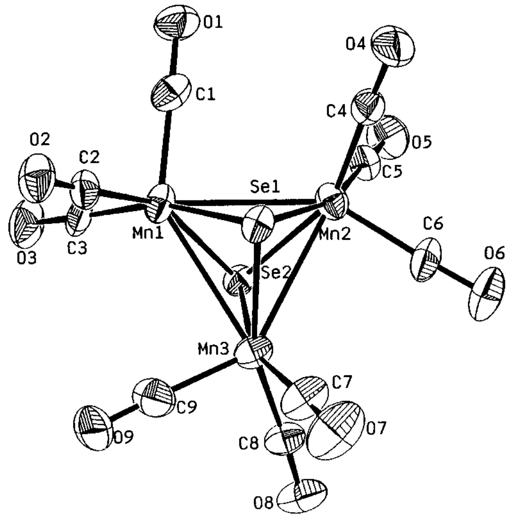
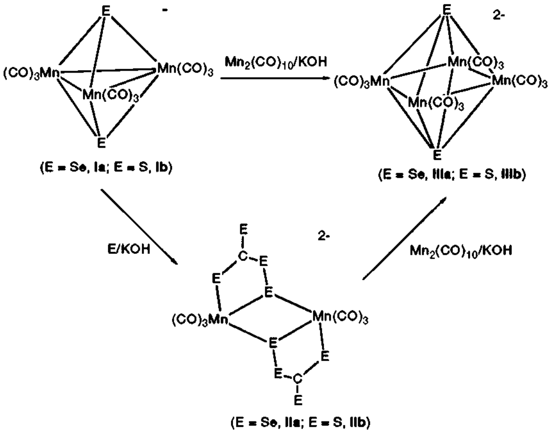


Figure 1. ORTEP diagram showing the structure and atom labeling for the anion **Ia**.

Scheme 1



The conditions for the preparations of the chalcogen−manganese carbonylates we describe here are very critical. Especially, the solvent system (MeOH/CH_2Cl_2) is crucial for the formations of the octahedral clusters **IIIa** and **IIIb**. The conversions would not occur if only MeOH was employed. However, the role of CH_2Cl_2 in these reactions is not understood. As long as the ratios are well controlled under suitable conditions, three types of complexes $[E_2Mn_3(CO)_9]^-$ (E = Se, **Ia**; E = S, **Ib**), $[C_2E_8Mn_2(CO)_6]^{2-}$ (E = Se, **IIa**; E = S, **IIb**), and $[E_2Mn_4(CO)_{12}]^{2-}$ (E = Se, **IIIa**; E = S, **IIIb**) can be synthesized in good yields.

Structures of Ia, IIa, IIIa, and IIb. According to the spectroscopic analyses, clusters **Ia** and **Ib** are isomorphous. Clusters **Ia** and **Ib** both display the trigonal bipyramidal metal core with the chalcogen atoms at the axial positions, each of which is a 48 electron system and represents the first case for the chalcogen−manganese system. X-ray analysis of **Ia** was carried out and the ORTEP diagram is displayed in Figure 1. Cluster **Ia** exhibits a near-idealized D_{3h} trigonal bipyramidal frame with three Mn−Mn bonds of similar lengths (2.813−2.858 Å) and nearly perfect internal Mn−Mn−Mn angles (59.26−60.83°). The average Se−Mn distance is 2.359 Å, which is comparatively shorter than those (2.402−2.458 Å) in

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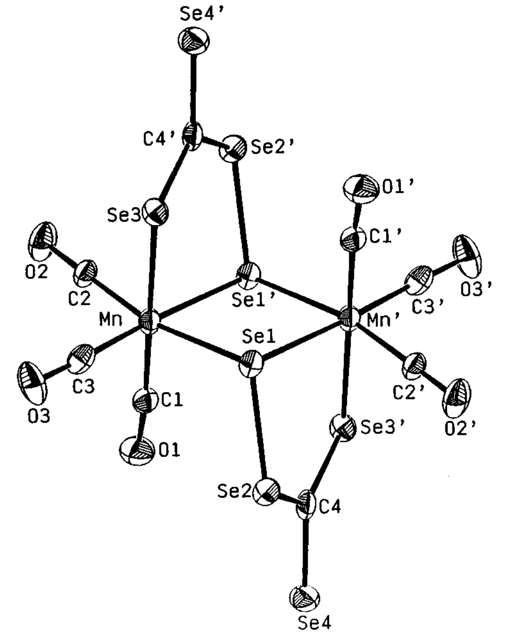

Figure 2. ORTEP diagram showing the structure and atom labeling for the dianion **IIa**.

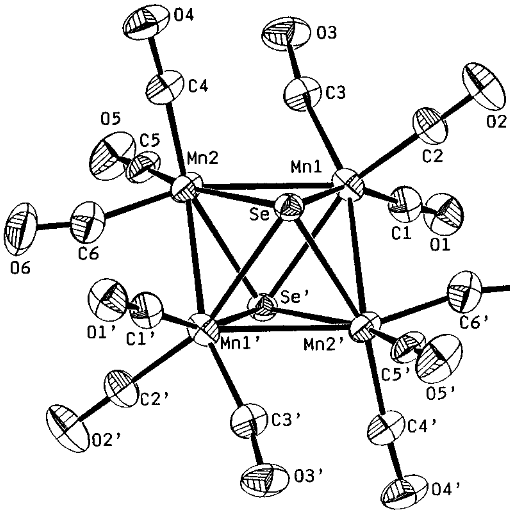

Figure 3. ORTEP diagram showing the structure and atom labeling for the dianion **IIIa**.

the square pyramidal complex[9] $[Se_2Mn_3(CO)_9]^{2-}$ and those (2.555(2)−2.581(2) Å) in the anion $[Mn(SePh)_4]^{2-}$.[18] The Se−Se distance of 3.398(2) Å is not within bonding distances.

Cluster **IIa** and **IIb** are isomorphous structures. The ORTEP diagrams of the anions **IIa** and **IIb** are shown in Figure 2 and 3, respectively. These two novel clusters each can be viewed to consist of two $Mn(CO)_3$ groups which are doubly bridged by two CE_4 fragments (E = Se or S) in the μ_2-η^2 fashion. The average Se−Mn bond length is 2.486 Å, which is comparable to those in clusters $[Mn_2(Se_2)_2(CO)_6]^{2-}$ (2.494 Å) and $[Mn_2(Se_4)_2(CO)_6]^{2-}$ (2.510 Å),[3] and the bridged Se−Mn distance (2.478(2) Å) is slightly shorter than the unbridged Se−Mn bonds (2.495(2) and 2.485(2) Å). There are rare examples of CE_4^{2-} as ligands in metal complexes. To our best knowledge, examples are limited to $[Zn(CSe_4)_2]^{2-}$.[19] Clusters **IIa** and **IIb** represent the first examples of CE_4^{2-} incorporated into transition metal carbonyls.

The sum of the covalent bond radii for selenium and carbon is 1.94 Å for a single bond and 1.74 Å for a double bond.[20] In cluster **IIa**, the C(4)−Se(4) (1.816(9) Å) is somewhat shorter than those of C(4)−Se(2) and C(4)−Se(3)′ (1.861(9) Å; 1.852(9) Å), indicating some double-bond character. The Se(1)−Se(2) distance (2.357(2) Å) is very close to those of elemental selenium (average 2.334(5) Å).[21] In cluster **IIb**, C(4)−S(4) (1.67(1) Å) is a bit shorter than those of C(4)−S(3)′ and C(4)−S(2) (1.76(1) Å; 1.69(1) Å) also indicative of some double-bond character. The S(1)−S(3) length of 2.074(4) Å is normal. The S−Mn bond lengths average 2.374 Å, comparable to those in the polynuclear complex $Mn_4(S_2)_2(CO)_{15}$ (2.34−2.38 Å),[22] but are slightly larger than that found for $[S_2Mn_3(CO)_9]^-$ (mean 2.246(2) Å).[4] As in the case of cluster **IIa**, the bridged S−Mn distance (2.355(3) Å) is slightly shorter than the unbridged S−Mn bonds (2.395(3) and 2.372(3) Å).

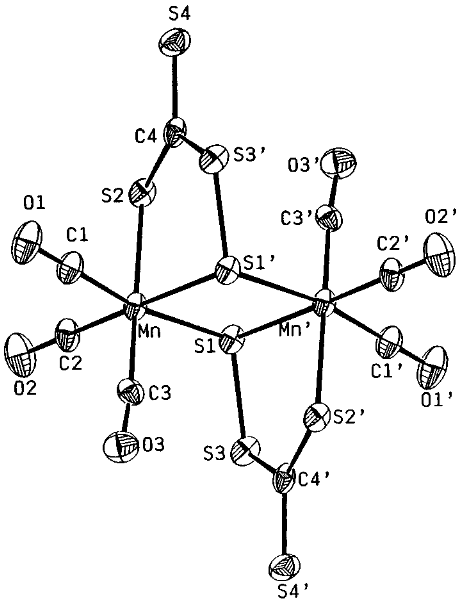

Figure 4. ORTEP diagram showing the structure and atom labeling for the dianion **IIb**.

According to the spectroscopic and elemental analyses, cluster **IIIa** is believed to be isostructural with cluster **IIIb**. The single-crystal X-ray analysis showed that cluster **IIIa** displays an octahedral metal core with two μ_4-Se atoms and the four Mn atoms are seven-coordinated. Cluster **IIIa** shows a near-idealized octahedral framework with four Mn−Mn bonds of similar lengths (2.698−2.712 Å) and nearly perfect internal Mn−Mn−Mn angles (89.96−90.04°). The average Se−Mn distance of 2.475 Å is normal. The octahedral cluster **IIIa** or **IIIb** obeys Wade's rule for a six-vertex *closo*-cluster containing seven skeletal pairs. Both of them offer the first examples of an E_2Mn_4 framework in the chalcogen−manganese system.

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Supporting Information Available: Complete listings of crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for $[Et_4N]$[**Ia**], $[PPN]_2$[**IIa**], $[PPN]_2$[**IIIa**], and $[PPN]_2$[**IIb**] (24 pages). Ordering information is given on any current masthead page.

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