Inorg. Chem. **1994,** *33,* 2303-2305 **2303**

Notes

Preparation of $[SeFe_3(CO)_9]^{2-}$ and Its Derivatives $[\{SeFe_3(CO)_9\}_2M]^{2-}$ (M = Hg, Cd)

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Received September 22, 1993

The chemistry of chalcogen-containing complexes has attracted much interest in recent years since chalcogenide-rich metal complexes often exhibit unusual structural and reactivity patterns.[1] Although an increased number of structurally characterized tellurium–iron carbonyl complexes has been reported, there has been very little work reported concerning selenium–iron carbonyl clusters. Two useful mixed selenium–iron carbonyl complexes for cluster building reactions are $Se_2Fe_2(CO)_6$ and $Se_2Fe_3(CO)_9$, which were first reported in 1958 by Hieber and Gruber.[2] However, surprisingly few anionic selenium–iron carbonyl clusters have been structurally characterized. Examples include $[Fe(CO)_2(Se_4)_2]^{2-}$,[3] $[\{Fe_2Se(CO)_6\}_2(Se_2)]^{2-}$,[4] and $[Fe_2(CO)_6(PSe_5)_2]^{2-}$.[5]

The work on these selenide-rich complexes has revealed that this area has the potential to be as rich as that of the tellurides, which has prompted us to investigate the chemistry of the selenium–iron carbonyl system. Here we wish to report the preparation of a tetrahedral anionic complex, $[SeFe_3(CO)_9]^{2-}$ (**I**), from a modified Hieber method and its derivatives, $[\{SeFe_3(CO)_9\}_2M]^{2-}$ (M = Hg, **II**; M = Cd, **III**).

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk line techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. SeO_2 (Strem), $Fe(CO)_5$ (Aldrich), $[Et_4N]Br$ (Merck), (PPN)Cl (Aldrich), $Hg(OAc)_2$ (Wako), and $Cd(OAc)_2{\cdot}2H_2O$ (Hanawa) were used as received. Infrared spectra were recorded on a Jasco 700 IR spectrometer using CaF_2 liquid cells. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Taiwan University, Taipei, Taiwan.

Preparation of $[Et_4N]_2[SeFe_3(CO)_9]$ ($[Et_4N]_2[I]$). To a solution of 0.61 g (5.50 mmol) of SeO_2 and 2.0 g (35.7 mmol) of KOH in 20 mL of MeOH was added 2 mL (14.8 mmol) of $Fe(CO)_5$. After being stirred for 6 h at room temperature, the solution was filtered and an aqueous solution of 3.0 g (14.3 mmol) of $[Et_4N]Br$ was added dropwise, precipitating the dark red product. This product was collected by filtration, washed with H_2O and ether, dried under vacuum, and then extracted with CH_2Cl_2 to give 1.76 g (2.32 mmol) of $[Et_4N]_2[SeFe_3(CO)_9]$ ($[Et_4N]_2[I]$) (46% based on Fe). IR (ν_{CO}, CH_2Cl_2) for $[Et_4N]_2[I]$: 1996 m, 1928 vs, 1901 s, 1875 m cm^{-1}. Anal. Calcd (found) for $[Et_4N]_2[I]$: C, 39.56 (36.90); H, 5.31 (5.30); N, 3.69 (3.50). The product is soluble in CH_2Cl_2, acetone, and MeCN.

Following a similar procedure, 0.28 g (2.5 mmol) of SeO_2 in 1.0 g (17.8 mmol) of KOH in MeOH solution reacted with 1 mL (7.4 mmol) of $Fe(CO)_5$ and then precipitated with 2.8 g (4.8 mmol) of (PPN)Cl gave 2.35 g (1.49 mmol) of $[PPN]_2[SeFe_3(CO)_9]$ ($[PPN]_2[I]$) (60% based on Fe). IR (ν_{CO}, CH_2Cl_2) for $[PPN]_2[I]$: 1996 m, 1928 vs, 1901 s, 1873 m cm^{-1}. Anal. Calcd (found) for $[PPN]_2[I]$: C, 61.74 (59.17); H, 3.84 (3.70); N, 1.78 (1.66).

Oxidation of $[Et_4N]_2[SeFe_3(CO)_9]$ ($[Et_4N]_2[I]$). To a solution of 1.76 g (2.32 mmol) of $[Et_4N]_2[I]$ in 40 mL of CH_2Cl_2 was added 2.00 g (6.36 mmol) of $[Cu(CH_3CN)_4BF_4$. The solution was allowed to stir at room temperature overnight and then filtered. After removal of solvent under vacuum, the residue was then extracted into hexane from which extraction 0.532 g (0.92 mmol) of $Se_2Fe_3(CO)_9$ (79% based on Se) was obtained. IR (ν_{CO}, hexane): 2056 s, 2038 vs, 2015 s cm^{-1}.

Preparation of $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Hg]$ ($[Et_4N]_2[II]$). To a mixture of 0.56 g (0.73 mmol) of $[Et_4N]_2[I]$ and 0.22 g (0.77 mmol) of $Hg(OAc)_2$ was added 30 mL of CH_3CN. The mixed solution was stirred for 4 h to give a brown solution. The solution was filtered, and solvent was removed to give an oil. The oil was then washed with ether and extracted with CH_2Cl_2 to give 0.51 g (0.35 mmol) of $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Hg]$ ($[Et_4N]_2[II]$) (96% based on the starting $[SeFe_3(CO)_9]^{2-}$). IR (ν_{CO}, CH_2Cl_2) for $[Et_4N]_2[II]$: 2021 m, 1992 s, 1948 m, br cm^{-1}. Crystals suitable for X-ray determination were grown from concentrated CH_2Cl_2 solution. Anal. Calcd (found) for $[Et_4N]_2[II]$: C, 28.00 (27.98); H, 2.76 (2.45); N, 1.92 (1.91). $[Et_4N]_2[II]$ is soluble in CH_2Cl_2, THF, and MeCN.

Preparation of $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Cd]$ ($[Et_4N]_2[III]$). To a mixture of 0.35 g (0.46 mmol) of $[Et_4N]_2[I]$ and 0.20 g (0.75 mmol) of $Cd(OAc)_2{\cdot}2H_2O$ was added 30 mL of acetone. The mixed solution was stirred overnight to give a brown solution. The solution was filtered, and solvent was removed to give an oil. The oil was washed with ether and then extracted with CH_2Cl_2 to give 0.27 g (0.20 mmol) of $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Cd]$ ($[Et_4N]_2[III]$) (87% based on starting $[SeFe_3(CO)_9]^{2-}$). IR (ν_{CO}, CH_2Cl_2) for $[Et_4N]_2[III]$: 2025 m, 1990 vs, 1944 m, br cm^{-1}. Anal. Calcd (found) for $[Et_4N]_2[III]$: C, 29.8 (28.2); H, 2.94 (3.01); N, 2.04 (1.90). $[Et_4N]_2[III]$ is soluble in CH_2Cl_2, THF, and MeCN. An X-ray analysis showed it to be isomorphous with $[Et_4N]_2[II]$.

X-ray Structural Characterization of $[Et_4N]_2[II]$. A summary of selected crystallographic data 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. Atomic scattering factors were taken from ref 6, and data reduction and structural refinement were performed using the NRCC-SDP-VAX packages.[7]

A brown crystal of $[Et_4N]_2[II]$ with dimensions $0.30 \times 0.50 \times 0.40$ mm^3 was selected for X-ray analysis. The crystal was mounted with epoxy on the tip of a glass fiber. Cell parameters were obtained from 25 reflections with 2θ angles in the range 22.94–27.66°. Systematic absences and intensity statistics indicated that the space group is $P2/n$. A total of 4240 unique reflections were collected, and the data were corrected for decay and absorption.[7] A total of 3550 reflections with $I > 2.5\sigma(I)$ were used in the refinement. The structure was solved by the heavy-atom method and 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 $R = 2.7\%$ and $R_w = 2.8\%$.

The selected atomic coordinates and isotropic displacement coefficients are given in Table 2. Selected bond distances and angles are listed in Table 3. Additional crystallographic data are available as supplementary material.

Results

The reaction of SeO_2/KOH with $Fe(CO)_5$ results in the formation of the dianion **I**, which can be isolated as a $[PPN]^+$ or $[Et_4N]^+$ salt in good yield. The IR spectrum of $[Et_4N]_2[I]$ shows absorptions characteristic of terminal CO ligands in the

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Table 1. Selected crystallographic Data for $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Hg]([Et_4N]_2[II])$

empirical formula	$Se_2Fe_6HgC_{34}H_{40}O_{18}N_2$
fw	1458.27
crystal syst	monoclinic
space group	$P2/n$
a, Å	12.881(2)
b, Å	8.574(1)
c, Å	22.488(6)
β, deg	104.25(2)
V, Å^3	2407
Z	2
D(calc), Mg m^{-3}	2.012
abs coeff, mm^{-1}	13.0
diffractometer	Nonius CAD-4
radiation [λ(Mo Kα)], Å	0.709 30
temp, °C	25
T_{min}/T_{max}	0.59/1.00
residuals[a] R, R_w	0.027, 0.028

[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 Atomic Coordinates and Isotropic Displacement Coefficients for $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Hg]$ $([Et_4N]_2[II])$

	x	y	z	B_{iso}
Hg	$^1/_4$	0.67489(4)	$^1/_4$	2.727(15)
Se	0.53940(5)	0.72180(7)	0.21077(3)	3.38(3)
Fe(1)	0.36967(6)	0.82928(9)	0.18301(4)	2.94(4)
Fe(2)	0.42652(7)	0.52805(9)	0.22971(4)	3.08(4)
Fe(3)	0.44135(7)	0.61529(10)	0.12016(4)	3.61(4)
O(1)	0.1523(4)	0.8291(6)	0.10405(22)	5.6(3)
O(2)	0.3873(4)	1.0494(5)	0.28488(22)	5.01(25)
O(3)	0.4283(4)	1.0814(6)	0.11106(24)	6.2(3)
O(4)	0.2585(4)	0.3015(5)	0.17328(23)	5.4(3)
O(5)	0.4559(4)	0.5102(6)	0.36272(22)	5.5(3)
O(6)	0.5859(4)	0.2869(7)	0.2431(3)	8.1(4)
O(7)	0.4771(4)	0.8119(6)	0.02182(23)	6.6(3)
O(8)	0.2364(5)	0.4971(7)	0.0476(3)	7.6(3)
O(9)	0.5851(5)	0.3726(6)	0.0982(3)	7.4(3)
C(1)	0.2360(5)	0.8228(7)	0.1368(3)	3.9(3)
C(2)	0.3764(4)	0.9615(7)	0.2471(3)	3.2(3)
C(3)	0.4053(5)	0.9798(8)	0.1393(3)	4.1(3)
C(4)	0.3207(5)	0.3925(7)	0.1947(3)	3.9(3)
C(5)	0.4401(5)	0.5238(7)	0.3108(3)	3.8(3)
C(6)	0.5250(6)	0.3828(8)	0.2362(4)	5.2(4)
C(7)	0.4640(5)	0.7354(8)	0.0609(3)	4.3(3)
C(8)	0.3158(6)	0.5418(8)	0.0778(3)	5.1(4)
C(9)	0.3158(6)	0.5418(8)	0.0778(3)	5.1(4)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Hg]$ $([Et_4N]_2[II])$

(A) Distances

Hg–Fe(1)	2.7462(9)	Hg-Fe(2)	2.7338(9)
Hg–Fe(3)	4.290(1)	Se–Fe(1)	2.312(1)
Se–Fe(2)	2.315(1)	Se–Fe(3)	2.305(1)
Fe(1)–Fe(2)	2.816(1)	Fe(1)–Fe(3)	2.619(1)
Fe(2)–Fe(3)	2.626(1)		

Carbonyl Ranges

C–O	1.118(8)–1.159(8)

(B) Angles

Fe(1)–Hg–Fe(1)′	122.37(3)	Fe(1)–Hg–Fe(2)	61.84(3)
Fe(1)–Hg–Fe(2)′	156.32(3)	Fe(1)′–Hg–Fe(2)	156.32(3)
Fe(1)′–Hg–Fe(2)′	61.84(3)	Fe(2)–Hg–Fe(2)′	125.16(3)
Fe(1)–Se–Fe(2)	74.98(3)	Fe(1)–Se–Fe(3)	69.11(4)
Fe(2)–Se–Fe(3)	69.28(4)	Se–Fe(1)–Fe(2)	52.56(3)
Se–Fe(1)–Fe(3)	55.32(3)	Fe(2)–Fe(1)–Fe(3)	57.65(3)
Se–Fe(2)–Fe(1)	52.47(3)	Se–Fe(2)–Fe(3)	55.18(3)
Fe(1)–Fe(2)–Fe(3)	57.40(3)	Se–Fe(3)–Fe(1)	55.57(3)
Se–Fe(3)–Fe(2)	55.54(3)	Fe(1)–Fe(3)–Fe(2)	64.95(3)

region 1996–1875 cm^{-1}, and the pattern is similar to those for the oxygen analog $[(\mu_3\text{-}O)Fe_3(CO)_9]^{2-}$ and the sulfur analog $[(\mu_3\text{-}S)Fe_3(CO)_9]^{2-}$.[8,9] It suggests that the anion I may exhibit the tetrahedral geometry for the metal core as in the structurally characterized $[(\mu_3\text{-}O)Fe_3(CO)_9]^{2-}$.[8] The elemental analyses are consistent with the formulation of $[PPN]_2[SeFe_3(CO)_9]$ or $[Et_4N]_2[SeFe_3(CO)_9]$ for the PPN$^+$ or Et$_4$N$^+$ salt of the dianion I. Unfortunately, several attempts at obtaining satisfactory X-ray analyses of $[Et_4N]_2[I]$ and $[PPN]_2[I]$ were unsuccessful due to the severe disorder of the cations and crystallographic problems. However, a preliminary X-ray study confirms the tetrahedral metal core for the dianion I.

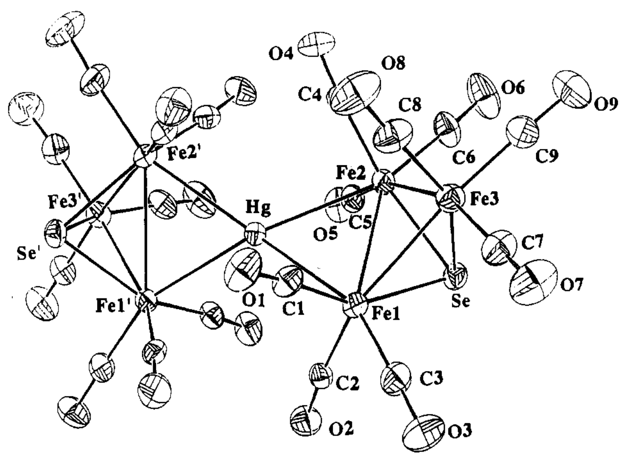

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion II.

Treatment of $[Et_4N]_2[I]$ with $[Cu(CH_3CN)_4]$ produces the previously characterized square-pyramidal $Se_2Fe_3(CO)_9$.[2] Further reaction of $[Et_4N]_2[I]$ with $Hg(OAc)_2$ readily gives the mercury derivative, $[Et_4N]_2[II]$, and the analogous reaction with $Cd(OAc)_2$ affords the cadmium derivative, $[Et_4N][III]$. On the basis of analyses and the similar IR absorption patterns, anions II and III possess isomorphous structures. A single crystal X-ray analysis of $[Et_4N]_2[II]$ shows it to be $[Et_4N]_2[\{SeFe_3(CO)_9\}_2Hg]$. The core geometry of II can be described as a Hg(II) ion tetrahedrally connected to two $[SeFe_3(CO)_9]^{2-}$ clusters by bridging the Fe–Fe bond. As shown in Figure 1, the dianion of $[Et_4N]_2[II]$ is located on the crystallographic 2-fold axis which passes through the Hg atom. Each iron atom is pseudooctahedrally coordinated and one lone pair of electrons is left uncoordinated on the pyramidal Se atom.

Discussion

Although the syntheses of the class of compounds $[EFe_3(CO)_9]^{2-}$ (E = O, S) have been reported,[8,9] the selenium analog $[SeFe_3(CO)_9]^{2-}$ has never been exploited probably due to a lack of a systematic route to the synthesis of this class of complexes. The employment of SeO_2 with $Fe(CO)_5$ in basic solution can produce $[SeFe_3(CO)_9]^{2-}$ (I) in good yield, and this methodology can also be extended to the synthesis of the sulfur analog $[SFe_3(CO)_9]^{2-}$.[10,11] The availability of the dianion I allows for further reactivity study.

Oxidation of the dianion I with $[Cu(CH_3CN)_4]BF_4$ provides an alternative to $Se_2Fe_3(CO)_9$. The formation of $Se_2Fe_3(CO)_9$ may be seen as a dimerization of cluster I accompanied by loss of $Fe(CO)_3$ groups. The metal bridged complexes $[\{SeFe_3(CO)_9\}_2M]^{2-}$ (M = Hg, Cd) can be considered as an aggregate of two dianion I fragments bridged by a mercury or cadmium metal in a μ_4 fashion. These reactivity patterns further support the tetrahedral arrangement for the metal core of the dianion I. The study of the dianion I toward $Hg(OAc)_2$ and $Cd(OAc)_2$

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reveals a lack of reactivity at the exposed selenium atom, which may be attributed to the lower basicity of the Se atom.

Although the ability of mercury to form bimetallic complexes with transition metal complex fragments has been recognized for quite some time,[12] this synthetic strategy is seldom used in the field of heavier main group element–transition metal clusters. There are several possible structural environments of a linking Hg atom in metal clusters, and $[Et_4N]_2[\mathbf{II}]$ represents the first structurally characterized heavier main group element–transition metal carbonyl cluster in which Hg atom occupies an edge position. The linking between transition metal clusters through metal–mercury chains in a μ_4 fashion is encountered in other examples such as $[\{\mu\text{-}C_2{}^tBu)Ru_3(CO)_9\}_2Hg]$,[13] $[\{(\mu\text{-}H)(\mu_3\text{-}S)Os_3(CO)_9\}_2Hg]$,[14] $[\{Cp(\mu_3\text{-}COCH_3)Fe_2Co(CO)_7\}_2Hg]$,[15] $[\{Cp(\mu_3\text{-}COCH_3)Fe_2Rh(CO)_7\}_2Hg]$,[15] $[\{\mu_3\text{-}COCH_3)Ru_3(CO)_{10}\}_2Hg]$,[16] $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$,[17] and $[\{Os_{10}C(CO)_{24}\}_2Hg]^{2-}$.[18]

The average Se–Fe bond length of **II** is 2.3108 Å, close to those in $[Fe(Se_4)_2(CO)_2]^{2-}$ (2.436 Å),[3] and $[\{Fe_2Se(CO)_6\}_2(Se_2)]^{2-}$ (2.386 Å).[4] The distances Hg–Fe(1) and Hg–Fe(2) average 2.74 Å and can be considered normal single bonds. In contrast, the Hg–Fe(3) distance, 4.290(1) Å, is indicative of the absence of significant contact.[19] In **II**, the Fe(2)–Fe(3) distance of 2.626(1) Å is comparable to the normal Fe–Fe bonds in many other clusters while the Fe(1)–Fe(2) bond distance is 2.816(1) Å, which is long but within the reasonable bonding distances.[19] The lengthening of the Fe(1)–Fe(2) edge in **II** is due to the presence of the bridging mercury atom. This effect of Hg bridging is also found for the Ru complex $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$.[17]

Our results suggest that the dianion **I** is a potential building block for the extended metal–metal-bonded system and that other condensation reactions between heavier main group element-transition metal clusters and mercury or cadmium salt might be a good route for the synthesis of high-nuclearity clusters.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 83-0208-M-003-004) and Dr. Chuen-Her Ueng (National Taiwan Normal University) for the X-ray structure determination.

Supplementary Material Available: Complete listings of crystallographic data, bond distances and angles, atomic positional parameters, and anisotropic thermal parameters for $[Et_4N]_2[\mathbf{II}]$ (6 pages). Ordering information is given on any current masthead page.

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