Dalton Communications

Crystal Structure of $[Na{\cdot}3thf][Fe(CO)_3(SePh)_3]$ and $[N(PPh_3)_2][Fe(CO)_3(SePh)_3]{\cdot}0.5thf$ (thf = tetrahydrofuran): Evidence for $Na^+\cdots SePh$ and Long-range $Na^+\cdots Fe^{II}$ Interactions

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The reaction between $Na[HFe(CO)_4]$ and $(PhSe)_2$ yielded $Na[Fe(CO)_3(SePh)_3]$ which crystallized as $[Na{\cdot}3thf][Fe(CO)_3(SePh)_3]$ in which three tetrahydrofuran (thf) molecules and the $[Fe(CO)_3(SePh)_3]^-$ anion surround the sodium cation; in the corresponding crystal structure of $[N(PPh_3)_2][Fe(CO)_3(SePh)_3]{\cdot}0.5thf$ the cations and anions are discrete entities.

The rational synthesis and reactivity of transition metal–thiolate complexes has been well developed and heavily exploited, nevertheless, the chemistry of analogous selenolates has received little attention until relatively recently, and the structural data on terminal metal–selenolates, in particular, are rare.[1-3] This communication describes the structures of the mononuclear iron(II) selenolate complexes, $[Na{\cdot}3thf][Fe(CO)_3(SePh)_3]$ **1** (thf = tetrahydrofuran) and $[N(PPh_3)_2][Fe(CO)_3(SePh)_3]{\cdot}0.5thf$ **2**. The former of these adopts a solid-state ion-pairing structure which may hold important ramifications for the understanding of the effect of alkali-metal cations upon anionic iron carbonyl complexes[4].

Reactions of the well defined complex $Na[HFe(CO)_4]$,[5] {obtained on mixing equimolar amounts of $[N(PPh_3)_2][HFe(CO)_4]$ (0.354 g, 0.5 mmol) and $NaBPh_4$ (0.171 g, 0.5 mmol) in thf followed by filtration} with 2 equivalents of $(PhSe)_2$ (0.313 g, 0.001 mol) in thf at ambient temperature for 4 h gave high yields (96%) of the $[Fe(CO)_3(SePh)_3]^-$ complex of sodium, which was crystallized from thf–hexane as dark brown-red, moderately air-sensitive crystals of formulation $[Na{\cdot}3thf][Fe(CO)_3(SePh)_3]$ [equation (1)]. At

$$\begin{aligned}
&[N(PPh_3)_2][HFe(CO)_4] + NaBPh_4 \longrightarrow \\
&\qquad\qquad Na[HFe(CO)_4] + [N(PPh_3)_2][BPh_4] \\
&\qquad\qquad\qquad\qquad \Big\downarrow {\scriptstyle +2(PhSe)_2 \atop -CO,\ -PhSeH} \\
&\qquad\qquad\qquad Na[Fe(CO)_3(SePh)_3] \qquad\qquad (1)
\end{aligned}$$

room temperature, complex **1** readily loses the co-ordinated solvent thf, but is otherwise stable and can be kept in non-polar hexane solvents under nitrogen for prolonged periods of time (1 month at least). Treatment of complex **1** with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) in thf for 2 h results in an infrared carbonyl spectrum identical with that of $[N(PPh_3)_2][Fe(CO)_3(SePh)_3]$ [ν(CO) shift from 2051s, 2036w, 1993s, 1977w cm^{-1} to 2037s, 1978s cm^{-1} in thf] obtained by reaction of 1 equivalent of $[N(PPh_3)_2][HFe(CO)_4]$ with 2 equivalents of $(PhSe)_2$ in thf at ambient temperature for 40 h.[5] Attempts to perform the cation-exchange reaction in the presence of $[N(PPh_3)_2][Fe(CO)_3(SePh)_3]$ and $NaBPh_4$ lead to decomposition only in thf at room temperature. The preparations of complexes **1** and **2** also show that the oxidative decarbonylation addition of $(PhSe)_2$ to $[cation][HFe(CO)_4]$ is accelerated by the assistance of a small alkali-metal counter cation {the reaction proceeds 10 times faster with Na^+ than with $[N(PPh_3)_2]^+$}.[6]

The structure of $[Na{\cdot}3thf][Fe(CO)_3(SePh)_3]$ † can be viewed in terms of either Na^+ in the cavity of *fac*-$FeSe_3$ or of three thf molecules and the *fac*-$[Fe(CO)_3(SePh)_3]^-$ anion held together by $Na^+\cdots SePh$ ionic interactions and Na^+–O(thf) bonds, featuring a highly distorted octahedral co-ordination sphere about sodium with an acute Se–Na–Se angle of 63.20(10)°, an O–Na–O angle of 94.2(5)°, and Se–Na–O angles of 94.0(3), 157.2(3) and 106.4(4)°. The co-ordination geometry around the iron(II) centre is also distorted octahedral with Se–Fe–Se 85.56(9)°, C–Fe–C 97.3(9)°, and Se–Fe–C angles of 84.7(7), 92.0(6) and 170.1(6)°. The Na^+ cation and Fe atom are located on a crystallographic three-fold axis. Each of the three Se–Na bond distances is 3.176(5) Å which is longer than the atomic radii of 3.00 Å for *d*(Na–Se),[8] and is predicted to possess 'strong' ionic interactions. The Fe···Na contact distance is 4.049(6) Å which is much longer than the corresponding distance of 3.09 Å in $Na_2[Fe(CO)_4]{\cdot}1.5C_4H_8O_2$ ($C_4H_8O_2$ = dioxane)[4] and also longer than the predicted Fe–Na bond length of 2.83 Å,[4] but is much shorter than the Fe···Na distance of 7.18 Å found in $[NaL]_2[Fe(CO)_4]$

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† Crystal data for **1**. $C_{33}H_{39}FeNaO_6Se_3$, M = 847.38, trigonal, space group $R3$, a = 14.402(3), c = 15.313(3) Å, U = 2750.7(8) $Å^3$, Z = 3, $F(000)$ = 1271, D_c = 1.535 g cm^{-3}, crystal dimensions 0.35 × 0.45 × 0.55 mm. The data were collected on a Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), using the θ–2θ scan mode. The last least-squares cycle was calculated with 33 atoms, 142 parameters and 573 [$I > 2\sigma(I)$] out of 810 reflections ($2\theta < 45°$). Absorption corrections were made using the NRCC-SDP-VAX package of programs;[7] maximum, minimum transmission 1.00, 0.68; largest residual peak = 0.200 e $Å^{-3}$, largest residual hole = −0.210 e $Å^{-3}$; R (R, all data) = 0.028 (0.057), R' (R', all data) = 0.027 (0.029); $w = 1/\sigma^2(F)$.

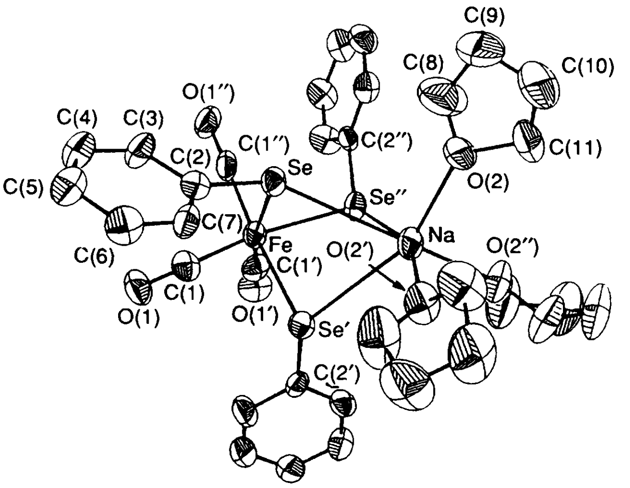

Fig. 1 The crystal structure of $[\mathrm{Na{\cdot}3thf}][\mathrm{Fe(CO)_3(SePh)_3}]$ **1**. Selected bond lengths (Å) and angles (°): Fe–Se 2.450(2), Na–Se 3.176(5), Na–O(2) 2.274(19), Fe–C(1) 1.759(20), C(1)–O(1) 1.154(12), Fe ··· Na 4.049(6); Se–Fe–Se 85.56(9), Se–Na–Se 63.20(10), Se–Na–O(2) 157.2(3), Se–Na–O(2) 106.4(4), Se–Na–O(2) 94.0(3), O(2)–Na–O(2) 94.2(5), Se–Fe–C(1) 170.1(6), Se–Fe–C(1) 92.0(6), Se–Fe–C(1) 84.7(7), C(1)–Fe–C(1) 97.3(9), Fe–Se–Na 91.12(8), Fe–Se–C(2) 106.9(3)

(L = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) which was claimed to show zero interaction between $\mathrm{Na^+}$ and Fe.[4] The $\mathrm{Na^+}$–O(thf) bond distance of 2.274(19) Å is shorter than the sum (2.37 Å) of the ionic radius of $\mathrm{Na^+}$ and the van der Waals radius of O.[4,8]

In contrast to **1**, $[\mathrm{N(PPh_3)_2}][\mathrm{Fe(CO)_3(SePh)_3}]{\cdot}0.5\mathrm{thf}$* crystallized as discrete $[\mathrm{N(PPh_3)_2}]^+$ cations and $[\mathrm{Fe(CO)_3(SePh)_3}]^-$ anions along with non-interacting thf molecules (Fig. 2). The $[\mathrm{Fe(CO)_3(SePh)_3}]^-$ anion represents the first example of a $\mathrm{FeSe_3}$ molecular fragment in a mononuclear iron complex. The reported terminal Fe–SePh bond length of 2.460(12) Å in tetrahedral $[\mathrm{Fe(SePh)_4}]^{2-}$ (ref. 9) is comparable with the Fe–SePh distance of 2.450(2) Å in **1**, and the average Fe–SePh bond length of 2.459(2) Å in **2**.

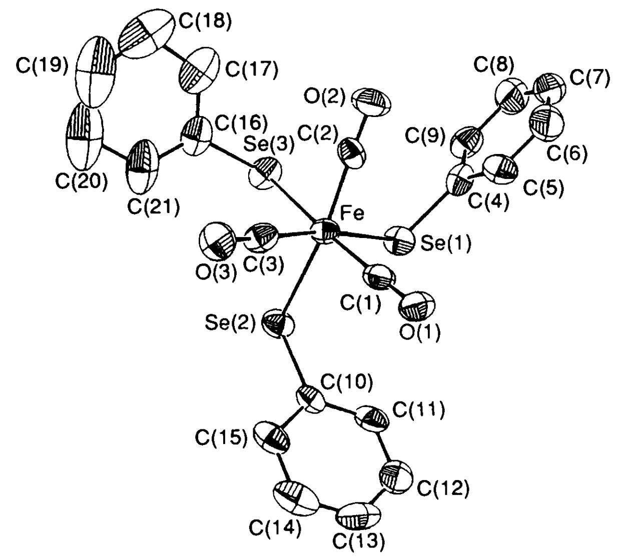

Fig. 2 The crystal structure of the $[\mathrm{Fe(CO)_3(SePh)_3}]^-$ anion in complex **2**. Selected bond lengths (Å) and angles (°): Fe–Se(1) 2.463(2), Fe–Se(2) 2.457(2), Fe–Se(3) 2.457(2), Fe–C(1) 1.743(12), Fe–C(2) 1.781(12), Fe–C(3) 1.741(11), C(1)–O(1) 1.153(14), C(2)–O(2) 1.148(15), C(3)–O(3) 1.160(14); Se(1)–Fe–Se(2) 84.86(7), Se(1)–Fe–Se(3) 85.00(7), Se(2)–Fe–Se(3) 85.85(8), Se(1)–Fe–C(1) 87.5(4), Se(1)–Fe–C(2) 93.9(4), Se(1)–Fe–C(3) 168.1(4)

The Se ··· Se contact distances in **2** are in the range 3.320(2)–3.347(3) Å indicative of the absence of direct Se–Se bonding, however intramolecular Se ··· Se interactions may be considered to be significant in this facial complex.[9]

Acknowledgements

We thank the National Science Council of the Republic of China (Taiwan) for support of this work.

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Received 4*th May* 1993; *Communication* 3/02542J

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* Crystal data for **2**. $\mathrm{C_{59}H_{48}FeNO_{3.5}P_2Se_3}$, $M = 1181.70$, monoclinic, space group $C2/c$, $a = 32.009(4)$, $b = 11.681(5)$, $c = 28.841(7)$ Å, $\beta = 95.10(2)°$, $U = 10\,741(5)$ Å^3, $Z = 8$, $F(000) = 4111$, $D_c = 1.461$ g cm^{-3}, crystal dimensions 0.13 × 0.50 × 0.50 mm. The data were collected on a Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å), using the θ–2θ scan mode. The last least-squares cycle was calculated with 118 atoms, 615 parameters and 2722 $[I > 2\sigma(I)]$ out of 7025 reflections ($2\theta < 45°$); maximum, minimum transmission 1.00, 0.62; largest residual peak = 0.490 e Å^{-3}, largest residual hole = -0.460 e Å^{-3}; R (R, all data) = 0.049 (0.187), R' (R', all data) = 0.046 (0.064); $w = 1/[\sigma^2(F) + 0.0003F^2]$. Atomic coordinates, thermal parameters and bond lengths and angles for both **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.