Heterotrinuclear complexes containing a hexaselenolato-zinc(II), -cadmium(II), -nickel(II) or -iron(II) core: crystal structures of [(OC)₃Fe(μ-SePh)₃M(μ-SePh)₃Fe(CO)₃] (M = Zn, Cd, Ni or Fe) and [Fe(CO)₂(phen)(SePh)₂] (phen = 1,10-phenanthroline)

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A series of linear trinuclear selenolate complexes of the general type [(OC)₃Fe(μ-SePh)₃M(μ-SePh)₃Fe(CO)₃] (M = Zn^{II} **1**, Cd^{II} **2**, Ni^{II} **3** or Fe^{II} **4**) has been synthesized by reaction of the appropriate [M(H₂O)$_n$]$^{2+}$ with the chelating metalloligand *fac*-[N(PPh₃)₂][Fe(CO)₃(SePh)₃] in acetonitrile. Their structures were elucidated on the basis of IR, UV/VIS, NMR spectra and X-ray crystallography. Compounds **1**–**4** are structurally related, each containing two tridentate metalloligands resulting in a MSe₆ co-ordination environment of virtual O_h symmetry. Further reaction of **4** with 3 equivalents of 1,10-phenanthroline (phen) initially afforded the intermediate [Fe(phen)₃][Fe(CO)₃(SePh)₃]₂ but eventually neutral [Fe(CO)₂(phen)(SePh)₂] **5** was formed as the sole product. Its crystal structure has been determined. This investigation shows that *fac*-[Fe(CO)₃(SePh)₃]⁻ serves as a tridentate chelating metalloligand and selenolate ligand-transfer reagent.

The study of transition-metal selenolate and tellurolate chemistry has been actively pursued in several laboratories recently,[1] motivated primarily by the bonding diversity,[2] reactivity,[3] potential use as precursors for M/Se materials,[4] and the relevance of such complexes to biomimetic chemistry.[5] (*e.g.*, the structure of the NiFeSe hydrogenase from *Desulfovibrio baculatus* revealed that the nickel is ligated to one Se atom, one or two S/Cl atoms, and three to four N/O atoms;[5f] the crystal structure of NiFe hydrogenase isolated from *Desulfovibrio gigas* is a Ni–Fe binuclear complex bridged by thiocysteines.[5g]) Some examples of complexes containing homoleptic hexathiolato-metal or hexaselenolatometal cores have been reported and characterized by X-ray crystallography.[6,7]

Recent work in this laboratory showed that *cis*-[Mn(CO)₄(ER)₂]⁻ complexes which contain delocalized lone pairs of electrons around chalcogen atoms are useful in the syntheses of heterotrimetallic Mn^I-Co^{III}-Mn^I-chalcogenolate complexes [(OC)₄Mn(μ-ER)₂Co(CO)(μ-E′R)₃Mn(CO)₃] (E = E′ = Te, R = Ph; E = Te, E′ = Se, R = Ph) and [(OC)₃Mn(μ-SePh)₃Co(μ-SePh)₃Mn(CO)₃]⁻.[7,8] In these reactions the complexes *cis*-[Mn(CO)₄(ER)₂]⁻ act as potential 'chelating metallo ligands', and the chelating properties of these manganese(I) chalcogenolate complexes offer novel routes toward heterometallic chalcogenolate species.

In order to investigate the chelating ability of *fac*-[Fe(CO)₃(SePh)₃]⁻,[9] we have studied its reactivity toward [M(H₂O)$_n$]$^{2+}$ fragments. In this paper we report the syntheses and characterization of the series of trinuclear clusters [(OC)₃Fe(μ-SePh)₃M(μ-SePh)₃Fe(CO)₃] (M = Zn **1**, Cd **2**, Ni **3** or Fe **4**), with the central M^{II} atom co-ordinated by six bridging benzeneselenolates leading to a M(SePh)₆ core of virtual O_h symmetry, and neutral [Fe(CO)₂(phen)(SePh)₂] **5** (phen = 1,10-phenanthroline). The formation of complex **5** from the intermediate [Fe(phen)₃][Fe(CO)₃(SePh)₃]₂ requires the transfer of selenolate and CO ligands from one iron(II) center to another.

Experimental

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glove-box (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH₂; acetonitrile from CaH₂–P₂O₅; hexane and tetrahydrofuran (thf) from sodium–benzophenone) and stored in dried, N₂-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use and transfers to reaction vessels were *via* stainless-steel cannula under N₂ at a positive pressure. The reagents iron pentacarbonyl, diphenyl diselenide, bis(triphenylphosphoranylidene)ammonium chloride, Zn(BF₄)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O, 1,10-phenanthroline and Fe(ClO₄)₂·6H₂O (Aldrich) were used as received. The complex *fac*-[N(PPh₃)₂][Fe(CO)₃(SePh)₃] was prepared by the literature method.[9a] Infrared spectra were recorded on Bio-Rad FTS-185 and FTS-7 FTIR spectrometers with sealed solution cells (0.1 mm) and KBr windows, NMR spectra on a Bruker AC 200 spectrometer, ¹H and ¹³C chemical shifts being relative to tetramethylsilane and UV/VIS spectra on a GBC 918 spectrophotometer. Cyclic voltammetric measurements were performed on a BAS-100B electrochemical analyzer, using glassy carbon as the working electrode, and [NBu^{n}₄][PF₆] as the supporting electrolyte. Analyses of carbon, hydrogen and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparations

[(OC)₃Fe(μ-SePh)₃M(μ-SePh)₃Fe(CO)₃] (M = Zn 1, Cd 2 or Ni 3). The complex *fac*-[N(PPh₃)₂][Fe(CO)₃(SePh)₃] (0.4 mmol, 0.458 g) dissolved in MeCN (5 cm³) was stirred under N₂, and Zn(BF₄)₂·6H₂O (0.2 mmol, 0.070 g), Cd(NO₃)₂·4H₂O (0.2 mmol, 0.062 g) or *fac*-[N(PPh₃)₂][Fe(CO)₃(SePh)₃] (1 mmol, 1.147 g) and Ni(NO₃)₂·6H₂O (0.5 mmol, 0.146 g) in MeCN solution added by cannula under a positive pressure of N₂ at ambient temperature. After stirring for 4 h, a brown solid was precipitated. The mother-liquor was removed *via* cannula and the solid washed with MeCN. The brown solid was dried under vacuum; thf–hexane (1 : 2 ratio) was added, and the dark brown solution filtered to remove the insoluble solid. The product was isolated by removing the solvent. The yield of dark brown [(OC)₃Fe(μ-SePh)₃Zn(μ-SePh)₃Fe(CO)₃] **1** was 0.13 g (50%).

Diffusion of hexane in a thf solution of this complex at $-15\,°C$ for 4 weeks afforded dark brown crystals suitable for X-ray crystallography. IR (thf): ν(CO) 2070vs and 2019s cm^{-1}. ^{1}H NMR (C$_4$D$_8$O): δ 7.21–7.62 (m, Ph). ^{13}C NMR (C$_4$D$_8$O): δ 128.5, 129.8, 130.0, 132.1 and 133.4. Absorption spectrum (thf): λ$_{max}$/nm (ε/M^{-1} cm^{-1}) 324 (23 920), 606 (470) (Found: C, 39.60; H, 2.55. Calc. for C$_{42}$H$_{30}$Fe$_2$O$_6$Se$_6$Zn: C, 39.36; H, 2.36%). The yield of complex **2** was 0.192 g (72%) of a dark red solid. Diffusion of hexane into a solution of [(OC)$_3$Fe(μ-SePh)$_3$Cd(μ-SePh)$_3$Fe(CO)$_3$] in thf at $-15\,°C$ for 4 weeks led to dark red crystals suitable for X-ray crystallography. IR (thf): ν(CO) 2072vs and 2021s cm^{-1}. ^{1}H NMR (C$_4$D$_8$O): δ 7.01–7.78 (m, Ph). ^{13}C NMR (C$_4$D$_8$O): δ 132.1, 130.0, 129.6 and 128.5. Absorption spectrum (thf): λ$_{max}$/nm (ε/M^{-1} cm^{-1}) 327 (8880) (Found: C, 37.86; H, 2.28. Calc. for C$_{42}$H$_{30}$CdFe$_2$O$_6$Se$_6$: C, 37.97; H, 2.28%). Complex **3** was isolated in 90.6% (0.578 g) yield. Diffusion of hexane–cyclohexane into a solution of [(OC)$_3$Fe(μ-SePh)$_3$Ni(μ-SePh)$_3$Fe(CO)$_3$] in thf at $-15\,°C$ for 3 weeks afforded dark redbrown crystals. IR (thf): ν(CO) 2070vs and 2019s cm^{-1}. ^{1}H NMR (C$_4$D$_8$O): δ 13.71 (br), 7.61 (br) and 7.26 (br) (Ph). ^{13}C NMR (C$_4$D$_8$O): δ 160.0, 132.1, 130.0 and 128.4. Absorption spectrum (thf): λ$_{max}$/nm (ε/M^{-1} cm^{-1}) 410 (9622) and 660 (788) (Found: C, 39.33; H, 2.43. Calc. for C$_{42}$H$_{30}$Fe$_2$NiO$_6$Se$_6$: C, 39.57; H, 2.37%).

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive; only small amounts of material should be prepared and handled with great caution.

[(OC)$_3$Fe(μ-SePh)$_3$Fe(μ-SePh)$_3$Fe(CO)$_3$] 4. A solution containing *fac*-[N(PPh$_3$)$_2$][Fe(CO)$_3$(SePh)$_3$] (0.4 mmol, 0.458 g) and Fe(ClO$_4$)$_2$·6H$_2$O (0.2 mmol, 0.073 g) in acetonitrile (10 cm^3) was stirred under nitrogen at ambient temperature for 1 h. A brown solution accompanied by a dark brown solid was formed. The mother-liquor was removed under a positive pressure of N$_2$ and the dark brown solid was washed twice with acetonitrile. Tetrahydrofuran was added to extract the product, and then hexane was slowly added to precipitate a dark brown solid [yield 0.205 g (80%)]. The dark brown thf solution was layered with hexane; storage for 4 weeks at $-15\,°C$ led to dark brown crystals of [(OC)$_3$Fe(μ-SePh)$_3$Fe(μ-SePh)$_3$Fe(CO)$_3$] suitable for X-ray crystallography. IR (thf): ν(CO) 2069vs and 2019s cm^{-1}. ^{1}H NMR (C$_4$D$_8$O): δ -7.82 (br), -33.23 (br) and 0.94 (br) (Ph). Absorption spectrum (thf): λ$_{max}$/nm (ε/M^{-1} cm^{-1}) 611 (644) and 338 (10 638) (Found: C, 39.66; H, 2.44. Calc. for C$_{42}$H$_{30}$Fe$_3$O$_6$Se$_6$: C, 39.66: H, 2.38%).

[Fe(CO)$_2$(phen)(SePh)$_2$] 5. A solution containing *fac*-[N(PPh$_3$)$_2$][Fe(CO)$_3$(SePh)$_3$] (0.458 g, 0.4 mmol) in acetonitrile (5 cm^3) was added to a mixture of 1,10-phenanthroline (0.109 g, 0.6 mmol) and Fe(ClO$_4$)$_2$·6H$_2$O (0.073 g, 0.2 mmol) in thf (5 cm^3). The reaction was monitored by FTIR spectroscopy. The IR spectrum, ν(CO) (MeCN–thf) 2040vs and 1980vs cm^{-1}, indicated the formation of the intermediate [Fe(phen)$_3$][Fe(CO)$_3$(SePh)$_3$]$_2$. After stirring overnight at room temperature the solvent was removed under reduced pressure. The residue was dissolved in thf (10 cm^3) under N$_2$, and the dark red-brown solution filtered to remove [N(PPh$_3$)$_2$][ClO$_4$]. The filtrate (in thf) was stored in a refrigerator ($-15\,°C$) for 3 weeks to induce precipitation of dark red-brown crystals of [Fe(CO)$_2$(phen)-(SePh)$_2$]. The crystals, suitable for X-ray crystallography, were recrystallized by vapor diffusion of hexane into a concentrated thf solution at $-15\,°C$. Yield 0.332 g (91%). IR (thf): ν(CO) 2013vs and 1967s cm^{-1}. ^{1}H NMR (C$_4$D$_8$O): δ 9.46 (d), 8.37 (d), 7.83 (s), 7.76 (dd), 7.6 (m), 6.65 (m) and 6.33 (m). ^{13}C NMR (C$_4$D$_8$O): δ 218.8 (s) (CO), 153.8 (s), 146.6 (s), 137.6 (s), 136.0 (s), 132.1 (s), 131.5 (s), 130.8 (s), 130.0 (s), 128.5 (s), 127.7 (s), 127.3 (s), 125.9 (s) and 125.5 (s). Absorption spectrum (thf): λ$_{max}$/nm (ε/M^{-1} cm^{-1}) 330 (8552) (Found: C, 51.58; H, 3.04; N, 4.53. Calc. for C$_{26}$H$_{18}$FeN$_2$O$_2$Se$_2$: C, 51.69; H, 3.00; N, 4.66%).

Crystallography

Crystallographic data for complexes **1**–**5** are collected in Table 1. All crystals were chunky: **1**, dark brown, *ca.* $0.40 \times 0.50 \times 0.60$ mm; **2**, dark red, $0.50 \times 0.50 \times 0.60$ mm; **3**, dark redbrown, $0.35 \times 0.50 \times 0.60$ mm; **4**, dark brown, $0.40 \times 0.50 \times 0.50$ mm; **5**, dark red-brown, $0.40 \times 0.60 \times 0.60$ mm. Each was mounted on a glass fiber and quickly coated in epoxy resin. The unit-cell parameters were obtained by least-squares refinement from 25 reflections with 2θ between 19.22 and 24.32° for **1**, $16.40 < 2\theta < 29.60°$ for **2**, $20.00 < 2\theta < 24.00°$ for **3**, $16.22 < 2\theta < 29.66°$ for **4**, and $18.80 < 2\theta < 25.26°$ for **5**. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and fixed hydrogen atoms contribution was based on *F*. Diffraction measurements were carried out at 25 °C on a Nonius CAD 4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.7107 Å) employing the θ–2θ scan mode.[10] A ψ-scan absorption correction was made. The NRCC-SDP-VAX package of programs was employed and atomic scattering factors were from ref. 12.
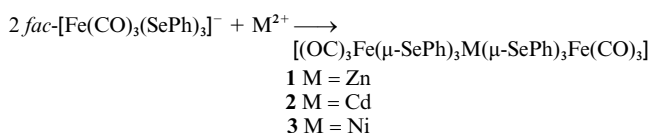
CCDC reference number 186/801.

Results and Discussion

As illustrated in Scheme 1, reaction of *fac*-[N(PPh$_3$)$_2$]-[Fe(CO)$_3$(SePh)$_3$] and Zn(BF$_4$)$_2$·6H$_2$O, Cd(NO$_3$)$_2$·4H$_2$O or Ni(NO$_3$)$_2$·6H$_2$O in a 2:1 molar ratio in MeCN gave trinuclear [(OC)$_3$Fe(μ-SePh)$_3$M(μ-SePh)$_3$Fe(CO)$_3$] (M = Zn **1**, Cd **2** or Ni **3**) as a dark brown solid by salt elimination ([N(PPh$_3$)$_2$][BF$_4$]/[N(PPh$_3$)$_2$][NO$_3$]) without the risk of adduct formation. Syntheses of **1**–**3** undertaken in thf solvent at ambient temperature proved unsuccessful. The heterotrimetallic complexes, which are stable and display no tendency to decompose under nitrogen at ambient temperature overnight, are sparingly soluble in common organic solvents like acetonitrile and hexane.

The IR carbonyl stretching and ^{1}H and ^{13}C NMR spectra are consistent with the presence of the six-co-ordination of d^{10} Zn^{II}, d^{10} Cd^{II}, d^8 Ni^{II} and low-spin octahedrally co-ordinated d^6 Fe^{II} with facial tricarbonyls. The electronic spectrum of complex **1** is dominated by ligand-to-metal charge-transfer bands at approximately 324 and 606 nm. It is notable that *fac*-[N(PPh$_3$)$_2$][Fe(CO)$_3$(SePh)$_3$] is an effective tridentate ligand for stabilizing six-co-ordinated d^{10} zinc(II)/cadmium(II) and d^8 nickel(II) cores. However, its reaction with Ni(NO$_3$)$_2$·6H$_2$O or NiCl$_2$ in thf led to decomposition at room temperature. The results suggest that this series of synthetic reactions are highly dependent on solvent and reactants. Compounds **1**–**3** are strongly colored and stable to both oxygen and moisture.

The definitive assignment of the structure of complex **1** was obtained by X-ray crystallography. An ORTEP[13] plot of the neutral trimetallic compound with its numbering scheme is shown in Fig. 1, selected bond distances and angles are given in Table 2. Complex **1** has a linear chain of one zinc(II) and two iron(II) atoms; two outer Fe atoms are co-ordinated by three bridging SePh ligands and three terminal carbonyls, while the central Zn^{II} is co-ordinated by six bridging benzeneselenolates giving a ZnSe$_6$ core of virtual O_h symmetry. Thus, two *fac*-[Fe(CO)$_3$(SePh)$_3$]$^-$ act as tridentate ligands to encapsulate the Zn^{II}. Following the proposal of Stiefel and Brown,[14] the six-co-ordinate polyhedron of D_3 symmetry can be defined by the two parameters Ø and *s/h*, *i.e.* the twist angle between two parallel

2 *fac*-[Fe(CO)$_3$(SePh)$_3$]$^-$ + M^{2+} ⟶

[(OC)$_3$Fe(μ-SePh)$_3$M(μ-SePh)$_3$Fe(CO)$_3$]
1 M = Zn
2 M = Cd
3 M = Ni

Scheme 1

Table 1 Crystallographic data for complexes **1–5**

	1·thf	**2·thf**	**3·1.5 C_6H_{12}·1.5 thf**	**4·thf**	**5·2H_2O**
Formula	$C_{46}H_{38}Fe_2O_7Se_6Zn$	$C_{46}H_{38}CdFe_2O_7Se_6$	$C_{57}H_{60}Fe_2NiO_{7.5}Se_6$	$C_{46}H_{38}Fe_3O_7Se_6$	$C_{26}H_{22}FeN_2O_4Se_2$
M	1353.62	1400.64	1509.55	1344.09	636.20
Crystal system	Triclinic	Triclinic	Cubic	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$Ia\bar{3}$	$P\bar{1}$	$I4_1/a$
$a/Å$	11.471(3)	11.337(3)	28.443(4)	11.465(5)	13.953(4)
$b/Å$	12.830(4)	13.266(4)		12.847(3)	
$c/Å$	19.210(8)	19.516(6)		19.208(7)	24.167(8)
$\alpha/°$	72.50(3)	70.07(3)		72.51(3)	
$\beta/°$	73.86(3)	73.29(3)		74.05(4)	
$\gamma/°$	67.32(3)	67.36(3)		67.37(4)	
$U/Å^3$	2445(1)	2505(1)	230 11(3)	2450(9)	4705(2)
Z	2	2	16	2	8
D_c/g cm^{-3}	1.839	1.857	1.743	1.822	1.796
μ/cm^{-1}	55.47	53.46	46.23	53.3	37.3
R'	0.053	0.037	0.062	0.075	0.069
R'	0.045	0.036	0.073	0.068	0.078
Goodness of fit	1.72	1.51	1.04	1.74	3.03

$R = \Sigma|(F_o - F_c)|/\Sigma F_o$. $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. Goodness of fit = $[\Sigma w(F_o - F_c)^2/(M - N)]^{\frac{1}{2}}$ where M = number of reflections and N = number of parameters.

Table 2 Selected bond distances (Å) and angles (°) for complexes **1–3**

Complex **1**

Se(1)–Zn	2.622(2)	Se(4)–Zn	2.644(2)
Se(2)–Zn	2.643(2)	Se(5)–Zn	2.613(2)
Se(3)–Zn	2.632(2)	Se(6)–Zn	2.597(2)
Se(1)–Fe(1)	2.464(3)	Se(4)–Fe(2)	2.460(2)
Se(2)–Fe(1)	2.464(2)	Se(5)–Fe(2)	2.461(2)
Se(3)–Fe(1)	2.454(2)	Se(6)–Fe(2)	2.453(2)
Se(1)–Zn–Se(2)	78.87(7)	Se(1)–Zn–Se(3)	78.10(7)
Se(1)–Zn–Se(4)	107.37(7)	Se(1)–Zn–Se(5)	97.00(8)
Se(1)–Fe(1)–Se(2)	85.47(8)	Se(1)–Zn–Se(6)	171.50(9)
Se(1)–Fe(1)–Se(3)	84.60(8)	Se(1)–Fe(1)–C(1)	94.1(4)
Se(1)–Fe(1)–C(2)	87.3(4)	Se(1)–Fe(1)–C(3)	170.8(4)
Se(2)–Fe(1)–Se(3)	85.08(8)	Zn–Se(2)–Fe(1)	81.55(7)
Zn–Se(2)–C(13)	119.4(3)	Fe(1)–Se(2)–C(13)	108.6(3)

Complex **2**

Cd–Se(1)	2.772(1)	Fe(1)–Se(1)	2.470(2)
Cd–Se(2)	2.800(2)	Fe(1)–Se(2)	2.469(2)
Cd–Se(3)	2.852(1)	Fe(1)–Se(3)	2.457(2)
Cd–Se(4)	2.822(1)	Fe(2)–Se(4)	2.471(2)
Cd–Se(5)	2.789(2)	Fe(2)–Se(5)	2.461(2)
Cd–Se(6)	2.758(1)	Fe(2)–Se(6)	2.463(2)
Se(1)–Cd–Se(2)	75.09(5)	Se(1)–Cd–Se(3)	73.13(4)
Se(1)–Cd–Se(4)	114.06(4)	Se(1)–Cd–Se(5)	101.32(5)
Se(1)–Cd–Se(6)	168.71(4)	Se(1)–Fe(1)–Se(2)	86.89(6)
Se(1)–Fe(1)–Se(3)	85.72(6)	Cd–Se(1)–Fe(1)	84.81(5)
Cd–Se(2)–Fe(1)	84.22(5)	Cd–Se(3)–Fe(1)	83.33(5)

Complex **3**

Ni–Se	2.511(2)	Fe–Se	2.460(4)
Fe–Ni–Fe	180.0	Se–Ni–Se	81.83(7)
Se–Ni–Se	98.18(7)	Se–Ni–Se	180.0
Se–Fe–Se	83.92(17)	Ni–Se–Fe	80.22(1)
Ni–Se–C(2)	116.0(7)	Fe–Se–C(2)	113.3(7)

Fig. 1 An ORTEP[15] drawing and labeling scheme of neutral [(OC)$_3$Fe(μ-SePh)$_3$M(μ-SePh)$_3$Fe(CO)$_3$] (M = Zn **1**, Cd **2** or Fe **4** with thermal ellipsoids drawn at the 20% probability level

lengthening may be due to steric effects of the six benzene-selenolates. The mean Fe^{II}–Se bond of length 2.459(2) Å is comparable with the average of 2.459(2) Å in *fac*-[N(PPh$_3$)$_2$]-[Fe(CO)$_3$(SePh)$_3$].[9a] The cofacial Se–Zn–Se angles is 78.73(7)° (average). The Se–Fe–Se angle [average 85.05(8)°] is not very different from that found in *fac*-[N(PPh$_3$)$_2$][Fe(CO)$_3$(SePh)$_3$] [average 85.24(8)°][9a] suggesting that binding to a second metal (Zn^{II}) has little influence on the Se–Fe^{II}–Se angles.

Complex **2** (Fig. 1, selected bond distances and angles in Table 2) is essentially isostructural with **1**. The six-co-ordinated Cd^{II} bearing six bridging selenolate ligands has the longest Cd^{II}–Se bonds [2.799(2) Å, average] among the reported cadmium complexes bearing bridging selenolate ligands, *e.g.* [{Cd(SeC$_6$H$_2$Bu^t-2,4,6)$_2$}$_2$] [average 2.646(4) Å],[2d] [{Cd$_2$-(μ-SePh)$_2$(SePh)$_2$(Et$_2$PC$_2$H$_4$PEt$_2$)}$_\infty$] (2.678 Å)[4c] and [Cd$_8$-(μ-S)(μ-SePh)$_{12}$(SePh)$_4$]$^{2-}$ (2.638 Å).[19]

Compound **3** displays intense charge-transfer transitions at 410 and 660 nm. The ^{1}H NMR spectrum exhibits broadening and shifting of resonances, indicative of two unpaired spins for d^8 nickel(II) in a distorted O_h ligand field.
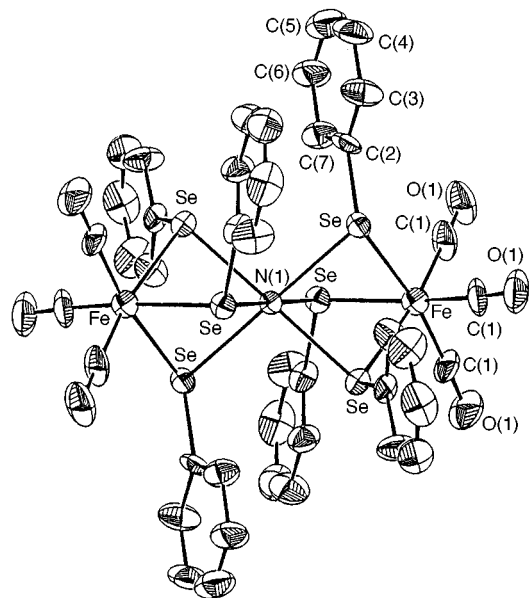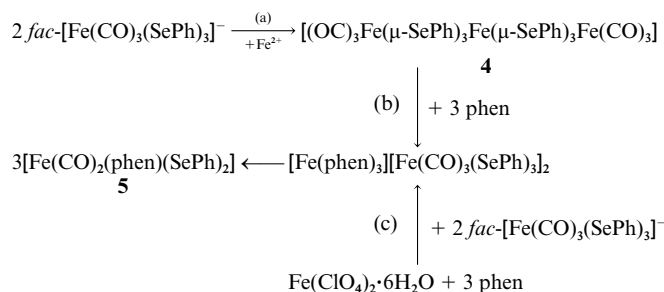
The X-ray structural analysis (Fig. 2) of complex **3** reveals a

triangular faces of the polyhedron and the ratio of the side of the triangle to the distance between the triangles.[15,16] In the Zn(SePh)$_6$ core of complex **1** $\varnothing$ = 48.4° and s/h = 1.47, indicating that the structure is elongated along one of the pseudo-C_3 axes, and adopts a conformation in which two adjacent triangles are almost staggered. The Fe$\cdots$Zn distances, average 3.32(2) Å [Zn$\cdots$Fe(1) 3.338(3) and Zn$\cdots$Fe(2) 3.302(3) Å], exclude any direct metal–metal interactions. The Zn^{II}–SePh bond distances [average 2.625(2), range from 2.597(2) to 2.644(2) Å] are significantly longer than the average of 2.515(3) Å in [(thf)$_4$Eu(μ-SePh)$_3$Zn(SePh)],[2b] 2.469(2) Å in [Zn(SePh)$_4$]$^{2-}$,[17] and 2.477(3) Å in [Zn$_4$(SePh)$_{10}$]$^{2-}$.[18] This

Fig. 2 An ORTEP drawing and labeling scheme of [(OC)₃Fe(μ-SePh)₃-Ni(μ-SePh)₃Fe(CO)₃] **3** with thermal ellipsoids drawn at the 30% probability level

centrosymmetric trinuclear iron–nickel–iron selenolate complex in which the Ni^{II} is in a distorted octahedral arrangement with the selenium atoms of benzeneselenolates in two parallel faces of the octahedron capped by tricarbonyliron(II) fragments. The structure of complex **3** contains two symmetrically independent molecules of **3** and both molecules locate at $\bar{3}$ with the same geometry. The arrangement of the selenolate substituents is symmetrical so that the Fe–Ni–Fe vector lies on a three-fold rotation axis. Neutral **3** appears to have no precedent in iron–nickel–selenolate chemistry. In concordance with the earlier discussion, the Ni(SePh)₆ core has Ø = 60° and s/h = 1.53. The Fe–Ni–Fe angle of 180.0° and the staggered conformation of two parallel triangular benzeneselenolate faces promise the best minimization of interactions between the selenolates.[20] The Se–Ni–Se angles are divided into two groups (Table 2), 81.95(7) (average) and 98.05(7)° (average, different facial groups). The Ni^{II}–Se bond distance is 2.509(2) Å (average), which is significantly longer than that in [Ni₂(μ-2,4,6-Me₃C₆H₂Se)₂(2,4,6-Me₃C₆H₂Se)₄]$^{2-}$ [2.341(2) Å average],[5b] in [Ni(SePh)₄]$^{2-}$ [2.401(3) Å average],[5b] and in [{Ni(μ-SePh)(SePh)(dmphen)}₂] (dmphen = 2,9-dimethyl-1,10-phenanthroline) [2.432(1) Å].[21] The Ni^{II}···Fe^{II} distance [3.201(6) Å] is not short enough to suggest a bonding interaction between the two metals.[5g]

Reaction of [Ni(η-C₅H₅)(C₅H₆)]⁺ and *fac*-[Fe(CO)₃(SePh)₃]⁻ in a 1:2 molar ratio in MeCN also yields complex **3**. In a sense, the triangular selenium atoms of the benzeneselenolates in the tridentate metallo ligand *fac*-[Fe(CO)₃(SePh)₃]⁻ act like cyclopentadienyl, a six-π-electron donor ligand. We are currently pursuing this relationship.

As illustrated in Scheme 2(a), reaction of *fac*-[N(PPh₃)₂]-[Fe(CO)₃(SePh)₃] and Fe(ClO₄)₂·6H₂O in a 2:1 molar ratio in

$$2 \; fac\text{-}[Fe(CO)_3(SePh)_3]^- \xrightarrow[+\,Fe^{2+}]{(a)} [(OC)_3Fe(\mu\text{-}SePh)_3Fe(\mu\text{-}SePh)_3Fe(CO)_3]$$

4

(b) | + 3 phen

3[Fe(CO)₂(phen)(SePh)₂] ⟵ [Fe(phen)₃][Fe(CO)₃(SePh)₃]₂
5

(c) | + 2 *fac*-[Fe(CO)₃(SePh)₃]⁻

Fe(ClO₄)₂·6H₂O + 3 phen

Scheme 2

Table 3 Selected bond distances (Å) and angles (°) for complexes **4** and **5**

Complex **4**

Fe–Se(1)	2.627(10)	Fe–Se(2)	2.640(3)
Fe–Se(3)	2.628(3)	Fe–Se(4)	2.641(3)
Fe–Se(5)	2.618(3)	Fe–Se(6)	2.594(10)
Fe(1)–Se(1)	2.469(3)	Fe(1)–Se(2)	2.463(5)
Fe(1)–Se(3)	2.457(5)	Se(1)–C(7)	1.878(17)
Se(2)–C(13)	1.949(14)	Se(3)–C(19)	1.938(14)
Se(1)–Fe–Se(2)	78.79(10)	Se(1)–Fe–Se(3)	78.37(10)
Se(1)–Fe–Se(4)	107.01(10)	Se(1)–Fe–Se(5)	96.87(10)
Se(1)–Fe–Se(6)	171.51(12)	Fe–Se(1)–Fe(1)	81.81(15)
Fe–Se(1)–C(7)	116.6(5)	Fe(1)–Se(1)–C(7)	113.0(5)

Complex **5**

Fe–Se	2.474(1)	Fe–N	1.989(8)
Fe–C(1)	1.773(12)	Se–C(8)	1.935(10)
Se–Fe–Se′	175.46(11)	Se–Fe–N	91.6(3)
Se–Fe–N′	91.8(3)	Se–Fe–C(1)	88.7(4)
Se–Fe–C(1′)	88.1(4)	N–Fe–C(1)	94.8(4)
N′–Fe–C(1)	176.2(4)	N–Fe–N′	81.3(3)
C(1)–Fe–C(1′)	89.0(5)		

MeCN gave trinuclear [(OC)₃Fe(μ-SePh)₃Fe(μ-SePh)₃Fe(CO)₃] **4** as a dark brown solid. Complex **4** exhibits a diagnostic ¹H NMR spectrum with the aryl proton resonances well removed from the diamagnetic region. The *o*- and *p*-protons resonate upfield, δ −7.8 and −33.2, while the *m*-protons are at δ 0.94 which is consistent with the central Fe^{II} having a high-spin and the two terminal Fe^{II} having low-spin configurations as observed in the analogue [(OC)₃Fe(μ-SPh)₃Fe(μ-SPh)₃-Fe(CO)₃].[22] Comparing **4** and [(OC)₃Fe(μ-SPh)₃Fe(μ-SPh)₃-Fe(CO)₃], the increase in the upfield shift of the *p*-, *o*-protons of the thiolate ligands (δ −12.2 and −43.8) compared to those of the selenolate ligands (δ −7.8 and −33.2) reflects the nature of the bonding between the metal and chalcogenolate ligands, *i.e.* weaker orbital overlap in the Fe–Se bonds.[23] The Mössbauer spectrum exhibited two doublets in a 2:1 intensity ratio. The isomer shifts occur at 0.23 and 0.35 mm s⁻¹ with quadrupole splittings of 0.31 and 0.93 mm s⁻¹ respectively for complex **4**.

The molecular structure of complex **4** is shown in Fig. 1 and selected bond distances and angles are summarized in Table 3. In the FeSe₆ core, Ø = 48.4 and s/h = 1.47.[14] The Fe···Fe distance averages to 3.32(2) Å [Fe(1)···Fe(2) 3.306(5) and Fe(2)···Fe(3) 3.338(5) Å]. The average Fe$^{II}_t$–Se distance (terminal Fe^{II}–SePh) of 2.462(6) Å is close to the value of 2.459(2) Å observed in *fac*-[Fe(CO)₃(SePh)₃]⁻.[9a] However, the six-co-ordinated Fe^{II} bearing six bridging selenolate ligands has longer Fe^{II}–Se bonds [2.625(3) Å, average], *e.g.* [Fe₁₂(SePh)₂₄] (average 2.441 Å).[24] This lengthening effect might result in cleavage of Fe–Se bonds under neutral Lewis-base ligands.

The reaction of complex **4** with 3 equivalents of 1,10-phenanthroline in MeCN solution initially affords the intermediate [Fe(phen)₃][Fe(CO)₃(SePh)₃]₂, but eventually neutral [Fe(CO)₂(phen)(SePh)₂] **5** is formed as the sole product [Scheme 2(b)].† In order to clarify the formation of **5**, as illustrated in Scheme 2(c), a straightforward synthetic reaction was conducted by addition of 2 equivalents of *fac*-[N(PPh₃)₂]-[Fe(CO)₃(SePh)₃] to a mixture of Fe(ClO₄)₂·6H₂O and 3 equivalents of 1,10-phenanthroline, in MeCN–thf under a nitrogen atmosphere at ambient temperature. The reaction finally led to the isolation of the dark red-brown complex **5**. Its formation from [Fe(phen)₃][Fe(CO)₃(SePh)₃]₂ requires the transfer of

† Crystals of [Fe(phen)₃][Fe(CO)₃(SePh)₃]₂·3H₂O·MeCN form in the monoclinic space group *C2/c* with cell dimensions *a* = 25.280(5), *b* = 14.802(2), *c* = 22.453(7) Å, β = 110.28(3)°, *U* = 7881(3) Å³, *Z* = 4, *R* = 0.042 and *R*′ = 0.037.

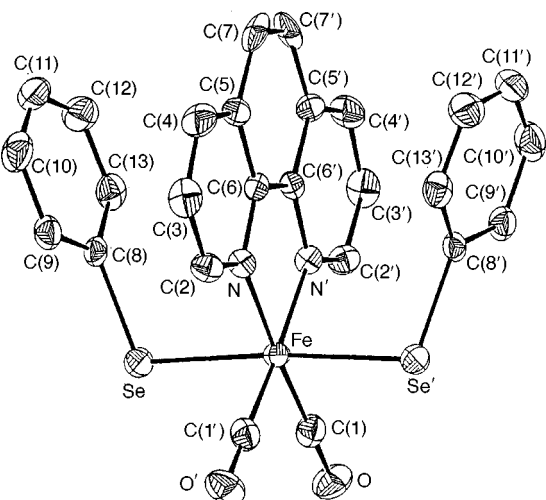**Fig. 3** An ORTEP drawing and labeling scheme of neutral [Fe(CO)$_2$(phen)(SePh)$_2$] with thermal ellipsoids drawn at the 30% probability level

selenolate and CO ligands from one iron(II) center to another. This redistribution reaction suggests that the complex *fac*-[Fe(CO)$_3$(SePh)$_3$]$^-$ serves as an intermetal selenolate-transfer reagent.[25] A carbon monoxide atmosphere prevents the formation of **5** when a mixture of [Fe(phen)$_3$][Fe(CO)$_3$(SePh)$_3$]$_2$ is exposed to 1 atm (101 325 Pa) CO in MeCN at room temperature. Complex **5** is a stable, diamagnetic species soluble in organic solvents. Its IR spectrum shows two strong CO stretching bands, supporting a *cis* position of two CO ligands. The electrochemistry of complex **5**, in thf with 0.05 M [NBu$^n_4$][PF$_6$] as supporting electrolyte, reveals two irreversible oxidations at −0.01 and 1.00 V (*vs.* Ag–AgCl).

The definitive assignment of the structure of complex **5** was obtained by X-ray crystallography. An ORTEP plot of the neutral complex with its numbering scheme is shown in Fig. 3. The molecules possess a crystallographic two-fold axis as defined by the equivalent atoms shown. The geometry about the Fe can be described as distorted octahedral with bond angles of 89.0(5)° for C(1)−Fe−C(1′), 81.3(3)° for N−Fe−N and 175.46(11)° for Se−Fe−Se confirming the spectroscopic assignment of a *cis-cis-trans* (*cct*) configuration. The Fe−SePh distances [2.474(1) Å] are comparable with terminal Fe−SePh of 2.459(2) Å in *fac*-[Fe(CO)$_3$(SePh)$_3$]$^{-}$,[9a] the Fe−SePh distance of 2.460(12) Å in tetrahedral [Fe(SePh)$_4$]$^{2-}$,[1b] and the Fe−SeMe distance of 2.448(1) Å in *cct*-[Fe(CO)$_2$(SeMe)$_2$(PMe$_3$)$_2$].[9d] Distances to the least-squares planes (1,10-phenanthroline ligand) from the carbon atoms of the phenyl rings range from 3.043(6) to 3.922(8) Å with an average value of 3.500(9) Å.

It is of interest that the benzeneselenolates occupy *trans* co-ordination sites, and the phenyl groups attached to seleniums lie above and below the 1,10-phenanthroline ligand in complex **5**.[26] When viewed along the Se−Fe−Se direction, the phenyl rings at Se and 1,10-phenanthroline are seen in an off-center face-to-face arrangement. This configuration lends itself to optimize intramolecular ring–ring displaced face-to-face and intramolecular non-bonded, weakly polar ring–ring interactions.[27]

Acknowledgements

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