Synthesis of $(Et_2C_2B_3H_5)Co(Me_4C_5CH_2Ph)$ (2). A 1.0-g (2.5-mmol) sample of **1** was dissolved in 5 mL of TMEDA, and three drops of water were added. The solution was stirred in air at room temperature for 2 h, and the volatiles were removed by rotary-evaporation. The residue was extracted with hexane, and the mixture was suction-filtered through silica to give a yellow solution. Evaporation gave yellow crystals (0.956 g, 2.45 mmol, 98%) of **2**. Exact mass: calcd for $^{59}Co^{12}C_{22}{}^{11}B_3{}^1H_{34}{}^+$, 390.2272; found, 390.2272.

Synthesis of $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2$ (3). A 250-mL three-necked round-bottom flask (A) containing a stirbar was connected via glass elbow joints to two 100-mL two-necked flasks (B and C), each of which was fitted with a septum cap and stirbar. In flask A was placed 60 mg (0.49 mmol) of $CoCl_2$, 190 mg (0.49 mmol) of **2** was placed in flask B, and 103 mg (0.49 mmol) of benzyltetramethylcyclopentadiene was placed in flask C. Flask A was connected to a vacuum line via its middle neck, and all three flasks were evacuated. THF (ca. 30 mL each) was distilled into the three vessels, and 0.2 mL of 2.5 M *n*-butyllithium in hexane was added to each of flasks B and C; both solutions turned dark red. After 30 min, the hydrocarbon anion solution in flask C was added *dropwise* to the stirred $CoCl_2$ in flask A; the latter solution turned deep green as the addition proceeded. After the reaction mixture was stirred for 1 h, the solution in flask B (containing the deprotonated anion $\mathbf{2}^-$) was added in one portion. The solution immediately turned a deep burgundy color. After overnight stirring, the solvent was removed to leave a red-brown solid, which was extracted in 50:50 hexane/CH_2Cl_2 and chromatographed on a silica column followed by silica plates (in the same solvent mixture) to give a deep red-brown band. Evaporation of the solvent gave 112 mg (0.17 mmol, 35%) of **3** as a burgundy-colored solid. Exact mass: calcd for $^{59}Co_2{}^{12}C_{38}{}^{11}B_3{}^1H_{51}{}^+$, 658.2934; found, 658.2948.

Synthesis of $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (4). Complex **1** (50 mg, 0.12 mmol) and 80 mg (0.27 mmol) of $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$[11] were sealed in vacuo into a Carius tube, and the mixture was heated at 200 °C for 4 h. The tube was opened in air, and the contents were extracted with CH_2Cl_2, giving a black solution, which was filtered through silica gel. The yellow filtrate was rotary-evaporated to give a yellow oil, which was thin-layer-chromatographed on silica in 50:50 hexane/CH_2Cl_2, giving two yellow bands. The high R_f band was **1**, 8 mg (0.02 mmol), and the low R_f band was **4**, 20 mg (0.030 mmol, 30%), a pale orange oil. Exact mass: calcd for $^{59}Co^{56}Fe^{12}C_{28}{}^{11}B_8{}^1H_{47}{}^+$, 586.3104; found, 586.3105.

Synthesis of $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe(Et_2C_2B_4H_4)$ (5) and $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe_2(Et_2C_2B_4H_4)_2$ (6). Complex **3** (112 mg, 0.170 mmol) and 200 mg (0.68 mmol) of $(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ were sealed in vacuo into a Carius tube, and the mixture was heated at 200 °C for 4 h. The tube was opened in air, and the contents were extracted with CH_2Cl_2, giving a brown solution which was filtered through silica gel. The red filtrate was chromatographed on a preparative-layer silica plate in 50:50 hexane/CH_2Cl_2, giving three red bands. The highest R_f band was recovered **3**, 68 mg (0.10 mmol), the middle band was **5** (15 mg, 0.02 mmol, 26% based on **3** consumed), obtained as a red oil on evaporation of solvent, and the lowest band was **6**, 1 mg (0.001 mmol, 1%), a red oil. Exact mass for **5**: calcd for $^{59}Co_2{}^{56}Fe^{12}C_{44}{}^{11}B_7{}^1H_{65}{}^+$, 844.3751; found, 844.3759. Exact mass for **6**: calcd for $^{59}Co_2{}^{56}Fe_2{}^{12}C_{50}{}^{11}B_{11}{}^1H_{59}{}^+$, 1030.4568; found, 1030.4564.

Synthesis of $(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (7). Compound **2** (237 mg, 0.61 mmol) was dissolved in THF and deprotonated in vacuo by addition of 0.24 mL of 2.5 M *tert*-butyllithium in hexane, giving a dark red solution of the $\mathbf{2}^-$ anion. To this solution was added 0.80 mL of benzyl bromide, which caused an immediate color change to yellow. Evaporation of the solvent gave a yellow solid, which was extracted in hexane. The mixture was filtered through silica, and the solvent was removed to give 220 mg (0.45 mmol, 74%) of yellow solid **7**. Exact mass for **7**: calcd for $^{59}Co^{12}C_{29}{}^{11}B_3{}^1H_{40}{}^+$, 480.2741; found, 480.2747.

Synthesis of $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (8) and $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (9). In a procedure analogous to that employed in the preparation of **5** and **6**, 100 mg (0.209 mmol) of **7** and 300 mg (1.03 mmol) of $(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ were sealed in vacuo into a Carius tube and the mixture was heated at 200 °C for 2 h. After cooling, the tube was opened and the contents were dissolved in 2:1 *n*-hexane/CH_2Cl_2. The solution was chromatographed on a silica gel column, giving four bands, of which the first two were unreacted **7** and the iron reagent. Band 3 was isolated as **8a**, a yellow oil (41 mg, 0.062 mmol, 30%), while band 4 was isolated as **9**, also a yellow oil (20 mg, 0.012 mmol, 11%). Exact mass for **8a**: calcd for $^{59}Co^{56}Fe^{12}C_{35}{}^{11}B_7{}^1H_{52}{}^+$, 666.3401; found, 664.3433. The composition of **9** was established via analysis of its unit-resolution mass spectral profile, which closely matches the calculated intensity pattern based on natural isotope abundances, supported by proton NMR and boron-11 NMR data.

Attempted Synthesis of $(Et_2C_2B_3H_2\text{-}5\text{-}CH_2Ph)Co_2(Me_4C_5CH_2Ph)_2$ (10). In an evacuated apparatus similar to that employed in the preparation of **3** from **2**, a solution of the $Me_4C_5CH_2Ph^-$ anion (prepared as above from 28 mg (0.013 mmol) of benzyltetramethylcyclopentadiene and an equimolar quantity of butyllithium in hexane) was slowly added to a solution of 0.13 mmol of $CoCl_2$ in THF in the lower flask. The solution was stirred for 20 min. In the upper flask, a solution of 63 mg (0.13 mmol) of **7** in THF was deprotonated with 0.013 mmol of butyllithium in hexane, and the dark orange solution was stirred for 20 min. This solution was then added through a filter, in vacuo, to the solution of the chloro(benzyltetramethylcyclopentadienyl)cobalt intermediate in the lower flask. The reaction mixture turned dark brown and was stirred for 16 h at room temperature with no further color changes. Following removal of the solvent in a rotary evaporator, the brown residue was extracted in 50:50 hexane/CH_2Cl_2 solution, and the resulting solution was placed on a silica column. Only bands identified as starting materials were obtained, and further careful chromatography of these bands gave no evidence of the desired **10**.

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Synthesis of the $PPh_4{}^+$ and $NEt_4{}^+$ Salts of $M(SePh)_4{}^{2-}$ (M = Mn, Fe, Co, Ni) and the Structure of $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$

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The syntheses of the $PPh_4{}^+$ and $NEt_4{}^+$ salts of the $M(SePh)_4{}^{2-}$ (M = Mn, Fe, Co, Ni) anions by reaction of the metal chlorides with LiSePh in the presence of the cations are described. $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$ crystallizes with four formula units in the orthorhombic space group $D_2^4\text{-}P2_12_12_1$ in a cell of dimensions $a = 14.787$ (1) Å, $b = 16.485$ (1) Å, and $c = 18.273$ (2) Å. Four benzeneselenol ligands provide slightly distorted tetrahedral coordination about the Fe^{II} center. The Fe–Se distances average 2.460 (12) Å; the Se–C distances average 1.907 (8) Å. The Se–Fe–Se angles range from 103.6 (1) to 114.9 (1)°. UV–vis and ^1H NMR data for the $PPh_4{}^+$ and $NEt_4{}^+$ salts of $M(SePh)_4{}^{2-}$ (M = Mn, Fe, Co, Ni) are assigned and discussed.

Introduction

Interest in metal coordination in metalloenzymes prompted the synthesis and characterization of $M(SPh)_4{}^{2-}$ complexes (M = Mn, Fe, Co, Ni, Zn, Cd).[1-3] These simple metal thiolates are useful precursors for soluble metal sulfides[4,5] and mixed-metal sulfides.[6] The number of stucturally characterized soluble metal sulfides

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[1] Holah, D. G.; Coucouvanis, D. *J. Am. Chem. Soc.* **1975**, *97*, 6917–6919.

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and mixed-metal sulfides is now large.[7-9] But only five mixed-metal selenides have been stucturally characterized: $Ni(Se_2)(WSe_4)_2^{2-}$,[10] which has no known sulfide analogue, $M(WSe_4)_2^{2-}$ (M = Ni, Pd),[10] and $M_2(WSe_4)_2^{2-}$ (M = Sn, Pb).[11] The possible use of $M(SePh)_4^{2-}$ (M = Mn, Fe, Co, Ni, Zn, Cd, Hg) anions as precursors in the synthesis of new mixed-metal selenides has prompted the present synthesis and characterization of new $M(SePh)_4^{2-}$ complexes (M = Mn, Fe, Co, Ni). Tetraselenophenolates of the zinc triad are known.[12,13]

Experimental Section

Syntheses. All the manipulations were carried out under N_2 with the use of standard Schlenk-line techniques. Solvents were distilled and dried. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. UV-vis spectra were recorded on a Perkin-Elmer 330 spectrophotometer. ^1H NMR spectra were obtained on a Varian XLA-400 spectrometer with a 5-mm tunable probe and a deuterium lock. All chemical shifts are referenced to TMS at δ 0 ppm. All reagents were purchased from Aldrich Chemical Co., Milwaukee, WI, except $MnCl_2\cdot 4H_2O$, which was purchased from J. T. Baker Chemical Co., Phillipsburg, NJ. LiSePh was prepared by a literature method.[14]

Preparation of $[NEt_4]_2[Mn(SePh)_4]$ (1). LiSePh (2.156 g, 13.2 mmol) was dissolved in MeCN (30 mL). A suspension of $MnCl_2\cdot 4H_2O$ (0.594 g, 3 mmol) in MeCN (20 mL) was slowly added to the selenophenolate solution with stirring. The mixture was heated to 60 °C and stirred for 0.5 h while a yellow solution formed. NEt_4Cl (0.998 g, 6 mmol) dissolved in MeCN (10 mL) was added to the selenophenolate solution. The solution was stirred for 0.25 h and filtered. The filtrate was diluted with diethyl ether to initiate crystallization, and the solution was cooled to −20 °C overnight to afford pink crystals of **1** (1.975 g, 70% yield). Anal. Calcd for $C_{40}H_{60}MnN_2Se_4$: C, 51.13; H, 6.44; Mn, 5.85; N, 2.98; Se, 33.61. Found: C, 51.25; H, 6.27; Mn, 5.38; N, 3.03; Se, 34.31.

Preparation of $[PPh_4]_2[Mn(SePh)_4]$ (2). LiSePh (4.303 g, 26.4 mmol) was dissolved in MeCN (75 mL). A suspension of $MnCl_2\cdot 4H_2O$ (1.188 g, 6 mmol) in MeCN (50 mL) was slowly added to the selenophenolate solution while it was being stirred. The mixture was heated to 60 °C and stirred for 0.5 h while a yellow solution formed. PPh_4Cl (4.50 g, 12 mmol) was dissolved in MeCN (25 mL), and this solution was added to the selenophenolate solution. The combined solution was stirred for 0.25 h and then filtered. Crystals immediately began to form. The solution was cooled to −20 °C overnight to afford large yellow crystals of **2** (4.564 g, 56% yield). Anal. Calcd for $C_{72}H_{60}MnP_2Se_4$: C, 63.68; H, 4.45; Mn, 4.05; P, 4.56; Se, 23.26. Found: C, 62.96; H, 4.64; Mn, 4.08; P, 4.33; Se, 22.64.

Preparation of $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$ (3). This compound was prepared in the same manner as **1** except $FeCl_2\cdot 4H_2O$ was used in place of $MnCl_2\cdot 4H_2O$. A brown solution formed. No diethyl ether was added, and the solution was cooled to −20 °C overnight to deposit brown crystals of **3** (1.542 g, 52% yield). Anal. Calcd for $C_{40}H_{60}FeN_2Se_4$ (no MeCN):[15] C, 51.08; H, 6.43; Fe, 5.94; N, 2.98; Se, 33.58. Found: C, 49.72; H, 6.53; Fe, 6.17; N, 2.81; Se, 32.47. Absorption spectrum (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 610 (1700), 422 (sh). ^1H NMR (Me_2SO-d_6): C_6H_5, −9.81 (*o*-H), 17.72 (*m*-H), −16.71 ppm (*p*-H).

Table I. Crystallographic Details

compd	$[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$
formula	$C_{42}H_{63}FeN_3Se_4$
fw	981.68
a, Å	14.787 (1)
b, Å	16.485 (1)
c, Å	18.273 (2)
V, Å^3	4454
Z	4
d_{calcd}, g cm^{-3}	1.463
space group	D_2^4-$P2_12_12_1$
T, °C	−120
λ, Å	1.540 562 (Cu Kα_1)
μ, cm^{-1}	68.0
transm coeff	0.370–0.699
$R(F_o^2)$	0.093
$R_w(F_o^2)$	0.119
$R(F_o)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.059
$R_w(F_o)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.054

Preparation of $[PPh_4]_2[Fe(SePh)_4]$ (4). This compound was prepared in the same manner as **2** except $FeCl_2\cdot 4H_2O$ was used in place of $MnCl_2\cdot 4H_2O$. A brown solution formed. The solution was cooled overnight to −20 °C to afford brown crystals of **4** (3.763 g, 46% yield). Anal. Calcd for $C_{72}H_{60}FeP_2Se_4$: C, 63.64; H, 4.45; Fe, 4.11; P, 4.56; Se, 23.24. Found: C, 61.00; H, 4.53; Fe, 4.08; P, 4.73; Se, 23.41. Absorption spectrum (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 610 (1720), 420 (sh). ^1H NMR (Me_2SO-d_6): C_6H_5, −9.69 (*o*-H), 17.76 (*m*-H), −16.77 ppm (*p*-H).

Preparation of $[NEt_4]_2[Co(SePh)_4]$ (5). This compound was prepared in the same manner as **1** except $CoCl_2\cdot 6H_2O$, was used in place of $MnCl_2\cdot 4H_2O$. A green solution formed. No diethyl ether was added, and the solution was cooled to −20 °C overnight to deposit green crystals of **5** (2.116 g, 75% yield). Anal. Calcd for $C_{40}H_{60}CoN_2Se_4$: C, 50.91; H, 6.41; Co, 6.24; N, 2.97; Se, 33.47. Found: C, 51.10; H, 6.38; Co, 6.46; N, 2.97; Se, 32.75. Absorption spectrum (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 693 (340), 430 (1500). ^1H NMR (Me_2SO-d_6): C_6H_5, −26.85 (*o*-H), 12.68 (*m*-H), −18.84 ppm (*p*-H).

Preparation of $[PPh_4]_2[Co(SePh)_4]$ (6). This compound was prepared in the same manner as **2** except $CoCl_2\cdot 6H_2O$, was used in place of $MnCl_2\cdot 4H_2O$. A green solution formed. The solution was cooled overnight to −20 °C to afford green crystals of **6** (6.255 g, 77% yield). Anal. Calcd for $C_{72}H_{60}CoP_2Se_4$: C, 63.49; H, 4.44; Co, 4.33; P, 4.55; Se, 23.19. Found: C, 61.48; H, 4.48; Co, 4.87; P, 4.72; Se, 23.64. Absorption spectrum (DMF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 693 (315), 425 (1520). ^1H NMR (Me_2SO-d_6): C_6H_5, −26.85 (*o*-H), 12.68 (*m*-H), −18.84 ppm (*p*-H).

Preparation of $[NEt_4]_2[Ni(SePh)_4]$ (7). This compound was prepared in the same manner as **1** except $NiCl_2\cdot 6H_2O$ was used in place of $MnCl_2\cdot 4H_2O$. A dark brown solution formed. No diethyl ether was added. The MeCN was pumped off and the precipitate was dissolved in warm propionitrile (70 °C). The solution was cooled to −20 °C overnight to deposit dark brown crystals of **7** (1.534 g, 54% yield). Anal. Calcd for $C_{40}H_{60}N_2NiSe_4$: C, 50.92; H, 6.41; N, 2.97; Ni, 6.22; Se, 33.48. Found: C, 48.15; H, 6.81; N, 2.70; Ni, 6.49; Se, 33.55. ^1H NMR (Me_2SO-d_6): C_6H_5, 4.80 (*o*-H), 16.91 (*m*-H), −8.51 ppm (*p*-H).

Preparation of $[PPh_4]_2[Ni(SePh)_4]$ (8). This compound was prepared in the same manner as **2** except $NiCl_2\cdot 6H_2O$ was used in place of $MnCl_2\cdot 4H_2O$. The dark brown solution that formed was cooled overnight to −20 °C to afford black crystals of **8** (6.524 g, 80% yield). Anal. Calcd for $C_{72}H_{60}NiP_2Se_4$: C, 63.50; H, 4.44; Ni, 4.31; P, 4.55; Se, 23.19. Found: C, 62.78; H, 4.48; Ni, 4.47; P, 4.39; Se, 23.26. ^1H NMR (Me_2SO-d_6): C_6H_5, 4.82 (*o*-H), 16.94 (*m*-H), −8.60 ppm (*p*-H).

Crystallographic Studies. Crystals of $[NEt_4]_2[Fe(SePh)_4]$ were grown by cooling a MeCN solution to −20 °C. A suitable crystal was mounted on a glass fiber and placed in the cold stream (−120 °C)[16] of an Enraf-Nonius CAD4 diffractometer, with which the unit cell was determined from 25 automatically centered reflections. Data collection proceeded smoothly. The intensities of five standard reflections monitored every 3 h throughout data collection remained constant within intensity statistics. Some crystallographic details are given in Table I; more information is available in Table IS.[17]

Procedures standard in this laboratory[18] were employed in the solution

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(16) The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Sotorem, Z. I. de Vic, 31320 Castanet-Tolosan, France.

(17) Supplementary material.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$

atom	*x*	*y*	*z*	B_{eq}
Fe(1)	0.241 52 (11)	−0.415 52 (10)	0.154 654 (93)	2.31 (4)
Se(1)	0.174 697 (91)	−0.376 147 (78)	0.036 088 (65)	2.84 (3)
Se(2)	0.400 287 (77)	−0.368 833 (78)	0.150 213 (73)	2.81 (3)
Se(3)	0.179 151 (86)	−0.344 813 (77)	0.260 913 (63)	2.73 (3)
Se(4)	0.223 032 (88)	−0.561 105 (76)	0.178 840 (68)	2.96 (3)
N(1)	0.095 91 (62)	0.300 31 (56)	0.365 46 (46)	2.3 (2)
N(2)	0.453 40 (58)	−0.162 38 (53)	0.340 81 (52)	2.5 (2)
N(3)	0.169 4 (12)	−0.065 72 (91)	0.427 13 (90)	7.8 (6)
C(1)	0.175 61 (79)	−0.260 50 (65)	0.032 03 (60)	2.8 (3)
C(2)	0.228 19 (70)	−0.212 04 (73)	0.077 94 (60)	2.8 (3)
C(3)	0.226 63 (86)	−0.129 39 (71)	0.071 82 (63)	3.4 (3)
C(4)	0.174 67 (97)	−0.090 53 (69)	0.022 18 (67)	3.6 (3)
C(5)	0.122 42 (84)	−0.134 49 (79)	−0.025 48 (57)	3.5 (3)
C(6)	0.121 90 (80)	−0.219 02 (83)	−0.019 34 (61)	3.4 (3)
C(7)	0.460 65 (85)	−0.405 18 (62)	0.235 89 (67)	2.8 (3)
C(8)	0.416 88 (79)	−0.437 56 (76)	0.295 78 (62)	3.1 (3)
C(9)	0.460 9 (10)	−0.467 33 (87)	0.358 70 (70)	4.5 (4)
C(10)	0.556 89 (99)	−0.462 30 (92)	0.359 05 (83)	5.0 (5)
C(11)	0.600 02 (83)	−0.429 55 (94)	0.299 86 (88)	4.7 (4)
C(12)	0.555 34 (75)	−0.401 46 (68)	0.238 70 (75)	3.4 (3)
C(13)	0.057 20 (78)	−0.375 08 (66)	0.283 81 (60)	2.6 (3)
C(14)	0.016 56 (79)	−0.345 77 (81)	0.346 72 (69)	3.5 (3)
C(15)	−0.072 08 (84)	−0.366 1 (10)	0.364 51 (79)	4.6 (4)
C(16)	−0.118 67 (82)	−0.419 82 (95)	0.320 26 (98)	5.1 (5)
C(17)	−0.080 12 (80)	−0.449 36 (73)	0.257 38 (93)	4.5 (4)
C(18)	0.008 20 (85)	−0.428 25 (64)	0.240 05 (72)	3.4 (3)
C(19)	0.243 97 (68)	−0.626 85 (71)	0.094 97 (60)	2.6 (3)
C(20)	0.250 11 (76)	−0.710 34 (69)	0.101 42 (66)	2.9 (3)
C(21)	0.268 01 (81)	−0.761 77 (69)	0.043 12 (74)	3.4 (3)
C(22)	0.280 99 (74)	−0.726 94 (78)	−0.025 76 (66)	3.3 (3)
C(23)	0.272 32 (82)	−0.643 46 (74)	−0.034 10 (61)	3.4 (3)
C(24)	0.255 98 (78)	−0.594 29 (71)	0.024 96 (68)	3.1 (3)
C(25)	−0.004 04 (94)	0.301 85 (83)	0.345 41 (83)	4.5 (4)
C(26)	−0.027 69 (88)	0.342 51 (77)	0.275 76 (73)	4.1 (4)
C(27)	0.133 23 (96)	0.384 55 (87)	0.369 87 (79)	4.6 (4)
C(28)	0.089 6 (13)	0.444 49 (87)	0.415 48 (83)	6.4 (5)
C(29)	0.103 89 (99)	0.260 61 (96)	0.436 54 (81)	4.9 (4)
C(30)	0.080 94 (94)	0.174 12 (99)	0.446 09 (86)	5.0 (5)
C(31)	0.144 3 (11)	0.252 6 (10)	0.307 39 (85)	5.0 (5)
C(32)	0.239 13 (80)	0.230 3 (10)	0.321 80 (88)	6.3 (5)
C(33)	0.510 77 (77)	−0.118 37 (64)	0.284 58 (75)	3.6 (3)
C(34)	0.534 9 (11)	−0.169 90 (86)	0.219 88 (86)	5.7 (5)
C(35)	0.369 79 (80)	−0.198 59 (74)	0.307 99 (71)	3.6 (3)
C(36)	0.307 38 (90)	−0.138 89 (78)	0.270 97 (75)	4.6 (4)
C(37)	0.508 74 (92)	−0.229 84 (72)	0.373 09 (83)	4.3 (4)
C(38)	0.472 67 (93)	−0.268 91 (83)	0.440 39 (79)	4.8 (4)
C(39)	0.425 36 (77)	−0.102 14 (63)	0.399 03 (65)	2.8 (3)
C(40)	0.502 08 (96)	−0.067 44 (81)	0.443 51 (74)	4.1 (4)
C(41)	0.091 4 (12)	−0.060 97 (93)	0.431 74 (88)	5.2 (5)
C(42)	−0.007 8 (11)	−0.057 3 (12)	0.428 15 (90)	6.2 (6)

Table III. Selected Bond Distances (Å) and Angles (deg) for the $[Fe(SePh)_4]^{2-}$ Anion in $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$

Fe–Se(1)	2.468 (2)	Se(2)–C(7)	1.899 (12)
Fe–Se(2)	2.472 (2)	Se(3)–C(13)	1.917 (12)
Fe–Se(3)	2.445 (2)	Se(4)–C(19)	1.902 (10)
Fe–Se(4)	2.456 (2)	Se···H_{av}	3.06 (19)
Se(1)–C(1)	1.908 (11)	Fe···H_{av}	3.10 (10)
Se(1)–Fe–Se(2)	105.6 (1)	Se(3)–Fe–Se(4)	106.3 (1)
Se(1)–Fe–Se(3)	114.9 (1)	Fe–Se(1)–C(1)	107.1 (4)
Se(1)–Fe–Se(4)	111.7 (1)	Fe–Se(2)–C(7)	108.7 (4)
Se(2)–Fe–Se(3)	103.6 (1)	Fe–Se(3)–C(13)	113.8 (3)
Se(2)–Fe–Se(4)	114.6 (1)	Fe–Se(4)–C(19)	113.2 (4)

and refinement of the structure. The Fe position was located by Patterson methods, and the remaining non-hydrogen atoms were found from successive difference electron density maps. The final cycle of full-matrix least-squares refinement was carried out on F_o^2 (5091 reflections and 451 variables) to give an $R(F_o^2)$ value of 0.093. Prior to this final refinement, H atoms were included at calculated positions (C–H = 0.95 Å). Methyl H atoms were located in each case in difference electron density maps and their positions idealized. Each hydrogen atom was given an isotropic themal parameter 1 Å^2 greater than the equivalent isotropic thermal parameter of the carbon atom to which it is attached. Final positional parameters of all non-hydrogen atoms are given in Table II. Anisotropic thermal parameters are given in Table IIS;[17] H atom positions are in Table IIIS;[17] structure amplitudes are in Table IVS.[17] Selected bond distances and bond angles are given in Table III. Additional metrical data are in Table VS.[17]

Results and Discussion

Synthesis. The general reaction

$$MCl_2\cdot 4H_2O + 4LiSePh \rightarrow Li_2[M(SePh)_4] + 2LiCl + 4H_2O$$

$$M = Mn, Fe, Co, Ni$$

in MeCN represents a convenient route to the simple tetraselenometalates. $Me_3SiSePh$ was used to synthesize the zinc and cadmium tetraselenophenolates,[12] and MSePh (M = Na, K) were used to make the mercury analogue.[13] The reaction of LiPh with Se in THF is a more convenient method of making the selenophenolate starting material.[14] The yields of the PPh_4^+ salts compare favorably with the standard syntheses of the analogous tetrathiophenolates.[19] The addition of excess LiSePh in the syntheses prevents the contamination of the products with the adamantoid cage complexes, $M_4(SePh)_{10}^{2-}$ (M = Mn, Fe, Co). In the thiol systems these compounds form when the SPh:M ratio is less than 4:1.[20–22] In the Ni system excess selenolate was used to prevent the formation of $[Ni(SePh)_2]_\infty$. Insoluble $[Ni(SPh)_2]_\infty$ was found to form in nickel thiophenolate systems when the SPh:Ni ratio was lower than 4:1. $[Ni(SPh)_2]_\infty$ also forms in alcoholic solution; to avoid this occurrence, MeCN was chosen as the solvent.[23]

In the solid state the PPh_4^+ salts are significantly more air stable than the NEt_4^+ salts. $[NEt_4]_2[Mn(SePh)_4]$ decomposes in seconds when exposed to air, but $[PPh_4]_2[Mn(SePh)_4]$ is stable in air for a half hour. Stability in air also increases in going from Mn to Ni; $[PPh_4]_2[Ni(SePh)_4]$ is stable in air for several hours. While in solution, all the complexes decompose rapidly when exposed to air.

Spectroscopy. In the UV–vis region the manganese and nickel complexes do not exhibit ligand-field transitions or M–Se charge-transfer bands. The $Fe(SePh)_4^{2-}$ anion absorbs at 610 nm, which corresponds to the $^5E \rightarrow {}^5T_2$ ligand-field transition of the anion. At approximately 420 nm the iron salts have a shoulder owing to charge-transfer bands. The cobalt complexes exhibit the $^4A_2 \rightarrow {}^5T_1(P)$ ligand-field transition at 693 nm. Both cobalt salts also show charge-transfer absorptions in the 430-nm region.

All four selenolate anions are paramagnetic. The $Mn(SePh)_4^{2-}$ complexes exhibit no NMR spectra. The Fe, Co, and Ni anions exhibit paramagnetically shifted ^1H NMR resonances for the phenyl hydrogen atoms. All three anions experience π-spin delocalization. Owing to their proximity to the paramagnetic metal centers, the ortho-hydrogen resonances in the Fe and Co complexes show significant broadening. The resonances of the ortho-hydrogen atoms in the Ni complexes are only slightly broadened. The meta and para peaks of all three anions are sharp and well-defined. For every anion the resonances of the meta-hydrogen atoms are shifted downfield and those of the ortho- and para-hydrogen atoms are shifted upfield.

Structure. The crystal structure of $[NEt_4][Fe(SePh)_4]\cdot MeCN$ consists of well-separated cations and anions and a solvent molecule; there are no unusual cation–anion interactions. The cations show the expected geometries. The $Fe(SePh)_4^{2-}$ anion (Figure 1) is similar to other structurally characterized $M(QPh)_4^{2-}$ anions (Q = S, Se).[2,3,12]

The $FeSe_4$ core is only slightly distorted from tetrahedral geometry. The Fe–Se distances range from 2.445 (2) to 2.472 Å

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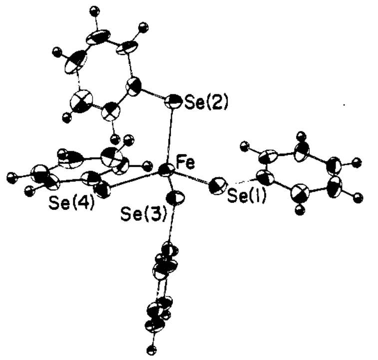

Figure 1. Structure of the $Fe(SePh)_4^{2-}$ ion with 50% probability ellipsoids shown. Hydrogen atoms are drawn artificially small.

Table IV. Dihedral Angles (deg) and Fe-Se-C Plane-Phenyl Ring Torsion Angles (deg)

[Se(1)-Fe-Se(2)]-[Se(3)-Fe-Se(4)]	84.6
[Se(1)-Fe-Se(3)]-[Se(2)-Fe-Se(4)]	90.8
[Se(1)-Fe-Se(4)]-[Se(2)-Fe-Se(3)]	96.3
[Fe-Se(1)-C(1)]-[ring 1]	16.2
[Fe-Se(2)-C(7)]-[ring 2]	12.8
[Fe-Se(3)-C(13)]-[ring 3]	5.2
[Fe-Se(4)-C(19)]-[ring 4]	9.7

and average 2.460 (12) Å; the average Se-C distance is 1.907 (8) Å. The Se-Fe-Se angles range from 103.6 (1) to 114.9 (1)°. The dihedral angles between the perpendicular Se-Fe-Se planes range from 84.6 to 96.3° (Table IV). Coucouvanis et al. proposed that the angular distortions in the MS_4 core result from interactions between the phenyl ortho-protons and the sulfur atoms.[3] Since Se would be polarized more easily than S, the chalcogen proton interaction would be expected to increase. However, the increased length of the Se-C bond over the S-C bond prevents any greater interaction. The average calculated Se···H and Fe···H distances in $[NEt_4][Fe(SePh)_4]$ are 3.06 and 3.10 Å, respectively, compared to average S···H and Fe···H distances in $[NEt_4][Fe(SPh)_4]$ of 2.96 and 2.99 Å, respectively.[3]

The $FeSe_4$ core is slightly less distorted than the $CdSe_4$ core (Se-Cd-Se angles range from 102.6 (1) to 115.0 (1)°) and significantly less distorted than the $ZnSe_4$ core (Se-Zn-Se angles range from 98.9 (1) to 119.2 (1)°).[12] In the $[PPh_4]_2[M(SPh)_4]$ (M = Fe, Zn) compounds the Fe and Zn structures have similar distortions.[3] The differences between the cores in $[NEt_4][Fe(SePh)_4]$ and $[NMe_4][Zn(SePh)_4]$ may result from a change in packing as a result of the change in cations. Evidence of packing force effects is found in the torsion angles between the M-Se-C planes and their respective phenyl rings. These angles should be 0° owing to π-interactions between the Se lone-pair electrons and the aromatic phenyl ring, but they range from 5.5 to 16.5°.

The differences between the average Fe-S and Fe-Se distances in the $Fe(QPh)_4^{2-}$ (Q = S, Se) anions is slightly over 0.1 Å. The differences between the average S-C and Se-C bonds is 0.14 Å. In the NEt_4^+ salts the average Fe-Q-C angles are smaller for Q = Se than for Q = S.[3] A similar effect is seen for the Zn and Cd species. The higher polarizability of the M-Se bond over the M-S bond is the probable cause of this effect.[12]

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Supplementary Material Available: Complete crystallographic details (Table IS), anisotropic thermal parameters (Table IIS), hydrogen atom positions (Table IIIS), and additional bond lengths and angles (Table VS) for $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$ (5 pages); structure amplitudes (Table IVS) (21 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Tetrabutylammonium (2-Aminobenzenethiolato(2−)-*S*,*N*)tetrachlorotechnetate(V)

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The reaction of $(n\text{-}Bu_4N)[TcO(abt)_2]$ (abt = 2-aminobenzenethiolato(2−)-*N*,*S*) with 12 M HCl in methanol gives the blue Tc(V) compound $(n\text{-}Bu_4N)[TcCl_4(abt)]$. Magnetic susceptibility measurements reveal this compound to have two unpaired electrons. This indicates that the ligand, with one hydrogen per nitrogen, is doubly anionic, establishing the metal oxidation state of +5. Infrared data show a single N-H stretching frequency at 3254 cm^{-1}. An X-ray crystal structure of $(n\text{-}Bu_4N)[TcCl_4(abt)]$ is also reported. Crystal data for $C_{22}H_{41}N_2SCl_4Tc$: triclinic, space group $P\bar{1}$ (No. 2), a = 11.5154 (8) Å, b = 13.6200 (9) Å, c = 10.5547 (8) Å, α = 95.205 (5)°, β = 116.970 (7)°, γ = 76.198 (4)°, and V = 1432.5 (4) $Å^3$ to give Z = 2 for D_{calc} = 1.401 g/cm^3. The structure solution and refinement based on 6893 reflections converged at R = 0.047 and R_w = 0.048.

Introduction

The technetium(V) oxidation state is dominated by complexes that contain at least one multiply bonded oxygen or nitrogen attached to the Tc(V) center. Many of these technetium-oxygen compounds are formed by the two-electron reduction of pertechnetate in the presence of ligands such as thiolates and thiocarboxylates, which tend to stabilize this oxidation state. Others are formed by the protonation of the oxygen and the loss of water to maintain the +5 oxidation state. Only a few Tc(V) compounds, such as TcF_5, $KTcF_6$, and $[Tc(diars)_2Cl_4]^+$, do not contain a technetium terminal oxo or a technetium nitrido core.[1]

We have obtained a novel Tc(V) complex lacking a Tc═O group during our investigations into the chemistry of technetium with the noninnocent ligand abt [abt = 2-aminobenzenethiolato(2−)-*N*,*S*, $(C_6H_4NHS^{2-}$; Habt = $(C_6H_4NH_2S)^-$; H_2abt = $(C_6H_4NH_2SH)^0$; H_3abt = $(C_6H_4NH_3SH)^+$]. When the red Tc(V) compound $(n\text{-}Bu_4N)[TcO(abt)_2]$ is reacted with concentrated HCl in the presence of methanol, the blue complex $(n\text{-}Bu_4N)[TcCl_4(abt)]$ can be isolated. The extended reaction gives the green complex $(H_3abt)[TcCl_6]$ as a minor product. The synthesis and characterization of $(n\text{-}Bu_4N)[TcCl_4(abt)]$ are described.

Experimental Section

Caution! Technetium-99 is a weak β^--emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12 × 10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[2]

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