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Spirocyclic Sulfur and Selenium Ligands as Molecular Rigid Rods in Coordination of Transition Metal Centers

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A set of analogous chalcogen-containing spirocycles, 2,6-dithiaspiro[3.3]heptane, 2,6-diselenaspiro[3.3]heptane, and 2-thia-6-selenaspiro[3.3]heptane [$E_2C_5H_8$, E = S (**1**), Se (**2**), and S/Se (**3**)], has been prepared and fully characterized by spectroscopic methods and by X-ray diffraction. The structural characterization of **2** was presented by us earlier, while the crystal structures of **1** and **3** are reported here for the first time. Molecules **1**–**3** are built around the central tetrahedral carbon atom and therefore are nonplanar. The E···E separation ranges from 4.690(1) Å in **1** to 4.906(1) Å in **2**. Molecule **3** has statistically mixed positions of sulfur and selenium atoms in the solid state with all geometric characteristics being intermediate between those of **1** and **2**. Compounds **2** and **3** have been tested as molecular rigid rod ligands in coordination reactions with transition metal complexes such as Cu(hfac)$_2$ (**4**), *cis*-Co(hfac)$_2$·2H$_2$O (**5**), and *cis*-Ni(hfac)$_2$·2H$_2$O (**6**) (hfac = hexafluoroacetylacetonate). Several coordination products built of two building blocks, M(hfac)$_2$ (M = Cu, Co, and Ni) and $Se_2C_5H_8$ (**2**), have been prepared in crystalline form and structurally characterized. The copper-based product (**7**) is comprised of the oligomeric units {[Cu(hfac)$_2$]$_3$·2μ^2-$Se_2C_5H_8$-*Se*,*Se′*} built on the axial Cu···Se interactions averaged at 2.909 Å. These units are further assembled into 1D polymeric chains via intermolecular Cu···F contacts at 2.829 Å. The $SSeC_5H_8$ (**3**) ligand was also used in the reaction with Cu(hfac)$_2$ to afford an analogue of **7**, namely {[Cu(hfac)$_2$]$_3$·2μ^2-$SSeC_5H_8$-*S*,*Se*} (**8**). Complex **8** exhibits statistically mixed positions of the donor sulfur and selenium atoms to give an average axial Cu···S/Se contact at 2.892 Å. In contrast to the copper complexes of composition 3:2, the stoichiometries of the isolated cobalt and nickel products are 1:1, [M(hfac)$_2$·$Se_2C_5H_8$] (M = Co (**9**) and Ni (**10**)). Complexes **9** and **10** exhibit 1D polymer structures having alternating metal units *cis*-M(hfac)$_2$ and ligands **2** with intermolecuar M···Se separations of 2.6046(8) and 2.5523(16) Å, respectively. In all products **7**–**10** the initial cis or trans geometry of M(hfac)$_2$ complexes is preserved and the spiro[3.3]heptane ligands act as bidentate linkers bridging transition metal centers via both donor ends. The magnetic properties of this series of new Cu^{II}, Co^{II}, and Ni^{II} complexes have been tested by variable-temperature magnetic susceptibility measurements.

Introduction

The design of new materials from molecular building blocks is a very rapidly developing field of chemical research driven by a variety of valuable applications.[1] The general synthetic strategy of assembling such materials is based on coordination of complementary metal units by various organic spacers having different structures and properties.[2] The geometry of the building blocks, in general, defines the structural organization of the complex system. Organic ligands that are capable of transmitting electronic and/or magnetic interactions from separated paramagnetic metal centers through the chain or network have attracted additional attention.[3] In this context, a set of rigid polyspiro ligands having a σ-bonded framework (Chart 1) is of special interest for self-assembling reactions since sulfur-containing molecules exhibited substantial through-bond electronic interac-

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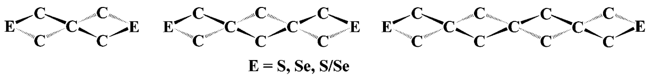
Chart 1



tions in mixed-valent metal complexes even when metal centers were remote.[4]

Despite these interesting properties, studies of this class of ligands as organic spacers in transmitting electronic interactions have been limited to the mixed valence ruthenium complexes only.[4] A series of complexes with metal carbonyls should be mentioned here,[5] but their characterization was rather limited. Moreover, only sulfur-containing systems, e.g. 2,6-dithiaspiro[3.3]heptane (**1**) and related polyspirocycles (Chart 1), have been examined in complexation and electron-transfer reactions.[4,5] Properties of the Se or mixed S/Se analogues, namely 2,6-diselenaspiro[3.3]heptane (**2**) and 2-thia-6-selenaspiro[3.3]heptane (**3**), have not been studied. The first synthesis of **2**, $Se_2C_5H_8$, was reported in 1937;[6] however, its crystal structure and reactivity have not been previously described. We recently reported the structural characterization of **2** and its first rhodium(II) complex.[7] We now examine the reactivity and the donor properties of spirocyclic selenium and mixed sulfur−selenium ligands **2** and **3** in coordination reactions with the 3d transition metals. To test their role as molecular rigid spacers in transmitting magnetic interactions between the individual paramagnetic centers, a series of hexafluoroacetylacetonate complexes, $M(hfac)_2$ (M = Cu, Co, and Ni), has been selected for this study. The later complexes have been used in the synthesis of molecular magnetic materials with various organic radical spacers.[3a,b] Herein, a family of new hybrid coordination products has been isolated and fully characterized by spectroscopic methods, magnetic susceptibility measurements, and single-crystal X-ray crystallography.

Experimental Section

General Procedures. All manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk techniques. Elemental analyses were performed by Canadian Microanalytical Service, Delta, BC, Canada. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets. NMR spectra were determined on a Varian Gemini NMR spectrometer at 300 MHz for proton and 75.1 MHz for carbon. Mass spectra were obtained on a Hewlett-Packard HP 5989/5970 GC-MS instrument at 70 eV. Synthesis of $S_2C_5H_8$ (**1**) was based on literature procedure.[8] The anhydrous $Cu(hfac)_2$ complex was prepared according to the recent report.[9] Syntheses of the aqua adducts, *cis*-$Co(hfac)_2(H_2O)_2$[10] and *cis*-$Ni(hfac)_2(H_2O)_2$,[11] were based on the known literature procedures.

2,6-Dithiaspiro[3.3]heptane (1). To a solution of 1,3-dibromo-2,2-bis(bromomethyl)propane (0.78 g, 2 mmol) in ethanol (15 mL) was added $Na_2S{\cdot}9H_2O$ (1.2 g, 5 mmol) dissolved in water (2.5 mL). The mixture was refluxed for 10 h. The solvent was removed in vacuo, the residue was extracted with chloroform, the extracts were dried ($MgSO_4$) and concentrated in vacuo, and the residue was chromatographed on silica gel (3:1 hexane−dichloromethane) to give **1** as a colorless solid. Yield: 0.10 g, 38%. IR (KBr, cm^{-1}): 2967 m, 2925 s, 2842 w, 1426 m, 1171 s, 1091 m, 990 w. ^1H NMR (300 MHz, $CDCl_3$): δ 3.26 (s, 8H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 39.8 (CH_2), 52.2 (C). EI-MS: *m/z* 132 (M^+). Mp: 31(1) °C.

2,6-Diselenaspiro[3.3]heptane (2). A solution of SuperHydride ($Li(C_2H_5)_3BH$) in THF (1.0 M, 20 mL, 20 mmol) was added all at once to selenium powder (0.80 g, 10 mmol) with vigorous stirring. Gas evolution occurred and ceased within 2 min. The solution gradually turned to a heterogeneous milky white suspension. Additional THF (10 mL) was added, the suspension was stirred for 20 min, and then a solution of 1,3-dibromo-2,2-bis(bromomethyl)propane (1.94 g, 5 mmol) in THF (10 mL) was added. The reaction mixture was refluxed for 4 h and stirred at room temperature for additional 12 h. The solvent was removed in vacuo, and the residue was chromatographed on neutral alumina (1:2 chloroform−hexane) to give **2** as a colorless solid. Yield: 0.80 g, 70%. IR (KBr, cm^{-1}): 2985 m, 2925 s, 2819 w, 1429 sh, 1418 m, 1243 w, 1220 w, 1207 w, 1134 s, 1125 s, 1055 w, 1036 w, 966 w, 939 m, 874 m, 797 w, 780 w, 719 m. ^1H NMR (300 MHz, $CDCl_3$,

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22 °C): δ 3.14 (s, 8H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): δ 28.7 (CH_2), 54.4 (C). EI-MS: *m*/*z* 228 (M^+, ^{80}Se). Mp: 68(1) °C.

2-Thia-6-selenaspiro[3.3]heptane (3). The synthesis was accomplished in three steps:

(1) To a solution of $C(CH_2Br)_4$ (3.88 g, 10 mmol) in THF (15 mL) was added potassium thioacetate (1.14 g, 10 mmol) under an argon atmosphere. The reaction mixture was stirred at reflux for 30 h. The precipitates were filtered off, the solvent was concentrated, and the residue was chromatographed on silica gel (CH_2Cl_2) to give thioacetic acid (2,2-bis(bromomethyl)-3-bromopropyl) ester, a colorless solid. Yield: 2.05 g, 54%.

(2) Sodium (0.14 g, 6 mmol) was added to methanol (10 mL) at room temperature to form a $NaOCH_3$ solution. To the solution cooled at 0 °C, thioacetic acid (2,2-bis(bromomethyl)-3-bromopropyl) ester (1.53 g, 4 mmol) was added, and the mixture was stirred at 0 °C for 2 h. Methanol was removed in vacuo, and the residue was chromatographed (hexane) to give 3,3-bis(bromomethyl)thietane, a colorless solid. Yield: 0.85 g, 81%.

(3) To Li_2Se in THF (1 mmol) was added 3,3-bis(bromomethyl)thietane (0.26 g, 1 mmol). The reaction mixture was stirred at reflux overnight. The solvent was concentrated, and the residue was chromatographed on neutral alumina (CH_2Cl_2) to give **3** as colorless crystals. Yield: 0.11 g, 60%. IR (KBr, cm^{-1}): 2930 s, 2842 w, 1423 s, 1238 s, 1170 s, 1131 s, 984 w. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.16 (s, 4H), 3.18 (s, 4H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 27.3 (CH_2Se), 41.1 (CH_2S), 53.3 (C). Mp: 45(1) °C.

[Cu(hfac)$_2$]$_3$·2Se$_2$C$_5$H$_8$ (7). Anhydrous $Cu(hfac)_2$ (0.015 g, 0.03 mmol) was loaded in a glass ampule of 9 mm diameter and 50 mm length, while $Se_2C_5H_8$ (0.007 g, 0.03 mmol) was placed in an ampule of a smaller diameter and length (3 × 10 mm). The latter was inserted inside the larger ampule to prevent direct contact of two reagents in the solid state and allow them to mix only in the gas phase. The outer ampule was sealed under vacuum and placed in a tube furnace at 35 °C for 10 h. Block-shaped green crystals of **7** grew in the end of the smaller ampule. Yield: 0.005 g, 52%. Anal. Calcd for $Cu_3C_{40}H_{22}O_{12}F_{36}Se_4$: C, 25.5; H, 1.20. Found: C, 23.8; H, 1.31. IR (KBr, cm^{-1}): 2963 w, 1648 m, 1538 m, 1474 m, 1259 s, 1208 s, 1147 s, 1105 m, 1020 m, 805 m, 680 m.

[Cu(hfac)$_2$]$_3$·2SeSC$_5$H$_8$ (8). Anhydrous $Cu(hfac)_2$ (0.015 g, 0.03 mmol) was loaded in a glass ampule (9 × 50 mm), while $SeSC_5H_8$ (0.006 g, 0.03 mmol) was placed in a smaller ampule (3 × 10 mm). The latter was inserted inside the larger ampule to prevent direct contact of two reagents in the solid state. The outer ampule was sealed under vacuum and placed in a tube furnace at 35 °C for 10 h. Block-shaped green crystals of **8** grew in the end of the smaller ampule. Yield: 0.005 g, 58%. Anal. Calcd for $Cu_3C_{40}H_{22}O_{12}F_{36}Se_2S_2$: C, 26.8; H, 1.26. Found: C, 26.2; H, 0.89. IR (KBr, cm^{-1}): 3134 w, 3062 w, 2960 w, 1646 m, 1618 m, 1560 w, 1538 m, 1482 m, 1260 s, 1208 s, 1146 s, 1106 w, 810 w, 674 w.

[*cis*-Co(hfac)$_2$·Se$_2$C$_5$H$_8$] (9). *cis*-$Co(hfac)_2$·$2H_2O$ (0.050 g, 0.10 mmol) and $Se_2C_5H_8$ (0.025 g, 0.11 mmol) were dissolved in a mixture of ether (1 mL) and benzene (10 mL) to give an orange solution. The mixture was then refluxed overnight to yield a brown solution. The solution was evaporated to dryness to afford a brown solid. Yield: 0.058 g, 83%. Crystals were obtained by sublimation of the above crude powder. Typically ca. 0.01 g of the brown powder was loaded in a glass ampule that was sealed under vacuum. The ampule was then placed in a tube furnace at 80 °C for 30 h. Needle-shaped brown crystals of **9** grew in the cold end of the ampule. Anal. Calcd for $CoC_{15}H_{10}O_4F_{12}Se_2$: C, 25.8; H, 1.44. Found: C, 26.1; H, 1.49. IR (KBr, cm^{-1}): 2963 w, 1636 s, 1532 m, 1473 m, 1258 s, 1206 s, 1143 s, 1093 m, 804 m, 668 m.

[*cis*-Ni(hfac)$_2$·Se$_2$C$_5$H$_8$] (10). *cis*-$Ni(hfac)_2$·$2H_2O$ (0.050 g, 0.10 mmol) and $Se_2C_5H_8$ (0.025 g, 0.11 mmol) were dissolved in a mixture of ether (1 mL) and benzene (10 mL) to give a green solution. The mixture was then refluxed overnight without a noticeable color change. The green solution was evaporated to dryness to afford a light-green solid. Yield: 0.062 g, 89%. Crystals were obtained by sublimation of the above crude powder. Typically ca. 0.01 g of the green powder was loaded in a glass ampule and the ampule sealed under vacuum and placed in a tube furnace at 105 °C for 72 h. Needle-shaped green crystals of **10** grew in the cold end of the ampule. Anal. Calcd for $NiC_{15}H_{10}O_4F_{12}Se_2$: C, 25.8; H, 1.44. Found: C, 25.9; H, 1.42. IR (KBr, cm^{-1}): 2963 w, 1648 m, 1525 w, 1477 m, 1260 s, 1199 m, 1146 s, 1097 s, 1023 m, 798 m, 672 w.

X-ray Crystallographic Procedures. The X-ray data sets were collected for **1**, **3**, and **7**−**10** at −100 °C (Bruker KRYO-FLEX) on a Bruker APEX CCD X-ray diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The frames were integrated with the Bruker SAINT software package,[12] and the data were corrected for absorption using the program SADABS.[13] The structures were solved and refined using the Bruker SHELXTL software.[14]

The colorless block crystal of $S_2C_5H_8$ (**1**) (0.25 × 0.15 × 0.05 mm) was found to be monoclinic, space group $P2_1/c$, with $a = 5.8013(4)$, $b = 19.2532(12)$, $c = 5.8183(4)$ Å, $\beta = 109.7090(10)°$, $V = 611.80(7)$ Å^3, and $Z = 4$. A total of 5251 reflections were collected in the range $2.12 \leq \theta \leq 28.16°$. All atoms were refined anisotropically. All hydrogen atoms were found in difference Fourier maps and were refined independently. The final refinement cycle was based on 1437 reflections, 96 parameters, and 0 restraints. The final R1 value was 0.0253 (wR2 = 0.0680) for 1355 reflections [$I > 2\sigma(I)$]. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.269 and −0.342 e/Å^3, with a goodness-of-fit value of 1.086.

The colorless block crystal of $SeSC_5H_8$ (**3**) (0.51 × 0.16 × 0.16 mm) was found to be monoclinic, space group $P2_1/c$, with $a = 5.8538(5)$, $b = 19.4846(18)$, $c = 5.8579(5)$ Å, $\beta = 109.1230(10)°$, $V = 631.28(10)$ Å^3, and $Z = 4$. A total of 5332 reflections were collected in the range $2.09 \leq \theta \leq 28.29°$. All atoms were refined anisotropically. All hydrogen atoms were found in difference Fourier maps and were refined independently. The sulfur and selenium atoms were found to be statistically mixed with the occupancies of 40:60%. The final refinement cycle was based on 1486 reflections, 116 parameters, and 0 restraints. The final R1 value was 0.0186 (wR2 = 0.0512) for 1417 reflections [$I > 2\sigma(I)$]. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.426 and −0.391 e/Å^3, with a goodness-of-fit value of 1.064.

The green block of $\{[Cu(hfac)_2]_3\cdot(Se_2C_5H_8)_2\}$ (**7**) (0.14 × 0.08 × 0.06 mm) was found to be triclinic, space group $P\bar{1}$, with $a = 11.1179(9)$, $b = 11.5052(10)$, $c = 12.3911(11)$ Å, $a = 90.6540(10)$, $\beta = 99.2800(10)$, $\gamma = 110.5090(10)°$, $V = 1461.1(2)$ Å^3, and $Z = 1$. A total of 12 366 reflections were collected in the range $1.67 \leq \theta \leq 28.26°$. All atoms of the $Cu(hfac)_2$ unit were refined anisotropically, except for one disordered CF_3 group for which disorder was modeled over three rotational orientations. The two orientations of the $Se_2C_5H_8$ ligands were found. This disorder affected the four outlying carbon atoms but had little effect on the positions of the selenium atoms and the central carbon atom. The

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(12) *SAINT*, version 6.02; Bruker AXS, Inc.: Madison, WI, 2001.

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(14) Sheldrick, G. M. *SHELXL-97*; University of Gottingen: Gottingen, Germany, 1997.

hydrogen atoms of the $Se_2C_5H_8$ ligands were included in the structure factor calculations at idealized positions, while the H atoms of the hfac units were found in difference Fourier maps and refined independently. The final refinement cycle was based on 6431 reflections, 483 parameters, and 106 restraints. The final R1 value was 0.0523 (wR2 = 0.1198) for 4604 reflections [$I > 2\sigma(I)$]. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.077 and −0.766 e/Å^3, with a goodness-of-fit value of 1.005.

The green block of {$[Cu(hfac)_2]_3 \cdot (SeSC_5H_8)_2$} (**8**) (0.17 × 0.11 × 0.09 mm) was found to be triclinic, space group $P\bar{1}$, with $a = 11.2238(15)$, $b = 11.4147(15)$, $c = 12.4732(17)$ Å, $\alpha = 91.251(2)$, $\beta = 98.773(2)$, $\gamma = 110.096(2)°$, $V = 1478.4(3)$ Å^3, and $Z = 1$. A total of 12 531 reflections were collected in the range $1.66 \le \theta \le 28.22°$. All atoms of the $Cu(hfac)_2$ unit were refined anisotropically, except for the disordered CF_3 groups for which disorder was modeled over two or three rotational orientations. The sulfur and selenium atoms were found to be statistically mixed with the occupancies of 45:55%. The two orientations of the $SeSC_5H_8$ ligand were found. This disorder affected only four carbon atoms but had little effect on the positions of the sulfur, selenium, and the central carbon atom. The hydrogen atoms of the $SSeC_5H_8$ ligands were included in the structure factor calculations at idealized positions, while the H atoms of the hfac units were found in difference Fourier maps and refined independently. The final refinement cycle was based on 6499 reflections, 448 parameters, and 30 restraints. The final R1 value was 0.0625 (wR2 = 0.1660) for 4809 reflections [$I > 2\sigma(I)$]. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.397 and −0.878 e/Å^3, with a goodness-of-fit value of 1.049.

The brown needle of [*cis*-$Co(hfac)_2 \cdot Se_2C_5H_8$] (**9**) (0.70 × 0.03 × 0.02 mm) was found to be monoclinic, space group $P2_1/n$, with $a = 7.5777(9)$, $b = 18.924(2)$, $c = 15.8309(18)$ Å, $\beta = 91.527(2)°$, $V = 2269.4(5)$ Å^3, and $Z = 4$. A total of 19 194 reflections were collected in the range $1.68 \le \theta \le 28.28°$. All atoms were refined anisotropically except for the disordered CF_3 groups, for which disorder was modeled over two or three rotational orientations. All hydrogen atoms were included in the structure factor calculations at idealized positions. The final refinement cycle was based on 5235 reflections, 307 parameters, and 36 restraints. The final R1 value was 0.0538 (wR2 = 0.1352) for 4093 reflections [$I > 2\sigma(I)$]. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.068 and −0.792 e/Å^3, with a goodness-of-fit value of 1.050.

The green needle of [*cis*-$Ni(hfac)_2 \cdot Se_2C_5H_8$] (**10**) (0.38 × 0.06 × 0.03 mm) was found to be monoclinic, space group $P2_1/n$, with $a = 7.5479(10)$, $b = 18.739(3)$, $c = 15.885(2)$ Å, $\beta = 90.667(2)°$, $V = 2246.7(5)$ Å^3, and $Z = 4$. A total of 18 741 reflections were collected in the range $1.68 \le \theta \le 28.32°$. All atoms were refined anisotropically except for the disordered CF_3 groups, which were refined using two orientations. All hydrogen atoms were included in the structure factor calculations at idealized positions. The final refinement cycle was based on 5259 reflections, 295 parameters, and 24 restraints. The final R1 value was 0.0865 (wR2 = 0.2186) for 4562 reflections [$I > 2\sigma(I)$]. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.479 and −1.211 e/Å^3, with a goodness-of-fit value of 1.127. Crystallographic data and X-ray experimental conditions for **1**, **3**, and **7**−**10** are listed in Tables 1 and 2. Selected distances and angles are given in Tables 3 and 4.

Magnetic Measurements. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. Measurements were performed on finely ground crystalline samples of **5** (23.1 mg), **7** (18.4 mg), **9** (29.7 mg), and **10** (4.2 mg) in the temperature range 1.8−300 K and with fields up to 7 T. The magnetic data were corrected for the sample holder and the diamagnetic contribution from Pascal's constants.[15]

Table 1. Crystallographic Data and Structural Refinement Parameters for $S_2C_5H_8$ (**1**) and $SeSC_5H_8$ (**3**)

	1	**3**
formula	$S_2C_5H_8$	$SeSC_5H_8$
fw	132.23	179.13
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	5.8013(4)	5.8538(5)
b (Å)	19.2532(12)	19.4846(18)
c (Å)	5.8183(4)	5.8579(5)
β (deg)	109.7090(10)	109.1230(10)
V (Å^3)	611.80(7)	631.28(10)
Z	4	4
T (K)	173(2)	173(2)
λ (Å)	0.710 73	0.710 73
D_{calc} (g·cm^{-3})	1.436	1.885
μ (mm^{-1})	0.737	6.149
data/restraints/params	1437/0/96	1486/0/116
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0253, 0.0680	0.0186, 0.0512
R1,[a] wR2[b] (all data)	0.0266, 0.0691	0.0197, 0.0516
GOF[c] on F^2	1.086	1.064

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$.

Results and Discussion

As a part of our broad coordination chemistry study of selenium-containing molecules of natural or synthetic origin,[7,16] in this work we study the structures, properties, and reactivity of a set of the spirocyclic ligands, $E_2C_5H_8$ (E = S (**1**), Se (**2**), S/Se (**3**)). Molecules **1**−**3** are the smallest in the series of polyspiro bidentate ligands (Chart 1) that are known to provide different metal-to-metal separations and substantial through-bond interactions in metal complexes. Since only the disulfur molecule (**1**) has been previously studied,[4,5] we have concentrated here on 2,6-diselenaspiro[3.3]heptane (**2**) but also tested the new mixed sulfur−selenium analogue, 2-thia-6-selenaspiro[3.3]heptane (**3**).

Our synthesis of **1** is based on a published procedure.[8] The synthesis of 2,6-diselenaspiro[3.3]heptane (**2**) dates back to 1937.[6] We have developed a different approach to synthesize **2** and the previously unknown mixed chalcogen analogue **3**. Compounds **1**−**3** were prepared in good yield and fully characterized. They were isolated as crystalline colorless solids at room temperature and have melting points of 31(1), 68(1), and 45(1) °C for **1**−**3**, respectively. These molecules are all volatile, and are soluble in common organic solvents including hexanes. Such properties make them excellent ligands for studying coordination reactions using both the gas phase and solution approaches.

We recently reported an X-ray diffraction study of **2**,[7] while the structures of the disulfur (**1**) and the mixed sulfur−

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(15) Boudreaux, E. A.; Mulay, L. N. *Theory and Applications of Molecular Paramagnetism*; John Wiley & Sons: New York, 1976.

(16) (a) Dikarev, E. V.; Petrukhina, M. A.; Li, X.; Block, E. *Inorg. Chem.* **2003**, *42*, 1966−1972. (b) Dikarev, E. V.; Becker, R. Y.; Block, E.; Shan, Z.; Haltiwanger, R. C.; Petrukhina, M. A. *Inorg. Chem.* **2003**, *42*, 7098−7105.

Table 2. Crystallographic Data and Structural Refinement Parameters for {[Cu(hfac)$_2$]$_3$·(Se$_2$C$_5$H$_8$)$_2$} (**7**), {[Cu(hfac)$_2$]$_3$·(2SeSC$_5$H$_8$)$_2$} (**8**), [*cis*-Co(hfac)$_2$·Se$_2$C$_5$H$_8$] (**9**), and [*cis*-Ni(hfac)$_2$·Se$_2$C$_5$H$_8$] (**10**)

	7	**8**	**9**	**10**
formula	$Cu_3Se_4O_{12}F_{36}C_{40}H_{22}$	$Cu_3Se_2S_2O_{12}F_{36}C_{40}H_{22}$	$CoSe_2O_4F_{12}C_{15}H_{10}$	$NiSe_2O_4F_{12}C_{15}H_{10}$
fw	1885.04	1791.24	699.08	698.83
cryst system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	11.1179(9)	11.2238(15)	7.5777(9)	7.5479(10)
b (Å)	11.5052(10)	11.4147(15)	18.924(2)	18.739(3)
c (Å)	12.3911(11)	12.4732(17)	15.8309(18)	15.885(2)
α (deg)	90.6540(10)	91.251(2)		
β (deg)	99.2800(10)	98.773(2)	91.527(2)	90.667(2)
γ (deg)	110.5090(10)	110.096(2)		
V (Å^3)	1461.1(2)	1478.4(3)	2269.4(5)	2246.7(5)
Z	1	1	4	4
T (K)	173(2)	173(2)	173(2)	173(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc} (g·cm^{-3})	2.142	2.005	2.046	2.173
μ (mm^{-1})	3.743	2.539	4.082	4.229
data/restraints/params	6431/106/483	6499/30/448	5235/36/307	5259/24/295
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0523, 0.1198	0.0625, 0.1660	0.0538, 0.1352	0.0865, 0.2186
R1,[a] wR2[b] (all data)	0.0798, 0.1329	0.0845, 0.1828	0.0702, 0.1453	0.0942, 0.2214
GOF[c] on F^2	1.005	1.049	1.050	1.127

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$.

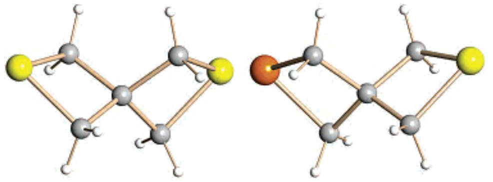


Figure 1. Ball-and-stick representations of the structures of **1** and **3**. Atomic color scheme: S = yellow; Se = orange; C = gray; H = light gray.

Table 3. Selected Distances (Å) and Angles (deg) in $E_2C_5H_8$ (**1**−**3**)

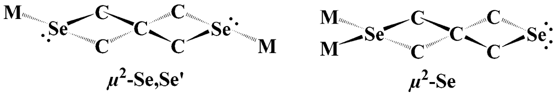
	1	**2**[7]	**3**[a]
E−C$_{av}$	1.835(13)	1.978(3)	1.908(6)
C−C$_{av}$	1.536(16)	1.537(4)	1.535(15)
E···E	4.690(1)	4.906(1)	4.792(6)
C−E−C$_{av}$	76.65(6)	72.03(11)	74.12(11)
C−C−C	96.1(1)−121.1(1)	98.1(2)−119.1(2)	97.0(1)−120.0(1)

[a] Average for the two mixed positions.

selenium (**3**) analogues remained unknown. Therefore, prior to coordination reactions, we obtained crystals of **1** and **3** by deposition from the gas phase and determined their molecular structures using single-crystal X-ray diffraction (Figure 1). This structural study has provided us with a unique series of three analogous molecules **1**−**3** to examine the effect of the replacement of sulfur by selenium on their geometry (Table 3) and reactivity.

Spirocyclic molecules **1**−**3** built around the tetrahedral carbon atom are nonplanar with the angles around the central C atom ranging from 96.1(1) to 121.1(1)° in **1** and from 98.1(2) to 119.1(2)° in **2**. The E−C distances are averaged to 1.835 Å in **1** and to 1.978(3) Å in **2**, while the average C−C distances are very close in **1** and **2** (Table 3). The C−E−C angles at the donor atoms are acute, averaged to 76.65(6)° in **1** versus 72.03(11)° in **2**. The differences in geometrical parameters of molecules **1** and **2** are in accord with the increased atomic radii of selenium compared with that of sulfur.[17]

Chart 2



For the molecule **3**, the spectroscopic methods unambiguously confirm its mixed sulfur−selenium SSeC$_5$H$_8$ nature (versus **3** being a mixture of **1** and **2**) in solution. However, in the solid state **3** crystallizes with a statistical distribution of sulfur and selenium atoms in every position that was refined at the 40:60% occupancies. As seen from the comparison of structures **1** and **2**, their geometries are very close and that probably makes it possible for the sulfur and selenium ends of **3** to alternate in the solid state. All geometric characteristics of the mixed sulfur−selenium molecule **3** are intermediate between those of **1** and **2**. For instance, an estimated separation between the two donor ends gradually increases along the series **1**−**3**−**2**.

The rigid bidentate ligands **1**−**3** have two lone electron pairs at each donor atom and therefore may exhibit two different bridging modes (Chart 2). Both should result in the formation of polymeric structures with metal complexes having two potential coordination sites. The μ^2-Se coordination of the monocyclic SeC$_2$H$_4$SiMe$_2$ ligand by two rhodium(II) centers has been observed in the polymeric complex [Rh$_2$(O$_2$CCF$_3$)$_4$·SeC$_2$H$_4$SiMe$_2$],[18] while the μ^2-Se,Se′-coordination has been found in [Rh$_2$(O$_2$CCH$_3$)$_4$·Se$_2$C$_5$H$_8$].[7]

From a system containing the bidentate diselenium ligand **2** and the copper(II) hexafluoroacetylacetonate complex Cu(hfac)$_2$, having two trans-oriented open Lewis acidic sites,[9] a new hybrid coordination product **7** has been prepared in the form of thermally stable but moisture-sensitive crystals. Spectroscopic methods indicated the presence of both building groups; a 3:2 composition of Cu(hfac)$_2$−diselenium ligand was confirmed by elemental analysis. The solid-state

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(17) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441−451.
(18) Block, E.; Dikarev, E. V. Unpublished results.

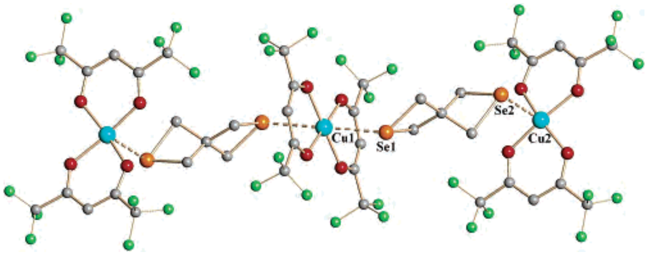

Figure 2. Ball-and-stick representation of the trinuclear copper unit in **7**. Atomic color scheme: Cu = blue; Se = orange; O = red; C = gray; F = green. H atoms are omitted for clarity.

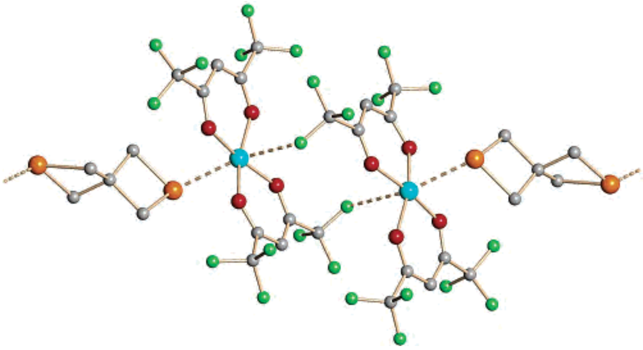

Figure 3. Fragment of packing of oligomeric units showing Cu•••F interactions in **7**. Atomic color scheme is the same as in Figure 2.

structure of **7** is comprised of the hybrid oligomeric units $\{[Cu(hfac)_2]_3{\cdot}2Se_2C_5H_8\}$ built on the axial Cu•••Se interactions (Figure 2). Within the centrosymmetric tricopper unit there are two crystallographically independent copper centers: the central Cu(1) atom is in a distorted octahedral CuO_4Se_2 environment, while the end Cu(2) atoms show a square pyramidal CuO_4Se arrangement. The Cu(1) atom has two symmetry related long metal−selenium interactions at 3.015(6) Å compared to the shorter Cu(2)•••Se(2) contact at 2.7873(9) Å. These intermolecular contacts are shorter than the sum of van der Waals radii for copper and selenium (3.3 Å)[17] and comparable to the Cu^{II}−Se distances in the selenocyanato complexes.[19] The initial trans-arrangement of the hexafluoroacetylacetonate ligands in **4** is preserved in coordination product **7**. The tricopper units are further assembled into 1D polymeric chains via the open Cu(2) ends which show intermolecular Cu•••F contacts at 2.829 Å with the neighboring oligomers (Figure 3). The latter distance is within the sum of van der Waals radii for the copper and fluorine atoms (2.87 Å).[17] These additional interactions complete a distorted octahedral CuO_4SeF environment around the Cu(2) atoms.

From the reaction of the bidentate mixed donor ligand **3** with $Cu(hfac)_2$, a new coordination product, $\{[Cu(hfac)_2]_3{\cdot}2SSeC_5H_8\}$ (**8**), was isolated. It was shown to be isostructural with the analogous copper complex **7**. Due to the fact that the different S and Se donor ends are statistically mixed in the structure of **8** (45:55), only averaged characteristics can be reported. Nevertheless, a comparison of geometrical parameters of **7** and **8** is interesting (Table 4). Average axial Cu•••S/Se contacts at 2.892 Å are slightly shorter in **8** versus **7** (2.909 Å). The copper-to-copper separation through the ligand is estimated at 8.8617(8) and 8.7679(9) Å in **7** and **8**, respectively.

In contrast to the copper complex **4** that has a trans-arrangement of hfac ligands and can be prepared[9] in the anhydrous $Cu(hfac)_2$ form, the starting cobalt and nickel complexes were of a cis-type and contained coordinated H_2O molecules, namely [*cis*-$M(hfac)_2{\cdot}2H_2O$] (M = Co (**5**), Ni (**6**)). All attempts to remove the axially bound H_2O ligands using an approach similar to that used by Maverick[9] for the preparation the anhydrous copper complex were unsuccessful. Sublimation of the crude cobalt product after 3 months of drying in a desiccator afforded crystals of the [*cis*-$Co(hfac)_2{\cdot}2H_2O$] (**5**) in high yield.[20] Therefore, substitution reactions of labile water molecules by the diselenium ligand **2** in the coordination sphere of [*cis*-$M(hfac)_2{\cdot}2H_2O$] were performed in solution to access the title products of cobalt and nickel. Both complexes were obtained in good yield as relatively air-stable solids. The presence of both building blocks in the hybrid products was confirmed by IR spectroscopy. In contrast to **7** and **8**, the stoichiometries of the cobalt and nickel complexes were consistent with a 1:1 ratio of the metal to ligand. Their solid-state structures were found to be infinite zigzag 1D polymers comprised of the alternating metal-containing units and organic spacers, $[M(hfac)_2{\cdot}\mu^2\text{-}Se_2C_5H_8\text{-}Se,Se']_\infty$ (M = Co (**9**) and Ni (**10**) (Figures 4 and 5). The chain structures are built on intermolecular M•••Se interactions of the metal centers to two different selenium ends of $Se_2C_5H_8$. The M•••Se distance of 2.6049(9) Å is a bit longer in **9** compared with that of 2.5523(16) Å in **10**, but both values are significantly shorter than those in the copper complexes. For comparison, the Ni^{II}−Se distance of coordinated 1,3-dimethyl-4-imidazoline-2-selenone was found to be 2.5927(12) Å.[21] The Se−M−Se′ bond angle is 88.51(3)° in **9** versus 89.48(5)° in **10**. The cis-configuration of the hexafluoroacetylacetonate ligands in the coordination sphere of Co^{II} and Ni^{II} is preserved upon coordination to **2**.

A comparison of geometrical parameters of 2,6-diselenaspiro[3.3]heptane in free (**2**) and complexed (**7**, **9**, and **10**) forms (Table 4) confirms that coordination does not cause any significant distortions in the structure of ligand.

To probe the influence of the spirocyclic organic spacers in transmitting magnetic interactions between the individual 3d paramagnetic metal centers in the hybrid products, we carried out magnetic susceptibility measurements on crystalline samples of complexes **7**, **9**, and **10** over the temperature range 1.8−300 K. As shown in Figure 6, the magnetic behavior of **7** ($g_{calc} = 2.10$) is typical of a Curie behavior

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(19) (a) Kivekas, R. *Finn. Chem. Lett.* **1978**, *2*, 71−73. (b) Tercero, J.; Diaz, C.; Ribas, J.; Mahia, J.; Maestro, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **2002**, 2040−2046.

(20) X-ray data for $[Co(hfac)_2{\cdot}(H_2O)_2]$ (**5**): $CoO_6C_{10}F_{12}H_6$; fw = 509.08; *C*2/*c*; *a* = 21.2490(12), *b* = 8.0736(4), *c* = 9.6680(5) Å; β = 95.4830(10)°; *V* = 1651.01(15) Å^3; *Z* = 4; D_{calcd} = 2.048 g/cm^3; *T* = 173(2) K. The final R1 (on F_o) was 0.0311, and wR2 (on F_o^2) = 0.0811 for 144 parameters, 0 restraints, and 1941 unique data (1851 reflections with $I > 2\sigma(I)$). See Supporting Information for structural details.

(21) Blake, A. J.; Casabo, J.; Devillanova, F. A.; Escriche, L.; Garau, A.; Isaia, F.; Lippolis, V.; Kivekas, R.; Muns, V.; Schroder, M.; Sillanpia, R.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1085−1092.

Table 4. Selected Distances (Å) and Angles (deg) in **2** and **7**−**10**

	2	**7**	**8**[a]	**9**	**10**
M−Se(S)		3.0315(6) 2.7873(9)	3.015(14) 2.769(9)	2.6049(9)	2.5523(16)
M−O$_{av}$		1.937(4)	1.950(3)	2.047(4)	2.025(7)
M···M		8.8617(8)	8.7679(9)	7.5777(9)	7.5479(10)
Se(S)−M−Se(S)’		180	180	88.51(3)	89.48(5)
O−M−O		171.68(17)	170.81(15)	88.38(14)	89.3(3)
Se(S)−C$_{av}$	1.978(3)	1.972(11)	1.900(17)	1.978(5)	1.994(10)
Se(S)···Se(S)	4.906(1)	4.960(1)	4.854(14)	4.919(2)	4.937(2)
C−Se(S)−C$_{av}$	72.0(1)	73.3(1)	75.8(1)	72.5(2)	72.4(4)
C−C−C	98.1(2)−119.1(2)	98.8(6)−122.2(9)	94.6(8)−130.5(11)	98.0(4)−117.6(4)	99.1(8)−116.3(8)

[a] Average values for the S and Se ends.

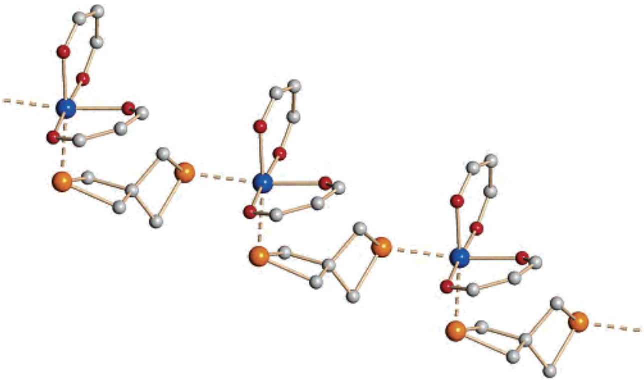

Figure 4. Ball-and-stick representation of the polymeric structure in **9**. Atomic color scheme: Co = dark blue; Se = orange; O = red; C = gray. The CF_3 groups and H atoms are omitted for clarity.

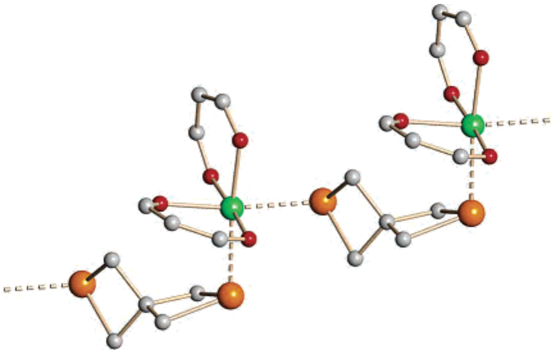

Figure 5. Ball-and-stick representation of the polymeric structure in **10**. Atomic color scheme: Ni = green; Se = orange; O = red; C = gray. The CF_3 groups and H atoms are omitted for clarity.

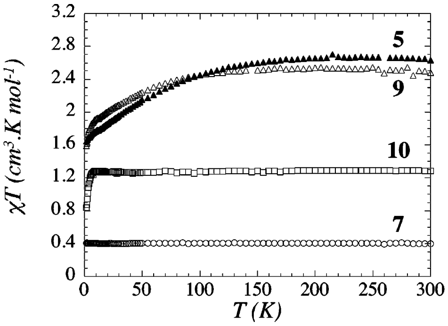

Figure 6. Temperature dependence of the χT product/metal ion (where $\chi = M/H$) at 1000 Oe for compounds **5**, **7**, **9**, and **10**.

with a Curie constant $C = 0.41$ cm^3 K mol^{-1} expected for the Cu^{II} metal ions. In addition to the long distance between the copper centers through the ligand, the coordination Cu···Se bonds in **7** seem weak, and therefore, the spirocyclic $Se_2C_5H_8$ ligand does not promote magnetic exchange between the Cu^{II} centers. For the nickel compound **10**, the susceptibility can be fitted to a Curie−Weiss law with $C = 1.28$ cm^3 K mol^{-1} (value expected for Ni^{II} metal ions with $g = 2.26$) and $\Theta = -1.4$ K. In the Ni case, the Weiss constant (i.e. the decrease of the χT product below 10 K) can reflect either antiferromagnetic interaction between magnetic centers along the chain through the $Se_2C_5H_8$ ligand (the Ni···Se contacts are much shorter in **10** compared to that in the copper complex **7**) or single ion zero-field splitting (ZFS) effect from the isolated Ni^{II} centers. Therefore experimental results have been modeled using two approaches: (i) an Heisenberg chain of antiferromagnetically coupled $S = 1$ model (with the following Hamiltonian: $H = -2J\Sigma_i S_i S_{i+1}$);[22] (ii) a model with an isolated Ni^{II} $S = 1$ ion and ZFS effect (with the following Hamiltonian $H = DS_z^2$).[22b] The best parameters obtained are $J/k_B = -0.2$ K and $D/k_B = -1.5$ K, respectively (in both cases $g = 2.28$). From these two approaches that lead to very good and qualitatively identical fittings, it is difficult to discriminate between the two models. Nevertheless on the basis of the result for the copper complex indicating that the $Se_2C_5H_8$ ligand is not an efficient magnetic pathway, it seems more likely that the ZFS effect is relevant to explain the low-temperature behavior of magnetic susceptibility for **10**. The magnetic susceptibility measurements for **9** reveal a paramagnetic Curie−Weiss behavior with $C = 2.85$ emu K/mol in agreement with typical values for high spin Co(II) metal ions in an octahedral coordination geometry[23] and $\Theta = -12.7$ K (fitted down to 40 K). The negative Weiss constant seen for **9** is not necessarily indicative of antiferromagnetic interaction between the Co^{II} ions. In fact, in Co^{II} systems it principally reflects the presence of spin−orbit coupling resulting in the splitting of the energy levels arising from the $^4T_{1g}$ ground term which stabilizes a doublet ground state.[23a] To illustrate this effect, the magnetic susceptibility of the monomeric starting material, $[Co(hfac)_2 \cdot (H_2O)_2]$ (**5**),[20] has been measured and compared to the data of the hybrid coordination polymer **9**. As shown in Figure 6, the decrease

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(22) (a) Meyer, A.; Gleizes, A.; Girerd, J. J.; Verdaguer, M.; Kahn, O. *Inorg. Chem.* **1982**, *21*, 1729−1739 (b) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

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in χT for **9** is essentially identical to that observed for **5** (the Curie Weiss fit leads to $C = 2.94$ emu K/mol and $\Theta = -16$ K), and therefore, it is mainly the result of spin−orbit coupling rather than antiferromagnetic interaction between the Co^{II} centers.

With study of the magnetic properties of these series of analogous complexes, it appears that the organic spacer **2** does not facilitate magnetic interactions between the paramagnetic metal centers.

In conclusion, a unique series of three analogous molecules **1**−**3**, $E_2C_5H_8$ (E = S, Se, S/Se), has now been prepared and fully characterized. The reactivity of **2** and **3** toward the 3d transition metal centers has been tested to confirm their bidentate μ^2-Se,Se′(S) preferences in coordination reactions. A new family of hybrid coordination products comprised of $M(hfac)_2$ units and spirocyclic ligands has been prepared and structurally characterized in the solid state.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.asc.org.

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