ity constant of $10^{17.5}$ [17b] the value of the stability constant of $\{MCy^-\}^*$ formed from M^{3+} and Cy^{4-} must be greater than $10^{5.5}$ M^{-1}. This is close to the values for rare earth–citrate complexes,[22] so the intermediate may be a metal atom coordinated to several of the acetate groups of CyDTA, outside the coordination cage. This would be similar to structure I without a proton on the nitrogen. For La^{3+} the value of K^*_{LaHCy} was 10^6 M^{-1} and therefore the association of Ce^{3+} and Cy^{4-} would be expected to be at least this large.

Glentworth and coworkers have observed a slight cerium ion catalysis of the radiocerium–CeCy⁻ exchange reaction. This phenomenon cannot be observed with our experimental method. His reaction may proceed by way of the $\{MCy^-\}^*$ intermediate proposed here.

Both metal ions cannot simultaneously be in the coordination cage, but one may be inside the cage and the other metal ion could coordinate with an acetate group outside the cage. Such a complex is known to inhibit the acid exchange reaction,[23] however, so an intermediate with both metal ions outside the coordination cage is more likely.

Mechanism.—The CyDTA complexes can therefore form and dissociate according to the scheme given in Figure 4. The pathway through which the reaction proceeds depends on the complexed metal, the scavenger metal, and the experimental conditions. The acid path is shown at the top of the figure and this pathway predominates for most experimental conditions. The intermediate I is observed with La^{3+} formation reactions because k^* is slow but with Sc^{3+} this intermediate is not observed. The structure of the ligand, the location of protons, and the size of the coordinating metal can have a large influence on the reaction rate.

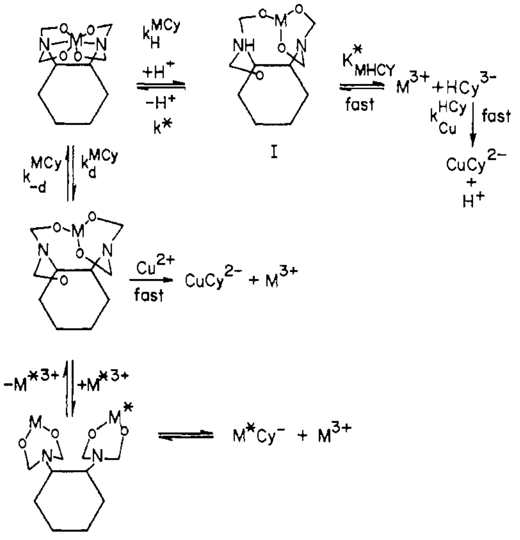

Figure 4.—Mechanism of formation and dissociation of CyDTA complexes of the rare earths.

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The Preparation of Bis(trifluoromethyl)-1,2-diselenetene and Some 1,2-Diselenolene Transition Metal Complexes

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The synthesis and properties of the heterocycle $Se_2C_2(CF_3)_2$ are described. Various attempts to prepare related compounds formally derived from ethylene-1,2-diselenol are discussed. The preparation and properties of a representative series of bis(trifluoromethyl)-1,2-diselenetene transition metal complexes are reported. The complexes are similar in behavior to the corresponding dithiolene species, though they are much less stable.

Introduction

Relatively few transition metal complexes having ligands with selenium as the donor atoms have been reported. However, work in this area is being actively pursued. Summaries of the earlier studies have been included in two recent reviews.[2,3] The most recent studies have dealt with the synthesis of seleno ligands and their complexes such as diselenocarbamates,[4–6] diselenoxanthates,[5] diselenophosphinates,[7] and diselenoacetylacetonates[8] and complexes of 1,2-bis(isopropylseleno)ethane[9] and of but-3-enyl selenides.[10] A number of mixed-donor set ligands involving selenium have

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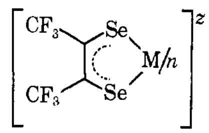
been reported. These include complexes of the tetradentate ligand tris(*o*-selenomethylbenzene)phosphine,[11] 1-diphenylphosphinobenzene-2-selenates,[12] benzene-1-seleno-2-thiolates,[13] dialkylselenophosphinates,[7] and dialkylselenothiophosphinates.[7] It seems that the selenium-containing complexes resemble the analogous sulfur complexes and that no marked changes in structure or properties result as a consequence of the interchange of sulfur for selenium. For example, it was observed[5] that the diselenocarbamate complexes resemble the dithiocarbamates in appearance, solubility, and chemical properties; their electronic spectra are also similar but they occur at longer wavelengths indicative of a slightly lower ligand field strength.

A representative series of bis(trifluoromethyl)-1,2-diselenetene complexes[14] (1,2-diselenolene complexes) (I) has been prepared for the purpose of comparing their electronic and structural properties with those of the analogous well-documented dithiolenes, the properties of which have been recently reviewed.[15]



I

Experimental Section

General Data.—Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Midwest Microlab, Inc., Indianapolis, Ind., and Spang Microanalytical Laboratory, Ann Arbor, Mich. and at M.I.T. by Mrs. Nancy E. Alvord.

All melting points were determined on a Kofler hot-stage microscope and are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrometer; electronic spectra, on a Cary 14 spectrometer.

Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 eV. Fluorine nmr spectra were recorded on a Varian HA-100 spectrometer operating at 94.1 MHz. Chemical shifts were measured relative to trifluoroacetic acid as an external standard.

Magnetic moments in solution were determined by the nmr method of Evans[16] using the TMS signals of the solvent and solution. Moments of solids were obtained by the Gouy method using $HgCo(SCN)_4$[17] as the calibrant. The polarographic data were obtained using a Heath-Built EUA-19-2 polarograph equipped with three electrodes. Both dichloromethane[18] and Spectrograde acetonitrile were employed as solvents with $[(C_4H_9)_4N][PF_6]$ and $[(C_3H_7)_4N][ClO_4]$, respectively, as the supporting electrolytes. Additional details are given in Table I. Electron paramagnetic resonance data were recorded on a Varian Model 4500 spectrometer equipped with a 100-kHz field modulation unit and a Varian V4533 cylindrical cavity.

Preparations. **$Se_2C_2(CF_3)_2$.**—Bis(trifluoromethyl)-1,2-diselenetene was prepared by the reaction of hexafluorobut-2-yne with refluxing selenium. A 30-mm Vycor tube with a side arm and an 8-mm inlet tube was charged with 100 g of selenium. The selenium (bp 688°) was brought to reflux by a vertical tube furnace maintained at 700°. A flow of nitrogen was maintained through the system. Then 72 g of $CF_3C\equiv CCF_3$ (Penisular Chemresearch) was added over 30 min through the inlet tube which ended just above the zone of refluxing selenium. The product distilled over as a dark red liquid. This was flash distilled to separate it from the elemental selenium carried over in the gas stream and was then fractionated. The fraction boiling at 78–79° (84 mm) was collected. A yield of 36 g (25% based on $CF_3C\equiv CCF_3$) of a dark-red liquid was obtained.

The nmr spectrum of this material showed a peak for CF_3 at 15.4 ppm to the low-field side of CF_3COOH (external standard). Satellites due to ^{77}Se were also observed with $J_{Se-F} = 5 \pm 1$ Hz. Impurity peaks of low intensity were also observed: two CF_3 resonances of equal intensity with a complex multiplet structure were observed at 21.5 and 24.8 ppm below trifluoroacetic acid; a third, sharp resonance was found at 22.6 ppm below CF_3COOH. The mass spectrum of this material showed strong multiplets corresponding to the ions $C_4F_6Se_2^+$, $C_4F_5Se_2^+$, and $C_3F_3Se_2^+$ and very weak multiplets corresponding to the ions $C_8F_{12}Se^+$, $C_8F_{11}Se^+$, and $C_7F_9Se^+$. The impurity associated with the two complex fluorine nmr resonances must be 2,3,4,5-tetrakis(trifluoromethyl)selenophene.

An analytical sample of $Se_2C_2(CF_3)_2$ was prepared by fractional distillation of the liquid on a Nester-Faust annular Teflon spinning-band column at 79° (84 mm). The final fractions contained no impurities detectable by nmr.

Anal. Calcd for $C_4F_6Se_2$: C, 15.02; F, 35.63; Se, 49.36. Found: C, 15.32; F, 39.74; Se, 47.96. The infrared spectrum of a thin film of the liquid showed $\nu_{C=C}$ at 1617 cm^{-1} (s) and ν_{CF_3} at 1285 (s, br), 1255 (s, br), 1170 (s, br), and 1130 (s, br) cm^{-1}; other bands were at 1670 (vw), 905 (sh), 897 (s), 802 (w), 710 (s), and 670 (s) cm^{-1}. The malodorous liquid was stored at 5° to retard polymerization reactions.

$[Se_2C_2(CF_3)_2]_2$.—Over a period of months at 0°, a small amount of orange plates deposited from the bis(trifluoromethyl)-1,2-diselenetene. These were recrystallized from hexane and then purified by sublimation at 70° (40 mm), mp 134–136°.

Anal. Calcd for $(C_4F_6Se_2)_n$: C, 15.02; F, 35.63; Se, 49.36. Found: C, 15.28; F, 38.29; Se, 47.77. The infrared spectrum of the material showed the following absorptions above 1300 cm^{-1}: 1637 (vw), 1556 (s), 1530 (sh), 1516 cm^{-1} (sh). The mass spectrum showed a strong multiplet corresponding to the parent ion $Se_4C_8F_{12}^+$; the spectrum was featureless for *m/e* values higher than that for this parent ion multiplet. Multiplets were also observed for the ions $Se_4C_8F_{11}^+$ and $Se_nC_4F_6^+$, $n = 4–2$.

Reaction of $Se_2C_2(CF_3)_2$ with $(C_6H_5)_3P$ and $(C_6H_5)_3As$.—A mixture of 0.52 g of $(C_6H_5)_3P$ and 0.64 g of $Se_2C_2(CF_3)_2$ in 20 ml of ether was allowed to stand for 4 hr. The solid which deposited was collected, washed with ether, and then recrystallized from absolute ethanol. White crystals (0.23 g) were obtained. They were identified as $(C_6H_5)_3PSe$ by comparison with a sample prepared directly (mp 186–187°; mmp 185–187°). The ether was evaporated to give a yellow-brown solid residue, but no pure compound could be isolated from this material. The reaction of $(C_6H_5)_3As$ (0.61 g) with $Se_2C_2(CF_3)_2$ (0.64 g) in 40 ml of dry ether gave no solid product after 5 hr at room temperature. The ether was evaporated, but the resulting residue was unstable and deposited elemental selenium. No product could be identified.

$NiSe_4C_4(CF_3)_4{}^0$.—A solution of 7.3 g of $Se_2C_2(CF_3)_2$ (22.8 mmol) in 100 ml of pentane was combined with a solution of 1.5 g of $Ni(CO)_4$ (11.4 mmol) in 30 ml of pentane under a nitrogen atmosphere. The solution turned blue-black immediately; after 30 sec gas evolution was noted and continued for about 5 min. The solution was allowed to stand overnight and then the solvent was removed *in vacuo* leaving dark red-brown crystals. An analytical sample was prepared by washing the product with three 10-ml portions of cold pentane.

Anal. Calcd for $C_8F_{12}NiSe_4$: C, 13.75; F, 32.63; Se, 45.21. Found: C, 13.62; F, 34.87; Se, 44.75. A strong odor, reminiscent of the ligand, could be detected after the material had stood for a few days. The complex did not melt below 350°. It dis-

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solves in dry benzene to give a red-brown solution from which the neutral species could be recovered. However, acetone or alcohol solutions of $NiSe_4C_4(CF_3)_4$ are green.

$[(C_6H_5)_4As][NiSe_4C_4(CF_3)_4]$.—A green solution of $NiSe_4C_4(CF_3)_4$ (0.37 g, 0.53 mmol) in 25 ml of methanol was treated with $(C_6H_5)_4AsCl$ (0.22 g, 0.53 mmol) in 10 ml of methanol. Addition of 30 ml of water caused a bright green solid to precipitate. This was recrystallized three times from an ethanol–water solvent pair to give 0.30 g (52%) of bright green crystals, mp 160.5–161.5°.

Anal. Calcd for $C_{32}H_{20}AsF_{12}NiSe_4$: C, 35.52; H, 1.86; F, 21.07; Se, 29.19. Found: C, 36.15; H, 2.01; F, 21.71; Se, 28.67.

χ^M_{cor} (dichloromethane, 34°) was 1368×10^{-6}; μ_{eff}, 1.84 BM; the electronic spectrum, recorded in CH_2Cl_2, showed bands at λ_{max} (in cm^{-1}): 16,130, 14,490, 12,195, 6960 (ϵ l. mol^{-1} cm^{-1}: 1570, 1800, 4640, 97).

$[(C_6H_5)_4As]_2[NiSe_4C_4(CF_3)_4]$.—A few drops of hydrazine were added to a solution of $NiSe_4C_4(CF_3)_4$ (0.27 g, 0.39 mmol) in 20 ml of methanol. The green solution immediately turned yellow-brown and the addition of 0.33 g (0.78 mmol) of $(C_6H_5)_4AsCl$ in 10 ml of methanol followed by 5 ml of water gave an orange-brown precipitate. This was recrystallized twice from an acetone–isobutyl alcohol solvent pair to give 0.33 g (56%) of orange-yellow crystals, mp 256–257°. The recrystallization was carried out rapidly to preclude the oxidation of the product to the monoanion in solution.

Anal. Calcd for $C_{56}H_{40}As_2F_{12}NiSe_4$: C, 45.90; H, 2.75; F, 15.56; Se, 21.55. Found: C, 45.74; H, 2.73; F, 15.89; Se, 21.36.

$[(C_4H_9)_4N][CuSe_4C_4(CF_3)_4]$.—A mixture of $[(C_6H_5)_3PuCI]_4$ (0.8 g) and $Se_2C_2(CF_3)_2$ (1.75 g) in 50 ml of benzene was shaken for 3 hr and then the resulting deep red solution was filtered to remove a small amount of insoluble material. The benzene was removed *in vacuo* and the resulting oil was shaken with several portions of pentane to remove the unreacted ligand. The residue was dissolved in 75 ml of ethanol–water (60% v/v) and allowed to stand overnight. It was again filtered to remove the solid that had collected. The addition of 0.57 g of $(C_4H_9)_4NBr$ in 10 ml of water caused a solid to precipitate. This was twice recrystallized from isobutyl alcohol–cyclohexane to give 0.5 g (21%) of dark red crystals, mp 89–92°.

Anal. Calcd for $C_{24}H_{36}CuF_{12}Se_4$: C, 30.47; H, 3.84; N, 1.48; F, 24.10; Se, 33.39. Found: C, 30.59; H, 3.86; N, 1.48; F, 24.29; Se, 33.28.

The $(C_6H_5)_4As^+$ and $C_{10}H_{10}N^+$ salts were prepared in a similar manner.

$[(C_6H_5)_4As]_2[CuSe_4C_4(CF_3)_4]$.—Treatment of an enthanolic solution of $[(C_4H_9)_4N][CuSe_4C_4(CF_3)_4]$ with a few drops of hydrazine did not give the dianion. Sodium amalgam was prepared by dissolving 0.03 g of sodium in 5 ml of mercury. This was shaken with a solution of $[(C_6H_5)_4As][CuSe_4C_4(CF_3)_4]$ (0.5 g) in 30 ml of dried and degassed tetrahydrofuran for 5 min. No obvious color change was observed. The amalgam was allowed to settle out and then the supernatant solution was poured into a solution of 0.2 g of $(C_6H_5)_4AsCl$ in 100 ml of degassed ethanol–water (1:2 v/v). A rapid stream of nitrogen bubbled through the solution for a few minutes caused the product to crystallize. Orange-brown crystals (0.40 g) slowly formed. The material was readily oxidized to the monoanion, so a satisfactory elemental analysis could not be obtained. However, an epr signal exhibiting both copper and selenium hyperfine interactions was observed for a tetrahydrofuran solution of the product. It was observed that prolonged contact of a tetrahydrofuran solution of the dianion with sodium amalgam resulted in further reaction to give a pale yellow solution which did not show an epr signal at room temperature.

$[(C_6H_5)_4As][VSe_6C_6(CF_3)_6]$.—The addition of $Se_2C_2(CF_3)_2$ (1.83 g, 5.7 mmol) to a solution of $[(C_6H_5)_4As][V(CO)_6]$ (1.15 g, 1.9 mmol) in 50 ml of dry dichloromethane gave a dark red-violet solution; rapid evolution of gas was observed. The solution was shaken mechanically under a nitrogen atmosphere for 4 hr. Slow addition of 50 ml of dry pentane to this solution caused the product to precipitate. The solid was recrystallized from dry dichloromethane–pentane to give 1.15 g (43%) of deep purple crystals. After the material had stood for 2 weeks, the odor of the ligand could be detected and some red selenium had deposited.

Anal. Calcd for $C_{36}H_{20}AsF_{18}Se_6V$: C, 31.02; H, 1.45; F, 24.53. Found: C, 31.00; H, 1.22; F, 23.85.

$[(C_6H_5)_4As]_2[VSe_6C_6(CF_3)_6]$.—Crude $[(C_6H_5)_4As][VSe_6C_6(CF_3)_6]$, prepared from 1.85 g (3.08 mmol) of $[(C_6H_5)_4As][V(CO)_6]$, was dissolved in 50 ml of acetone to give a dark green-brown solution. It was filtered to remove some insoluble material. The addition of $(C_6H_5)_4AsCl$ (1.30 g, 3.08 mmol) in 10 ml of ethanol followed by 100 ml of water caused the product to precipitate. It was collected and then recrystallized twice from CH_2Cl_2–pentane to give 2.4 g (44%) of dark green crystals, mp 196–200° dec.

Anal. Calcd for $C_{60}H_{40}As_2F_{18}Se_6V$: C, 40.54; H, 2.27; F, 19.24; Se, 26.65. Found: C, 40.42; H, 2.30; F, 17.94; Se, 26.77.

χ^M_{cor} (solid, 22°) was 1425×10^{-6}; μ_{eff}, 1.84 BM; the electronic spectrum, recorded in CH_2Cl_2, showed bands at λ_{max} (in cm^{-1}): 34,500 (sh), 25,900, 23,400 (sh), 17,700, 10,300 (ϵ, l. mol^{-1} cm^{-1}: 10,000, 4800, 3600, 4060, 1680).

$MoSe_6C_6(CF_3)_6$.—Bis(trifluoromethyl)-1,2-diselenetene (2.0 g, 6.4 mmol) was added to a solution of $Mo(CO)_6$ (0.56 g, 2.1 mmol) in 25 ml of *n*-octane. The initially red solution was refluxed under nitrogen for 2 hr; it became very dark red-brown after 5 min and a black solid began to deposit on the walls of the flask after 15 min. After cooling, the supernatant liquid was decanted and the solid was washed with three 10-ml portions of dry pentane. Well-formed, deep red-purple crystals (1.3 g, 59%) were obtained. An analytical sample was prepared by Soxhlet extraction of the crystals with *n*-pentane.

Anal. Calcd for $C_{12}F_{18}MoSe_6$: C, 13.65; F, 32.39; Se, 44.87. Found: C, 13.09; F, 32.13; Se, 44.84.

$[(C_4H_9)_4N]_2[MoSe_6C_6(CF_3)_6]$.—The addition of hydrazine (0.5 ml) to a solution of $MoSe_6C_6(CF_3)_6$ (0.4 g) in 20 ml of ethanol caused an immediate color change from purple to dark green. Addition of $(C_4H_9)_4NBr$ (0.27 g) in 10 ml of water gave a bright green precipitate. This was recrystallized from acetone–isobutyl alcohol to give 0.45 g (77%) of dark green crystals, mp 256.5–258.5°.

Anal. Calcd for $C_{44}H_{72}F_{18}MoN_2Se_6$: C, 34.30; H, 4.71; F, 22.19; Se, 30.75. Found: C, 34.33; H, 4.39; F, 20.53; Se, 28.27.

$WSe_6C_6(CF_3)_6$.—A solution of $W(CO)_6$ (1.0 g, 2.8 mmol) and $Se_2C_2(CF_3)_2$ (2.70 g, 8.5 mmol) in 50 ml of dry *n*-octane was refluxed under nitrogen for 1 week. The solution turned deep red-violet after 12 hr and a black solid deposited on the walls of the flask after 48 hr. After cooling, the supernatant liquid was decanted and the solid (1.2 g) was washed with three 10-ml portions of dry pentane. The crude material was purified by Soxhlet extraction with *n*-pentane. Red-violet crystals (0.5 g, 15%) with a pronounced green reflex were obtained. The material does not melt below 320°, but it does sublime above *ca.* 170°.

Anal. Calcd for $C_{12}F_{18}Se_6W$: C, 12.60; F, 29.90; Se, 41.42. Found: C, 12.33; F, 27.89; Se, 39.72.

$[(C_4H_9)_4N]_2[WSe_6C_6(CF_3)_6]$.—This complex was prepared as dark blue-violet crystals, mp 265–268° dec, by a procedure similar to that described for the corresponding molybdenum complex.

Anal. Calcd for $C_{44}H_{72}F_{18}N_2Se_6W$: C, 32.45; H, 4.46; N, 1.72. Found: C, 32.28; H, 4.64; N, 1.58.

$[(C_4H_9)_4N][FeS_4C_4(CF_3)_4]$.—A mixture of $Fe(CO)_5$ (0.68 ml, 5 mmol) and $Se_2C_2(CF_3)_2$ (4.80 g, 15 mmol) in 100 ml of dry pentane was refluxed under nitrogen for 8 hr. The solution gradually turned from light red to a very dark red-brown and a black solid deposited on the walls of the flask. After cooling, the mixture was filtered under nitrogen and the solid collected (2.8 g) was washed with several volumes of dry pentane. The infrared spectrum showed no carbonyl absorptions. However, the material was unstable in solution and slowly decomposed on standing; it could not be recrystallized. The crude product was treated with 75 ml of ethanol and filtered; the addition of 0.5 ml of hydrazine gave a deep red solution. The product was precipitated by the addition of $(C_4H_9)_4NBr$, followed by 75 ml of water. The product was very difficult to crystallize, but dark-red crystals (1.1 g, 23%) were finally obtained by slow evaporation of an ethanol solution.

Anal. Calcd for $C_{24}H_{36}F_{12}FeNSe_4$: C, 30.72; H, 3.07; N, 1.49. Found: C, 30.56; H, 3.71; N, 1.66.

A similar method was employed to prepare $[(C_6H_5)_4As][FeSe_4C_4(CF_3)_4]$ from $Fe(CO)_5$ (0.40 ml, 2.94 mmol) and $Se_2C_2(CF_3)_2$ (3.40 g, 10.6 mmol). Red-brown crystals (1.4 g, 44%), mp 214–218° dec, were obtained.

When the reaction was carried out using a 2:1 molar ratio of ligand to $Fe(CO)_5$, the black solid obtained from the pentane solution contained CO groups (infrared bands at 2040, 2065, 2095 cm^{-1}). Attempts to purify the material by Soxhelet extraction with CCl_4 gave a variety of products that could not be reproducibly prepared and were not identified.

$[(C_4H_9)_4N][CoSe_4C_4(CF_3)_4]$.—Bis(trifluoromethyl)-1,2-diselenetene (8.6 g, 26.9 mmol) was added to a stirred solution of $Co_2(CO)_8$ (2.0 g, 5.9 mmol) in 200 ml of dry pentane under a nitrogen atmosphere at 0°. Slow evolution of gas was observed, and during 1 hr the solution became deep purple. It was then refluxed under nitrogen for 3 hr and during this time a black solid deposited on the walls of the flask. This material had carbonyl stretching modes in its infrared spectrum (2063 and 2090 cm^{-1}) as well as bands at 1535 and 1555 cm^{-1}. However, the carbonyl species was unstable, as evidenced by deposition of elemental selenium, and no carbonyl-containing complexes were characterized. The black solid was treated with a solution of hydrazine (1 ml) in ethanol (100 ml). The resulting dark brown mixture was filtered to remove a small amount of insoluble material. The filtrate was treated with excess tetrabutylammonium chloride, followed by enough water to precipitate the complex. Again, this material was difficult to crystallize, but a small amount of black crystals (mp 165.5–167°) was obtained from acetone–isobutyl alcohol.

Anal. Calcd for $C_{24}H_{36}CoF_{12}NSe_4$: C, 30.62; H, 3.86; N, 1.49. Found: C, 29.99; H, 3.34; N, 1.16.

Electron Paramagnetic Resonance. $[CuSe_4C_4(CF_3)_4]^{2-}$.—The solution spectrum (Figure 1) of $[(C_6H_5)_4As]_2[CuSe_4C_4(CF_3)_4]$ (*ca.* 10^{-2} *M*) in chloroform–dimethylformamide (1:1 v/v) was recorded. Both the copper and selenium hyperfine structure could be observed; the ^{63}Cu and ^{65}Cu components were not separately resolved. The values obtained were $\langle g \rangle = 2.060 \pm 0.001$, $\langle A_{Cu} \rangle = 81.7 \pm 2.5$ G (236 ± 8 MHz), and $\langle A_{Se} \rangle = 70.3 \pm 2.5$ G (203 ± 8 MHz).

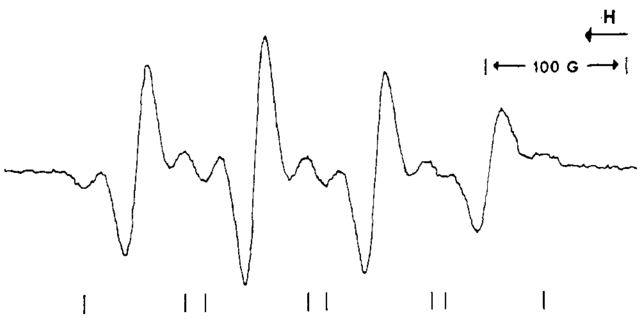

Figure 1.—The electron paramagnetic resonance spectrum of $CuSe_4C_4(CF_3)_4^{2-}$ in chloroform–dimethylformamide (1:1 v/v) solution at room temperature. The values are $\langle g \rangle = 2.060$, $\langle A_{Cu} \rangle = 81.7$ G, and $\langle A_{Se} \rangle = 70.3$ G.

For comparison, the previously unreported spectrum of $CuS_4C_4(CF_3)_4^{2-}$ was measured with $\langle g \rangle = 2.045 \pm 0.001$ and $\langle A_{Cu} \rangle = 78.3 \pm 2.5$ G (226 ± 8 MHz). The spectra of $NiSe_4C_4(CF_3)_4^-$ and $VSe_6C_6(CF_3)_6^{2-}$ are reported elsewhere.[19]

Results and Discussion

The heterocycle $Se_2C_2(CF_3)_2$ was readily prepared by the reaction of selenium vapor with hexafluorobut-2-yne as a deep red, malodorous liquid (bp 78° (84 mm)). Very little product was obtained from the reaction of selenium with hexafluorobut-2-yne at temperatures below the boiling point of selenium. In a number of reactions varying amounts of 2,3,4,5-tetrakis(trifluoromethyl)selenophene were produced as a by-product which could only be completely removed by multiple fractional distillation. A satisfactory elemental analysis for fluorine and selenium could not be obtained for this material. However, the fluorine nmr spectrum of a purified sample showed only the peak assigned to $Se_2C_2(CF_3)_2$ and the mass spectrum showed a strong multiplet with the appropriate intensity distribution corresponding to the parent ion $Se_2C_4F_6^+$. This, together with the isolation of well-characterized complexes of the ligand, confirms its formulation as bis(trifluoromethyl)-1,2-diselenetene. A polarogram of the material (in CH_2Cl_2 with 0.1 *M* $(C_3H_7)_4NClO_4$ as the supporting electrolyte) showed only a one-electron reduction ($E_{1/2} = -0.50 \pm 0.03$ V). Like the corresponding sulfur species, the compound slowly gives an orange crystalline dimer. Again, a satisfactory elemental analysis for fluorine and selenium could not be obtained, but the mass spectrum showed a strong multiplet corresponding to the parent ion $Se_4C_8F_{12}^+$.

In view of the ready formation of $Se_2C_2(CF_3)_2$ it was anticipated that other ligand systems could be easily synthesized. This was not the case. It is perhaps not surprising that a phenyl-substituted species could not be prepared in view of the rather specialized nature of the acyloin reaction[20] with P_4S_{10} and the fact that P_2Se_5 is not well-characterized and little of its chemistry is known. Recent studies[21] have indicated that the material is an amorphous solid.

The fact that the *cis*-1,2-dicyanoethylene-1,2-diselenolate anion could not be prepared was more surprising. However the material reported[22] to be $Na[CNCSe_2]$ did not dimerize, with elimination of selenium, under a variety of conditions including treatment with triphenylphosphine in an attempt to abstract the selenium as triphenylphosphine selenide.

The methods used to prepare the diselenolene complexes were similar to those previously employed to prepare the corresponding dithiolene[15] species. Overall, the properties of the two types of complexes are very similar. Like the sulfur-containing compounds, the diselenolenes undergo redox reactions to give a series of complexes related by one-electron-transfer reactions. The polarographic half-wave potentials measured for these species are given in Table I. The redox reactions were reversible. The half-wave poten-

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TABLE I

POLAROGRAPHIC HALF-WAVE POTENTIALS[a] FOR 1,2-DITHIOLENE AND 1,2-DISELENOLENE COMPLEXES

		$E_{1/2}$,[b] V	
Species	Couple	L = $Se_2C_2(CF_3)_2$	L = $S_2C_2(CF_3)_2$
NiL_2^-	$0 + e^- = -1$	+0.89	+0.89
	$-1 + e^- = -2$	−0.17	−0.17
CuL_2^-	$-1 + e^- = -2$	−0.42	(−0.10)
VL_3^-	$-1 + e^- = -2$	+0.07[c]	+0.08[c]
	$-2 + e^- = -3$	−1.05[c]	−1.10[c]
MoL_3^{2-}	$0 + e^- = -1$	+0.78	(+0.83)
	$-1 + e^- = -2$	+0.22	(+0.25)
	$-2 + e^- = -3$	−1.56	(−1.5)
WL_3^{2-}	$0 + e^- = -1$	+0.70	(+0.76)
	$-1 + e^- = -2$	+0.16	(+0.21)

[a] Recorded in CH_2Cl_2 using a rotating Pt electrode and 0.1 *M* $(C_3H_7)_4NClO_4$ as the supporting electrolyte, except as otherwise noted. [b] Measured in volts *vs.* sce. Values in parentheses are estimated from the reported values measured in CH_3CN. [c] Measured with a dropping mercury electrode.

tials were virtually unaffected by the substitution of selenium for sulfur in the ligand system except for the copper complex. In this case, the dianion can be readily oxidized to the monoanion; this fact was reflected in the difficulty encountered in preparing a pure sample of $CuSe_4C_4(CF_3)_4^{2-}$.

The selenium-containing complexes, notably in the most oxidized state and with the first-row transition metals, were much less stable than the sulfur-containing compounds. Neutral complexes with chromium, cobalt, and iron, for example, could not be characterized. The material obtained from the reaction of the appropriate metal carbonyl with $Se_2C_2(CF_3)_2$ was unstable with respect to elimination of elemental selenium. In the reactions involving cobalt and iron, products containing both carbonyl and selenetene ligand groups were obtained when a 2:1 molar ratio of selenetene to metal was employed, but these were unstable and could not be characterized. The neutral species $NiSe_4C_4(CF_3)_4$ was relatively stable with no evidence for elimination of selenium, but even here, after several weeks, an odor reminiscent of the ligand could be detected. The complex $VSe_6C_6(CF_3)_6^-$ was also unstable and eliminated selenium on standing. However, the complexes with second- and third-row transition metal complexes were quite stable.

In view of the similar behavior of the dithiolene and diselenolene complexes, it is reasonable to assume that they have the same geometry. In fact, the crystal structure of $MoSe_6C_6(CF_3)_6$ has been determined[23] and it has been found to have the trigonal-prismatic geometry first found[24] for $ReS_6C_6(C_6H_5)_6$.

Further, the epr spectrum of the paramagnetic nickel complexes ($S = 1/2$) containing the anion $NiSe_4C_4(CF_3)_4^-$ showed the pronounced *g* value anisotropy[19] characteristic of the sulfur complexes.[25] This has been interpreted[19] in terms of a planar configuration for the complex having a b_{3g} ground state. The observation of ligand hyperfine structure in the frozen-glass spectrum, due to ^{77}Se (7.58% abundant, $I = 1/2$), has led to an estimate of 70–90% ligand character for the electron in the half-filled molecular orbital. Although an analytically pure sample of salts of the anion $CuSe_4C_4(CF_3)_4^{2-}$ could not be prepared, the solution epr spectrum confirms the formation of the dianion, Figure 1. Both copper and selenium hyperfine interactions were observed. The magnitude of the selenium hyperfine interaction indicates a large degree of covalency in the complex.

No isotropic or anisotropic ligand hyperfine interaction was observed[19] in the epr spectrum of the paramagnetic ($S = 1/2$) vanadium complex $[(C_6H_5)_4As]_2[VSe_6C_6(CF_3)_6]$ and this result has been interpreted as having the unpaired electron in an a_1' molecular orbital that is largely metal d_{z^2} in character for the presumably prismatic complex. This latter feature is in accord with the semiempirical molecular orbital calculations of the analogous sulfur complexes.[26]

A tabulation of the infrared frequency for the perturbed C=C stretching mode for the complexes prepared is found in Table II. This frequency is uniformly higher for the diselenolene complexes compared to the corresponding dithiolene species, even though it is about the same for the parent heterocycles and their dimers. The effect is most pronounced for species in their most oxidized form. The increase in double-bond character indicates that the electron density is more extensively delocalized onto the ligand in the diselenolenes compared to the dithiolene complexes. It is, however, quite significant that both the epr data[19] and the infrared data indicate that the unpaired electron is more extensively delocalized onto the ligand in $NiSe_4C_4(CF_3)_4^-$ than in $NiS_4C_4(CF_3)_4^-$.

TABLE II

PERTURBED C=C FREQUENCY FOR DISELENOLENE AND DITHIOLENE COMPLEXES

Compound	Color	$\nu_{C=C}$, cm^{-1}	$\nu_{C=C}$, cm^{-1} (sulfur analog)
$Se_2C_2(CF_3)_2$	Red (liquid)	1617	1621
$[Se_2C_2(CF_3)_2]_2$	Yellow	1556	1560
$NiSe_4^0$	Blue-black	1496	1422
$NiSe_4^-$	Green	1520	1502
$NiSe_4^{2-}$	Orange	1530	1534
$CuSe_4^-$ [a]	Red-brown	1573	1572
$CuSe_4^{2-}$ [a]	Red-brown	1511	1503
VSe_6^- [a]	Purple	. . .	. . .
VSe_6^{2-} [a]	Green-brown	1517	1504
$MoSe_6^0$	Purple	1479	1455
$MoSe_6^{2-}$	Green	1550	1538
WSe_6^0	Red-violet	1500	1474
WSe_6^{2-}	Blue-violet	1555	1541
$FeSe_4^-$ [a]	Red-brown	1558	1538
$CoSe_4^-$ [a]	Dark brown	1518	1502

[a] $(C_6H_5)_4As^+$ as cation; in all other cases, $(C_4H_9)_4N^-$ was the cation.

The behavior of the iron and cobalt systems is less straightforward. In both cases, the product of the reaction of the metal carbonyl with $Se_2C_2(CF_3)_2$ could

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be reduced by hydrazine in ethanol to give a species with the empirical formula $MSe_4C_4(CF_3)_4^-$, M = Co or Fe. It was very difficult to obtain crystalline samples of these anions, however. In order to determine the degree of association of $[(C_6H_5)_4As][FeSe_4C_4(CF_3)_4]$ in solution, the equivalent conductivities for acetonitrile solutions were measured as a function of $\sqrt{c}$. The resulting plot was nonlinear. The measured magnetic moments for this complex were μ_{eff} (solid, 22°) 1.11 BM (monomeric formulation) and 1.58 BM (dimeric formulation) and μ_{eff} (acetone, 34°) 2.51 BM (monomeric formulation) and 3.04 BM (dimeric formulation). These results suggest that a monomer $\rightleftarrows$ dimer equilibrium exists here. A polarogram of this material in CH_2Cl_2 using a rotating platinum electrode showed a reversible one-electron wave at $E_{1/2} = +0.58$ V and an irreversible two-electron wave at $E_{1/2} = -0.78$ V.

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Hindered Ligand Systems. IV. Complexes of *cis,cis*-1,3,5-Tris(pyridine-2-carboxaldimino)cyclohexane. Trigonal-Prismatic *vs.* Octahedral Coordination[1]

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Trigonal-prismatic coordination of the metal atom is known to occur in $Zn((py)_3tach)(ClO_4)_2$, where $(py)_3$tach is *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane. X-Ray powder patterns of this compound and the corresponding Co(II) and Mn(II) compounds are virtually indistinguishable. However, the patterns of the Ni(II) and Fe(II) compounds differ from each other as well as the others, which suggests that either or both may have a different geometry. No unaccountably large differences occur in any of the vibrational spectra between 400 and 3600 cm^{-1}, but the electronic spectra of the Ni(II) and Fe(II) complexes suggest octahedral or near-octahedral configurations in each case. Ligand field calculations lend some support to this tentative conclusion since the calculations suggest that the tendency toward the octahedral configuration ought to decrease according to: low-spin Fe(II) > Ni(II) > high-spin Co(II) > high-spin Mn(II) = Zn(II). Conformational preferences within the ligand favor trigonal-prismatic coordination. Consequently, a competition between the two geometries may exist. Energy level diagrams for d^7 and d^8 trigonal prismatic complexes have been derived. The spectrum of $Co((py)_3tach)^{2+}$ has been assigned and the magnetic moment (5.0 BM), which is in accord with accepted values for octahedral coordination, has been shown to be also consistent with the predicted ground state of the trigonal prism. On the basis of the d^8 energy level diagram, a remote possibility exists that the spectrum of a trigonal-prismatic complex would be difficult to distinguish from that of an octahedral species.

Lions and Martin[2] have reported the preparation of complexes derived from the Schiff base adduct of pyridine-2-carboxaldehyde and what was thought to be isomerically pure *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) with Fe(II), Co(II), and Co(III). Octahedral coordination was assigned to each. Our own interest in this system was derived from our past studies,[3-5] particularly the one that indicated[3] that the synthesis of the triamine results in both possible stereoisomers, research done by others,[6,7] and another important observation. Space-filling molecular models of the *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane ligand system ($(py)_3$tach) indicated that, in the absence of a major perturbation caused by the metal ion, metal complexes ought to have a trigonal-prismatic coordination geometry, rather than the octahedral coordination assigned by Lions and Martin. The peculiar nature of this ligand seems to have also been recognized by others[7] but without reference to the possible coordination geometry. Consequently, we deliberately chose to examine the coordination geometry of a complex of this ligand in which the metal ion would have no ligand field preference for either an octahedral or a trigonal-prismatic configuration. The X-ray diffraction study of $Zn((py)_3tach)^{2+}$, using ClO_4^- as the counterion, was described recently.[8] As it was hoped, trigonal-prismatic coordination had been realized.

Other examples of trigonal-prismatic coordination are relatively few. Early structural studies[9] have indicated this geometry exists in MoS_2 and WS_2. More

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