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# Coordination Chemistry of 2,2′-Dipyridyl Diselenide: X-ray Crystal Structures of PySeSePy, [Zn(PySeSePy)$Cl_2$], [(PySeSePy)Hg($C_6F_5$)$_2$], [Mo($SePy)_2(CO)_3$], [W($SePy)_2(CO)_3$], and [Fe($SePy)_2(CO)_2$] (PySeSePy = $C_5H_4NSeSeC_5H_4N$; SePy = [$C_5H_4N$(2-Se)-*N,Se*])

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The coordination chemistry of 2,2′-dipyridyl diselenide (PySeSePy) **(2)** ($C_{10}H_8N_2Se_2$) has been investigated and its crystal structure has been determined (monoclinic, $P2_1/c$, $a = 10.129(2)$ Å, $b = 5.7332(12)$ Å, $c = 19.173(3)$ Å, $\beta = 101.493(8)°$, $Z = 4$). In metal complexes the ligand was found to coordinate in three different modes, as also confirmed by X-ray structure determination. N,N′-coordination was found in the zinc complex [Zn(PySeSePy)-$Cl_2$] **(3)** ($C_{10}H_8Cl_2N_2Se_2Zn$, triclinic, $P\bar{1}$, $a = 7.9430(10)$ Å, $b = 8.147(2)$ Å, $c = 11.999(2)$ Å, $\alpha = 93.685(10)°$, $\beta = 107.763(10)°$, $\gamma = 115.440(10)°$, $Z = 2$) and Se,Se′-coordination in the adduct of the ligand with bis(pentafluorophenyl)mercury(II) [PySeSePyHg($C_6F_5$)$_2$] **(5)** ($C_{10}H_8F_{10}HgN_2Se_2$, monoclinic, $P2_1/n$, $a = 7.7325(10)$ Å, $b = 5.9974(14)$ Å, $c = 25.573$, $\beta = 98.037(10)°$, $Z = 2$), which however displays only weak interactions between selenium and mercury. The reaction of the ligand with norbornadiene carbonyl complexes of molybdenum and tungsten leads to reductive cleavage of the selenium−selenium bond with oxidation of the metal center and concomitant addition of the resulting selenolate to the metal carbonyl fragment. Thus the 7-coordinate complexes [Mo($SePy)_2(CO)_3$] **(6)** ($C_{13}H_8MoN_2O_3Se_2$, monoclinic, $P2_1/n$, $a = 9.319(3)$ Å, $b = 12.886(5)$ Å, $c = 13.231(6)$ Å, $\beta = 109.23(3)°$, $Z = 4$) and [W($SePy)_2(CO)_3$] **(7)** ($C_{13}H_8N_2O_3Se_2W$, monoclinic, $P2_1/n$, $a = 9.303(2)$ Å, $b = 12.853(2)$ Å, $c = 13.232(2)$ Å, $\beta = 109.270(10)°$, $Z = 4$) were obtained. The same *N,Se*-coordination pattern emerges from the reaction of [$Fe_2(CO)_9$] with **(2)** leading to [Fe($SePy)_2(CO)_2$] **(8)** ($C_{12}H_8FeN_2O_2Se_2$, monoclinic, $P\bar{1}$, $a = 8.6691(14)$ Å, $b = 12.443(2)$ Å, $c = 14.085(2)$ Å, $\alpha = 105.811(10)°$, $\beta = 107.533(8)°$, $\gamma = 92.075(10)°$, $Z = 4$).

## Introduction

Metal complexes with neutral or anionic ligands containing selenium and nitrogen donors have not been extensively studied,[1a] although they are interesting for several reasons. First, they can provide insight into the competitive coordination behavior between the hard and soft Lewis bases nitrogen and selenium toward the same metal center. Secondly, they are potential precursors for the generation of semiconducting materials, if an appropriate metal center is chosen.[2] It is also conceivable that complexes of this kind with platinum[3] or even other metal centers[4] could be useful as cytostatic drugs.

A ligand that contains two sets of N/Se donor atoms is 2,2′-dipyridyl diselenide, which was first synthesized in 1962.[5] Though it has been known for such a long time and its physical properties[6] and use in organic synthesis[7] and biochemistry[8] have been studied, the crystal structure has not been determined nor has the coordination chemistry been investigated. This is in contrast to the analogous disulfide, whose coordination chemistry has received more attention[9] and whose X-ray structure is known.[10]

Here we report modified procedures for the preparation of pyridine-2-selenol and 2,2′-dipyridyl diselenide, together with the X-ray structures of the latter compound and some complexes with group 6, group 8, and group 10 metal centers.

## Experimental Section

Unless otherwise stated all reactions were carried out under dry nitrogen. Solvents were dried by standard methods with subsequent distillation under nitrogen.

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The starting materials gray selenium (Janssen), 2-bromopyridine (Fluka), glacial acetic acid (Riedel de Haën), chloropentafluorobenzene (Aldrich), $NaBH_4$ (Aldrich), $ZnCl_2$ (Aldrich), $Zn(NO_3)_2$ (Aldrich), and $HgCl_2$ (Merck) were used as received.

$Na_2Se_2$,[11] $Hg(C_6F_5)_2$,[12] $Mo(C_7H_8)(CO)_4$,[13] $W(C_7H_8)(CO)_4$[14] ($C_7H_8$ = norbornadiene), and $Fe_2(CO)_9$[15] were produced by literature methods. For the preparations of pyridine-2-selenol ($C_5H_4NSeH$ = PySeH) and 2,2′-dipyridyl diselenide ($C_5H_4NSeSeC_5H_4N$ = PySeSePy) modified literature methods[5,6c] were used (vide infra).

For the spectroscopic characterization of the compounds the following devices were used: NMR spectra, Bruker AC 200; UV/vis spectra, Perkin-Elmer Lambda 15; IR spectra, Biorad FTS 165; mass spectra, Finnigan MAT 8430.

NMR spectra were recorded at the following frequencies and referred to the given standards: $^1H$, 200.1 MHz, signal of the remaining protons of the deuterated solvent; $^{13}C$, 50.3 MHz, solvent signal; $^{77}Se$, 38.2 MHz, dimethyl selenide, external. Heteronuclear NMR spectra were recorded proton-decoupled.

The elemental analyses were carried out by the analytical laboratory of the Chemical Institute of the University, except that of compound **5**, which was carried out by Microanalytisches Labor Beller, Göttingen, Germany.

**PySeH (1).** $Na_2Se_2$ is prepared by the method of Klayman and Griffin[11] from gray selenium (30 g, 0.38 mol) and $NaBH_4$ (10 g, 0.27 mol) in ethanol (500 mL). After the reaction is complete the ethanol is removed under vacuum and the remaining dark gray to purple residue is dissolved in ethylene glycol monoethyl ether (500 mL). 2-Bromopyridine (20.1 g, 0.127 mol) is added at once and the mixture refluxed for 24 h. The resulting brown solution is filtered, the ethylene glycol monoethyl ether removed in vacuum, and the residue taken up with water (320 mL, not degassed). Glacial acetic acid (80 mL) is added and the immediately precipitated red selenium is filtered off after 1 h stirring. The clear yellow filtrate is evaporated to dryness and the remaining pale yellow solid is extracted in a Soxhlet apparatus with $CH_2Cl_2$ (500 mL). After removal of the solvent and drying under vacuum, the pure product is obtained as a yellow powder (19.8 g, 98%).

$^1H$-NMR ($CDCl_3$): $\delta$ 9.95 (s, broad, 1 H), 7.83 (m, 1 H), 7.75 (m, 1 H), 7.37 (m, 1 H), 6.96 (m, 1 H). $^{13}C$-NMR ($CDCl_3$): $\delta$ 169.4, 138.7, 137.6, 137.1, 116.4. Anal. Calcd for $C_5H_5NSe$: C, 38.0; H, 3.19; N, 8.9. Found: C, 37.8; H, 3.16; N, 8.6. Mp: 138−148 °C.

The selenol is sensitive to moist air but can be stored over a period of many months at −60 °C under nitrogen in the dark without noticeable decomposition.

**PySeSePy (2).** Pyridine-2-selenol (5 g, 31.6 mmol) is suspended in 250 mL of water and $H_2O_2$ (1.6 mL of a 35% solution) is added dropwise via a syringe. Almost immediately an orange oil and a pale yellow solid form. After 1 h of stirring, the orange oil also solidifies and the aqueous phase together with the solid is extracted four times with 50-mL portions of diethyl ether. The ether phase is dried over magnesium sulfate and the solvent removed in a vacuum, yielding an orange oil. Light petroleum (20 mL, fraction 30−40 °C) is added to the oil and the mixture placed in an ultrasonic bath to give the pure product as a pale yellow solid, which is filtered off and dried in vacuum. A further crop of the product is obtained by reducing the light petroleum filtrate to a third and collecting the precipitate by filtration. Yield: 4.21 g (84%).

$^1H$-NMR ($CDCl_3$): $\delta$ 8.45 (m, 2 H), 7.79 (m, 2 H), 7.54 (m, 2 H), 7.08 (m, 2 H). $^{13}C$-NMR ($CDCl_3$): $\delta$ 154.4, 149.6, 137.6, 123.7, 121.3. $^{77}Se$-NMR ($CDCl_3$): $\delta$ 447. UV/vis: $\lambda$ 281, 257 nm ($4 \times 10^{-5}$ M DMSO solution); $\lambda$ 284 nm ($10^{-4}$ M toluene-solution). MS (EI): *m/z* 316 ($M^+$), 235 ($M^+ - Se$). Anal. Calcd for $C_{10}H_8N_2Se_2$: C, 38.2; H, 2.57; N, 8.9. Found: C, 38.1; H, 2.52; N, 8.7. Mp: 49 °C.

The compound is stable to air and moisture and quite soluble in most organic solvents. Single crystals were obtained as pale yellow prisms from diethyl ether/light petroleum (fraction 30−40 °C) at −30 °C.

**[Zn(PySeSePy)$Cl_2$] (3).** To a solution of $ZnCl_2$ (anhydrous, 100 mg, 0.73 mmol) in MeCN (10 mL) a solution of PySeSePy (229 mg, 0.73 mmol) in the same solvent (10 mL) is added dropwise over a period of 20 min. A yellow precipitate forms rapidly and the reaction mixture is stirred for a further 1/2 h. Then diethyl ether (20 mL) is added dropwise to the mixture, which is then stirred for 1 h. The yellow precipitate is filtered off, washed twice with portions of diethyl ether (20 mL), and dried under vacuum to give the pure product (293 mg, 89%).

$^1H$-NMR (DMSO-$d_6$): $\delta$ 8.47 (m, 2 H), 7.74 (m, 4 H), 7.25 (m, 2 H). $^{13}C$-NMR (DMSO-$d_6$): $\delta$ 153.2, 149.9, 138.2, 123.3, 121.9. $^{77}Se$-NMR (DMSO-$d_6$): $\delta$ 439. UV/vis: $\lambda$ 281 nm, 257 nm ($5 \times 10^{-5}$ M DMSO solution). Anal. Calcd for $C_{10}H_8Cl_2N_2Se_2Zn$: C, 26.7; H, 1.79; N, 6.2. Found: C, 26.7; H, 1.70; N, 6.4. Mp: 255 °C dec.

The product is stable to air and moisture and soluble only in DMF and DMSO. Single crystals were obtained as yellow plates from DMF/diethyl ether by diffusion.

**[Zn(PySeSePy)$(NO_3)_2$] (4).** This reaction was carried out without protective atmosphere. The solid ligand PySeSePy (100 mg, 0.32 mmol) is added in one portion to a solution of $Zn(NO_3)_2 \cdot 6\,H_2O$ (96 mg, 0.32 mmol) in acetone (10 mL). A yellow precipitate rapidly forms, and the mixture is stirred for 3 h. The solvent is removed under vacuum and diethyl ether (10 mL) is added to the yellow residue. The resulting suspension is stirred for 10 min, and the yellow solid is filtered off, washed three times with portions of diethyl ether (5 mL), and dried under vacuum to yield the pure product (144 mg, 90%).

$^1H$-NMR (DMSO-$d_6$): $\delta$ 8.46 (m, 2 H), 7.74 (m, 4 H), 7.24 (m, 2 H). $^{13}C$-NMR (DMSO-$d_6$): $\delta$ 153.2, 149.9, 138.2, 123.3, 122.0. $^{77}Se$-NMR: $\delta$ 439. UV/vis: $\lambda$ 281 nm, $\lambda$ 258 nm ($10^{-4}$ M DMSO solution). Anal. Calcd: C, 23.9; H, 1.6; N, 11.1. Found: C, 23.8; H, 1.54, N, 11.0. Mp: slow decomposition from 130 °C, rapid decomposition from 180 °C.

The product is stable to moisture and air and soluble in DMF and DMSO.

**[PySeSePyHg$(C_6F_5)_2$] (5).** This reaction was carried out without protective atmosphere. PySeSePy (100 mg, 0.32 mmo) and $Hg(C_6F_5)_2$ (171 mg, 0.32 mmol) are dissolved in diethyl ether (10 mL). After 10 min of stirring the solvent is removed in vacuum to give the product as a brown-orange solid (quantitative yield).

Anal. Calcd for $C_{22}H_8F_{10}HgN_2Se_2$: C, 31.1; H, 0.95; N, 3.3. Found: C, 31.3; H, 1.08; N, 3.3. Mp: 85−86 °C.

The product is stable to air and moisture and soluble in a variety of organic solvents such as diethyl ether, toluene, and dichloromethane with dissociation into PySeSePy and $Hg(C_6F_5)_2$.

Single crystals were obtained as dark red plates from diisopropyl ether/petroleum ether (fraction 40−70 °C).

**[Mo{$C_5H_4N$(2-Se)-*N,Se*}$_2$(CO)$_3$] (6).** Solid PySeSePy (200 mg, 0.64 mmol) and [$Mo(C_7H_8)(CO)_4$] ($C_7H_8$ = norbornadiene) (192 mg, 0.64 mmol) are mixed and toluene (10 mL) is added. The solution immediately becomes red and gas evolution is noted. After 3 h of stirring, during which the solution darkens, the solvent is evaporated under reduced pressure and *n*-heptane (10 mL) is added to the remaining red-brown solid. Then the reaction vessel is placed into an ultrasonic bath for about 20 s and the resulting suspension is stirred for 3 h. The red-brown solid is filtered off and dried under vacuum (236 mg, 75%).

$^1H$-NMR ($C_6D_6$): $\delta$ 8.28 (m, 2 H), 6.46 (m, 2 H), 6.24 (m, 2 H), 5.89 (m, 2 H). $^{13}C$-NMR ($C_6D_6$): $\delta$ 239.0, 169.2, 148.6, 136.7, 129.8, 119.2. $^{77}Se$-NMR ($C_6D_6$): $\delta$ 5. IR: 2013 s, 1925 s, 1903 s, 1846 sh $cm^{-1}$. Anal. Calcd: C, 31.6; H, 1.64; N, 5.7. Found: C, 31.6, H, 1.68, N, 5.6. Mp: decomposition from 130 °C.

The complex in the solid state is not very sensitive to air and moisture; but solutions are sensitive. An oxygen-free benzene-$d_6$ solution was stable for several days. It is also soluble in toluene and very soluble in dichloromethane.

Single crystals were obtained from toluene/*n*-heptane at −30 °C as large, dark red blocks.

**[W{$C_5H_4N$(2-Se)-*N,Se*}$_2$(CO)$_3$] (7).** Solid PySeSePy (200 mg, 0.64 mmol) and [$W(C_7H_8)(CO)_4$] ($C_7H_8$ = norbornadiene) (248 mg, 0.64 mmol) are mixed and toluene (15 mL) is added. After 48 h of stirring, the now dark red solution is filtered, the residue washed with toluene (5 mL), and the solvent removed from the filtrate under reduced pressure. The remaining dark red solid is extracted once with *n*-heptane

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**Table 1.** Crystallographic Parameters for **2**, **3**, **5**, **6**, **7**, and **8**

| | **2** | **3** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|
| chem formula | $C_{10}H_8N_2Se_2$ | $C_{10}H_8Cl_2N_2Se_2Zn$ | $C_{10}H_8F_{10}HgN_2Se_2$ | $C_{13}H_8MoN_2O_3Se_2$ | $C_{13}H_8N_2O_3Se_2W$ | $C_{12}H_8FeN_2O_2Se_2$ |
| fw | 314.10 | 450.37 | 848.81 | 494.07 | 581.98 | 425.97 |
| cryst syst | monoclinic | triclinic | monoclinic | monoclinic | monoclinic | triclinic |
| space group | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) |
| $a$ (Å) | 10.129(2) | 7.9430(10) | 7.3725(10) | 9.319(3) | 9.303(2) | 8.6691(14) |
| $b$ (Å) | 5.7332(12) | 8.147(2) | 5.9974(14) | 12.886(5) | 12.853(2) | 12.443(2) |
| $c$ (Å) | 19.173(3) | 11.999(2) | 25.573(3) | 13.231(6) | 13.232(2) | 14.085(2) |
| $\alpha$ (deg) | 90 | 93.685(10) | 90 | 90 | 90 | 105.811(10) |
| $\beta$ (deg) | 101.493(8) | 107.763(10) | 98.037(10) | 109.23(3) | 109.270(10) | 107.533(8) |
| $\gamma$ (deg) | 90 | 115.440(10) | 90 | 90 | 90 | 92.075(10) |
| $V$ (Å$^3$) | 1091.0(4) | 650.3(2) | 1119.6(3) | 1500.3(10) | 1493.5(5) | 1382.3(4) |
| $Z$ | 4 | 2 | 2 | 4 | 4 | 4 |
| $T$ (°C) | −100 | −100 | −100 | −130 | −100 | −100 |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.912 | 2.300 | 2.518 | 2.187 | 2.588 | 2.047 |
| $\mu$ (cm$^{-1}$) | 67.38 | 78.72 | 102.23 | 57.35 | 126.17 | 63.54 |
| final $R$ indices [$I > 2\sigma(I)$], R1[a] | 0.0446 | 0.0447 | 0.0344 | 0.0292 | 0.0378 | 0.0535 |
| $R$ indices (all data), wR2[b] | 0.1191 | 0.1186 | 0.0812 | 0.0778 | 0.0986 | 0.1451 |
| GoF ($S$)[c] | 1.029 | 0.978 | 0.984 | 1.133 | 1.012 | 0.969 |

[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] $\mathrm{GoF} = S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

(3 mL) by means of an ultrasonic bath and the undissolved residue filtered off and dried under vacuum to give the pure product (248 mg, 67%).

$^1$H-NMR ($C_6D_6$): $\delta$ 8.41 (m, 2 H), 6.25 (m, 4 H), 5.93 (m, 2 H). $^{13}$C-NMR ($C_6D_6$, [Cr(acac)$_3$]): $\delta$ 232.7, 169.4, 148.3, 136.8, 130.9, 119.7. $^{77}$Se-NMR ($C_6D_6$): $\delta$ −15. IR: 2004 s, 1911 s, 1890 s cm$^{-1}$. Anal. Calcd: C, 26.8; H, 1.39; N, 4.8. Found: C, 27.3; H, 1.42; N, 4.7. Mp: decomposition from 90 °C.

The properties are the same as those of the corresponding molybdenum complex. Single crystals were obtained from dichloromethane/*n*-heptane at −30 °C as red prisms.

**[Fe(SePy)$_2$(CO)$_2$] (8).** Solid PySeSePy (300 mg, 0.96 mmol) and $Fe_2(CO)_9$ (348 mg, 0.96 mmol) are mixed, and toluene (20 mL) is added. After 3 h of stirring the solution is still clear but has taken on a dark red color. The solvent is removed under vacuum and the oily residue extracted once with *n*-heptane (50 mL) in an ultrasonic bath. The red solution is filtered and immediately cooled to −70 to −80 °C. The precipitating red-purple solid is filtered off (the use of a precooled glass filter is recommended) and dried in a vacuum to give the product (277 mg, 67%).

$^1$H-NMR ($C_6D_6$): $\delta$ 8.33 (m, 2 H), 6.46 (m, 2 H), 6.35 (m, 2 H), 5.95. $^{13}$C-NMR ($C_6D_6$): $\delta$ 215.7, 170.2, 149.7, 139.1, 129.0, 119.0. $^{77}$Se ($C_6D_6$): $\delta$ −99. IR: 2023 s, 1980 s, 1968 s, 1945 sh cm$^{-1}$. Anal. Calcd: C, 33.8; H, 1.89; N, 6.6. Found: C, 33.8; H, 1.96; N, 6.3. Mp: 115−117 °C dec.

The solid is not very sensitive to air and moisture, but should be stored under nitrogen at low temperature (−30 °C). After ca. 1 h, a solution in $C_6D_6$ displays noticeable decomposition. The complex is very soluble in toluene, diethyl ether, and dichloromethane and to a much lesser extent in petroleum ether.

Single crystals were obtained from a diethyl ether solution at −30 °C.

**X-ray Structural Studies.** The crystal structures of compounds **2**, **3**, **5**, **7**, and **8** were determined on a Siemens P4 four-circle diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) at −100 °C in $\omega$-scan mode. The crystal structure of compound **6** was determined on a Stoe STADI-4 four-circle diffractometer with the same radiation at −130 °C in $\omega/\theta$-scan mode. Cell constants were refined from setting angles (Siemens) or $\pm\omega$ angles (Stoe) of ca. 60 reflections in the $2\theta$ range 6−25° (Siemens) or 20−23° (Stoe). For all compounds $\psi$-scans for absorption correction were performed.

All structures were solved by direct methods (SHELXS 86).[16] All non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods based upon $F^2$ (SHELXL 93).[17] Hydrogen atoms were included using a riding model with isotropic thermal parameters. Crystallographic data and final *R* values are given in Table 1.

## Results and Discussion

The ligand 2,2′-dipyridyl diselenide contains pairs of hard (nitrogen) and soft (selenium) donors, and thus a great variety of coordination modes is conceivable. Some possibilities are given in Scheme 1.

Complexes of type **i**, in which 2,2′-dipyridyl diselenide acts as an N,N′-chelating ligand, are formed with zinc(II) salts $ZnX_2$ (X = $Cl^-$, $NO_3^-$). Compound **3** (X = $Cl^-$) resembles the well-known complexes of $ZnCl_2$ with other N,N′-chelating ligands such as 1,10-phenanthroline[18a] and 2,2′-bipyridine.[18c] This result is attributable to the preference for hard−hard interactions between zinc(II) and nitrogen, rather than a hard−soft interaction between zinc(II) and selenium. The latter cannot however be completely excluded, because the shortest zinc−selenium distances in the crystal correspond approximately to the sum of the van der Waals radii[19] (vide infra). However this is probably only a packing effect. Exchanging chlorine for nitrate, leading to **4**, affords no change in coordination, as seen by the almost identical NMR data. Attempts to coordinate more than one ligand to the zinc failed. A satisfactory crystal structure of the nitrate could not be obtained because the diselenide bridge of the ligand and the nitrates were disordered. The first effect could be caused by the absence of the above-mentioned weak interaction between zinc and selenium, so that even in the solid state more than one position of the diselenide bridge is possible.

A compound of type **v**, in which the coordination only occurs through the selenium atoms, seems to be found in **5**, which is however an adduct rather than a genuine complex. The selenium−mercury distance is 3.4780(6) Å, implying at best a weak interaction, which can be compared with the interactions between other aromatic diselenides and e.g. iodine.[20] The weakness of the interaction is demonstrated by the fact that this adduct exists only in the solid state and decomposes in solution immediately into its components, as evidenced by proton NMR,

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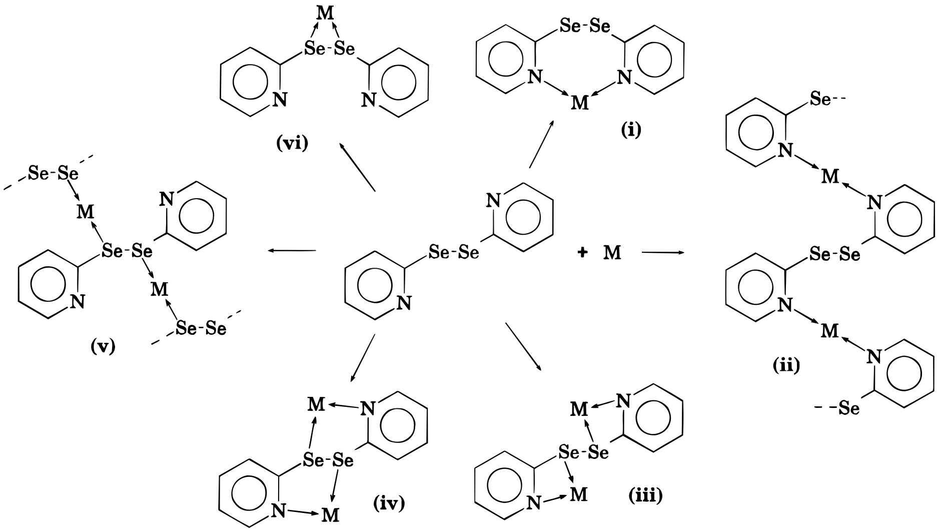
**Scheme 1**



which shows the signals for the free diselenide. The color changes on dissolution from brown-orange to light yellow, the color of the free diselenide in solution. The intense color of the adduct may be due to a charge transfer transition in the visible area of the electromagnetic spectrum, but the decomposition in solution precludes the recording of UV/visible spectra.

The reaction between 2,2′-dipyridyl diselenide and norbornadiene tetracarbonyl complexes of molybdenum and tungsten leads to the displacement of norbornadiene and the loss of one carbonyl group, with reductive cleavage of the selenium-selenium bond and oxidation of the metal center from oxidation state 0 to +2 (eq 1).

$$\mathrm{PySeSePy} + [\mathrm{M(CO)_4(C_7H_8)}] \rightarrow [\mathrm{M(SePy)_2(CO)_3}] + \mathrm{C_7H_8} + \mathrm{CO} \quad (1)$$

$$\mathrm{M} = \mathrm{Mo, W;\ C_7H_8} = \text{norbornadiene}$$

This type of reaction is well-known for metal carbonyls and usually leads to $\mu$-SeR-bridged (R = alkyl or aryl) binuclear complexes.[1b] However, to the best of our knowledge, this is the first time that olefin/carbonyl complexes have been used for this purpose. The reaction takes place under very mild conditions in good yields and produces mononuclear complexes with the unusual coordination number seven at the metal center. That no bridging by the selenolate is observed in these complexes is presumably associated with the nitrogen donor, which stabilizes the metal center by additional coordination, thus fulfilling the 18-electron rule. Similar reactions between $[\mathrm{CpMo(CO)_2}]_2$ (containing an Mo−Mo triple bond) and nitrogen-heterocyclic disulfides have recently been reported, also leading to mononuclear rather than $\mu$-SR-bridged complexes.[9d]

The assumption of oxidation state +2 for the metal center and −2 for the selenium atoms in **6** and **7** is shown to be reasonable by the $^{77}$Se-NMR data. In both cases a drastic shift to higher field relative to the diselenide is observed (from $\delta = 439$ ppm to $\delta = 5$ ppm and $\delta = -15$ ppm, respectively, see above), hence indicating increased shielding of the selenium nucleus in the complexes. Additionally the slightly greater shielding effect in the tungsten complex can be interpreted in terms of stronger back-bonding from the metal to the selenium than in the molybdenum complex.

An example of reductive cleavage of the selenium−selenium bond using a complex containing a metal−metal single bond is the reaction between the diselenide and diiron enneacarbonyl $[\mathrm{Fe_2(CO)_9}]$. The course of the reaction is similar to that of the norbornadiene−carbonyl complexes (cf. eq 1) and is depicted in eq 2.

$$\mathrm{PySeSePy} + [\mathrm{Fe_2(CO)_9}] \rightarrow [\mathrm{Fe(SePy)_2(CO)_2}] + 2\,\mathrm{CO} + [\mathrm{Fe(CO)_5}] \quad (2)$$

The product contains two selenolate ligands coordinated via the nitrogen and the selenium atoms at the iron center, which bears two additional carbonyl groups **(8)**, thus completing its noble gas configuration. The preparation of a similar thio-analogous complex with the 2-quinolinethiolato ligand has been reported recently,[21] but involved a different synthetic route starting from iron pentacarbonyl and the thiol. The chemical shift of the selenium atoms in **8** is even further toward high field compared with the diselenide than for the complexes **6** and **7**, thus indicating a strong shielding of the selenium nuclei. This might be caused by the higher electron density at the iron center in oxidation state II than at the molybdenum or tungsten atoms in the same oxidation state and hence more effective back-bonding from iron to selenium. It is interesting to note that the NMR spectra of **(8)** differ substantially depending whether they are recorded in benzene-$d_6$ or deuterochloroform. The complex apparently reacts almost immediately with deuterochloroform to give a product of unknown composition whose stability in solution is much greater than that of **8**. This point is still under investigation.

**X-ray Crystallography.** The crystal structure of **2** is shown in Figure 1, with bond lengths and angles in Table 2. The structure is similar to that of the corresponding disulfide,[10] which crystallizes in the same space group but with different cell parameters (the cell in ref 10 corresponded to $P2_1/c$ and can be reorientated to $P2_1/n$ with $a = 13.310$ Å, $b = 5.581$ Å, $c = 14.902$ Å, and $\beta = 111.43°$); the two compounds do not appear to be isostructural.

The diselenide shows no crystallographic symmetry. Two approximately ideal planes (interplanar angle = 84.2°) can be laid through Se2−Se1−C1−C2 (torsion angle = 0.6(5)°) and Se1−Se2−C6−C7 (torsion angle = −0.8(6)°) and can be brought into register by rotation about the Se−Se bond. In the disulfide the corresponding S−S−C−C torsion angles are 5.1

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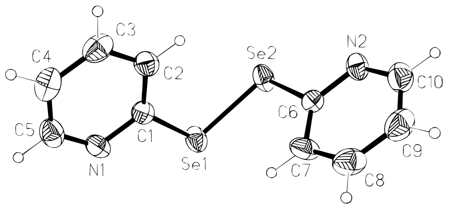

**Figure 1.** Molecule of compound **2** in the crystal. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **2**

| | | | |
|---|---|---|---|
| Se1−C1 | 1.932(6) | C1−C2 | 1.369(9) |
| Se1−Se2 | 2.2969(9) | N2−C6 | 1.331(8) |
| Se2−C6 | 1.934(6) | N2−C10 | 1.339(8) |
| N1−C5 | 1.325(8) | C6−C7 | 1.377(8) |
| N1−C1 | 1.339(8) | | |
| C1−Se1−Se2 | 102.8(2) | C2−C1−Se1 | 126.5(5) |
| C6−Se2−Se1 | 103.7(2) | C6−N2−C10 | 116.1(5) |
| C5−N1−C1 | 117.0(6) | N2−C6−C7 | 125.3(6) |
| N1−C1−C2 | 124.0(6) | N2−C6−Se2 | 109.4(4) |
| N1−C1−Se1 | 109.5(4) | C7−C6−Se2 | 125.3(5) |

and 10.2°, respectively, so that even after rotation about the S−S bond the rings stay somewhat inclined to each other. The commonly observed approximate coplanarity of ring and E−E bonds (C−C−E−E or N−C−E−E torsion angles ca. 0°) in such molecules has been explained in terms of a minimization of S···S lone pair repulsion.[10] The C−E−E−C torsion angles are similar: 87.1° for E = S and 84.3(2)° for E = Se.

In both compounds the nitrogen atoms point away from the E-E bonds to the "outside" of the molecule ("trans,trans"), except for one disorder component of the disulfide. Semiempirical CNDO/2 calculations[22] indicated that the cis,cis conformation of disulfides should be slightly more stable than cis,trans or trans,trans, and this was indeed observed for 3,3′-dihydroxydi-2-pyridyl disulfide.[23]

Short contacts are observed between Se1 and H7 ($d$ = 2.909 Å) and Se2 and H2 ($d$ = 2.911 Å), which are significantly shorter than the distances between Se1 and H2 ($d$ = 3.104 Å) and Se2 and H7 ($d$ = 3.089 Å). This interaction is associated with a distortion of the geometry at the carbon atoms C1 and C6: the Se1−C1−N1 and the Se1−C1−C2 angles are 109.5(4) and 126.5(5),° respectively, and the Se2−C6−N2 and Se2−C6−C7 angles are 109.4(4) and 125.3(5)°, respectively. It thus seems reasonable to propose repulsive Se...H interactions. Equivalent features are found in the disulfide, for which however a 1,4-sulfur−carbon interaction was mentioned.[10]

The C−Se−Se−C torsion angle and the Se−Se and the Se−C bond lengths of 2.2969(9) (Se1−Se2), 1.932(6) (Se1−C1), and 1.934(6) Å (Se2−C6) are in accordance with the values in other aromatic diselenides,[24] ranging from 2.29(1) to 2.343(1) Å for Se−Se and from 1.910 to 1.934(6) Å for Se−C. (For disulfides a correlation between shorter S−S bonds and 0°/180° X−C−S−S torsion angles has been discussed in terms of interactions of sulfur 3p$\pi$ orbitals with the aromatic $\pi$ system).[25] The coordination at selenium can be regarded as essentially tetrahedral (C1−Se1−Se2 = 102.8(2)°, Se1−Se2−C6 = 103.7(2)°) if the lone pairs are taken into account.

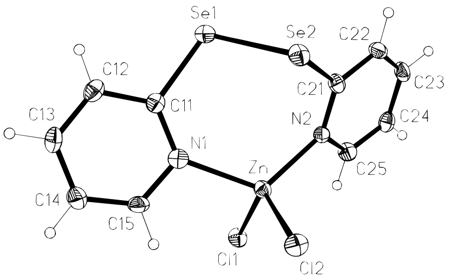

**Figure 2.** Molecule of compound **3** in the crystal. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **3**

| | | | |
|---|---|---|---|
| Se1−C11 | 1.926(5) | N1−C15 | 1.346(7) |
| Se1−S2 | 2.3148(9) | N1−C11 | 1.348(7) |
| Se2−C21 | 1.926(5) | C11−C12 | 1.390(8) |
| Zn−N2 | 2.046(4) | N2−C21 | 1.338(6) |
| Zn−N1 | 2.077(5) | N2−C25 | 1.347(6) |
| Zn−Cl2 | 2.2283(13) | C21−C22 | 1.386(7) |
| Zn−Cl1 | 2.2613(13) | | |
| C11−Se1−Se2 | 104.6(2) | C11−N1−Zn | 132.6(4) |
| C21−Se2−Se1 | 99.8(2) | N1−C11−C12 | 123.6(5) |
| N2−Zn−N1 | 120.8(2) | N1−C11−Se1 | 121.3(4) |
| N2−Zn−Cl2 | 114.31(13) | C12−C11−Se1 | 115.0(4) |
| N1−Zn−Cl2 | 103.79(12) | C21−N2−C25 | 118.5(4) |
| N2−Zn−Cl1 | 101.80(12) | C21−N2−Zn | 122.6(3) |
| N1−Zn−Cl1 | 98.82(13) | C25−N2−Zn | 118.8(3) |
| Cl2−Zn−Cl1 | 116.99(5) | N2−C21−C22 | 122.3(5) |
| C15−N1−C11 | 116.0(5) | N2−C21−Se2 | 117.8(4) |
| C15−N1−Zn | 111.3(3) | C22−C21−Se2 | 119.9(4) |

The crystal structure of **3** is shown in Figure 2, with bond lengths and angles in Table 3. The main feature of the structure is a seven-membered ring formed by the zinc atom and the atoms N1, C11, Se1, Se2, C21, and N2 of the N,N′-chelating 2,2′-dipyridyl diselenide. This ring conformation is such that all ring atoms lie on the same side of a plane through the zinc and both nitrogen atoms. The atoms Se1, C11, N1, and Zn and Se2, C21, N2, and Zn also lie in two almost ideal planes. The geometry of the diselenide as a chelating ligand differs substantially from that of the free ligand (values in brackets); the inclination of the pyridyl rings is reduced to 40.1° (from 84.2°), whereas the C11−Se1−Se2−C21 torsion angle is larger at 98.2(2)° (84.3(2)°) to minimize the ring strain. The angles at the carbon atoms C11 and C21 lie near to the ideal 120° (see Table 3, cf. C1 and C6 in the free ligand) as a consequence of the changed positions of the nitrogen atoms, since no steric repulsion between H12/Se2 and H22/Se1 (cf. H2/Se2 and H7/Se1 in the free ligand) can take place. The Se−Se bond (2.3148(9) Å) is slightly lengthened with respect to the free ligand. The Se−Se−C−N torsion angles are 179°.

The zinc atom is coordinated in a distorted tetrahedral manner by the two nitrogen and two chlorine atoms, with maximum and minimum angles at zinc of 120.8(2)° (N1−Zn−N2) and 98.82(13)° (N1−Zn−Cl1). Furthermore, the compression of the tetrahedron is reflected in the Cl1−Zn−Cl2 angle of 116.99(5)°, attributable to minimization of Cl−Cl interactions. The zinc−selenium distances are significantly different (3.758 for Zn−Se1 and 3.338 Å for Zn−Se2); the smaller value is close to the sum of the van der Waals radii of 3.3 Å.[19a]

The zinc−chlorine and the zinc−nitrogen bond lengths both differ slightly among themselves (2.2613(13), 2.2283(13) Å and 2.077(5), 2.046(4) Å, respectively), but otherwise are in agreement with those for other complexes of zinc dichloride with various nitrogen donor ligands such as 1,10-phenanthroline,[18a] pyridine,[18b] and 2,2′-dipyridine[18c] ranging from 2.198 to 2.228 Å (Zn−Cl) and from 2.046 to 2.072 Å (Zn−N), respectively.

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(24) (a) Marsh, R. E. *Acta Crystallogr.* **1952**, *5*, 458. (b) Woodard, C. M.; Brown, D. S.; Lee, J. D.; Massey, A. G. *J. Organomet. Chem.* **1976**, *121*, 333. (c) Jones, P. G.; Kienitz, C.; Thöne, C. *Z. Kristallogr.* **1994**, *209*, 83.

(25) Simmons, C. J.; Lundeen, M.; Seff, K. *Inorg. Chem.* **1979**, *18*, 3444.

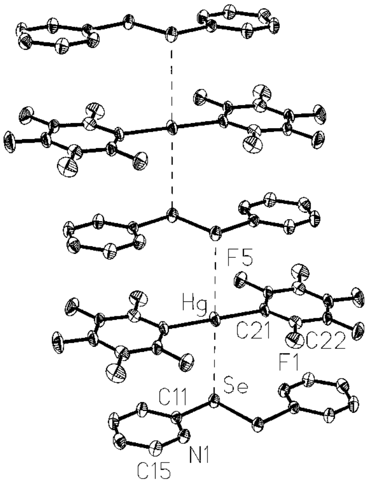

**Figure 3.** Steplike stacking of adduct **5** in the crystal. Ellipsoids correspond to 50% probability levels. Only the asymmetric unit is numbered. Hydrogen atoms are omitted for clarity.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for **5**[a]

| | | | |
|---|---|---|---|
| Hg−C21 | 2.066(4) | N1−C11 | 1.329(6) |
| Hg−Se | 3.4780(6) | N1−C15 | 1.339(6) |
| Se−C11 | 1.917(4) | C11−C12 | 1.401(6) |
| Se−Se#2 | 2.3515(11) | | |
| C21#1−Hg−C21 | 180.0 | C11−N1−C15 | 117.3(4) |
| C21#1−Hg−Se | 89.83(12) | N1−C11−C12 | 123.9(4) |
| C21−Hg−Se | 90.17(12) | N1−C11−Se | 118.1(3) |
| Se#1−Hg−Se | 180.0 | C12−C11−Se | 118.0(3) |
| C11−Se−Se#2 | 92.52(14) | C26−C21−C22 | 116.1(4) |
| C11−Se−Hg | 90.32(12) | C26−C21−Hg | 120.8(3) |
| Se#2−Se−Hg | 90.77(3) | C22−C21−Hg | 123.1(3) |

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y + 1$, $-z + 1$; #2, $-x + 1$, $-y + 1$, $-z + 1$.

The structure of compound **5** is shown in Figure 3, with bond lengths and angles in Table 4.

Compound **5** consists of 2,2′-dipyridyl diselenide and bis(pentafluorophenyl)mercury(II) molecules stacked alternately in such a way that the selenium and the mercury atoms form a "staircase" (see the dashed lines in Figure 3). The asymmetric unit contains only a half molecule of each component. The missing halves are generated by inversion at $(^1/_2,^1/_2,^1/_2)$ (the position of the mercury atom) for the mercury component and at $(0,^1/_2,^1/_2)$ (the center of the selenium−selenium bond) for the diselenide. The pyridine rings are almost parallel to the pentafluorophenyl rings (interplanar angle 4.6°). The diselenide in this adduct shows a geometry completely different from that of the free or the nitrogen−coordinated ligand: the whole molecule is planar, as indicated by the torsion angle C12−C11−Se−Se#1 178.4(3)°; as far as we know this is unique for an aromatic diselenide with no further annelation at selenium. All angles at selenium are close to 90°, leading to a trigonal pyramidal coordination geometry. The mercury component is also planar: the Hg−C21−C22−C23 torsion angle is 175.4(3)°. This is also in contrast to free bis(pentafluorophenyl)mercury(II), where the rings are inclined by 59.4(12)°.[26] The environment of the mercury (including the weak Hg−Se interactions, vide infra) is tetragonal planar with all angles close to 90°. Most bond lengths show no great deviations from the expected values. A notable exception is the Se−Se bond with 2.3515(11) Å, much longer than in the free ligand (2.2969(9) Å). A similar lengthening of S−S bonds in disulfides when the C−S−S−C torsion angles are 180° has previously been noted and attributed to increased repulsion between the lone pairs at the sulfur atoms.[27] However, the Se−Se bond lengths in the diphenyldiselenide−iodine complex (2.29(1) Å (free ligand) vs 2.347[20a] Å) may indicate that the Se−Se bond is weakened anyway on formation of complexes or adducts. The Hg−C bonds (2.066(4) Å) are somewhat shorter than in free bis(pentafluorophenyl)mercury(II) (2.095 Å). The first effect can be caused by two factors: First, the planarity of the diselenide leads to an electronic repulsion of the free electron pairs at the selenium atoms. Second, the charge transfer interaction with the mercury atom diminishes the electron density between the selenium atoms, thus weakening the Se−Se bond; it also increases the electron density at the mercury atom and thus shortens the mercury−carbon bonds by partial delocalization into the electron-withdrawing pentafluorophenyl rings. With a value of 3.4780(6) Å the contact between selenium and mercury cannot be regarded as a true bond, because it is even greater than the sum of the van der Waals radii (3.4 Å[19]) and about 1 Å longer than the covalent Hg−Se bond in the selenolate complex $Hg(SeNC_5H_4)_2$ with 2.458(1) Å[2]. Nevertheless this soft−soft interaction is strong enough to induce a planarization of the components, thus overriding steric and electronic causes of nonplanar geometries in the pure components.

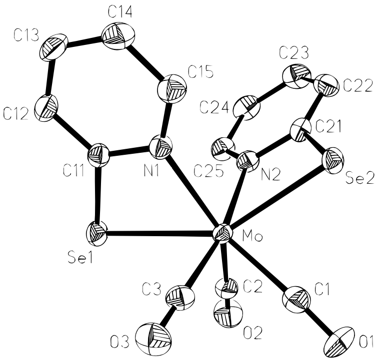

**Figure 4.** Molecule of compound **6** in the crystal. Ellipsoids correspond to 50% probability levels. Hydrogen atoms are omitted for clarity.

The crystal structure of **6** is shown in Figure 4, with bond lengths and angles in Table 5. The complex shows seven-coordinate molybdenum. The four-membered rings derived from the chelating N,Se-coordination of the two 2-selenopyridines are coplanar with the adjacent pyridine rings, as seen from the torsion angles Se1−C11−N1−C15 = −177.5(3)°/Mo−Se1−C11−N1 = −3.4(2)° and Se2−C21−N2−C25 = −178.7(3)°/Mo−Se2−C21−N2 = 0.1(2)°. The two combined planes subtend an angle of 97.5°. The orientation of the 2-selenopyridines toward each other is such that a nitrogen lies opposite a selenium atom and vice versa. Due to steric constraints of chelation, the angles at the selenium, carbon, and nitrogen atoms belonging to the four-membered rings are significantly smaller than normal: 104.5(2) and 107.4(2)° for the nitrogen atoms, 109.1(2) and 111.8(2)° for the carbon atoms (cf. 120° ideal value), and 77.09(11) and 77.79(11)° for the selenium atoms (cf. ≈ 100°).[1c] The coordination geometry at the molybdenum atom can be regarded as distorted capped trigonal prismatic, as shown in Figure 5. The accompanying atomic distances of the coordination polyhedron are given in Table 6.

The trigonal planes of the prism (C1−C2−C3/Se2−N1−N2) are almost ideally parallel (interplanar angle 2°).

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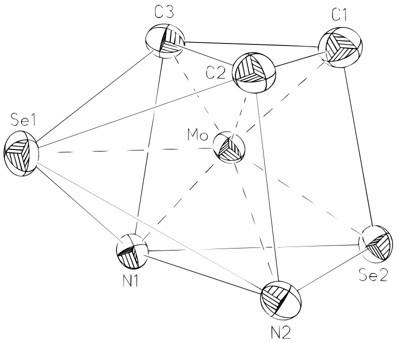

**Figure 5.** Coordination polyhedron of compound **6**.

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for **6**

| | | | |
|---|---|---|---|
| Mo−C1 | 1.964(4) | Se2−C21 | 1.891(3) |
| Mo−C2 | 1.966(4) | N1−C15 | 1.338(5) |
| Mo−C3 | 2.011(4) | N1−C11 | 1.353(4) |
| Mo−N2 | 2.206(3) | C11−C12 | 1.382(5) |
| Mo−N1 | 2.247(3) | N2−C25 | 1.340(4) |
| Mo−Se2 | 2.6411(8) | N2−C21 | 1.344(4) |
| Mo−Se1 | 2.6558(10) | C21−C22 | 1.384(5) |
| Se1−C11 | 1.896(3) | | |
| C1−Mo−C2 | 74.4(2) | N2−Mo−Se1 | 93.64(8) |
| C1−Mo−C3 | 76.4(2) | N1−Mo−Se1 | 66.46(8) |
| C2−Mo−C3 | 103.28(14) | Se2−Mo−Se1 | 147.41(2) |
| C1−Mo−N2 | 113.87(14) | C11−Se1−Mo | 77.09(11) |
| C2−Mo−N2 | 81.93(13) | C21−Se2−Mo | 77.79(11) |
| C3−Mo−N2 | 169.56(13) | C15−N1−C11 | 119.1(3) |
| C1−Mo−N1 | 142.19(14) | C15−N1−Mo | 136.4(2) |
| C2−Mo−N1 | 143.12(13) | C11−N1−Mo | 104.5(2) |
| C3−Mo−N1 | 86.69(13) | N1−C11−C12 | 121.3(3) |
| N2−Mo−N1 | 83.85(11) | N1−C11−Se1 | 111.8(2) |
| C1−Mo−Se2 | 73.45(11) | C12−C11−Se1 | 126.9(3) |
| C2−Mo−Se2 | 118.32(11) | C25−N2−C21 | 119.6(3) |
| C3−Mo−Se2 | 117.99(10) | C25−N2−Mo | 133.0(2) |
| N2−Mo−Se2 | 65.72(8) | C21−N2−Mo | 107.4(2) |
| N1−Mo−Se2 | 85.65(8) | N2−C21−C22 | 122.0(3) |
| C1−Mo−Se1 | 139.13(11) | N2−C21−Se2 | 109.1(2) |
| C2−Mo−Se1 | 80.69(11) | C22−C21−Se2 | 128.8(3) |
| C3−Mo−Se1 | 78.49(11) | | |

**Table 6** Selected Bond Lengths (Å) for the Coordination Polyhedron of **6** (See Figure 5)

| | | | |
|---|---|---|---|
| Se1−N1 | 2.708 | N1−N2 | 2.975 |
| Se1−N2 | 3.558 | N1−C3 | 2.928 |
| Se1−C2 | 3.038 | N2−C2 | 2.741 |
| Se1−C3 | 2.994 | C1−C2 | 2.376 |
| Se2−N1 | 3.335 | C1−C3 | 2.459 |
| Se2−N2 | 2.655 | C2−C3 | 3.118 |
| Se2−C1 | 2.807 | | |

The Mo−N bond lengths (2.247(3) and 2.206(3) Å) lie in a range that is also observed in molybdenum complexes with the analogous pyridine-2-thiolato ligand[28] (2.157(5)[28b] −2.328(5) Å[28f]). The Mo−Se bond lengths (2.6558(10) and 2.6411(8) Å) are in agreement with reported values (2.633(2)−2.661(1)Å).[29]

The crystal structure of **7** is shown in Figure 6, with bond lengths and angles in Table 7.

Complex **7** is isostructural to complex **6**, and we therefore do not discuss it further.

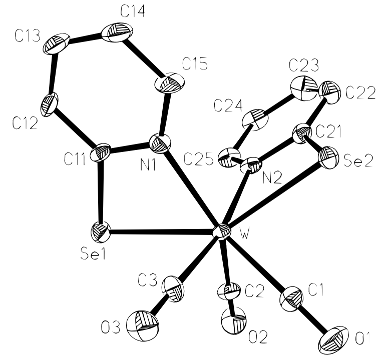

**Figure 6.** Molecule of compound **7** in the crystal. Ellipsoids correspond to 50% probability levels. Hydrogen atoms are omitted for clarity.

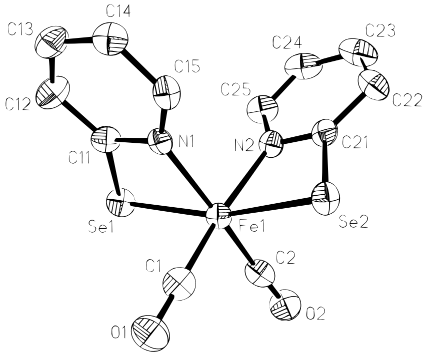

**Figure 7.** One of the two independent molecules of compound **8** in the crystal. Ellipsoids correspond to 50% probability levels. Hydrogen atoms are omitted for clarity.

**Table 7.** Selected Bond Lengths (Å) and Angles (deg) for **7**

| | | | |
|---|---|---|---|
| W−C2 | 1.946(8) | Se2−C21 | 1.882(6) |
| W−C1 | 1.976(7) | N1−C11 | 1.351(8) |
| W−C3 | 2.017(6) | N1−C15 | 1.371(8) |
| W−N2 | 2.205(5) | C11−C12 | 1.401(8) |
| W−N1 | 2.232(5) | N2−C21 | 1.338(8) |
| W−Se2 | 2.6354(7) | N2−C25 | 1.341(8) |
| W−Se1 | 2.6579(9) | C21−C22 | 1.390(9) |
| Se1−C11 | 1.899(6) | | |
| C2−W−C1 | 74.2(3) | N2−W−Se1 | 92.79(14) |
| C2−W−C3 | 103.2(3) | N1−W−Se1 | 66.19(14) |
| C1−W−C3 | 76.0(3) | Se2−W−Se1 | 146.47(2) |
| C2−W−N2 | 82.3(2) | C11−Se1−W | 77.2(2) |
| C1−W−N2 | 115.4(2) | C21−Se2−W | 77.8(2) |
| C3−W−N2 | 168.4(2) | C11−N1−C15 | 118.5(6) |
| C2−W−N1 | 142.6(3) | C11−N1−W | 105.7(4) |
| C1−W−N1 | 142.8(3) | C15−N1−W | 135.9(5) |
| C3−W−N1 | 86.6(2) | N1−C11−C12 | 122.3(6) |
| N2−W−N1 | 82.9(2) | N1−C11−Se1 | 110.9(4) |
| C2−W−Se2 | 118.9(2) | C12−C11−Se1 | 126.8(5) |
| C1−W−Se2 | 75.2(2) | C21−N2−C25 | 120.4(6) |
| C3−W−Se2 | 118.6(2) | C21−N2−W | 107.2(4) |
| N2−W−Se2 | 65.58(14) | C25−N2−W | 132.3(4) |
| N1−W−Se2 | 85.13(14) | N2−C21−C22 | 121.4(6) |
| C2−W−Se1 | 80.4(2) | N2−C21−Se2 | 109.4(4) |
| C1−W−Se1 | 138.3(2) | C22−C21−Se2 | 129.3(5) |
| C3−W−Se1 | 78.3(2) | | |

Compound **8** crystallizes with two independent molecules per asymmetric unit. The crystal structure of one molecule of **8** is shown in Figure 7, with bond lengths and angles in Table 8.

The structure of complex **8** is very similar to that of compounds **6** and **7**, displaying the same features: two four-membered rings each including the metal center, a coordinating nitrogen and selenium atom and a carbon atom of the pyridine ring, the planarity of these rings with the adjacent pyridine rings (interplanar angles between these rings: 2.1 and 1.3° at Fe1 and 3.1 and 1.6° at Fe2, respectively), interplanar angles of the

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**Table 8.** Selected Bond Lengths (Å) and Angles (deg) for **8** (Two Columns Correspond to Two Independent Molecules)

| | | | | | |
|---|---|---|---|---|---|
| Se1−C11 | 1.887(8) | 1.894(8) | Fe1−N1 | 2.005(6) | 2.008(7) |
| Se1−Fe1 | 2.457(2) | 2.4394(14) | N1−C15 | 1.325(10) | 1.349(10) |
| Se2−C21 | 1.901(8) | 1.885(9) | N1−C11 | 1.359(10) | 1.352(10) |
| Se2−Fe1 | 2.442(2) | 2.4502(14) | C11−C12 | 1.383(12) | 1.398(11) |
| Fe1−C1 | 1.757(9) | 1.779(9) | N2−C21 | 1.333(11) | 1.344(10) |
| Fe1−C2 | 1.786(9) | 1.771(9) | N2−C25 | 1.355(11) | 1.348(10) |
| Fe1−N2 | 2.003(7) | 1.995(7) | C21−C22 | 1.409(12) | 1.378(11) |

| | | | | | |
|---|---|---|---|---|---|
| C11−Se1−Fe1 | 75.3(2) | 75.3(2) | N1−Fe1−Se1 | 72.0(2) | 71.9(2) |
| C21−Se2−Fe1 | 74.6(3) | 75.1(2) | Se2−Fe1−Se1 | 165.43(6) | 163.75(6) |
| C1−Fe1−C2 | 91.9(4) | 92.5(4) | C15−N1−C11 | 120.7(7) | 119.2(7) |
| C1−Fe1−N2 | 169.7(3) | 169.4(3) | C15−N1−Fe1 | 134.7(6) | 135.8(6) |
| C2−Fe1−N2 | 90.2(3) | 90.5(3) | C11−N1−Fe1 | 104.5(5) | 105.0(5) |
| C1−Fe1−N1 | 92.7(3) | 92.1(3) | N1−C11−C12 | 120.1(8) | 122.5(8) |
| C2−Fe1−N1 | 170.0(3) | 169.7(3) | N1−C11−Se1 | 108.2(6) | 107.5(6) |
| N2−Fe1−N1 | 86.9(3) | 86.7(3) | C12−C11−Se1 | 131.7(7) | 130.0(6) |
| C1−Fe1−Se2 | 97.5(3) | 97.5(3) | C21−N2−C25 | 120.1(7) | 120.2(7) |
| C2−Fe1−Se2 | 92.3(3) | 93.5(3) | C21−N2−Fe1 | 104.4(5) | 104.4(6) |
| N2−Fe1−Se2 | 72.3(2) | 72.1(2) | C25−N2−Fe1 | 135.4(6) | 135.4(5) |
| N1−Fe1−Se2 | 95.8(2) | 95.1(2) | N2−C21−C22 | 122.6(8) | 121.3(8) |
| C1−Fe1−Se1 | 91.1(3) | 92.8(3) | N2−C21−Se2 | 108.6(6) | 108.7(6) |
| C2−Fe1−Se1 | 99.1(3) | 98.6(3) | C22−C21−Se2 | 128.7(7) | 130.1(7) |
| N2−Fe1−Se1 | 98.5(2) | 96.9(2) | | | |

combined planes of 84.8 (Fe1) and 84.6° (Fe2), and the orientation of one nitrogen atom of one four-membered ring opposite a selenium atom in the other one. As in the complexes **6** and **7**, the angles at the selenium, carbon, and nitrogen atoms of the four-membered rings are again significantly smaller than the normal values: 104.5(5), 104.4(5), 105.0(5), and 104.4(6)° for the nitrogen atoms, 108.2(6), 108.6(6), 107.5(6), and 108.7(6)° for the carbon atoms (cf. 120° ideal value), and 75.3(2), 74.6(3), 75.3(2) and 75.1(2)° for the selenium atoms (cf. ≈ 100°).[1c] The coordination geometry at the iron atom is distorted octahedral.

The Fe−N distances (2.005(6), 2.003(7), 1.995(7), and 2.008(7) Å) are much shorter than in the comparable complex tetraethylammonium tris(pyridine-2-thiolato)ferrate(II)[30] (2.141(3)−2.173(4) Å) and resemble that in bis[(carbonyl)(quinoline-2-thiolato-*N*,*S*)]iron(II).[21] The Fe−Se bond lengths (2.457(2), 2.442(2), 2.4394(14), and 2.4502(14) Å) are in agreement with reported values (2.411(1)−2.421(1) Å).[31]

## Conclusions

The coordination chemistry of 2,2′-dipyridyl diselenide displays a great variety of possibilities that derive from the existence of a set of hard and soft donor atoms and the lability of the selenium-selenium bond toward reductive cleavage. We are optimistic that it will be possible in the future to realize further coordination modes of this ligand as depicted in Scheme 1. This will form the object of further investigations.

## Note Added in Proof

During revision of this manuscript a report appeared in this journal on the preparation and structure of homoleptic tin and lead pyridineselenolates.[32] Syntheses involved either reductive cleavage of the diselenide by the metal or metathesis of the selenolate and an appropriate metal chloride.

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**Supporting Information Available:** A table of complete crystallographic information in CIF format (25 pages). Ordering information is given on any current masthead page.

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