The Synthesis of a Novel *Cyclo*-Se_3-Bridged Trinuclear Ru Complex

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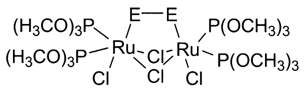
Abstract: The reaction of $[\{RuCl[P(OCH_3)_3]_2\}_2(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$ with four equivalents of $NaPF_6$ gave $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}Se_2)](PF_6)_3$ and $[\{Ru[P(OCH_3)_3]_2(CH_3CN)(\mu\text{-}Cl)\}_2(\mu\text{-}cyclo\text{-}Se_3)\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}](PF_6)_4$. The former is a $Ru^{II}Ru^{III}$ mixed-valent paramagnetic compound. The X-ray structural analysis of the latter compound revealed that it has a novel μ-*cyclo*-Se_3 neutral ligand and three Ru^{II} atoms.

Keywords: bridging ligands · *cyclo*-triselenium ligand · dinuclear Ru^{III} complex · selenium · trinuclear Ru^{II} complex

Introduction

Chalcogen ligands have been recognized as an important group, especially when they are in polymetallic complexes such as the iron-sulfur clusters in nitrogenase[1] and synthetic polymetallic chalcogenide clusters. The remarkably strong donating ability of inorganic sulfur ligands and their structural diversity in bridged-metal centers have for many years tempted synthetic chemists to synthesize functionally and structurally novel cluster complexes.[2] The syntheses and reactions of polymetallic complexes containing heavier chalcogens have also been a research target.[3] The larger ionic radii, the ligands' softer properties, and the increased propensity for catenation would cause a significant difference in the reactivity of the sulfur-analogue complexes. Since the first report of the disulfide-bridged Ru^{III} dinuclear complex, $[\{RuCl[P(OCH_3)_3]_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**1**), we have developed novel reactions on the bridging disulfide ligand of **1** and related complexes;[4, 5] for example reactions with alkenes and ketones that involve C–H bond activation and C–S bond formation on the bridging disulfide ligand.[6–8] These reactions clearly show that, under certain conditions, a disulfide ligand can act like a transition metal center in organometallic complexes. This opens up a new area both in sulfur chemistry and organometallic chemistry. Recently, we prepared the selenium analogue of **1**, $[\{RuCl[P(OCH_3)_3]_2\}_2(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$ (**2**) (Scheme 1),[9] and observed substitution reactions of the terminal and bridging chloride ligands similar to those in **1**. In the present paper, the synthesis of the *cyclo*-Se_3-bridged trinuclear ruthenium complex prepared from **2** is reported. The reaction is unique to **2**, and is not observed for **1**.



1: E = S
2: E = Se

Results and Discussion

Treatment of **2** with an appropriate equivalent of $AgCF_3SO_3$ resulted in the formation of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2(\mu\text{-}Se_2)(\mu\text{-}Cl)_2](CF_3SO_3)_2$ (**3**), and $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}Se_2)](CF_3SO_3)_4$ (**4**), similar to the sulfur analogue.[10] Although the elemental-analysis data of **3** were satisfactory, several unassignable peaks were observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra. In solution, **3** seems unstable and equilibrates with a couple of unknown species by disproportionation. Nevertheless, in situ prepared **3** could be treated with 2,3-dimethylbutadiene to give a complex carrying a bridging ligand of a C_4S_2 six-membered ring, $[\{Ru[P(OCH_3)_3]_2(CH_3CN)\}_2\{\mu\text{-}SeCH_2C(CH_3){=}C(CH_3)CH_2Se\}(\mu\text{-}Cl)_2](CF_3SO_3)_2$ (**5**).[11] This reaction parallels that of the sulfur analogue.[12]

The reaction of **2** with four equivalents of $NaPF_6$ in CH_3CN/H_2O gave a mixture of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}Se_2)](PF_6)_3$ (**6**) and an unknown diamagnetic complex, after standard workup and recrystallization by layer diffusion of Et_2O onto a solution of the crude product in CH_3CN (Scheme 1).[13] In the $^{31}P\{^1H\}$ NMR spectrum of the recrystallized products, a septet signal from the PF_6^- counter anion at

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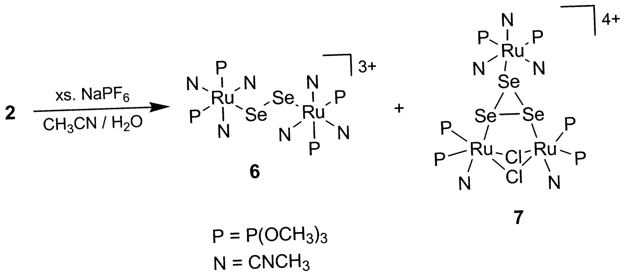


Scheme 1.

$\delta = -143.1$ ($J_{PF} = 704$ Hz) and three signals (doublets at $\delta = 120.9$ and 123.8 ($J_{PP} = 71$ Hz) and a singlet at $\delta = 122.7$) are observed.

Since the paramagnetic compound **6** does not give any $^{31}P\{^1H\}$ NMR signal, the three signals must correspond to the unknown complex. The three signals are always observed, and the total intensity relative to that of the PF_6 anion varies from batch to batch. X-ray diffraction studies were carried out to determine the structures of **6** and the unknown complex, and the latter revealed the novel *cyclo*-Se_3 structure of the complex, $[\{Ru[P(OCH_3)_3]_2(CH_3CN)(\mu\text{-}Cl)\}_2(\mu\text{-}cyclo\text{-}Se_3)\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}](PF_6)_4$ (**7**). In the $^{31}P\{^1H\}$ NMR spectrum, the two doublets are assigned to the two nonequivalent $P(OCH_3)_2$ ligands on the chloride-bridged two Ru atoms, whereas the one singlet must arise from the two equivalent $P(OCH_3)_3$ ligands on the remaining Ru atom.

Figure 1 shows the structure of **6**. The Se–Se bond length in **6** (2.2623(12) Å) is similar to that in the starting complex **2** (2.27 Å).[9] The structure of **7** is shown in Figure 2, in which the novel *cyclo*-Se_3 group bridges the three Ru atoms. Two of the three Ru atoms are further doubly bridged by two chloride ligands. The three Se–Se bond lengths in the *cyclo*-Se_3 are approximately the same (2.4356(7), 2.4452(8), and 2.4454(8) Å), and are longer than the Se–Se bond in the starting complex **2** (2.27 Å).[9] The major bond distances in **6** and **7** are listed in Tables 1 and 2, respectively. The oxidation states of the three Ru atoms and the formal charge of the *cyclo*-Se_3 group can be assigned as three Ru^{II} and neutral Se_3 by taking into account the charge of the complex cation of **7**. Considering the almost uniform Ru–P bond lengths for all three metal sites, it is less probable that Se_3^{2-} is the oxidation state of the ligand.

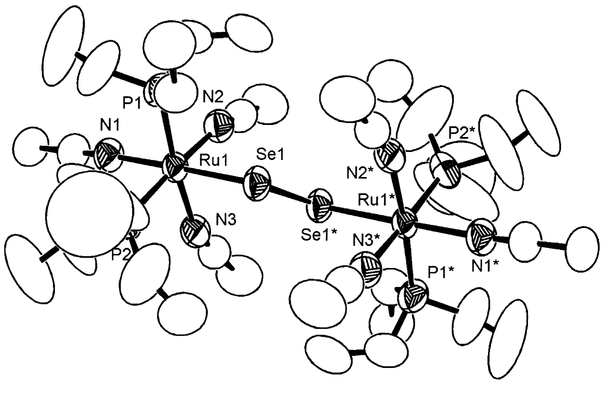


Figure 1. The structure of the complex cation **6** drawn at the 50% probability level. Methyl H atoms are omitted for clarity.

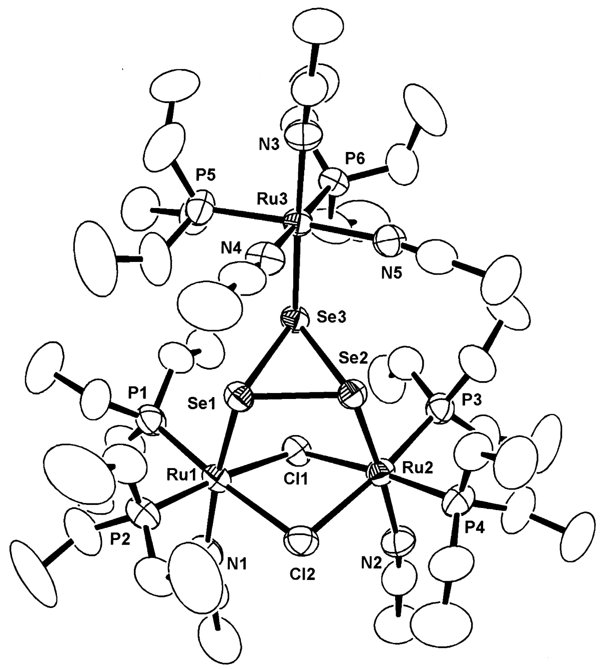


Figure 2. The structure of the complex cation of **7** drawn at the 50% probability level. Methyl H atoms are omitted for clarity.

Table 1. Selected structural parameters of **6**.

Bond lengths [Å]			
Ru1–P1	2.2310(18)	Ru1–P2	2.225(2)
Ru1–Se1	2.4379(7)		
Se1–Se1*	2.2623(12)	Ru1–N1	2.078(6)
Ru1–N2	2.140(6)	Ru1–N3	2.142(6)
Bond angles [°]			
Ru1-Se1-Se1*	104.90(4)		

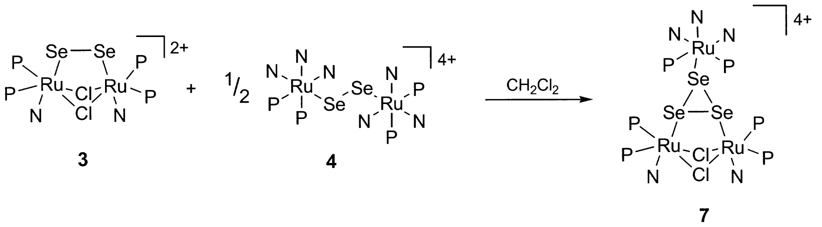
Table 2. Selected structural parameters of **7**.

Bond lengths [Å]			
Ru1–Cl1	2.4480(14)	Ru1–Cl2	2.4990(15)
Ru2–Cl1	2.4674(14)	Ru2–Cl2	2.4965(15)
Ru1–P1	2.2433(16)	Ru1–P2	2.2353(16)
Ru2–P3	2.2403(16)	Ru2–P4	2.2463(16)
Ru3–P5	2.2514(17)	Ru3–P6	2.2569(15)
Ru1–Se1	2.3623(7)	Se1–Se2	2.4452(8)
Ru2–Se2	2.3581(7)	Se2–Se3	2.4356(7)
Ru3–Se3	2.3967(7)	Se3–Se1	2.4454(8)
Ru1–N1	2.063(5)	Ru2–N2	2.069(5)
Ru3–N3	2.067(5)	Ru3–N4	2.113(5)
Ru3–N5	2.118(5)		
Bond angles [°]			
Se2-Se1-Se3	59.74(2)		
Se3-Se2-Se1	60.13(2)		
Se1-Se3-Se2	60.13(2)		

A number of catena-polychalcogenide complexes have been reported.[14, 15, 16, 17] For example, Ibers et al. found $[V_2(\eta^2\text{-}Se_2)_2(\mu\text{-}\eta^2Se_2)_2(Se_5)]^{2-}$ to have a pentaselenide bridging ligand with different Se–Se bond lengths (2.453(3), 2.360(3), 2.339(3), and 2.431(3) Å).[14] There are only a few examples of fully characterized complexes that have a *cyclo*-trichalcogen.

Novel *cyclo*-Te_3^{2+} ligands were found in the mononuclear molybdenum complex, $[Mo(CO)_4(\eta^3\text{-}Te_3)]^{2+}$[18] and tungsten complex, $[W(CO)_4(\eta^3\text{-}Te_3)]^{2+}$.[19] As another example of a *cyclo*-polychalcogen complex, $[Te_4Nb_3O(Te)_2I_6]^+$, is found in the literature and has Te_4^{4+} as a bridging ligand.[20] Rozière et al. have reported the complex $W_2(CO)_{10}Se_4^{2+}$, which has a Se_4^{2+} core and is regarded as the dimer of $W(CO)_5Se_2^+$, based on the two different Se–Se bond lengths (2.208 (1) and 3.017(1) Å).[21] In the literature, neutral *cyclo*-Se_7 is found in $[Re_2I_2(CO)_6(Se_7)]$, in which the Se–Se bond lengths are in the range 2.309–2.346 Å with the exception of 2.558(3) Å for the bridging Se–Se bond.[22] A *bicyclo*-Se_{10}^{2-} is found in $[Ph_3PNPPPh_3]Se_{10}\cdot DMF$, in which the Se–Se bond lengths are 2.31–2.46 Å with two exceptions of 2.572(3) and 2.759(3) Å.[23] The novel *cyclo*-Te_4 is found in $[Te_4\{Cr(CO)_5\}_4]$.[24]

Complex **7** seems to consist structurally of **3** and a half unit of **4**. In a reaction solution, **7** was formed via the intermediate complexes **3** and **4** by replacing the chloride ligands of **2** (Scheme 2), as the $^{31}P\{^1H\}$ NMR spectra of the reaction solution showed. A solution of **2** in CD_3CN with aqueous $NaPF_6$ was sealed in an NMR tube, and the room-temperature aging was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 15 minutes, a broad resonance arising from **3** appeared at $\delta = 118.98$ ppm, whereas the signal from **2** ($\delta = 123.84$, s) was not observed because of the fast replacement of the chloride ligands. As the reaction proceeded further, the signal of **3** decreased, and that of **7** arose and increased. Furthermore, the reaction of **3** with 0.5 equivalents of **4** was examined in CH_2Cl_2 and CH_3CN to confirm the formation of **7′** ($CF_3SO_3^-$ salt of **7**) by $^{31}P\{^1H\}$ NMR spectroscopy as well as X-ray diffraction and elemental analysis. The reaction showed that **3** is the key intermediate for the formation of **7**. The cleavage of the Se–Se bond in **4** may be one of the characteristic reactivities of the bridging diselenide ligand, since the sulfur analogue does not show such reactivity.



Scheme 2.

Experimental Section

All the experiments were carried out under a dry atmosphere of nitrogen or argon by using standard Schlenk techniques, or in a dry N_2 box. Dry solvents were purchased from Kanto chemical Co. [D$_3$]Acetonitrile was dried over CaH_2 and then distilled by trap-to-trap prior to use. Complexes **3** and **4** were prepared as described in the literatures.[11] The NMR spectra were recorded on a JEOL Lambda 270 spectrometer operating at 270 MHz for ^1H and at 109 MHz for ^{31}P. The chemical shifts are reported in δ (ppm) downfield from Me_4Si for ^1H and from H_3PO_4 (85%, external reference) for ^{31}P. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer PE 2400II Elemental Analyzer.

Complex 4: Complex **4** was prepared similarly to the sulfur analogue, as described in the literature.[8] Complex **2** (399 mg, 0.40 mmol) and $AgCF_3SO_3$ (417 mg, 1.62 mmol) were dissolved in a mixture of CH_3CN (2 mL) and acetone (4 mL), and the solution was stirred for 3 h at room temperature. The resulting mixture was separated in a centrifuge to remove AgCl, and the supernatant was evaporated to dryness in vacuo. The beige residue was washed with Et_2O (2 × 10 mL) and THF (10 mL) to give the acetonyl complex $[\{Ru(CH_3CN)_2(P(OCH_3)_3)_2\}(\mu\text{-}SeSeCH_2COCH_3)\{Ru(CH_3CN)_3(P(OCH_3)_3)_2\}](CF_3SO_3)_3$. This crude product was dissolved in CH_3CN (2 mL) and was treated with CF_3SO_3H (0.05 mL) with stirring for 1 h at room temperature. After evaporation to dryness in vacuo, the residue was washed with Et_2O (2 × 10 mL) to give **4** as a dark blue powder (609 mg, 0.36 mmol, 90%). ^1H NMR (270 MHz, CD_3CN): $\delta = 3.84$ (vt, $^3J_{PH} = 81$ Hz, 36H; $P(OCH_3)_3$); $^{31}P\{^1H\}$ NMR (109 MHz, CD_3CN): $\delta = 115.15$(s); UV/Vis (CH_3CN): λ_{max} (ε_{max}) = 704 (1.04×10^4), 515 (9.19×10^2), 338 nm (5.56×10^3 $cm^{-1}M^{-1}$); elemental analysis calcd (%) for $C_{28}H_{54}F_{12}N_6O_{24}P_4Ru_2S_4Se_2$: C 19.79, H 3.20, N 4.95; found: C 19.59, H 3.07, N 4.63.

Complexes 6 and 7: A degassed solution of $NaPF_6$ (109.2 mg, 0.65 mmol) in water (10 mL) was added to a solution of **2** (101.6 mg, 0.10 mmol) in CH_3CN (5 mL). After the mixture had been stirred for 3 h at ambient temperature, CH_2Cl_2 (10 mL) was added to separate the organic- and water-soluble compounds. The extracted organic phase was transferred to a Schlenk tube with a syringe. The CH_2Cl_2 solution was concentrated under reduced pressure, then Et_2O (8 mL) was slowly layered onto it. The brown needles of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}_2(\mu\text{-}Se_2)](PF_6)_3$ (**6**) together with the brown plates of $[\{Ru[P(OCH_3)_3]_2(CH_3CN)(\mu\text{-}Cl)\}_2(\mu\text{-}cyclo\text{-}Se_3)\{Ru[P(OCH_3)_3]_2(CH_3CN)_3\}](PF_6)_4$ (**7**) were obtained.

Compound 6: After separation of the organic- and water-soluble compounds, the volatile species were removed under reduced pressure, and **6** was extracted from the residue with CH_2Cl_2. Recrystallization of the CH_2Cl_2 solution gave analytically pure crystals of **6**. Elemental analysis calcd (%) for $C_{24}H_{54}F_{18}N_6O_{12}P_7Ru_2Se_2$: C 18.75, H 3.54, N 5.47; found: C 18.70, H 3.45, N 5.35.

Compound 7: After separation of the organic- and water-soluble compounds, the volatile species were removed under reduced pressure. The residue was washed with CH_2Cl_2, and was recrystallized from CH_3CN/Et_2O to give analytically pure crystals of **7** in 38% yield. $^{31}P\{^1H\}$ NMR (109 MHz, CD_3CN): $\delta = -143.1$ (sept, $^1J_{PF} = 704$ Hz, PF_6), 120.9 (d, $^2J_{PP} = 71$ Hz), 122.7 (s), 123.8 (d); elemental analysis calcd (%) for $C_{28}H_{69}Cl_2F_{24}N_5O_{18}P_{10}Ru_3Se_3$: C 15.71, H 3.25, N 3.27; found: C 16.23, H 3.21, N 3.53.

The CF_3SO_3 salt of **7**, **7′** was obtained by the reaction of **3** (160 mg, 0.12 mmol) with **5** (104 mg, 0.061 mmol) in CH_2Cl_2 (1.5 mL) and CH_3CN (0.5 mL). Yield: 215 mg (81%); elemental analysis calcd (%) for $C_{32}H_{69}Cl_2F_{12}N_5O_{30}P_6Ru_3S_4Se_3$: C 17.82, H 3.22, N 3.25; found: C 18.01, H 3.20, N 3.39.

X-ray crystallography: Diffraction data for complexes **6** and **7** were collected on a Bruker SMART 1000 CCD diffractometer by using $Mo_{K\alpha}$ radiation with $\lambda = 0.71069$ Å. All the intensity data were processed with a SAINT plus program package. Absorption correction was applied to the integrated intensity with a SADABS program. The structure solution was performed with a SHELXTL software package. Details of the two crystallographic analyses are summarized in Table 3. The crystallographic analysis of **7′** was also carried out with the analogous procedure described above.

CCDC-151559 (**6**), 151560 (**7**), and 178660 (**7′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Table 3. Crystallographic data for **6**, **7** and **7′**.

	6	**7**	**7′**
empirical formula	$C_{24}H_{54}F_{18}N_6O_{12}P_7Ru_2Se_2$	$C_{28}H_{69}Cl_2F_{24}N_5O_{18}P_{10}Ru_3Se_3$	$C_{32}H_{69}Cl_2F_{12}N_5O_{30}P_6Ru_3S_4Se_3$
M_w	1537.58	2140.57	2156.97
T [K]	293(2)	293(2)	124(2)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
cell dimensions			
a [Å]	11.7740(10)	12.6862(8)	12.7589(15)
b [Å]	12.4173(10)	24.8375(15)	25.164(3)
c [Å]	12.4381(10)	24.1938(15)	24.145(3)
α [°]	111.0210(10)	90	90
β [°]	112.6310(10)	102.7110(10)	102.338(2)
γ [°]	102.436(2)	90	90
V [Å^3]	1428.9(2)	7436.5(8)	7573.3(16)
Z	1	4	4
λ [Å]	0.71073 ($Mo_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)
d_{calcd} [g cm^{-3}]	1.787	1.912	1.892
μ [mm^{-1}]	2.108	2.474	2.445
observed reflns.	4129	8410	11293
$R1$[a] [$I > 2\sigma(I)$]	0.0647	0.0356	0.0507
$wR2$[b] [$I > 2\sigma(I)$]	0.1791	0.0500	0.1207
$R1$ (all data)	0.0928	0.1069	0.0970
$wR2$ (all data)	0.1980	0.1148	0.1380
GOF[c]	1.001	1.022	0.897

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)/\Sigma(n-p)]^{1/2}$, in which n = number of reflections and p = number of parameters.

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