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Oxidative Additions of *cyclo*-Octasulfur and *cyclo*-Octaselenium to the Cobalt(II) Complex of 1,3-Bis(dimethylphosphino)propane (dmpp): Crystal Structures and Spectroscopic Properties of $[Co(S_2O)(dmpp)_2]PF_6$ and $[Co(Se_2)(dmpp)_2]BF_4$

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Introduction

Side-on-bonded disulfur and diselenium complexes,[2] which are analogous to well-studied side-on-bonded dioxygen complexes, have attracted great interest not only in coordination chemistry but also in the biological and catalytic fields.[3] However, because sulfur and selenium fragments have a strong propensity to bridge two or more metal centers, it is often difficult to prepare their mononuclear side-on-bonded complexes.[3,4] In a previous paper,[5] we reported that reactions of S_8 with $[Co^{II}(dmpe)_2]^{2+}$ (dmpe = 1,2-bis(dimethylphosphino)ethane) yielded two novel complexes, $[Co(S_2O\text{-}\kappa^2 S)(dmpe)_2]ClO_4$ ([**1**]ClO_4) and $[Co(S_2PMe_2)_2(dmpe)]BF_4$ ([**2**]BF_4). These results provided us with two intriguing mechanistic features to investigate: an easy oxygenation of a disulfur fragment coordinated to a Co(III) center and a facile P−C(bridge) bond cleavage of dmpe. In this study, we have examined oxidative-addition reactions of S_8 with Co(II) complexes of dmpp, depe (=1,2-bis(diethylphosphino)ethane), and dppe (=1,2-bis(diphenylphosphino)ethane) and those of Se_8 with $[Co(dmpp\ and\ dmpe)_2]^{2+}$. The crystal structures and absorption spectra of $[Co(S_2O)(dmpp)_2]PF_6$ ([**3**]PF_6) and $[Co(Se_2)(dmpp)_2]BF_4$ ([**4**]BF_4) are reported.

To our knowledge, only two examples have been reported so far for the oxidative additions of E_8 (E = S and Se) to Co(II) and Co(I) complexes, i.e., $[\{Co(CN)_5\}_2(\mu\text{-}E_2)]^{6-}$, obtained from reactions of E_8 with $[Co(CN)_5]^{3-}$,[6] and $[(\eta^5\text{-}C_5H_5)Co(PMe_3)(S_2)]$, obtained from the reaction of S_8 with $[(\eta^5\text{-}C_5H_5)Co(PMe_3)(CS_2\text{-}\kappa^2 S)]$,[7] while there are extensive studies for analogous reactions involving Rh(I) and Ir(I) phosphine complexes.[8−10]

Experimental Section

General Procedures and Measurements. The phosphines dmpe[11] and dmpp[12] were prepared according to literature methods, while depe and dppe were used as purchased from Strem Co. Ltd. Preparation of the Co(II) phosphine complexes and their reactions with S_8 and Se_8 were performed under an atmosphere of dinitrogen using standard Schlenk techniques. Removal of the reaction solutions, column chromatographic separations, and recrystallizations of the products were carried out in the open air. UV−visible absorption spectra were obtained on a JASCO V-560 or a Hitachi U-3410 spectrophotometer, infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotometer by the Nujol mull method, and elemental analyses (C, H, N) were performed on an LECO CHN-900 analyzer.

Reaction of S_8 with $[Co(dmpp)_2]^{2+}$. To a dark green methanol solution (50 cm^3) of $[Co(dmpp)_2]^{2+}$, prepared by a reaction of $Co(BF_4)_2 \cdot 6H_2O$ (0.71 g, 2.1 mmol) with dmpp (0.68 g, 4.2 mmol), was added a toluene solution (80 cm^3) of S_8 (0.55 g, 2.1 mmol) at room temperature, and the mixture was stirred for 1 d. The resulting brown solution was evaporated to dryness under reduced pressure, and the residue was extracted with 1 dm^3 of water. The filtered extract was placed on a column (ϕ 2 × 50 cm) of SP-Sephadex C-25 (Na^+ form). The adsorbed products were eluted with an aqueous Na_2SO_4 solution (0.01−0.2 mol dm^{-3}), separating into three bands: the first, an eluted red ($\lambda_{max} = 355$ nm) band; the second, an eluted yellow ($\lambda_{max} = 302$ nm) band; and the third, an unmoved brown band. The red band was collected, and the eluate was concentrated to a small volume (ca. 5 cm^3) under reduced pressure. Methanol (ca. 20 cm^3) was added to the concentrate to precipitate Na_2SO_4, which was filtered off. The resulting filtrate was concentrated to ca. 5 cm^3, and an aqueous solution (5 cm^3) of $NaPF_6$ (1.0 g, 6.0 mmol) was added. The mixture was allowed to stand overnight to deposit red crystals of $[Co(S_2O)(dmpp)_2]PF_6$ ([**3**]PF_6), which were collected by filtration and recrystallized from aqueous acetone and then from a mixture of nitromethane and diethyl ether. Yield: 0.13 g (10%). Anal. Calcd for $C_{14}H_{36}CoF_6OP_5S_2$: C, 27.46; H, 5.93. Found: C, 27.67; H, 5.81.

Reaction of Se_8 with $[Co(dmpp)_2]^{2+}$. To a dark green methanol solution (60 cm^3) containing $Co(BF_4)_2 \cdot 6H_2O$ (0.72 g, 2.1 mmol) and dmpp (0.70 g, 4.3 mmol) was added a toluene solution (75 cm^3) of Se_8 (1.27 g, 2.1 mmol), and the mixture was stirred for 2 d at room temperature. The resulting dark brown solution was evaporated to dryness under reduced pressure, and the residue was extracted with methanol (50 cm^3). The filtered extract was concentrated to ca. 10 cm^3 under reduced pressure, depositing dark brown crystals of $[Co(Se_2)(dmpp)_2]BF_4$ ([**4**]BF_4). The crystals were collected by filtration and recrystallized from a mixture of acetone and ethanol and then from a mixture of acetone and diethyl ether. Yield: 0.08 g (6%). Anal. Calcd for $C_{14}H_{36}BCoF_4P_4Se_2$: C, 26.61; H, 5.74. Found: C, 26.58; H, 5.64.

Reactions of S_8 with $[Co(depe\ and\ dppe)_2]^{2+}$ and of Se_8 with $[Co(dmpe)_2]^{2+}$. These reactions were carried out similarly to that above, and the details are described in the Supporting Information. From the $S_8/[Co(depe)_2]^{2+}$ reaction system were obtained orange crystals of $[Co(S_2O)(depe)_2]BPh_4$ ([**5**]BPh_4). Yield: 1.3%. Anal. Calcd for $C_{34}H_{68}BCoOP_4S_2$: C, 60.69; H, 7.87. Found: C, 61.36; H, 7.81. And from the $Se_8/[Co(dmpe)_2]^{2+}$ reaction system were obtained brown crystals of $[Co(Se_2)(dmpe)_2]PF_6$ ([**6**]PF_6). Yield: 8.0%. Anal. Calcd for $C_{12}H_{32}$-

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[2] In this paper, we use the terms "disulfur" and "diselenium" complexes, though it is chemically more reasonable to define them as S_2^{2-} (disulfide) and Se_2^{2-} (diselenide) complexes, in accordance with a notation suggested in ref 3a.

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Table 1. Crystallographic Data for $[Co(S_2O)(dmpp)_2]PF_6$ ([**3**]PF_6) and $[Co(Se_2)(dmpp)_2]BF_4$ ([**4**]BF_4)

	[**3**]PF_6	[**4**]BF_4
empirical formula	$C_{14}H_{36}CoF_6OP_5S_2$	$C_{14}H_{36}BCoF_4P_4Se_2$
fw	612.35	631.99
T/°C	23	23
λ(Mo Kα)/Å	0.710 73	0.710 73
space group	$P2_1/c$	$P2_1/c$
a/Å	13.652(5)	9.631(4)
b/Å	11.792(3)	8.934(3)
c/Å	16.253(3)	28.377(3)
β/deg	98.05(2)	97.32(2)
V/Å^3	2590(1)	2421(1)
Z	4	4
ρ_{calc}/Mg m^{-3}	1.570	1.733
μ(Mo Kα)/mm^{-1}	1.181	4.009
$R(F)$,[a] $R_w(F)$[b]	0.061, 0.063	0.041, 0.035

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + (0.020|F_o|)^2$.

$CoF_6P_5Se_2$: C, 21.77; H, 4.87. Found: C, 22.16; H, 4.85%. A reaction of S_8 with $[Co(dppe)_2]^{2+}$ gave a white powder of $Ph_2P(S)CH_2CH_2P(S)Ph_2$. Yield: 69%. Anal. Calcd for $C_{26}H_{24}P_2S_2$: C, 67.51; H. 5.23. Found: C, 67.45; H, 5.29.

Crystallography. A red columnar crystal of [**3**]PF_6 (0.62 × 0.30 × 0.25 mm) and a dark brown columnar crystal of [**4**]BF_4 (0.48 × 0.32 × 0.28 mm) were each glued on the top of a glass fiber with epoxy resin. The X-ray intensities ($2\theta_{max} = 60°$) were collected on an automated Rigaku AFC-5 or -5R four-circle diffractometer. Absorption corrections were applied by the numerical integration method.[13] The structures were solved by direct methods using the SHELXS86 program[14] and refined on F with the observed ($I > 3\sigma(I)$) independent reflections. All calculations were carried out using a TeXsan software package.[15] The crystallographic data are summarized in Table 1.

Results and Discussion

Oxidative Additions of *cyclo*-Octasulfur. A reaction of S_8 with $[Co(dmpe)_2](BF_4)_2$ in a mixed toluene/methanol solution for 1 d afforded S_2O^{2-} and $S_2PMe_2^-$ complexes, **1** and **2**, respectively, whereas a reaction with $[Co^I(dmpe)_2]^+$ did not give characterizable products.[5] A reaction of S_8 with $[Co(dmpp)_2]^{2+}$ afforded red crystals of $[Co(S_2O)(dmpp)_2]PF_6$ ([**3**]PF_6) as the only characterizable product. Chromatographic separation of a water-soluble extract from the reaction mixture showed no evidence for the formation of a $S_2PMe_2^-$ complex corresponding to **2**. During cation-exchange column chromatography, a very small amount of a yellow band appeared, in addition to a red band of **3** and an uneluted (even with a saturated NaCl solution) brown band. The minor yellow product was probably $[Co(dmpp)_3]^{3+}$ because its absorption spectrum was analogous to that of $[Co(dmpe)_3]^{3+}$.[16] However, isolation of the complex was not possible owing to low yield and instability. Large amounts of the uneluted brown complex at the top of the column and the residue remaining after extraction of the reaction mixture with water seem to be highly charged cluster compounds or complex polymers formed during the oxidative-addition reaction.

The molecular structure of $[Co(S_2O)(dmpp)_2]^+$ (**3**) is shown in Figure 1, with selected bond lengths and angles given in the caption. The coordination geometry around the Co center and the structural parameters of the S_2O^{2-} moiety are very similar to those of $[Co(S_2O\text{-}\kappa^2S)(dmpe)_2]^+$ (**1**).[5] The six-membered chelate rings formed by dmpp have a typical chair conformation. The S(2) atom is chiral and has an $S(R)$ configuration in the $\Delta(\Lambda)$ complex.[17] The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained to determine the structure in solution, but the spectra of **3** as well as those of **1** were too complicated to analyze owing to the low symmetry of the complexes and couplings to four inequivalent P nuclei.

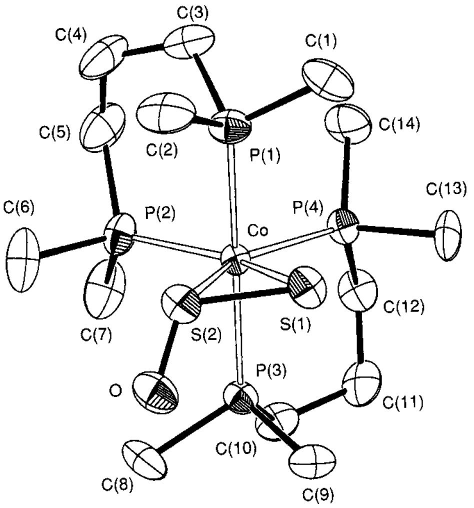

Figure 1. Perspective drawing (50% probability level) of the cationic part of [**3**]PF_6. Selected distances and angles: Co−S(1) 2.299(2), Co−S(2) 2.286(2), S(1)−S(2) 2.027(3), S(2)−O 1.484(5) Å; S(1)−Co−S(2) 52.47(7), Co−S(2)−O 118.1(2), S(1)−S(2)−O 113.5(3)°. Hydrogen atoms are omitted for clarity.

Complex **5**, obtained from a reaction of S_8 with $[Co(depe)_2]^{2+}$, is air stable and was characterized as a S_2O^{2-} complex, an analogue of **1** and **3**, by FAB mass, IR, and UV−vis spectroscopy. The FAB mass spectrum shows a characteristic envelope at $m/z = 551$ corresponding to $[Co(S_2O)(depe)_2]^+$. The IR spectrum of [**5**]BPh_4 gives the ν(S−S) and ν(S−O) bands at 527 and 1025 cm^{-1}, respectively, which are almost the same energies as those of the corresponding bands of [**1**]BPh_4 (523 and 1050 cm^{-1}) and [**3**]BPh_4 (523 and 1030 cm^{-1}). Furthermore, the UV−vis absorption spectra of [**1**]PF_6, [**3**]PF_6, and [**5**]PF_6 in acetonitrile are quite similar (Figure S1, Supporting Information). An X-ray diffraction study of [**5**]BPh_4 was also attempted. Although a completely satisfactory analysis was not obtained,[19] a $S_2O\text{-}\kappa^2S$ coordination mode was suggested.

Our previous study using XPS and UV−vis absorption spectroscopy suggested that **1** could be described as a Co(III)−S_2O^{2-} complex.[5] This is also the case for complexes **3** and **5** because of the similarity of their absorption spectra. Therefore, in the reaction, the Co(II) center of [Co(dmpe, dmpp, or

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(19) For details, see the Supporting Information. (a) Crystal data for [**5**]BPh_4: $C_{44}H_{68}BCoOP_4S_2$, fw = 870.78, T = 23 °C, λ(Mo Kα) = 0.710 73 Å, space group $P2_1/n$, a = 11.992(9) Å, b = 13.27(1) Å, c = 29.202(9) Å, β = 97.28(5)°, V = 4610(4) Å^3, Z = 4, ρ_{calc} = 1.25 Mg m^{-3}, μ(Mo Kα) = 0.634 mm^{-1}, R1(F^2: $I > 2\sigma(I)$) = 0.120. (b) Crystal data for [**6**]PF_6: $C_{12}H_{32}CoF_6P_5Se_2$, fw = 662.10, T = 23 °C, λ(Mo Kα) = 0.710 73 Å, space group $P2_1/c$, a = 13.288(3) Å, b = 11.117(2) Å, c = 16.504(3) Å, β = 95.97(2)°, V = 2424.7(7) Å^3, Z = 4, ρ_{calc} = 1.814 Mg m^{-3}, μ(Mo Kα) = 4.083 mm^{-1}, R(F: $I > 3\sigma(I)$) = 0.099.

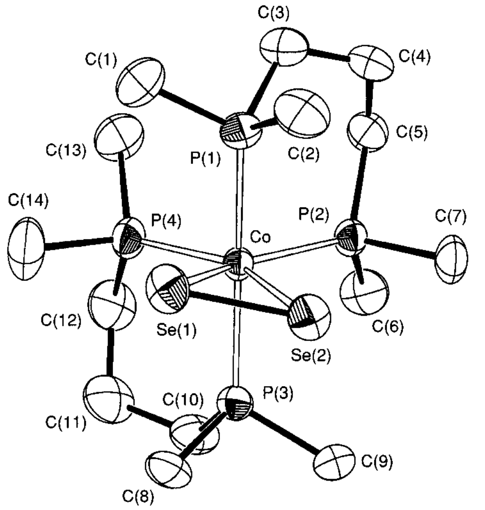

Figure 2. Perspective drawing (50% probability level) of the cationic part of [**4**]BF_4. Selected distances and angles: Co−Se(1) 2.4156(8), Co−Se(2) 2.423(1), Se(1)−Se(2) 2.2944(9) Å; Se(1)−Co−Se(2) 56.61(2), Co−Se(1)−Se(2) 61.86(3), Co−Se(2)−Se(1) 61.53(3)°. Hydrogen atoms are omitted for clarity.

depe)$_2]^{2+}$ must be oxidized by S_8, which would induce fragmentation of S_8. Although the detailed mechanism of this oxidative-addition reaction is still unclear, it seems likely, from comparison with the following Se_2^{2-} complexes, that an intermediate Co(III)−S_2^{2-} complex, [Co(S_2)(dmpe, dmpp, or depe)$_2]^+$, is formed during the reaction and the S_2^{2-} fragment coordinated to Co(III) is probably oxidized by atmospheric oxygen during the course of isolation and purification.

In contrast to the S_8 reactions with the above dmpe, dmpp, and depe complexes, a reaction of S_8 with [Co(dppe)$_2$](BF_4)$_2$ in toluene/methanol gave a white precipitate of $Ph_2P(S)CH_2CH_2P(S)Ph_2$ in an almost quantitative yield, and no Co(III) complexes containing di- or polysulfur fragments were isolated. This result also contrasts with the formation of [(Rh or Ir)(S_2)(dppe)$_2]^+$ from a reaction of S_8 with [(Rh or Ir)(dppe)$_2$]Cl.[9] Severe interligand steric interactions with dppe are expected for *cis*-$[Co^{III}X_2(dppe)_2]^{n+}$-type complexes, which have not yet been reported.

Oxidative Additions of *cyclo*-Octaselenium. A reaction of Se_8 with [Co(dmpp)$_2]^{2+}$ afforded [Co(Se_2)(dmpp)$_2$]BF_4 ([**4**]BF_4). The IR spectrum of [**4**]BF_4 shows a ν(Se−Se) band at 310 cm^{-1} and a relatively broad, weak band at 172 cm^{-1} due to ν(Co−Se). An X-ray structure analysis of [**4**]BF_4 was performed, and a perspective drawing of **4** is shown in Figure 2, with selected bond lengths and angles given in the caption. The Co(dmpp)$_2$ moiety has a structure similar to those of **3** and [Co(O_2)(dmpp)$_2$]$BF_4 \cdot H_2O$ ([**7**]$BF_4 \cdot H_2O$).[20] The Se(1)−Se(2) bond length (2.2944(9) Å) corresponds to an Se−Se single bond when compared with Se−Se bond lengths in other side-on-bonded diselenium complexes.[9a,21] The Se−Se bond twists from the Co, P(2), P(4) plane to reduce steric interactions around the Co center; the dihedral angle between the Co, Se(1), Se(2) plane and the Co, P(2), P(4) plane is 12.2°. Similar twists of η^2-E_2 groups were also found in [Ir(S_2 and Se_2)(dppe)$_2]^+$ (12.8 and 14.0°, respectively),[8,9a] but the corresponding dihedral angle of 6.8° in **3** is smaller.

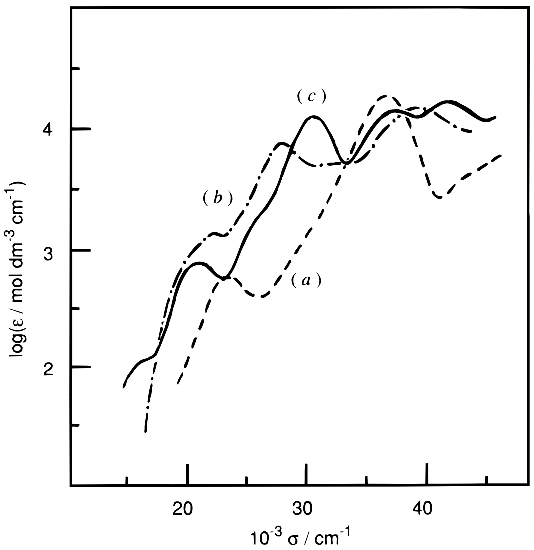

Figure 3. Comparison of the absorption spectra of [Co(O_2, S_2O, and Se_2)(dmpp)$_2]^+$: (a) O_2^{2-} complex **7** (- - -); (b) S_2O^{2-} complex **3** (− •−); (c) Se_2^{2-} complex **4** (—).

Figure 3 compares the absorption spectra of the dmpp complexes **7** (O_2^{2-}), **3** (S_2O^{2-}), and **4** (Se_2^{2-}). The spectral pattern of **4** in the region 17 500−35 000 cm^{-1} is similar to that of **7**, while each absorption band of **4** is considerably red-shifted compared to the corresponding band of **7**. The absorption band of **4** at 20 800 cm^{-1} with medium intensity ($\epsilon = 731$ dm^3 mol^{-1} cm^{-1}) was assigned to the first d−d transition by comparison with the spectrum of **7**.[20] A much weaker ligand-field strength of Se_2^{2-} than of O_2^{2-} parallels the fact that selenolates (RSe^-) give weaker ligand-field perturbations than alkoxides (RO^-).[22] The corresponding absorption of **3** splits into two bands around 20 000 and 22 300 cm^{-1}. This splitting seems to result from the difference in ligand-field strength between the $-S^-$ and $-S(O)^-$ donor groups of S_2O^{2-}. It may be reasonable to assume that $-S^-$ has a weaker ligand-field strength than $-S(O)^-$ because thiolates (RS^-) give weaker ligand-field perturbations than sulfenates ($RS(O)^-$: coordinated through S).[22] On the basis of these considerations, we can anticipate that the ligand-field strength of $-S^-$, which would be the same as that of the S_2^{2-} ligand, will be nearly equal to that of Se_2^{2-} because the position of the lower energy splitting component of **3** is almost the same as the position of the first d−d transition band of **4**. A weak but distinct shoulder around 16 500 cm^{-1} for the Se_2^{2-} complex **4** is presumably assigned as the spin-forbidden d−d transition band, which is enhanced by coordination of the heavy donor atom Se via a spin−orbit coupling mechanism.

The charge-transfer absorption of the Se_2^{2-} complex **4** shows two components: $\sigma = 30\,530$ ($\epsilon = 12\,340$) and $\sigma = 37\,300$ cm^{-1} ($\epsilon = 13\,800$ dm^3 mol^{-1} cm^{-1}). The former would be assignable to an Se(σ) → Co($d\sigma^*$) CT band, since similarly intense absorption bands in this region are observed for selenolato−Co(III) complexes without phosphine coligands.[23] The latter absorption component of **4** is preferably assigned to

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a P(σ) → Co(dσ*) CT band, which corresponds to the P(σ) → Co(dσ*) LMCT band of **7** at 36 000 cm^{-1}.[20] In the spectrum of the S_2O^{2-} complex **3**, the corresponding CT absorption seems to split into at least three components: two bands at 27 860 (ϵ = 7920) and 32 190 cm^{-1} (ϵ = 5250 dm^3 mol^{-1} cm^{-1}) and a broad shoulder around 37 000 cm^{-1} (ϵ = ca. 10 000 dm^3 mol^{-1} cm^{-1}). This suggests that the S(σ) → Co(dσ*) CT band splits further into two components corresponding to the S(σ) → Co(dσ*) and S(O)(σ) → Co(dσ*) transitions. It has been well documented for thiolato– and sulfenato–Co(III) complexes that the S(O)(σ) → Co(dσ*) CT bands of sulfenates show remarkable red shifts from the S(σ) → Co(dσ*) bands of the thiolates.[23,24] Accordingly, the lowest energy component (27 860 cm^{-1}) would be assigned to the S(O)(σ) → Co(dσ*) CT transition and the component observed at 32 190 cm^{-1} would be assigned to the S(σ) → Co(dσ*) transition. Thus the $E_2(O)^{2-}(\sigma)$ → Co(dσ*) CT energies become lower in the following order: $O_2^{2-} > SS(O)^{2-} > Se_2^{2-} > SS(O)^{2-}$.

A reaction of Se_8 with $[Co(dmpe)_2](BF_4)_2$ gave $[Co(Se_2)(dmpe)_2]^+$ (**6**), which shows a ν(Se–Se) band at 301 cm^{-1} and a ν(Co–Se) band at 173 cm^{-1} in the IR spectrum. These values are similar to those of [**4**]BF_4. An X-ray analysis was also attempted for [**6**]PF_6,[19] but a satisfactory refinement could not be achieved owing to severe positional disorders for the C atoms of dmpe, related to chelate ring deformations, and for the F atoms of PF_6^-.

Conclusion

Oxidative additions of S_8 to $[Co(dmpp\ and\ depe)_2]^{2+}$ afford the S_2O^{2-} complexes **3** and **5**, respectively. Any $S_2PMe_2^-$ or $S_2PEt_2^-$ complex corresponding to **2** is not detected in the reaction mixtures. The facile P–C bond cleavage is so far limited to the reaction of S_8 with $[Co(dmpe)_2]^{2+}$, although the mechanism is not clear at present. The oxidative-addition reactions of Se_8 with $[Co(dmpp\ and\ dmpe)_2]^{2+}$ give the side-on-bonded Se_2^{2-} complexes **4** and **6**, which are stable to air in the solid state and in solution. The behaviors of these complexes toward oxidation of the E_2^{2-} fragments are similar to those of analogous rhodium and iridium complexes of disulfur and diselenium, $[(Rh\ or\ Ir)(S_2\ or\ Se_2)(dmpe\ or\ dppe)_2]^+$; the disulfur complexes can be oxidized to give S_2O or S_2O_2 complexes by using oxidizing agents such as periodate and *m*-chloroperbenzoic acid,[9,18,25] while no such oxidized diselenium complexes have thus far been reported.

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Supporting Information Available: Text presenting detailed descriptions of the reactions and the crystallographic studies, Figure S1, showing absorption spectra of $[Co(S_2O)(dmpe,\ dmpp,\ and\ depe)_2]^+$, and X-ray crystallographic files, in CIF format, for [**3**]PF_6 and [**4**]BF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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