

## Group 9 Chalcogenometalates

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The compounds  $[\text{K}(18\text{-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$  (**1**),  $[\text{K}(2.2.2\text{-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]\cdot\text{C}_6\text{H}_5\text{CH}_3$  (**2**), and  $[\text{K}(18\text{-crown-6})(\text{DMF})_2][\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]$  (**3**) (DMF = dimethylformamide) have been prepared from the reaction of  $[\text{Ir}(\text{NCCH}_3)_2(\text{COE})_2][\text{BF}_4]$  (COE = cyclooctene) with polyselenide anions in acetonitrile/DMF. Analogous reactions utilizing  $[\text{Rh}(\text{NCCH}_3)_2(\text{COE})_2][\text{BF}_4]$  as a Rh source produce homologues of the Ir complexes; these have been characterized by <sup>77</sup>Se NMR spectroscopy.  $[\text{NH}_4]_3[\text{Ir}(\text{S}_6)_3]\cdot\text{H}_2\text{O}\cdot 0.5\text{CH}_3\text{CH}_2\text{OH}$  (**4**) has been synthesized from the reaction of  $\text{IrCl}_3\cdot n\text{H}_2\text{O}$  with aqueous  $(\text{NH}_4)_2\text{S}_m$ . In the structure of  $[\text{K}(18\text{-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$  (**1**) the Ir(III) center is chelated by three  $\text{Se}_4^{2-}$  ligands to form a distorted octahedral anion. The structure contains a disordered racemate of the  $\Delta\lambda\lambda\lambda$  and  $\Lambda\delta\delta\delta$  conformers. The  $\text{K}^+$  cations are pulled out of the planes of the crowns and interact with Se atoms of the  $[\text{Ir}(\text{Se}_4)_3]^{3-}$  anion.  $[\text{K}(2.2.2\text{-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]\cdot\text{C}_6\text{H}_5\text{CH}_3$  (**2**) possesses no short  $\text{K}\cdots\text{Se}$  interactions; here the  $[\text{Ir}(\text{Se}_4)_3]^{3-}$  anion crystallizes as the  $\Delta\lambda\lambda\delta/\Lambda\delta\delta\lambda$  racemate. In the crystal structure of  $[\text{K}(18\text{-crown-6})(\text{DMF})_2][\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]$  (**3**), the  $\text{K}^+$  cation is coordinated by an 18-crown-6 ligand and two DMF molecules and the anion comprises an octahedral Ir(III) center bound by two chelating  $\text{Se}_4^{2-}$  chains and two trans acetonitrile groups. The  $[\text{Ir}(\text{Se}_4)_3]^{3-}$  and  $[\text{Rh}(\text{Se}_4)_3]^{3-}$  anions undergo conformational transformations as a function of temperature, as observed by <sup>77</sup>Se NMR spectroscopy. The thermodynamics of these transformations are:  $[\text{Ir}(\text{Se}_4)_3]^{3-}$ ,  $\Delta H = 2.5(5)$  kcal mol<sup>-1</sup>,  $\Delta S = 11.5(2.2)$  eu;  $[\text{Rh}(\text{Se}_4)_3]^{3-}$ ,  $\Delta H = 5.2(7)$  kcal mol<sup>-1</sup>,  $\Delta S = 24.7(3.0)$  eu.

## Introduction

The chemistry of chalcogenometalates has been well-developed over the past decade.<sup>1–6</sup> There has been limited attention paid to and success with group 9 chalcogenometalates, even though  $[\text{Ir}(\text{S}_5)_3]^{3-}$ <sup>7</sup> was among the first polychalcogenometalate anions to be isolated. To this day it has not been structurally characterized. The  $[\text{Rh}(\text{S}_5)_3]^{3-}$  anion has also been reported<sup>8a</sup> and its structure has been determined,<sup>8b</sup> but it is unstable and appears to decompose to polymeric  $[\text{RhS}_{10}]^-$  in both aqueous and nonaqueous solutions. In view of the known  $[\text{M}(\text{Se}_4)_2]^{2-}$  anions with Mn,<sup>9,10</sup> Ni,<sup>10,11</sup> Pd,<sup>10</sup> Pt,<sup>10,12</sup> Zn,<sup>10,11,13</sup> Cd,<sup>10,11,13,14</sup> Hg,<sup>10,11,13–16</sup> and Pb,<sup>11</sup> one would expect the square-planar anions  $[\text{M}(\text{Se}_4)_2]^{3-}$  (M = Rh(I), Ir(I)) to exist. Our attempts to prepare such species have been unsuccessful, but

they have led<sup>17</sup> to the synthesis of homoleptic, octahedral chalcogenometalates of the type  $[\text{M}(\text{Q}_n)_3]^{z-}$  (M = Ir(III), Rh(III)). Previously known species of this type appear to be limited to  $[\text{Sn}(\text{S}_4)_3]^{2-}$ ,<sup>18</sup>  $[\text{Pt}(\text{S}_5)_3]^{2-}$ ,<sup>19–21</sup>  $[\text{Pt}(\text{S}_6)_3]^{2-}$ ,<sup>22,23</sup>  $[\text{Rh}(\text{S}_5)_3]^{3-}$ ,<sup>8b</sup>  $[\text{Pt}(\text{Se}_4)_3]^{2-}$ ,<sup>12,24</sup> and  $[\text{Sn}(\text{Se}_4)_3]^{2-}$ .<sup>25,26</sup>

Here we report the syntheses and characterization of  $[\text{K}(18\text{-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$  (**1**),  $[\text{K}(2.2.2\text{-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]\cdot\text{C}_6\text{H}_5\text{CH}_3$  (**2**),  $[\text{K}(18\text{-crown-6})(\text{DMF})_2][\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]$  (**3**), and  $[\text{NH}_4]_3[\text{Ir}(\text{S}_6)_3]\cdot\text{H}_2\text{O}\cdot 0.5\text{CH}_3\text{CH}_2\text{OH}$  (**4**), as well as a preliminary identification of the Rh homologues of the selenoiridates. We also discuss the rich variety of conformers of  $[\text{M}(\text{Se}_4)_3]^{z-}$  that have been observed to crystallize, depending not only upon M but also on crystallization conditions and counteraction.<sup>12</sup> In addition we have utilized <sup>77</sup>Se VT-NMR spectroscopy as a method for determining the dynamics of conformational changes in  $[\text{M}(\text{Se}_4)_3]^{3-}$  (M = Rh, Ir) anions.

## Experimental Section

**Syntheses.** All manipulations were carried out under an Ar atmosphere with the use of standard Schlenk-line techniques. Solvents were freshly distilled prior to use. <sup>77</sup>Se chemical shifts are referenced to Ph<sub>2</sub>Se<sub>2</sub> at 460 ppm. K<sub>2</sub>Se was prepared by the reaction of stoichiometric amounts of K and gray Se in liquid ammonia.  $[\text{IrCl}$

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**Table 1.** Crystallographic Details

	[K(18-crown-6)] <sub>3</sub> [Ir(Se <sub>4</sub> ) <sub>3</sub> ] (1)	[K(2.2.2-crypt)] <sub>3</sub> [Ir(Se <sub>4</sub> ) <sub>3</sub> ]· C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (2)	[K(18-crown-6)(DMF)] <sub>2</sub> - [Ir(NCCH <sub>3</sub> ) <sub>2</sub> (Se <sub>4</sub> ) <sub>2</sub> ] (3)	[NH <sub>4</sub> ] <sub>3</sub> [Ir(S <sub>6</sub> ) <sub>3</sub> ]·H <sub>2</sub> O· 0.5CH <sub>3</sub> CH <sub>2</sub> OH (4)
chem form	C <sub>36</sub> H <sub>72</sub> IrK <sub>3</sub> O <sub>18</sub> Se <sub>12</sub>	C <sub>61</sub> H <sub>116</sub> IrK <sub>3</sub> N <sub>6</sub> O <sub>18</sub> Se <sub>12</sub>	C <sub>22</sub> H <sub>44</sub> IrKN <sub>4</sub> O <sub>8</sub> Se <sub>8</sub>	CH <sub>17</sub> IrN <sub>3</sub> O <sub>1.5</sub> S <sub>18</sub>
fw	2049.96	2478.62	1355.59	864.57
cryst syst	hexagonal	monoclinic	triclinic	monoclinic
space group	<i>P</i> 6 <sub>3</sub> / <i>m</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	14.676(14)	15.547(6)	8.421(8)	26.802(5)
<i>b</i> , Å	14.676(14)	18.839(12)	8.886(10)	12.543(5)
<i>c</i> , Å	16.316(16)	32.91(2)	14.220(14)	15.920(5)
α, deg	90	90	83.48(6)	90
β, deg	90	97.98(6)	75.70(5)	109.91(2)
γ, deg	120	90	79.50(6)	90
<i>V</i> , Å <sup>3</sup>	3043.4(9)	9545(10)	1011(2)	5032(3)
ρ(calc), <sup>a</sup> g/cm <sup>3</sup>	2.237	1.661	2.226	2.273
temp. °C	-167(2)	-167(2)	-167(2)	-167(2)
<i>Z</i>	2	4	1	8
μ, cm <sup>-1</sup>	96	62	106	243
Δρ, e/Å <sup>3</sup>	1.55	0.69	2.69	1.80
<i>R</i> ( <i>F</i> ) <sup>b</sup>	0.0770	0.0628	0.0807	0.0714
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>c</sup>	0.1689	0.1172	0.1654	0.1676

<sup>a</sup> ρ(obs) was not measured. <sup>b</sup>  $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $F_o^2 > 2\sigma(F_o^2)$  <sup>c</sup>  $R_w(F_o^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}$ ;  $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ ;  $w^{-1} = \sigma^2(F_o^2)$ ,  $F_o^2 < 0$ .

(COE)<sub>2</sub>)<sub>2</sub> and [RhCl(COE)<sub>2</sub>]<sub>2</sub> (COE = cyclooctene) were prepared by published methods.<sup>27</sup>

**[K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] (1).** A solution of nominal composition [K(18-crown-6)]<sub>2</sub>[Se<sub>4</sub>] was generated in situ by the reaction of K<sub>2</sub>Se (189 mg, 1.2 mmol), Se (284 mg, 3.6 mmol), and 18-crown-6 (1.2 mmol, 317 mg) in 20 mL of DMF. The solution was cooled to -50 °C after 1 h of stirring. [IrCl(COE)<sub>2</sub>]<sub>2</sub> (135 mg, 0.15 mmol) (COE = cyclooctene) was reacted with AgBF<sub>4</sub> (79 mg, 0.4 mmol) in 10 mL of CH<sub>3</sub>CN to generate [Ir(NCCH<sub>3</sub>)<sub>2</sub>(COE)<sub>2</sub>][BF<sub>4</sub>] in situ. This solution was slowly filtered into the [K(18-crown-6)]<sub>2</sub>[Se<sub>4</sub>] solution with stirring. A color change from dark green to red-brown occurred immediately. The solution was stirred at -50 °C for 15 min before being warmed to 25 °C where it was stirred for an additional 30 min. It was filtered and concentrated under vacuum to 10 mL, and then it was layered with 20 mL of diethyl ether. Crystals were isolated after 5 days; yield, 639 mg (75%). <sup>77</sup>Se NMR (DMF): δ 633, 560 ppm. Anal. Calcd for C<sub>36</sub>H<sub>72</sub>IrK<sub>3</sub>O<sub>18</sub>Se<sub>12</sub>: C, 21.09; H, 3.54. Found C, 20.86; H, 3.26.

**[K(2.2.2-cryptand)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2).** K<sub>2</sub>Se (126 mg, 0.80 mmol) and Se (190 mg, 2.4 mmol) were dissolved in 20 mL of DMF, and the resultant solution was allowed to stir for 1 h. [IrCl(COE)<sub>2</sub>]<sub>2</sub> (135 mg, 0.15 mmol) and AgBF<sub>4</sub> (79 mg, 0.40 mmol) were dissolved in 10 mL of acetonitrile in a flask wrapped in aluminum foil, and the solution was stirred for 1 h. The K<sub>2</sub>Se<sub>n</sub> solution was cooled to -55 °C, and the Ir-containing solution was slowly filtered into it. Once the addition was complete, the resultant solution was kept at -55 °C for 15 min before being warmed to 25 °C where it was kept an additional 30 min. The solution was filtered into a flask containing 2.2.2-cryptand (915 mg, 2.43 mmol), which dissolved with agitation. This solution was divided into three 50 mL Schlenk flasks, and each was layered with 10 mL of toluene. One day later each was layered with 10 mL of toluene and 10 mL of diethyl ether. On the following day each flask was layered with an additional 10 mL of diethyl ether. All three flasks were then agitated slightly. Crystals were isolated after 2 weeks; yield, 270 mg (36%). <sup>77</sup>Se NMR (DMF, 25 °C): δ 630, 534 ppm. Anal. Calcd for C<sub>61</sub>H<sub>116</sub>IrK<sub>3</sub>N<sub>6</sub>O<sub>18</sub>Se<sub>12</sub>: C, 29.56; H, 4.72; N, 3.39. Found: C, 30.64, H, 4.95, N, 4.18.

**[K(18-crown-6)(DMF)]<sub>2</sub>[Ir(NCCH<sub>3</sub>)<sub>2</sub>(Se<sub>4</sub>)<sub>2</sub>] (3).** K<sub>2</sub>Se (94 mg, 0.60 mmol), Se (284 mg, 3.6 mmol), and 18-crown-6 (317 mg, 1.2 mmol) were stirred in 15 mL of DMF for 3 h and then cooled to -50 °C. [IrCl(COE)<sub>2</sub>]<sub>2</sub> (135 mg, 0.15 mmol) was stirred with AgBF<sub>4</sub> (79 mg, 0.4 mmol) for 1 h in 10 mL of acetonitrile in a covered flask to generate [Ir(NCCH<sub>3</sub>)<sub>2</sub>(COE)<sub>2</sub>][BF<sub>4</sub>] in situ. This solution was cannulated into the polyselenide solution with rapid stirring. The color of the solution changed from dark green to red-brown. The solution was stirred for an additional 1 h at 25 °C before being filtered. The filtrate was then concentrated under vacuum to 15 mL and layered with 20 mL of diethyl ether. After 7 days crystals were isolated; yield, 212 mg (52%). <sup>77</sup>Se NMR (DMF, 25 °C): δ 649, 648 ppm. Anal. Calcd for C<sub>22</sub>H<sub>44</sub>IrKN<sub>4</sub>O<sub>8</sub>Se<sub>8</sub>: C, 19.49; H, 3.27. Found: C, 19.48; H, 2.98.

**[NH<sub>4</sub>]<sub>3</sub>[Ir(S<sub>6</sub>)<sub>3</sub>]·H<sub>2</sub>O·0.5CH<sub>3</sub>CH<sub>2</sub>OH. (4)** A 30 mL aliquot of a 25 wt % aqueous solution of (NH<sub>4</sub>)<sub>2</sub>S was warmed to 50 °C. Elemental S (5 g, 0.156 mol) was slowly added to the solution of (NH<sub>4</sub>)<sub>2</sub>S with rapid stirring. Once all of the S had dissolved, IrCl<sub>3</sub>·*n*H<sub>2</sub>O (1 g) in 10 mL of H<sub>2</sub>O was slowly added to this solution. The solution was stirred at 50 °C for 1 h and then cooled to 25 °C. It was filtered and layered with a 1:1 mixture of ethanol and 2-propanol. Golden-yellow octagonal platelets were isolated after 1 week. These crystals were washed with CS<sub>2</sub> to remove elemental S and then dried briefly under vacuum; yield, 1.38 g. This compound decomposes once redissolved, rapidly liberating elemental S. Anal. Calcd for CH<sub>17</sub>IrN<sub>3</sub>O<sub>1.5</sub>S<sub>18</sub>: C, 2.71; H, 2.27; N, 4.73; Ir, 21.66. Found: C, 3.03; H, 1.79; N, 4.77; Ir, 23.17.

Synthesis of Rh homologues of [Ir(Se<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> and [Ir(NCCH<sub>3</sub>)<sub>2</sub>(Se<sub>4</sub>)<sub>2</sub>]<sup>-</sup> was carried out by the same procedure as that described above with the substitution of [RhCl(COE)<sub>2</sub>]<sub>2</sub> for [IrCl(COE)<sub>2</sub>]<sub>2</sub>.

**Crystallographic Studies.** Intensity data were collected from single crystals of [K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] (1), [K(2.2.2-cryptand)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2), and [K(18-crown-6)(DMF)]<sub>2</sub>[Ir(NCCH<sub>3</sub>)<sub>2</sub>(Se<sub>4</sub>)<sub>2</sub>] (3) with the use of a Picker diffractometer. Peak-profile data were collected from a single crystal of [NH<sub>4</sub>]<sub>3</sub>[Ir(S<sub>6</sub>)<sub>3</sub>]·H<sub>2</sub>O·0.5CH<sub>3</sub>CH<sub>2</sub>OH (4) on an Enraf-Nonius CAD4 diffractometer. The data for 1–4 were processed and then corrected for absorption. The structures were solved by direct methods (SHELXS<sup>28</sup>) and refined with the use of the SHELXL-93<sup>29</sup> least-squares program. The SHELXTL PC graphics programs<sup>30</sup> were employed. Structure refinements were straightforward for all but compound 2 where unresolved solvent molecules were present. Consequently, the BYPASS<sup>31</sup> subroutine in the program package PLATON<sup>32</sup> was used to account for these molecules. With this procedure potential solvent regions in the crystal structure are identified from considerations of space filling. The contributions to the total structure factors of the observed electron densities in these regions are calculated by a discrete Fourier transform, and the results are incorporated into the structure factors for further least-squares refinement of the ordered part of the structure. The process is iterated. Some crystallographic details are listed in Table 1 for compounds 1–4.

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**Table 2.** Fractional Coordinates, Equivalent Isotropic Displacement Parameters, and Site Occupancies for the Anion of [K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] (1)

atom	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>	occupancy
Ir(1)	2/3	1/3	3/4	0.0502(5)	1
Se(1)	0.83409(12)	0.61562(12)	0.67905(10)	0.0487(4)	1
Se(2)	0.6860(2)	0.4729(2)	0.63855(14)	0.0315(5)	0.50
Se(3)	0.8159(2)	0.4399(2)	0.8258(2)	0.0373(6)	0.50

**Table 3.** Fractional Coordinates and Equivalent Isotropic Displacement Parameters for the Anion of [K(2.2.2-cryptand)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2)

atom	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
Ir(1)	0.75708(6)	0.23126(5)	0.64035(3)	0.0272(3)
Se(1)	0.8522(2)	0.30986(13)	0.68526(8)	0.0341(7)
Se(2)	0.8063(2)	0.29646(13)	0.75058(8)	0.0391(8)
Se(3)	0.6590(2)	0.31340(13)	0.73271(8)	0.0375(8)
Se(4)	0.6365(2)	0.22182(13)	0.68366(8)	0.0325(7)
Se(5)	0.8357(2)	0.13374(13)	0.67805(8)	0.0406(8)
Se(6)	0.8098(2)	0.03247(14)	0.63789(9)	0.0507(9)
Se(7)	0.6628(2)	0.04754(14)	0.62118(9)	0.0559(9)
Se(8)	0.6678(2)	0.15935(13)	0.58947(8)	0.0420(8)
Se(9)	0.8799(2)	0.23025(13)	0.59838(8)	0.0360(7)
Se(10)	0.8358(2)	0.30149(14)	0.54117(8)	0.0402(8)
Se(11)	0.7811(2)	0.39598(13)	0.57632(8)	0.0421(8)
Se(12)	0.6773(2)	0.33384(13)	0.60924(8)	0.0350(7)

**Table 4.** Fractional Coordinates and Equivalent Isotropic Displacement Parameters for the Anion of [K(18-crown-6)(DMF)<sub>2</sub>][Ir(NCCH<sub>3</sub>)<sub>2</sub>(Se<sub>4</sub>)<sub>2</sub>] (3)

atom	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
Ir(1)	0	1/2	0	0.0234(4)
Se(1)	0.1414(3)	0.4696(3)	0.23853(14)	0.0375(6)
Se(2)	0.2614(2)	0.3213(3)	0.01102(14)	0.0333(6)
Se(3)	-0.0601(2)	0.6118(2)	0.16057(13)	0.0311(6)
Se(4)	0.3716(2)	0.4502(3)	0.10754(14)	0.0371(6)
N(1)	0.118(2)	0.663(2)	-0.0565(11)	0.043(5)
C(1)	0.183(2)	0.772(2)	-0.0894(13)	0.025(5)
C(2)	0.271(3)	0.896(3)	-0.1300(14)	0.043(6)

**Table 5.** Fractional Coordinates and Equivalent Isotropic Displacement Parameters for the Anion of [NH<sub>4</sub>]<sub>3</sub>[Ir(S<sub>6</sub>)<sub>3</sub>]·H<sub>2</sub>O·0.5CH<sub>3</sub>CH<sub>2</sub>OH (4)

atom	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
Ir(1)	0.33591(2)	0.49640(7)	0.43879(5)	0.0316(2)
S(1)	0.2635(2)	0.5692(4)	0.4718(3)	0.0391(11)
S(2)	0.2013(2)	0.4660(4)	0.4527(3)	0.0416(12)
S(3)	0.1427(2)	0.5174(4)	0.3382(3)	0.0493(13)
S(4)	0.1570(2)	0.4484(4)	0.2322(3)	0.0460(12)
S(5)	0.2234(2)	0.5236(4)	0.2224(3)	0.0468(13)
S(6)	0.2888(2)	0.4389(4)	0.2924(3)	0.0416(11)
S(7)	0.3181(2)	0.3296(4)	0.4884(3)	0.0443(12)
S(8)	0.3834(2)	0.2352(4)	0.5453(4)	0.0550(14)
S(9)	0.3853(2)	0.1342(5)	0.4451(4)	0.060(2)
S(10)	0.4412(2)	0.1973(4)	0.3979(4)	0.0547(14)
S(11)	0.4098(2)	0.3332(4)	0.3271(3)	0.0486(13)
S(12)	0.4170(2)	0.4512(4)	0.4191(3)	0.0390(11)
S(13)	0.3451(2)	0.6623(4)	0.3758(3)	0.0434(12)
S(14)	0.3369(2)	0.7914(4)	0.4482(3)	0.0427(11)
S(15)	0.4127(2)	0.8456(4)	0.5174(3)	0.0508(13)
S(16)	0.4375(2)	0.7668(5)	0.6377(3)	0.0503(13)
S(17)	0.4533(2)	0.6130(4)	0.6096(3)	0.0447(12)
S(18)	0.3848(2)	0.5288(4)	0.5899(3)	0.0418(12)

The final positional parameters of the anions all are given in Tables 2–5. Additional atomic positional parameters and crystallographic details are given in the Supporting Information.

## Results

**Syntheses.** At either 25 or -55 °C a pale yellow solution of [Ir(NCCH<sub>3</sub>)<sub>2</sub>(COE)<sub>2</sub>][BF<sub>4</sub>] in acetonitrile will react with a dark green solution in DMF of what is nominally [K(18-crown-

6)]<sub>2</sub>[Se<sub>4</sub>] to afford a red-brown solution that contains [K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] (1). Single crystals of this compound can be grown by slow diffusion of diethyl ether into a filtered reaction mixture or by slow evaporation of the reaction mixture under reduced pressure.

[K(2.2.2-cryptand)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] is synthesized in a manner similar to that of [K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>]. However, in this synthesis the encapsulating agent 2.2.2-cryptand is added after the reaction of [Ir(NCCH<sub>3</sub>)<sub>2</sub>(COE)<sub>2</sub>][BF<sub>4</sub>] with 2.67 equiv of Se<sub>4</sub><sup>2-</sup>. This procedure helps to prevent the precipitation of [K(2.2.2-cryptand)]<sub>2</sub>[Se<sub>5</sub>] and [K(2.2.2-cryptand)]<sub>2</sub>[Se<sub>6</sub>], both of which are insoluble in the solution. Crystals of [K(2.2.2-cryptand)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2) were grown with great difficulty by the slow diffusion of diethyl ether and toluene into a concentrated solution of this compound in DMF.

[Ir(NCCH<sub>3</sub>)<sub>2</sub>(COE)<sub>2</sub>][BF<sub>4</sub>] also reacts with 2 equiv of K<sub>2</sub>Se and 12 equiv of Se initially suspended in DMF to produce [K(18-crown-6)(DMF)<sub>2</sub>][Ir(NCCH<sub>3</sub>)<sub>2</sub>(Se<sub>4</sub>)<sub>2</sub>] (3). Single crystals can be isolated from a filtered reaction mixture into which diethyl ether is allowed to diffuse for a week.

The reaction of IrCl<sub>3</sub>·nH<sub>2</sub>O with [NH<sub>4</sub>]<sub>2</sub>[S<sub>m</sub>] at 50 °C in water affords [NH<sub>4</sub>]<sub>3</sub>[Ir(S<sub>6</sub>)<sub>3</sub>]. Crystals of [NH<sub>4</sub>]<sub>3</sub>[Ir(S<sub>6</sub>)<sub>3</sub>]·H<sub>2</sub>O·0.5CH<sub>3</sub>-CH<sub>2</sub>OH (4) can be grown by diffusion of 1:1 2-propanol/ethanol into a filtered reaction mixture. This compound, though stable in the solid state under an inert atmosphere for several months, rapidly liberates S upon dissolution into either aqueous or nonaqueous solvents.

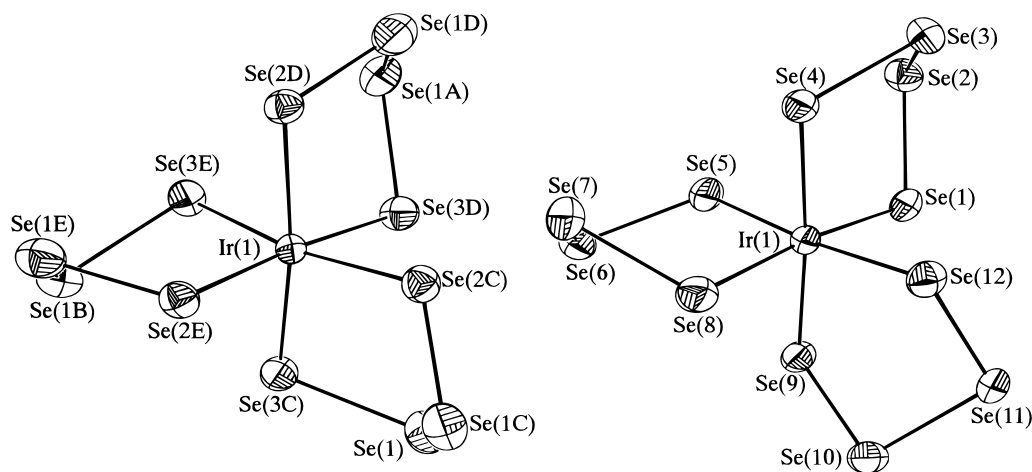
**Structures.** (a) [K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] (1). In the crystal structure of [K(18-crown-6)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>] the [Ir(Se<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> anion has crystallographically imposed symmetry  $\bar{6}$  with the  $\Delta\lambda\lambda\lambda$  (Figure 1) and  $\Lambda\delta\delta\delta$  conformers being superimposed upon one another in a 1:1 ratio. In the structure there are strong interactions between the K<sup>+</sup> ion, which is out of the plane of the crown ether, and some Se atoms (Figure 2), with K<sup>+</sup>···Se interactions ranging from 3.535(4) to 3.646(5) Å. The resultant geometry about the Ir(III) center is distorted from octahedral symmetry, with the two independent Ir–Se distances being 2.654(8) Å (shorter K<sup>+</sup>···Se interaction) and 2.319(8) Å (longer K<sup>+</sup>···Se interaction). Whereas it is possible that some of this distortion is an artifact of the crystallographically imposed  $\bar{6}$  symmetry at the Ir site and the resultant disorder, distortions of metal–selenium bonds have previously been observed in [Na(15-crown-5)]<sub>2</sub>[M(Se<sub>4</sub>)<sub>2</sub>] (M = Zn, Cd, Hg)<sup>33</sup> and in [K(18-crown-6)]<sub>2</sub>[Hg(Se<sub>4</sub>)<sub>2</sub>].<sup>14</sup> In the latter instance a 0.1 Å difference was observed in Hg–Se bond lengths, with the longest Hg–Se bond involving a Se atom that has a close interaction with the K<sup>+</sup> ion. Previous Ir–Se bond distances for organometallic species containing single Se<sub>4</sub><sup>2-</sup> units range between 2.468(2) and 2.547(2) Å.<sup>34,35</sup>

(b) [K(2.2.2-cryptand)]<sub>3</sub>[Ir(Se<sub>4</sub>)<sub>3</sub>]·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2). The octadentate ligation of 2.2.2-cryptand about K<sup>+</sup> greatly inhibits close K<sup>+</sup>···Se interactions both by saturating the coordination sphere of the K<sup>+</sup> cation and by providing steric bulk. As a consequence of this, the octahedral geometry about the Ir(III) center in the present [Ir(Se<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> anion is more regular than it is in 1. Selected metrical details for this anion are given in Table 6. There is a small tetragonal distortion, as the two trans Ir–Se bond lengths are 2.513(3) and 2.507 Å, whereas the four basal Ir–Se bond lengths range from 2.433(3) to 2.447(3) Å. The largest angular deviation from an idealized octahedral

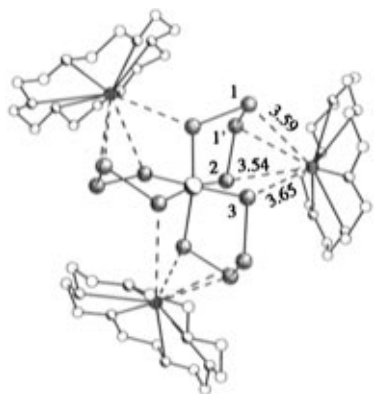
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**Figure 1.**  $\Delta\lambda\lambda\lambda$ - $[\text{Ir}(\text{Se}_4)_3]^{3-}$  and  $\Delta\lambda\lambda\delta$ - $[\text{Ir}(\text{Se}_4)_3]^{3-}$  anions as viewed down the three-fold axes of the octahedra. Here and in Figures 3 and 4 the 50% displacement ellipsoids are shown.



**Figure 2.**  $[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$  showing some of the  $\text{K}\cdots\text{Se}$  interactions with relevant distances.

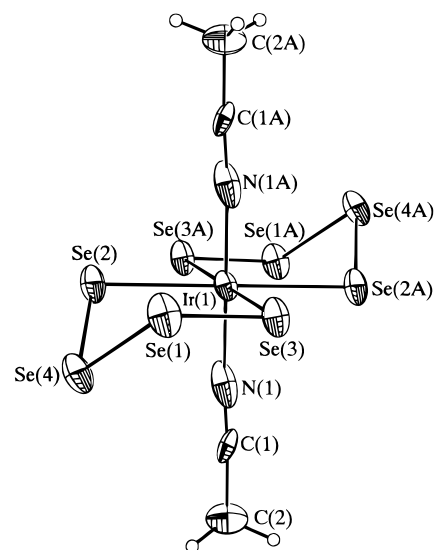
**Table 6.** Selected Bond Distances (Å) and Angles (deg) for the Anion of  $[\text{K}(\text{2.2.2-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]\cdot\text{C}_6\text{H}_5\text{CH}_3$  (2)

Ir(1)–Se(1)	2.441(3)	Se(3)–Se(4)	2.355(4)
Ir(1)–Se(4)	2.513(3)	Se(5)–Se(6)	2.324(4)
Ir(1)–Se(5)	2.447(3)	Se(6)–Se(7)	2.293(4)
Ir(1)–Se(8)	2.433(3)	Se(7)–Se(8)	2.357(4)
Ir(1)–Se(9)	2.507(3)	Se(9)–Se(10)	2.336(4)
Ir(1)–Se(12)	2.443(3)	Se(10)–Se(11)	2.346(4)
Se(1)–Se(2)	2.371(4)	Se(11)–Se(12)	2.373(4)
Se(2)–Se(3)	2.306(3)		
Se(8)–Ir(1)–Se(1)	173.87(10)	Se(1)–Ir(1)–Se(5)	86.01(11)
Se(12)–Ir(1)–Se(5)	174.39(11)	Se(1)–Ir(1)–Se(9)	83.93(10)
Se(9)–Ir(1)–Se(4)	175.36(9)	Se(1)–Ir(1)–Se(12)	90.21(11)

geometry about the Ir center is approximately  $8^\circ$ . The anion is a racemic mixture of the  $\Delta\lambda\lambda\delta$  (Figure 1) and  $\Lambda\delta\delta\lambda$  conformers.

(c) **[K(18-crown-6)(DMF)<sub>2</sub>][Ir(NCCH<sub>3</sub>)<sub>2</sub>(Se<sub>4</sub>)<sub>2</sub>] (3).** In the crystal structure of  $[\text{K}(\text{18-crown-6})(\text{DMF})_2][\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]$  the  $[\text{K}(\text{18-crown-6})(\text{DMF})_2]^+$  cations and the  $[\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]^-$  anions (each with crystallographically imposed  $\bar{1}$  symmetry) are well-separated from one another. The  $\text{K}^+$  cation is eight coordinate, being bonded to the six ether O atoms of the crown and to O atoms of two trans DMF molecules. The Ir(III) center is octahedrally coordinated by two chelating  $\text{Se}_4^{2-}$  ligands and two trans  $\text{CH}_3\text{CN}$  molecules (Figure 3). Bond distances and angles for the anion are given in Table 7. The two independent Ir–Se distances are 2.494(3) and 2.496(3) Å. The Ir–N distance is 1.89(2) Å. The Se–Se distances range from 2.329–(3) to 2.352(3) Å. The five-membered  $\text{Ir}(\text{Se}_4)$  ring is in the half-envelope conformation.

(d)  **$[\text{NH}_4]_3[\text{Ir}(\text{S}_6)_3]\cdot\text{H}_2\text{O}\cdot 0.5\text{CH}_3\text{CH}_2\text{OH}$  (4).** The crystal structure consists of well-separated cations and anions as well



**Figure 3.** View of the  $[\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]^-$  anion.

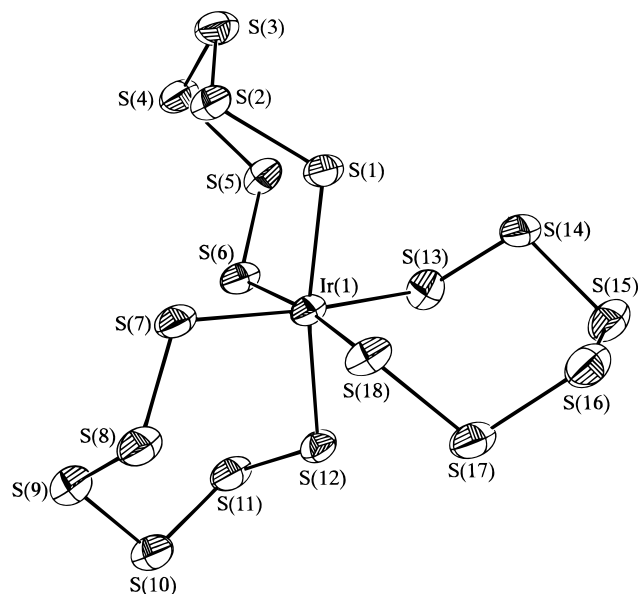
**Table 7.** Bond Distances (Å) and Angles (deg) for the Anion of  $[\text{K}(\text{18-crown-6})(\text{DMF})_2][\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]$  (3)<sup>a</sup>

Ir(1)–N(1)	1.89(2)	Se(1)–Se(3)	2.352(3)
Ir(1)–Se(3)	2.494(3)	Se(2)–Se(4)	2.330(3)
Ir(1)–Se(2)	2.496(3)	N(1)–C(1)	1.20(2)
Se(1)–Se(4)	2.329(3)	C(1)–C(2)	1.43(3)
N(1)–Ir(1)–N(1')	180	Se(4)–Se(1)–Se(3)	99.86(13)
N(1)–Ir(1)–Se(3)	88.9(5)	Se(4)–Se(2)–Ir(1)	101.76(12)
Se(3)–Ir(1)–Se(3)	180	Se(1)–Se(3)–Ir(1)	104.37(11)
N(1)–Ir(1)–Se(2)	92.1(5)	Se(1)–Se(4)–Se(2)	96.53(13)
Se(3)–Ir(1)–Se(2)	98.88(9)	C(1)–N(1)–Ir(1)	176(2)
Se(2)–Ir(1)–Se(2')	180	N(1)–C(1)–C(2)	177(2)

<sup>a</sup> Primed atoms are related to the corresponding unprimed atoms by the crystallographic center of symmetry.

as disordered water and ethanol molecules. These solvent molecules appear to be hydrogen bonded to one another. The  $[\text{Ir}(\text{S}_6)_3]^{3-}$  anion is formed by chelation of three  $\text{S}_6^{2-}$  ligands about an Ir(III) center. The structure contains a racemic mixture of the  $\Delta\lambda\lambda\delta$  (Figure 4) and  $\Lambda\delta\delta\lambda$  conformers. The resultant  $\text{IrS}_6$  rings have approximate pseudo-chair conformations. Bond distances and angles are given in Table 8 for  $[\text{Ir}(\text{S}_6)_3]^{3-}$ . There are no large distortions of the octahedral geometry about the Ir(III) center: Ir–S distances range from 2.343(5) to 2.368(4) Å, and S–Ir–S angles range from 85.2(2) to 100.4(2) $^\circ$ .

**<sup>77</sup>Se NMR Spectroscopy.** Table 9 lists the <sup>77</sup>Se NMR resonances for the Se-containing compounds reported here. The



**Figure 4.** View of the  $[\text{Ir}(\text{S}_6)_3]^{3-}$  anion demonstrating the pseudo-chair ring conformations.

**Table 8.** Selected Bond Distances (Å) and Angles (deg) for the Anion of  $[\text{NH}_4]_3[\text{Ir}(\text{S}_6)_3] \cdot \text{H}_2\text{O} \cdot 0.5\text{CH}_3\text{CH}_2\text{OH}$  (4)

Ir(1)–S(7)	2.343(5)	S(18)–S(17)	2.046(6)
Ir(1)–S(18)	2.350(5)	S(7)–S(8)	2.051(7)
Ir(1)–S(6)	2.354(4)	S(13)–S(14)	2.042(7)
Ir(1)–S(1)	2.359(4)	S(5)–S(6)	2.029(6)
Ir(1)–S(13)	2.359(5)	S(14)–S(15)	2.067(6)
Ir(1)–S(12)	2.368(4)	S(11)–S(10)	2.058(8)
S(1)–S(2)	2.050(6)	S(17)–S(16)	2.057(7)
S(4)–S(3)	2.044(7)	S(16)–S(15)	2.054(7)
S(4)–S(5)	2.068(6)	S(10)–S(9)	2.050(7)
S(2)–S(3)	2.064(7)	S(8)–S(9)	2.051(8)
S(12)–S(11)	2.044(7)		
S(7)–Ir(1)–S(18)	85.2(2)	S(1)–S(2)–S(3)	105.6(3)
S(7)–Ir(1)–S(6)	87.6(2)	S(11)–S(12)–Ir(1)	113.6(2)
S(18)–Ir(1)–S(6)	172.1(2)	S(4)–S(3)–S(2)	107.2(3)
S(7)–Ir(1)–S(1)	89.6(2)	S(17)–S(18)–Ir(1)	113.9(2)
S(18)–Ir(1)–S(1)	85.3(2)	S(8)–S(7)–Ir(1)	115.0(2)
S(6)–Ir(1)–S(1)	97.7(2)	S(14)–S(13)–Ir(1)	114.3(2)
S(7)–Ir(1)–S(13)	173.8(2)	S(6)–S(5)–S(4)	108.9(3)
S(18)–Ir(1)–S(13)	100.4(2)	S(5)–S(6)–Ir(1)	117.1(3)
S(6)–Ir(1)–S(13)	87.0(2)	S(13)–S(14)–S(15)	106.7(3)
S(1)–Ir(1)–S(13)	88.1(2)	S(12)–S(11)–S(10)	106.7(3)
S(7)–Ir(1)–S(12)	97.6(2)	S(18)–S(17)–S(16)	106.1(3)
S(18)–Ir(1)–S(12)	87.7(2)	S(15)–S(16)–S(17)	105.9(3)
S(6)–Ir(1)–S(12)	90.1(2)	S(9)–S(10)–S(11)	107.8(3)
S(1)–Ir(1)–S(12)	169.5(2)	S(16)–S(15)–S(14)	106.6(3)
S(13)–Ir(1)–S(12)	85.5(2)	S(9)–S(8)–S(7)	104.9(3)
S(2)–S(1)–Ir(1)	114.3(2)	S(10)–S(9)–S(8)	105.1(3)
S(3)–S(4)–S(5)	106.1(3)		

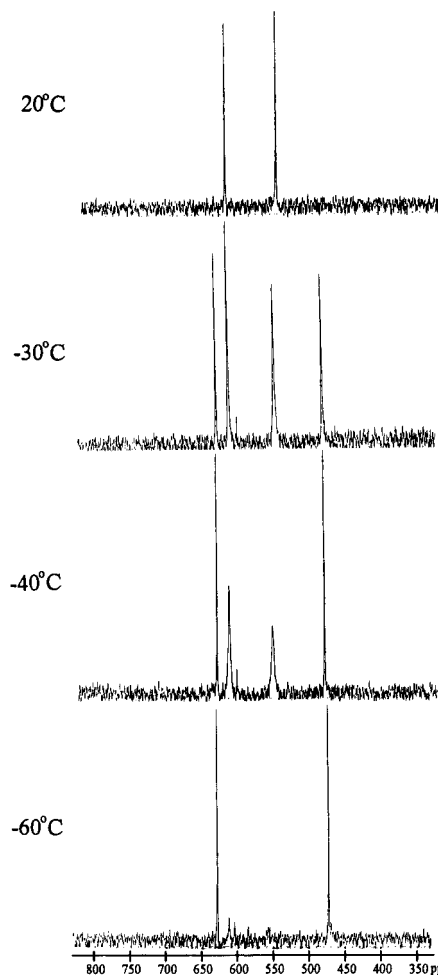
**Table 9.**  $^{77}\text{Se}$  NMR Resonances (ppm)

compound	$\delta$ , +25 °C	$\delta$ , –70 °C
$[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$ (1)	633, 560	647, 488
$[\text{K}(\text{2.2.2-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]$ (2)	630, 534	635, 482, 614, 603, 450
$[\text{K}(\text{18-crown-6})]_3[\text{Rh}(\text{Se}_4)_3]$	704, 602	637, 484
$[\text{K}(\text{18-crown-6})(\text{DMF})_2][\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]$ (3)	649, 648	
$[\text{K}(\text{18-crown-6})][\text{Rh}(\text{NCCH}_3)_2(\text{Se}_4)_2]$	772 (broad) <sup>a</sup>	

<sup>a</sup> This resonance appears to comprise several peaks.

$^{77}\text{Se}$  VT-NMR behavior of all of the complexes discussed is reversible; no precipitation was observed at low temperature.

The  $^{77}\text{Se}$  NMR spectrum at 20 °C of a sample of  $[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$  (1) dissolved in DMF shows two resonances of equal intensity at 633 and 560 ppm. When this sample is



**Figure 5.** Variable-temperature  $^{77}\text{Se}$  NMR spectra of  $[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$  in a DMF solution at +20, –30, –40, and –60 °C.

cooled in 10 °C increments from +20 °C to –70 °C, two new peaks at 647 and 488 ppm grow into the spectrum as the original peaks at 633 and 560 ppm become less intense. Figure 5 shows the spectra obtained at +20, –30, –40, and –60 °C. By –70 °C only the peaks at 647 and 488 ppm are apparent. From these NMR data the values  $\Delta H = 2.5(5)$  kcal mol<sup>–1</sup> and  $\Delta S = 11.5(2.2)$  eu may be derived for what we believe is an equilibrium between two conformers, A and B, of  $[\text{Ir}(\text{Se}_4)_3]^{3-}$ . These data do not, however, enable us to elucidate the identity of the conformers present.  $^{77}\text{Se}$  NMR spectra obtained for  $[\text{K}(\text{2.2.2-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]$  are not identical with those obtained for  $[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$ . At 20 °C the  $^{77}\text{Se}$  NMR spectrum of a sample of  $[\text{K}(\text{2.2.2-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]$  dissolved in DMF displays two resonances at 630 and 534 ppm, as compared to 633 and 560 ppm for  $[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$ . The differences in these spectra at 20 °C may result from the persistence in solution of the K $\cdots$ Se interactions found in the crystal structure of  $[\text{K}(\text{18-crown-6})]_3[\text{Ir}(\text{Se}_4)_3]$ . When this sample of  $[\text{K}(\text{2.2.2-cryptand})]_3[\text{Ir}(\text{Se}_4)_3]$  is cooled, initially two new peaks arise at 635 and 428 ppm. However, three minor resonances at 614, 603, and 450 ppm are observed below –50 °C. These resonances, which have intensities that are less than 10% of those of the resonances at 630 and 534 ppm, may arise from the presence of small amounts of conformers in addition to A and B.

The  $^{77}\text{Se}$  NMR spectrum at 20 °C of a solution that we believe contains  $[\text{K}(\text{18-crown-6})]_3[\text{Rh}(\text{Se}_4)_3]$  displays two resonances at 704 and 602 ppm. As this solution is cooled, resonances at 637 and 484 ppm arise and the original resonances become less intense. Assuming a conformational equilibrium similar to that

proposed for  $[\text{Ir}(\text{Se}_4)_3]^{3-}$ , we derive the values of  $\Delta H = 5.2(7)$  kcal mol<sup>-1</sup> and  $\Delta S = 24.7(3.0)$  eu. The two conformers in equilibrium are not necessarily the same for the Rh and Ir systems. No Rh–Se coupling is observed in these spectra. Neither is coupling observed in <sup>77</sup>Se NMR spectra of  $[\text{M}(\text{Se}_4)_3]^{2-}$  (M = Pt, Sn), where it is also expected.<sup>25,26</sup>

Whereas solutions of  $[\text{K}(18\text{-crown-6})_3[\text{Ir}(\text{Se}_4)_3]$  are stable for several months under an argon atmosphere, solutions of  $[\text{Rh}(\text{Se}_4)_3]^{3-}$  exhibit the dark green color of polyselenides after approximately 3 h at +25 °C or 13 h at –30 °C. Concomitant with this obvious decomposition is the appearance of a single peak at 274 ppm in the <sup>77</sup>Se NMR spectrum. Since the <sup>77</sup>Se NMR spectrum of  $\text{Se}_n^{2-}$  has only been observed for samples at low temperatures,<sup>36</sup> this resonance probably arises from some other source, possibly from a  $[\text{RhSe}_n]^{2-}$  polymer similar in nature to that proposed for the analogous polysulfide system.<sup>8</sup> Crystals isolated from these solutions are  $[\text{K}(18\text{-crown-6})_2]_2[\text{Se}_5]$ . Crystallizations at low temperatures produced powders.

## Discussion

**Conformations.** From earlier studies of  $[\text{M}(\text{en})_3]^{n+}$  systems (M = Cr(III),<sup>37</sup> Ru(II),<sup>38</sup> Co(III),<sup>39</sup> Rh(III),<sup>40</sup> en = ethylenediamine), the relative stabilities of the various conformers in solution were established to be  $\Delta\lambda\lambda\delta > \Delta\lambda\lambda\lambda \approx \Delta\lambda\delta\delta > \Delta\delta\delta\delta$ .<sup>41</sup> We restrict the following discussion to the  $\Delta$  conformers of the  $[\text{M}(\text{Se}_4)_3]^{n-}$  (M = Sn, Pt, Ir) systems. The observed conformers are as follows: M = Sn,  $\Delta\lambda\delta\delta$ ;<sup>25,26</sup> Pt,  $\Delta\lambda\lambda\delta$  (concentrated solution, +25 °C)<sup>24</sup> and  $\Delta\lambda\delta\delta$  (dilute solution, –40 °C);<sup>12</sup> Ir,  $\Delta\lambda\lambda\lambda$  (K(18-crown-6) salt), and  $\Delta\lambda\lambda\delta$  (K(2.2.2-cryptand) salt). Not surprisingly, the stabilities<sup>42</sup> established for the  $[\text{M}(\text{en})_3]^{n+}$  systems do not apply to the  $[\text{M}(\text{Se}_4)_3]^{n-}$  systems. The changes in conformation with temperature in the latter system are consistent with differences in stability of around ~5 kcal mol<sup>-1</sup>; hence, those factors affecting stability of a given conformer are subtle at best and mysterious at worst. Surely one subtle factor is the cation–anion interaction. Such interactions resulting from hydrogen bonding were invoked for [Co-

(en)<sub>3</sub>]<sup>3+</sup>;<sup>37</sup> similarly we can invoke K<sup>+</sup>•••Se interactions in the present Ir system.<sup>17</sup>

**Reactions.** Whereas they are prepared similarly,  $[\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]^-$  could be viewed as an intermediate in the formation of  $[\text{Ir}(\text{Se}_4)_3]^{3-}$ . Thus, when 4 equiv of Se are added to a solution containing  $[\text{Ir}(\text{NCCH}_3)_2(\text{Se}_4)_2]^-$  and 2 equiv of LiBEt<sub>3</sub>H are added slowly,  $[\text{Ir}(\text{Se}_4)_3]^{3-}$  is produced quantitatively after 2 h of stirring. This result is surprising given the kinetic inertness of Ir(III) complexes.<sup>43,44</sup> However, the labilization of Rh(III) complexes has been proposed to result from electron transfer from catalytic amounts of Rh(I) to Rh(III).<sup>45</sup> It is possible that in the above reaction catalytic amounts of Ir(I) are formed, thereby labilizing the acetonitrile ligands.

Pt(II)<sup>12</sup> and Ir(I) complexes react with  $\text{Se}_n^{2-}$  to afford Pt(IV) and Ir(III) species, respectively. Whereas the Pt(IV) species  $[\text{Pt}(\text{Se}_4)_3]^{2-}$  can be reduced with LiBEt<sub>3</sub>H to afford the Pt(II) species  $[\text{Pt}(\text{Se}_4)_2]^{2-}$ , we have been unable to isolate  $[\text{Ir}(\text{Se}_4)_2]^{3-}$  from the attempted reduction of  $[\text{Ir}(\text{Se}_4)_3]^{3-}$  with a variety of reductants. Although many analogies can be drawn between isoelectronic Pt(II) and Ir(I) complexes, there are many differences in the stabilities of complexes of these low-valent metals. For example, we have found no examples of Rh(I) or Ir(I) complexes in solution containing only pure  $\sigma$ -donor ligands and only one such example in the solid state.<sup>46</sup> Further,  $[\text{PtCl}_4]^{2-}$  exists, but  $[\text{IrCl}_4]^{3-}$  has not been reported. In general, two  $\pi$ -acceptor ligands, such as CO or PR<sub>3</sub>, are required to stabilize Rh(I) or Ir(I).<sup>47</sup> Q<sub>n</sub><sup>2-</sup> ligands (Q = S, Se) may not possess empty d-orbitals low enough in energy to stabilize Ir(I) or Rh(I). Thus,  $[\text{M}(\text{Se}_4)_3]^{3-}$  (M = Rh, Ir) may not be stable even though numerous  $[\text{M}(\text{Se}_4)_2]^{2-}$  species (M = Fe, Mn, Ni, Pd, Pt, Zn, Cd, Hg) exist.

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**Supporting Information Available:** Tables giving structure determination summaries, positional coordinates (including hydrogen-atom coordinates) and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for compounds 1–4 (53 pages). Ordering information is given on any current masthead page.

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