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# Synthesis and Characterization of the New Selenometalate Anion $[Ir(Se_4)_3]^{3-}$

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The chemistry of the chalcogenometalate anions $[M_xQ_y]^{z-}$, Q = S, Se, Te, continues to expand rapidly.$^{1-6}$ Although the metals M range over groups 5−14, and concentrate in groups 10−12, it is curious that $[Co_3(Se_4)_6]^{3-}$ $^{7,8}$ is the only example from group 9. Whereas square-planar or tetrahedral anions of the type $[M(Q_n)_2]^{z-}$ are common, with *n* most often 4, octahedral complexes of the type $[M(Q_n)_3]^{z-}$ appear to be limited to $[Pt(S_5)_3]^{2-}$,$^{9-11}$ $[Pt(Se_4)_3]^{2-}$,$^{12,13}$ and $[Sn(Se_4)_3]^{2-}$.$^{14,15}$ One would expect the $[Ir(Se_4)_2]^{3-}$ anion to exist, as examples of known $[M(Se_4)_2]^{z-}$ anions include M = Mn,$^{16,17}$ Ni,$^{17,18}$ Pd,$^{17}$ Pt,$^{13,17}$ Zn,$^{17-19}$ Cd,$^{17-19}$ Hg,$^{17,18,20}$ and Pb.$^{18}$ In an attempt to synthesize the square-planar Ir(I) anion $[Ir(Se_4)_2]^{3-}$, we have instead synthesized the octahedral Ir(III) anion $[Ir(Se_4)_3]^{3-}$, the second example of a chalcogenometalate of group 9.

All manipulations were carried out under an argon atmosphere. $[K(18\text{-crown-}6)]_2[Se_4]$ was generated in situ by the reaction of $K_2Se$ (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. $[IrCl(COE)_2]_2$ (135 mg, 0.15 mmol) (COE = cyclooctene) was reacted with $AgBF_4$ (79 mg, 0.4 mmol) in 10 mL of $CH_3CN$ to generate $[Ir(CH_3CN)_2(COE)_2][BF_4]$ in situ. This solution was slowly filtered into the $[K(18\text{-crown-}6)]_2[Se_4]$ solution with stirring. A color change from dark green to red-brown was immediately observed. While being stirred, the solution was kept at −50 °C for 15 min; it was then allowed to warm to room temperature, where it was kept for an additional 30 min. The mixture was filtered, and the filtrate was concentrated under vacuum to 10 mL and subsequently layered with 20 mL of diethyl ether. Crystals were isolated after 5 days. Total yield was 464 mg (75% based on Ir). The reaction can be carried out stoichiometrically to produce the same compound; excess $Se_4^{2-}$ merely improves the yield. The compound is very air-sensitive, even as a solid, but it can be stored for several months under an argon atmosphere without noticeable decomposition.

In the crystal structure of $[K(18\text{-crown-}6)]_3[Ir(Se_4)_3]$,$^{21}$ the $[Ir(Se_4)_3]^{3-}$ anion has crystallographically imposed $\bar{6}$ symmetry with the $\Lambda\delta\delta\delta$ and $\Delta\lambda\lambda\lambda$ conformers being superimposed upon one another in a 1:1 ratio. The $\Delta\lambda\lambda\lambda$ conformer is shown in Figure 1. There are strong interactions between the $K^+$ ion, which is out of the plane of the crown ether, and several Se atoms (Figure 2), with K· · ·Se interactions ranging from 3.535(4) to 3.646(5) Å. The resultant geometry about Ir is distorted from idealized octahedral symmetry, with the two independent Ir−Se distances being 2.646(2) Å (K· · ·Se interaction = 3.54 Å) and 2.312(3) Å (K· · ·Se interaction = 3.65 Å). Previously reported Ir−Se bond distances for organometallic species containing single $Se_4^{2-}$ units range from 2.468(2) to 2.547(2) Å.$^{22,23}$ 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,$^{24}$ distortions of metal−selenium bonds have previously been observed in $[Na(15\text{-crown-}5)]_2[M(Se_4)_2]$ (M = Zn, Cd, Hg)$^{25}$ and in $[K(18\text{-crown-}6)]_2[Hg(Se_4)_2]$.$^{26}$ In the latter example, 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 $K^+$ ion.

The $^{77}$Se NMR spectrum of a DMF solution of $[K(18\text{-crown-}6)]_3[Ir(Se_4)_3]$ at room temperature shows two singlets at 633 and 560 ppm. Singlets at 790 and 680 ppm were found in a previous $^{77}$Se NMR study of the $[Pt(Se_4)_3]^{2-}$ anion.$^{13}$ Since no $J_{Pt-Se}$ coupling was observed for $[Pt(Se_4)_3]^{2-}$, it is not known which of these resonances belongs to the metal-bound Se and which to the ring-bound Se. When a DMF solution of $[K(18\text{-crown-}6)]_3[Ir(Se_4)_3]$ is cooled, the peaks at 633 and 560 ppm decrease in size and new peaks at 647 and 488 ppm arise. By −70 °C only these latter peaks are apparent. If we assume that conformer **A** of the $[Ir(Se_4)_3]^{3-}$ anion is in equilibrium with

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(21) Crystal data for $[K(18\text{-crown-}6)]_3[Ir(Se_4)_3]$: $C_{36}H_{72}IrK_3O_{18}Se_{12}$, hexagonal, space group $C^2_{6h}$-$P6_3/m$, Z = 2, *a* = 14.676(14) Å, *c* = 16.316(16) Å, *V* = 3043 Å$^3$ at 113 K. Data were collected in $\omega$ scan mode out to $2\theta$(Mo K$\alpha_1$) = 53°. The anion has crystallographically imposed $\bar{6}$ symmetry and has been modeled by a 1:1 disorder of the $\Lambda\delta\delta\delta$ and $\Delta\lambda\lambda\lambda$ conformers. The final model, involving anisotropic displacement parameters for all atoms except C(2) (which became nonpositive definite), converged to $R(F^2) = 0.169$ for 2193 observations and 115 variables. The conventional *R* index, *R*(*F*), is 0.077 for those 1235 reflections having $F_o^2 > 2\sigma(F_o^2)$. Displacement parameters are normal, suggesting that atom Se(1) is common to both conformers.

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(24) Whereas twinning, more properly trilling, of a monoclinic structure in $P2_1/c$ with $a \approx c$ and $\beta \approx 120°$ can emulate $6/m$ symmetry, this seems unlikely in the present instance. The only unusual aspect of the structure is the difference in Ir−Se bond lengths; in all other respects, solution and refinement of the structure were normal.

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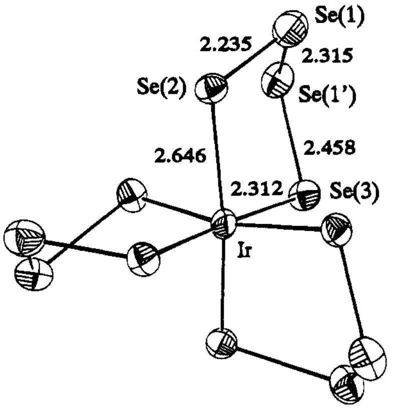

**Figure 1.** The $\Delta\lambda\lambda\lambda$ conformer of the $Ir(Se_4)_3{}^{3-}$ ion. The labeling scheme, principal distances, and 50% probability ellipsoids are shown. Estimated standard deviations are 0.002–0.003 Å for Ir–Se and 0.003–0.004 Å for Se–Se.

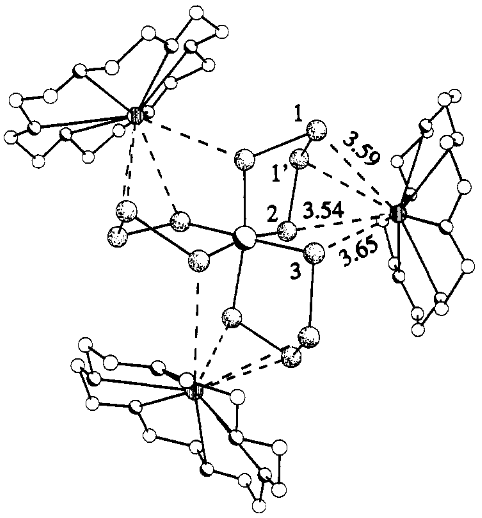

**Figure 2.** Part of the crystal structure of $[K(18\text{-crown-}6)]_3[Ir(Se_4)_3]$. The orientation of the cations, the interactions of $K^+$ ions with the Se atoms, and relevant distances are shown. Hydrogen atoms have been omitted for the sake of clarity.

conformer **B**, then from these NMR data the values $\Delta H = 2.5(5)$ kcal mol$^{-1}$ and $\Delta S = 11.5(2.2)$ cal mol$^{-1}$ K$^{-1}$ may be derived for this conversion. Identification of the conformations of **A** and **B** is not possible from the $^{77}$Se NMR data. The small energy difference between conformers **A** and **B** is consistent with the observations of various conformers among the octahedral $[M(Se_4)_3]^{z-}$ anions. As none of these has been resolved, we restrict discussion to the $\Delta$ conformers. Whereas the present $[Ir(Se_4)_3]^{3-}$ anion crystallizes as the $\Delta\lambda\lambda\lambda$ conformer, $[Pt(Se_4)_3]^{2-}$ crystallizes as the $\Delta\lambda\lambda\delta$[12] and $\Delta\lambda\delta\delta$[13] conformers, and $[Sn(Se_4)_3]^{2-}$ crystallizes as the $\Delta\lambda\delta\delta$ conformer.[14,15]

Polyselenide ligands form complexes with transition metals both in low oxidation states (e.g. Cu(I)[27,28] ) and also in unusually high oxidation states (e.g. Ni(IV)[29,30] ). In the present instance, the use of Ir(I) to synthesize the proposed Ir(I) anion $[Ir(Se_4)_2]^{3-}$ was a reasonable choice. However, as in the related Pt chemistry where a Pt(II) source led to the Pt(IV) anion $[Pt(Se_4)_3]^{2-}$, Ir(I) was oxidized to Ir(III) (presumably by $Se_n{}^{2-}$) and $[Ir(Se_4)_3]^{3-}$ resulted. The Pt(II) species $[Pt(Se_4)_2]^{2-}$ was successfully synthesized by the reduction of $[Pt(Se_4)_3]^{2-}$ with $LiBEt_3H$.[13] Attempts are underway to reduce $[Ir(Se_4)_3]^{3-}$ to $[Ir(Se_4)_2]^{3-}$. In addition, Rh chemistry analogous to the present Ir chemistry is being pursued, as is related sulfidometalate and tellurometalate chemistry.[31]

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**Supporting Information Available:** Listings of crystallographic details, positional and displacement parameters, and bond lengths and angles (9 pages). Ordering information is given on any current masthead page.

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(31) The $^{77}$Se NMR spectrum of a Rh reaction mixture analogous to the Ir one described above displays two singlets at 708 and 606 ppm, providing strong evidence for the presence of $[Rh(Se_4)_3]^{3-}$. No $J_{Rh-Se}$ coupling was observed. However, no Rh-containing product has been successfully isolated yet.