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Synthesis and Structure of the New Organometallic Polyoxovanadates, $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ and $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$

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A 1,5-cyclooctadieneiridium complex of $V_4O_{12}^{4-}$, $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ is synthesized as a tetra-*n*-butylammonium salt by reacting $[(\eta\text{-}C_8H_{12})IrCl]_2$ with either $[(n\text{-}C_4H_9)_4N]_3V_5O_{14}$ or $[(n\text{-}C_4H_9)_4N]VO_3$ in CH_3CN. The reaction of $[(\eta\text{-}C_8H_{12})IrCl]_2$ with $[(n\text{-}C_4H_9)_4N]VO_3$ in CH_3CN also yields $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ as a tetra-*n*-butylammonium salt. X-Ray structural analyses revealed that the $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ and $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ anions contain a $V_4O_{12}^{4-}$ ring coordinated to one or two $(\eta\text{-}C_8H_{12})Ir^+$ moieties, respectively.

Recently, we1) and others2) reported the synthesis of $[(C_5Me_5)Rh]_4(V_6O_{19})$, the first polyoxovanadate supported organometallic complex. Unfortunately, the synthetic methods employed require starting materials that are water-stable, and are thus not general routes to reactive organometallic polyoxovanadates. Here we report syntheses of two new complexes, $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ and $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$, that are performed in nonaqueous media. This route should serve as a general synthetic pathway to reactive polyoxovanadate supported organometallic compounds.

Addition of a solution of $[(C_8H_{12})IrCl]_2$ 3) (0.12 g, 0.18 mmol, in 2 cm^3 CH_3CN) to a solution of $[(n\text{-}C_4H_9)_4N]_3V_5O_{14}$ 4) (0.40 g, 0.33 mmol, in 2 cm^3 CH_3CN) under dry nitrogen produced a brown

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precipitate. This material was collected by filtration, washed with 2x2 cm^3 of diethyl ether, and dried under vacuum to yield 0.09 g of $[(n\text{-}C_4H_9)_4N]_2\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}$, **1** (0.061 mmol, 34% yield based on Ir).5) The same compound was also obtained by adding a solution of $[(n\text{-}C_4H_9)_4N]VO_3$ 6) (0.50 g, 1.5 mmol, in 3 cm^3 CH_3CN) to a solution of $[(C_8H_{12})IrCl]_2$ (0.26 g, 0.39 mmol, in 5 cm^3 CH_3CN), collecting the brown precipitate which formed by filtration, washing with 3x2 cm^3 of diethyl ether, and drying under vacuum (0.32 g, 0.22 mmol, 59% yield based on V). Reaction of $[(C_8H_{12})IrCl]_2$ (0.042 g, 0.063 mmol) with $[(n\text{-}C_4H_9)_4N]VO_3$ (0.20 g, 0.59 mmol) in 2 cm^3 CH_3CN under dry nitrogen for 30 min followed by addition of 20 cm^3 of diethyl ether produced an orange precipitate. This material was collected by filtration, washed with 2x2 cm^3 of diethyl ether, and dried under vacuum to yield 0.12 g of $[(n\text{-}C_4H_9)_4N]_3[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]$, **2**(0.084 mmol, 67% yield based on Ir).7)

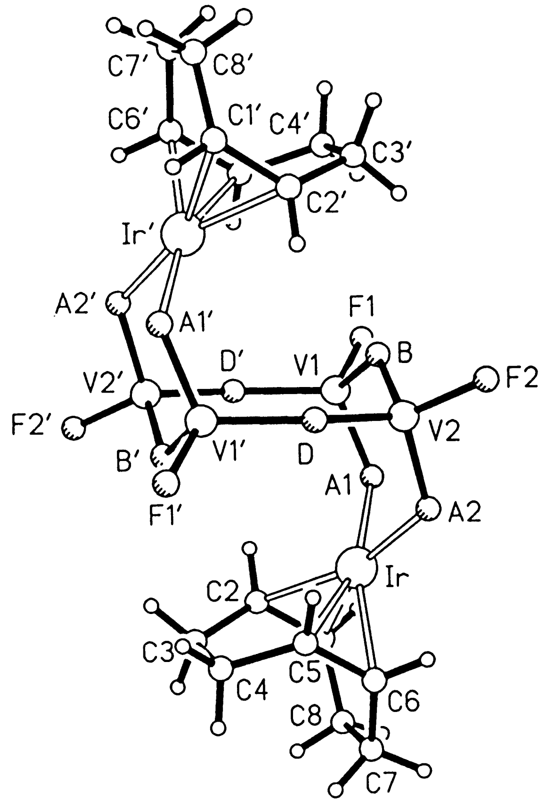

Fig. 1. Structure of the anion in **1**. Oxygen atoms are represented by shaded spheres and are labeled only by their subscripts. All other atoms are represented by open spheres and are labeled, except for hydrogen atoms, by their atomic symbol and, in the case of vanadium and carbon, their subscripts. Atoms with primed labels are related to atoms with unprimed labels by the crystallographic inversion center at (1/4, 1/4, 0) in the unit cell.

X-Ray structural analyses of crystalline **1** and **2** revealed that the anions $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ and $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ have closely related structures, consisting of a $V_4O_{12}{}^{4-}$ ring with two (**1**) or one (**2**) $(\eta\text{-}C_8H_{12})Ir^+$ moieties bonded to two terminal oxygens of adjacent vanadium atoms (see Figs. 1 and 2).8-10) Although the anion of **1** possesses only rigorous crystallographic inversion symmetry, it approximates closely its maximum possible symmetry of C_{2h}. Average values of structurally equivalent bond lengths and angles of interest are as follows: V-O_A, 1.671(7, 2, 2, 2) Å;11) V-O_B, 1.794(7, 10, 10, 2) Å; V-O_D, 1.780(7, 13, 13, 2) Å; V-O_F, 1.614(8, 6, 6, 2) Å; Ir-O, 2.050(7, 1, 1, 2) Å; Ir-C, 2.104(13, 6, 11, 4) Å; V-O_D-V, 146.3(4)°; V-O_B-V, 125.3(5)°; O_B-V-O_D, 109.3(3, 2, 2, 2)°; V-O_A-Ir, 121.8(3, 12, 12, 2)°; O-Ir-O, 88.2(3)°. Although it has no rigorous crystallographic symmetry, the anion of **2** approximates C_s symmetry with the Ir atom and the oxygen atoms O_B and O_E lying on the pseudo mirror plane.

Average values of structurally equivalent bond length and angles of interest include the following: V-O_A, 1.68(1, 2, 2, 2) Å; V-O_B, 1.78(1, 1, 1, 2) Å; $V_{1,2}$-O_D, 1.75 (1, 2, 2, 2) Å; $V_{3,4}$-O_D, 1.82(1, 1, 1, 2)Å; V-O_E, 1.77(1, 2, 2, 2)Å; V-O_F, 1.60(1, 2, 2, 2,) Å; V-O_G, 1.59(2, 2, 2, 2) Å; V-O_H, 1.56(2, 4, 4, 2)Å; Ir-O, 1.97(1, 4, 4, 2) Å; Ir-C, 2.20(2, 4, 9, 4) Å; Ir-O_A-V, 123(1, 3, 3, 2)°; V-O_B-V, 131(1)°; V-O_D-V, 141(1, 3, 3, 2)°; V-O_E-V, 155(1)°; O_B-V-O_D, 109(1, 2, 2, 2)°; O_D-V-O_E, 110(1, 2, 2, 2)°. Unlike the $V_4O_{12}^{4-}$ ring in $HV_4O_{12}^{3-}$, which has a bent structure,12) the rings in the present anions assume a more planar configuration, each having all four V atoms nearly in the same plane. Coordination around Ir atoms in both complexes is square planar and is almost identical to that found in acetylacetonato(1,5-cyclooctadiene)iridium, [(η-C_8H_{12})Ir(acac)].13)

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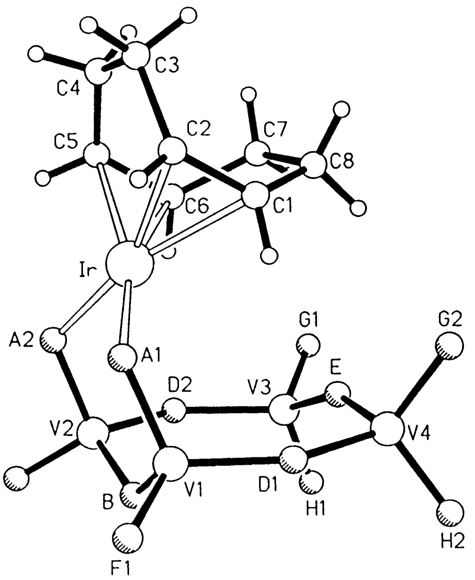

Fig. 2. Structure of the anion in **2**. Oxygen atoms are represented by shaded spheres and are labeled only by their subscripts. All other atoms are represented by open spheres and are labeled, except for hydrogen atoms, by their atomic symbol and, in the case of vanadium and carbon, their subscripts.

References

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5) Anal. Found: C, 38.87; H, 6.56; N, 2.06; Ir, 24.79; V, 13.98%. Calcd for $C_{48}H_{96}N_2Ir_2V_4O_{12}$: C, 38.92; H, 6.53; N, 1.89; Ir, 25.95; V, 13.75%. IR (Nujol, 1000 - 700 cm^{-1}): 969 (s), 922 (w), 901 (w), 882 (w), 845 (m), 796 (s), 726 (m). ^1H NMR (CD_3CN, 300 MHz): δ 3.8 (br, 8), 3.11 (m, 16), 2.4 (br, 8), 1.62 (m, 16), 1.45 (m, 8), 1.37 (m, 16), 0.97 (t, 24). ^{51}V NMR (CD_3CN, 78.9 MHz): δ -446.

6) [(*n*-C_4H_9)$_4$N]VO_3 was prepared by adding V_2O_5 (4.0 g, 22 mmol) to 200 cm^3 of aqueous 0.4 M [(*n*-C_4H_9)$_4$N]OH solution, stirring the solution for 18 h, filtering off a small amount of insoluble material, and then evaporating the solution to complete dryness under vacuum at 60 °C (14 g, 41 mmol, 93% yield based on V). The analytical sample was obtained by dissolving 1.0 g of the

crude material in 4 cm^3 of acetone, precipitating by adding 8 cm^3 of diethyl ether, washing the precipitate with 2x3 cm^3 of diethyl ether, and drying under vacuum for 18 h (0.5 g, 50% yield). Anal. Found: C, 55.85; H, 10.72; N, 4.06; V, 14.67%. Calcd for $C_{16}H_{36}NVO_3 \cdot 0.1H_2O$: C, 55.99; H, 10.63; N, 4.08; V, 14.84%.

7) Anal. Found: C, 47.17; H, 8.50; N, 3.10; Ir, 13.62; V, 14.23%. Calcd for $C_{56}H_{120}N_3IrV_4O_{12}$: C, 47.25; H.8.50; N, 2.95; Ir, 13.50; V, 14.31%. IR (Nujol, 1000 - 700 cm^{-1}): 957 (m), 943 (m), 926 (m), 915 (sh), 891 (w), 855 (sh), 827 (s), 802 (s), 736 (m). ^{1}H NMR (CD_3CN, 360 MHz): δ 3.83 (br, 4), 3.18 (m, 24), 2.48 (br, 4), 1.63 (m, 24), 1.38 (m, 28), 0.97 (m, 36). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.5 MHz): 59.9 (s, 4), 59.3 (s, 12), 32.8 (s, 4), 24.4 (s, 12), 20.4 (s, 12), 13.9 (s, 12). ^{51}V NMR (CH_3CN, 78.9 MHz): δ -524.

8) The reflections were collected on a Nicolet P$\bar{1}$ diffractometer, and the structures were solved using (SHELXTL) "direct methods" techniques.

9) Crystals of compound **1** were obtained by dissolving the compound in *N*,*N*-dimethylformamide at 45°C, adding diethyl ether to the point of saturation, and cooling the mixture to ambient temperature. Single crystals of $[(n\text{-}C_4H_9)_4N]_2\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}$ (formula weight 1481.50) are at 20 ± 1 °C monoclinic, space group $C2/c$ with $a = 22.243(4)$, $b = 18.475(3)$, $c = 15.937(3)$ Å, $\beta = 94.58(2)°$, $V = 6528(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.51$ g·cm^{-3}. $R = 0.045$ and $R_w = 0.056$ for 3261 independent absorption-corrected reflections having $2\theta_{MoK\alpha} < 48.3°$ and $I > 3\sigma(I)$.

10) Crystals of compound **2** were obtained by adding diethyl ether to the reaction mixture without stirring to make a second layer and allowing the mixture to stand for 12 h. Single crystals of $[(n\text{-}C_4H_9)_4N]_3[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]$ (formula weight 1423.57) are at 20 ± 1 °C, orthorhombic, space group $Pna2_1$, with $a = 17.185(3)$, $b = 18.165(3)$, $c = 22.433(4)$ Å, $V = 7003(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.35$ g·cm^{-3}. $R = 0.049$ and $R_w = 0.055$ for 3254 independent absorption-corrected reflections having $2\theta_{MoK\alpha} < 48.3°$ and $I > 3\sigma(I)$.

11) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number is the number of individual measurements which are included in the averaged value.

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