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Synthesis and Crystal Structure of $[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]_2(\mathrm{Cr_2O_7})\cdot 8\mathrm{H_2O}$ ($\mathrm{Cp}^*=\eta^5\text{-}\mathrm{C_5Me_5}$). A Novel Two-Dimensional Hydrogen-Bonding Network

Joon T. Park,# Takanori Nishioka, Takayoshi Suzuki,* and Kiyoshi Isobe*
Institute for Molecular Science, Okazaki 444

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Synopsis. The title complex, prepared from a reaction of $[(\mathrm{IrCp^*Cl})_2(\mu\text{-Cl})_2]$ with $\mathrm{K_2CrO_4}$ in water, has been characterized via a single-crystal X-ray diffraction study. In the solid state the tri-μ-hydroxo-diiridium complex cations, the dichromates having the staggered conformation, and the water molecules of crystallization are entirely connected by hydrogen bonds forming a novel two-dimensional layer structure.

In previous papers,[1,2] we have reported the syntheses, structures, and reactivities of cubane-type organometallic oxometalates involving MCp^* ($\mathrm{M}=\mathrm{Rh^{III}}$, $\mathrm{Ir^{III}}$) group in the cubane framework. The reactions of $[(\mathrm{MCp^*Cl})_2(\mu\text{-Cl})_2]$ with $\mathrm{NaVO_3}$ and with $\mathrm{Na_2MoO_4}$ in water have yielded a quadruple cubane-type cluster, $[(\mathrm{MCp}^*)_4\mathrm{V_6O_{19}}]$[1] and a triple cubane-type one, $[(\mathrm{MCp}^*)_4\mathrm{Mo_4O_{16}}]$,[2] respectively. However, chemistry of polyoxochromates has not been well-established,[3,4] compared to that of polyoxovanadates, -molybdates, and -tungstates.[5] In order to synthesize a new type of oxochromate clusters and to develop our studies on the organometallic oxometalates, the reaction of $[(\mathrm{MCp^*Cl})_2(\mu\text{-Cl})_2]$ with $\mathrm{K_2CrO_4}$ has been performed, and the obtained product has been characterized via a single-crystal X-ray diffraction study.

Experimental

$[(\mathrm{MCp^*Cl})_2(\mu\text{-}\mathrm{Cl})_2)]$ ($\mathrm{M}=\mathrm{Rh}$ (**1**), Ir (**2**))[6] and $[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]\mathrm{OH}$ (**3**)[7] were prepared by the literature methods. Infrared spectra were obtained with a Hitachi 270-30 spectrophotometer by the Nujol mull method.

Preparation of $[(\mathrm{RhCp}^*)_2(\mu\text{-OH})_3]_2(\mathrm{Cr_2O_7})\cdot 8\mathrm{H_2O}$ (4): An aqueous solution (15 cm^3) of $\mathrm{K_2CrO_4}$ (8.44 g, 43.5 mmol) was added dropwise to an aqueous suspension (6 cm^3) of **1** (1.50 g, 2.43 mmol), and the reaction mixture was stirred for 18 h at room temperature. The resulting yellow precipitate was collected by filtration and dried in vacuo. Yield 1.45 g (84.4% based on Rh). Anal. Found: C, 33.84; H, 5.48%. Calcd for $\mathrm{C_{40}H_{82}Cr_2O_{21}Rh_4}$: C, 33.96; H, 5.84%.

Preparation of $[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]_2(\mathrm{Cr_2O_7})\cdot 8\mathrm{H_2O}$ (5): Compound **5** was prepared similarly by using an aqueous solution (15 cm^3) of $\mathrm{K_2CrO_4}$ (7.00 g, 36.0 mmol) and an aqueous suspension (5 cm^3) of **2** (1.00 g, 1.23 mmol). Yield 1.05 g (94.4% based on Ir). Anal. Found: C, 27.13; H, 4.75%. Calcd for $\mathrm{C_{40}H_{82}Cr_2Ir_4O_{21}}$: C, 27.11; H, 4.66%.

Crystal Structure Analysis. The rhodium compound, **4**, yielded red-orange thin plate crystals which are not suitable for X-ray analysis. The iridium compound, **5**, however, formed brownish yellow prismatic crystals on slow evaporation of an aqueous methanol solution at room temperature. A crystal (an approximate dimension of $0.7\times0.3\times0.1$ mm^3) of them was mounted on a glass fiber and used for data collection. Intensity data were collected at 23 °C with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) on a Rigaku automated four-circle diffractometer AFC-5. The θ–2θ scan technique was employed at a scan rate of 8° min^{-1} in θ and a scan width of $1.3+0.5\tan\theta/°$. A total of 16618 reflections with $2\theta\leq60°$ were measured, and the intensities were corrected for Lorentz-polarization factors. Absorption corrections were made by the Gauss numerical integration method.[8] Final lattice parameters were determined by least-squares treatment using the setting angles of 25 reflections in the range $25°<2\theta<30°$. Crystal data are FW=1771.95, triclinic, space group $P\,\bar{1}$, $a=14.701(2)$, $b=17.565(4)$, $c=10.717(2)$ Å, $\alpha=90.97(2)$, $\beta=94.64(1)$, $\gamma=85.85(2)°$, $V=2751.0(9)$ Å^3, $Z=2$, $D_\mathrm{x}=2.139$, $D_\mathrm{m}=2.13$ Mg m^{-3}, and $\mu(\mathrm{Mo}\,K\alpha)=10.09$ mm^{-1}.

The structure was solved by the heavy-atom method using the SHELXS-86 program.[9] Non-hydrogen atoms were located in subsequent Fourier syntheses and were refined anisotropically. All the H atoms were not included in the structure factor calculations. The function, $\Sigma w||F_\mathrm{o}|-|F_\mathrm{c}||^2$, was minimized with $w^{-1}=\sigma^2(|F_\mathrm{o}|)+(0.020|F_\mathrm{o}|)^2$ by the full-matrix least-squares method. Complex neutral-atom scattering factors were used.[10] Final R (R_w) value was 0.081 (0.096), and S(goodness of fit)=2.530 for 7953 reflections with $I>3.0\,\sigma(I)$.[11] The calculations were carried out using the Xtal 3.2 software[12] on a Fujitsu S-4/IX workstation.[13]

Results and Discussion

Formation of Dichromate. Treatment of a saturated aqueous solution of $\mathrm{K_2CrO_4}$ with a red aqueous suspension of **1** and with an orange one of **2** at room temperature formed yellow precipitates, **4** and **5**, respectively. Compounds **4** and **5** are soluble in methanol, but not in water, dichloromethane, or chloroform, and crystallize from an aqueous methanol solution as red-orange plates for **4** and brownish yellow prisms for **5**, respectively. The reaction with sodium chromate instead of the potassium salt gave the same result, suggesting that the product is independent on the cations of the chromates. The infrared spectra of **4** and **5** are very similar to each other, indicating that both complexes are isomorphous, and exhibit strong bands around 940 and 765 cm^{-1}. These characteristic bands do not correspond to any absorption of $\mathrm{CrO_4^{2-}}$, but are assigned to $\nu_\mathrm{a}(\mathrm{O_3^TCr})$ and $\nu_\mathrm{a}(\mathrm{Cr_2O^B})$ of $\mathrm{Cr_2O_7^{2-}}$,[14] respectively. The crystal structure of **5** was confirmed by

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#On leave from Department of Chemistry, KAIST, Taejon 305-701, Korea.

an X-ray diffraction study, as illustrated in Fig. 1. The crystal consists of two crystallographically independent $[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]^+$, a dichromate, and eight molecules of water of crystallization.

While a reaction of $[(\mathrm{MCp}^*\mathrm{Cl})_2(\mu\text{-Cl})_2]$ with $\mathrm{NaVO_3}$[1] or $\mathrm{Na_2MoO_4}$[2] in water yielded an organometallic oxometalate cluster having a cubane-type framework with the $\mathrm{V_6O_{19}}$ or $\mathrm{Mo_4O_{16}}$ core, the reaction with $\mathrm{CrO_4^{2-}}$ did not give an oxochromate cluster with the MCp^* group, but gave the dichromate salt.

$$2[(\mathrm{MCp}^*\mathrm{Cl})_2(\mu\text{-Cl})_2] + 2\mathrm{K_2CrO_4} + 5\mathrm{H_2O} \longrightarrow [(\mathrm{MCp}^*)_2(\mu\text{-OH})_3]_2(\mathrm{Cr_2O_7}) + 4\mathrm{KCl} + 4\mathrm{HCl}$$

The condensation reaction from $\mathrm{CrO_4^{2-}}$ to $\mathrm{Cr_2O_7^{2-}}$ is attributed to the acidity of the reaction mixture due to hydrolysis of $[(\mathrm{MCp}^*\mathrm{Cl})_2(\mu\text{-Cl})_2]$.

$$[(\mathrm{MCp}^*\mathrm{Cl})_2(\mu\text{-Cl})_2] + 4\mathrm{H_2O} \longrightarrow [(\mathrm{MCp}^*)_2(\mu\text{-OH})_3]\mathrm{OH} + 4\mathrm{HCl}$$

In fact, the pH values of aqueous solutions of **1** (7.1×10^{-5} mol dm^{-3}) and **2** (5.1×10^{-5} mol dm^{-3}) are 5.2 and 3.9, respectively. Since the chromate exists as an equilibrium mixture of $\mathrm{HCrO_4^-}$ and $\mathrm{Cr_2O_7^{2-}}$ in aqueous solutions of pH 2—6,[16]

$$2\mathrm{HCrO_4}^- \rightleftharpoons \mathrm{Cr_2O_7}^{2-} + \mathrm{H_2O}$$

it is expected that the dichromate salt having a low solubility was precipitated from the reaction mixture. Compound **5** was also obtained directly from a reaction of aqueous solutions of **3** (the pH value of an aqueous solution of **3** is 9.5 at 1.1×10^{-4} mol dm^{-3}) and $\mathrm{K_2Cr_2O_7}$ in 64% yield.

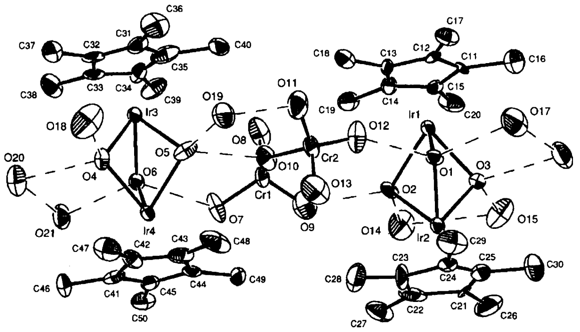

Fig. 1. ORTEP[15] drawing of **5** with atom numbering scheme. Bond lengths (l/Å) and angles (ϕ/°) are Ir–O = 2.09(2)—2.15(2), Ir–C$^\mathrm{R}$ = 2.09(3)—2.16(3), Cr–O$^\mathrm{T}$ = 1.56(2)—1.62(2), Cr–O$^\mathrm{B}$ = 1.76(2) and 1.80(2), O–Ir–O = 70.5(6)—75.7(6), Ir–O–Ir = 91.8(7)—94.1(6), O$^\mathrm{T}$–Cr–O$^\mathrm{T}$ = 108(1)—113(1), O$^\mathrm{T}$–Cr–O$^\mathrm{B}$ = 106.8(9)—112(1), and Cr–O$^\mathrm{B}$–Cr = 136(1), where C$^\mathrm{R}$, O, O$^\mathrm{T}$, and O$^\mathrm{B}$ denote ring carbon of Cp*, hydroxy oxygen bridged two iridium atoms, terminal oxygen of dichromate, and bridging oxygen of dichromate, respectively.

$$2[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]\mathrm{OH} + \mathrm{K_2Cr_2O_7} \longrightarrow [(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]_2(\mathrm{Cr_2O_7}) + 2\mathrm{KOH}$$

Furthermore, acidification of a mixture of aqueous solutions of **3** and $\mathrm{K_2CrO_4}$ by addition of nitric acid caused precipitation of **5** in 64% yield.

$$2[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]\mathrm{OH} + \mathrm{K_2CrO_4} + 2\mathrm{H}^+ \longrightarrow [(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3]_2(\mathrm{Cr_2O_7}) + 2\mathrm{K}^+ + 2\mathrm{H_2O}$$

However, without addition of any acid a precipitate of an uncharacterized product, whose infrared spectrum was apparently different from the one of **5**, was formed in a relatively low yield. These results described above support that the condensation reaction of $\mathrm{CrO_4^{2-}}$ to $\mathrm{Cr_2O_7^{2-}}$ has occurred due to the acidity of reaction mixture.

Crystal Structure of 5: A Novel Two-Dimensional Hydrogen-Bonding Network. The X-ray crystal structure analysis of $[(\mathrm{IrCp}^*)_2(\mu\text{-OH})_3](\mathrm{CH_3CO_2})\cdot14\mathrm{H_2O}$ was reported previously.[7] The structure of the tri-μ-hydroxodiiridium moiety in the acetate salt is very similar to that of **5**. The crystal structure of **5**, however, has two interesting features. One is the structure of the dichromate, which has a nearly staggered conformation about the terminal $\mathrm{CrO_3^T}$ groups. When the dichromate in **5** was viewed from the Cr···Cr direction, the torsion angles of O$^\mathrm{T}$–Cr···Cr–O$^\mathrm{T}$ are 44(1), 46(1), and 50(1)°, the angle being 0° and 60° for the ideal eclipsed and staggered conformations, respectively. Although a large number of dichromate salts with different cations have been analyzed by X-rays,[4,17,18] almost all the dichromates have an eclipsed conformation, in which the torsion angles are less than 21°. Recent ab initio SCF calculation for the isolated $\mathrm{Cr_2O_7^{2-}}$ has also given an energetic minimum for the nearly eclipsed conformation with the torsion angle of 7—9°.[19] A few exceptions of the staggered conformations for $\mathrm{Cr_2O_7^{2-}}$ have been reported,[18] and in all of them the dichromates are bound to the cations through the hydrogen bonds in the crystal. In **5**, all of the oxygen atoms in the dichromate are hydrogen-bonded either to the diiridium complex cations or to the water molecules of crystallization (vide infra). Therefore, the conformational fixation of the staggered form in **5**, which is less stable than the eclipsed one in the isolated state, is due to a restriction by the hydrogen bonds.

The other remarkable feature in the crystal structure of **5** is the hydrogen-bonding network. As illustrated in Fig. 2 and tabulated in Table 1, all the oxygen atoms of the tri-μ-hydroxodiiridium complexes, the dichromates, and water molecules of crystallization are involved in hydrogen bonds forming a novel two dimensional network. The hydrogen-bonding networks in the crystal are separated by hydrophobic layers of Cp* ligands as shown in Fig. 3. The layered packing of complex **5** in the solid state may be attributed to the amphiphilic

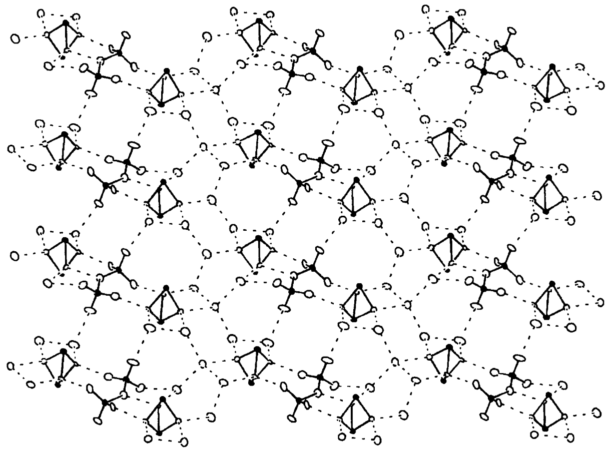

Fig. 2. A hydrogen-bonding network in **5**. Atoms with shadow show Ir or Cr, and C atoms are omitted for clarity.

Table 1. Hydrogen-Bonding Distances (l/Å) in **5**

O(1)···O(12)	2.75(2)	O(1)···O(17)	2.89(3)
O(2)···O(9)	2.74(3)	O(2)···O(14)	2.81(3)
O(3)···O(15)	2.87(2)	O(3)···O(16)	2.83(3)
O(4)···O(18)	2.78(3)	O(4)···O(20)	2.80(3)
O(5)···O(10)	2.83(2)	O(5)···O(19)	2.82(3)
O(6)···O(7)	2.82(2)	O(6)···O(21)	2.75(2)
O(11)···O(19)	2.87(3)	O(14)···O(15)	2.90(3)
O(16)···O(17)	2.81(3)	O(20)···O(21)	2.87(3)
O(8)$^{\rm i}$···O(21)	2.93(3)	O(13)$^{\rm ii}$···O(17)	2.89(3)
O(14)···O(18)$^{\rm iii}$	2.82(3)	O(15)$^{\rm iv}$···O(16)	2.76(3)
O(15)···O(19)$^{\rm iii}$	2.78(3)	O(18)$^{\rm v}$···O(20)	2.74(3)

Symmetry codes: (i) $-x$, $1-y$, $1-z$; (ii) $-x$, $2-y$, $2-z$; (iii) $1+x$, y, z; (iv) $-1-x$, $2-y$, $2-z$; (v) $1-x$, $1-y$, $1-z$.

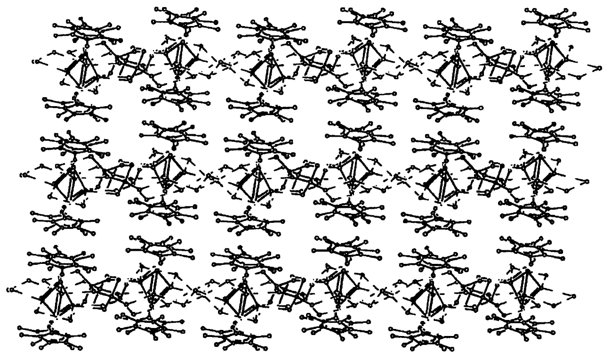

Fig. 3. Layer structure in **5**.

nature of $[(MCp^*)_2(\mu\text{-OH})_3]^+$. The hydrogen bonds between a μ-hydroxo ligand and a counter anion or a water molecule may also exist in the related complexes, $[(RhCp^*)_2(\mu\text{-OH})_3]OH\cdot 11H_2O$ and $[(IrCp^*)_2(\mu\text{-OH})_3](CH_3CO_2)\cdot 14H_2O$, although the detailed structure of the hydrogen bonds is not described.[7] The novel two-dimensional hydrogen-bonding network and the layer structure in **5** will be interesting for the design of donor–acceptor systems and proton-transfer in the solid state.

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