ramidal or the trigonal-bipyramidal geometry.[42] Thus, reaction of Hppy with any Ir(III) starting material containing simple monodentate ligands might lead to modification of the stereochemistry favored by trans-directing effects of Ir–C bonds via formation of a common 5-coordinate monomer and then a bridged dimer. The success of $Ir(acac)_3$ in promoting formation of *fac* tris complexes in reaction with Hppy and related ligands may arise from inhibition of formation of this common 5-coordinate intermediate as a result of the bidentate nature of $acac^-$.

The luminescence lifetime of each of the *fac*-$Ir(R\text{-}ppy)_3$ complexes (Table I) is approximately 2–3 μs in nitrogen-saturated acetonitrile at room temperature. The similarities in the lifetimes and emission energies of all of the *fac*-$Ir(R\text{-}ppy)_3$ complexes indicate that they, like $Ir(ppy)_3$,[22,23] each emit from an MLCT excited state. Each complex is characterized by a reversible oxidative wave in cyclic voltammetry in acetonitrile (+0.55 to +1.08 V vs SCE), which indicates the relative ease of oxidation of Ir(III) to Ir(IV) in these species. The position of the oxidative wave follows a pattern in which more positive values are found for complexes of ligands bearing electron-withdrawing substituents and less positive values result from ligands with electron-donating substituents (see Table I).

We are presently characterizing excited-state electron-transfer reactions of these *fac* tris-ortho-metalated complexes of Ir(III). These studies are intended to fully characterize the excited-state reducing power of *fac* tris-ortho-metalated Ir(III) complexes.

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Sulfur-Bridged Incomplete Cubane-Type Mixed-Metal Cluster Compounds of Molybdenum(IV) and Tungsten(IV). Syntheses, Characterization, and X-ray Structures of $[Mo_2WS_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ and $[MoW_2S_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$

Molybdenum sulfur compounds have attracted much attention, and a large number of sulfur-bridged molybdenum compounds have appeared.[1] Among them, many molybdenum compounds with incomplete cubane-type Mo_3S_4 cores[2] have been reported and some tungsten analogues with W_3S_4 cores[3] also studied.

We now report the syntheses, characterization, and X-ray structures of incomplete cubane-type molybdenum(IV)–tungsten(IV) mixed-metal aqua cluster compounds $[Mo_2WS_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ (Mo_2W') and $[MoW_2S_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ (MoW_2'), which complete a series of clusters having the following cores:

$$Mo_3S_4 \qquad Mo_2WS_4 \qquad MoW_2S_4 \qquad W_3S_4$$

Only a few triangular molybdenum-tungsten mixed-metal compounds are known;[4-7] however, no reports on mixed-metal compounds with any sulfur bridge(s) have appeared so far.[8] Once aqua ions are prepared, the derivatives are prepared easily by substitution reactions.[9] The aqua ions $[Mo_3S_4(H_2O)_9]^{4+}$ (Mo_3)[2g,h] and $[W_3S_4(H_2O)_9]^{4+}$ (W_3)[3a,b,g] are well-known, and their X-ray structures have been determined.[2h,3b]

$(NH_4)_2WS_4$[10] (1.00 g, 2.87 mmol) and bis(μ-sulfido)(cysteinato)molybdenum(V) dimer $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$[11] (1.85 g, 2.87 mmol) were dissolved in water (50 mL), and small portions (ca. 2 mL each) of $NaBH_4$ (3.0 g in 20 mL H_2O) and 6 M HCl (20 mL) were added alternately to the solution. Then, an additional amount (80 mL) of 6 M HCl was added to the solution, which was heated at above 90 °C for 5 h with introduction of an air stream. During heating, 1 M HCl was added occasionally to keep the volume of the solution constant (ca. 150 mL). The solution was cooled to room temperature and filtered by suction. The filtrate was subjected to Sephadex G-15 column chromatography (4.0 cm × 85 cm, 1 M HCl). The sixth ($MoW_2(aq)^{4+}$ (MoW_2); gray) and seventh bands[12,13] ($Mo_2W(aq)^{4+}$ (Mo_2W); green) were concentrated by use of a cation exchanger, Dowex 50W-X2 (2 M HCl). Sephadex G-15 column chromatography (2.0 cm × 150 cm, 1 M HCl) was applied again for purification. This concentration–purification process is repeated again; yields of Mo_2W and MoW_2 (in solution) are 17% and 3%, respectively. The crystalline compounds[14] Mo_2W' (green plates) and MoW_2'

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(12) Other bands: 1st, $Mo_4S_4(aq)^{5+}$ (green); 2nd, $Mo_3O_2S_2(aq)^{4+}$ (gray); 3rd, unknown (greenish yellow); 4th, unknown (yellowish green); 5th, $Mo_3OS_3(aq)^{4+}$ (green); 8th, $Mo_3S_4(aq)^{4+}$ (green).

(13) The mixture of Mo_3 and W_3 clusters is clearly separated into two bands by Sephadex G-15 column chromatography, while the Mo_2W (or MoW_2) cluster is not separated by the method, which supports the existence of the mixed-metal clusters.

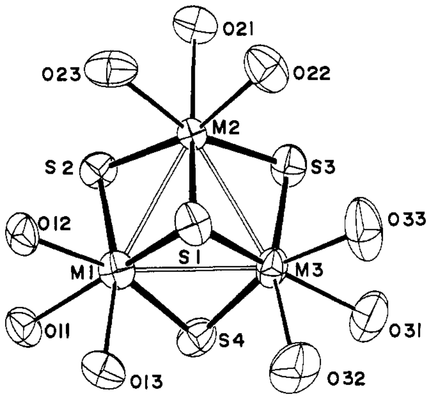

Figure 1. ORTEP view of $[Mo_2WS_4(H_2O)_9]^{4+}$ (Mo_2W').

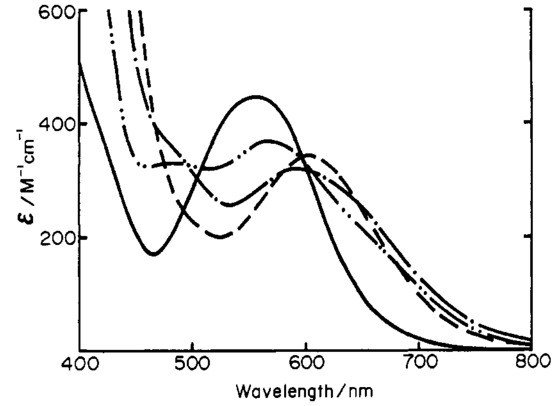

Figure 2. Electronic absorption spectra in 2 M HPTS: —, $[W_3S_4(H_2O)_9]^{4+}$ (W_3); -··-, $[MoW_2S_4(H_2O)_9]^{4+}$ (MoW_2); -·-, $[Mo_2WS_4(H_2O)_9]^{4+}$ (Mo_2W); ---, $[Mo_3S_4(H_2O)_9]^{4+}$ (Mo_3).

(gray plates) were prepared by a procedure similar to that for the syntheses of $[Mo_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4{\cdot}9H_2O$ (Mo_3')[2h] and $[W_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4{\cdot}7H_2O$ (W_3').[3b] The mixed-metal clusters are stable: the absorption spectra of the clusters in 2 M HCl or freshly prepared 2 M HPTS solution do not change for several days in the air.

X-ray structure analyses[15] of Mo_2W' and MoW_2' revealed the existence of incomplete cubane-type Mo_2W $(\mu_3\text{-}S)(\mu\text{-}S)_3$ (Figure 1) and MoW_2 $(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores, respectively. The clusters Mo_3', Mo_2W', MoW_2', and W_3' are isomorphous. Molybdenum and tungsten atoms in both crystals are statistically disordered: the use of a weighted ((2Mo + W)/3) value of the atomic scattering factors of Mo and W gave reasonable temperature factors for the three metal atoms in Mo_2W', and another weighted value ((Mo + 2W)/3) is used satisfactorily for MoW_2'. Elemental analyses and the agreement between calculated and observed densities for both crystals also support the formulas. The averaged W–W distance in W_3' (2.724 [17] Å) is very slightly shorter than the averaged Mo–Mo distance in Mo_3' (2.735 [8] Å), and the averaged metal–metal distances in Mo_2W' (2.728 [6] Å) and MoW_2' (2.723 [6] Å) lie between them, though this may not be really statistically significant.

Table I. Binding Energies (eV) of $[Mo_{3-n}W_nS_4(H_2O)_9]^{4+}$ (n = 0–3)[a]

	Mo $3d_{3/2}$	Mo $3d_{5/2}$	W $4f_{5/2}$	W $4f_{7/2}$
Mo_3	233.6	230.7		
Mo_2W	233.5	230.6	36.0	34.0
MoW_2	233.4	230.5	35.9	33.8
W_3			35.9	33.8

[a] C_{1s} = 285.0 eV.

Electronic spectra of Mo_2W (λ_{max} = 490_{sh} nm, ϵ = 298 M^{-1} cm^{-1}; λ_{max} = 595 nm, ϵ = 322 M^{-1} cm^{-1}) and MoW_2 (490 nm, ϵ = 320; 568 nm, ϵ = 363) in the visible region are shown in Figure 2 together with those of Mo_3 (602 nm, ϵ = 351) and W_3 (557 nm, ϵ = 446).[16] No peaks were observed in the near-infrared region for all the four clusters. In the mixed-metal aqua ions, Mo_2W and MoW_2, fairly large splittings of the absorption peaks are observed. The longer peak wavelength positions of the four aqua ions shift to longer wavelengths when the tungsten atom is replaced by molybdenum. It should be noted, however, that the peak at shorter wavelength for MoW_2 and the shoulder for Mo_2W appear even at the shorter wavelength side of the peak of W_3.

Binding energies of molybdenum ($3d_{3/2}$ and $3d_{5/2}$) and tungsten ($4f_{5/2}$ and $4f_{7/2}$) are obtained from XPS spectra of Mo_3', Mo_2W', MoW_2', and W_3' (Table I). The binding energies of Mo in Mo_3' change little on the replacement of Mo with W, and those of W in W_3' change little on the replacement of W with Mo, also, which is in contrast to the case of $[M_3(\mu\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ (M_3 = $Mo_{3-n}W_n$ (n = 0–3)), where the binding energies of Mo in the Mo_3 species decrease on the replacement of Mo with W and those of W in the W_3 species increase on the replacement of W with Mo.[6b] The former have only bridging S atoms and terminal H_2O ligands whereas the latter have O, H_2O, and μ-CH_3COO groups, and no direct comparison can be made. However, the difference between the binding energy changes in the two types of clusters could be attributed to the softness of sulfur compared to oxygen: sulfur bridges work as a buffer for the electron density changes on the Mo and W atoms.

Other properties are under investigation.[17]

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Supplementary Material Available: Listings of crystallographic details, atomic coordinates, thermal parameters, and bond distances and angles and Figure 3, showing far-IR spectra (17 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(14) Anal. Found (calcd) for Mo_2W': Mo, 12.3 (12.68); W, 12.5 (12.15); C, 22.47 (22.22); H, 4.22 (4.26). Found (calcd) for MoW_2': Mo, 5.7 (5.99); W, 23.2 (22.96); C, 21.38 (21.00); H, 3.35 (4.02).

(15) Crystal data: Mo_2W', triclinic system, space group $P\bar{1}$, a = 15.317 (4) Å, b = 16.693 (4) Å, c = 12.055 (5) Å, α = 95.48 (3)°, β = 108.94 (3)°, γ = 102.44 (2)°, V = 2801.0 (17) Å^3, Z = 2, D_c = 1.794 g cm^{-3}, D_m = 1.79 g cm^{-3}, Mo Kα, $2\theta_{max}$ = 50°, R = 0.0599 for 5416 reflections ($|F_o| \geq 6\sigma|F_o|$); MoW_2', triclinic system, space group $P\bar{1}$, a = 15.361 (5) Å, b = 16.721 (4) Å, c = 12.062 (4) Å, α = 95.57 (2)°, β = 108.93 (2)°, γ = 102.35 (3)°, V = 2816.0 (15) Å^3, Z = 2, D_c = 1.888 g cm^{-3}, D_m = 1.89 g cm^{-3}, Mo Kα, $2\theta_{max}$ = 50°, R = 0.0765 for 4382 reflections ($|F_o| \geq 5\sigma|F_o|$). The structures were solved by direct methods (SHELXS) and refined by least squares. Details will be described elsewhere.

(16) The electronic spectrum of the Mo_2W cluster is clearly different from that of the mixture of 66% Mo_3 and 33% W_3 clusters. The same is true for MoW_2.

(17) For example, the peak positions of the far-IR spectra of the four aqua ions in the 550–400-cm^{-1} region shift to lower wavenumbers when the molybdenum atom is replaced by tungsten (Figure 3 (supplementary material)).