

products that are available from thermochemical data alone. The details of the computational procedure will be given elsewhere, but the essence is as follows. Starting with a product of ordinary partition functions, as in (1), we use the steepest descent procedure¹³ to determine the density of states $\rho(E)$ for the particular dissociation channel. Then a generalized partition function is computed as

$$Q = \int_0^{\infty} \rho(E) f(E) dE \quad (2)$$

Here $f(E)$ is the energy deposition function. The branching fraction q is given by $q = Q/N$. If $f(E) = \exp(-\beta E)$ then (2) leads back to (1). If we specify both $\langle E \rangle$ and, say, $\langle E^2 \rangle$ then $f(E) = \exp(-\beta E - \gamma E^2)$, where the value of γ is such so as to reproduce the value of $\langle E^2 \rangle$, etc.

To achieve a distribution in energy that is wider than thermal we have used $f(E) = \exp(-\alpha E^{1/2} - \beta E - \gamma E^2)$, which is the distribution of maximal entropy subject to given values for $\langle E^{1/2} \rangle$, $\langle E \rangle$, and $\langle E^2 \rangle$. For the present results shown in Figure 1, $\langle E^{1/2} \rangle$, $\langle E \rangle$, and $\langle E^2 \rangle^{1/2}$ have the values 4.3, 5.7, and 8.5 eV, respectively. For the narrower, thermallike distribution the corresponding values are 4.12, 4.3, and 4.6 eV.

The computational results for C_2H_6 and other systems suggest that there are two primary reasons for the differences between the multiphoton ionization^{1,2} and the electron impact mass spectrum: (i) Energy input into the secondary ions is absent in the latter.⁹ That, however, can also be achieved in the former using short (picosecond) laser pulses. (ii) The energy distribution of the parent ion produced by electron impact is wider. That is consistent with the very wide energy distributions assumed in the QET-type computations¹⁴ and indicated by threshold-law considerations.^{15,16} The narrower laser-pumped distributions makes them more useful for analytical applications of mass spectrometry.

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Preparation and Structures of Novel Di- and Trinuclear Clusters of Iridium(II) without Carbonyl Ligands

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Despite rapid development of the chemistry of metal-metal-bonded complexes¹ there are still large untouched areas. One of these underinvestigated fields is that of iridium cluster compounds with ligands other than carbon monoxide.²

We wish to report here the synthesis and structure of an Ir(II) complex, $Ir_2(\mu^2-I)_2I_2(COD)_2$ (**1**) (COD = 1,5-cyclooctadiene)

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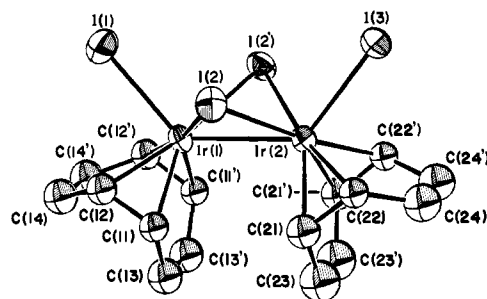


Figure 1. ORTEP view of $[Ir(COD)I_2]_2$. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

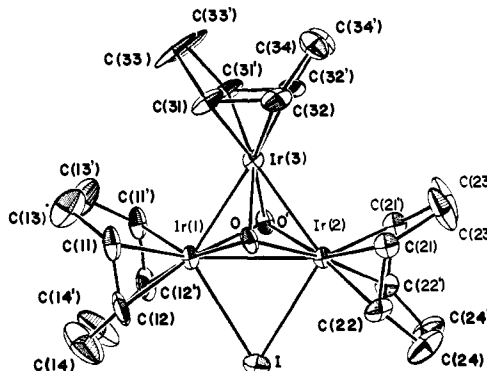


Figure 2. ORTEP view of $Ir_3(\mu^3-O)_2(\mu^2-I)(COD)_3$.

which we expect to be a starting material for the synthesis of cluster compounds. Reaction of **1** with silver acetate afforded, among other products, the trinuclear cluster $Ir_3(\mu^3-O)_2(\mu^2-I)(COD)_3$ (**2**). It is a bioxo-capped trimer of a configuration unprecedented among late transition metals.

Reaction of equimolar amounts of $Ir_2(OMe)_2(COD)_2^3$ and I_2 in CH_2Cl_2 for 30 min, followed by partial evaporation of the solvent and precipitation with hexane, afforded the dark red crystalline compound **1**. An ORTEP drawing is given in Figure 1.⁴ The dimeric molecule has crystallographically imposed C_{2v} symmetry and is composed of two square pyramids sharing an edge. The Ir-Ir distance is 2.914 (1) Å and indicative of bonding interaction between the two metal atoms. The fact that there is an 18-electron count for each metal center if an Ir-Ir bond is assumed supports this.

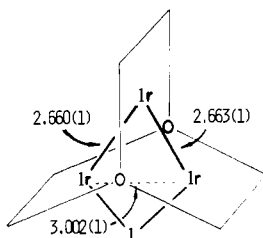
Reaction of **1** with $Ag(O_2CCH_3)$ in CH_2Cl_2 leads instantaneously to a voluminous precipitate of AgI. The reaction mixture, after filtration, was investigated by TLC. On silica gel we find that a large fraction of the product mixture is irreversibly adsorbed at the starting point. Of the moving zones the one corresponding to the trimeric cluster **2** is the most abundant fraction. It was isolated by column chromatography (silica gel, CH_2Cl_2) reproducibly in yields of ca. 5%. While we are not suggesting, in light of the low yield, that this is a good synthesis for **2**, we report it here because the cluster is a surprising molecule for Ir to form. The synthetic procedures are presently under revision. The cluster compound is depicted in Figure 2.⁵ It consists of an isosceles triangle of Ir atoms, bicapped by μ^3-O atoms and containing one μ^2-I bridge. This leads to a square-prismatic coordination polyhedron for Ir1 and Ir2 whereas Ir3 exhibits a square-planar coordination geometry. The trimer is then composed of the three-coordination polyhedra sharing the O...O edge.

Bioxo-capped trinuclear clusters are unprecedented among the late transition metals but are an important structural type for

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(4) Dark red crystals from CH_2Cl_2 /hexane-acetone; orthorhombic $Pnma$; $a = 16.248$ (9) Å, $b = 10.827$ (10) Å, $c = 11.739$ (9) Å; $Z = 4$; $R = 0.032$, $R_w = 0.043$.

(5) Dark red crystals from CH_2Cl_2 /hexane-acetone; monoclinic $C2/c$; $a = 22.205$ (3) Å, $b = 11.967$ (2) Å, $c = 19.042$ (4) Å; $\beta = 99.09$ (2)°; $Z = 8$; $R = 0.046$, $R_w = 0.063$.



group 5 and 6 elements with d^2 configuration.⁶ The bonding properties of the latter are well understood in terms of a MO description. Despite the structural similarities, the electronic properties of **2** are distinctly different and the MO description of the group 5 and 6 trimers is not applicable to **2**.

Assignment of oxidation states II to Ir1 and Ir2 and I to Ir3 (consistent with the preferred coordination geometries of the respective oxidation states)⁷ leads to an 18-electron count for each of the three Ir centers if a bonding interaction is assumed to take place between Ir1 and Ir3 as well as Ir2 and Ir3 but not between Ir1 and Ir2. This view is consistent with the observed bond distances of 3.002 (1), 2.660 (1), 2.663 (1) Å for Ir1–Ir2, Ir1–Ir3, and Ir2–Ir3, respectively.

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Transient Circular Dichroism of the Luminescent State of Ru(bpy)₃²⁺

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We have recently developed a new technique capable of measuring transient circular dichroism (CD) spectra on a nano-second time scale.^{1,2} In this report we describe the application of this technique to the measurement of the CD spectrum of the excited-state absorption of (Δ) -Ru(bpy)₃²⁺. While CD spectra of a few very long-lived triplet excited states of chiral organic molecules have been measured with modifications of standard steady-state photoelastic modulation methods,³⁻⁵ this is the first report of a time-resolved excited-state CD spectrum.

CD spectra have been useful for assigning ground-state spectral transitions in Ru(bpy)₃²⁺.^{6,7} The excited-state spectrum of Ru(bpy)₃²⁺ has not been completely assigned.⁸⁻¹⁰ We have

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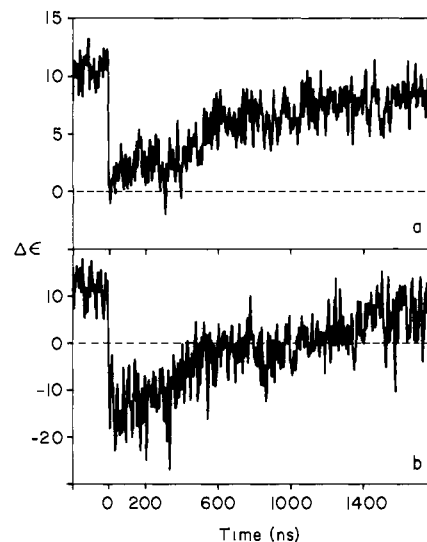


Figure 1. Time-resolved CD signal of Ru(bpy)₃²⁺ in H₂O at 20 °C excited with a 7-ns, 355-nm pulse from a Nd:YAG laser: (a) signal at 420 nm, note a positive CD before the laser fires and subsequent disappearance upon excitation; (b) signal at 315 nm, note the initial positive ground-state CD and subsequent negative CD of the excited state. The kinetics at both wavelengths are consistent with the previously reported lifetime of the luminescent state.¹¹

measured the CD spectrum of this state to address issues concerning the nature of this state. This state is amenable to CD spectroscopy as the lifetime is approximately 640 ns at 20 °C in water¹¹ and the quantum yields for racemization and decomposition are low.^{12,13}

The transient CD technique used here has been described previously.^{1,2} CD is determined by measuring the change in eccentricity of an elliptically polarized probe beam produced by passing linearly polarized light from a xenon flash lamp through a strained, fused quartz plate. A solution of Ru(bpy)₃²⁺ in water is excited with a 355-nm, 7-ns light pulse from a Nd:YAG laser. The sample, resolved in the manner described by Dwyer and Gyarfas,¹⁴ is flowed through a 2-mm path-length cell with strain-free quartz windows.

The ground-state circular dichroism of metal tris(bipyridyls) has been studied in detail.^{15,16} Qualitatively, for ligand-centered transitions the magnitude of the CD can be explained in terms of the degree of coupling between the transition moments on the different ligands. For example, the coupled interligand transition of ground-state M(diimine)₃, centered near 300 nm exhibits a large CD ($\Delta\epsilon > 100$).^{16,17} For this transition in Co(bpy)₂(NO₂)₂³⁺ $\Delta\epsilon \approx 20$,¹⁷ and in Co(bpy)(ethylenediamine)₂³⁺ $\Delta\epsilon \approx 10$.¹⁸ Hence for the absorption of Ru(bpy)₃²⁺ a very small CD would be expected ($\Delta\epsilon \approx 10$) for a $\pi^*\pi^*$ transition localized on a single bipyridyl ligand, while a larger CD would be expected from a transition coupled between two or more ligands.

Figure 1 shows representative CD signals as a function of time. At 420 nm (Figure 1a) there is a positive CD signal before the laser fires (ground-state signal) and subsequent disappearance of the signal upon photolysis (complete ground-state depletion). At 315 nm (Figure 1b) there is a positive CD in the ground state and then a negative CD in the excited state. The lifetime of the signal is the same within our experimental resolution as that previously reported for the luminescence (640 ns).¹¹

Figure 2a shows the ground-state CD of Ru(bpy)₃²⁺ from 310 to 480 nm obtained by averaging the signal for 50 ns before photolysis for 64 averages. This is in excellent agreement with

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