

guanine bases and is quite selective in binding to the purines.

Because water is a reasonable nucleophile it has been presumed that *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] in vivo first undergoes aquation and then the aquated species react with the nuclear DNA.<sup>34</sup> The aquation has been presumed to occur in the intracellular fluid after transport through the membrane of the *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] has taken place. On the basis of the poor selectivity exhibited by the *cis* and *trans* aquo species, it would appear that a direct bimolecular displacement of chloride or some even more strongly bound carrier ligand would be necessary to have the high selectivity that has been observed.

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**Supplementary Material Available:** Raman spectra, 3 pages. Ordering information is given on any current masthead page.

## References and Notes

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## Communications to the Editor

### Preparation and Crystal Structure of Ir<sub>7</sub>(CO)<sub>12</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>8</sub>H<sub>11</sub>)(C<sub>8</sub>H<sub>10</sub>), a Heptanuclear Iridium Cluster Showing Three Stages of Cyclooctadiene Coordination and Dehydrogenation

Sir:

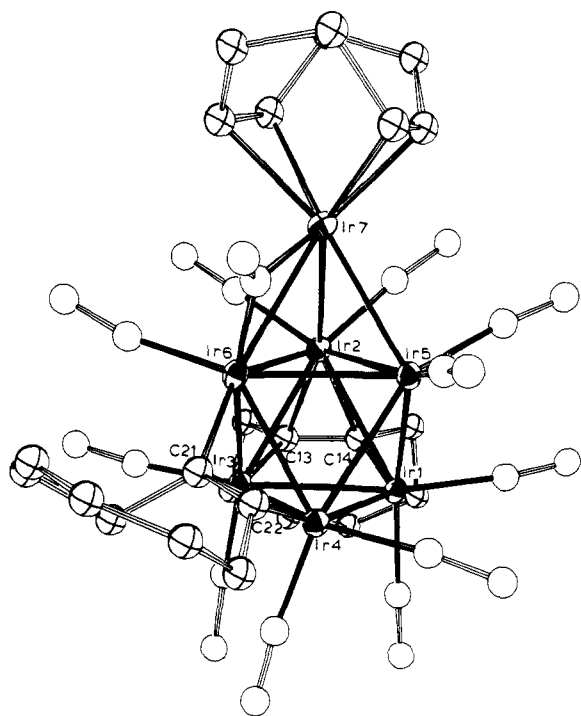
Recent interest in the preparation and properties of large metal cluster compounds<sup>1</sup> has resulted in the structural characterization of large clusters involving cobalt,<sup>2</sup> nickel,<sup>3,4</sup> ruthenium,<sup>5</sup> rhodium,<sup>6,7</sup> osmium,<sup>8,9</sup> and platinum,<sup>10</sup> but the corresponding chemistry of iridium is underdeveloped. The hexanuclear compounds Ir<sub>6</sub>(CO)<sub>15</sub><sup>2-</sup> and Ir<sub>6</sub>(CO)<sub>16</sub> are moderately well characterized by infrared and powder x-ray comparison with the known cobalt and rhodium compounds, but Ir<sub>8</sub>(CO)<sub>20</sub><sup>2-</sup> and Ir<sub>8</sub>(CO)<sub>22</sub><sup>2-</sup> have been formulated solely on the basis of elemental analyses.<sup>11</sup> We wish to report the preparation and first x-ray structural characterization of a large iridium cluster, Ir<sub>7</sub>(CO)<sub>12</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>8</sub>H<sub>11</sub>)(C<sub>8</sub>H<sub>10</sub>). The compound also is a rare example of a large cluster with hydrocarbon ligands. Previous examples include the arene derivatives Ru<sub>6</sub>(CO)<sub>14</sub>(arene)C,<sup>12</sup> of which the mesitylene complex has been structurally characterized,<sup>13</sup> and the compounds formulated as Rh<sub>6</sub>(CO)<sub>14</sub>(diene),<sup>14</sup> in which, for example, diene = 1,5-cyclooctadiene. The title compound contains not only coordinated cyclooctadiene, but also singly and doubly dehydrogenated cyclooctadiene moieties.

The reaction of Ir<sub>4</sub>(CO)<sub>12</sub> with 1,5-cyclooctadiene in refluxing chlorobenzene (18 h) provided a complex mixture of products.<sup>15</sup> Column chromatography of the mixture (Florisil/pentane) developed a green fraction, which after further purification by TLC (silica gel/pentane) afforded a green-

black crystalline solid (yield ~3%).<sup>16</sup> The field desorption mass spectrum (*m/e* 2008 (<sup>193</sup>Ir, M<sup>+</sup>)<sup>17</sup> and <sup>1</sup>H NMR data<sup>18</sup> obtained for this compound are consistent with the formulation Ir<sub>7</sub>(CO)<sub>12</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>8</sub>H<sub>11</sub>)(C<sub>8</sub>H<sub>10</sub>). A single-crystal x-ray diffraction study was undertaken to determine the geometry of the metal framework together with the binding modes of the organic ligands.<sup>19</sup>

As shown in Figure 1, the seven iridium atoms adopt a capped octahedral geometry with Ir(7) above the Ir(2)-Ir(5)-Ir(6) face. Eleven of the twelve carbonyl ligands are bound terminally to the six metal atoms of the octahedral fragment, two per metal except for Ir(6), which has one terminal carbonyl and shares the twelfth carbonyl with Ir(7). In addition to the bridging carbonyl, the apical iridium atom coordinates a normal, chelating 1,5-cyclooctadiene ligand. Shown at the lower left of Figure 1 is a cyclooctadiene ligand missing one olefinic proton; the bridging vinyl moiety is  $\pi$  bonded to Ir(4) and  $\sigma$  bonded to Ir(6). The Ir(6)-C(21)  $\sigma$ -bond length is 2.02 (3) Å, the distances in the  $\pi$  bond are Ir(4)-C(21) = 2.18 (3) Å and Ir(4)-C(22) = 2.29 (4) Å, and the C(21)-C(22) bond length is 1.51 (5) Å. Located beneath the Ir(1)-Ir(2)-Ir(3) face of the cluster in the center background of the view is the acetylenic portion of a cycloocta-1-en-5-yne ligand, coordinated as a [ $2\sigma + \pi$ ] four-electron donor. The Ir(2)-C distances are both 2.20 (4) Å, the  $\sigma$ -bond distances are 2.08 (3) and 2.04 (4) to Ir(1) and Ir(3), respectively, and the C(13)-C(914) length is 1.32 (5) Å. The additional olefinic portions of the C<sub>8</sub>H<sub>11</sub> and C<sub>8</sub>H<sub>10</sub> ligands are uncoordinated.

Only three heptanuclear cluster complexes have been characterized previously and each has a capped octahedral geometry. Both Rh<sub>7</sub>(CO)<sub>16</sub><sup>3-</sup><sup>21</sup> and Os<sub>7</sub>(CO)<sub>21</sub><sup>9</sup> have the



**Figure 1.** Perspective view of the  $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  molecule. Carbons C(13) and C(14) are associated with the alkyne portion of the  $\text{C}_8\text{H}_{10}$  ligand, C(21) and C(22) with the vinylic portion of  $\text{C}_8\text{H}_{11}$ .

**Table I.** Iridium-Iridium Lengths in the  $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  Cluster

Ir(1)–Ir(3)	2.690 (2)	Ir(3)–Ir(6)	2.783 (2)
Ir(1)–Ir(2)	2.738 (2)	Ir(3)–Ir(4)	2.862 (2)
Ir(1)–Ir(5)	2.744 (2)	Ir(4)–Ir(6)	2.665 (2)
Ir(1)–Ir(4)	2.791 (2)	Ir(4)–Ir(5)	2.764 (2)
Ir(2)–Ir(3)	2.678 (2)	Ir(5)–Ir(7)	2.676 (2)
Ir(2)–Ir(6)	2.799 (2)	Ir(5)–Ir(6)	2.764 (2)
Ir(2)–Ir(5)	2.817 (2)	Ir(6)–Ir(7)	2.689 (2)
Ir(2)–Ir(7)	2.979 (2)		

same number of valence electrons (98) as the  $\text{Ir}_7$  cluster;  $\text{Rh}_7(\text{CO})_{16}\text{I}^{2-7}$  has an additional electron pair due to the bridging iodine atom. The former two clusters adopt near- $\text{C}_{3v}$  structures and exhibit relatively small deviations from their mean metal-metal bond lengths (2.76 (1) and 2.855 (6) Å, respectively). In the latter case, the extra electron pair apparently resides in an orbital locally antibonding with respect to the capping rhodium atom, which causes significant lengthening of the apical Rh–Rh bonds (mean 2.926 (5) Å) relative to the remainder (mean 2.770 (5) Å). The Rh–Rh bond associated with the bridging iodide is especially lengthened to 3.000 (5) Å. The Ir–Ir bond lengths in  $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  are summarized in Table I. The values vary over a considerable range, from 2.665 (2) to 2.979 (2) Å, and show a larger, average deviation from the mean (2.763 (2) Å) than any of the previous structures. The longest Ir–Ir distance, Ir(2)–Ir(7) = 2.979 (2) Å, involves the apical iridium atom, but the other apical distances, Ir(5)–Ir(7) = 2.676 (2) and Ir(6)–Ir(7) = 2.689 (2) Å, are actually shorter than the average. The formal distribution of valence electrons among the metal centers is also much less symmetrical for  $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  than for  $\text{Os}_7(\text{CO})_{21}$ ; Ir(2) and Ir(4) are electron rich whereas Ir(5) and Ir(6) are electron poor relative to the analogous centers in the osmium compound.<sup>22</sup> However, for the  $\text{Ir}_7$  structure, no correlation of bond distances with the formal electron distribution is apparent.

The structure of  $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  is direct evidence that iridium carbonyl cluster species can possess

sufficient reactivity for olefinic C–H bond cleavage, heretofore a feature of the chemistry of trinuclear ruthenium and osmium carbonyl clusters.<sup>23</sup> Furthermore, coordination of the “enyl” moiety to an edge and of the “yne” moiety to a face of the  $\text{Ir}_7$  polyhedron parallels the manner in which such groups are bound to an edge or to a face of a triangular cluster framework.<sup>24,25</sup> This recurrence of localized coordination modes in the large cluster provides support for the proposition that such modes also will occur in similar environments on metal surfaces.<sup>26</sup>

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- (19) Crystals of the heptairidium cluster complex  $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  belong to the monoclinic system, space group  $P2_1/n$ . Cell constants of  $a = 10.941$  (2) Å,  $b = 11.090$  (2) Å,  $c = 33.561$  (5) Å,  $\beta = 96.30$  (2), and  $V = 4047.7$  Å<sup>3</sup> were calculated from the settings of 15 reflections with  $2\theta$  values  $>20^\circ$  (Mo K $\alpha$  radiation). The intensities of 8009 independent reflections were measured on a Syntex P1 automated diffractometer and corrected for absorption effects. Of these reflections, 3307 with  $I \geq 3\sigma(I)$  were observed and used in the refinement. The locations of the seven iridium atoms were obtained using direct methods and the positions of other atoms of the structure determined from a difference Fourier calculated with phases obtained by refinement of the metal atom positions.<sup>20</sup> Least-squares refinement of the complete structure with anisotropic thermal parameters for the metal atoms and isotropic thermal parameters for all other atoms converged with  $R = 0.055$  and  $R_w = 0.062$ .
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**Magnetic Exchange Interactions in  
 Copper(II) Dimers Bridged by Aromatic Diamines.  
 Crystal and Molecular Structure of  
 $\mu$ -Benzidine-bis(2,2',2''-triaminotriethylamine)-  
 dicopper(II) Nitrate**

Sir:

The determination of the spatial and time-dependent delocalization of electrons in molecules or more complex systems is an important problem.<sup>1,2</sup> For example, it is relevant to electron transfer in redox reaction precursors<sup>3</sup> and electron transport chains.<sup>4</sup> Mixed-valence compounds provide the opportunity to monitor the propagation time of an electron from one region of the molecule to another.<sup>5-7</sup> It is also possible to study electron dynamics in biradical systems that are involved in magnetic exchange interactions. The frequency of *electron exchange* between the two radical centers parallels the magnitude of the magnetic exchange interaction (as gauged by the exchange parameter  $J$  in the spin Hamiltonian  $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ).<sup>8</sup> In a series of nitroxyl biradicals, then, the biradical which is *not* involved in a magnetic exchange interaction will *not* have electrons exchanging between the two radical centers. This noninteracting biradical has an electronic structure consisting of two *localized* nitroxyl radical moieties. Recent work on nitroxyl biradicals has shown that electrons can exchange *intramolecularly* via a through-bond mechanism.<sup>9</sup>

Determining the presence and magnitude of a magnetic exchange interaction between the copper(II) centers in a copper(II) dimer with an extended organic bridge is one means of learning whether the extended organic moiety does support electron exchange between two paramagnetic centers. It was with this in mind that we prepared a series of copper(II) dimers with extended aromatic amine bridges having the composition of  $[\text{Cu}_2(\text{tren})_2(\text{DA})]\text{X}_4$ , where DA is various aromatic diamines such as benzidine (BZD), *o*-tolidine (OT), or *p*-phenylenediamine (PPD); tren is 2,2',2''-triaminotriethylamine; and X is  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , or  $\text{PF}_6^-$ . In this paper we communicate the structural and magnetic properties of these complexes.<sup>10</sup>

The single-crystal x-ray structure of  $[\text{Cu}_2(\text{tren})_2(\text{BZD})](\text{NO}_3)_4$  was solved using 8154 ( $I > 2\sigma(I)$ ) unique reflections collected on a Syntex P2<sub>1</sub> diffractometer equipped with a graphite monochromator,  $\lambda$  ( $\text{Cu K}\alpha_1$ ) = 1.54178 Å. The crystal data are as follows:  $\text{C}_{24}\text{H}_{48}\text{N}_{14}\text{O}_{12}\text{Cu}_2$ , mol wt 851.83; monoclinic, space group  $P2_1/c$ ;  $a = 29.799$  (4),  $b = 13.960$  (2),  $c = 18.732$  (3) Å;  $\beta = 106.49$  (1)°;  $V = 7471.9$  Å<sup>3</sup>;  $Z = 8$ ;  $\rho_{\text{calcd}} = 1.51$ ,  $\rho_{\text{obsd}} = 1.52$  g/cm<sup>3</sup>. The asymmetric unit consists of 104 nonhydrogen atoms (2 formula weights, 937 variables) and, as such, only Gauss-Seidel block refinements were used to refine the structure to final discrepancy indices<sup>11</sup> of  $R = 0.11$  and  $R_w = 0.16$ . All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of the 96 hydrogen atoms were calculated with fixed bond lengths of 1.05 Å and assigned isotropic thermal parameters of 9.5 Å<sup>2</sup>. The

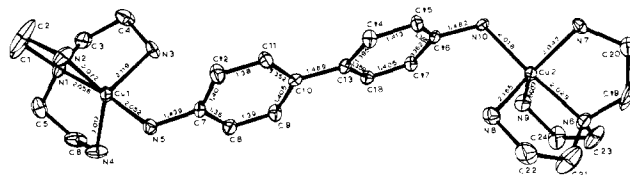


Figure 1. Perspective view of the  $[\text{Cu}_2(\text{tren})_2(\text{BZD})]^{4+}$  cation for one of the two independent dimers. The bond distances about the copper(II) ions and in the BZD bridge are quite similar for the two units.

two crystallographically independent dimers are related by a translation of *almost*  $(\frac{1}{2}, 0, 0)$ .

The geometry of one of the dimeric cations is illustrated in Figure 1 which shows the trigonal-bipyramidal coordination about each copper(II) ion. The bond distances and angles are quite similar for the two dimers which give copper-copper distances within each dimer of 12.270 (2) and 12.074 (2) Å. The phenyl rings of the BZD bridge are planar with dihedral angles of 13.8 and 22.5° about the C-C bond connecting them for each dimer. The nitrate anions exhibit weak (O-N distance  $> 2.9$  Å) hydrogen-bonding interactions with the tren nitrogens. There are copper-copper *interdimer* separations as short as 7.499 (2) Å.

Variable-temperature (4.2–286 K) magnetic susceptibility data for  $[\text{Cu}_2(\text{tren})_2(\text{BZD})](\text{NO}_3)_4$  show an antiferromagnetic exchange interaction with a maximum in the susceptibility data at 6 K. The data were least-squares fit to equations for an isotropic magnetic exchange interaction (exchange parameter  $J$  in a spin Hamiltonian of  $-2J\hat{S}_1\hat{S}_2$ ) to give  $J = -3.2$  cm<sup>-1</sup> and a Curie-Weiss constant of  $\theta = 0.75^\circ$ . The  $g$  values used in the fitting were taken from the Q-band EPR spectrum, which shows signals at  $g = 2.030$ , 2.124, and 2.191. Replacement of the  $\text{NO}_3^-$  counterion with  $\text{ClO}_4^-$  or  $\text{PF}_6^-$  leads to very similar magnetic susceptibility results with  $J$  values fit to  $-3.0$  and  $-2.6$  cm<sup>-1</sup>, respectively. The lack of a counterion dependence for the exchange parameter  $J$  is clear indication that the magnetic exchange interaction is propagated by the benzidine bridge. A similar complex,  $[\text{Cu}_2(\text{tren})_2(\text{OT})](\text{PF}_6)_4$ , shows a slightly weaker exchange interaction with  $J$  fit to  $-2.3$  cm<sup>-1</sup>.

Further substantiation for the fact that the benzidine bridge is propagating the interaction is found in the susceptibility data for the  $[\text{Cu}_2(\text{tren})_2(\text{PPD})]\text{X}_4$  compounds. All three of these *p*-phenylenediamine compounds exhibit a stronger antiferromagnetic interaction than found for the BZD compounds. For example, the data for the  $\text{NO}_3^-$  compound were fit to give  $J = -26$  cm<sup>-1</sup> with the average  $g$  value fixed at 2.115 (EPR).

The copper(II)-BZD compounds demonstrate that electrons can exchange between two metal ions separated by  $> 12$  Å via a biphenyl moiety. This is relevant to previous work which suggests that, in certain redox reactions between transition metal ions, the electron transfer occurs through extended ligands such as the *p*-dicarboxylic acid of biphenyl.<sup>12,13</sup> These same compounds are the first stable nonpolymeric copper(II) complexes of BZD and PPD, two reagents which are used to monitor the enzymatic activity of various cuproproteins such as ceruloplasmin<sup>14,15</sup> and laccase.<sup>14b</sup>

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**References and Notes**

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