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Structural Features of the Heptanuclear Iridium Cluster $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$. An Organometallic Cluster Complex Showing Stages of Cyclooctadiene Coordination and Dehydrogenation

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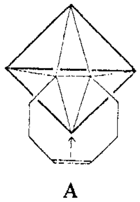
The organometallic cluster complex $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ obtained as a minor product of the reaction between $Ir_4(CO)_{12}$ and 1,5-cyclooctadiene in chlorobenzene has been investigated structurally by using crystallographic methods. The complex crystallizes in the centric monoclinic space group $P2_1/n$ with $a = 10.941$ (2) Å, $b = 11.090$ (2) Å, $c = 33.561$ (5) Å, $\beta = 96.30$ (2)°, $V = 4047.7$ Å^3, and d(calcd) = 3.303 g cm^{-3} for $Z = 4$. Diffraction data were collected with a Syntex $P\bar{1}$ automated diffractometer, and the structure was refined to $R_F = 0.055$ and $R_{wF} = 0.062$ for 3307 reflections with $F_o^2 > 3\sigma(F_o^2)$. The molecule consists of a monocapped octahedral core of seven iridium atoms. A normal cyclooctadiene ligand is chelated to the apical metal atom. π bonded to one metal and bridging one edge of the cluster is a singly deprotonated, vinylic, C_8H_{11} moiety. A doubly deprotonated C_8H_{10} ligand is bonded to one triangular face of the cluster in the manner of an alkyne. These ligands are the products of C–H bond cleavage, and the cluster illustrates the steps of cyclooctadiene dehydrogenation by the polyiridium species.

Introduction

Metal cluster complexes have received considerable recent interest due to their potential utility as catalysts.[1] This interest has led to rapid growth in the area of organocluster chemistry and to significant progress in the development of synthetic routes to higher order cluster complexes consisting of more than four metal atoms.[2-4]

Carbonyl cluster complexes of Ru and Os have been shown to readily activate the carbon–hydrogen bonds of coordinated organic ligands.[5] Related complexes of Rh and Ir show a lower affinity for C–H bond activation and offer the opportunity to investigate dehydrogenation reactions under controlled conditions. Shapley has examined the reaction between $Ir_4(CO)_{12}$ and 1,5-cyclooctadiene in careful detail.[6] Under mild conditions, using Me_3NO as a decarbonylating agent, the series of complexes $Ir_4(CO)_{12-2x}(C_8H_{12})_x$ (x = 1–3) have been synthesized. Pyrolysis of the bis- and tris(cyclooctadiene) species in refluxing cyclohexane produced $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ and $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$, respectively, by deprotonation of one diene ligand. In a previous report we presented a scheme showing how cyclooctadiene deprotonation might occur upon coordination to the Ir_4 cluster.[6] Intermediates which were proposed to lead ultimately to the *closo*-Ir_4C_2 cages of $Ir_4(CO)_7(C_8H_{12})(C_8H_{10})$ and $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ (A) included a [$\sigma + \pi$]-bound vinylic C_8H_{11} ligand (B) and a [$2\sigma + \pi$]-coordinated C_8H_{10} species (C). When the $Ir_4(CO)_{12}$–1,5-COD reaction was carried out under more extreme conditions (refluxing chlorobenzene), dehydrogenation products were obtained directly along with the higher order cluster complex $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$. This species shows, within a single molecular unit, the proposed stages of cyclooctadiene deporotonation. It is also a rare example of a higher order cluster complex containing organic ligands. We present herein the complete account of the structure determination of $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$. A preliminary report of these results appeared previously.[7]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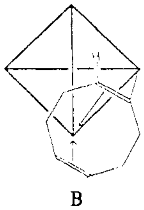
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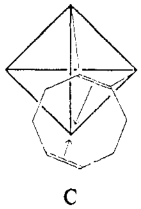
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Experimental Section

Dark green crystals of $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ were provided by Professor J. R Shapley of the University of Illinois.

Table I. Crystallographic Data for $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$

formula wt: 2003.19
crystal system: monoclinic
space group: $P2_1/n$
a = 10.941 (2) Å
b = 11.090 (2) Å
c = 33.561 (5) Å
β = 96.30 (2)°
V = 4047.7 Å^3
d(calcd) = 3.303 g cm^{-3}
Z = 4
radiation: Mo Kα
μ = 244.95 cm^{-1}

crystal size: 0.097 × 0.162 × 0.169 mm
bounding planes: {100}, {001}, {011}, {01$\bar{1}$}
transmission coeff: max = 0.119; min = 0.040
scan rate: 4°/min
2θ limits: $3 \leqslant 2\theta \leqslant 50°$
scan range: ±0.7°
data collected: 8009
data $F_o^2 > 3\sigma(F_o^2)$: 3307
p = 0.04

Preliminary photographs indicated monoclinic symmetry and systematic absences $k = 2n + 1$ for $0k0$ and $h + l = 2n + 1$ for $h0l$, which are consistent with space group $P2_1/n$, a nonstandard setting of the centric, monoclinic space group $P2_1/c$. The crystal described in Table I was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. An orientation matrix and refined cell constants were determined from the centered settings of 15 reflections by using Mo Kα radiation. Data were collected by the conventional θ–2θ scan technique and corrected for Lorentz, polarization, and absorption effects.

The locations of the seven iridium atoms were apparent from an E map calculated with phases determined by the tangent formula (MULTAN). Isotropic least-squares refinement of the seven metal atoms alone converged with $R_F = 0.097$ showing clearly how the metal contribution dominates the diffraction effect. The locations of all other carbon and oxygen atoms of the structure were obtained from a difference Fourier map calculated with phases obtained from the metal-atom refinement. Final refinement with anisotropic thermal parameters for the metal atoms and isotropic thermal parameters for the carbon and oxygen atoms converged with $R_F = 0.055$ and $R_{wF} = 0.062$. The value of the standard deviation of an observation of unit weight is 1.49 electrons. Sources of scattering factors, computer programs, and calculational procedures have been noted previously.[8] The final positional parameters and isotropic thermal parameters are listed in Table II. Anisotrtopic thermal parameters of the metal atoms are listed in Table III. Values of $10|F_o|$ and $10|F_c|$ in electrons for the 3307 reflections used in the refinement are available as supplementary material.

Discussion

Description of the $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ Molecule. Figures 1–3 show various views of the cluster complex and the atom-labeling scheme. Stereoscopic views showing the coordination of the C_8H_{11} and C_8H_{10} ligands are presented in Figures 4 and 5. Bond distances and angles are contained in Tables IV and V.

The inner Ir_7 core of the molecule may be described as a monocapped octahedron with metal atoms Ir1 to Ir6 defining

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Table II. Positional and Isotropic Thermal Parameters for the Atoms of the $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ Molecule

atom	*x*	*y*	*z*	*B*, Å^2
Ir1	0.16090 (13)	0.08591 (12)	0.11253 (5)	*a*
Ir2	0.33432 (14)	−0.05053 (12)	0.15693 (5)	*a*
Ir3	0.35246 (13)	−0.00803 (13)	0.07924 (5)	*a*
Ir4	0.34150 (13)	0.24628 (13)	0.09286 (5)	*a*
Ir5	0.31161 (13)	0.19786 (12)	0.17201 (5)	*a*
Ir6	0.51072 (13)	0.11388 (13)	0.13610 (5)	*a*
Ir7	0.50105 (13)	0.09125 (13)	0.21546 (5)	*a*
C1	0.023 (4)	0.120 (4)	0.143 (1)	4.2 (5)
O1	−0.049 (3)	0.138 (3)	0.163 (1)	6.4 (7)
C2	0.064 (3)	0.103 (3)	0.062 (1)	5.4 (6)
O2	0.009 (3)	0.124 (3)	0.034 (1)	7.1 (7)
C3	0.272 (4)	−0.074 (3)	0.205 (1)	5.0 (6)
O3	0.216 (3)	−0.093 (3)	0.233 (1)	6.2 (6)
C4	0.456 (3)	−0.173 (3)	0.163 (1)	4.7 (5)
O4	0.532 (3)	−0.241 (3)	0.166 (1)	5.5 (6)
C5	0.300 (6)	0.004 (4)	0.032 (2)	6.3 (7)
O5	0.252 (3)	0.017 (3)	−0.007 (1)	6.1 (7)
C6	0.484 (4)	−0.102 (4)	0.063 (1)	5.2 (6)
O6	0.563 (3)	−0.163 (3)	0.056 (1)	6.0 (6)
C7	0.321 (4)	0.276 (3)	0.039 (1)	4.3 (5)
O7	0.299 (3)	0.294 (3)	0.005 (1)	7.1 (6)
C8	0.219 (4)	0.353 (4)	0.106 (1)	5.1 (6)
O8	0.138 (3)	0.429 (3)	0.112 (1)	5.9 (7)
C9	0.361 (3)	0.362 (3)	0.186 (1)	4.9 (5)
O9	0.385 (3)	0.456 (2)	0.192 (1)	6.2 (5)
C10	0.215 (5)	0.183 (3)	0.213 (1)	4.9 (5)
O10	0.149 (3)	0.184 (3)	0.237 (1)	5.7 (6)
C11	0.644 (3)	0.016 (3)	0.128 (1)	3.8 (5)
O11	0.734 (3)	−0.044 (3)	0.129 (1)	5.9 (5)
C12	0.597 (3)	0.207 (3)	0.183 (1)	5.1 (5)
O12	0.664 (2)	0.292 (2)	0.192 (1)	7.2 (6)
C13	0.257 (3)	−0.146 (3)	0.102 (1)	6.3 (6)
C14	0.165 (4)	−0.100 (3)	0.120 (1)	7.1 (6)
C15	0.047 (3)	−0.173 (3)	0.134 (1)	6.2 (6)
C16	−0.049 (3)	−0.192 (4)	0.098 (1)	8.9 (8)
C17	−0.004 (3)	−0.264 (7)	0.061 (1)	7.8 (8)
C18	0.087 (7)	−0.306 (6)	0.050 (2)	9.1 (8)
C19	0.206 (4)	−0.328 (3)	0.052 (1)	6.5 (8)
C20	0.274 (3)	−0.280 (3)	0.094 (1)	5.3 (5)
C21	0.541 (3)	0.240 (3)	0.095 (1)	6.4 (5)
C22	0.509 (4)	0.371 (4)	0.100 (1)	6.7 (6)
C23	0.527 (4)	0.475 (3)	0.078 (1)	8.1 (7)
C24	0.645 (4)	0.536 (3)	0.088 (1)	10.8 (8)
C25	0.754 (5)	0.464 (4)	0.084 (3)	9.6 (8)
C26	0.798 (4)	0.357 (5)	0.082 (2)	11.1 (8)
C27	0.756 (4)	0.236 (5)	0.068 (1)	6.3 (8)
C28	0.609 (3)	0.222 (3)	0.059 (1)	6.5 (7)
C29	0.457 (3)	0.116 (4)	0.275 (1)	4.8 (6)
C30	0.540 (3)	0.207 (3)	0.269 (1)	5.2 (6)
C31	0.677 (4)	0.195 (5)	0.290 (1)	8.1 (7)
C32	0.754 (4)	0.113 (4)	0.266 (1)	7.5 (7)
C33	0.692 (4)	0.033 (4)	0.236 (2)	6.1 (6)
C34	0.600 (4)	−0.054 (4)	0.249 (1)	6.7 (6)
C35	0.575 (4)	−0.074 (4)	0.294 (1)	6.3 (7)
C36	0.473 (4)	0.005 (4)	0.302 (1)	7.8 (7)

[a] Atoms refined with anisotropic thermal ellipsoids.

Table III. Anisotropic Thermal Parameters for the Iridium Atoms of $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir1	2.29 (6)	2.16 (6)	2.67 (9)	0.38 (5)	0.30 (6)	0.01 (6)
Ir2	2.53 (6)	1.92 (6)	2.84 (9)	0.17 (5)	0.12 (6)	0.18 (6)
Ir3	2.77 (7)	2.20 (6)	2.80 (9)	0.19 (5)	0.61 (6)	−0.25 (6)
Ir4	2.75 (6)	2.05 (6)	2.93 (9)	0.33 (5)	0.61 (6)	0.21 (6)
Ir5	2.57 (7)	2.08 (6)	2.53 (9)	0.27 (5)	0.51 (6)	−0.03 (6)
Ir6	2.31 (6)	2.14 (6)	3.11 (9)	0.15 (5)	0.35 (6)	0.03 (6)
Ir7	2.64 (6)	2.44 (7)	2.93 (9)	0.13 (5)	−0.09 (6)	0.16 (6)

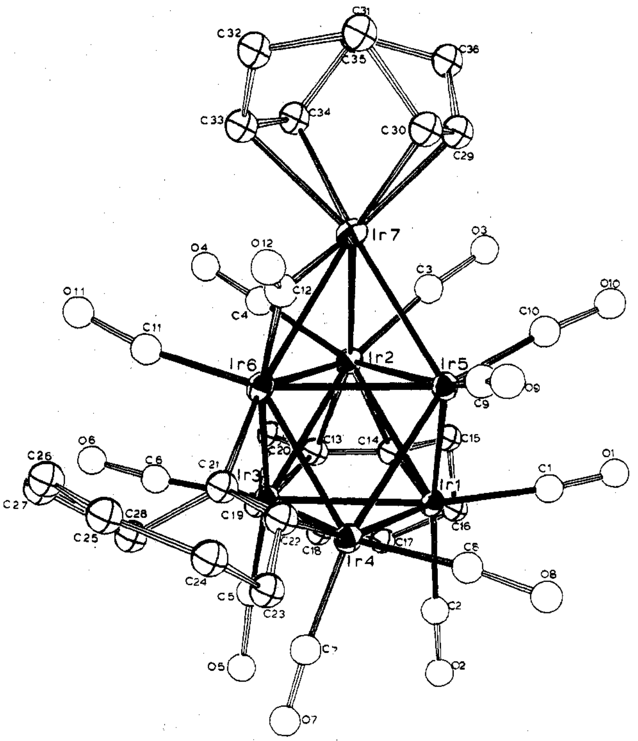


Figure 1. View of the $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ molecule. The singly deprotonated C_8H_{11} ligand is shown in the left foreground bonded along the Ir4–Ir6 edge of the cluster. In the center background is shown the C13–C14 bond of the C_8H_{10} ligand bonded to the Ir1, Ir2, Ir3 face.

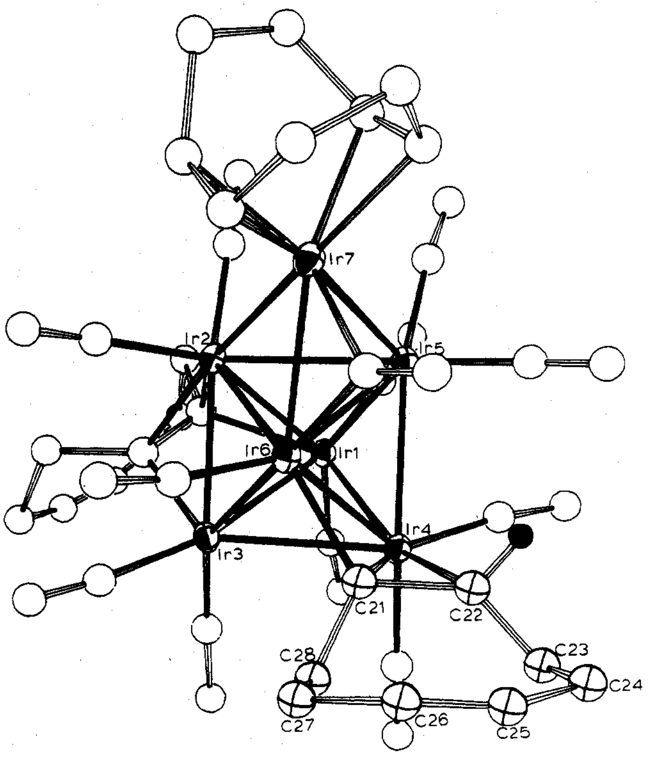


Figure 2. View showing the bonding of the C_8H_{11} ligand to Ir4 and along the Ir4–Ir6 bond. The single hydrogen atom of the C21–C22 bond is shown in an idealized position.

the octahedral region of the cluster and Ir7 atop one triangular face. Metal atoms Ir1, Ir3, and Ir4 occupy basal positions, each bonded to four other metal atoms (Figure 1). The apical metal atom Ir7 bonds with three metal atoms, and metals Ir2, Ir5, and Ir6, occupying meridional sites, bond with five other metal atoms. Iridium–iridium bond lengths within the cluster show considerable variation, ranging from the Ir4–Ir6 length of 2.665 (2) Å, the shortest of the cluster, to the Ir2–Ir7 length of 2.979 (2) Å. Shorter lengths of the cluster are roughly comparable to the single bond length of 2.693 Å reported for

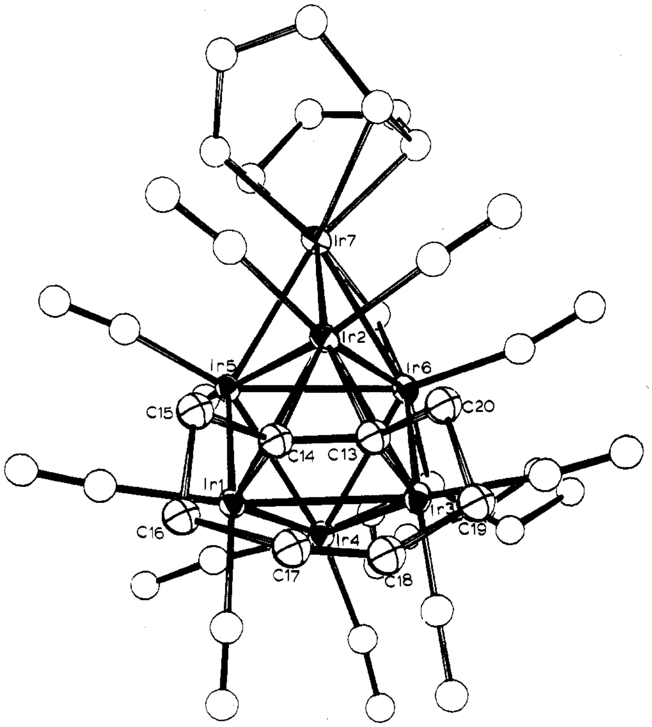
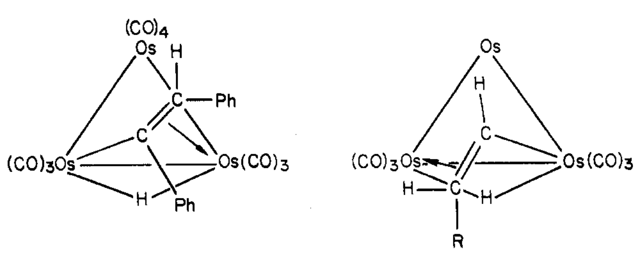


Figure 3. View showing the bonding of the C_8H_{10} ligand to the Ir1, Ir2, Ir3 face of the cluster. The C13–C14 bond is π bonded to Ir2 and σ bonded to metals Ir1 and Ir3.



I, R = H, Et

$Ir_4(CO)_{12}$;[9] the longest length exceeds the 2.903 (1) Å value of the hydride-bridged two-electron, three-center bond of $[(\eta^5\text{-}C_5(CH_3)_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$.[10] Each metal atom within the octahedral region of the cluster has two carbonyl ligands all bonded terminally with one exception, CO(12), which bridges the bond between Ir6 and the apical metal Ir7. In place of terminal carbonyl ligands, Ir7 has a bidentate cyclooctadiene ligand occupying two coordination sites. By a conventional electron count this metal is a 17-electron center. The other two organic ligands of the structure are bound to an edge and a face of the Ir_7 core. A singly deprotonated cyclooctadiene moiety is coordinated as a vinylic $[\sigma + \pi]$ three-electron donor along the Ir4–Ir6 bond. The C21–C22 bond is π bonded to Ir4 and σ bonded to Ir6 through C21 (Figure 2). A number of examples of vinylic ligands coordinated along metal–metal bonds of the triangular triosmium cluster I have been characterized structurally, and we have noted previously that this mode of coordination appears to

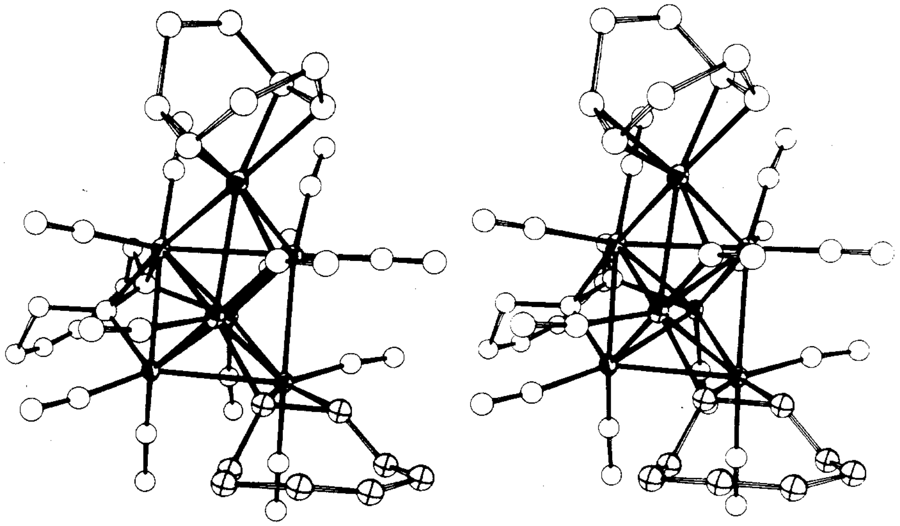


Figure 4. Stereoscopic view showing the bonding of the C_8H_{11} ligand.

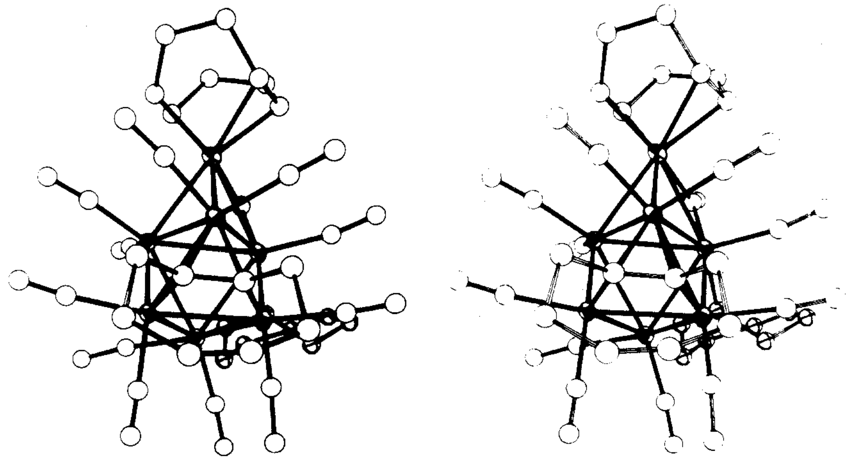


Figure 5. Stereoscopic view showing the bonding of the C_8H_{10} ligand.

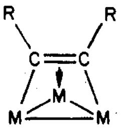
Table IV. Bond Distances for the $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ Molecule (Å)

Iridium–Iridium Lengths			
Ir1–Ir2	2.738 (2)	Ir3–Ir4	2.862 (2)
Ir1–Ir3	2.690 (2)	Ir3–Ir6	2.783 (2)
Ir1–Ir4	2.791 (2)	Ir4–Ir5	2.764 (2)
Ir1–Ir5	2.744 (2)	Ir4–Ir6	2.665 (2)
Ir2–Ir3	2.678 (2)	Ir5–Ir6	2.764 (2)
Ir2–Ir5	2.817 (2)	Ir5–Ir7	2.676 (2)
Ir2–Ir6	2.799 (2)	Ir6–Ir7	2.689 (2)
Ir2–Ir7	2.979 (2)		
Iridium–Organic Ligand Lengths			
C13–Ir2	2.21 (3)	C22–Ir4	2.29 (4)
C13–Ir3	2.04 (4)	C29–Ir7	2.12 (4)
C14–Ir2	2.19 (4)	C30–Ir7	2.20 (4)
C14–Ir1	2.08 (3)	C33–Ir7	2.22 (4)
C21–Ir4	2.18 (3)	C34–Ir7	2.19 (4)
C21–Ir6	2.02 (3)		
Iridium–Carbonyl Carbon Lengths			
C1–Ir1	1.94 (4)	C7–Ir4	1.84 (5)
C2–Ir1	1.90 (3)	C8–Ir4	1.88 (5)
C3–Ir2	1.82 (5)	C9–Ir5	1.94 (4)
C4–Ir2	1.90 (3)	C10–Ir5	1.83 (4)
C5–Ir3	1.64 (7)	C11–Ir6	1.86 (3)
C6–Ir3	1.91 (5)	C12–Ir6	2.02 (4)
		C12–Ir7	2.05 (3)
Carbon–Carbon Lengths			
C13–C14	1.32 (5)	C25–C26	1.30 (6)
C14–C15	1.64 (5)	C26–C27	1.48 (6)
C15–C16	1.54 (5)	C27–C28	1.61 (5)
C16–C17	1.58 (7)	C28–C21	1.51 (5)
C17–C18	1.30 (7)	C29–C30	1.39 (5)
C18–C19	1.42 (8)	C30–C31	1.60 (6)
C19–C20	1.54 (5)	C31–C32	1.53 (6)
C20–C13	1.53 (4)	C32–C33	1.46 (7)
C21–C22	1.51 (5)	C33–C34	1.39 (6)
C22–C23	1.40 (5)	C34–C35	1.57 (7)
C23–C24	1.46 (5)	C35–C36	1.46 (6)
C24–C25	1.45 (6)	C36–C30	1.53 (6)

$C\text{-}O_{av} = 1.17\ (5)$

shorten the associated Os–Os bond.[11] A similar effect seems to be operative in the present case, with the Ir4–Ir6 length the shortest metal–metal bond of the structure.

The remaining organic ligand of the cluster is a doubly deprotonated cyclooctadiene which, like the C_8H_{11} moiety, bonds to the cluster through one carbon–carbon bond of the ring. It sits atop the Ir1, Ir2, Ir3 triangular face as a $[2\sigma + \pi]$ four-electron donor (Figure 3). This mode of coordination is also found typically for simple triangular clusters containing alkyne ligands (II).[8] Other examples of cycloocta-1-en-5-yne bound in the manner of an alkyne are known. The "butterfly" clusters $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$[6] and $Ru_4(CO)_{11}(C_8H_{10})$[5] with the acetylenic carbon–carbon bond inserted into one edge of an M_4 tetrahedron (III) have been characterized structurally and compared with related alkyne complexes. The $Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$ cluster was obtained as the major product of the reaction which also produced $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$. It is perhaps significant that the longest Ir–Ir bond of the present molecule occurs at the position opposite to the C13–C14 π bond to Ir2. To our knowledge there are no simple examples of cluster complexes characterized structurally which have metal–metal bonds trans to π-bonded alkynes for comparison.



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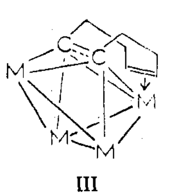
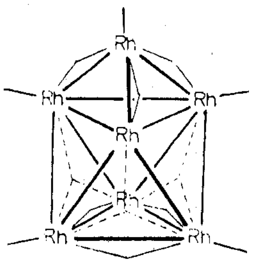
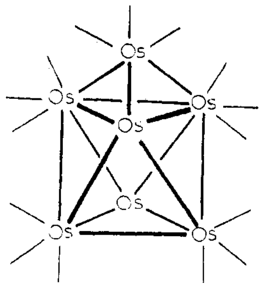


III

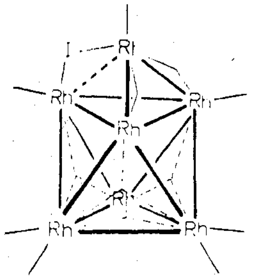
Structural Features of M_7 Clusters. Three other metal cluster complexes have been reported which show the capped octahedral M_7 core. Two of these are isoelectronic with $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ ($Rh_7(CO)_{16}{}^{3-}$[12] and $Os_7(CO)_{21}$[13]) while the third, $Rh_7(CO)_{16}I^{2-}$[14], has an additional electron pair due to the bridging iodine atom. The isoelectronic pair of carbonyl clusters $Rh_7(CO)_{16}{}^{3-}$ (IV) and $Os_7(CO)_{21}$ (V), both of approximate C_{3v} symmetry, show rather different metal–metal bonding patterns. The Os–Os lengths at the triangular base of $Os_7(CO)_{21}$ are the longest of the molecule, averaging to 2.902 Å, while for $Rh_7(CO)_{16}{}^{3-}$ and also $Rh_7(CO)_{16}I^{2-}$, the shortest lengths of 2.72 and 2.741 Å, respectively, are found at these positions. Basal lengths of $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ show considerable variation, ranging from 2.690 (2) to 2.862 (2) Å. Lengths to the apical metal of $Os_7(CO)_{21}$ are the shortest of the structure, averaging to 2.819 Å, slightly shorter than the Os–Os single-bond value of 2.877 (3) Å for $Os_3(CO)_{12}$. The two independent bonds at this position of $Rh_7(CO)_{16}{}^{3-}$ are quite different, 2.73 (1) and 2.81 (1) Å, while for $Rh_7(CO)_{16}I^{2-}$ (VI), there is considerable lengthening due to the presence of the iodine. Values of 3.000 (5), 2.886 (5), and 2.893 (5) Å have been reported for the apical bonds of this complex anion, although, disorder of iodine and bridging carbonyl ligands limits the significance of these lengths. As for the basal bonds, the lengths to Ir7 of $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ show considerable variation, ranging from 2.676 (2) to 2.979 (2) Å, the latter value being very close to the iodine-bridged length of $Rh_7(CO)_{16}I^{2-}$. The absence of a systematic pattern for the Ir–Ir lengths in the present structure must be related to some degree to regional differences in change distribution within the cluster. Isolated metal atoms of the Ir_7 unit include a 17-electron metal (Ir7), four 18-electron metals (Ir1, Ir3, Ir5, Ir6), a 19-electron metal (Ir4), and a 20-electron metal (Ir2). The anomalously long



IV



V



VI

Table V. Bond Angles for the $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ Molecule (deg)

Angles about Ir1			
Ir2–Ir1–Ir3	59.13 (5)	C2–Ir1–Ir3	93 (1)
Ir2–Ir1–Ir4	90.83 (6)	C2–Ir1–Ir4	94 (1)
Ir2–Ir1–Ir5	61.85 (5)	C2–Ir1–Ir5	146 (1)
Ir3–Ir1–Ir4	62.92 (5)	C1–Ir1–C2	93 (1)
Ir3–Ir1–Ir5	92.51 (6)	C14–Ir1–Ir2	52 (1)
Ir4–Ir1–Ir5	59.92 (5)	C14–Ir1–Ir3	70 (1)
C1–Ir1–Ir2	111 (1)	C14–Ir1–Ir4	131 (1)
C1–Ir1–Ir3	167 (1)	C14–Ir1–Ir5	111 (1)
C1–Ir1–Ir4	127 (1)	C14–Ir1–Cl	98 (2)
C1–Ir1–Ir5	88 (1)	C14–Ir1–C2	102 (1)
C2–Ir1–Ir2	145 (1)		
Angles about Ir2			
Ir1–Ir2–Ir3	59.56 (5)	C4–Ir2–Ir6	90 (1)
Ir1–Ir2–Ir5	59.19 (5)	C4–Ir2–Ir7	76 (1)
Ir1–Ir2–Ir6	87.70 (6)	C3–Ir2–C4	98 (1)
Ir1–Ir2–Ir7	113.91 (6)	C13–Ir2–Ir1	68 (1)
Ir3–Ir2–Ir5	91.16 (6)	C13–Ir2–Ir3	48 (1)
Ir3–Ir2–Ir6	61.04 (5)	C13–Ir2–Ir5	125 (1)
Ir3–Ir2–Ir7	116.35 (6)	C13–Ir2–Ir6	108 (1)
Ir5–Ir2–Ir6	58.97 (5)	C13–Ir2–Ir7	162 (1)
Ir5–Ir2–Ir7	54.90 (5)	C13–Ir2–C3	121 (1)
Ir6–Ir2–Ir7	55.36 (5)	C13–Ir2–C4	87 (1)
C3–Ir2–Ir1	105 (1)	C14–Ir2–Ir1	48 (1)
C3–Ir2–Ir3	162 (1)	C14–Ir2–Ir3	69 (1)
C3–Ir2–Ir5	86 (1)	C14–Ir2–Ir5	105 (1)
C3–Ir2–Ir6	130 (1)	C14–Ir2–Ir6	126 (1)
C3–Ir2–Ir7	76 (1)	C14–Ir2–Ir7	158 (1)
C4–Ir2–Ir1	153 (1)	C14–Ir2–C3	95 (1)
C4–Ir2–Ir3	96 (1)	C14–Ir2–C4	115 (1)
C4–Ir2–Ir5	139 (1)	C14–Ir2–C13	35 (1)
Angles about Ir3			
Ir1–Ir3–Ir2	61.32 (5)	C6–Ir3–Ir2	109 (1)
Ir1–Ir3–Ir4	60.25 (5)	C6–Ir3–Ir4	129 (1)
Ir1–Ir3–Ir6	88.95 (6)	C6–Ir3–Ir6	92 (1)
Ir2–Ir3–Ir4	90.52 (6)	C5–Ir3–C6	88 (2)
Ir2–Ir3–Ir6	61.61 (5)	C13–Ir3–Ir1	71 (1)
Ir4–Ir3–Ir6	56.32 (5)	C13–Ir3–Ir2	54 (1)
C5–Ir3–Ir1	100 (2)	C13–Ir3–Ir4	130 (1)
C5–Ir3–Ir2	155 (2)	C13–Ir3–Ir6	114 (1)
C5–Ir3–Ir4	93 (1)	C13–Ir3–C5	107 (2)
C5–Ir3–Ir6	139 (2)	C13–Ir3–C6	98 (1)
C6–Ir3–Ir1	168 (1)		
Angles about Ir4			
Ir1–Ir4–Ir3	56.82 (5)	C7–Ir4–C8	97 (1)
Ir1–Ir4–Ir5	59.20 (5)	C21–Ir4–Ir1	135 (1)
Ir1–Ir4–Ir6	89.31 (6)	C21–Ir4–Ir3	85 (1)
Ir3–Ir4–Ir5	88.48 (6)	C21–Ir4–Ir5	101 (1)
Ir3–Ir4–Ir6	60.35 (5)	C21–Ir4–Ir6	48 (1)
Ir5–Ir4–Ir6	61.17 (5)	C21–Ir4–C7	93 (1)
C7–Ir4–Ir1	110 (1)	C21–Ir4–C8	138 (1)
C7–Ir4–Ir3	91 (1)	C22–Ir4–Ir1	160 (1)
C7–Ir4–Ir5	166 (1)	C22–Ir4–Ir3	124 (1)
C7–Ir4–Ir6	130 (1)	C22–Ir4–Ir5	101 (1)
C8–Ir4–Ir1	78 (1)	C22–Ir4–Ir6	77 (1)
C8–Ir4–Ir3	135 (1)	C22–Ir4–C7	90 (1)
C8–Ir4–Ir5	74 (1)	C22–Ir4–C8	100 (1)
C8–Ir4–Ir6	133 (1)	C22–Ir4–C21	39 (1)
Angles about Ir5			
Ir1–Ir5–Ir2	59.97 (5)	C9–Ir5–Ir2	159 (1)
Ir1–Ir5–Ir4	60.88 (5)	C9–Ir5–Ir4	89 (1)
Ir1–Ir5–Ir6	88.28 (6)	C9–Ir5–Ir6	102 (1)
Ir1–Ir5–Ir7	124.39 (6)	C9–Ir5–Ir7	96 (1)
Ir2–Ir5–Ir4	89.73 (6)	C10–Ir5–Ir1	99 (1)
Ir2–Ir5–Ir6	60.19 (5)	C10–Ir5–Ir2	97 (1)
Ir2–Ir5–Ir7	65.64 (5)	C10–Ir5–Ir4	151 (1)
Ir4–Ir5–Ir6	57.65 (5)	C10–Ir5–Ir6	148 (1)
Ir4–Ir5–Ir7	116.34 (6)	C10–Ir5–Ir7	92 (1)
Ir6–Ir5–Ir7	59.22 (5)	C9–Ir5–C10	95 (1)
C9–Ir5–Ir1			
Angles about Ir6			
Ir2–Ir6–Ir3	57.35 (5)	C11–Ir6–Ir7	102 (1)
Ir2–Ir6–Ir4	92.17 (6)	C12–Ir6–Ir2	115 (1)
Ir2–Ir6–Ir5	60.84 (5)	C12–Ir6–Ir3	169 (1)
Ir2–Ir6–Ir7	65.73 (5)	C12–Ir7–Ir4	112 (1)
Ir3–Ir6–Ir4	63.32 (5)	C12–Ir6–Ir5	79 (1)
Ir3–Ir6–Ir5	90.10 (6)	C12–Ir6–Ir7	49 (1)
Ir3–Ir6–Ir7	123.03 (7)	C11–Ir6–C12	96 (1)
Ir4–Ir6–Ir5	61.18 (5)	C21–Ir6–Ir2	142 (1)
Ir4–Ir6–Ir7	119.38 (7)	C21–Ir6–Ir3	90 (1)
Ir5–Ir6–Ir7	58.76 (5)	C21–Ir6–Ir4	53 (1)
C11–Ir6–Ir2	103 (1)	C21–Ir6–Ir5	105 (1)
C11–Ir6–Ir3	93 (1)	C21–Ir6–Ir7	140 (1)
C11–Ir6–Ir4	139 (1)	C21–Ir6–C11	97 (1)
C11–Ir6–Ir5	158 (1)	C21–Ir6–C12	94 (1)
Angles about Ir7			
Ir2–Ir7–Ir5	59.46 (5)	C30–Ir7–C29	37 (1)
Ir2–Ir7–Ir6	58.91 (5)	C33–Ir7–Ir2	122 (1)
Ir5–Ir7–Ir6	62.02 (5)	C33–Ir7–Ir5	161 (1)
C12–Ir7–Ir2	107 (1)	C33–Ir7–Ir6	102 (1)
C12–Ir7–Ir5	81 (1)	C33–Ir7–C12	80 (1)
C12–Ir7–Ir6	48 (1)	C33–Ir7–C29	93 (2)
C29–Ir7–Ir2	120 (1)	C33–Ir7–C30	80 (2)
C29–Ir7–Ir5	102 (1)	C34–Ir7–Ir2	101 (1)
C29–Ir7–Ir6	163 (1)	C34–Ir7–Ir5	157 (1)
C29–Ir7–C12	127 (1)	C34–Ir7–Ir6	121 (1)
C30–Ir7–Ir2	153 (1)	C34–Ir7–C12	119 (2)
C30–Ir7–Ir5	105 (1)	C34–Ir7–C29	76 (2)
C30–Ir7–Ir6	136 (1)	C34–Ir7–C30	88 (1)
C30–Ir7–C12	90 (1)	C34–Ir7–C33	39 (1)
Selected Carbon Atom Bond Angles			
Ir2–C13–Ir3	78 (1)	C22–C21–C28	111 (3)
Ir2–C13–C14	72 (2)	Ir4–C22–C23	127 (3)
Ir2–C13–C20	124 (2)	Ir4–C22–C21	66 (2)
Ir3–C13–C14	109 (2)	C21–C22–C23	132 (4)
Ir3–C13–C20	126 (2)	Ir7–C29–C30	75 (2)
C14–C13–C20	124 (3)	Ir7–C29–C36	115 (3)
Ir2–C14–Ir1	80 (1)	C30–C29–C36	129 (3)
Ir2–C14–C13	73 (2)	Ir7–C30–C29	68 (2)
Ir2–C14–C15	127 (3)	Ir7–C30–C31	114 (2)
Ir1–C14–C13	109 (2)	C29–C30–C31	118 (3)
Ir1–C14–C15	121 (3)	Ir7–C33–C34	69 (2)
C13–C14–C15	127 (3)	Ir7–C33–C32	113 (3)
Ir4–C21–Ir6	78 (1)	C32–C33–C34	118 (5)
Ir4–C21–C22	74 (2)	Ir7–C34–C33	71 (2)
Ir4–C21–C28	124 (2)	Ir7–C34–C35	118 (3)
Ir6–C21–C22	122 (2)	C33–C34–C35	124 (4)
Ir6–C21–C28	126 (2)	Ir6–C12–Ir7	83 (1)

Ir2–Ir7 bond is between electron-rich and electron-deficient centers.

Structural changes resulting from the presence of the iodine ligand in the complex anion above and the vinylic ligand in the present molecule show clearly how ligands can serve to influence bond strength within higher order clusters. Observations of this type are quite important as they relate directly to the role that ligands play in promoting the structural rearrangment of the metal framework by either weakening or strengthening metal–metal bonds. Further, it is important to establish that bonding patterns which have been found for smaller molecular systems appear also in localized regions of larger clusters, supporting the extension to higher order polymetallic systems.

Acknowledgment. We thank Professor J. R. Shapley for supplying crystals of $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$ and the University of Colorado Computing Center for a generous allocation of computational time.

Registry No. $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$, 65762-17-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of μ-Peroxo-bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] Tetraiodide. Effect of Chelate Ring Size on the Structures and Stabilities of Dioxygen Complexes[1]

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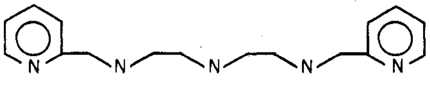
Received February 12, 1979

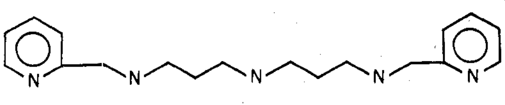
The structure of μ-peroxo-bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] tetraiodide, $[Co(PYDIEN)]_2O_2I_4$, $Co_2C_{32}H_{46}N_{10}O_2I_4$, has been determined by single-crystal X-ray diffraction. The opaque crystals are orthorhombic, conforming to the space group *Fdd*2, with unit cell dimensions $a = 26.73$ (2) Å, $b = 32.19$ (1) Å, and $c = 10.049$ (6) Å; $Z = 8$. The observed density of 1.90 (1) $g{\cdot}cm^{-3}$ agrees well with the calculated value of 1.89 $g{\cdot}cm^{-3}$. Least-squares refinement gave an R index of 0.045 for 2167 observed reflections with intensities greater than 3σ. The O–O distance of 1.489 (8) Å and the Co–O–O angle of 112.5 (4)° are characteristic of peroxide bound to tripositive cobalt. The two pyridyl groups and the dioxygen moiety are cis to one another, the central (aliphatic) nitrogen donor of the ligand is trans to a pyridyl ring, and one of the secondary amino groups is trans to dioxygen in the distorted octahedral complex. The results of the structure determination provide an explanation for the difference in the oxygen affinities of $[Co(PYDIEN)]^{2+}$ and the cobaltous complex of 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT). Some of the Co–N bonds in $[Co(PYDIEN)]_2O_2I_4$ are shorter and thus stronger than those in $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O$, the structure of which has been reported previously. Donation of electron density from the ligand to cobalt increases the tendency of cobalt to transfer electron density to dioxygen and is probably the major factor affecting the stability of the oxygen complex. That the extent of donation from cobalt to dioxygen is different in the two structures can be seen by comparison of the Co–O and O–O bond distances.

Introduction

In a recent paper,[2a] the cobalt(II) complex of PYDIEN (**1**)



1, PYDIEN



2, PYDPT

was shown to have an affinity for molecular oxygen which is about 4 orders of magnitude larger than the oxygen affinity exhibited by the cobalt(II) complex of PYDPT (**2**). Differences in intrinsic basicity can account for differences in oxygen affinity;[2b] however, the intrinsic basicities of the ligands are approximately equal. Indeed, the ligands differ only in the number of methylene groups between the three central amine nitrogen atoms. A study[3] of ligands analogous to PYDIEN and PYDPT, in which the pyridyl groups have been replaced by imidazolyl groups, has confirmed that additional methylene groups between the aliphatic nitrogen atoms drastically decrease the oxygen affinity of the cobaltous complex. It would appear that the stability of the oxygen complex is affected by properties of the ligand other than basicity.

The molecular structure of $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O$ was recently determined[4] by single-crystal X-ray diffraction. This work was performed in order to determine whether the structure of this complex could account for its lowered stability in solution. The structure did not exhibit any features which would prevent the close approach of dioxygen to the cobalt ion. Thus, it is unlikely that the stability of the complex is lowered by direct steric interaction between the ligand and dioxygen. Comparison with structural data for related complexes[5,6] gives no clue to the reason for the reduced stability of the oxygen complex of cobaltous PYDPT.

The crystal structure of $[Co(PYDIEN)]_2O_2I_4$ is reported in this paper. This structure was undertaken to determine whether any structural differences between the oxygen complexes containing PYDIEN and PYDPT exist. The difference in their stabilities might be explained by differences in geometry about the cobalt ion. A full comparison of the two structures is made; relevant data on the structure of $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O^4$ are included to facilitate this comparison.

Experimental Section

Materials. Reagent grade cobaltous chloride ($CoCl_2{\cdot}6H_2O$) and sodium iodide (NaI) were obtained from Fisher Scientific Co. and were used without further purification. 2-Pyridinecarboxaldehyde and bis(2-aminoethyl)amine were purchased from Aldrich Chemical Co. and the former was distilled prior to use. High-purity oxygen, nitrogen, and hydrogen gases were obtained from Airco Gas Products, Inc., and used as obtained. All other compounds employed in this research were reagent grade chemicals and solvents.

Preparation of 1,9-Bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN). In a typical reaction, 0.10 mol of 2-pyridinecarboxaldehyde and 0.050 mol of bis(2-aminoethyl)amine were mixed together in 150 mL of absolute ethanol. The yellow solution was then heated to boiling and allowed to cool to room temperature. Raney nickel catalyst was then added and the mixture was shaken under 60 psi of hydrogen gas for 8 h. The catalyst was filtered from the clear solution and washed

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