

Acetylacetonato(1,5-cyclooctadiene)iridium(I)

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Abstract. $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_7\text{O}_2)]$, $\text{C}_{13}\text{H}_{19}\text{IrO}_2$, $M_r = 399.51$, monoclinic, $C2/m$, $a = 17.523(2)$, $b = 7.069(1)$, $c = 10.245(1)$ Å, $\beta = 94.28(1)^\circ$, $Z = 4$, $D_c = 2.096$ Mg m $^{-3}$, $\mu(\text{Mo } K\alpha) = 10.49$ mm $^{-1}$. Final $R = 0.017$ for 1855 reflections. Mean bond lengths are Ir–O 2.042(3) and Ir–C 2.092(3) Å. The molecular geometry is compared with that in the analogous Rh complex.

Introduction. A crystal $0.375 \times 0.090 \times 0.053$ mm was used for data collection. 5192 reflections of the type $\pm h, k, \pm l$ were measured in the range $3^\circ < 2\theta < 60^\circ$ on a Picker FACS-I diffractometer with crystal-monochromated Mo $K\alpha$ radiation. Further experimental and refinement details have been deposited. Cell dimensions were obtained by least squares from 12 high-angle ($2\theta > 54^\circ$) reflections and are in agreement with those reported by Davignon, Dereigne, Bonnaire & Manoli (1971). Intensities were corrected for Lorentz, polarization and absorption effects (Ferguson, Mau & Whimp, 1979). Equivalent reflections were averaged to give 1855 unique reflections with $I > 3\sigma(I)$.

Systematic absences indicate a C-centring operation only, so that the possible space groups are Cm , $C2$ or $C2/m$. With $Z = 4$ the Patterson map is inconsistent with Cm . The Patterson and subsequent Fourier syntheses show that the molecule either lies in a general position in $C2$ and has approximate mirror symmetry or has exact mirror symmetry and lies on the mirror plane in $C2/m$. Refinement in the noncentrosymmetric $C2$ was attempted and converged with $R_w \{ = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} \} = 0.019$. The improved fit (relative to the $C2/m$ refinement below) of this model to the data was significant on the basis of the R -factor ratio test (*International Tables for X-ray Crystallography*, 1974). However, the resultant molecular geometry of the 1,5-cyclooctadiene ligand was unreasonable. Consequently this model was rejected and the space group is assumed to be $C2/m$.

Scattering factors and the real and imaginary anomalous-scattering terms for Ir were taken from *International Tables for X-ray Crystallography* (1974). Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined. H atoms were

located from a difference synthesis and their positional parameters refined with thermal parameters equal to the isotropic equivalent of the atom to which they were bound. Refinement converged with $R = 0.017$ ($R_w = 0.022$), the shift in the final cycle being no more than 0.5 times that of the parameter e.s.d.* The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma(F_o) + 0.005|F_o|^2]^{-1}$. An extinction parameter

* Lists of structure factors, thermal parameters, H-atom coordinates and experimental details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35644 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and equivalent isotropic thermal parameters (Willis & Pryor, 1975), with e.s.d.'s in parentheses

	x	y	z	B_{eq} (Å 2)
Ir	0.16763 (1)	0.0	0.18284 (1)	2.929
O(1)	0.2832 (1)	0.0	0.1665 (3)	3.76
O(2)	0.1463 (2)	0.0	-0.0155 (3)	4.08
C(1)	0.0565 (1)	0.0995 (5)	0.2021 (3)	4.00
C(2)	0.0516 (2)	0.2188 (7)	0.3234 (5)	6.13
C(3)	0.1193 (3)	0.2179 (8)	0.4154 (4)	6.83
C(4)	0.1849 (2)	0.0987 (5)	0.3752 (2)	3.98
C(5)	0.3148 (2)	0.0	0.0580 (4)	3.52
C(6)	0.2770 (2)	0.0	-0.0664 (4)	3.73
C(7)	0.1983 (2)	0.0	-0.0970 (3)	3.38
C(8)	0.4008 (2)	0.0	0.0698 (6)	5.13
C(9)	0.1686 (3)	0.0	-0.2392 (4)	4.99

Table 2. Bond lengths (Å) and angles ($^\circ$)

Ir–O(1)	2.045 (3)	Ir–O(1)–C(5)	124.6 (2)
Ir–O(2)	2.039 (3)	Ir–O(2)–C(7)	124.2 (2)
Ir–C(1)	2.094 (3)	O(1)–C(5)–C(6)	126.0 (3)
Ir–C(4)	2.091 (3)	O(2)–C(7)–C(6)	126.5 (3)
C(1)–C(1')	1.406 (7)	C(5)–C(6)–C(7)	127.1 (3)
C(4)–C(4')	1.395 (7)	O(1)–C(5)–C(8)	115.3 (4)
C(1)–C(2)	1.510 (5)	O(2)–C(7)–C(9)	114.7 (4)
C(2)–C(3)	1.459 (6)	C(6)–C(5)–C(8)	118.7 (4)
C(3)–C(4)	1.507 (5)	C(6)–C(7)–C(9)	118.8 (4)
O(1)–C(5)	1.278 (5)	O(1)–Ir–O(2)	91.6 (1)
O(2)–C(7)	1.281 (4)	C(1')–C(1)–C(2)	123.9 (2)
C(5)–C(6)	1.392 (5)	C(4')–C(4)–C(3)	124.0 (3)
C(7)–C(6)	1.391 (5)	C(1)–C(2)–C(3)	115.8 (3)
C(5)–C(8)	1.502 (5)	C(4)–C(3)–C(2)	115.2 (3)
C(7)–C(9)	1.510 (5)		

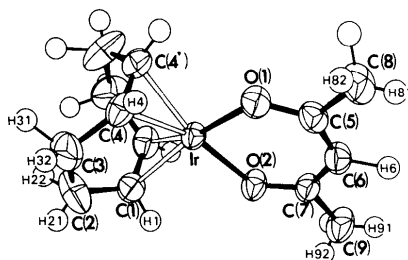


Fig. 1. ORTEP drawing (Johnson, 1965) of the molecule showing the atom labelling. Ellipsoids are drawn to include 50% probability and H atoms are scaled arbitrarily for clarity. The crystallographic mirror plane contains the Ir(acac) ring and bisects the olefinic bonds.

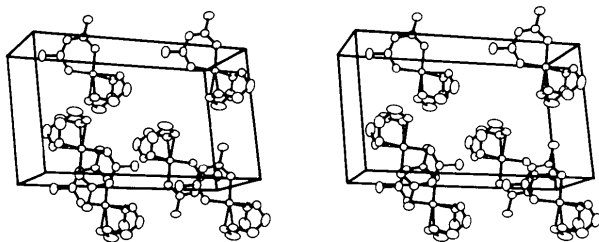


Fig. 2. Stereoscopic drawing of the molecular packing viewed roughly along *b*.

[$0.52(3) \times 10^{-4}$] was refined (Zachariassen, 1967). Final atomic coordinates are listed in Table 1, bond lengths and angles in Table 2. The molecular geometry is illustrated in Fig. 1 and the crystal packing in Fig. 2.

Discussion. The olefinic function of the tridentate chelating ligand *o*-bis(diphenylphosphino)stilbene (bdpps) in the isomorphous complexes [IrCl₃(bdpps)] and [RhCl₃(bdpps)] is thought (Robertson, Tucker & Whimp, 1981) to be bound more strongly to Ir^{III} than Rh^{III} due to enhanced metal–olefin back-bonding when the metal is Ir. We expected this trend to be more evident for unit oxidation state *d*⁸ complexes of these metals where, formally at least, the metal is more electron rich. However, the ¹H NMR chemical shift of the 1,5-cyclooctadiene (cod) olefinic protons on coordination (Robinson & Shaw, 1965) indicates less olefinic character in acetylacetonato(1,5-cyclooctadiene)rhodium(I), [Rh(acac)(cod)], than in the title complex [Ir(acac)(cod)] which could reflect greater back-donation to the olefin in the Rh complex. In an attempt to resolve this problem we have determined the structure of [Ir(acac)(cod)] to compare the molecular geometry with that in [Rh(acac)(cod)] (Tucker, Scutcher & Russell, 1975).

There are three quantities that may be used to measure the nature and strength of the metal–cod interaction: the *M*–C lengths, the olefinic C–C lengths and the rehybridization of the olefinic C atoms upon coordination as measured by the angle of bend-back α

(Stalick & Ibers, 1970). Although shorter, the mean Ir–C distance [2.092 (3) Å] in [Ir(acac)(cod)] does not differ significantly from the mean Rh–C distance [2.103 (7) Å] in [Rh(acac)(cod)]. There is a complication in that the Ir–O distance [mean 2.042 (3) Å] in [Ir(acac)(cod)] is significantly shorter than the equivalent Rh–O distance [mean 2.060 (5) Å]. Were it reasonable to assume a constant covalent radius for a transition metal the implication would be that the Rh–C bond is *relatively* stronger than the Ir–C bond. The difference ($[\text{Rh–C} - \text{Rh–O}] - [\text{Ir–C} - \text{Ir–O}] = 0.007 \text{ \AA}$), however, is not significant. An equivalent measure in the previously mentioned [*M*^{III}(bdpps)] complexes ($[\text{Rh–C} - \text{Rh–Cl}] - [\text{Ir–C} - \text{Ir–Cl}] = -0.050 \text{ \AA}$) is significant and substantially larger. Neither the olefinic C=C lengths nor the degree of olefin rehybridization differ significantly between [Ir(acac)(cod)] and [Rh(acac)(cod)], although the latter quantity is necessarily poorly determined in an X-ray experiment. In conclusion, any differences in bonding of the cod ligand between [Ir(acac)(cod)] and [Rh(acac)(cod)] are small and less than the combined experimental errors.

The O–Ir–O angle [91.6 (1)°] in [Ir(acac)(cod)] is significantly larger than the O–Rh–O angle [89.8 (2)°] in [Rh(acac)(cod)] but other bond lengths and angles in [Ir(acac)(cod)] do not differ from those in the Rh complex (Tucker, Scutcher & Russell, 1975).

A final difference synthesis shows four peaks, in approximately square-planar arrangement perpendicular to the Ir–C(6) vector, in the vicinity of the Ir atom (0.175, –0.106, 0.176, 0.6 e Å⁻³ at 0.77 Å from Ir and its symmetry-related peak, 0.125, 0.000, 0.145, 1.6 e Å⁻³ at 0.80 Å from Ir and 0.209, 0.000, 0.224, 1.3 e Å⁻³ at 0.82 Å from Ir). With *sp_xp_yd_{x²-y²}* hybridization for the σ -bonding orbitals of the metal, and if it is remembered that the *d_{yz}* and *d_{xz}* orbitals are of the correct symmetry for metal–olefin back-bonding, these peaks may reflect in part the excess electron density in the filled *d_{z²}* and *d_{xy}* orbitals.

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The Structure of *trans*-Diaquabis[(±)-hydrogen malato]cobalt(II) Dihydrate

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Abstract. $[\text{Co}\{(\pm)\text{-C}_4\text{H}_5\text{O}_5\}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $\text{C}_8\text{H}_{14}\text{CoO}_{12} \cdot 2\text{H}_2\text{O}$, triclinic, $P\bar{1}$, $a = 7.406$ (1), $b = 7.647$ (1), $c = 7.362$ (1) Å, $\alpha = 99.12$ (1), $\beta = 103.73$ (1), $\gamma = 63.72$ (1)°, $V = 362.5$ Å³, $Z = 1$, $d_c = 1.82$, $d_m = 1.80$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.31$ mm⁻¹, $R = 0.026$ and $R_w = 0.044$ for 1250 counter-collected reflections. The sixfold coordination polyhedron around the Co²⁺ ion consists of α -carboxylate and hydroxyl O atoms from each of two hydrogen malate ligands and two water molecules (*trans* configuration). The molecular symmetry is $\bar{1}$.

Introduction. Suitable crystals of the title compound for X-ray diffraction were grown by evaporation of an aqueous solution of the salt which had been prepared from the reaction of cobalt(II) carbonate and (±)-malic acid. A crystal with approximate dimensions 0.15 × 0.20 × 0.20 mm, which gave sharp optical extinction under crossed polarizers, was used. Unit-cell dimensions and X-ray intensity data were obtained using an automated diffractometer equipped with Zr-filtered Mo $K\alpha$ radiation. 1281 independent reflections out to 50° in 2θ were measured using the θ - 2θ scan technique.

The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$. 1250 reflections had $F_o > \frac{1}{2}\sigma(F_o)$ and were used in the structure solution and refinement. The structure was solved using conventional heavy-atom methods. With $Z = 1$, the formula unit is required to have crystallographic $\bar{1}$ symmetry. There are two independent water molecules and one independent hydrogen malate in the asymmetric unit. Refinement was by a full-matrix least-squares procedure, although the H atom parameters were not varied. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w , was taken to be $[\sigma(F_o)]^{-2}$. The structure converged to a

conventional R index, $\sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.026 and a weighted R_w index, $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, of 0.044. The goodness-of-fit was 1.49. In the last cycle of least-squares refinement the largest shift in any positional or thermal parameter was less than 5×10^{-3} times its own estimated standard deviation. A total of 106 parameters including one scale factor was refined yielding a data: parameter ratio of 11.8:1. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of F_o , $\sin \theta/\lambda$ or Miller indices indicated no unusual trends. The final difference map was essentially

Table 1. *Fractional positional parameters and their standard deviations* ($\times 10^4$ for nonhydrogen atoms; $\times 10^3$ for hydrogen atoms)

The isotropic temperature factors, B_{eq} (in Å²), for the nonhydrogen atoms were calculated from the anisotropic coefficients following the definition given by Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Co	0	0	0	1.75
O(1)	1373 (2)	1283 (2)	-1150 (2)	2.13
O(2)	3651 (2)	2532 (2)	-608 (2)	2.28
O(3)	1589 (2)	971 (2)	2341 (2)	2.19
O(4)	3129 (3)	2420 (2)	5823 (2)	3.09
O(5)	2476 (4)	5524 (2)	5975 (2)	4.52
O(6)	-2555 (2)	2695 (2)	263 (2)	2.82
O(7)	2426 (3)	-996 (2)	5318 (2)	3.61
C(1)	2600 (3)	1877 (3)	-66 (3)	1.75
C(2)	2847 (3)	1819 (3)	2048 (3)	1.70
C(3)	2275 (3)	3890 (3)	2962 (3)	2.28
C(4)	2659 (3)	4012 (3)	5065 (3)	1.97
H(O3)	212	37	337	
H(O4)	333	258	709	
H(C2)	432	108	251	
H1(C3)	316	430	265	
H2(C3)	86	462	252	
H1(O6)	-370	270	23	
H2(O6)	-238	338	121	
H1(O7)	189	-22	628	
H2(O7)	236	-210	545	