

Di- μ -chloro-bis[chloro(η^6 -*p*-cymene)osmium(II)]*

BY S. F. WATKINS AND F. R. FRONCZEK

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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Abstract. $(C_{10}H_{14}Cl_2Os)_2$, $M_r = 790.7$, monoclinic, $P2_1/n$, $a = 9.821(3)$, $b = 11.571(2)$, $c = 10.583(2)$ Å, $\beta = 113.42(2)^\circ$, $V = 1103.6(5)$ Å³, $Z = 2$, $D_c = 2.380$ Mg m⁻³ (D_m was not measured). The structure was solved by heavy-atom methods and refined by weighted full-matrix constrained least squares to a conventional R of 0.0248 over 2617 diffractometer data. Each Os of the centrosymmetric dimer is bonded to two bridging Cl [both 2.450(1) Å], a terminal Cl [2.389(2) Å], and the η^6 ring. Although the substituted ring is planar, the Os–C and C–C distances vary non-systematically. There is no direct interaction between metal atoms [Os...Os = 3.742(1) Å].

Introduction. The title compound was prepared during a study of the mechanism of reactions of triply-bridged dimeric arene complexes (Arthur & Stephenson, 1981). The diffraction analysis was undertaken to provide a structural model for possible reaction mechanisms, and also as a group exercise for a graduate seminar in X-ray crystallography.

A clear orange prismatic crystal was cleaved to produce a specimen measuring 0.14 × 0.14 × 0.34 mm. It was mounted with its direction of elongation approximately along the ϕ axis of an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator set for Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å, 45 kV, 20 mA, take-off angle 2.8°). Lattice constants at ~295 K were derived by least-squares refinement of 25 well centered reflections from all eight octants ($40^\circ < 2\theta < 42^\circ$).

The intensities of 3527 reflections in two octants having $1^\circ < \theta < 30^\circ$ were measured using a $\theta:2\theta$ scan technique, with $\Delta\theta = (0.6 + 0.35 \tan \theta)^\circ$ and an additional 25% on either side of $\theta(\text{peak})$ to provide an estimate of background. The intensity measured during a survey scan at 5° min⁻¹ determined the final scan

speed: if $I < 0.5\sigma(I)$, the intensity was judged too weak to observe; if $I > 50\sigma(I)$, the intensity measured during the survey scan was used; otherwise, a final scan speed was computed such that $I \sim 50\sigma(I)$, but in no case was the scan time allowed to exceed 180 s.

During data collection, three reflections were re-measured after every hour of X-ray exposure, and two other reflections were recentered after every 200 data points. No significant change in any of these measurements was observed. After all intensity data were collected, three reflections at $\chi \approx 90^\circ$, but with different $\sin \theta/\lambda$ and intensity values, were measured by the ψ -scan technique ($0 \leq \psi \leq 350^\circ$, $\Delta\psi = 10^\circ$). These data were then used to apply a numerical absorption correction to all intensity data [$\mu(\text{Mo } K\alpha) = 12.7$ mm⁻¹, minimum relative transmission factor = 60%]. All reflections $h0l$, $h + l$ odd, and $0k0$, k odd, were too weak to observe as required by space group $P2_1/n$.

A total of 2617 reflections with $I > 3\sigma(I)$ were used in the structure solution (Patterson and difference electron density Fourier syntheses) and weighted full-matrix least-squares refinement. The final refinement model incorporated the following features: anisotropic thermal parameters were refined for all nonhydrogen atoms; each non-methyl H, initially in a computed position, was constrained to 'ride' 1.02 Å from the attached C with a common isotropic thermal parameter (final value of $B = 3.2$ Å²); methyl H atoms were constrained as tetrahedral rigid groups with a common isotropic thermal parameter (C–H = 1.03 Å, HCH = 109.5°, $B = 6.4$ Å²); an isotropic extinction parameter was refined; a parameter was refined which adjusted the weight of each structure amplitude, $w^{-1} = \sigma^2(F_o) + gF_o^2$, such that the final goodness-of-fit $\sum w\Delta^2/(n - v)$ was 1.00 ($\Delta = |F_o - |F_c||$, $n = 2617$, $v = 131$, $g = 0.0003$). No parameter shifted more than 0.5 σ on the last cycle, and the largest peak on the final difference map was ca 0.5 e Å⁻³ in the region of Os.

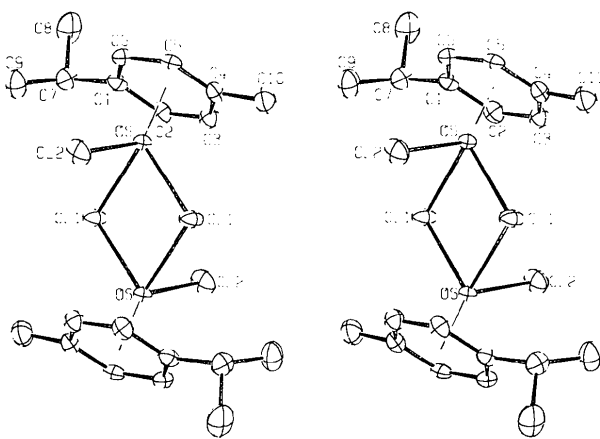
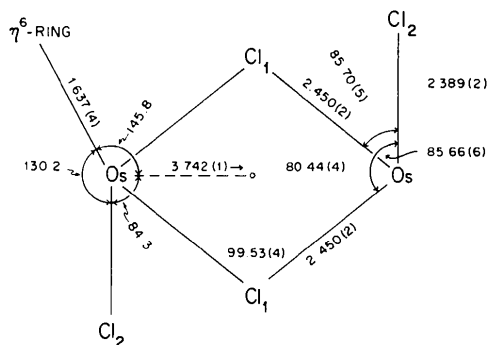
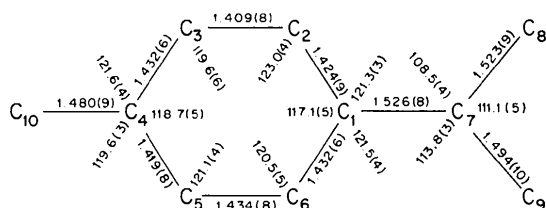
The final residual factors were $R = \sum \Delta/\sum F_o = 0.0248$, $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.0336$ ($R = 0.0309$ and $R_w = 0.0345$ over all 2935 unique measured reflections). The scattering factors used were those in *International Tables for X-ray Crystallography* (1974, pp. 99–101), but corrected for disper-

* This structural analysis was undertaken as a group exercise during a graduate seminar in crystallography. Class members were: K. A. Abboud, T. J. Delord, J. T. Donner, T. A. Ekman, M. A. Gutierrez, H. W. Lee, J. H. Medley, M. A. Oliver, R. V. Piccione, W. E. Puckett, D. R. Salinovich, E. M. Skelly, R. D. Snelling and M. M. Soroczak.

Table 1. Positional parameters ($\times 10^5$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

U_{eq} is as defined in *International Tables for X-ray Crystallography* (1974, p. 316).

	x	y	z	U_{eq}
Os	69337 (2)	44125 (1)	57293 (2)	244 (1)
Cl(1)	47254 (14)	44208 (11)	35646 (12)	409 (4)
Cl(2)	75554 (17)	61918 (11)	49434 (16)	510 (5)
C(1)	79578 (53)	29112 (40)	52033 (50)	337 (15)
C(2)	68883 (55)	25479 (42)	57156 (48)	372 (16)
C(3)	68973 (59)	29275 (42)	69847 (54)	400 (17)
C(4)	80158 (56)	37210 (40)	78107 (46)	340 (15)
C(5)	90951 (49)	41003 (43)	73258 (49)	320 (14)
C(6)	90775 (48)	37007 (41)	60366 (48)	329 (14)
C(7)	78956 (63)	24990 (48)	38119 (57)	422 (17)
C(8)	89295 (93)	14612 (54)	40849 (79)	754 (34)
C(9)	82093 (83)	34225 (52)	29767 (64)	589 (25)
C(10)	79984 (78)	42041 (58)	90992 (60)	537 (23)

Fig. 1. A stereoview of the $(C_{10}H_{14}Cl_2Os)_2$ molecule.Fig. 2. A schematic representation of the organic and inorganic moieties of the $(C_{10}H_{14}Cl_2Os)_2$ molecule containing bond distances (\AA) and angles ($^\circ$).

sion (Cromer & Liberman, 1970). Atomic coordinates are listed in Table 1, and Figs. 1 and 2 show the molecule.*

Discussion. The two halves of this dimeric molecule are related by a crystallographic inversion center and are joined by two Cl atoms symmetrically bridging two Os atoms. The interior angles of the four-atom bridge plane, and the large distance between Os atoms, indicate a complete lack of metal-metal bonding. The Cl atom terminally bonded to Os is nearly perpendicular to the bridge plane, but tilts 5.7° toward the adjacent Os atom. The ring centroid of the η -bonded *p*-cymene is $1.637(2)$ \AA from Os, 145.5° from the $Os \cdots Os'$ line, and in the plane containing the Os and terminal Cl atoms.

The C_6 ring is flat, with maximum deviation $0.003(2)$ \AA from the mean plane and $\chi^2 = 0.8$. This is in contrast to the slight folding reported in a somewhat analogous Ru^{II} monomer (Bennett, Robertson & Smith, 1972). However, the ring reported here is not regular since the C-C bond lengths differ significantly around the ring ($\chi^2 = 54$) and in a way apparently unrelated to the extra-annular substitution. Further, the organic substituents are not coplanar with C_6 but are bent slightly toward Os (methyl = 3.6° , isopropyl = 1.2°). Finally, the two methyl groups of the isopropyl moiety are not symmetrically placed with respect to the C_6 plane: C(8) is $1.409(2)$ \AA above and C(9) is $0.940(2)$ \AA below this plane; that is, the isopropyl group is twisted about the C(1)-C(7) bond by 25.8° . The general features of the *p*-cymene ligand are remarkably similar to those observed in *trans*-2,2'-azo-*p*-cymene (Wetherington, Holmes & Moncrief, 1974).

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References

- ARTHUR, T. & STEPHENSON, T. A. (1981). *J. Organomet. Chem.* Submitted.
 BENNETT, M. A., ROBERTSON, G. B. & SMITH, A. K. (1972). *J. Organomet. Chem.* **43**, C41-C43.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 WETHERINGTON, J. B., HOLMES, K. D. JR & MONCRIEF, J. W. (1974). *Acta Cryst.* **B30**, 246-249.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36281 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.