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Stereochemistry of Transition Metal Cyclooctatetraenyl Complexes. Tris(cyclooctatetraene)dichromium, a Novel Stereochemistry for a Compound Containing a Quadruple Metal–Metal Bond

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Received March 26, 1976 AIC602341

The crystal structure of $(C_8H_8)_3Cr_2$ has been determined from single-crystal, three-dimensional, x-ray diffraction data collected by counter methods. The crystals belong to the monoclinic system, space group $P2_1$, with unit cell constants $a = 10.485$ (3), $b = 11.819$ (4), $c = 7.571$ (2) Å, and $\beta = 99.64$ (2)°. The calculated density is 1.49 g cm^{-3} for $Z = 2$. Two forms of intensity data were collected with 2θ(Mo K$\bar{\alpha}$) $\leq 50°$. Averaging of the data set, with due regard given to the anomalous dispersion effect, yielded 2443 unique reflections of which 85 were considered to be "unobserved". The structure was refined by anisotropic least-squares methods, and the absolute configuration of the molecule was determined. The final values for the conventional and weighted R indices were 0.028 and 0.032, respectively. The crystal structure consists of discrete, binuclear molecules with no crystallographic symmetry. Cr(1) bonds to a "π-butadiene" fragment of C_8H_8 ring 1, and Cr(2) interacts similarly with the second C_8H_8 ligand. The third C_8H_8 ring lies below the Cr–Cr vector and forms π bonds to both metal atoms. The highest symmetry for this molecule is $2mm$ (C_{2v}); however, a 12.4° twisting of the C_8H_8 ligands 1 and 2 relative to one another reduces steric repulsion between these rings and lowers the molecular symmetry to 2 (C_2). Thus the chirality of the molecule is of little chemical significance. The metal–metal distance is 2.214 (1) Å. A quadruple Cr–Cr bond can be postulated to explain this short distance.

Introduction

1,3,5,7-Cyclooctatetraene (COT) complexes of the type $(COT)_3M_2$ (M = Cr, Mo, W) have been reported by Breil and Wilke.[1] Nothing is known about the structural details of these compounds, which are reported to be diamagnetic.[2] A compound of similar stochiometry, $(COT)_3Ti_2$, possesses a distorted "triple decker" structure, six carbon atoms of the central ring bonding "π butadienelike" to the metal atoms of the two (η-COT)Ti moieties.[3] A similar stereochemistry for a compound of the group 6A elements would be unprecedented. In order to elucidate the structure and bonding in the $(COT)_3M_2$ complexes, we have characterized $(COT)_3Cr_2$ (I) by single-crystal x-ray diffraction techniques.

Experimental Section

Black crystals of I were kindly supplied by Dr. Breil.[25] A wedge-shaped specimen was placed in an argon filled glass capillary. Crystalline quality was checked and preliminary unit cell constants and space group data were obtained by Weissenberg and precession photography. The crystal was transferred to a Siemens AED automated diffractometer. Theta values for 53 Mo K$\bar{\alpha}$, Mo Kα_1, or Mo Kα_2 intensity maxima θ_{max} of a number of high angle reflections were measured by scanning the reflections in θ with a thin slit collimator inserted before the counter window. A least-squares procedure was used to derive the unit cell constants from the θ_{max} measurements. Crystal data appear in Table I.

Table I. Crystal Data

Formula	$C_{24}H_{24}Cr_2$
Molecular wt	416.45
Color	Black
Crystal size	0.13 × 0.97 × 0.86 mm
Crystal system	Monoclinic
Cell dimensions	$a = 10.485$ (3) Å[a]
	$b = 11.819$ (4) Å
	$c = 7.571$ (2) Å
	$\beta = 99.64$ (2)°
	$V = 925$ Å^3
	$Z = 2$
	$d_c = 1.49$ g cm^{-3}
	d_m = not measured[b]
μ(Mo K$\bar{\alpha}$), cm^{-1}	12.3
Systematic absences	$0k0$, $k = 2n + 1$
Space group	$P2_1$
λ(Mo K$\bar{\alpha}$), Å	0.710 69

[a] Numbers in parentheses following numerical values here and throughout the paper are the standard deviations in the least significant digit. [b] The extreme air and moisture sensitivity of the compound prevented a reliable density measurement.

The intensities of the left half (PL), right half (PR), and full peak (PK) were measured by three θ–2θ scans of time t, t, and $2t$ s, respectively. Stationary-crystal, stationary-counter background measurements, BL and BR, of t s were made at the left and right ends of the peaks, respectively. Zirconium filtered Mo K$\bar{\alpha}$ radiation was used. Data collection time and coincident losses were minimized by the automated selection of one of three scan speeds and one of six Zr attenuators for each reflection. The symmetrical scan ranges (1.20–1.80° in 2θ) were chosen from a function of the Bragg angle. During data collection one reflection 006 was remeasured periodically. Apart from an abrupt 10% intensity drop half-way through the experiment, the variations in the intensity of this reflection were random. Two forms of data ($2\theta \leq 50°$) were measured. At the end of data collection the crystal faces were measured and indexed.

The intensities were given by $I_0 = k[0.5(\text{PL} + \text{PR} + \text{PK}) - (\text{BL} + \text{BR})]$, where k is a scaling constant which contains corrections for the scanning speed, attenuator, and standard reflection fluctuation. The data were also corrected for absorption. The transmittance A varied from 0.51 to 0.87.[4] The data were then converted to structure factor amplitudes $|F_o|$, $|F_o| = (I_0/ALp)^{1/2}$, where Lp is the Lorentz and polarization correction. Of the 3264 reflections measured, 3147 had $I_0 \geq 2\sigma(I_0)$, where $\sigma(I_0) = k[0.25(\text{PL} + \text{PR} + \text{PK}) + \text{BL} + \text{BR}]$, and were considered "observed". The other reflections were labeled "unobserved" and were assigned weights w of zero. The "observed" $|F_o|$'s were assigned w equal to $1/\sigma^2(|F_o|)$, $\sigma^2(|F_o|)$ being derived from $\sigma^2(I) = \sigma^2(I_0) + (0.03I_0)^2$.

Averaging of the equivalent data yielded 1714 reflections (50 "unobserved") and 2443 reflections (85 "unobserved") assuming point group symmetry $2/m$ or 2, respectively. The former averaging is not valid for the space group $P2$ when anomalously scattering atoms are present; thus the latter data set was used in the final stages of refinement.

The structure was solved by the heavy-atom technique. The locations of two unique chromium atoms in general positions were derived from a sharpened Patterson synthesis; thus the space group was shown to be $P2_1$. The positions of the 24 carbon atoms were taken from a subsequent Fourier map.

The structure was refined by full-matrix and later by large block least-squares techniques. The function minimized was $\sum w\Delta^2$, where $\Delta = ||F_o| - |F_c||$. Relativistic scattering factors[5] were used for all atoms except H.[6] The real and imaginary components of the anomalous scattering factor of the Cr atoms[7] were included in the calculation of F_c. The discrepancy indices R and R_w are defined as $\sum\Delta/\sum|F_o|$ and $[\sum w\Delta^2/\sum w|F_o|^2]^{1/2}$, respectively. The origin of the unit cell was fixed by holding the y parameter of Cr(1) constant.

Isotropic refinement yielded $R = 0.072$ and $R_w = 0.093$. Anisotropic refinement lowered these values to 0.042 and 0.055, respectively. A difference density synthesis confirmed the structure

Table II. Positional and Thermal Parameters for $(C_8H_8)_3Cr_2$

	x	y	z	$U_{11}{}^a$ or $U_{iso}{}^b$	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cr(1)	0.194 14 (4)	0.000 00	0.195 40 (5)	0.0335 (3)	0.0355 (2)	0.0282 (2)	0.0016 (2)	−0.0049 (2)	0.0064 (2)
Cr(2)	0.397 67 (4)	0.055 68 (5)	0.268 95 (5)	0.0353 (3)	0.0291 (2)	0.0239 (2)	−0.0011 (2)	−0.0013 (2)	0.0056 (2)
C(11)	0.003 2 (5)	0.103 5 (4)	0.089 5 (6)	0.067 (3)	0.069 (2)	0.067 (2)	0.036 (2)	0.009 (2)	0.018 (2)
C(12)	0.064 5 (4)	0.126 7 (3)	0.262 6 (6)	0.048 (2)	0.044 (2)	0.084 (3)	0.008 (2)	−0.016 (2)	0.021 (2)
C(13)	0.102 2 (3)	0.053 9 (4)	0.407 3 (4)	0.039 (2)	0.076 (2)	0.045 (2)	−0.001 (2)	−0.020 (2)	0.017 (1)
C(14)	0.090 8 (4)	−0.061 6 (4)	0.419 4 (5)	0.063 (3)	0.077 (3)	0.051 (2)	0.014 (2)	0.013 (2)	0.028 (2)
C(15)	−0.012 3 (8)	−0.139 6 (4)	0.352 7 (9)	0.131 (6)	0.054 (3)	0.121 (4)	−0.005 (3)	0.007 (3)	0.077 (4)
C(16)	−0.114 7 (8)	−0.138 6 (6)	0.213 0 (14)	0.091 (5)	0.106 (5)	0.182 (7)	−0.064 (4)	−0.086 (5)	0.081 (5)
C(17)	−0.145 4 (5)	−0.067 2 (8)	0.065 0 (10)	0.036 (3)	0.161 (7)	0.117 (5)	−0.014 (4)	−0.076 (5)	0.011 (3)
C(18)	−0.093 7 (5)	0.025 3 (6)	0.014 3 (6)	0.052 (3)	0.153 (6)	0.064 (3)	0.042 (3)	−0.033 (3)	−0.011 (2)
C(21)	0.520 2 (4)	0.036 2 (3)	0.555 5 (4)	0.066 (2)	0.052 (2)	0.032 (2)	−0.016 (2)	0.002 (1)	0.002 (1)
C(22)	0.421 5 (4)	0.115 5 (3)	0.537 4 (4)	0.051 (2)	0.065 (2)	0.030 (1)	−0.025 (2)	−0.015 (2)	0.014 (1)
C(23)	0.394 2 (4)	0.206 6 (3)	0.417 4 (5)	0.046 (2)	0.043 (2)	0.053 (2)	−0.001 (2)	−0.019 (1)	0.010 (2)
C(24)	0.463 3 (4)	0.239 0 (3)	0.278 5 (4)	0.056 (2)	0.030 (1)	0.048 (2)	−0.003 (1)	−0.003 (1)	0.004 (2)
C(25)	0.595 7 (4)	0.243 0 (3)	0.262 0 (5)	0.061 (3)	0.047 (2)	0.047 (2)	−0.018 (2)	0.005 (1)	0.016 (2)
C(26)	0.707 3 (4)	0.194 7 (3)	0.344 0 (5)	0.052 (2)	0.058 (2)	0.053 (2)	−0.014 (2)	−0.010 (2)	0.014 (2)
C(27)	0.734 2 (4)	0.107 3 (3)	0.471 8 (5)	0.042 (2)	0.055 (2)	0.067 (2)	0.001 (2)	−0.010 (2)	−0.005 (2)
C(28)	0.655 4 (4)	0.038 3 (3)	0.548 6 (5)	0.060 (2)	0.049 (2)	0.054 (2)	0.000 (2)	0.005 (2)	−0.017 (2)
C(31)	0.240 0 (3)	−0.171 9 (3)	0.135 8 (5)	0.043 (2)	0.038 (2)	0.060 (2)	−0.003 (1)	−0.013 (1)	0.016 (2)
C(32)	0.181 7 (3)	−0.125 4 (3)	−0.024 7 (4)	0.039 (2)	0.060 (2)	0.047 (2)	−0.008 (2)	−0.027 (2)	0.009 (1)
C(33)	0.198 5 (3)	−0.016 2 (3)	−0.085 8 (3)	0.040 (2)	0.074 (2)	0.025 (1)	0.006 (2)	−0.010 (1)	−0.001 (1)
C(34)	0.297 9 (3)	0.066 0 (3)	−0.026 4 (3)	0.054 (2)	0.053 (2)	0.028 (1)	0.007 (2)	0.004 (1)	0.007 (1)
C(35)	0.437 1 (3)	0.053 2 (3)	−0.001 0 (3)	0.047 (2)	0.053 (2)	0.028 (1)	−0.001 (2)	−0.001 (1)	0.014 (1)
C(36)	0.513 0 (3)	−0.031 7 (3)	0.091 6 (4)	0.032 (2)	0.056 (2)	0.046 (2)	−0.004 (1)	−0.019 (1)	0.012 (1)
C(37)	0.480 3 (3)	−0.106 1 (2)	0.217 5 (4)	0.045 (2)	0.036 (2)	0.047 (2)	0.009 (1)	−0.008 (1)	0.002 (1)
C(38)	0.353 7 (3)	−0.135 5 (3)	0.256 6 (4)	0.043 (2)	0.034 (1)	0.050 (2)	0.000 (1)	0.001 (1)	0.006 (1)
H(11)	0.019 (4)	0.167 (3)	0.004 (5)	0.05					
H(12)	0.110 (4)	0.199 (3)	0.289 (5)	0.05					
H(13)	0.159 (4)	0.090 (3)	0.508 (5)	0.05					
H(14)	0.142 (4)	−0.098 (3)	0.507 (5)	0.05					
H(15)	0.002 (4)	−0.191 (3)	0.411 (5)	0.05					
H(16)	−0.165 (4)	−0.189 (3)	0.216 (5)	0.05					
H(17)	−0.238 (4)	−0.076 (3)	−0.013 (4)	0.05					
H(18)	−0.129 (4)	0.034 (3)	−0.116 (4)	0.05					
H(21)	0.512 (4)	−0.035 (3)	0.623 (4)	0.05					
H(22)	0.360 (4)	0.101 (3)	0.603 (5)	0.05					
H(23)	0.310 (4)	0.237 (3)	0.413 (5)	0.05					
H(24)	0.411 (4)	0.299 (3)	0.191 (5)	0.05					
H(25)	0.599 (4)	0.285 (3)	0.183 (5)	0.05					
H(26)	0.805 (4)	0.218 (3)	0.308 (5)	0.05					

	x	y	z	$U_{iso}{}^b$
H(27)	0.815 (4)	0.085 (3)	0.498 (5)	0.05
H(28)	0.700 (4)	−0.034 (3)	0.606 (4)	0.05
H(31)	0.186 (4)	−0.236 (3)	0.178 (5)	0.05
H(32)	0.097 (4)	−0.156 (3)	−0.080 (5)	0.05
H(33)	0.133 (4)	0.010 (3)	−0.168 (4)	0.05
H(34)	0.281 (4)	0.135 (3)	−0.064 (5)	0.05
H(35)	0.472 (4)	0.106 (3)	−0.049 (5)	0.05
H(36)	0.597 (4)	−0.019 (3)	0.095 (4)	0.05
H(37)	0.548 (4)	−0.142 (3)	0.301 (5)	0.05
H(38)	0.358 (4)	−0.180 (3)	0.362 (5)	0.05

[a] The form of the anisotropic thermal ellipsoids is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The form of the isotropic temperature factor is: $\exp[-8\pi^2U\sin^2\theta/\lambda^2]$.

and yielded reasonable positions for the 24 hydrogen atoms. The H atoms were assigned mean-square vibration amplitudes of 0.05 Å². Anisotropic refinement (only the positional parameter of the H atoms being varied) converged at $R = 0.028$ and $R_w = 0.032$.[8] On the last cycle no parameter shifted more that 10% of its error, estimated from the diagonal elements of the inverted least-squares matrix. An examination of $\langle w\Delta^2\rangle$ as a function of $|F_o|$, $\sin\theta/\lambda$, and the Miller indices confirmed the relative validity of the weighting scheme. The error of fit is 1.68. Refinement of the structure with $\Delta f''$ of the Cr atoms given the opposite sign yielded $R = 0.036$ and $R_w = 0.043$, values which are clearly larger than those obtained using the correct sign for $\Delta f''$. Thus the absolute configuration of the compound is most likely to be that defined by the positional parameters obtained from the original refinement[9] (Table II).

The numbering scheme of the Cr and C atoms is that given in Figure 1. The C atoms are numbered C(*ij*), where *i* specifies the COT ring in which that atom appears. Hydrogen atoms are numbered after the carbon atoms to which they are attached. Bond distances and bond angles are listed in Tables III and IV, respectively.

Description of the Crystal Structure

Crystals of I consist of discrete, binuclear molecules. The intermolecular contacts are normal, the shortest being H(17)–H(36) ($x - 1, y, z$), 2.14 (5) Å.

As can be seen in Figure 1, the structure of I bears no resemblance to that of $(COT)_3Ti_2$. In I the Cr atoms participate in three distinct types of bonding. First, Cr(1) and Cr(2) forms sandwich bonds to a "butadiene" fragment of COT rings 1 and 2, respectively. Second, both Cr atoms are sandwich bonded to two "pentadienyl" fragments of COT ring 3, C(34) and C(38) being the atoms common to both fragments. Third, the Cr atoms form a strong metal–metal bond. While no crystallographic symmetry is imposed on the molecule, I possesses approximate 2*mm* (C_{2v}) symmetry and almost exact 2 (C_2) symmetry. The distortion from 2*mm* symmetry probably results from steric crowding of H(12) with H(23) and H(13) with H(22). Thus the angle between the bonds C(12)–C(13) and C(22)–C(23) is 12.4°; 2*mm* symmetry requires this angle to be zero. The chirality of the molecule is thus of little chemical significance. If we assume that the errors estimated from the least-squares refinement are too small by a factor of 2, the bond lengths between Cr atoms and the 1-4η-COT rings obey 2 symmetry and the remaining bonds obey 2*mm* symmetry satisfactorily. When

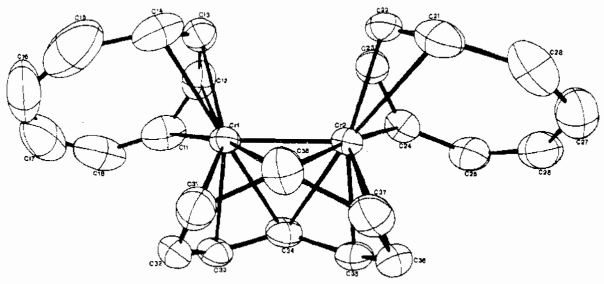

Figure 1. A perspective drawing of $(C_8H_8)_3Cr_2$. Hydrogen atoms have been omitted for the sake of clarity.

Table III. Selected Bond Distances (Å) in $(C_8H_8)_3Cr_2$

Cr(1)–Cr(2)	2.214 (1)	C(12)–C(13)	1.398 (5)
Cr(1)–C(11)	2.369 (5)	C(22)–C(23)	1.407 (5)
Cr(2)–C(21)	2.341 (3)	Av	1.402 (6)
Av	2.355 (20)[a]		
		C(11)–C(18)	1.420 (8)
Cr(1)–C(12)	2.140 (4)	C(14)–C(15)	1.447 (8)
Cr(2)–C(22)	2.127 (3)	C(21)–C(28)	1.428 (6)
Av	2.134 (9)	C(24)–C(25)	1.416 (6)
		Av	1.429 (14)
Cr(1)–C(13)	2.104 (3)		
Cr(2)–C(23)	2.112 (3)	C(15)–C(16)	1.376 (12)
Av	2.108 (6)	C(17)–C(18)	1.306 (10)
		C(25)–C(26)	1.356 (6)
Cr(1)–C(14)	2.279 (4)	C(27)–C(28)	1.359 (6)
Cr(2)–C(24)	2.272 (3)	Av	1.349 (30)
Av	2.276 (5)		
		C(16)–C(17)	1.397 (12)
Cr(1)–C(31)	2.153 (3)	C(26)–C(27)	1.412 (6)
Cr(1)–C(33)	2.146 (3)	Av	1.404 (10)
Cr(2)–C(35)	2.153 (3)		
Cr(2)–C(37)	2.162 (3)	C(31)–C(32)	1.380 (5)
Av	2.154 (7)	C(32)–C(33)	1.393 (5)
		C(35)–C(36)	1.395 (4)
Cr(1)–C(32)	2.218 (3)	C(36)–C(37)	1.382 (4)
Cr(2)–C(36)	2.208 (3)	Av	1.388 (8)
Av	2.213 (7)		
		C(31)–C(38)	1.442 (5)
Cr(1)–C(34)	2.286 (3)	C(33)–C(34)	1.441 (5)
Cr(1)–C(38)	2.307 (3)	C(34)–C(35)	1.448 (5)
Cr(2)–C(34)	2.309 (3)	C(37)–C(38)	1.450 (5)
Cr(2)–C(38)	2.305 (3)	Av	1.445 (4)
Av	2.302 (11)		
		C–H Av	0.94 (10)
C(11)–C(12)	1.388 (6)		
C(13)–C(14)	1.375 (7)		
C(21)–C(22)	1.387 (5)		
C(23)–C(24)	1.427 (5)		
Av	1.394 (23)		

[a] These are average values. The standard deviations of the mean are the larger of the estimates calculated by the formulas $[\Sigma_{i=1}^{N}(l_i - \bar{l})/(N-1)]^{1/2}$ and $[\Sigma_{i=1}^{N}\sigma^2(l_i)/N]^{1/2}$.

Table IV. Selected Bond Angles (deg) in $(C_8H_8)_3Cr_2$

C(12)–C(11)–C(18)	134.1 (4)	C(32)–C(31)–C(38)	129.6 (3)
C(13)–C(14)–C(15)	132.7 (4)	C(32)–C(33)–C(34)	130.3 (3)
C(22)–C(21)–C(28)	135.6 (3)	C(34)–C(35)–C(36)	128.4 (3)
C(23)–C(24)–C(25)	134.5 (3)	C(36)–C(37)–C(38)	129.4 (3)
Av[a]	134.2 (12)	Av	129.4 (8)
C(11)–C(12)–C(13)	130.2 (4)	C(31)–C(32)–C(33)	126.8 (3)
C(12)–C(13)–C(14)	130.3 (3)	C(35)–C(36)–C(37)	128.2 (3)
C(21)–C(22)–C(23)	130.5 (3)	Av	127.5 (10)
C(22)–C(23)–C(24)	127.5 (3)		
Av	129.6 (14)	C(33)–C(34)–C(35)	129.1 (3)
		C(31)–C(38)–C(37)	129.1 (3)
C(14)–C(15)–C(16)	134.8 (5)	Av	129.1 (3)
C(11)–C(18)–C(17)	137.0 (5)		
C(24)–C(25)–C(26)	136.9 (3)	Cr(1)–C(34)–Cr(2)	57.6 (2)
C(21)–C(28)–C(27)	134.8 (4)	Cr(1)–C(38)–Cr(2)	57.4 (2)
Av	135.9 (12)	Av	57.5 (2)
C(15)–C(16)–C(17)	131.9 (7)		
C(16)–C(17)–C(18)	133.6 (6)		
C(25)–C(26)–C(27)	132.9 (4)		
C(26)–C(27)–C(28)	131.8 (4)		
Av	132.6 (9)		

[a] See Table III.

Table V. Selected Best Weighted[a] Least-Squares Planes in $(C_8H_8)_3Cr_2$

Equations of the Best Planes

Plane No.	
1	$0.9517X^{b} - 0.1159Y - 0.2842Z + 0.4059 = 0$
2	$-0.4766X - 0.6008Y - 0.6418Z + 5.1804 = 0$
3	$0.7015X - 0.4917Y - 0.5159Z + 0.9702 = 0$
4	$0.0148X - 0.6578Y - 0.7530Z + 3.3292 = 0$
5	$0.8430X - 0.3188Y - 0.4334Z - 2.1847 = 0$
6	$-0.2206X - 0.6505Y - 0.7268Z + 1.4145 = 0$
7	$0.6923X - 0.4439Y - 0.5689Z - 1.9576 = 0$
8	$0.0184X - 0.6592Y - 0.7518Z - 0.3149 = 0$

Deviations (Å) of Atoms from Their Best Planes

1	C(11), −0.002 (5); C(12), 0.003 (4); C(13), −0.002 (4); C(14), 0.001 (5); Cr(1),[c] 1.6935 (5)
2	C(21), −0.002 (3); C(22), 0.004 (3); C(23), −0.004 (3); C(24), 0.002 (3); Cr(2),[c] 1.6717 (5)
3	C(11), −0.032 (5); C(14), 0.008 (4); C(15), 0.019 (7); C(16), −0.078 (9); C(17), −0.017 (7); C(18), 0.067 (6)
4	C(21), −0.004 (3); C(24), −0.028 (3); C(25), 0.055 (4); C(26), −0.015 (4); C(27), −0.051 (4); C(28), 0.040 (4)
5	C(31), 0.000 (4); C(32), 0.000 (3); C(33), 0.000 (3); Cr(1),[c] −1.3093 (4)
6	C(35), 0.000 (3); C(36), 0.000 (3); C(37), 0.000 (3); Cr(2),[c] −1.3175 (5)
7	C(31), −0.009 (3); C(33), 0.008 (3); C(34), −0.006 (3); C(38), 0.007 (3); C(32),[c] 0.146 (3); Cr(1),[c] −1.5494 (4)
8	C(34), 0.007 (3); C(35), −0.009 (3); C(37), 0.009 (3); C(38), −0.007 (3); C(36),[c] 0.145 (3); Cr(2),[c] −1.5576 (5)

Dihedral Angles (deg) between Various Best Planes

∠1,3 = 150.6[d]	∠5,6 = 70.4	∠6,8 = 13.8
∠2,4 = 150.6[d]	∠5,7 = 13.7	∠7,8 = 42.9

[a] The Cartesian coordinates X, Y, Z are related to the monoclinic coordinates x, y, z as follows: $X, Y, Z = ax + cz \cos\beta, by, cz \sin\beta$. [b] The weight of an atom was the inverse of the variance of that atom along the normal of the best plane. [c] This atom was not included in the best plane calculation. [d] This angle is the supplement of the angle derived from the above given equations.

possible, we will refer to average values with standard deviations estimated from the distribution of the above described populations.

The average bond lengths between the Cr atoms and the terminal C atoms of the "butadiene" fragments are unequal, 2.355 (20) and 2.276 (5) Å, probably because of the steric crowding referred to previously. The interaction of the Cr atoms with the central C atoms of these fragments is stronger and essentially symmetric, these Cr–C bond lengths averaging 2.134 (9) and 2.108 (6) Å. No significant difference is shown by the average values of the inner and outer C–C bonds of the coordinated "butadiene" fragment, 1.402 (6) and 1.394 (23) Å, respectively. More localized C–C bonding is probably present in the uncoordinated "butadiene" residue, the inner and outer C–C bonds averaging 1.404 (10) and 1.349 (30) Å, respectively. The C–C bonds between the coordinated and uncoordinated "butadiene" fragments appear to have some double bond character since the bond lengths average 1.429 (14) Å. COT rings 1 and 2 are in the bent conformation. The dihedral angles between the best planes defined by atoms C(*n*1), C(*n*2), C(*n*3), C(*n*4) and by atoms C(*n*1), C(*n*4), C(*n*5), C(*n*6), C(*n*7), C(*n*8) are 150.6° for $n = 1$ and $n = 2$. The C–H bonds of the coordinated "butadiene" fragments are inclined, on the average, 14 (4)° toward the Cr atoms with respect to the plane of the four C atoms.

The bonds Cr–C(COT ring 3) show a systematic variation; that is, average values of 2.154 (7), 2.213 (7), and 2.302 (11) Å are found when C is like C(31), C(32), and C(34), respectively. Since C(34) and C(38) bond to both Cr atoms, it is not surprising that these Cr–C bonds are the longest of the three types. The inner C–C bonds (average 1.388 (8) Å) of the "pentadienyl" fragment are shorter than the outer C–C bonds (average 1.445 (4) Å). The third COT ring folds away from the two Cr atoms along the line defined by atoms C(34) and C(38). The angle between the normals of the best planes of the two "pentadienyl" fragments is 48.0°. Examination of the dihedral angles listed in Table V indicates that the third COT ring is also folded, albeit to a lesser extent, along the line segments C(31)–C(33) and C(35)–C(37). The H atoms bonded to C(31), C(32), or C(33) lie on the Cr(1) side of the plane through these three carbon atoms, and the H atoms bonded to C(34), C(35), or C(37) show a similar feature. On the average, the corresponding C–H bonds are inclined 21 (3)° with respect to the relevant carbon atom planes.

The short Cr–Cr distance of 2.214 (1) Å indicates that this bond is multiple in character. Each Cr atom obtains four electrons from a 1-4η-COT ring and another four electrons from the bridging ligand, the electrons of C(34) and C(38) being shared equally by the metal atoms. The Cr atoms need four more electrons in order to obtain a closed shell configuration. The assumption of a Cr–Cr quadruple bond meets this need.

Discussion

The dihedral angles of COT rings 1 and 2 (150.6°) are larger than that reported for $(COT)Ru(CO)_3$, 136.3 (5)°,[10] but smaller than that found for the *tetrahapto* ring in $(COT)_2Zr\cdot THF$, 159.4°.[11] The dihedral angle of a bent COT ring reflects the interplay of at least two types of forces: (1) π conjugation which favors a planar conformation, and (2) C–C–C valence angle strain which favors a nonplanar ring. In a symmetry based, molecular orbital description of butadiene–metal sandwich bonding, two bonds may be formed by the two filled butadiene π orbitals and two empty metal orbitals; two more bonds may be formed by a back donation of charge from filled metal orbitals and the empty butadiene π^* orbitals. A detailed discussion of this bonding scheme has been published.[12] If a butadiene species is a fragment of a COT ring, the back-bonded charge might be stabilized on the ring by conjugation with the uncoordinated "butadiene" residue. Thus metal to COT ligand charge transfer should stimulate an increase in delocalized ring π bonding and, as a by-product, tend to enlarge the dihedral angle. Thus the Cr atoms of I appear to be better π bases than the Ru atom of $(COT)Ru(CO)_3$ but poorer π bases than the Zr atom of $(COT)_2Zr\cdot THF$.

A few examples of the bonding of two transition metals to a COT ligand have been investigated by x-ray diffraction methods. With the exception of $COT\{Fe(CO)_3\}_2$,[13] a description of these compounds has appeared in a review.[14] In each case cited, the metal atoms bridged by the COT ligand form long, single, metal–metal bonds. The average metal–carbon distance of the COT carbon atoms bonding to both metal atoms is generally much longer than the other metal–C(COT) bonds; for example, in $(COT)Fe_2(CO)_5$[15] the difference in the lengths of these two types of bonds is nearly 0.4 Å. In I this difference is less than 0.15 Å. Undoubtedly the short, multiple bond character of the Cr–Cr interaction works to strengthen the Cr(1)–C(34,38)–Cr(2) interactions with respect to the corresponding interaction in $(COT)Fe_2(CO)_5$.

The Cr–Cr distance in I (2.214 (1) Å) is 0.23 Å longer than the Cr–Cr bond length of 1.980 (5) Å in $(Li\cdot THF)_4Cr_2(CH_3)_8$,[16] of 1.975 (5) Å in $[Li\cdot O(C_2H_5)_2]_4Cr_2[(CH_2)_4]_4$,[17] and of 1.975 Å in $Cr_2(C_3H_5)_4$.[18] Quadruple Cr–Cr bonds presumably exist in the latter three compounds. Strong quadruple bonds have also been postulated to explain the short Cr–Cr bond distances in $Cr_2(O_2CCH_3)_4\cdot 2H_2O$, 2.362 (1) Å,[19] and $MgCr_2(CO_3)_4\cdot 6H_2O$, 2.22 Å.[20] The large variations in Cr–Cr quadruple bond distances have received comment by other authors, but no explanation for this fact has been offered.[21] We will only point out that the Cr atoms in those compounds with Cr–Cr distances less than 2.0 Å have 16 electron configurations while the other compounds possess Cr atoms with 18 electrons in their valence shell. A similar problem is involved in the interpretation of the variation of the Cr–Cr distance in two recently investigated diamagnetic compounds, $\{[\eta\text{-}(CH_3)_5C_5]CrO\text{-}\mu\text{-}O\}_2$ (II)[22,23] and $\{[\eta\text{-}(CH_3)_5]Cr(CO)_2\}_2$ (III).[24] On the basis of the rare gas rule, one might expect that both compounds contain Cr–Cr triple bonds. The Cr–Cr distances are 2.512 (1) Å in II and 2.280 (2) Å in III. Consideration of the formal oxidation states of the Cr atoms in these complexes, +5 in II and +1 in III, helps to explain the variation in the bond lengths; the Cr atoms of II have fewer electrons available for metal–metal bonding than the Cr atoms of III. The detection of these multiple bonds in compounds with widely varying stereochemistries shows that such interactions are important in the inorganic and organometallic chemistry of chromium.

Since the importance of metal–metal bonding is believed to increase as one moves down the periodic table and since the compounds $(COT)_3Mo_2$ and $(COT)_3W_2$ are known,[1] we suggest that these complexes possess structures similar to that of I.

Registry No. I, 59982-80-8.

Supplementary Material Available: A listing of observed and calculated structure amplitudes (24 pages). Ordering information is given on any current masthead page.

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