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Crystallographic Study of Dicarbonylpentamethylcyclopentadienylchromium Dimer, a Complex with a Cr≡Cr Bond[1]

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The crystal structure of dicarbonylpentamethylcyclopentadienylchromium dimer has been determined by a single-crystal three-dimensional X-ray diffraction study. The structure consists of discrete centrosymmetric $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ units, each with a short Cr–Cr bond distance [2.280 (2) Å]. The Cr–Cr triple bond length in $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ is greater than the Cr–Cr quadruple bond lengths in $Li_4[Cr_2(CH_3)_8]\cdot 4C_4H_8O$ [1.98 Å] and $Cr_2(C_3H_5)_4$ [1.98 Å] but less than the Cr–Cr distance in $Cr_2(O_2CCH_3)_4\cdot 2H_2O$ [2.362 Å] for which a quadruple bond has also been suggested. Carbonyl groups, two per chromium, are staggered with respect to the Cr–Cr axis and the Cr–C–O atoms are nearly collinear [angles 170.8 (6), 174.8 (6)°]. Detailed analysis of bond distances and angles suggests that the carbonyl groups are essentially terminal. The $(CH_3)_5C_5$ rings exhibit nearly perfect C_{5v} symmetry and are trans with respect to the Cr–Cr axis. However, Cr–C(ring) distances are nonequivalent; this is ascribed to steric crowding between the ring and carbonyl groups which forces the latter to lie over the Cr–Cr bond [Cr′–Cr–CO angles 73.0 (3), 79.1 (3)°]. Short contacts are also observed between the carbonyl groups and the molecule appears to be quite crowded sterically. Crystallographic data are as follows: space group $P2_1/n$; unit cell $a = 8.717$ (6) Å, $b = 14.716$ (4) Å, $c = 9.867$ (5) Å, $\beta = 112.00$ (5)°; $U = 1173$ Å^3; d_{calcd} for $Z = 2$ is 1.408 and d_{obsd} is 1.41 (2) g/cm^3. Diffractometer data (1411 independent reflections with $F^2 \geqslant 3\sigma$) were used to refine the structure anisotropically to final values of $R_F = 0.053$ and $R_{wF} = 0.061$.

Introduction

Binuclear transition metal complexes containing metal–metal bonds have been studied extensively in recent years.[2] Many of these complexes, with nominal bond orders ranging from 1 to 4, have been characterized structurally.[3-7] Considerable attention has been given to bonds of high order because, as a class, they constitute the strongest known chemical bonds[2a] and because no simple theory has been able to account for the M–M bond distances observed in a wide variety of compounds.

The chromium complex $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$[8] and the molybdenum complexes $[(\pi\text{-}C_9H_9)Mo(CO)_2]_2$[9] and $[(\pi\text{-}R_5C_5)Mo(CO)_2]_2$ ($R = CH_3$,[10] C_6H_5[11]) constitute a group of π-organometallic compounds which, on the basis of spectroscopic properties and the effective atomic number rule, were presumed to contain unbridged M–M triple bonds. Of these, $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ promised to be interesting in two respects: as the first example of a compound with a Cr–Cr triple bond and/or the first example of an unbridged π-organometallic complex containing a multiple M–M bond. Consequently, a structural study of this compound was undertaken.

Experimental Section

The compound was prepared and purified by the method of King and Efraty.[8] Dark green crystals, suitable for X-ray analysis, were obtained by slow evaporation from hexane. A crystal approximately 0.50 mm long and 0.18 mm in square cross section was cut to a cube and mounted in a sealed glass capillary parallel to the crystal axis *c*. Weissenberg photographs indicated a monoclinic space group with systematic absences of $h0l$ when $h + l$ is odd and of $0k0$ when k is odd; these conditions define the space group as $P2_1/n$ (No. 14, $P2_1/n$). The unit cell parameters $a = 8.717$ (6) Å, $b = 14.716$ (4) Å, $c = 9.867$ (5) Å, and $\beta = 112.00$ (5)° were obtained by a least-squares fit of 40 reflections using graphite-monochromated Mo Kα radiation (λ 0.71069 Å) and an Enraf-Nonius CAD-3 automated diffractometer. The unit cell volume U, based on these dimensions, is 1173 Å^3. A density of 1.408 g/cm^3 was calculated for $Z = 2$ and this agreed with that of 1.41 (2) g/cm^3 measured by flotation of several crystals in aqueous potassium iodide solution.

Data were collected at room temperature (22 ± 1°) with the Enraf-Nonius diffractometer. Graphite-monochromated Mo Kα radiation was detected with a scintillation counter and a pulse height analyzer set to admit approximately 90% of the Kα peak. A θ–2θ scan was used to collect a unique data set to a maximum of $\theta = 30°$. Reflections with $\theta < 2°$ were shielded from the counter by the beamstop and were not recorded. The scan range S was a function of θ chosen according to $S = (2.0 + 0.1 \tan\theta)°$. A circular aperture 1.3 mm in diameter was placed 4.1 cm from the crystal. Each reflection was scanned before being recorded and zirconium foil attenuators

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(1) A preliminary account of this work has appeared: J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty, and R. B. King, *J. Chem. Soc., Chem. Commun.*, 1333 (1972).

(2) Review articles include the following: (a) F. A. Cotton, *Rev. Pure Appl. Chem.*, 17, 25 (1967); (b) F. A. Cotton, *Accounts Chem. Res.*, 2, 240 (1969); (c) M. C. Baird, *Progr. Inorg. Chem.*, 9, 1 (1968); (d) B. P. Biryukov and Y. T. Struchkov, *Russ. Chem. Rev.*, 39, 789 (1970).

(3) These complexes may conveniently be divided into five categories for tabulation purposes: (i) inorganic unbridged, (ii) inorganic bridged, (iii) π-organometallic bridged, (iv) σ-organometallic unbridged, and (v) π-organometallic unbridged. Some examples for the first four categories of binuclear complexes containing metal–metal multiple bonds are given in ref 4–7. Except for the present work, there is no structurally categorized compound containing a M–M multiple bond for category v of which we are aware.

(4) Inorganic unbridged: (a) $[Mo_2Cl_8]^{4-}$, J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 8, 7 (1969); (b) $[Re_2Br_8]^{2-}$, P. A. Koz'min, V. G. Kuznetzov, and Z. V. Popova, *Zh. Strukt. Khim.*, 6, 651 (1965); F. A. Cotton, B. G. DeBoer, and M. Jeremic, *Inorg. Chem.*, 9, 2143 (1970); (c) $Re_2Cl_6[P(C_2H_5)_3]_2$, F. A. Cotton and B. M. Foxman, *ibid.*, 7, 2135 (1968); (d) $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$, M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc., Ser. A*, 303, 175 (1968).

(5) Inorganic bridged: (a) $Cr_2(O_2CCH_3)_4\cdot 2H_2O$ and $Rh_2(O_2CCH_3)_4\cdot 2H_2O$, F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *J. Amer. Chem. Soc.*, 92, 2926 (1970); *Acta Crystallogr., Sect. B*, 27, 1664 (1971); (b) $Mo_2(O_2CCF_3)_4$, F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, 1, 161 (1971); (c) $Mo_2(O_2CCF_3)_4\cdot 2C_5H_5N$, F. A. Cotton and J. G. Norman, Jr., *J. Amer. Chem. Soc.*, 94, 5697 (1972); (d) $K_3Mo_2(SO_4)_4\cdot 3.5H_2O$, F. A. Cotton, B. A. Frenz, and T. R. Webb, *ibid.*, 95, 4431 (1973); (e) $[Re_2(n\text{-}C_3H_7CO_2)_4][ReO_4]_2$, C. Calvo, N. C. Jayadevan, C. J. L. Lock, and R. Restivo, *Can. J. Chem.*, 48, 219 (1970).

(6) π-Organometallic bridged: (a) $Cr_2(C_3H_5)_4$, T. Aoki, A. Furusaki, Y. Tomiie, K. Ono, and K. Tanaka, *Bull. Chem. Soc. Jap.*, 42, 545 (1969); (b) $Mo_2(C_3H_5)_4$, F. A. Cotton and J. R. Pipal, *J. Amer. Chem. Soc.*, 93, 5441 (1971); (c) $(\pi\text{-}C_5H_5)_2V_2(CO)_5$, F. A. Cotton, B. A. Frenz, and L. Kruczynski, *ibid.*, 95, 951 (1973); (d) $[(t\text{-}C_4H_9)_2C_2Fe(CO)_2]_2$, K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608 (1971).

(7) σ-Organometallic unbridged: (a) $Li_4[Cr_2(CH_3)_8]\cdot 4C_4H_8O$, J. Krausse, G. Marx, and G. Schodl, *J. Organometal. Chem.*, 21, 159 (1970); (b) $Mo_2(CH_2Si(CH_3)_3)_6$, F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971).

(8) R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 93, 4950 (1971); 94, 3773 (1972).

(9) R. B. King, *Chem. Commun.*, 986 (1967).

(10) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 8, 287 (1967).

(11) A. Efraty, unpublished results.

were automatically inserted if the intensity of the diffracted beam exceeded 6000 counts/sec. Background measurements were made at the beginning and end of each scan with the counter stationary; the total time for background counts was equal to the total scan time. The scan rate was $^1/_6°$ sec^{-1} and each reflection was scanned repeatedly to a maximum of six scans or until 6000 total counts were obtained. Intensities were placed on a common scale by dividing by the number of scans. The intensity of a standard reflection, measured at 40 reflection intervals, was consistent to ±2% over the period of data collection and showed no significant trend.

A total of 3629 diffraction maxima were collected and corrected for Lorentz and polarization effects. The absorption coefficient μ = 9.9 cm^{-1} for Mo Kα radiation is so small that absorption corrections were not considered necessary for a crystal of the size used to collect data. Standard deviations were assigned to F^2 values according to

$$\sigma(F^2) = \frac{1}{Lp}(N_t + (0.02N_n)^2)^{1/2}$$

where N_t is the total count (background plus scan) and N_n is the net count (scan minus background). An estimate of the overall scale factor was obtained using Wilson's method and subsequently refined. Of the 3629 measured reflections, 1803 with $F^2 \geqslant \sigma$ were used in the initial stages of refinement.

The structure was solved by the heavy-atom method. Space group $P2_1/n$ has four general positions, and the presence of two molecules per cell requires one monomer per asymmetric unit. Approximate coordinates for the unique chromium atom were readily obtained from a normal sharpened Patterson map.[12] A Fourier synthesis based on the chromium phases revealed the positions of all carbon and oxygen atoms. The atomic coordinates so determined showed both halves of the dimer related by a center of symmetry at the origin.

Isotropic refinement was initiated using the atomic scattering factors of Cromer and Waber[13] for chromium, oxygen, and carbon. All atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion corrections were applied to chromium.[14] Initial refinement was based on F^2 and weights were set according to $w = 1/\sigma^2$. Three refinement cycles of all chromium, oxygen, and carbon positional and isotropic thermal parameters, followed by one cycle with anisotropic thermal parameters for chromium, reduced $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ to 0.098.

Further refinement was based on F and a weighting scheme was chosen by an analysis of variance[15] to make $|\Delta F|/\sigma$ independent of F_o. This procedure led to the following assignments for $\sigma(F_o)$: $\sigma(F_o) = 2.05 - 0.09F_o$ for $0 < F_o \leqslant 11$; $\sigma(F_o) = 1.05$ for $11 < F_o < 22$; $\sigma(F_o) = 0.27 + 0.034F_o$ for $F_o \geqslant 22$. One cycle of refinement, again with anisotropic chromium temperature factors, reduced R_F to 0.093 and $R_{wF} = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$, the function minimized, to 0.105. A difference Fourier at this point revealed broad, diffuse maxima which could be interpreted as arising from the methyl group hydrogen atoms. Hydrogen atoms were placed at these positions; however, some coordinates were varied slightly within these areas to give more nearly the expected C-H bond lengths and tetrahedral angles. C-H distances thus determined varied from 1.05 to 1.10 Å while the H-C-H angles varied from 107 to 111°. Hydrogen atoms were included for further refinement[14b] with isotropic temperature factors equal to those of the carbon atom to which they are bonded. Hydrogen atoms were not refined. One cycle of refinement with hydrogen atoms included reduced R_F to 0.087 and R_{wF} to 0.098.

An attempt was made to refine the structure further using anisotropic temperature factors for oxygen and carbon; however, nonpositive definite temperature factors were obtained for all carbon and oxygen atoms. Examination of the parameter changes for successive cycles showed them to be oscillating and diverging. It was therefore decided to restrict parameter changes to 25% of their calculated values. Since this procedure was expected to result in slow convergence, 1411 reflections with $F^2 \geqslant 3\sigma$ were used for further refinement. Six cycles of refinement reduced R_F and R_{wF} to their final values of 0.053 and 0.061, respectively. A final difference Fourier showed no significant features. A list of observed and calculated structure factors is available.[16]

Final atomic parameters are listed in Table I while Figure 1 shows the unit cell contents viewed along *b*. Root-mean-square amplitudes of vibration along the principal ellipsoid axes are listed in Table II. As expected, they increase in going from chromium toward the exterior of the molecule. Thus, the methyl carbon atoms and the carbonyl oxygen atoms show the largest amplitudes; however, these amplitudes are not unreasonably large for a structure of this type.

Description of the Structure and Discussion

The structure consists of discrete, centrosymmetric $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ dimers (Figure 2). Intermolecular contacts less than 4 Å are listed in Table III; none of these is short enough to indicate intermolecular interactions significantly stronger than those arising from van der Waals forces.

Within each dimer, centrosymmetrically related chromium atoms are separated by 2.280 (2) Å (Table IV); this short distance is indicative of a strong M-M interaction. It is longer than the Cr-Cr bond lengths in $Li_4[Cr_2(CH_3)_8]\cdot 4C_4H_8O$ [1.98 Å][7a] and $Cr_2(C_3H_5)_4$ [1.98 Å][6a] but significantly shorter than the Cr-Cr distance in $Cr_2(O_2CCH_3)_4\cdot 2H_2O$ [2.362 Å];[5a] quadruple Cr-Cr bonds have been suggested for these three compounds. Each chromium atom is bonded to two nearly perpendicular carbonyl groups [C(1)-Cr-C(2) angle 88.9 (3)°]. Atoms Cr, Cr′, C(1), C(1′), O(1), and O(1′) are coplanar to 0.01 Å (plane 1), as are atoms Cr, Cr′, C(2), C(2′), O(2), and O(2′) (plane 2). Thus, the carbonyl groups are staggered with respect to the Cr-Cr′ axis; however, they are far from perpendicular to it as evidenced by the rather small Cr′-Cr-CO angles [73.0 (3), 79.1 (3)°]. These angles indicate that each carbonyl group lies to some extent over the M-M bond. Structural studies of a number of metal carbonyl complexes without bulky axial groups[17] have shown M-M-C angles somewhat smaller than 90°. For example, the average M-M-CO (equatorial) angles in $[Cr_2(CO)_{10}]^{2-}$ and $[Mn_2(CO)_{10}]$ were found to be 87 and 86°, respectively. In the present structure, the decrease is considerably larger and we attribute this primarily to nonbonding repulsions between the ligands. Steric crowding in the molecule is considered in more detail below.

The cyclopentadienyl ring centers (CR) are 1.857 Å removed from the nearest chromium atom and lie 0.510 Å above and below plane 1. The rings are trans with respect to the chromium atoms and staggered with respect to each other as required by the center of symmetry and the Cr′-Cr-CR angle [158.7°]. Three of the Cr-C(ring) distances [Cr-C(3), Cr-C(4), and Cr-C(5)] are equivalent to within their estimated standard deviation, as are the remaining two. Atoms C(6) and C(7) are further from Cr than C(3)-C(5) by approximately 0.03 Å; this difference is small but significant. Although not required crystallographically, the $(CH_3)_5C_5$ rings exhibit nearly perfect C_{5v} symmetry. The ring carbon atoms are coplanar to 0.008 Å while individual C(ring)-C(ring) distances are all equivalent. C(ring)-C(CH_3) distances are also equivalent and average to 1.510 ± 0.004 Å which is close to the accepted value[18] of 1.506 Å for sp^2-sp^3

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[12] In addition to local programs for the IBM 360/67 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program; Busing, Martin and Levy's ORFLS least-squares program; Busing, Martin, and Levy's ORFFE error function program; and Johnson's ORTEP II thermal ellipsoid plotting program.

(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(14) (a) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 213-216. (b) Hydrogen scattering factors were obtained from ref 14a, pp 201-209.

(15) The analysis of variance was performed using program NANOVA obtained from Dr. I. Bernal; see J. S. Ricci, Jr., C. A. Eggers, and I. Bernal, *Inorg. Chim. Acta*, 6, 97 (1972).

(16) See paragraph at end of paper regarding supplementary material.

(17) (a) $[Cr_2(CO)_{10}]^{2-}$, L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 7312 (1970), and references therein; (b) $Mn_2(CO)_{10}$, L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, 16, 419 (1963); (c) $Tc_2(CO)_{10}$, M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1140 (1965).

(18) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, (1965).

Table I. Fractional Atomic Coordinates and Anisotropic Thermal Parameters[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	48,831 (1)	53,825 (1)	59,615 (1)	108 (2)	25 (1)	72 (1)	−6 (1)	42 (1)	−2 (1)
O(1)	14,413 (5)	54,315 (4)	37,055 (5)	127 (9)	85 (3)	176 (8)	22 (5)	31 (7)	−17 (5)
O(2)	58,453 (3)	69,418 (7)	65,069 (5)	367 (25)	44 (3)	174 (11)	−20 (5)	147 (11)	6 (4)
C(1)	28,194 (7)	53,790 (4)	44,943 (6)	126 (12)	48 (3)	113 (8)	5 (6)	41 (7)	1 (5)
C(2)	54,689 (8)	63,037 (8)	50,211 (7)	190 (19)	33 (3)	111 (10)	−5 (5)	76 (9)	−3 (4)
C(3)	64,740 (7)	57,730 (4)	82,041 (6)	136 (14)	52 (3)	86 (8)	−25 (5)	53 (8)	−24 (4)
C(4)	57,870 (7)	49,009 (4)	82,319 (5)	133 (14)	39 (3)	69 (7)	12 (4)	43 (7)	4 (3)
C(5)	40,527 (7)	50,105 (4)	77,344 (6)	124 (13)	42 (3)	87 (8)	−6 (4)	50 (7)	−3 (4)
C(6)	36,613 (8)	59,374 (4)	74,098 (6)	157 (15)	43 (4)	85 (8)	22 (5)	58 (8)	−1 (4)
C(7)	51,610 (8)	64,029 (4)	77,149 (7)	225 (21)	37 (3)	95 (9)	2 (6)	82 (9)	−6 (4)
C(8)	83,010 (10)	59,993 (6)	87,330 (9)	183 (9)	93 (6)	165 (12)	−46 (7)	65 (10)	−40 (6)
C(9)	67,250 (9)	40,373 (5)	87,986 (8)	210 (16)	55 (4)	126 (11)	36 (6)	60 (9)	16 (5)
C(10)	28,368 (9)	42,763 (5)	77,078 (8)	201 (27)	58 (4)	135 (14)	−37 (7)	85 (14)	2 (6)
C(11)	19,704 (9)	63,687 (5)	69,693 (8)	205 (23)	77 (5)	143 (14)	61 (7)	78 (13)	3 (7)
C(12)	53,600 (12)	74,260 (5)	76,675 (9)	391 (35)	40 (4)	179 (15)	−8 (8)	145 (16)	−17 (6)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(1)	9028	5415	8625	597	H(9)	2208	4452	8473	480
H(2)	8542	6577	8162	597	H(10)	6269	7575	7219	605
H(3)	8762	6173	9924	597	H(11)	4154	7710	6980	605
H(4)	6311	3680	9566	493	H(12)	5760	7681	8769	605
H(5)	6677	3566	7916	493	H(13)	1871	6960	6267	550
H(6)	8090	4180	9410	493	H(14)	1056	5989	6051	550
H(7)	1905	4165	6640	480	H(15)	1537	6364	7878	550
H(8)	3500	3626	8115	480					

[a] Chromium, oxygen, and carbon coordinates are $\times 10^5$; hydrogen coordinates are $\times 10^4$. [b] Anisotropic temperature factors are $\times 10^4$ and are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic temperature factors for hydrogen are $\times 10^2$.

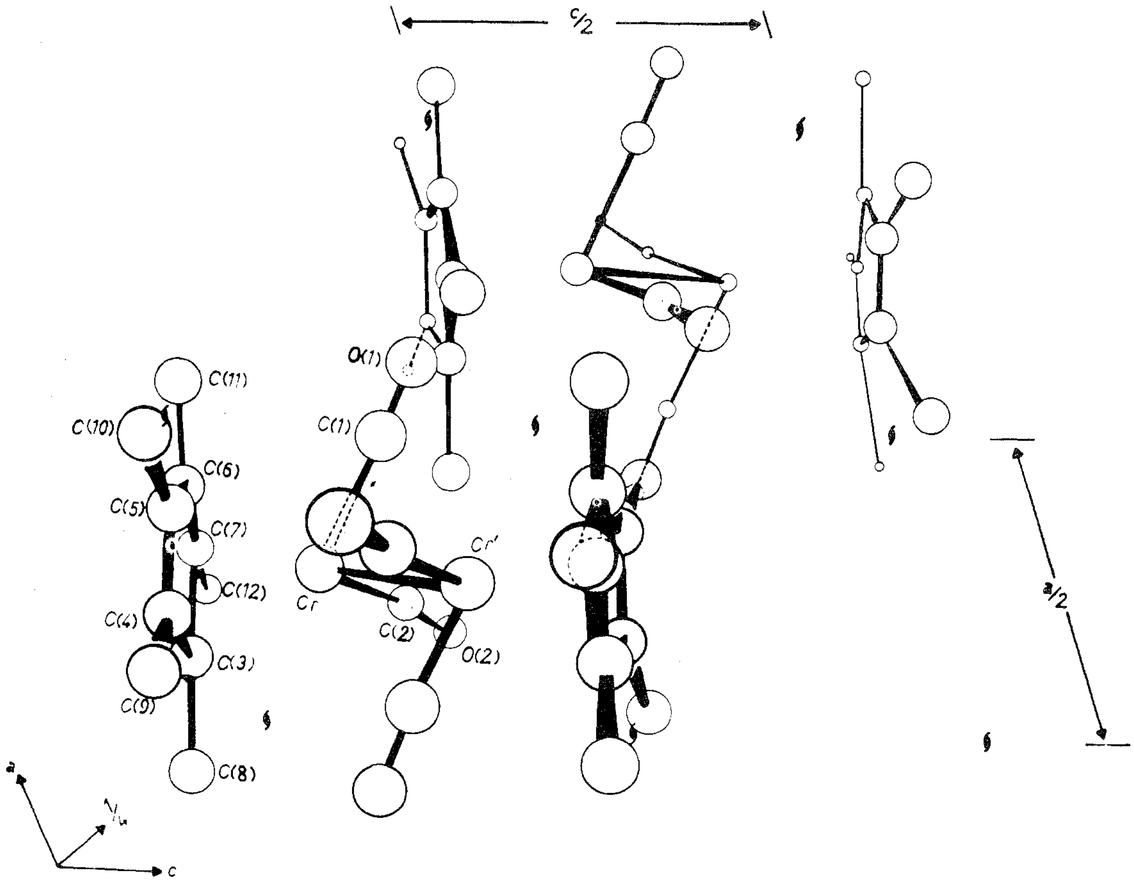

Figure 1. The unit cell contents viewed along *b*. Hydrogen atoms are omitted for clarity.

hybridization. Last, all methyl groups are bent from the cyclopentadienyl ring plane by approximately 4.5° and are exo with respect to Cr.

Nonbonding intramolecular contacts (Table IV) suggest that the molecule is sterically crowded. For example, each carbonyl carbon atom, in addition to a bonding contact with Cr, shows a short Cr′· · ·C(CO) distance, two short C(CO)· · ·C(CO) distances, and a short C(CO)· · ·C(ring) distance. Interestingly, ring atoms C(6) and C(7), which show the shortest C(CO)· · ·C(ring) distances, give the longest Cr–C(ring) distances, suggesting that asymmetric bonding of the cyclopentadienyl ring results from steric hindrance. The carbonyl groups appear locked in place and may not rotate away from the Cr–Cr bond without

Table II. Root-Mean-Square Thermal Displacements (Å)[a]

Atom	Min	Med	Max
Cr	0.162 (2)	0.171 (3)	0.189 (2)
O(1)	0.193 (9)	0.265 (8)	0.335 (6)
O(2)	0.188 (10)	0.243 (8)	0.372 (10)
C(1)	0.205 (10)	0.211 (10)	0.239 (9)
C(2)	0.171 (19)	0.197 (9)	0.273 (11)
C(3)	0.146 (20)	0.209 (9)	0.293 (12)
C(4)	0.145 (16)	0.200 (10)	0.234 (9)
C(5)	0.160 (14)	0.205 (11)	0.256 (9)
C(6)	0.167 (9)	0.190 (9)	0.266 (8)
C(7)	0.166 (15)	0.203 (9)	0.225 (8)
C(8)	0.190 (10)	0.260 (16)	0.366 (16)
C(9)	0.203 (11)	0.233 (13)	0.300 (9)
C(10)	0.177 (18)	0.247 (13)	0.348 (8)
C(11)	0.208 (13)	0.253 (13)	0.355 (9)
C(12)	0.162 (23)	0.252 (13)	0.309 (10)

[a] Values were computed for the principal axes of the thermal ellipsoids, the orientations of which are shown in Figure 2.

Table III. Intermolecular Contacts Less Than 4 Å

Atoms	Distance, Å	Atoms	Distance, Å
O(1)· · ·C(15)′	3.336	C(10)· · ·C(12)′	3.814
O(1)· · ·C(10)′	3.484	O(1)· · ·C(11)′	3.853
O(2)· · ·C(8)′	3.663	O(2)· · ·C(11)′	3.905
O(2)· · ·C(9)′	3.760	C(1)· · ·C(12)′	3.925

Table IV. Interatomic Distances (Å) and Angles (deg)[a,b]

Atoms	Distance	Atoms	Distance
Cr-Cr′	2.280 (2)	C(1)-O(1)	1.162 (7)
Cr-C(1)	1.842 (6)	C(2)-O(2)	1.171 (8)
Cr′· · ·C(1)	2.474 (5)	C(3)-C(4)	1.420 (8)
Cr-C(2)	1.822 (6)	C(4)-C(5)	1.416 (8)
Cr′· · ·C(2)	2.633 (5)	C(5)-C(6)	1.413 (9)
Cr-C(3)	2.200 (6)	C(6)-C(7)	1.407 (9)
Cr-C(4)	2.197 (6)	C(3)-C(7)	1.411 (9)
Cr-C(5)	2.202 (6)	C(3)-C(8)	1.515 (10)
Cr-C(6)	2.232 (6)	C(4)-C(9)	1.505 (10)
Cr-C(7)	2.236 (6)	C(5)-C(10)	1.506 (10)
C(1)· · ·C(2)	2.561 (8)	C(6)-C(11)	1.512 (10)
C(1)· · ·C(2)′	2.838 (9)	C(7)-C(12)	1.514 (10)
C(CO)· · ·C(ring) Contacts < 3.3 Å			
C(1)· · ·C(3)	3.017 (9)	C(2)· · ·C(5)	3.026 (9)
C(1)· · ·C(6)	2.814 (9)	C(2)· · ·C(7)	2.770 (9)
C(1)· · ·C(11)	3.158 (10)		
Atoms	**Angle**	**Atoms**	**Angle**
Cr-C(1)-O(1)	170.8 (6)	C(10)-C(5)-C(6)	125.6 (6)
Cr-C(2)-O(2)	174.8 (6)	C(11)-C(6)-C(5)	126.6 (6)
Cr′-Cr-C(1)	73.0 (3)	C(11)-C(6)-C(7)	125.7 (6)
Cr′-Cr-C(2)	79.1 (3)	C(12)-C(7)-C(3)	125.1 (7)
Cr′-Cr-CR	158.7	C(12)-C(7)-C(6)	126.0 (7)
C(1)-Cr-C(2)	88.9 (3)	C(8)-C(3)-C(7)	126.0 (7)
C(3)-C(4)-C(5)	107.2 (5)	C(8)-C(3)-C(4)	126.0 (6)
C(4)-C(5)-C(6)	108.7 (5)	C(1)-Cr-CR	118.2
C(5)-C(6)-C(7)	107.5 (5)	C(2)-Cr-CR	117.3
C(6)-C(7)-C(3)	108.6 (5)	CR-C(4)-C(9)	175.8
C(7)-C(3)-C(4)	107.9 (5)	CR-C(5)-C(10)	175.0
C(9)-C(4)-C(3)	126.0 (6)	CR-C(6)-C(11)	175.4
C(9)-C(4)-C(5)	126.7 (5)	CR-C(7)-C(12)	175.1
C(10)-C(5)-C(4)	125.4 (6)	CR-C(3)-C(8)	176.6

[a] Values in parentheses are estimated standard deviations justified to the last significant figure of the preceding number. [b] CR corresponds to the center of the cyclopentadienyl ring.

further reducing an already short C(CO)· · ·C(ring) contact or increasing an already long Cr-C(ring) distance.

Similar steric effects have been observed[19] in [π-(C_5H_5)Cr-$(CO)_3]_2$ which contains a long Cr-Cr single bond; indeed, the Cr-Cr bond length was found to be 0.06 Å longer than the Mo-Mo distance in the isomorphous compound [π-(C_5H_5)-$Mo(CO)_3]_2$. This unusual increase was attributed to repulsive forces between the ligands in the chromium compound. In an analogous way, the observed Cr-Cr distance in the present structure may not represent the intrinsic strength of the Cr-Cr triple bond in this compound; the observed distance may result from a compromise between the attractive M-M and M-L forces and the repulsive forces between the ligands. To determine the extent to which steric factors affect the Cr-Cr bond length, it would be interesting to determine the structure of [(π-$(CH_3)_5C_5$)$Mo(CO)_2]_2$. Short L· · ·L distances [$C(CH_3)$· · ·$C(CH_3)$ = 2.98 Å] have also been observed[7a] in $Li_4[Cr_2(CH_3)_8]\cdot 4C_4H_8O$; however, there the M-L distances were long [Cr-$C(CH_3)$ = 2.20 Å] and the Cr-Cr bond was extremely short. Overall, these results suggest that steric effects may also be important in other first-row complexes containing M-M bonds; their importance might be expected to increase as the ligands become more bulky and as the M-M bond strength increases.

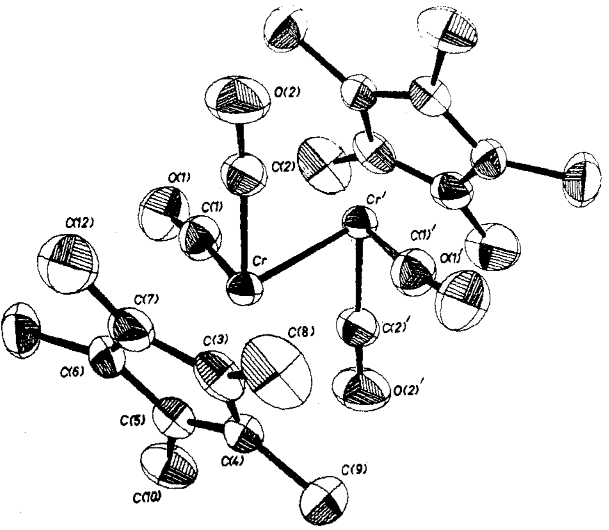

Figure 2. The molecular structure showing the atom-numbering scheme and the 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Structural evidence suggests that both carbonyl groups are essentially terminal. The Cr-C-O angles [170.8 (6), 174.8 (6)°] are in the range usually found for terminal carbonyl groups. In $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$, for example, M-C-O angles averaged to 173°. However, in the present structure, the direction of bend is that which would be produced from nonbonded repulsions between the cyclopentadienyl and carbonyl groups and deviations from 180° may, in part, be attributed to this. A similar explanation has been offered for the Cr-C-O angles in [(π-C_5H_5)$Cr(CO)_3]_2$. The Cr-C(CO) distances differ only slightly from each other and average to 1.83 Å. Both lie within the range of 1.77-1.92 Å observed[20] for carbonyl groups in several mononuclear complexes containing chromium; they are closest to the average of 1.84 Å reported[20b] for the arene complex $C_6H_6Cr(CO)_3$. Carbonyl 1 [C(1)-O(1)], with the longer Cr-C(CO) bond length, shows the shorter Cr′· · ·C(CO) contact. The Cr′· · · C(1) distance is only slightly longer than the respective V-C-(CO) distances of 2.44 (1) and 2.40 (1) Å found for the "grossly unsymmetrical bridging carbonyl groups" in the

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[19] R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, 96, 749 (1974).

[20] (a) $Cr(CO)_6$, L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, 34, 1350 (1938); W. Rudorff and U. Hofmann, *Z. Phys. Chem., Abt. B*, 28, 351 (1935); (b) $(C_6H_6)Cr(CO)_3$, M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1314 (1965); (c) $(C_4H_4S)Cr(CO)_3$, M. F. Bailey and L. F. Dahl, *ibid.*, 4, 1306 (1965), and references therein.

structurally related vanadium complex $(\pi\text{-}C_5H_5)_2V_2(CO)_5$.[6c] Since chromium is smaller than vanadium, a secondary bonding interaction between C(1) and the remote chromium atom is expected to be weaker than the corresponding interaction in the vanadium complex.

The ir spectrum of $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ is consistent with the structural findings above. Carbonyl stretching frequencies (1876, 1857 cm^{-1}, KBr)[8] were found in the region usually assigned to terminal carbonyl groups. Two bands are expected from group theory considerations (point group C_i), one for each unique carbonyl group; presumably, the lower frequency corresponds to carbonyl 1. The ir spectrum of $(\pi\text{-}C_5H_5)_2V_2(CO)_5$ shows five carbonyl stretching bands; the low-frequency band (1815 cm^{-1}, KBr)[21] is considerably below those found in $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ and this is also consistent with a greater degree of bridging in the former compound. The pmr spectrum[8] of $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ showed only a sharp singlet at τ 8.37 due to the methyl protons. Either the difference in shielding of nonequivalent methyl groups is too small to be detected on the nmr time scale or the molecule exhibits fluxional properties in solution. The second explanation is favored, particularly since $(\pi\text{-}C_5H_5)_2V_2(CO)_5$, with nonequivalent vanadium atoms, also showed a singlet pmr spectrum.[21]

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Registry No. $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$, 37299-12-0.

Supplementary Material Available. A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2540.

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Model Compounds of Biological Molybdenum. I. Flavin and Mixed-Ligand Complexes of Molybdenum(IV) and -(V)

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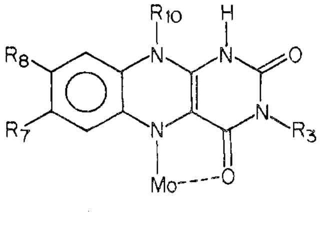
The first solid flavin complexes of molybdenum(IV) have been isolated and characterized by dta, tga, ir, vis-uv, nmr, and epr data. Their general formulation is $MoOCl_3$(H-flavine), with the organic ligand being a monocation complexed as a bidentate ligand through its primary binding site, C=O(4) and N(5). Ir data are cited in support of this mode of bonding. The first solid molybdenum(V)-flavine complex has been isolated and partially characterized; its epr spectrum suggests that it is monomeric. Mixed-ligand complexes of oxomolybdenum(IV) containing both a flavine molecule and a sulfur-donor ligand have been synthesized for the first time. It is believed that these compounds may approximate the first coordination sphere environment of molybdenum in certain biological-molybdenum species.

It is now well established that molybdenum is an essential component of at least five different redox enzymes.[1-3] Despite a very large number of papers, which deal mainly with studies of the mammalian enzyme xanthine oxidase, several important questions remain unanswered. (1) What is (are) the oxidation state(s) of the metal in the resting enzymes, and what oxidation state changes take place during normal substrate turnovers? (2) Do atom as well as electron transfers involving the molybdenum take place during turnovers? (3) What groups (*e.g.*, from coenzyme flavines and/or from the apoenzyme itself) are permanently attached to the molybdenum, and what groups (if any) attach and detach during turnovers? In other words, what does the immediate (first coordination sphere) environment of the molybdenum look like before, during, and after a redox turnover? We have been preparing and characterizing a number of compounds of molybdenum with the aim of simulating the active sites of biological molybdenum, with the emphasis on the oxidation state of the metal and its first coordination sphere environment. These compounds are then to be assayed for their redox behavior with various redox substrates including the actual biological substrates. In this paper we describe the preparation and characterization of 12 new compounds of molybdenum in oxidation states IV and V. (See Table I.) A later paper will deal with the pertinent redox reactions of these and other new products.

In Chart I are shown structural formulas, compound names, and name abbreviations for the ligands employed in this work. For the four flavine ligands **3-6** the abbreviation takes on an initial H when the complex forms, since N(1) becomes protonated. Thus HEAMIA, HTMIA, HRTA, and HRTB stand for the respective flavine molecules after they are complexed resulting in the generalized structure



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