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Molecular Structures and Barriers to Internal Rotation in Bis(η^5-cyclopentadienyl)hexacarbonylditungsten and Its Molybdenum Analog

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The crystal structure of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ has been determined and that of its molybdenum analog redetermined with increased accuracy. The W-W distance (3.222 (1) Å) is slightly shorter than the Mo-Mo distance (3.235 (1) Å), in continuation of the trend already found from the chromium to the molybdenum compound. The free energy of activation for (presumably rotational) interconversion of the gauche and anti rotamers of the tungsten compound in solution has been evaluated from proton nmr spectra over a temperature range (−20 to +60°); it is slightly higher than that in the molybdenum compound. Possible reasons for the observed trends, namely, Cr >> Mo > W for the M-M distances and Cr < Mo ⩽ W for the free energies of activation of gauche-anti interconversion, are discussed. The crystallographic data for $(\eta^5\text{-}C_5H_5)_2$-$Mo_2(CO)_6$ are essentially identical with those reported previously by Wilson and Shoemaker; the present work merely gives the enhanced precision needed to reveal clearly the difference between *d*(Mo-Mo) and *d*(W-W). For $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ the crystallographic data are space group $P2_1/c$, $a = 10.374$ (1) Å, $b = 7.971$ (1) Å, $c = 12.047$ (2) Å, $\beta = 125.83$ (1)°, and $Z = 2$.

Introduction

Previous studies in this laboratory have revealed that in solutions of both $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$[1] and its chromium analog[2] there are solvent-dependent equilibria between anti and gauche rotamers. From line shape analysis of nmr spectra at various temperatures the barriers to internal rotation in the two cases were evaluated, with the result that the barrier is several kilocalories lower in the chromium compound. This at first appeared surprising since, naively, *d*(Cr-Cr) was expected to be less than *d*(Mo-Mo), which should have led to greater steric forces and, hence, a higher barrier. In order to gain more insight into the problem, the structure of the chromium compound was determined crystallographically[2] and compared with the known structure of the molybdenum compound.[3] It was found that *d*(Cr-Cr) is actually ~0.06 Å greater than *d*(Mo-Mo). An explanation for this was proposed.[2]

On the basis of the proposed explanation, and even for purely empirical reasons, the obvious questions became: (1) is *d*(W-W) in the analogous tungsten compound greater or smaller than *d*(Mo-Mo) and (2) is the barrier to rotation in the tungsten compound higher or lower than that in the molybdenum compound? To answer these questions the appropriate nmr and X-ray crystallographic studies were carried out on $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$. When it was found that the differences, in both bond lengths and rotational barriers, between the molybdenum and tungsten compounds were very small, it was decided to collect a new and better set of X-ray data for the molybdenum compound so that the small difference between *d*(W-W) and *d*(Mo-Mo) could be established at a high confidence level.

Experimental Section

Nuclear Resonance Measurements. These were made as previously[1,2] and the line shape analyses also were done in the same way as before. The temperature dependence of the gauche:anti equilibrium ratio was so slight that it could be treated as invariant at 0.75 from −20 to +60°, the range through which line shape analysis was carried out. The spectra throughout this range were extremely similar in appearance to those previously published[1] for the molybdenum compound.

Crystal Data and Structure Determination for $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$. A deep red crystal was selected from the product of recrystallization out of toluene. The crystal, measuring about 0.3 × 0.3 × 0.06 mm along *b*, *c*, and *a*, respectively, was mounted in a sealed capillary and examined photographically to establish its suitability for data collection. Further checking by ω and θ-2θ scans, after placing the specimen on a diffractometer, confirmed that it was a single crystal of good quality. Additional preliminary work, generally following the outline given elsewhere,[2,4] allowed assignment of a unit cell in the monoclinic system.

X-Ray diffraction data were collected on a Syntex four-circle diffractometer using graphite-monochromatized Mo Kα radiation and θ-2θ scans of variable rate and range. The scanning rate was 2.0°/min for most reflections but ranged up to 24°/min for those of highest intensity. The base scan range of 1.7° was varied to take account of spectral dispersion, and individual background measurements were made at both limits of each scan. Of the 2767 integrated intensities measured in the range $2\theta < 60.0°$, 1548 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected with the usual Lorentz and polarization factors. Four standard-reflection measurements repeated every 100 data points were stable and showed no discernible time dependence. With a linear absorption coefficient[5] of 150.9 cm^{-1}, the maximum and minimum transmissions are respectively 49 and 9%. The clearly required absorption corrections[6] were applied to give the set of structure factors used in structure determination.

For calculation of lattice parameters, fifteen of the strongest reflections in the range $50° \leqslant 2\theta \leqslant 60°$ were selected to give a variety of crystal orientations. Based on angular settings for these reflections at 20 ± 2°, the refined parameters obtained from the Syntex software package are (Mo Kα_1, λ 0.709300 Å) $a = 10.374$ (1) Å, $b = 7.971$ (1) Å, $c = 12.047$ (2) Å, and $\beta = 125.83$ (1)°. The pattern of systematic absences verified[7] assignment of the space group as $P2_1/c$ with $Z = 2$.

A three-dimensional Patterson map, as expected, was dominated by W-W interactions. Analysis of the map gave the position for a tungsten atom. A trial structure based on tungsten alone was refined by least squares and the remainder of the structure, excluding hydrogen atoms, was developed from Fourier difference syntheses. Anisotropic least-squares refinement of the structure gave at this point a discrepancy factor value of $R_1 = 0.028$.

A difference map based on the refined model had principal positive density features near the expected hydrogen atom positions. Therefore, starting with the calculated hydrogen atom positions, further cycles of full-matrix refinement were carried out with positional and isotropic thermal parameters for hydrogen atoms allowed to vary; two apparently ill-behaved hydrogen atoms were reset to their initial descriptions for each of the three cycles. Comparison

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[1] R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, **7**, 153 (1973).

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

[3] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

[4] F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, **50**, 227 (1973).

[5] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[6] The computer programs used throughout this work are as described previously.[2]

[7] F. C. Wilson and D. P. Shoemaker, *Naturwissenschaften*, **43**, 57 (1956).

of observed and calculated structure factors suggested significant extinction effects, since for each of the 47 largest reflections $|F_c|$ exceeded $|F_o|$ and the difference generally increased with the magnitude of $|F_o|$. Final cycles of refinement, including an isotropic extinction coefficient and the now well-behaved hydrogen atoms (for a data:parameter ratio of 11.9) gave $R_1 = 0.023$ and $R_2 = 0.039$ as customarily defined.[2,4] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $p = 0.06$ in the previously defined expression for the weights,[2,4] and atomic scattering factors were from ref 8. Corrections for anomalous scattering by tungsten are those of Cromer and Liberman.[9] In the last cycle of refinement no parameter changed by more than 0.15 esd. A final difference map was judged to be free of significant features.

A list of observed and calculated structure factors is available.[10] The observed structure factors have been corrected for secondary extinction.[11] Atomic coordinates and thermal parameters are given in Tables I and II. Bond distances and selected bond angles are given in Tables III and IV. The labeling of atoms is shown in Figure 1.

Data and Structure Refinement. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$. A single crystal measuring about 0.3 × 0.3 × 0.08 mm along *b*, *c*, and *a*, respectively, was selected from a sample of the compound which had been recrystallized from toluene. Following the data collection procedures given above, 1471 unique reflections in the range $2\theta < 55.0°$ were taken as observed. After correction for Lorentz and polarization effects, absorption corrections were made using a linear absorption coefficient[5] of 15.3 cm^{-1}. The calculated maximum and minimum of transmission are 91 and 74%.

Wilson's lattice description[12] of $P2_1/c$ with $Z = 2$ and unit cell parameters of $a = 10.38$ Å, $b = 8.02$ Å, $c = 12.03$ Å, and $\beta = 125° 47'$ was verified. Based on angular settings for 15 strong reflections ($2\theta \pm 2°$) in the range $25° < 2\theta < 30°$, the unit cell parameters were recalculated to be (Mo Kα; λ 0.71069 Å) $a = 10.387$ (1) Å, $b = 8.031$ (1) Å, $c = 12.039$ (2) Å, and $\beta = 125.58$ (1)°.

After two cycles of anisotropic refinement ($R_1 = 0.026$) starting with Wilson's atomic parameters, a difference Fourier map gave good positions for the five hydrogen atoms. Least-squares refinement with $p = 0.04$, corrections for anomalous scattering by molybdenum,[9] but no correction for extinction, ultimately gave $R_1 = 0.021$ and $R_2 = 0.029$. In the last cycle of refinement all parameter shifts were less than 0.10 esd. A final difference map was judged to be free of significant features. A list of observed and calculated structure factors is available.[10] Atomic coordinates and thermal parameters are given in Tables V and VI. Bond distances and selected bond angles are given in Tables VII and VIII. The atoms are labeled according to Figure 1 with Mo substituted for W.

Results

Structures. The molybdenum and tungsten compounds are isomorphous as well as isostructural with each other and also with the chromium compound.[2]

The cyclopentadienyl rings in the structures under study are normal in every respect. In the molybdenum compound the carbon atoms form a plane with a mean deviation of 0.003 Å; the perpendicular distance from Mo to the plane of the ring is 2.009 Å. The C-C distances range from 1.399 to 1.408 Å and average to 1.404 (5) Å. The calculated deviations of hydrogen atoms from the mean plane of carbon atoms range from +0.06 to −0.03 Å with a mean deviation of 0.04 Å. The average C-H distance of 0.85 (4) Å is below the expected value but comparable to the value derived for $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$.[2]

For the tungsten compound, the parameters associated with the cyclopentadienyl ring show more scatter. The carbon atoms comprise a plane with a mean deviation of 0.005 Å; the perpendicular distance from W to the ring is 2.010 Å. The C-C distances average 1.41 (1) Å with a mean deviation of 0.01 Å. The C-H distances average to 0.93 (7) Å and range from 0.76 to 1.10 Å. They deviate from the cyclopentadienyl ring by 0.06 Å on the average. In view of their proximity to a tungsten atom and the evident limitations of absorption and extinction corrections, it is perhaps remarkable only that the hydrogen atoms refined to give reasonable averaged bond parameters.

Table I. Atomic Coordinates for $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$

Atom type[a]	Coordinates with standard deviations[b]		
	x	*y*	*z*
W	0.17781 (2)	−0.00779 (2)	0.13909 (2)
O_1	0.1426 (6)	0.3458 (5)	0.0116 (5)
O_2	0.3440 (6)	0.2307 (7)	0.3922 (5)
O_3	−0.0543 (7)	−0.0345 (7)	0.2234 (6)
C_1	0.1473 (7)	0.2140 (6)	0.0537 (6)
C_2	0.2796 (7)	0.1430 (8)	0.2970 (7)
C_3	0.0221 (8)	−0.0202 (7)	0.1853 (7)
Cp_1	0.2413 (8)	−0.2939 (6)	0.1645 (8)
Cp_2	0.2198 (7)	−0.2434 (7)	0.0429 (7)
Cp_3	0.3383 (8)	−0.1185 (8)	0.0770 (8)
Cp_4	0.4320 (8)	−0.0993 (9)	0.2212 (8)
Cp_5	0.3698 (9)	−0.2067 (8)	0.2721 (8)
H_1	0.189 (6)	−0.369 (6)	0.172 (5)
H_2	0.132 (7)	−0.303 (7)	−0.054 (6)
H_3	0.354 (8)	−0.039 (7)	0.011 (8)
H_4	0.505 (15)	−0.024 (10)	0.262 (13)
H_5	0.404 (9)	−0.212 (9)	0.347 (8)

[a] Atom labeling follows Figure 1. [b] In each table the number in parentheses is the estimated standard deviation in the least significant figure.

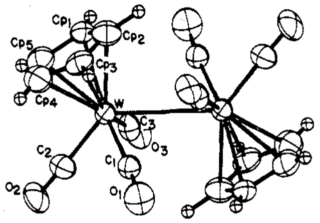

Figure 1. An ORTEP diagram of the $(\eta^5\text{-}C_5H_5)W_2(CO)_6$ molecule with 50% probability thermal ellipsoids. The hydrogen atoms, included with an arbitrary isotropic thermal parameter of 1.0, have the same numerical subscripts as the carbon atoms to which they are bonded.

Intermolecular packing in the effectively identical crystals is marked by the absence of any particular critical interaction. Rather, the crystal packing seems determined by a pattern of O-O approaches in the range of 3.1-3.2 Å, O-Cp approaches in the range 3.3-3.4 Å, and Cp-Cp distances at 3.75 Å. No hydrogen atom is closer than 2.6 Å to an atom in another molecule.

With averaged M-CO (M = Mo, W) distances of 1.98 Å, the increase of 0.04 Å relative to 1.94 Å for Mo-CO in Mo(dien)(CO)$_3$[13] is the same as for the analogous pair of chromium compounds.[2] The W to C_5H_5 ring distance of 2.01 Å is the same as that observed in $(\eta^5\text{-}C_5H_5)W(CO)_3AuP(C_6H_5)_3$[14] where W-Cp ring is 2.01 Å and ⟨W-CO⟩ is 1.97 Å.

Nmr Results. From the line-shape analysis the following Arrhenius activation parameters were obtained: $E_a = 15.2 \pm 0.4$ kcal mol^{-1}; $\log A = 12.1 \pm 1.0$. The uncertainties are derived from a computerized least-squares fitting of eight points in the temperature range −20 to +60°. From these the activation parameters according to absolute reaction rate theory were calculated: $\Delta G^{\ddagger} = 16.2 \pm 0.5$ kcal mol^{-1}; $\Delta H^{\ddagger} = 14.6 \pm 0.4$ kcal mol^{-1}; $\Delta S = -5.2 \pm 4.0$ cal mol^{-1} deg^{-1}.

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(8) "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in preparation.

(9) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

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

(11) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963).

(12) F. C. Wilson, Ph.D. Thesis, Massachusetts Institute of Technology, 1957.

(13) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 4, 314 (1965).

(14) J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, 8 (1969).

Table II. Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$

	Anisotropic parameters ($Å^2$) with standard deviations[a]						
Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[b]
W	2.11 (1)	2.53 (1)	2.06 (1)	−0.09 (1)	0.82 (1)	−0.22 (1)	2.41
O_1	4.3 (2)	3.1 (2)	4.8 (2)	−0.6 (1)	1.7 (2)	0.3 (2)	4.3
O_2	3.8 (2)	7.2 (3)	3.5 (2)	−1.5 (2)	1.3 (2)	−2.5 (2)	4.6
O_3	4.8 (3)	7.4 (3)	3.7 (2)	−1.6 (2)	3.1 (2)	−1.1 (2)	4.5
C_1	2.9 (2)	2.9 (2)	2.7 (2)	−0.4 (1)	1.3 (2)	−0.3 (1)	3.0
C_2	2.7 (3)	4.8 (3)	3.2 (3)	0.0 (2)	1.4 (2)	−0.6 (2)	3.6
C_3	3.2 (2)	3.9 (2)	2.6 (2)	−1.0 (2)	1.4 (2)	−0.3 (2)	3.3
Cp_1	3.5 (3)	2.6 (2)	4.9 (4)	−0.1 (2)	1.8 (3)	−0.1 (2)	3.8
Cp_2	3.4 (3)	3.2 (2)	3.8 (3)	0.9 (2)	1.3 (2)	−0.8 (2)	3.5
Cp_3	3.8 (3)	4.3 (3)	6.2 (4)	1.0 (2)	3.5 (3)	0.4 (3)	4.0
Cp_4	2.5 (3)	4.5 (3)	5.1 (4)	0.5 (2)	1.4 (3)	−0.3 (2)	4.1
Cp_5	3.4 (3)	4.3 (3)	3.4 (3)	1.7 (2)	0.8 (2)	0.9 (2)	3.8
H_1							1.3 (9)
H_2							2.8 (12)
H_3							3.0 (13)
H_4							5.9 (26)
H_5							4.1 (17)

[a] The B_{ij} are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$. [b] Except for hydrogen atoms, $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Distances in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$

Bond type	Length, Å	Bond type	Length, Å
W-W	3.222 (1)	C_3-O_3	1.130 (8)
W-C_1	1.975 (5)	Cp_1-Cp_2	1.41 (1)
W-C_2	1.956 (6)	Cp_2-Cp_3	1.44 (1)
W-C_3	1.996 (7)	Cp_3-Cp_4	1.42 (1)
W-Cp_1	2.344 (5)	Cp_4-Cp_5	1.41 (1)
W-Cp_2	2.377 (6)	Cp_5-Cp_1	1.38 (1)
W-Cp_3	2.359 (6)	Cp_1-H_1	0.85 (5)
W-Cp_4	2.326 (6)	Cp_2-H_2	1.09 (6)
W-Cp_5	2.305 (6)	Cp_3-H_3	1.10 (7)
C_1-O_1	1.155 (6)	Cp_4-H_4	0.85 (11)
C_2-O_2	1.163 (8)	Cp_5-H_5	0.76 (7)

Table IV. Selected Bond Angles in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$

Type of angle	Angle, deg	Type of angle	Angle, deg
W-C_1-O_1	174.4 (5)	C_1-W-C_2	77.7 (2)
W-C_2-O_2	178.2 (6)	C_1-W-C_3	106.3 (2)
W-C_3-O_3	173.2 (6)	C_2-W-C_3	79.8 (2)
Cp_5-Cp_1-Cp_2	108.1 (6)	Cp_1-W-Cp_2	34.6 (3)
Cp_1-Cp_2-Cp_3	108.2 (6)	Cp_2-W-Cp_3	35.4 (2)
Cp_2-Cp_3-Cp_4	106.4 (7)	Cp_3-W-Cp_4	35.2 (3)
Cp_3-Cp_4-Cp_5	107.9 (7)	Cp_4-W-Cp_5	35.4 (3)
Cp_4-Cp_5-Cp_1	109.4 (7)	Cp_5-W-Cp_1	34.6 (2)

Table V. Atomic Coordinates for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$

	Coordinates with standard deviations		
Atom type[a]	x	y	z
Mo	0.17785 (2)	−0.00803 (2)	0.13872 (2)
O_1	0.1412 (3)	0.3453 (3)	0.0142 (2)
O_2	0.3408 (3)	0.2280 (3)	0.3910 (2)
O_3	−0.0516 (3)	−0.0345 (3)	0.2260 (2)
C_1	0.1452 (3)	0.2138 (3)	0.0536 (3)
C_2	0.2780 (3)	0.1411 (4)	0.2976 (3)
C_3	0.0246 (3)	−0.0219 (3)	0.1862 (3)
Cp_1	0.2425 (4)	−0.2920 (4)	0.1639 (4)
Cp_2	0.2228 (4)	−0.2406 (4)	0.0432 (4)
Cp_3	0.3375 (4)	−0.1195 (4)	0.0775 (4)
Cp_4	0.4301 (4)	−0.0971 (4)	0.2201 (4)
Cp_5	0.3703 (4)	−0.2036 (4)	0.2727 (4)
H_1	0.189 (5)	−0.372 (6)	0.171 (4)
H_2	0.149 (4)	−0.271 (4)	−0.042 (3)
H_3	0.351 (4)	−0.080 (5)	0.023 (3)
H_4	0.503 (7)	−0.034 (6)	0.271 (5)
H_5	0.404 (4)	−0.219 (4)	0.357 (4)

[a] Atom labeling follows Figure 1 with Mo substituted for W.

Discussion

This work shows that the surprising trends previously observed in the compounds $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ for the M-M distances (Cr > Mo) and rotational barriers (Cr < Mo) extend monotonically to the tungsten analog, although the differences between the molybdenum and tungsten compounds are very small. The structural variations through the series of three compounds are well represented by the selected molecular dimensions which are compared in Table IX. This table also gives comparable results[15] for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$. The latter are considerably less precise and are shown here only to emphasize that the substitution of one CO group by CH_3NC has no significant effect on the remainder of the molecular structure. This result is important since it is a necessary one in order for CH_3NC-substituted molecules to be safely regarded as dynamically comparable to the unsubstituted parent molecules in studies designed to reveal the details of fluxional bebehavior.[15-19]

As Table IX clearly shows, the bond lengths and angles within half of a $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ molecule are not significantly different in the molybdenum and tungsten compounds. Also, in spite of the slightly shorter M-M distance for the tungsten compound the nonbonded contacts of the type $C_{1,3}$-$C_{3',1'}$ differ negligibly. However, for both the Mo and W compounds these contacts are significantly less severe (by ~0.08 Å) than for the Cr compound. Thus, the structural results might appear to lead to the expectation that the rotational barriers would vary in such a way that for the Mo and W compounds we would have Mo ≈ W with that in the Cr compound noticeably higher. This is not, in fact, what is found, but the inconsistency can be explained.

The activation parameters for all three compounds are collected for comparison in Table X. It may first be seen that the various energy terms, as well as the $\Delta S^{\ddagger}$ values, are the same within experimental error for the Mo and W compounds, which is consistent with the conclusion implied by the structural data. Only for the $\Delta G^{\ddagger}$ values might there be any significant implication that there is a lower value for the Mo compound, but since the apparent difference is equal to the sum of the uncertainties, this is

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(15) R. D. Adams, M. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6594 (1973).

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(17) R. D. Adams and F. A. Cotton, *Syn. Inorg. Metal-Org. Chem.*, **2**, 277 (1972).

(18) R. D. Adams and F. A. Cotton, *Inorg. Chem.*, **13**, 249 (1974).

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Table VI. Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$

	Anisotropic parameters (Å^2) with standard deviations[a]						
Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[b]
Mo	2.05 (1)	2.57 (1)	2,20 (1)	−0.09 (1)	0.80 (1)	−0.24 (1)	2.46
O_1	4.9 (1)	3.0 (1)	5.0 (1)	−0.6 (1)	2.1 (1)	0.3 (1)	4.4
O_2	4.0 (1)	7.4 (1)	3.8 (1)	−1.1 (1)	1.4 (1)	−2.8 (1)	4.8
O_3	4.6 (1)	7.0 (1)	3.9 (1)	−0.9 (1)	2.9 (1)	−0.5 (1)	4.6
C_1	2.8 (1)	3.1 (1)	2.9 (1)	−0.5 (1)	1.2 (1)	−0.7 (1)	3.1
C_2	2.6 (1)	4.5 (1)	2.9 (1)	−0.4 (1)	1.0 (1)	−0.7 (1)	3.5
C_3	2.9 (1)	3.8 (1)	2.5 (1)	−0.4 (1)	1.1 (1)	−0.3 (1)	3.2
Cp_1	3.4 (1)	2.7 (1)	5.1 (2)	0.5 (1)	1.8 (1)	0.4 (1)	3.9
Cp_2	3.4 (1)	3.9 (1)	4.4 (1)	0.8 (1)	1.7 (1)	−1.0 (1)	3.9
Cp_3	4.2 (1)	4.8 (1)	5.8 (2)	1.1 (1)	3.5 (1)	0.3 (1)	4.3
Cp_4	2.2 (1)	4.6 (1)	5.8 (2)	0.1 (1)	1.3 (1)	−0.6 (1)	4.2
Cp_5	3.6 (1)	4.3 (1)	3.7 (1)	1.3 (1)	1.0 (1)	0.8 (1)	4.2
H_1							7.1 (10)
H_2							4.2 (7)
H_3							4.8 (8)
H_4							8.1 (13)
H_5							4.9 (8)

[a] The B_{ij} are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$. [b] Except for hydrogen atoms, $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table VII. Bond Distances in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$

Bond type	Length, Å	Bond type	Length, Å
Mo-Mo	3.235 (1)	C_3-O_3	1.144 (4)
Mo-C_1	1.984 (3)	Cp_1-Cp_2	1.406 (5)
Mo-C_2	1.964 (3)	Cp_2-Cp_3	1.402 (5)
Mo-C_3	1.983 (3)	Cp_3-Cp_4	1.408 (5)
Mo-Cp_1	2.347 (3)	Cp_4-Cp_5	1.406 (5)
Mo-Cp_2	2.378 (3)	Cp_5-Cp_1	1.399 (4)
Mo-Cp_3	2.348 (3)	Cp_1-H_1	0.88 (4)
Mo-Cp_4	2.312 (3)	Cp_2-H_2	0.89 (3)
Mo-Cp_5	2.304 (3)	Cp_3-H_3	0.81 (3)
C_1-O_1	1.148 (3)	Cp_4-H_4	0.82 (5)
C_2-O_2	1.151 (3)	Cp_5-H_5	0.87 (3)

Table VIII. Selected Bond Angles in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$

Type of angle	Angle, deg	Type of angle	Angle, deg
Mo-C_1-O_1	173.4 (2)	C_1-Mo-C_2	77.9 (1)
Mo-C_2-O_2	178.0 (3)	C_1-Mo-C_3	105.9 (1)
Mo-C_3-O_3	173.3 (3)	C_2-Mo-C_3	79.2 (1)
Cp_5-Cp_1-Cp_2	107.9 (3)	Cp_1-Mo-Cp_2	34.6 (1)
Cp_1-Cp_2-Cp_3	108.2 (3)	Cp_2-Mo-Cp_3	34.5 (1)
Cp_2-Cp_3-Cp_4	107.9 (3)	Cp_3-Mo-Cp_4	35.2 (1)
Cp_3-Cp_4-Cp_5	107.7 (3)	Cp_4-Mo-Cp_5	35.4 (1)
Cp_4-Cp_5-Cp_1	108.3 (3)	Cp_5-Mo-Cp_1	35.0 (1)

Table IX. Comparison of Selected Dimensions of the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ Molecules and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$

	$(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$			$(\eta^5\text{-}C_5H_5)_2$-$Mo_2(CO)_5$-$(CNCH_3)$[a]
	M = Cr	M = Mo	M = W	
M-M, Å	3.281 (1)	3.235 (1)	3.222 (1)	3.230 (1)
M-$C_{1,3}$ (av), Å	1.868	1.984	1.986	1.96
M-C_2, Å	1.846	1.964	1.956	1.95
$C_{1,3}$-$O_{1,3}$, Å	1.142	1.146	1.14_2	1.16_5
C_2-O_2, Å	1.146	1.151	1.16_3	1.18
$C_{1,3}$-$C_{3',1'}$, Å	2.720	2.810	2.80_1	
∠$MC_{1,3}O_{1,3}$ (av), deg	172.43	173.37	173.7_8	172
∠MC_2O_2, deg	178.73	178.02	178.1_9	176
∠$M'MC_{1,3}$ (av), deg	71.18	71.18	71.2_8	70.4

[a] From $(\eta^5\text{-}C_5H_5)Mo(CO)_3$–half only.

questionable. However, the direct experimental observations do suggest that at any given temperature the rate for the Mo compound is slightly greater than that for the W compound, in accord with the apparent difference in $\Delta G^{\ddagger}$ values.

Table X. M-M Distances and Rotational Activation Parameters[a] (298°K) for the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ Molecules

M	d(M-M), Å	Log A	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Cr	3.281 (1)	14.2 (6)	13.7 (5)	12.1 (7)	13.1 (5)	+4.5 (30)
Mo	3.235 (1)	13.0 (10)	15.3 (5)	15.0 (7)	14.7 (5)	−1.0 (40)
W	3.222 (1)	12.1 (10)	15.2 (4)	16.2 (5)	14.6 (4)	−5.2 (40)

[a] E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ in kcal mol^{-1}; $S^{\ddagger}$ in cal mol^{-1} deg^{-1}; figures in parentheses are esd's occurring in last decimal place.

The direct observation of line shapes clearly shows that at any given temperature rotation is faster for the Cr compound than for the Mo compound. This is reflected in the activation parameters. However, the overall difference in $\Delta G^{\ddagger}$ values appears to be due in significant measure (roughly half) to a more favorable entropy of activation.

While we recognize that the uncertainties in the thermodynamic activation parameters are large enough to behoove a cautious approach in their interpretation, it does seem clear that, whereas the structural results imply that the barrier in the Cr compound might be higher than in the Mo compound, the difference is, in fact, roughly 1.5 kcal mol^{-1} in the opposite sense. However, the entropy of activation for the Cr compound appears to be significantly more positive than for the Mo and W compounds.

A possible resolution of the apparent inconsistency between structural and kinetic data can be found in our original reasoning[2] as to why the Cr-Cr bond length is significantly longer than the Mo-Mo bond length. The relevant point here is that at its *equilibrium length,* the Cr-Cr bond is *substantially weaker* than the Mo-Mo bond. Therefore during the process of rotation, the Cr-Cr bond can and will stretch more than the Mo-Mo bond. If it is assumed that part of the barrier (E_a or $\Delta H^{\ddagger}$) to rotation in all three cases is attributable to energy required to stretch the M-M bonds, then for the Cr-Cr case, that component will be significantly less than it is in the other two cases. Moreover, the stretching of the Cr-Cr bond may be more extensive than that of the other two bonds thereby allowing more freedom in the transition state, which would account for a more favorable entropy of activation. Whether the latter consideration is really important is difficult to say with certainty. In any case, however, our original concept concerning the relative weakness of the Cr-Cr bond appears to explain not only the greater length of that bond, as shown previously, but to explain also the greater rotational lability of the Cr compound.

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Supplementary Material Available. A listing of 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-74-1086.

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Bonding Studies of Bis(tetramethylurea)dichlorooxovanadium(IV)

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The bonding in the X-ray-determined low-symmetry complex bis(tetramethylurea)dichlorooxovanadium(IV) was studied by optical and electron spin resonance spectroscopy and by molecular orbital calculations of the Wolfsberg-Helmholz type and compared with the bonding in high-symmetry complexes such as $VOCl_4{}^{2-}$. Assignments of the d–d optical transitions were made on the basis of calculated and experimental intensities as well as considerations of the expected effects of substituents and electrostatic terms. The molecular orbital calculations indicated a removal of all degeneracy in the vanadium d-orbital energy levels while the experimental optical spectra were ambiguous on this point. Of particular interest from the MO calculations is the finding of a bonding molecular orbital which is delocalized over the equatorial ligands and the vanadyl oxygen in $VO(tmu)_2Cl_2$. The esr data indicated that the overall average environment for the d_{xy} unpaired electron was very similar for $VO(tmu)_2Cl_2$ and $VOCl_4{}^{2-}$.

I. Introduction

A combined experimental and theoretical investigation of the electronic structure and chemical bonding of low-symmetry transition metal complexes is in progress in our laboratory in order to extend the knowledge of the dependence of bonding upon symmetry. This is considered important since many spectroscopic theories have been derived and/or tested mainly for cases of relatively high symmetry while many complexes of practical use such as industrial catalyst systems and biological complexes are of low symmetry. In previous papers we have studied the bonding of low-symmetry Cu(II) complexes.[1-3] Cu(II) was chosen since it has one unpaired electron which is normally involved in σ-type bonding to the ligands and can be easily studied by electron spin resonance spectroscopy. In order to extend this investigation to systems in which the unpaired electron is in the π system we have initiated similar studies of vanadyl complexes. The appearance of a three-dimensional X-ray structure determination[4] for bis(tetramethylurea)dichlorooxovanadium(IV), $VOCl_2 \cdot 2tmu$, made it an obvious choice for an initial study of this type.

II. Experimental Section

The complex was prepared according to the general method of du Preez and Sadie[5] and checked by comparison with their published ir data and elemental analysis. Digital electronic absorption spectra were obtained from a Cary 17 spectrophotometer and resolved into gaussian components by the use of the Fortran program BiGauss written by Cavell.[6] Esr studies were carried out on a Strand-Magnion, Varian hybrid spectrometer on 10^{-2}–10^{-3} *M* solutions of the complex dissolved in $CHCl_3$.

For the theoretical calculations the extended Huckel method was used. The calculation procedure used is different from what has been employed in previous studies. Rather than converging on a charge self-consistent solution based on either the theoretical charge dependence of the H_{ii} terms[7] or a scaled charge dependence for the metal ion with fixed ligand values,[8] we have chosen to calculate to charge self-consistency for the organic ligand and the vanadyl oxygen,[9] to use the neutral chloride H_{ii} values to correct for Madelung energy,[10] and empirically to adjust the vanadium 3d orbital H_{ii} value until a correct ground state is obtained and the esr, optical, and molecular orbital coefficient data are in general agreement with experiment. This is not a severe approximation since one adjustable parameter is being used simultaneously to fit a number of experimental parameters. The purpose of this approach is to see what the effect of the low-symmetry ligand environment is on the vanadium–ligand bonds, *i.e.*, what mixing and/or splitting of molecular orbitals occurs in this X-ray-determined low-symmetry complex which do not occur in high-symmetry classical complexes. The final values of the coulomb integrals, H_{ii}, are given in Table I (microfilm edition only). The orientation chosen for the calculations puts the vanadyl oxygen along the $+z$ direction, the vanadium at the origin, the chlorines in the general x and $-x$ directions, and the tmu ligands along the general y and $-y$ directions.

In order to check whether the final calculated organic ligand charge distributions and energy levels are realistic, CNDO2,[11] MINDOII,[12] and CNDO-CI[13] calculations were performed on the tetramethylurea. The charge distributions and energies calculated by the various methods for tmu are given in Table II (microfilm edition only).

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