J. Am. Chem. Soc. **1982**, *104*, 5651-5657

Preparation, Properties, and Structures of the Clusters Hexakis(μ_3-oxo)pentakis(η^5-cyclopentadienylvanadium), $[(\eta^5\text{-}C_5H_5)_5V_5O_6]$, and Tetrakis($\mu_3$-oxo)tetrakis($\eta^5$-cyclopentadienylchromium), $[(\eta^5\text{-}C_5H_5)_4Cr_4O_4]$

Frank Bottomley,* Daniel E. Paez, and Peter S. White

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2. *Received February 2, 1982*

Abstract: The reaction of N_2O with Cp_2V or Cp_2Cr gives $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$, respectively ($Cp = \eta^5\text{-}C_5H_5$). The structures of the clusters show that they are similar. $Cp_5V_5O_6$ (which has a magnetic moment of 0.93 μ_B at 25 °C) is a trigonal bipyramid of V atoms with an oxygen atom over each triangular face. The V(axial)–O distance of 1.861 (6) Å is shorter than the V(equatorial)–O distance of 1.992 (6) Å. The Cp rings that cap each V atom have perpendicular distances from the axial V atoms of 1.997 Å and from the equatorial V atoms of 1.973 Å. The differing equatorial and axial V–Cp and V–O distances are due to the different formal oxidation states of the V atoms, the axial V being V(IV), the equatorial V(III). The V(axial)–V(equatorial) average distance, 2.752 (2) Å, is at the minimum determined by the steric requirements of the Cp rings and is not significantly different from the V(equatorial)–V(equatorial) distance of 2.740 (2) Å. $Cp_4Cr_4O_4$ (which is antiferromagnetic) is a distorted tetrahedron of Cr atoms with an oxygen over each triangular face and a Cp ring capping each Cr atom (average Cr–Cp 1.920 Å); $Cp_4Cr_4O_4$ is therefore a cubane-like molecule. The Cr–Cr distances occur in pairs: 2.702 (6) and 2.712 (2) Å; 2.811 (6) and 2.841 (6) Å; and 2.897 (5) and 2.900 (6) Å; and the O–Cr–O and Cr–O–Cr angles are correspondingly found in three sets of four angles. The average values are for O–Cr–O: 83.2 (2), 86.2 (1), and 90.1 (1); for Cr–O–Cr: 88.8(1), 93.8(1), and 96.7(2). The $Cp_4Cr_4O_4$ cluster has D_2 symmetry. The shortest Cr–Cr distances (average 2.707 Å) are at a minimum determined by the steric requirements of the attached Cp rings. In both $Cp_4Cr_4O_4$ and $Cp_5V_5O_6$, the M–O distances are indicative of single bonds. The M–M interaction is discussed and compared with the metal–metal interactions in other clusters and dimers. Crystal data for $Cp_5V_5O_6$: monoclinic, $P2_1/c$, a = 9.825 (4) Å, b = 15.584 (9) Å, c = 19.592 (8) Å, β = 123.83 (3)°, final R = 0.069, R_w = 0.086 for 426 variables and 2180 observed reflections; for $Cp_4Cr_4O_4$: monoclinic, $P2_1/c$, a = 10.45 (2) Å, b = 20.94 (1) Å, c = 11.02 (2) Å, β = 124.24 (2)°, final R = 0.030, R_w = 0.046 for 334 variables and 2162 observed reflections.

We have been systematically investigating the reactions between dinitrogen oxide (N_2O, nitrous oxide or "laughing gas") and organometallic complexes of the early transition metals.[1-3] Our aims had been to prepare complexes containing N_2O as a ligand (only one of which, $[Ru(NH_3)_5(N_2O)]^{2+}$, has to date been characterized[4]) and to use N_2O as a mild oxygen donor to prepare complexes containing the M═O moiety. It has become apparent that N_2O complexes are extremely unstable with respect to disproportionation and oxidation and also that N_2O functions as a source of bridging rather than terminal oxygen atoms.[3] This latter property has resulted in a facile route to oxo-bridged molecular clusters and dimers of the early transition metals, in contrast to the polymers usually obtained on oxidation of complexes of these metals. We describe here the use of N_2O to prepare the two related clusters given in the title, $(\eta^5\text{-}C_5H_5)_5V_5(\mu_3\text{-}O)_6$ and $(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}O)_4$, hereafter referred to as $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$. Brief reports of parts of this work have appeared previously.[5,6] In a separate paper, a theoretical approach to the electronic and molecular structures of these complexes is discussed.[7]

Experimental Section

Instruments. Infrared spectra were measured as Nujol or Fluorolube mulls or in toluene solution between KBr or CaF_2 plates, respectively, on a Perkin-Elmer 457 IR spectrophotometer and ESR spectra on a locally modified version of the Varian E-4 ESR spectrometer. Magnetic moments were measured at room temperature by the Faraday method (Alpha Scientific magnet and power supply units with a Cahn electrobalance) and over a variable-temperature range by Professor A. B. P. Lever, York University, Ontario, Canada. Microanalyses were performed by the Analytische Laboratorien, Engelskirchen, West Germany. A locally modified version of the vacuum line described by Shriver[8] was used for the manipulation of compounds under argon or vacuum.

Synthesis of $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$. Both $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$ were synthesized by a similar procedure. Successful preparation required rigorously air- and water-free conditions. All solvents were stored under vacuum over CH_3Li and oven-dried glassware was flamed under vacuum before use.

A solution of Cp_2M[9] (M = V or Cr) (4.5 g, 25 mM) in toluene (100 cm^3) was incubated with 1 molar equiv of N_2O (measured by using a calibrated bulb attached to the vacuum line) for 72 h at room temperature. The solution changed color from purple to black (Cp_2V) or red to dark blue (Cp_2Cr). The solvent was removed in vacuo and the residue sublimed under vacuum at 120 °C (Cp_2V) or 100 °C (Cp_2Cr) for 12 h to remove unreacted Cp_2V (0.9 g, 5.2 mM) or Cp_2Cr (1.9 g, 10.4 mM). The temperature was then increased to 285 °C ($Cp_5V_5O_6$) or 300 °C ($Cp_4Cr_4O_4$) and the residue sublimed under vacuum for a further 12 h. The sublimed products were finally recrystallized from toluene/hexane as shiny black rhombohedra of $Cp_5V_5O_6$ (0.68 g, 17%) or bright blue rhombohedra of $Cp_4Cr_4O_4$ (0.39 g, 21%). Yields are based on the amount of Cp_2M actually consumed, not on the initial amount of Cp_2M. Anal. Calcd for $C_{25}H_{25}V_5O_6$: C, 44.4; H, 3.7; V, 37.7. Found: C, 44.3; H, 3.9; V (as V_2O_5) 34.7. Calcd for $C_{20}H_{20}Cr_4O_4$: C, 45.1; H, 3.8; Cr, 39.1. Found: C, 44.8; H, 4.2; Cr (as Cr_2O_3), 39.4.

Crystal Structure Determinations

Collection and Reduction of Intensity Data. Crystals were obtained as described above and were covered with air-free "Apiezon" grease and

---

(1) Bottomley, F.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* **1978**, 234–35.

(2) Bottomley, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5238–5242.

(3) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

(4) Bottomley, F.; Brooks, W. V. F. *Inorg. Chem.* **1977**, *16*, 501–2.

(5) Bottomley, F.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 28–29.

(6) Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 5581–82.

(7) Bottomley, F.; Grein, F. *Inorg. Chem.*, in press.

(8) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

(9) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. I, pp 64–79.

0002-7863/82/1504-5651$01.25/0

Table I. Crystal Data for $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$

	$Cp_5V_5O_6$	$Cp_4Cr_4O_4$
M_r	676.2	532.4
crystal class	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	9.825 (4)	10.45 (2)
b, Å	15.584 (9)	20.94 (1)
c, Å	19.592 (8)	11.02 (2)
β, deg	123.83 (3)	124.24 (2)
Z	4	4
Mo K$\bar{\alpha}$ radiation, Å	0.71069	0.71069
absorption coeff μ, mm^{-1}	1.79	2.10
crystal dimensions, mm	0.28 × 0.48 × 0.14	0.08 × 0.22 × 0.50
calculated density, Mg m^{-3}	1.80	1.77
no. of independent reflections	3250	2616
2θ(max), deg	45	45
no. with $I > 3\sigma(I)$	2180	2162
no. of variables	426	334
$R = \Sigma\Delta\|F\|/\Sigma\|F\|$	0.069	0.030
$R_w = (\Sigma w(\Delta F)^2/\Sigma wF^2)^{1/2}$	0.086	0.046
max residual intensity, e Å^{-3}	1.11	0.41
min residual intensity, e Å^{-3}	−0.87	−0.38

Table II. Fractional Atomic Coordinates (esd) for $Cp_5V_5O_6$

atom	x	y	z
V(1)	0.16062 (17)	0.86334 (10)	0.64208 (8)
V(2)	0.11515 (19)	0.97010 (10)	0.84217 (9)
V(3)	0.23963 (16)	0.99894 (10)	0.74879 (8)
V(4)	0.23033 (17)	0.83572 (10)	0.79756 (8)
V(5)	−0.05493 (16)	0.91660 (9)	0.68099 (8)
O(1)	0.0502 (7)	0.8066 (4)	0.6821 (3)
O(2)	0.3392 (7)	0.8886 (4)	0.7475 (3)
O(3)	0.0615 (7)	0.9675 (3)	0.6337 (3)
O(4)	0.0257 (7)	0.8648 (4)	0.7906 (3)
O(5)	0.3164 (7)	0.9475 (4)	0.8571 (3)
O(6)	0.0361 (7)	1.0252 (4)	0.7435 (3)
C(11)	0.1657 (15)	0.7464 (7)	0.5716 (7)
C(12)	0.3155 (13)	0.7906 (8)	0.6043 (6)
C(13)	0.2792 (12)	0.8689 (6)	0.5658 (6)
C(14)	0.1086 (13)	0.8749 (7)	0.5108 (6)
C(15)	0.0374 (12)	0.7979 (7)	0.5139 (6)
C(21)	0.1082 (19)	1.0860 (7)	0.9140 (8)
C(22)	0.2307 (15)	1.0330 (8)	0.9710 (7)
C(23)	0.1661 (14)	0.9563 (8)	0.9721 (6)
C(24)	−0.0032 (18)	0.9637 (9)	0.9152 (9)
C(25)	−0.0414 (16)	1.0416 (8)	0.8788 (7)
C(31)	0.4098 (20)	1.0673 (9)	0.7222 (9)
C(32)	0.4834 (14)	1.0654 (8)	0.8076 (8)
C(33)	0.3978 (22)	1.1126 (8)	0.8248 (10)
C(34)	0.2690 (19)	1.1459 (8)	0.7506 (16)
C(35)	0.2819 (18)	1.1164 (11)	0.6904 (9)
C(41)	0.2609 (17)	0.7362 (8)	0.8918 (8)
C(42)	0.2303 (14)	0.6925 (6)	0.8231 (7)
C(43)	0.3612 (15)	0.7088 (7)	0.8161 (7)
C(44)	0.4711 (13)	0.7619 (8)	0.8808 (7)
C(45)	0.4052 (15)	0.7760 (8)	0.9258 (6)
C(51)	−0.3020 (13)	0.8767 (10)	0.6584 (8)
C(52)	−0.2932 (13)	0.8447 (6)	0.5937 (10)
C(53)	−0.2853 (13)	0.9126 (9)	0.5506 (7)
C(54)	−0.2938 (11)	0.9877 (7)	0.5852 (6)
C(55)	−0.3048 (12)	0.9645 (9)	0.6506 (7)

mounted in sealed tubes under nitrogen. The space groups and symmetries were determined by using Weissenberg and precession photographs, and intensity data were collected on a Picker FACS-1 4-circle computer-controlled diffractometer. Data for the crystals are listed in Table I. Cell dimensions, at 25 °C, were determined from 12 Friedel pairs of reflections accurately centered on the diffractometer.

Table III. Fractional Atomic Coordinates (esd) for $Cp_4Cr_4O_4$

atom	x	y	z
CR(1)	0.39464 (6)	0.35968 (3)	0.46417 (6)
CR(2)	0.14551 (6)	0.29317 (3)	0.20847 (6)
CR(3)	0.35024 (6)	0.37975 (3)	0.20076 (6)
CR(4)	0.11548 (6)	0.41878 (3)	0.24802 (6)
O(1)	0.3678 (3)	0.30417 (11)	0.31004 (25)
O(2)	0.3339 (3)	0.43254 (11)	0.33572 (25)
O(3)	0.1275 (3)	0.37075 (11)	0.10371 (25)
O(4)	0.1756 (3)	0.34400 (11)	0.36891 (24)
C(11)	0.4944 (5)	0.3200 (2)	0.6916 (4)
C(12)	0.4802 (5)	0.3870 (2)	0.6966 (4)
C(13)	0.5787 (5)	0.4162 (2)	0.6622 (4)
C(14)	0.6500 (4)	0.3668 (2)	0.6345 (4)
C(15)	0.5995 (4)	0.3083 (2)	0.6524 (4)
C(21)	−0.0766 (5)	0.2512 (2)	0.0215 (5)
C(22)	0.0451 (5)	0.2139 (2)	0.0402 (4)
C(23)	0.1182 (5)	0.1858 (2)	0.1779 (4)
C(24)	0.0468 (5)	0.2042 (2)	0.2460 (5)
C(25)	−0.0751 (5)	0.2457 (2)	0.1487 (5)
C(31)	0.5669 (5)	0.3576 (2)	0.2104 (5)
C(32)	0.5716 (4)	0.4225 (2)	0.2447 (4)
C(33)	0.4465 (5)	0.4536 (2)	0.1206 (5)
C(34)	0.3667 (4)	0.4077 (2)	0.0099 (4)
C(35)	0.4380 (5)	0.3482 (2)	0.0639 (4)
C(41)	−0.0423 (6)	0.4516 (3)	0.3133 (6)
C(42)	−0.1333 (5)	0.4344 (2)	0.1643 (6)
C(43)	−0.0983 (5)	0.4763 (3)	0.0904 (5)
C(44)	0.0108 (6)	0.5177 (2)	0.1878 (6)
C(45)	0.0465 (5)	0.5041 (2)	0.3243 (6)

Table IV. Distances in the $Cp_5V_5O_6$ (Å) (esd)

V(1)–V(3)	2.763 (2)	V(3)–O(5)	1.983 (6)
V(1)–V(4)	2.759 (2)	V(3)–O(6)	1.986 (6)
V(1)–V(5)	2.748 (2)	V(4)–V(5)	2.744 (2)
V(1)–O(1)	1.876 (6)	V(4)–O(1)	1.999 (5)
V(1)–O(2)	1.861 (6)	V(4)–O(2)	1.988 (6)
V(1)–O(3)	1.853 (6)	V(4)–O(4)	1.990 (6)
V(2)–V(3)	2.745 (2)	V(4)–O(5)	2.003 (6)
V(2)–V(4)	2.744 (2)	V(5)–O(1)	1.995 (6)
V(2)–V(5)	2.754 (2)	V(5)–O(3)	1.994 (5)
V(2)–O(4)	1.870 (7)	V(5)–O(4)	2.000 (6)
V(2)–O(5)	1.864 (6)	V(5)–O(6)	1.985 (6)
V(2)–O(6)	1.846 (6)	V(1)–Cp(1)[a]	2.003
V(3)–V(4)	2.737 (3)	V(2)–Cp(2)	1.994
V(3)–V(5)	2.740 (2)	V(3)–Cp(3)	1.977
V(3)–O(2)	1.986 (6)	V(4)–Cp(4)	1.973
V(3)–O(3)	1.998 (6)	V(5)–Cp(5)	1.969

[a] V–Cp is the perpendicular distance to the centroid of the η^5-C_5H_5 ring.

Structure Solution and Refinement. Preliminary positions for the metal atoms were derived by using MULTAN direct methods procedures.[10] The positions of these atoms were used in the phasing of Fourier syntheses and the positions of all non-hydrogen atoms subsequently determined by successive Fourier and partial refinement techniques.[11] The structures were refined by standard least-squares techniques, minimizing the function $\sum w(\Delta F)^2$, with weighting schemes of the form $w = 1/(\sigma(F)^2 + kF^2)$ based on counting statistics. Scattering factors were taken from the International Tables for Crystallography[12] and were corrected for the effects of anomalous dispersion (both real and imaginary parts). The structures were refined by using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were observed in difference-Fourier syntheses at low R values and included in the calculations with their isotropic thermal parameters and positions being refined. Extinction corrections were made in the refinement, and absorption corrections were also applied to the observed intensities.

In the final refinement of $Cp_5V_5O_6$, it was found that some of the C atoms of two of the rings had unusually high thermal parameters (these

---

(10) Main, P.; Woolfson, M. M.; Germain, G. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(11) Programs used were those of Larson, A. C.; Gabe, E. J. "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Korningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; 81–89.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table V. Angles in the $Cp_5V_5O_5$ Core (Deg) (esd)

O(1)-V(1)-O(2)	92.47 (24)	V(1)-O(2)-V(3)	91.8 (3)
O(1)-V(1)-O(3)	92.97 (25)	V(1)-O(2)-V(4)	91.5 (3)
O(2)-V(1)-O(3)	92.1 (3)	V(3)-O(2)-V(4)	87.04 (23)
O(4)-V(2)-O(5)	93.3 (3)	V(1)-O(3)-V(3)	91.60 (24)
O(4)-V(2)-O(6)	92.6 (3)	V(1)-O(3)-V(5)	91.13 (23)
O(5)-V(2)-O(6)	92.5 (3)	V(3)-O(3)-V(5)	86.68 (22)
O(2)-V(3)-O(3)	84.34 (24)	V(2)-O(4)-V(4)	90.6 (3)
O(2)-V(3)-O(5)	76.53 (24)	V(2)-O(4)-V(5)	90.7 (3)
O(2)-V(3)-O(6)	131.78 (24)	V(4)-O(4)-V(5)	86.92 (23)
O(3)-V(3)-O(5)	132.89 (24)	V(2)-O(5)-V(3)	91.0 (3)
O(3)-V(3)-O(6)	76.55 (23)	V(2)-O(5)-V(4)	90.35 (25)
O(5)-V(3)-O(6)	84.91 (24)	V(3)-O(5)-V(4)	86.73 (23)
O(1)-V(4)-O(2)	85.18 (23)	V(2)-O(6)-V(3)	91.4 (3)
O(1)-V(4)-O(4)	75.54 (24)	V(2)-O(6)-V(5)	91.8 (3)
O(1)-V(4)-O(5)	132.58 (24)	V(3)-O(6)-V(5)	87.23 (23)
O(2)-V(4)-O(4)	132.3 (3)	Cp(1)-A-Cp(2)[a]	177.3
O(2)-V(4)-O(5)	76.01 (24)	Cp(1)-A-Cp(3)	87.7
O(4)-V(4)-O(5)	85.7 (3)	Cp(1)-A-Cp(4)	88.7
O(1)-V(5)-O(3)	85.37 (23)	Cp(1)-A-Cp(5)	90.7
O(1)-V(5)-O(4)	75.43 (24)	Cp(2)-A-Cp(3)	90.4
O(1)-V(5)-O(6)	132.28 (23)	Cp(2)-A-Cp(4)	89.7
O(3)-V(5)-O(4)	132.29 (24)	Cp(2)-A-Cp(5)	92.4
O(3)-V(5)-O(6)	76.67 (24)	Cp(3)-A-Cp(4)	117.3
O(4)-V(5)-O(6)	84.8 (3)	Cp(3)-A-Cp(5)	123.5
V(1)-O(1)-V(4)	90.72 (23)	Cp(4)-A-Cp(5)	119.1
V(1)-O(1)-V(5)	90.42 (25)		
V(4)-O(1)-V(5)	86.81 (22)		

[a] Cp-A-Cp is the angle subtended by the normals to the η^5-C_5H_5 rings projected through the V atoms into the V_5O_6 rhombohedron.

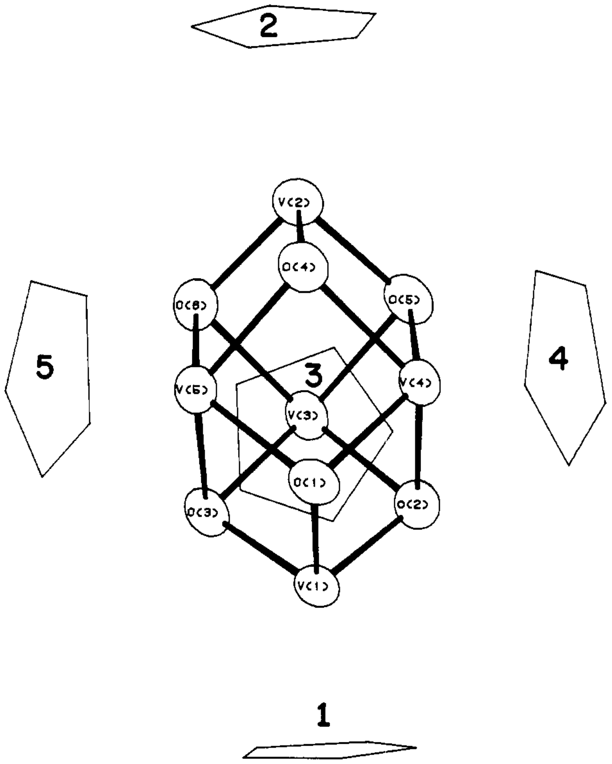

Figure 1. $Cp_5V_5O_6$ cluster showing the atom and ring numbering schemes.

can be seen in the ORTEP[13] plot in Figure 3). It appears that there is either disorder or rotation of these rings. No attempt was made to investigate this problem. The rather high final R value for $Cp_5V_5O_6$ compared to $Cp_4Cr_4O_4$ is certainly due to this ring libration.

The positional parameters from the final refinement of $Cp_5V_5O_6$ are given in Table II, from the final refinement of $Cp_4Cr_4O_4$ in Table III. Tables of hydrogen-atom positions, thermal parameters, equations of mean planes, and $|F_o|$ and $|F_c|$ for both structures are available as supplementary material for this paper. The distances and angles derived from the final positional parameters are given for the $Cp_5V_5O_6$ core in Tables IV and V and for the $Cp_4Cr_4O_4$ core in Tables VI and VII. The distances are uncorrected for libration. The numbering schemes are shown in Figures 1 and 2. The C-C, V-C, and Cr-C distances and C-C-C angles are given in the supplementary material.

Table VI. Distances in $Cp_4Cr_4O_4$ Core (esd)

Cr(1)-Cr(2)	2.900 (6)	Cr(3)-Cr(4)	2.897 (5)
Cr(1)-Cr(3)	2.702 (6)	Cr(3)-O(1)	1.934 (3)
Cr(1)-Cr(4)	2.811 (6)	Cr(3)-O(2)	1.936 (3)
Cr(1)-O(1)	1.944 (4)	Cr(3)-O(3)	1.949 (6)
Cr(1)-O(2)	1.930 (3)	Cr(4)-O(2)	1.936 (6)
Cr(1)-O(4)	1.936 (6)	Cr(4)-O(3)	1.944 (4)
Cr(2)-Cr(3)	2.841 (4)	Cr(4)-O(4)	1.918 (3)
Cr(2)-Cr(4)	2.712 (2)	Cr(1)-Cp(1)[a]	1.912
Cr(2)-O(1)	1.944 (6)	Cr(2)-Cp(2)	1.920
Cr(2)-O(3)	1.940 (3)	Cr(3)-Cp(3)	1.925
Cr(2)-O(4)	1.932 (4)	Cr(4)-Cp(4)	1.922

[a] Cr-Cp is the perpendicular distance to the centroid of the η^5-C_5H_5 ring.

Table VII. Angles in the $Cp_4Cr_4O_4$ Core (Deg) (esd)

O(1)-Cr(1)-O(2)	90.31 (17)	Cr(1)-O(2)-Cr(3)	88.70 (16)
O(1)-Cr(1)-O(4)	83.05 (16)	Cr(1)-O(2)-Cr(4)	93.33 (15)
O(2)-Cr(1)-O(4)	86.28 (15)	Cr(3)-O(2)-Cr(4)	96.89 (17)
O(1)-Cr(2)-O(3)	85.89 (14)	Cr(2)-O(3)-Cr(3)	93.89 (14)
O(1)-Cr(2)-O(4)	83.15 (17)	Cr(2)-O(3)-Cr(4)	88.60 (14)
O(3)-Cr(2)-O(4)	89.70 (15)	Cr(3)-O(3)-Cr(4)	96.17 (18)
O(1)-Cr(3)-O(2)	90.43 (15)	Cr(1)-O(4)-Cr(2)	97.14 (17)
O(1)-Cr(3)-O(3)	85.92 (14)	Cr(1)-O(4)-Cr(4)	93.67 (15)
O(2)-Cr(3)-O(3)	83.27 (17)	Cr(2)-O(4)-Cr(4)	89.59 (16)
O(2)-Cr(4)-O(3)	83.41 (17)	Cp(1)-A-Cp(2)[a]	119.7
O(2)-Cr(4)-O(4)	86.60 (15)	Cp(1)-A-Cp(3)	94.7
O(3)-Cr(4)-O(4)	89.96 (16)	Cp(1)-A-Cp(4)	109.3
Cr(1)-O(1)-Cr(2)	96.46 (17)	Cp(2)-A-Cp(3)	116.0
Cr(1)-O(1)-Cr(3)	88.36 (15)	Cp(2)-A-Cp(4)	93.3
Cr(2)-O(1)-Cr(3)	94.23 (15)	Cp(3)-A-Cp(4)	123.1

[a] Cp-A-Cp is the angle subtended by the normals to the η^5-C_5H_5 rings projected through the Cr atom into the Cr_4O_4 rhombohedron.

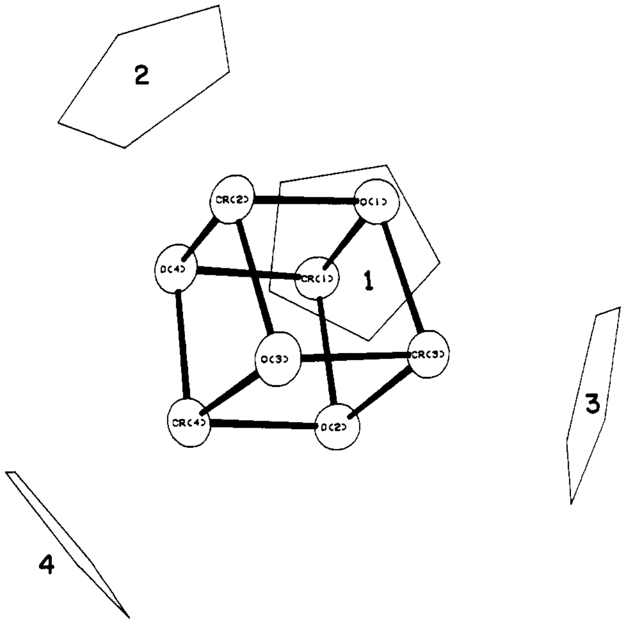

Figure 2. $Cp_4Cr_4O_4$ cluster showing the atom and ring numbering schemes.

Results and Discussion

Synthesis of $Cp_5V_5O_6$. Toluene solutions of Cp_2V absorb N_2O at −78 °C in a 1:1 molar ratio. The color of the solution changes from purple to wine-red. There is no gas evolution. The solution

---

(13) Johnson, C. K. Report ORNL-5138; ORTEP-II: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

appears to be stable with respect to gas evolution or color change for at least 30 min at −78 °C. We presume that it contains a Cp_2V-N_2O complex, but all attempts to isolate this complex failed. Addition of hexane to the solution at −78 °C precipitated a solid from which Cp_2V, $Cp_5V_5O_6$, and a mauve material could be obtained by sublimation and fractional recrystallization. The mauve material could also be obtained from the reaction between O_2 and Cp_2V in toluene.[14] It had the approximate composition $Cp_3V_2O_3$ (Anal. Found: C, 50.7; H, 4.4; V(as V_2O_5), 30.3; $Cp_3V_3O_2$ requires C, 52.2; H, 4.4; V, 29.5), was air stable, and had a paramagnetism of 1.40 μ_B (calculated for that formulation). From the analysis and the magnetic moment, it appears that the mauve material is more highly oxidized than $Cp_5V_5O_6$ and is therefore unlikely to be an intermediate in the formation of the cluster. Crystals of $Cp_5V_5O_6$ can be manually separated from the mixture obtained by reaction of N_2O with Cp_2V at −78 °C. This indicates that neither sublimation nor heat is necessary for formation of the cluster, though sublimation is the best purification procedure. It should also be noted that N_2O is necessary for the formation of $Cp_5V_5O_6$; O_2 does not give the cluster, only the mauve material.

Because of the low yield of $Cp_5V_5O_6$ and the concurrent formation of the mauve material (which may contain more than one compound), we have not been able to follow the formation of $Cp_5V_5O_6$; neither do we know the fate of the Cp ring lost from Cp_2V in the process.

Synthesis of $Cp_4Cr_4O_4$. On addition of N_2O to a toluene solution of Cp_2Cr at −78 °C, there is no immediate color change or gas evolution. Over a period of several hours, the solution slowly evolves N_2, becomes dark, and precipitates a blue solid. The same sequence of events occurs when the reaction is conducted at room temperature. The blue solid is not pure $Cp_4Cr_4O_4$ but contains at least one other species. Removal of solvent from the mixture and sublimation under high vacuum at 300 °C gives a dark blue sublimate, which on recrystallization from hexane gives blue $Cp_4Cr_4O_4$. However, the hexane solution shows varying shades of blue-green. If the sublimation is conducted at 230 instead of 300 °C, a reduced yield of $Cp_4Cr_4O_4$ is obtained, but the residue is now dark green in color. Increasing the sublimation temperature to 300 °C produces a mixed sublimate of a grass-green material and blue $Cp_4Cr_4O_4$. Although we can separate $Cp_4Cr_4O_4$ from the green solid, the reverse has so far proved impossible (efforts are continuing). The facts that it is indistinguishable from $Cp_4Cr_4O_4$ in the infrared spectrum, is hexane soluble, and is thermally stable suggest that the green solid is also a $Cp_mCr_mO_n$ cluster.

In 1960, Fischer, Ulm, and Fritz described $(CpCrO)_4$, obtained from Cp_2Cr and O_2 in benzene.[15,16] They suggested an eight-membered ring structure on the basis of IR spectroscopy, but the properties they report for their material make it certain that it is the same as our cubane-like $Cp_4Cr_4O_4$. They suggested that $Cp_4Cr_4O_4$ did not appear until a high-temperature sublimation was performed, but this is not true when N_2O is used as oxidant.

Properties of $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$. Both $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$ are among the most air- and water-sensitive materials we have handled, being rapidly decomposed to mauve (from $Cp_5V_5O_6$) or brown-black (from $Cp_4Cr_4O_4$) materials by traces of air, even in the crystalline state. This is very surprising since $Cp_5V_5O_6$ formally contains V(III) and V(IV), and $Cp_4Cr_4O_4$ is formally an oxide of Cr(III) and as such would be expected to be air and water stable. Presumably, the lack of electrons for π backbonding to Cp is responsible for the instability, which must involve the rings. Both clusters were moderately soluble in hexane and very soluble in toluene.

Fischer, Ulm, and Fritz reported that $[CpCrO]_4$ had two absorption bands in the infrared spectra that were due to vibrations of the Cr_4O_4 core at 750 and 551 cm^{-1}. We have been unable to confirm the band at 750 cm^{-1}, which occurs in the same region as an intense Cp ring absorption. We did observe a band at 545 cm^{-1}. For $Cp_6Ti_6O_8$, Caulton et al.[17] observed bands due to the Ti_6O_8 core at 728 and 598 cm^{-1}. For both $Cp_4Cr_4O_4$ and $Cp_6Ti_6O_8$, three triply degenerate vibrations of T_{1u} ($Cp_6Ti_6O_8$) and T_2 ($Cp_4Cr_4O_4$) symmetry are expected. These primarily correspond to an asymmetric vibration of the metals, an asymmetric vibration of the oxygen atoms, and a combined "antitranslation" mode in which vibrations of the metals and of the oxygens are opposed to one another.[18] We assign the high-frequency band to this antitranslation vibration and the low-frequency band to the oxygen vibration for $Cp_6Ti_6O_8$ and $Cp_4Cr_4O_4$. The third band, involving primarily the metals, is presumed to be at very low frequency.

For $Cp_5V_5O_6$, we clearly observed a band at 775 cm^{-1} but could not identify any other bands. For the V_5O_6 core, eight vibrations are expected, five of E' and three of A_2'' symmetry. We assign the 775-cm^{-1} band to the antitranslation of the V_5 trigonal bipyramid and O_6 prism of E' symmetry.

The magnetic moment of $Cp_5V_5O_6$ obeyed the Curie–Weiss law with $\theta = -48°$ and $\mu_{eff} = 0.93\ \mu_B$ at 293 K, the values quoted being uncorrected for any ligand diamagnetism. For $Cp_4Cr_4O_4$ at 293 K, an effective moment of 2.49 μ_B was found. However, the effective moment decreased with temperature to a value of 1.15 μ_B at 80 K. The results are compatible with antiferromagnetic behavior, with the Nẽel temperature being greater than 326 K. Fischer, Ulm, and Fritz also reported antiferromagnetic behavior for their material but stated only that "approximately one unpaired electron per $Cp_4Cr_4O_4$ is present".

An attempt was made to investigate the magnetic behavior by using ESR spectroscopy. However for $Cp_4Cr_4O_4$, no signal above noise could be observed in the solid state, in toluene solutions, or in toluene solutions frozen at 80 K. For $Cp_5V_5O_6$, no signal was observed in either the solid state or in liquid toluene solutions. In the glassy state, an extremely broad featureless signal centered at $g = 1.972$ appeared. We are continuing to investigate the magnetic properties of these clusters.

Structures of the Clusters

General Comments. The crystals of both $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$ contain molecular clusters of one formula unit. The shortest intermolecular contacts are an H···H of 2.4 Å (equal to twice the accepted van der Waals radius of H[19]) in $Cp_5V_5O_6$ and H···O of 2.3 Å in $Cp_4Cr_4O_4$. The shortest intermolecular O···O contact is 4.78 Å in $Cp_5V_5O_6$ and 4.36 Å in $Cp_4Cr_4O_4$. Hence, we are dealing with molecular clusters and not with the polymers usually found for organometallic oxides. $Cp_6Ti_6O_8$ is also a molecular cluster.[17]

Examination of the structures of $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$ (Figures 3 and 4) and $Cp_6Ti_6O_8$[17] shows that their common features are oxygen atoms located above the triangular faces of a trigonal bipyramid, a distorted tetrahedron, and an octahedron, respectively. In $Cp_6Ti_6O_8$, all 24 Ti–O distances are equal within experimental error, averaging 1.973 (3) Å.[17] In $Cp_5V_5O_6$, the six V(axial)–O distances average 1.861 (5) Å, with a maximum deviation of 0.015 Å from this average; the 12 V(equatorial)–O distances average 1.992 (6) Å, maximum deviation 0.011 Å. In $Cp_4Cr_4O_4$, the 12 Cr–O distances average 1.937 (4) Å, with a maximum deviation of 0.019 Å. We compare these distances with other metal–oxygen bond distances in order to decide on a bond order for the M–O bonds in the M_nO_m core. In order to make comparisons, it is necessary to make some decision about the oxidation states of the metals in the clusters. We will consider Cp as (η^5-$C_5H_5^-$), a six-electron donor, and oxygen as O^{2-}. This gives formal oxidation states of $Ti(3^2/_3)$, $V(3^2/_5)$, and Cr(3), and therefore, the distances should be compared to Ti–O distances

---

[14] Brown polymeric materials of formula $(CpVO)_n$ and $(Cp_3V_2O_5)_n$ have also been obtained from the reaction between O_2 and Cp_2V in benzene.[15]

[15] Ulm, K. Ph.D. Dissertation, Universität München, 1961; 17–18.

[16] Fischer, E. O.; Ulm, K.; Fritz, H. P. *Chem. Ber.* **1960**, *93*, 2167–2173.

[17] Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829–31.

[18] We thank W. V. F. Brooks for a group theoretical analysis of M_6O_8, M_5O_6, and M_4O_4 core vibrations.

[19] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; 260.

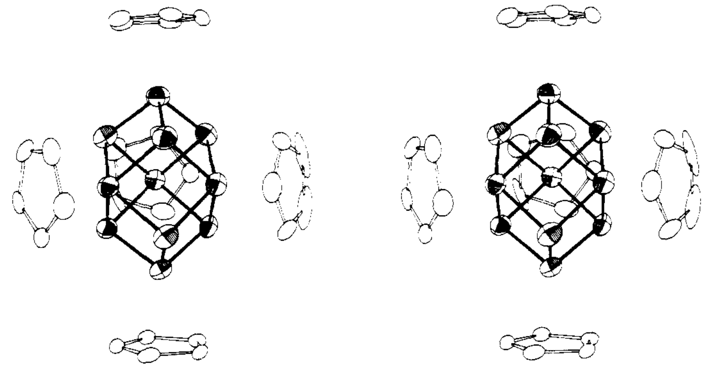

Figure 3. ORTEP view of $Cp_5V_5O_6$.

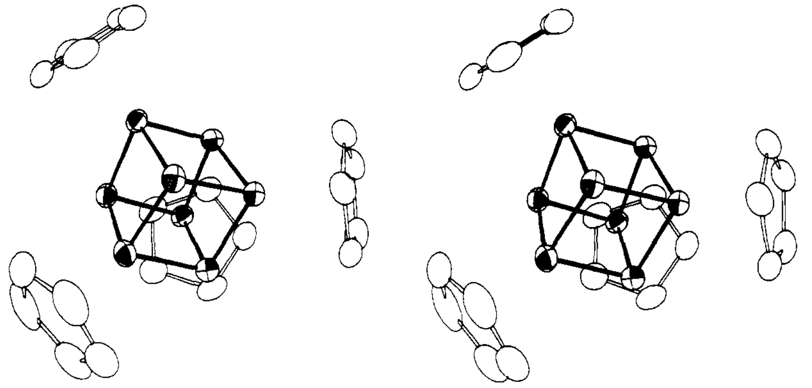

Figure 4. ORTEP view of $Cp_4Cr_4O_4$.

in CpTi(III) and CpTi(IV) compounds, V–O in CpV(III) and CpV(IV) compounds, and Cr–O in CpCr(III) compounds. For CpTi(IV) complexes, Ti–O distances range from 1.75 to 1.80 Å with a weighted average of 1.787 (2) Å.[3,20] These distances are considered to represent Ti(IV)–O single bonds, with considerable π donation of electrons from O to Ti(IV) in the shorter examples. We have been unable to find any examples of CpTi(III)–O distances. Cp_2Ti(III)–O distances range from 2.08 to 2.18 Å[21] and represent Ti(III)–O single bonds with some π donation of electrons from Ti(III) to the O-containing ligand. However, these distances will be longer than expected for CpTiO compounds. On the basis of the difference between Cp_2Ti–O and CpTi–O in $(\eta\text{-O})_2[\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4][Ti(\eta^5\text{-}C_5(CH_3)_5]_2$ (Cp_2Ti(IV)–O = 1.961 (3), CpTi(IV)–O = 1.789 (3) Å,[3] difference = 0.172 Å), a CpTi(III)–O distance is estimated as 1.97 Å. We therefore conclude that the Ti–O distance in $Cp_6Ti_6O_8$ (1.973 (3) Å) represents a Ti–O single bond. It may represent a bond order somewhat less than 1, certainly not more. Only one compound containing a Ti═O moiety is known; the Ti—O distance is 1.613 (5) Å.[22]

There are no CpV–O distances with which those of $Cp_5V_5O_6$ can be compared. In general, V(III)–O single-bond distances are close to 2.0 Å and V(IV)–O close to 1.93 Å;[23,24] the π-acid nature of the Cp ligand will be expected to shorten these distances to some extent. In complexes containing the V(IV)═O moiety, the V–O distance decreases to 1.54–1.60 Å.[23,24] Despite the approximations necessary in the comparison, the V–O distances of 1.861 (5) and 1.992 (6) Å in $Cp_5V_5O_6$ are appropriate to a V–O single bond, though a somewhat greater bond order cannot be discounted.

One compound is known that contains a CpCr(III)–O unit, namely, $Cp_2Cr_3(CF_3CO_2)_6$; the Cr–O distances average 1.996 Å.[25] Complexes containing CpCr(II)–O show Cr–O distances in the range 1.91–1.98 Å;[26] those containing Cr(III)–O but without Cp rings have Cr–O distances close to 1.96 Å.[27] The Cr═O moiety occurs in Cr(V) complexes such as $[CrCl_4O]^-$ and has a Cr—O distance of 1.52 Å.[28] The 1.937 Å observed for the Cr–O distance in $Cp_4Cr_4O_4$ is therefore at the lower end of the Cr–O single-bond range.

It is clear from the above comparison that in all three clusters, $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$, the M–O bonds are basically single bonds. This result is important in the detailed discussion of the structures below and in the discussion of the electronic and structural properties of $Cp_mM_mA_n$ clusters.[7]

The Cp rings are planar and in no way unusual, although in $Cp_5V_5O_6$, two of them are disordered or librating (equations of the planes are available with the supplementary material). The

---

(20) Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169–174. Skapski, A. C.; Troughton, P. G. H. *Acta Crystallogr., Sect. B* **1970**, *B26*, 716–722. Petersen, J. L. *Inorg. Chem.* **1980**, *19*, 181–185. Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014. Thewalt, U.; Klein, H.-P. *Z. Anorg. Allg. Chem.* **1981**, *479*, 113–118. Thewalt, U.; Kebbel, B. *J. Organomet. Chem.* **1978**, *150*, 59–66.

(21) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Organomet. Chem.* **1981**, *212*, 341–349. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767–1775. Guggenberger, L. J.; Tebbe, F. N. *Ibid.* **1976**, *98*, 4137–4143. Eremenko, I. L.; Skripkin, Yu. V.; Pasynskii, A. A.; Kalinnikov, V. T.; Struchkov, Yu. T.; Aleksandrov, G. G. *J. Organomet. Chem.* **1981**, *220*, 159–164.

(22) Guilard, R.; Latour, J.-M.; Lecomte, C.; Marchon, J.-C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1228–1237.

(23) Johnson, G. K.; Schlemper, E. O. *J. Am. Chem. Soc.* **1978**, *100*, 3645–3646.

(24) Selbin, J. *Coord. Chem. Rev.* **1966**, *1*, 293–314. Rice, C. E.; Robinson, W. R.; Tofield, B. C. *Inorg. Chem.* **1976**, *15*, 345–348. Pasquali, M.; Marchetti, F.; Floriani, C.; Merlino, S. *J. Chem. Soc., Dalton Trans.* **1977**, 139–149. Hendrick, K.; Raston, C. L.; White, A. H. *Ibid.* **1976**, 26–32.

(25) Cotton, F. A.; Rice, G. W. *Inorg. Chim. Acta* **1978**, *27*, 75–78.

(26) Hardy, A. D. U.; Sim, G. A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1463–1465. Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* **1979**, *18*, 120–125.

(27) Abu-Dari, K.; Ekstrand, J. D.; Freyberg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 108–112. Raymond, K. N.; Isied, S. S.; Brown, L. D.; Fronczek, F. R. Nibert, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 1767–1774. Wieghardt, K.; Schmidt, W.; Endres, H.; Wolfe, C. R. *Chem. Ber.* **1979**, *112*, 2837–2846.

(28) Gahan, B.; Garner, D. C.; Hill, L. H.; Mabbs, F. E.; Hargrave, K. D.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1977**, 1726–1729.

M–Cp ring distances (defined by the perpendicular to the center of the planar ring) average 2.062 Å in $Cp_6Ti_6O_8$. This compares with the average Cp–Ti distance in the CpTi(IV) complexes used for the comparison of Ti–O distances above, 2.047 Å.[3,20] An increase in the Ti–Cp distance as the formal oxidation state of the titanium increases from II to IV in Cp_2Ti complexes has been noted previously; Cp_2Ti(II) distances are close to 2.01 Å,[29] Cp_2Ti(III) close to 2.045 Å,[21,30] and Cp_2Ti(IV) close to 2.06 Å.[20] Comparable Cp–Ti distances are not available, but the Cp–Ti distance of 2.062 Å in $Cp_6Ti_6O_8$ is clearly in the range of Ti(IV) rather than Ti(II).

Literature values for the V–Cp perpendicular distance show a steady increase as the oxidation state increases: 1.87–1.92 Å in V(I),[31,32] 1.91–1.92 Å in V(II),[33] 1.94–1.96 Å in V(III),[34] and 1.96–2.05 Å in V(IV)[34,35] complexes. The V(axial)–Cp and V(equatorial)–Cp distances of 1.997 and 1.973 Å, respectively, indicate differing electron densities at the different types of V atom and oxidation states of III–IV.

In $Cp_4Cr_4O_4$, the Cr–Cp distances average 1.920 Å, with a range of 1.912–1.925 Å. The structures of only two other CpCr(III) complexes are known; both have Cp–Cr distances of 1.87 Å,[25,36] and a survey of complexes containing the CpCr unit gives an average distance of 1.87 Å. Hence the distances in $Cp_4Cr_4O_4$ are long, indicative of the high metal oxidation state.

In both structures there are remarkably short intramolecular O···O contacts. The shortest in $Cp_5V_5O_6$ is 2.444 (8) and in $Cp_4Cr_4O_4$, 2.572 (5) Å. In $Cp_6Ti_6O_8$,[17] the shortest O···O is 2.57 Å. These distances are all much shorter than twice the van der Waals radius of oxygen (3.0 Å[19]).

Structure of $Cp_5V_5O_6$. Within the general framework discussed above, $Cp_5V_5O_6$ manifests three details of interest. Firstly, the average V(axial)–O distance, 1.861 (5) Å, is much shorter than the average V(equatorial)–O distance, 1.992 (6) Å. Secondly, the average V(axial)–Cp distance, 1.997 Å, is significantly longer than the average V(equatorial)–Cp distance, 1.973 Å. Thirdly, there is no significant difference in the V–V distances, which range from 2.738 (3) to 2.762 (2) Å. The six V(axial)–V(equatorial) distances range from 2.744 (2) to 2.762 (2) Å, with an average of 2.752 (2) Å; the three V(equatorial)–V(equatorial) distances range from 2.738 (3) to 2.743 (2) Å, with an average of 2.740 (2) Å. Using a 3σ criterion, we find that the axial and equatorial distances are the same, and the V_5 core of $Cp_5V_5O_6$ is a perfect trigonal bipyramid.

The differences between the shorter V(axial)–O and longer V(equatorial)–O and between the longer V(axial)–Cp and shorter V(equatorial)–Cp distances are easily explained if the axial V atoms are considered to be V(IV) and the equatorial are V(III). As noted above, precise comparison with CpV–O distances in complexes of clearly discernable oxidation state is not possible. The difference between the average V–O distances, 0.131 Å, is larger than that observed for compounds not containing Cp as a ligand, reflecting the need for V–Cp backdonation. This need is also shown by the longer V(IV)(d^1)–Cp distances of the axial V compared to the V(III)(d^2)–Cp of the equatorial V. The different V(axial)–O and V(equatorial)–O distances are also reflected in the V–O–V angles, which average 91.1 (7)° for V(axial)–O–V(equatorial) and 86.9 (3)° for V(equatorial)–O–V(equatorial).

Before discussing the V–V distances, we need to consider the steric constraints on the cluster. Combining the observed V–V and V–Cp distances and angles (Table V) with idealized Cp ring geometry (C–C, 1.40, C–H, 1.08 Å; C–C–H, 126°), we find that the intramolecular H···H contact between an axial and an equatorial Cp ring is 2.36 Å assuming independent free rotation of the rings. The same contact between equatorial Cp rings is 3.9 Å. The 2.36 Å contact is less than twice the van der Waals radius of H. Although some reduction in steric strain can be achieved by either staggering the rings without rotation or by "cogwheel" rotation, it is obvious that the V(axial)–V(equatorial) distance could not be significantly shorter than the observed average of 2.752 Å; the V(equatorial)–V(equatorial) distance is not sterically determined. The equivalence of the axial–equatorial V–V distances is in marked contrast to $[Ni_5(CO)_{12}]^{2-}$[37,38] in which the Ni(axial)–Ni(equatorial) distance, 2.81 Å, is 0.45 Å longer than the Ni(equatorial)–Ni(equatorial) distance; this latter cluster also shows deviations in the direction of C_{2v} rather than idealized D_{3h} geometry.

It is difficult from either the V–V distances or the physical properties of $Cp_5V_5O_6$ to assess the magnitude of the V–V interaction. The magnetic moment of 0.93 μ_B is much lower than expected for the two unpaired electrons that would result from the assignment of the two axial V atoms as V(IV) d^1 and the three equatorial V atoms as spin-paired V(III) d^2. Therefore a direct V–V interaction is implied. Comparison with other clusters or dimers of vanadium is limited by the small number of such compounds. Cotton has suggested that the V–V distance of 2.462 (2) Å in $Cp_2V_2(CO)_5$ represents at least a V–V single bond.[31] The V–V distance of 2.200 (2) Å in $[V_2(2,6\text{-}(CH_3O)_2C_6H_3)_4]$ is presumed to represent a triple V–V bond.[39] It has been suggested that the threshold distance for spin pairing of V(IV) in an oxide matrix is 2.92 Å.[23] These distances point to a moderate V–V interaction in $Cp_5V_5O_6$, but it is unlikely to reach a formal bond order of 1.

Perhaps the most persuasive evidence for a V–V interaction is the acute V–O–V angles, averaging 91.1 (7) and 86.9 (3)°. Since the μ_3-oxygen bridge could hold the cluster together without any V–V interaction whatever, one would expect that without an interaction the V–O–V angles would approach the idealized tetrahedral angle. This would make the V–V distances 3.15–3.25 Å, close to the nonbonded distance of 3.13 Å in the $V_{10}O_{28}{}^{6-}$ ion.[40] The observed angles and distances, therefore, represent a moderate interaction between the V atoms.

The short O···O contacts in $Cp_5V_5O_6$ indicate that V–V interaction may not be the only one in the cluster. Some O–O bonding is possible.

Structure of $Cp_4Cr_4O_4$. The most obvious feature of $Cp_4Cr_4O_4$ within the general framework is its distortion. Although the 12 Cr–O distances are equal within experimental error (all except one distance of 1.918 (3) Å are within three standard deviations of the average of 1.937 (4) Å), the six Cr–Cr distances are markedly unequal, occurring in sets of two: 2.900 (6), 2.897 (5) Å; 2.841 (4), 2.811 (6) Å; and 2.712 (2), 2.702 (6) Å. The 12 O–Cr–O and 12 Cr–O–Cr angles are in sets of four: 83.1 (2), 83.1 (2), 83.3 (2), 83.4 (2)°; 86.3 (1), 85.9 (1), 85.9 (1), 86.6 (1)°; and 90.3 (2), 89.7 (1), 90.4 (1), 90.2 (2)° for O–Cr–O; and 88.4 (1), 88.7 (2), 88.6 (1), 89.6 (2)°; 94.2 (1), 93.3 (1), 93.9 (1), 93.7 (1)°; and 96.2 (2), 96.5 (2), 96.9 (2), 97.1 (2)° for Cr–O–Cr; and the angles between the normals to the Cp rings

---

(29) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 982–984. Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367–375.

(30) Forder, R. A.; Prout, K. *Acta Crystallogr., Sect. B* **1974**, *B30*, 491–495. Melmed, K. M.; Coucouvanis, D.; Lippard, S. J. *Inorg. Chem.* **1973**, *12*, 232–236.

(31) Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* **1978**, *160*, 93–100.

(32) Rehder, D.; Müller, J.; Kopf, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1013–1017. Gusev, A. I.; Aleksandrov, G. G.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1969**, *10*, 655.

(33) Antipin, M. Yu.; Lobkovskii, E. B.; Semenenko, K. N.; Soloveichik, G. L.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1979**, *20*, 942.

(34) Fachinetti, G.; Floriani, C.; Villa, A. C.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1612–1617. Fieselmann, B. F; Stucky, G. D. *J. Organomet. Chem* **1977**, *137*, 43–54.

(35) Muller, E. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91–112. Muller, E. G.; Walkins, S. F.; Dahl, L. F.; *Ibid.* **1976**, *111*, 73–89. Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422–6433. Wiberg, N.; Haring, H.-W.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *B35*, 599–603.

(36) Wiberg, N.; Haring, H.-W.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *B33*, 1365–1370.

(37) Ruff, J. K.; White, R. P., Jr.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 2159–2176.

(38) Longoni, G.; Chini, P.; Lower, L. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 5034–5036.

(39) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886–7891.

(40) Evans, H. T. *Inorg. Chem.* **1966**, *5*, 967–977.

projected through the Cr atoms are in three sets of two: 119.7, 123.1°; 93.3, 94.7°; and 109.3, 116.0°. Assuming that the Cr–Cr distances of 2.811 (6) and 2.841 (4) Å and the associated Cr–O–Cr and O–Cr–O angles are equal, then $Cp_4Cr_4O_4$ has D_2 symmetry (see also Figure 2 of ref 6). As discussed elsewhere,[7] the cause of the distortion from idealized T_d symmetry is the electronic structure of $Cp_4Cr_4O_4$. However, the actual Cr–Cr distances observed may have steric constraints. If independent free rotation of the Cp rings is assumed, the two shortest Cr–Cr distances result in H···H contacts between the rings attached to Cr(1) and Cr(3) and between those of Cr(2) and Cr(4) of 2.38 Å. As with $Cp_5V_5O_6$, the steric strain can be relieved somewhat by staggering the rings, but the Cr–Cr distance of 2.702 (6) Å is close to the sterically determined minimum for a D_2 structure when the other Cr–Cr distances remain relatively short. The shortest Fe–Fe distances of 2.661 (5) and 2.643 (4) Å in $[Cp_4Fe_4S_4]^+$ combined with the D_{2d} geometry of this cation gives a minimum H···H contact for free rotation of the rings of 1.97 Å and an H···H contact in the staggered conformation of 2.45 Å. The other Fe–Fe distances are of necessity longer, 3.19 and 3.32 Å.[41] In $Cp_4Co_4P_4$ (D_{2d}), the two extremely short Co–Co distances, 2.501 (2) and 2.507 (2) Å, give an H···H contact, assuming free rotation, of 1.65 Å and with staggering of the rings of 2.30 Å. The distortion is now very severe, the other four Co–Co distances being 3.366 Å.[42] In all three clusters the shortest M–M distances are at a steric but not necessarily electronic minimum.

Given this steric constraint and the lack of comparable Cr clusters, it is as difficult as with $Cp_5V_5O_6$ to assess the magnitude of the Cr–Cr interaction. The three average distances, 2.707 (4), 2.826 (5), and 2.899 (5) Å, are longer than twice the atomic radius of Cr, 2.6 Å. However, Cr–Cr distances of from 2.61 to 3.43 Å have been considered to represent Cr–Cr single bonds.[43,44] As Vahrenkamp has noted, many of the distances are determined more by packing of the ligands than any metal–metal interaction.[44] In several tetrabridged dinuclear species of general formula $[Cr_2(\mu\text{-}O_2Cr)_4X_2]$ the Cr–Cr distances are between 2.22 and 2.53 Å and represent quadruple Cr–Cr bonds; Cr–Cr distances of less than 1.90 Å have been observed when no axial ligands X are present.[45] If one uses a distance criteria alone, the Cr–Cr interactions in $Cp_4Cr_4O_4$ may represent bond orders of close to 1. As with $Cp_5V_5O_6$, the most persuasive evidence for a Cr–Cr interaction comes from the acute Cr–O–Cr angles of 88.4–97.1°. A tetrahedral angle about oxygen would give Cr–Cr distances close to 3.16 Å. That such a distance is possible is shown by $Cp_4Co_4S_4$, a cluster with Co–Co distances as large as 3.34 Å, which is held together as a unit,[46] albeit by the larger μ_3-S bridge.

The antiferromagnetic behavior of $Cp_4Cr_4O_4$ also indicates direct interaction between the formally Cr(III) d^3 ions, although it does not suggest a magnitude for the interaction. We also note, as for $Cp_5V_5O_6$, that the O–O distances in $Cp_4Cr_4O_4$ are such that they can interact and assist in cluster bonding.

Structure of $Cp_6Ti_6O_8$. In view of the results and discussion of the structures of $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$, it is worth applying the same arguments to $Cp_6Ti_6O_8$. The average Ti–Ti distance in $Cp_6Ti_6O_8$ is 2.891 (1) Å,[17] which is shorter than twice the atomic radius of Ti (2.94 Å). However an even shorter distance, 2.725 (2) Å in $(\eta\text{-}O)_2[\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4][Ti[\eta^5\text{-}C_5(CH_3)_5]]_2$, cannot represent a Ti–Ti bond since the complex formally contains two Ti(IV) (d^0) ions,[3] but a much longer distance, 3.336 (4) Å in $(\eta^5\text{-}C_5H_5)_2Ti\overline{\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_5)Ti}(\eta^5\text{-}C_5H_5)$, is considered to represent a Ti–Ti single bond.[47] As with $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$, perhaps the most convincing evidence of a Ti–Ti interaction is the Ti–O–Ti bond angles, which average 94.2°. This is much less than the tetrahedral angle. No bond order can be given to the interaction until more information on Ti–Ti bonds becomes available. Assuming independent free rotation of the Cp rings, the minimum H···H intramolecular ring contact is 2.61 Å, indicating that the Ti–Ti distances are not determined by steric repulsions. Again, an O–O interaction can contribute to the stabilization.

Acknowledgment. We thank Professor E. O. Fischer for providing us with unpublished observations on $[CpCrO]_4$, Professor K. G. Caulton for similar help with $Cp_6Ti_6O_8$, and Dr. A. B. P. Lever for the magnetic measurements. David I. McGee and Germaine C. Pataki provided assistance with the preparations and determination of physical properties. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada. D.E.P. thanks the Gran Mariscal de Ayacucho Foundation of Venezuela for the award of a scholarship.

Registry No. $Cp_5V_5O_6$, 79173-26-5; $Cp_4Cr_4O_4$, 79417-63-3; Cp_2V, 1277-47-0; Cp_2Cr, 1271-24-5; N_2O, 10024-97-2; V, 7440-62-2; Cr, 7440-47-3.

Supplementary Material Available: Tables of $|F_o|$ and $|F_c|$, anisotropic thermal parameters, fractional atomic coordinates and isotropic thermal parameters of the hydrogen atoms, metal–carbon and carbon–carbon bond distances, carbon–carbon–carbon bond angles, and equations of mean planes for $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$ (47 pages). Ordering information is given on any current masthead page.

---

(41) Trinh-Toan; Fehlhammer, W. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 402–407.

(42) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2175–2183.

(43) McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1968**, 1858–1865. Pasynskii, A. A.; Eremenko, I. L.; Rakitin, Yu. V.; Novolortsev, V. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 57–64. Calderon, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W. *Ibid.* **1974**, *64*, C10–12. Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749–754. Goh, L.-Y.; D'Aniello, M. J.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I., Friedrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192–197.

(44) Rottinger, E.; Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 2199–2205.

(45) Bino, A.; Cotton, F. A.; Kaim, W. *J. Am. Chem. Soc.* **1979**, *101*, 2506–2507 and references therein.

(46) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2164–74.

(47) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072–8078.