Figure 7 is an example of such a compound with a structure analogous to that of a known[39] Ru₆C(CO)₁₄(mesitylene) complex. The stereochemistry is uniquely defined by the order of listed bonds at each of the external cluster atoms as in the previous examples, so it is not necessary to establish a stereochemical descriptor to define stereochemistry at the carbide carbon. Consequently, we simply list vertices attached to carbon in ascending order, realizing that the remaining notational ordering will uniquely define the enantiomer being considered. Bonding information where stereochemistry is not defined will be designated by enclosure in brackets.

These examples should suffice to show that this linear notation system provides a workable method to denote structures and gives unique registry numbers for any cluster residue. Some advantages of the system are that it requires less learning effort than standard nomenclature systems, the number of arbitrary rules and conventions is small, and the system is not limited to particular types of polyhedra with particular types of symmetry. It is also obvious that the numeric form of the notation system makes it suitable for computer-oriented search operations, and we think that the ability of the method to allow the laboratory chemist to obtain a unique registry or identification number could prove to be an additional useful feature.

One important disadvantage is that a good drawing or model of the compound to be denoted is required before the correct stereochemical notation can be obtained. If the absolute configuration at a particular chiral center in unknown, or if one is dealing with a racemic mixture, the notation is too specific; one name is required for each possible isomer. We suggest that brackets be used both where stereochemical information is redundant (as above) and also where such information is missing. A compound whose constitution is known but whose stereochemistry is yet to be determined would then be indicated by bracketing the entire linear notation. In the case of racemic mixtures we suggest that one simply list the notations for both enantiomers.

The question as to whether or not the proposed scheme is completely general and applicable to all compounds must obviously be answered no. It turns out that the stereochemistry of a complex cluster is actually rather easy to denote because the extensive three-dimensional cluster bonding restricts the available molecular shapes and conformations. These restrictions would not hold, for example, for inorganic or organic moieties attached to the cluster where a conformational description might be required. An illustration is provided by the restricted staggered X-ray structure of the metallodicarborane (8-CH₃OC₂B₉H₁₀)₂Ni found by Janousek et al.[40] They have proposed a system of locants and descriptors to treat the stereochemistry of cases of this type, but clearly a more general method is desirable. We recognize this problem, and we have devised simple extensions of the present rules to provide linear notations including conformational isomerism, which will be reported in a full paper. Suggestion for the application of the linear notation system to coordination compounds and bridged dinuclear or polynuclear compounds will also be advanced.

Finally, following suggestions of reviewers, we would like to comment more specifically on potential uses of this notation scheme. We do not suggest that it provides descriptive names to be used in research papers or textbooks. Primarily the linear notation uniquely specifies connectivity and stereochemistry of a three-dimensional cluster of atoms, and the numerical notation itself or a shortened version is a unique registration number for the compound. As such it can be used to compare structures to establish whether or not they are identical, or it can be used in computer searches of files of cluster compounds, with the assumption that clusters have been catalogued with this method. The advantages of structure-generated registry numbers that can be determined by the user rather than sequentially assigned registry numbers (Chemical Abstracts) are factors to be considered in assessing utility.

In large cluster compounds, the notation also does not easily allow by-hand reconstruction of the structure from the linear sequence of atomic symbols and connectivity numbers. However, the linear notation is tantamount to a connection table augmented with stereochemical descriptors, and a computer program capable of producing a three-dimensional representation from this type of input data has recently been described by Wenger and Smith.[41] In principle then, the visualization of structures using the linear notation is a solved problem. Practical procedures associated with implementation of the visualization process and with the problems of searching for classes of clusters or particular substructures are under investigation.

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A Bent, Staggered (μ-H)[Cr₂(CO)₅]₂⁻ Monoanion. Crystal Structure of KHCr₂(CO)₁₀

J. Roziere,*[1a] P. Teulon,[1a] and M. D. Grillone[1b]

In recent years the nature of the metal–hydrogen–metal bond in the binuclear transition-metal complexes (μ-H)[M(CO)₅]₂⁻ (M = group 6B metal) and related compounds has attracted much attention. Particular interest in the chemical reactivity of such systems stems in part from their use as reagents for the synthesis of organometallic derivatives as well as from their potential activity in catalytic systems.[2,3] For instance, these species have recently been observed in solutions of M(CO)₆ and potassium hydroxide, which serve as homogeneous catalysts for the water gas shift reaction.[4] From the structural viewpoint, previous investigations have placed particular emphasis on the MHM bridge geometry in relation to the extent of direct metal–metal overlap in the three-center two-electron-bridged hydride bond.

As discussed in a review of structural studies on transition-metal hydride complexes,[5] the geometry of group 6B

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MHM carbonylates or derivatives can be classified according to their $(OC)_{ax}$--$M(CO)_{ax}$ "backbone" (linear or bent) and the relative orientation of the equatorial carbonyls on each metal center (linear, eclipsed or bent, staggered). The two combinations have been reported for the tungsten (and molybdenum) derivatives. In particular, it has been shown for the $(\mu\text{-H})[W(CO)_5]_2^-$ monoanion that the counterion can have an appreciable effect on the geometry of the W–H–W bond. For the tetraethylammonium (Et_4N^+) salt a linear, eclipsed metal carbonyl structure exists, whereas for the bis(triphenylphosphine)nitrogen(1+) (PPN^+) salt a bent, staggered carbonyl configuration is observed, with a stronger metal-metal interaction, since the W–W separation is 0.11 Å shorter in the bent form.[6] However, unlike that of the tungsten monoanion, the geometry of the chromium analogue apparently does not show the same dependance upon cation substitution.[7-9]

Previous workers have concluded that the $(\mu\text{-H})[Cr(CO)_5]_2^-$ anion is considerably less susceptible than the tungsten analogue to a twisting deformation from a linear, eclipsed to a bent, staggered configuration.[8,9] However a recent publication has described the $(\mu\text{-H})[Cr(CO)_5]_2^-$ anion in a configuration that is intermediate between the linear, eclipsed and the bent, staggered configuration.[10] The influence of lattice effects on $(\mu\text{-H})[Mo(CO)_5]_2$ has also been investigated.[11] This X-ray diffraction study of $K[(\mu\text{-H})Cr_2(CO)_{10}]$ has been undertaken to evaluate the influence of the cation–anion interactions on the geometry of the $(\mu\text{-H})[Cr(CO)_5]_2^-$ anion. Our interest was further stimulated because the solid-state Raman and infrared spectra of $K[(\mu\text{-H})Cr_2(CO)_{10}]$ were quite different from those of the $[Et_4N]^+$ salt, not only in the carbonyl stretching region but in regions characteristic of the MHM bridge vibrations, indicating a higher degree of bending and/or asymmetry in the bridge.[12]

Experimental Section

Crystals of $K[(\mu\text{-H})Cr_2(CO)_{10}]$ were prepared from $Cr(CO)_6$ and KOH by following the published procedure.[1] Preliminary precession and Weissenberg photographs indicated the Laue symmetry to be C_i-$\bar{1}$. A crystal of approximate dimensions (0.3 × 0.2 × 0.1 mm³) was protected from air and moisture by coating with paraffin oil and mounted in a Lindemann glass capillary. Precise lattice constants and the orientation matrix were determined by least-squares refinements of the angular positions of 25 reflections collected and centered on an Enraf-Nonius CAD 4 fully automated diffractometer: $a = 6.943$ (3) Å, $b = 8.326$ (2) Å, $c = 27.837$ (5) Å, $\alpha = 90.99$ (1)°, $\beta = 93.38$ (1)°, $\gamma = 101.77$ (2)°, $V = 1572.99$ Å³, $Z = 4$. Diffraction data were collected at 295 K from $2\theta = 4°$ up to $2\theta = 60°$ with use of graphite-monochromatized Mo Kα X-ray radiation ($\lambda = 0.71069$ Å). The profile analysis of a few low-angle reflections indicated that an $\omega\text{-}^4/_3\theta$ scan method was the most appropriate for data collection. Scan widths were calculated with the formula $SW = A + B \tan \theta$ where the values of A and B were 1.20 and 0.35, respectively. For each reflection the calculated scan angle was extended by 25% on either side to estimate the background count. Three standard reflections were monitored every 60 reflections and showed no significant change in intensity. Data were corrected for Lorentz and polarization effects and for absorption (calculated μ for Mo Kα radiation 17.4 cm⁻¹;

Table I. Positional Parameters (×10⁴)

	x	y	z
Cr(1)	1914 (3)	2074 (2)	7939 (1)
Cr(2)	648 (3)	8801 (2)	7240 (1)
Cr(3)	1259 (3)	6906 (2)	145 (1)
Cr(4)	8803 (3)	8133 (2)	5142 (1)
K(1)	3996 (5)	2403 (3)	1252 (1)
K(2)	6639 (5)	3066 (3)	6339 (1)
C(1)	2398 (21)	3931 (16)	8298 (5)
C(2)	-525 (21)	1317 (16)	8204 (5)
C(3)	6917 (21)	9093 (16)	1616 (4)
C(4)	5629 (23)	7192 (17)	2339 (6)
C(5)	9272 (22)	6986 (15)	2563 (5)
C(6)	-350 (24)	7037 (16)	6765 (5)
C(7)	-752 (24)	7621 (17)	7736 (5)
C(8)	-1599 (21)	9705 (16)	711 (5)
C(9)	2022 (21)	10089 (15)	6778 (5)
C(10)	7145 (23)	2091 (18)	2572 (6)
C(11)	2612 (20)	8951 (14)	331 (4)
C(12)	-954 (22)	7308 (16)	422 (5)
C(13)	2146 (22)	6059 (15)	727 (5)
C(14)	3428 (20)	6416 (15)	9820 (4)
C(15)	9617 (21)	2369 (15)	442 (5)
C(16)	7465 (23)	6155 (17)	5337 (5)
C(17)	8119 (23)	9168 (17)	5694 (5)
C(18)	1120 (21)	7762 (18)	5448 (6)
C(19)	522 (22)	2770 (16)	5429 (5)
C(20)	6539 (21)	8480 (14)	4789 (4)
O(1)	2669 (17)	5190 (12)	8525 (4)
O(2)	-194 (16)	800 (13)	8382 (4)
O(3)	6218 (16)	9913 (13)	1356 (4)
O(4)	4284 (17)	6690 (13)	2524 (3)
O(5)	9978 (16)	6366 (12)	2881 (3)
O(6)	-929 (19)	6059 (11)	6486 (3)
O(7)	-1545 (16)	6926 (13)	8025 (3)
O(8)	3018 (15)	9830 (12)	2968 (3)
O(9)	2850 (16)	10887 (12)	6487 (4)
O(10)	5871 (19)	2629 (14)	2440 (5)
O(11)	3509 (15)	212 (10)	452 (3)
O(12)	-2338 (17)	7598 (12)	583 (4)
O(13)	2772 (16)	5561 (12)	1080 (3)
O(14)	4707 (16)	6206 (11)	-384 (3)
O(15)	136 (16)	1903 (12)	803 (3)
O(16)	6576 (18)	4910 (12)	5474 (4)
O(17)	7632 (18)	9782 (14)	6021 (4)
O(18)	2462 (17)	7520 (13)	5652 (4)
O(19)	104 (18)	3344 (13)	5783 (4)
O(20)	5164 (15)	8657 (11)	4575 (3)
H(1)	194 (14)	16 (10)	777 (3)
H(2)	0	500	0
H(3)	1000	1000	500

transmission coefficients from 0.71 to 0.79). The final data set for $KHCr_2(CO)_{10}$ consisted of 9500 independent reflections of which 4003 with $I > 3\sigma(I)$ were used in the refinements.

The structure was determined by heavy-atom methods. The initial positions of the three independent Cr atoms were interpreted from the strongest peaks of an unsharpened three-dimensional Patterson map and used in subsequent Fourier summations to locate the remaining non-hydrogen atoms. Scattering factors including both the real and imaginary components of anomalous dispersion were included. Full-matrix least-squares refinements with anisotropic temperature factors for all the non-hydrogen atoms were conducted by minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_c(F_o^2) + (0.01F_o)^2$ (F_o and F_c are the observed and calculated structure amplitudes).

A difference Fourier map calculated by using low-angle data ($(\sin \theta)/\lambda < 0.4$ Å⁻¹) provided sufficient residual density to locate the hydrogen atoms in the structure. The hydrogen atoms in special positions 0, ¹/₂, 0 and 0, 0, ¹/₂ were fixed with isotropic temperature factors of 5 Å²; the positional parameters of the third hydrogen atom were refined. The final values of the discrepancy indices were $R = 0.074$, $R_w = 0.092$, and $\sigma_1 = 1.56$ with $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and $\sigma_1 = [\sum \mu(|F_o| - |F_c|)^2/(N - M)]^{1/2}$, where N is the number of observations and M the number of parameters varied.

Positional parameters are given in Table I. Final thermal parameters and a list of observed and calculated structure factors are

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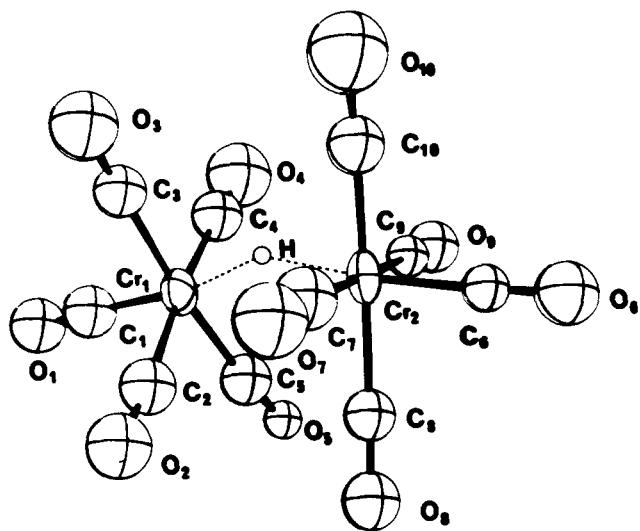
Figure 1. Geometry of the bent, staggered $(\mu\text{-}H)[Cr(CO)_5]_2^-$ anion in $KHCr_2(CO)_{10}$ with the atoms represented by their 50% probability ellipsoids for thermal motion. The Cr(1)–Cr(2) distance is 3.260 (3) Å, and the staggering of the anion is 36 (1)°. The hydrogen atom was located as follows: Cr(1)–H(1) = 1.65 (7), Cr(2)–H(1) = 1.90 (7) Å; Cr(1)–H(1)–Cr(2) = 132 (3)°. Important bond lengths: Cr(1)–C(1) = 1.79 (1), Cr(1)–C(2) = 1.88 (1), Cr(1)–C(3) = 1.84 (1), Cr(1)–C(4) = 1.91 (1), Cr(1)–C(5) = 1.85 (1), Cr(2)–C(6) = 1.95 (1), Cr(2)–C(7) = 1.91 (1), Cr(2)–C(8) = 1.89 (1), Cr(2)–C(9) = 1.87 (2), Cr(2)–C(10) = 1.89 (2) Å.

available as supplementary material.

Results and Discussion

The crystal is composed of discrete molecular anions $(\mu\text{-}H)[Cr(CO)_5]_2^-$ and potassium cations. The outcome of this crystal structure determination, however, turned out to be more complicated than expected from the vibrational spectra. There are three crystallographically independent sites for the molecular anions, two having a crystallographically imposed $\bar{1}$ symmetry and the third being not constrained to lie on a crystallographic center of symmetry. The two centrosymmetric anions belong to the linear, eclipsed type, and the third anion appears to be the first structurally characterized example of a highly bent, staggered chromium carbonylate with a metal–hydrogen–metal bridge. The geometry of the linear, eclipsed configuration of the chromium monoanion has largely been discussed in previous publications on neutron diffraction

structural studies.[7-9] In particular, it has been found in $[Et_4N][(\mu\text{-}H)Cr_2(CO)_{10}]$ that the H atom is in an off-axis position situated 0.3 Å from the Cr–Cr axis. Because of the presence of a crystallographic center of inversion, what is actually observed is a disordered superposition of two slightly bent identical anions with a pseudo-D_{4h} non-hydrogen geometry.[7]

The two linear $(\mu\text{-}H)[Cr(CO)_5]_2^-$ monoanions in $K[(\mu\text{-}H)Cr_2(CO)_{10}]$ closely resemble those of Et_4N^+ and PPN^+ salts.[7,8] The Cr–Cr distances of 3.343 (3) and 3.356 (3) Å compare well with those found in Et_4N^+ (3.386 (6) Å) and PPN^+ (3.359 (2) Å) salts.

The bent, staggered $(\mu\text{-}H)[Cr(CO)_5]_2^-$ anion is represented in Figure 1. For nonsubstituted dimeric carbonylates the distance between metals varies in the order "linear" $(\mu\text{-}H)$-$[M(CO)_5]_2^- >$ "bent" $(\mu\text{-}H)[M(CO)_5]_2^- > [M_2(CO)_{10}]^{2-}$, where "linear" and "bent" refer to the $(OC)_{ax}M\text{-}\text{-}M(CO)_{ax}$ backbone.

In $(\mu\text{-}H)[W(CO)_5]_2^-$ a decrease in W–W distance of ca. 0.11 Å is coincident with the bend.[6] In the present case a similar reduction is observed. The Cr–Cr distance is 3.260 (3) Å, which is about 0.09 Å shorter than the corresponding distances of the linear, eclipsed forms in the same salt (0.13 Å with respect to the Et_4N^+ salt).[7] The Cr–Cr distance is still 0.05 Å shorter than that of the same anion in an intermediate configuration, observed recently in $[K(crypt-222)][(\mu\text{-}H)\text{-}Cr_2(CO)_{10}]$.[10] This reduction in the Cr--Cr separation is accompanied by a greater bending of the Cr–H–Cr bond in $K[(\mu\text{-}H)Cr_2(CO)_{10}]$. The bend in the molecular anion framework as defined by the angle of intersection of extension of the C(1)–Cr(1) and C(6)–Cr(2) vectors is 165 (1)°, which can be compared with the corresponding angle of 169° in the $[K(crypt-222)]^+$ salt.[10]

The two independent $Cr(CO)_5$ groups are rotated with respect to each other about the Cr--Cr line, giving rise to a staggered carbonyl arrangement. The dihedral angle between appropriate pairs of planes passing through two trans equatorial carbonyl groups, the axial carbonyl group, and the Cr atom of each $Cr(CO)_5$ moiety is 36°. In $[K(crypt-222)][(\mu\text{-}H)Cr_2(CO)_{10}]$, the corresponding angle is only 19°. This twisting distortion from an eclipsed configuration and the bent stucture of the metal carbonyl framework have been interpreted as resulting from a particular interaction between one of the $Cr(CO)_5$ groups and the K^+ ion.[10] The extent to which the geometry of $[(\mu\text{-}H)Cr(CO)_5]_2^-$ in $K[(\mu\text{-}H)Cr(CO)_{10}]$ is influenced by crystal-packing forces and cation interactions
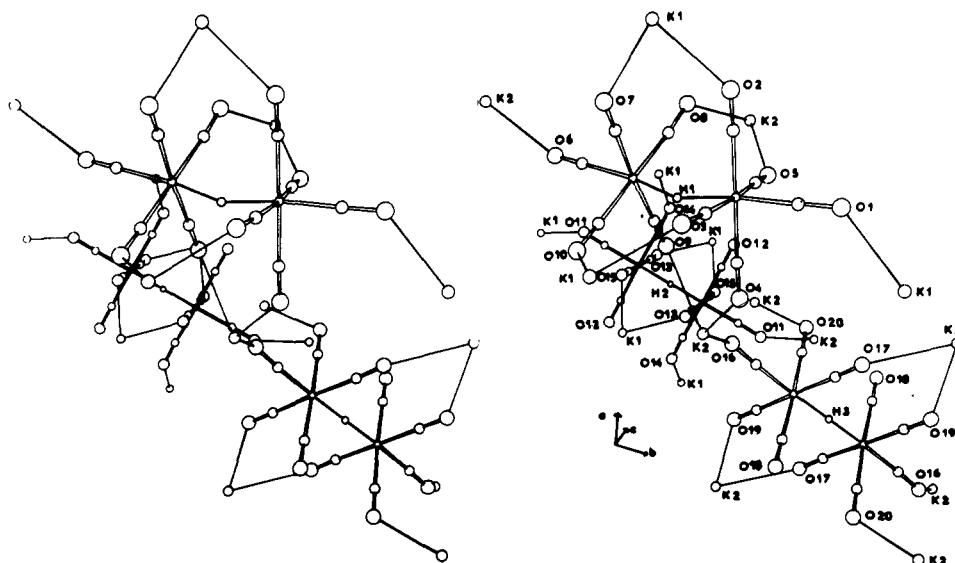

Figure 2. Stereoscopic view showing the interactions between carbonyl oxygens and the potassium ions.

is difficult to quantify. A stereoscopic view showing carbonyl oxygen and potassium ion interactions is given in Figure 2. Each of the two crystallographically nonequivalent potassium ions is surrounded by nine oxygen atoms with K$^+$··O distances ranging from 2.72 (1) to 3.47 (1) Å and with K$^+$··O–C angles ranging from 123 (1) to 146 (1)°. The three $(\mu$-H)[Cr-(CO)$_5$]$_2^-$ ions have a similar environment; however, the two shortest K$^+$··O contacts (2.72 (1) and 2.77 (1) Å) involve the two axial carbonyl oxygen atoms of the bent, staggered anion. Similar tight ion pairings in alkali salts of carbonylate anions have been observed for [(μ-SH)W$_2$(CO)$_{10}$]$^-$ and Fe(CO)$_4^{2-}$ [13,14] and are thought to contribute to the significant anion distortion. The strong interactions between the axial carbonyl groups and the potassium ions in the title compound may be responsible for the unusual anion solid-state configuration.

Registry No. KHCr$_2$(CO)$_{10}$, 61453-56-3.

Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factor amplitudes (39 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Tetrakis(2,4,6-trimethoxyphenyl)divanadium(II) Bis(tetrahydrofuranate)

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Received December 18, 1981

In our continuing studies of multiple bonds between metal atoms[1] the versatility of inorganic and organic ligands functioning as simple three-atom bridges, as illustrated schematically in **1**, has been well established. Complexes with bond

1
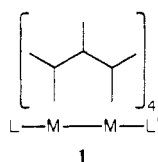
orders of 1,[2] 2,[3] 2.5,[4] 3,[5] 3.5,[6] and 4[7] between the metal atoms have been structurally characterized, and several discussions have appeared detailing how the identity of the three atoms present in the bridging moiety may be responsible for differences in the metal–metal bond distance.[7,8] There is, however, one prominent structural anomaly.

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(4) See, for example: Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599 (Ru^{II}–Ru^{III}).
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(7) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3464.
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In 1977 we reported the structural characterization of the divanadium(II) compound, V$_2$(dmp)$_4$·2THF[9] (dmp = 2,6-dimethoxyphenyl). In contrast to the formally analogous chromium(II) and molybdenum(II) complexes, M$_2$(dmp)$_4$ (M = Cr, Mo),[10] which can be represented as in **1**, the vanadium complex has only two of the ligands in this relationship to the V$_2$ unit while the other two 2,6-dimethoxyphenyl ligands are so placed that both methoxy oxygen atoms are coordinated to vanadium atoms and a phenyl carbon atom is symmetrically positioned directly above the midpoint of the V≡V bond, forming an isosceles V–C–V triangle.

The work reported here was undertaken to see if this unusual structure was confined only to this one compound (perhaps as an artifact of crystal-packing forces) or whether it is the inherently preferred one for a V$_2^{4+}$ complex with ligands of the 2,6-dialkoxyphenyl type. As before, in connection with the chromium compounds,[9,10] we used the 2,4,6-trimethoxyphenyl (tmp) ligand in place of the 2,6-dimethoxyphenyl ligand, and since the pertinent lithium reagent is readily accessible, the presence of the *p*-methoxy group should cause little if any significant electronic effect, but it would guarantee that a different form of molecular packing will occur.

Experimental Section

The title compound was prepared in a manner analogous to that described for the V$_2$(dmp)$_4$·2THF complex starting from VCl$_3$·(THF)$_3$[11] and (2,4,6-trimethoxyphenyl)lithium.[12] Large air-sensitive black crystals were obtained from the reaction mixture, immersed in epoxy cement, sealed in glass capillaries, and placed on an Enraf-Nonius CAD-4 automated diffractometer. While several crystals showed signs of rapid loss of solvent, one approximately equidimensional (0.70 × 0.65 × 0.65 mm) crystal was deemed suitable for study. Twenty-five reflections in the range 20° < 2θ < 40° were located by using the standard CAD-4 random automatic searching routine. On the basis of angular settings for these reflections, the refined lattice parameters obtained from the Enraf-Nonius software package are (Mo Kα, λ = 0.71073 Å) a = 14.272 (1) Å, b = 24.746 (3) Å, c = 12.669 (2) Å, and V = 4474 (2) Å^3. Systematic absences indicated the orthorhombic space group *Pbca*. With Z = 4 and a formula weight of 914.84, the calculated density is 1.358 g cm^{-3}.

Intensity data were collected at room temperature (graphite-monochromatized Mo Kα radiation) to 2θ = 45° by using the ω–2θ method and a scan range determined by $\Delta\omega$ = (0.80 + 0.35 tan θ)° with a 25% extension at either end for background determination. Of the 3898 symmetry-independent reflections measured, 1896 observations with $I > 3\sigma(I)$ were retained as observed data and corrected for Lorentz and polarization effects. Three standard reflections measured repeatedly every 100 data points indicated an overall loss of intensity of 45% presumably due to loss of THF of crystallization. The data were subsequently corrected for this loss in intensity with use of the program CHORTA,[13] and successful refinement of the structure indicated the reliability of the method used.

A three-dimensional Patterson map gave the position of the one independent vanadium atom. A difference Fourier synthesis based on the refined vanadium position revealed all of the non-hydrogen positions. All atoms were assigned isotropic thermal parameters, and least-squares refinement then gave discrepancy indices

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.904$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.122$$

where

$$w = 1/\sigma^2(F_o)$$

Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms to convergence at R_1 = 0.062 and R_2 =

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