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 $K^+\cdots O$ distances ranging from 2.72 (1) to 3.47 (1) Å and with $K^+\cdots O–C$ angles ranging from 123 (1) to 146 (1)°. The three $(\mu\text{-H})[Cr(CO)_5]_2^-$ ions have a similar environment; however, the two shortest $K^+\cdots O$ 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 $[(\mu\text{-SH})W_2(CO)_{10}]^-$ 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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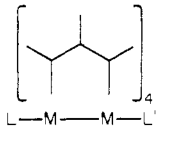
In our continuing studies of multiple bonds between metal atoms[1] the versatility of inorganic and organic ligands functioning as simple three-atom bridges, as illustrated schematically in **1**, has been well established. Complexes with bond orders of 1,[2] 2,[3] 2.5,[4] 3,[5] 3.5,[6] and 4[7] between 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.



1

In 1977 we reported the structural characterization of the divanadium(II) compound, $V_2(dmp)_4\cdot 2THF$[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, 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 $V_2(dmp)_4\cdot 2THF$ complex starting from $VCl_3\cdot(THF)_3$[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 $20° < 2\theta < 40°$ 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 $2\theta = 45°$ by using the ω–2θ method and a scan range determined by $\Delta\omega = (0.80 + 0.35 \tan\theta)°$ 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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0020-1669/83/1322-0560$01.50/0

Table I. Positional Parameters and Their Estimated Standard Deviations for $V_2(tmp)_4 \cdot 2THF$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
V(1)	0.03279 (8)	0.49009 (4)	0.07724 (9)	C(18)	0.1695 (6)	0.3877 (3)	0.0708 (6)
O(1)	−0.0429 (3)	0.4602 (2)	−0.3132 (3)	C(19)	0.1222 (7)	0.2799 (3)	−0.3810 (6)
O(2)	0.1069 (3)	0.4209 (2)	0.0079 (3)	C(21)	−0.1047 (5)	0.4558 (2)	0.0348 (5)
O(3)	0.1500 (4)	0.2996 (2)	−0.2786 (4)	C(22)	−0.1104 (5)	0.4235 (3)	0.1236 (5)
O(4)	−0.1782 (3)	0.4857 (2)	−0.1173 (3)	C(23)	−0.1849 (5)	0.3897 (3)	0.1540 (5)
O(5)	−0.0269 (3)	0.4270 (2)	0.1833 (3)	C(24)	−0.2611 (5)	0.3903 (3)	0.0860 (6)
O(6)	−0.3408 (3)	0.3591 (2)	0.1035 (4)	C(25)	−0.2647 (5)	0.4212 (3)	−0.0067 (5)
O(S)	0.3566 (5)	0.2870 (2)	0.1350 (5)	C(26)	−0.1860 (5)	0.4525 (2)	−0.0262 (5)
C(11)	0.0308 (5)	0.4425 (2)	−0.1529 (5)	C(27)	−0.2431 (6)	0.4773 (3)	−0.2043 (5)
C(12)	0.0143 (4)	0.4255 (2)	−0.2573 (5)	C(28)	−0.0316 (6)	0.4167 (3)	0.2957 (5)
C(13)	0.0498 (5)	0.3791 (3)	−0.3038 (5)	C(29)	−0.3320 (6)	0.3125 (3)	0.1687 (6)
C(14)	0.1102 (5)	0.3476 (2)	−0.2427 (5)	C(S1)	0.3860 (9)	0.2802 (4)	0.0330 (8)
C(15)	0.1329 (5)	0.3598 (3)	−0.1394 (5)	C(S2)	0.3811 (7)	0.2390 (4)	0.1942 (8)
C(16)	0.0909 (5)	0.4071 (2)	−0.0987 (5)	C(S3)	0.3860 (8)	0.1937 (4)	0.1159 (7)
C(17)	−0.0757 (7)	0.4439 (4)	−0.4161 (6)	C(S4)	0.4187 (8)	0.2221 (4)	0.0189 (8)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table IIA. Important Interatomic Distances (Å) and Bond Angles (deg) for $V_2(tmp)_4 \cdot 2THF$[a]

	Distances		
V(1)–V(1)′	2.223 (2)	O(2)–C(16)	1.411 (5)
–O(2)	2.195 (3)	O(4)–C(26)	1.420 (5)
–O(4)	2.218 (3)	O(5)–C(22)	1.413 (5)
–O(5)	2.227 (3)	C(11)–C(16)	1.404 (6)
–C(11)	2.126 (5)	C(21)–C(22)	1.382 (6)
–C(21)	2.203 (5)	–C(26)	1.395 (6)
–C(21)′	2.204 (5)		
	Angles		
V(1)–V(1)′–O(2)	91.27 (9)	C(11)–V(1)–C(12)	90.7 (2)
–O(4)	122.3 (1)	–C(21)′	119.4 (1)
–O(5)	121.7 (1)	V(1)–O(2)–C(16)	119.6 (3)
–C(11)	92.5 (1)	–O(4)–C(26)	92.5 (3)
–C(21)	59.7 (1)	–O(5)–C(22)	92.4 (3)
–C(21)′	59.7 (1)	–C(11)–C(16)	121.9 (3)
O(2)–V(1)–O(4)	81.5 (1)	O(2)–C(16)–C(11)	114.6 (4)
–O(5)	83.1 (1)	V(1)–C(21)–V(1)′	60.6 (1)
–C(11)	175.7 (2)	–C(22)	94.4 (3)
–C(21)	91.8 (2)	–C(26)	153.8 (4)
–C(21)′	89.5 (2)	V(1)–C(21)′–C(22)′	154.5 (4)
O(4)–V(1)–O(5)	114.1 (1)	–C(26)′	93.8 (3)
–C(11)	94.8 (2)	C(22)–C(21)–C(26)	111.6 (5)
–C(21)	172.9 (2)	O(5)–C(22)–C(21)	110.5 (5)
–C(21)′	63.1 (2)	O(4)–C(26)–C(21)	110.6 (4)
O(5)–V(1)–C(11)	96.5 (2)		
–C(21)	62.5 (2)		
–C(21)′	172.5 (2)		

[a] Estimated standard deviations in the least significant digits are included in parentheses.

0.080, the error in an observation of unit weight being 2.16. A final difference synthesis showed random fluctuations not exceeding ±0.43 e/Å³. Final positional parameters are given in Table I. A table of anisotropic thermal parameters is available as supplementary material as are values of observed and calculated structure factor amplitudes.

Results and Discussion

Figure 1 shows an ORTEP plot of the entire molecule and defines the atom-numbering scheme. Pertinent bond distances and angles are listed in Table IIA while the less important data are available as supplementary material (Table IIB). The molecules reside on crystallographic centers of inversion.

The arrangement of the 2,4,6-trimethoxyphenyl ligands about the two vanadium atoms is entirely analogous to that found in the $V_2(dmp)_4$ molecule.[9] There are two ligands that are bidentate and form conventional three-atom bridges between the two metal atoms; the other two ligands are of the curious tridentate type where the phenyl ring bridges the two vanadium atoms and one methoxy oxygen atom is coordinated to each of the metal atoms.

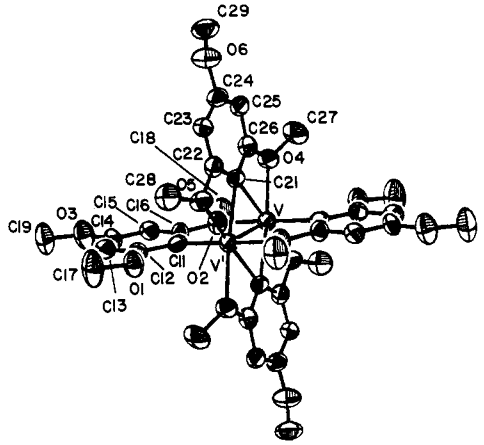

Figure 1. ORTEP view of the $V_2(tmp)_4$ molecule. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

There is a small but statistically real difference between the V≡V bond length observed here, 2.223 (2) Å, and that found previously in the 2,6-dimethoxy compound, 2.200 (2) Å, viz., 0.023 (3) Å. Such a change, while small, is probably too large to be accounted for purely by packing forces or other extramolecular factors. It may, therefore, most reasonably be attributed to the presence of the additional methoxy group in the para position, which could have a significant effect on the ring carbon atom that lies over the V≡V bond. This, in turn, evidently weakens the bond slightly.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $V_2(tmp)_4 \cdot 2THF$, 83830-97-1.

Supplementary Material Available: Tables of structure factors, additional bond distances and angles (Table IIB) and thermal parameters (Table III) (13 pages). Ordering information is given on any current masthead page.

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Phosphazenes. 1. Reactions of Hexachlorocyclotriphosphazene with Methyllithium

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Reactions of organometallic reagents with chlorophosphazenes have received considerable attention in the last few years. However, only recently has some understanding

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