configuration finally adopted. The final positional and thermal parameters for the nongroup atoms along with their estimated standard deviations are given in Table V. Table VI lists the derived positions of the 16 group atoms belonging to the phenyl and naphthyl rings. The root mean square amplitudes of vibration for the anisotropic atoms are given in Table VII.[35] Table VIII lists the idealized positions of the hydrogen atoms.[35] A listing of the structure amplitudes (10 $|F_o|$ vs. 10 $|F_c|$) is also available.[35]

Acknowledgments. This work was supported by the National Science Foundation and the Japanese Society for the Promotion of Science under the Japan-U.S. Cooperative Science Program (6R021/0IP75-09438). We thank Mr. Osamu Teranaka for experimental assistance. J.A. acknowledges receipt of a UNESCO Fellowship while on leave from the University of Islamabad, Pakistan.

Supplementary Material Available: Table VII, the root mean square amplitudes of vibration, Table VIII, the idealized positions of the hydrogen atoms, and a listing of the observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 3: S. Otsuka, K. Tani, I. Kato, and O. Teranaka, *J. Chem. Soc., Dalton Trans.*, 2216 (1974).
(2) (a) Osaka University; (b) Northwestern University.
(3) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971.
(4) G. Wilke, Plenary Lecture at 7th International Conference on Organometallic Chemistry, Venice, Italy, Sept 1–5, 1975.
(5) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J. Chem. Soc., Chem. Commun.*, 10 (1972).
(6) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961).
(7) L. Horner, F. Schedlbauer, and P. Beck, *Tetrahedron Lett.*, 1421 (1964).
(8) L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).
(9) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).
(10) O. Kospium, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4843 (1968).
(11) K. Naumann, G. Aon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).
(12) S. Otsuka, A. Nakamura, T. Kano, and K. Tani, *J. Am. Chem. Soc.*, **93**, 4301 (1971).
(13) A. F. Peerdeman, J. P. C. Holst, L. Horner, and H. Winkler, *Tetrahedron Lett.*, 811 (1965).
(14) R. Luckenbach, *Justus Liebigs Ann. Chem.*, 1618 (1974).
(15) (a) O. Behrens, Dissertation, Bochum University, 1973; (b) C. Krüger, *Chem. Ber.*, **109**, 3574 (1976).
(16) D. L. Weaver, *Inorg. Chem.*, **9**, 2250 (1970).
(17) R. J. Cross and N. H. Tennent, *J. Chem. Soc., Dalton Trans.*, 1444 (1974).
(18) E. Cernia, G. M. Giongo, F. Marcati, W. Marconi, and N. Palladino, *Inorg. Chim. Acta*, **11**, 195 (1974). The phospholene was assigned erroneously as 1-phenyl-3-methyl-3-phospholene by these authors.
(19) G. Wittig, H. J. Cristau, and H. Braun, *Angew. Chem.*, **79**, 721 (1967); *Justus Liebigs Ann. Chem.*, **751**, 17 (1971).
(20) Upon coordination, the designation of the phosphorus center is changed to *S* according to rules of nomenclature, although no change in the actual configuration of the phosphine itself takes place. See, e.g., R. S. Chan, C. K. Ingold, and V. Prelog, *Angew. Chem.*, **78**, 413 (1966).
(21) S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98**, 5850 (1976).
(22) S. Otsuka et al., to be published.
(23) A. C. Cope, *J. Am. Chem. Soc.*, **71**, 3929 (1949).
(24) R. N. Icke and B. B. Wisegarver, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1962, p 723.
(25) W. Theilacker and H. Winkler, *Chem. Ber.*, **87**, 690 (1954).
(26) A. Fredga, B. Sjoberg, and R. Sandber, *Acta Chem. Scand.*, **11**, 1609 (1957).
(27) J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3453 (1966).
(28) L. D. Quin, J. P. Giratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968).
(29) H. Hoffmann and O. Schellenbeck, *Chem. Ber.*, **99**, 1134 (1966).
(30) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
(31) In addition to various local programs for the CDC 6400 computer, programs used in this work include local versions of Zalkin's FORDAP Fourier program, the Busing and Levy ORFFE function and error program, and the AGNOST absorption program (which includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration). Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. The diffractometer was run under the Vanderbilt Disk System as described by P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975).
(32) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A.
(33) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(34) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, **53**, 189 (1970).
(35) Supplementary material.

The Probable Existence of a Triple Bond between Two Vanadium Atoms

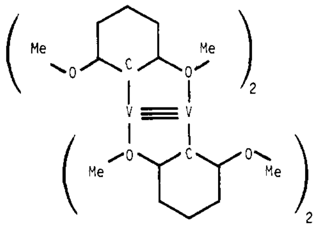
F. Albert Cotton* and Michelle Millar

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received June 17, 1977*

Abstract: A recent report of the preparation of a compound to which the formula V_2(2,6-dimethoxyphenyl)$_4$·THF was assigned, and for which a structure having as its key component a triple bond between the vanadium atoms was proposed, has prompted us to investigate this substance by x-ray crystallography. We find that the solid actually contains two molecules of THF, which are not coordinated and therefore are easily lost. The actual structure differs in detail from that suggested but does contain a V–V triple bond, with $d_{V-V} = 2.200\ (2)$ Å. The essential symmetry of the molecular structure is C_{2h}. The two vanadium atoms and two of the $(MeO)_2C_6H_3$ groups are coplanar, and each of these groups is bound through C(1) to one V atom and through one oxygen atom to the other, and so arranged as to conform to C_{2h} symmetry. The other two $(MeO)_2C_6H_3$ groups are placed above and below this plane and perpendicular to it with their common plane including the V atoms and with their C(1) atoms over the midpoint of the V–V bond. They each interact through both oxygen atoms with the vanadium atoms. The compound, $V_2(C_8H_9O_2)_4 \cdot 2C_4H_8O$, crystallizes in space group $P2_1/c$ with unit cell dimensions $a = 13.804\ (3)$ Å, $b = 12.308\ (3)$ Å, $c = 23.456\ (4)$ Å, $\beta = 102.35\ (1)°$, and $V = 3893\ (1)$ Å^3, with $Z = 4$. It was necessary to collect data at -70 °C to prevent the crystals from disintegrating by solvent loss, a process which occurs quickly at ambient temperature even in a sealed capillary.

The existence of triple bonds between transition metal atoms is now very well established. Aside from those between atoms of rhenium in $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$,[1] $La_4Re_2O_{10}$,[2] and $Re_2Cl_4(PR_3)_4$,[3,4] there is an extensive series of M_2X_6 compounds[5] formed by the elements Mo and W, in which X groups may be alkyl, R_2N, or RO, as well as related compounds such a $M_2(NR_2)_4X_2$ where X represents Cl, Br, or I. In the first transition series, there are several structurally proven examples of triple bonds. One is found[6a] in $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$, where d_{Cr-Cr} = 2.280 (2) Å; molybdenum and tungsten analogues exist, as well as similar compounds with C_5H_5 instead of C_5Me_5.[6b] Two Fe≡Fe bonds, one bridged by three CO groups in $(t\text{-}Bu_2Ph_2C_4)_2Fe_2(\mu\text{-}CO)_3$,[7] and the other by three hydrogen atoms, in $[HC(CH_2PPh_2)_3]_2Fe_2H_3$,[8] have also been reported. In view of the occurrence of quadruple bonds between atoms of the first-row element chromium,[9] as well as the extensive occurrence of such bonds between atoms of heavier elements such as molybdenum, tungsten, technetium, and rhenium,[10] we have been interested in—and optimistic about—the possibility that multiple bonds might be found to occur more widely between pairs of metal atoms in the first transition series.

In the actual preparation of such a compound involving vanadium, we have been anticipated by Siedel, Kreisel, and Mennenga[11] (SKM), who prepared a dark-colored, crystalline compound for which they proposed the structure I. This proposal was prompted by their observations that the compound is binuclear (mass spectrum) and diamagnetic, and by the likelihood that a pair of d^3 V(II) atoms would tend, like pairs of d^3 Mo(III) and W(III) atoms in the cases cited above,[5] to form a triple bond. We have conducted an x-ray crystallographic investigation of this compound to determine with certainty if it does afford the first recognized example of a V–V triple bond. As shown below it does contain such a bond, although the structure is more complex than that depicted as I.



I

Experimental Section

Preparation. The procedure, which we describe here in detail, was patterned on that briefly outlined by SKM.[11] All manipulations were carried out under an atmosphere of dry nitrogen. To $VCl_3(THF)_3$[12] (2.5 g, 6.7 mmol) and 2,6-dimethoxyphenyllithium[13] (3.85 g, 26.8 mmol) was added ca. 75 mL of cold (−78 °C) tetrahydrofuran. The mixture was stirred at −60 °C until all the starting material had dissolved and the color of the solution was deep purple.[14] The solution was allowed to warm gradually to 20 °C over a period of 15 h and then filtered to give 1.1 g of black, crystalline product. As the x-ray analysis shows, this substance, which is doubtless identical with SKM's product, is $V_2(C_8H_9O)_4\cdot 2THF$ (not the monosolvate as previously claimed).[11]

Crystal Selection and Data Collection. During preliminary examination of several crystals it appeared that molecules of solvent were lost when the crystals were in contact with mineral oil or other protective coating at room temperature over a period of a few hours. This problem, as well as problems associated with the fragility and air sensitivity of the crystals, was circumvented by conducting the centering procedure and data collection at low temperature. A rectangular crystal measuring approximately 0.48 × 0.48 × 0.30 mm was immersed in mineral oil in a sealed capillary and immediately placed on a Syntex $P\bar{1}$ four-circle automated diffractometer equipped with a cryostat set to maintain the atmosphere around the crystal at −70 °C. Least-squares refinement of 15 intense reflections in the range 20° $< 2\theta <$ 30° gave an orientation matrix for calculation of setting angles and cell parameters. A monoclinic cell later shown by systematic absences and successful refinement to belong to the space group $P2_1/c$ was used. The cell dimensions are a = 13.804 (3) Å, b = 12.308 (3) Å, c = 23.456 (4) Å, β = 102.35 (1)°, and V = 3893 (1) Å^3. For Z = 4 and a formula weight of 794.74 the calculated density is 1.356 g cm^{-3}.

Intensity data were collected using graphite-monochromatized Mo Kα radiation and a $\theta/2\theta$ scan rate varying from 4 to 24°/min, depending upon the intensity of the reflection. Background measurements were made at both limits of each scan. Of the 5559 integrated intensities collected in the range 0° $< 2\theta \leq$ 45°, 2652 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected[15] for Lorentz and polarization effects. The standard reflections measured repeatedly every 100 data points showed no significant decline in intensity. No absorption correction was made since the linear absorption coefficient, 5.695 cm^{-1}, is small.

Structure Solution and Refinement.[15] From the three-dimensional Patterson map the positions for both vanadium atoms were deduced. A difference Fourier synthesis based on refined vanadium atom positions revealed six atoms coordinated to the vanadium atoms. These eight atoms were refined to give discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.405$$

$$R_2 = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.499$$

The weighting factor, w, is equal to $4F_o^2/\sigma(F_o^2)^2$. All remaining nonhydrogen atoms appeared on the next difference map. Refinement was continued with isotropic thermal parameters to discrepancy indices of R_1 = 0.158 and R_2 = 0.238. The vanadium atoms and then all the remaining atoms except the methoxy carbon atoms and the tetrahydrofuran atoms were assigned anisotropic thermal parameters and further least-squares refinement led to R_1 = 0.074 and R_2 = 0.099 at convergence; the error in an observation of unit weight was 2.03. No attempt was made to locate the hydrogen atoms. A final difference map had no peaks with intensity greater than 1 e/Å^3. There were some peaks in the region surrounding the methoxy carbon atoms and tetrahydrofuran molecules, suggesting that disorder in these regions had not been completely accounted for. However, the refinement was considered complete and adequate to reveal all structural features of chemical significance.

A table of observed and final calculated structure factors is available as supplementary material.

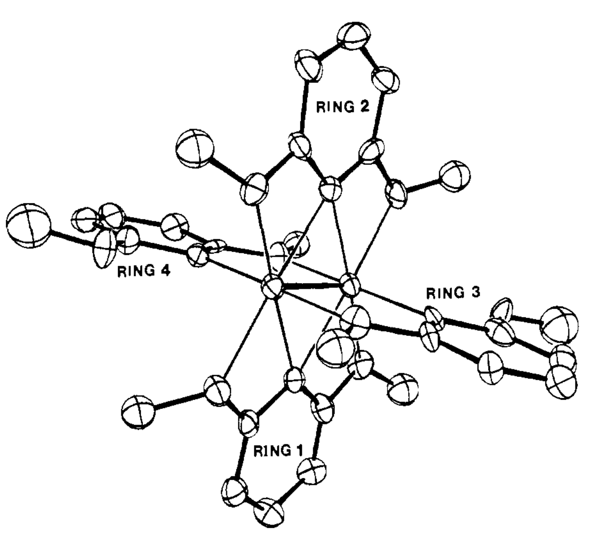


Figure 1. An ORTEP view of the V_2(2,6-dimethoxyphenyl)$_4$ molecule. Atoms are represented by their ellipsoids of thermal vibration, scaled to enclose 50% of the electron density.

Results

The positional and thermal parameters are recorded in Table I. Figure 1 shows the entire molecule in perspective. Figure 2a shows the essentially planar portion of the molecule consisting of the two vanadium atoms and ligands 3 and 4, which are related to the V_2 moiety in the manner suggested by SKM. Table IIa gives the distances and angles involving vanadium atoms for this part of the molecule. Similarly, Figure 2b shows the essentially planar part of the molecule consisting of V(1), V(2), and the other two ligands (which are *not* related to the V_2 moiety in the proposed way) and Table IIb lists distances and angles involving vanadium atoms for this part of the molecule. Table III lists interatomic distances and angles involving only ligand atoms for each of the four ligands. Table IV gives

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V1	0.7981 (1)	0.5294 (1)	0.26078 (7)	0.00211 (8)	0.0024 (1)	0.00102 (3)	−0.0003 (2)	0.00088 (9)	−0.0000 (1)
V2	0.7116 (1)	0.3784 (1)	0.24333 (7)	0.00236 (9)	0.0021 (1)	0.00106 (3)	−0.0000 (2)	0.00074 (9)	−0.0001 (1)
O13	0.7724 (5)	0.6515 (5)	0.3255 (3)	0.0028 (4)	0.0028 (5)	0.0015 (1)	−0.0001 (8)	0.0014 (4)	−0.0002 (5)
O12	0.5688 (5)	0.3542 (6)	0.2710 (3)	0.0030 (4)	0.0038 (5)	0.0016 (2)	−0.0027 (8)	0.0012 (4)	0.0002 (5)
O23	0.9399 (5)	0.5527 (5)	0.2325 (3)	0.0030 (4)	0.0032 (5)	0.0013 (1)	−0.0023 (8)	0.0014 (4)	0.0001 (5)
O22	0.7364 (5)	0.2564 (5)	0.1783 (3)	0.0043 (4)	0.0016 (5)	0.0016 (2)	−0.0008 (8)	0.0014 (4)	−0.0006 (5)
O33	0.8962 (4)	0.4591 (5)	0.3378 (3)	0.0026 (4)	0.0036 (5)	0.0011 (1)	−0.0019 (8)	0.0001 (4)	−0.0005 (5)
O32	0.7044 (6)	0.1452 (6)	0.2985 (3)	0.0067 (5)	0.0029 (5)	0.0012 (1)	−0.0027 (9)	0.0006 (5)	0.0014 (5)
O43	0.8094 (5)	0.7623 (6)	0.2026 (3)	0.0050 (5)	0.0028 (5)	0.0019 (2)	−0.0025 (9)	0.0011 (5)	0.0007 (5)
O42	0.6123 (4)	0.4486	0.1672 (3)	0.0025 (4)	0.0033 (5)	0.0013 (1)	0.0002 (8)	−0.0002 (4)	0.0004 (5)
O1	0.7593 (8)	0.4924 (10)	0.5424 (5)	7.5 (3)					
O2	0.7291 (7)	0.5991 (8)	−0.0496 (4)	5.5 (2)					
C11	0.6669 (7)	0.5035 (8)	0.2996	0.0026 (5)	0.0032 (7)	0.0008 (2)	0.002 (1)	0.0004 (5)	0.0009 (7)
C14	0.6845 (7)	0.6004 (8)	0.3317 (4)	0.0029 (6)	0.0027 (7)	0.0008 (2)	0.002 (1)	−0.0002 (6)	0.0007 (6)
C15	0.6249 (7)	0.6403 (9)	0.3669 (4)	0.0034 (6)	0.0038 (8)	0.0012 (2)	0.002 (1)	0.0011 (6)	0.0009 (7)
C16	0.5404 (7)	0.5787 (9)	0.3711 (5)	0.0025 (6)	0.0051 (9)	0.0015 (2)	0.001 (1)	0.0013 (6)	−0.0007 (8)
C17	0.5185 (7)	0.4812 (9)	0.3403 (4)	0.0025 (6)	0.0054 (9)	0.0012 (2)	−0.000 (1)	0.0007 (6)	0.0000 (8)
C18	0.5828 (7)	0.4480 (8)	0.3051 (5)	0.0028 (6)	0.0027 (7)	0.0013 (2)	−0.001 (1)	−0.0000 (6)	−0.0007 (7)
C21	0.8399 (7)	0.4050 (8)	0.2035 (4)	0.0017 (5)	0.0027 (7)	0.0009 (2)	0.000 (1)	0.0003 (5)	0.0002 (6)
C24	0.9231 (7)	0.4606 (8)	0.1970 (4)	0.0031 (6)	0.0025 (7)	0.0010 (2)	0.002 (1)	0.0008 (6)	−0.0001 (7)
C25	0.9860 (8)	0.4318 (9)	0.1593 (5)	0.0040 (6)	0.0040 (8)	0.0014 (2)	0.004 (1)	0.0010 (7)	0.0004 (8)
C26	0.9607 (8)	0.3363 (10)	0.1267 (5)	0.0035 (6)	0.0067 (10)	0.0016 (2)	0.003 (1)	0.0023 (6)	0.0018 (8)
C27	0.8789 (7)	0.2724 (9)	0.1324 (4)	0.0033 (6)	0.0047 (8)	0.0010 (2)	0.003 (1)	0.0007 (6)	−0.0001 (7)
C28	0.8220 (7)	0.3105 (9)	0.1698 (4)	0.0027 (6)	0.0048 (8)	0.0008 (2)	0.001 (1)	0.0006 (6)	0.0015 (7)
C31	0.8004 (7)	0.3007 (8)	0.3178 (4)	0.0037 (6)	0.0016 (7)	0.0013 (2)	0.002 (1)	0.0022 (6)	−0.0000 (7)
C34	0.8775 (7)	0.3522 (8)	0.3556 (4)	0.0024 (5)	0.0016 (7)	0.0012 (2)	0.001 (1)	0.0006 (6)	0.0002 (6)
C35	0.9352 (8)	0.3098 (9)	0.4065 (5)	0.0044 (7)	0.0035 (8)	0.0014 (2)	0.003 (1)	0.0018 (6)	0.0013 (7)
C36	0.9091 (8)	0.2037 (9)	0.4225 (5)	0.0045 (7)	0.0053 (9)	0.0015 (2)	0.004 (1)	0.0016 (7)	0.0009 (8)
C37	0.8313 (8)	0.1449 (9)	0.3867 (5)	0.0035 (6)	0.0042 (8)	0.0016 (2)	0.002 (1)	0.0009 (7)	0.0009 (8)
C38	0.7818 (7)	0.1981 (8)	0.3364 (5)	0.0035 (6)	0.0031 (8)	0.0015 (2)	−0.000 (1)	0.0016 (6)	−0.0015 (7)
C41	0.7085 (7)	0.6067 (8)	0.1859 (4)	0.0028 (6)	0.0030 (7)	0.0014 (2)	0.002 (1)	0.0023 (6)	0.0009 (7)
C44	0.7282 (7)	0.7121 (9)	0.1668 (4)	0.0039 (6)	0.0033 (8)	0.0014 (2)	0.001 (1)	0.0016 (6)	0.0010 (7)
C45	0.6726 (8)	0.7609 (9)	0.1173 (4)	0.0042 (6)	0.0047 (8)	0.0011 (2)	0.002 (1)	0.0016 (6)	0.0004 (8)
C46	0.5919 (8)	0.7049 (9)	0.0848 (5)	0.0057 (7)	0.0048 (9)	0.0018 (2)	0.005 (1)	0.0029 (7)	0.0017 (8)
C47	0.5681 (7)	0.5995 (9)	0.0987 (5)	0.0026 (6)	0.0059 (9)	0.0013 (2)	0.002 (1)	0.0002 (6)	0.0011 (8)
C48	0.6280 (7)	0.5566 (8)	0.1495 (4)	0.0028 (5)	0.0036 (8)	0.0009 (2)	−0.000 (1)	0.0025 (5)	−0.0002 (6)
C10	0.7725 (8)	0.7711 (9)	0.3271 (5)	2.9 (2)					
C19	0.5027 (9)	0.2701 (11)	0.2836 (5)	4.0 (3)					
C20	1.0057 (8)	0.6354 (10)	0.2198 (5)	3.3 (2)					
C29	0.7291 (8)	0.1413 (10)	0.1700 (5)	3.3 (2)					
C30	0.9680 (8)	0.5239 (9)	0.3759 (5)	3.2 (2)					
C39	0.6778 (10)	0.0377 (12)	0.3120 (6)	5.2 (3)					
C40	0.8406 (10)	0.8645 (12)	0.1828 (6)	5.3 (3)					
C49	0.5350 (8)	0.3851 (9)	0.1292 (5)	2.9 (2)					
C1	0.7940 (12)	0.4444 (14)	0.4926 (7)	7.2 (4)					
C2	0.7191 (11)	0.3579 (13)	0.4683 (6)	5.9 (4)					
C3	0.6271 (10)	0.3809 (12)	0.4980 (6)	5.7 (4)					
C4	0.6528 (9)	0.4904 (12)	0.5265 (6)	4.8 (3)					
C5	0.6917 (9)	0.5151 (11)	−0.0187 (5)	4.1 (3)					
C6	0.7731 (10)	0.4847 (12)	0.0326 (6)	5.2 (3)					
C7	0.8374 (12)	0.5833 (15)	0.0413 (8)	7.8 (5)					
C8	0.8080 (12)	0.6564 (15)	−0.0105 (7)	7.1 (4)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

equations for the mean plane of each ligand, the deviations of individual atoms from the planes, and the dihedral angles between mean planes.

The structure determination revealed the stoichiometry of the crystals to be V_2(2,6-dimethoxyphenyl)$_4$·2THF. The tetrahydrofuran molecules do not interact with the vanadium atoms and are readily lost from the crystals when they are removed from the mother liquor.

The vanadium dimer and two molecules of tetrahydrofuran comprise the asymmetric unit. Although the dimer has no crystallographic symmetry, the approximate symmetry of the molecule is C_{2h} ($2/m$). The short distance between the two vanadium atoms, 2.200 (2) Å, is indicative of a strong vanadium-vanadium interaction.

The four 2,6-dimethoxyphenyl groups coordinate to the metal atoms in two different modes of ligation. The first pair of ligands (3 and 4) and the two vanadium atoms are essentially coplanar (see Table IV for dihedral angles between ligand planes). Each vanadium atom is coordinated to the unique phenyl carbon atom, C(1) of one ligand and to a methoxy oxygen of the second ligand; the nonbonded methoxy oxygen atoms are 3.17 Å from the nearest vanadium atom. The second pair of ligands (1 and 2) and the vanadium atoms are also virtually coplanar; this plane is approximately perpendicular to the plane defined by ligands 3 and 4. Both methoxy oxygen atoms are coordinated to a vanadium atom. The phenyl carbon atom, C(1), is symmetrically positioned directly above the two vanadium atoms so as to form an equilateral triangle C(1)–V(1)–V(2), with sides of ~2.20 Å.

Each metal atom is coordinated by six ligand atoms and the other metal atom. As can be seen in Figure 2b, these atoms form an incomplete, distorted hexagonal bipyramid about each V atom, incomplete in the sense that the vertex trans to the other metal atom is unoccupied.

Table II. Interatomic Distances (Å) and Bond Angles (deg) Involving Vanadium Atoms[a]

A. Vanadium Atoms and Ligands 3 and 4			
V(1)-V(2)	2.200 (2)	C(41)-V(1)-V(2)	91.6 (2)
V(1)-C(41)	2.143 (8)	C(31)-V(2)-V(1)	91.9 (2)
V(2)-C(31)	2.134 (8)	O(33)-V(1)-V(2)	92.0 (1)
V(1)-O(33)	2.190 (5)	O(42)-V(2)-V(1)	92.2 (1)
V(2)-O(42)	2.183 (5)	C(41)-V(1)-O(33)	176.4 (3)
V(1)-O(43)	3.192 (5)	O(42)-V(2)-C(31)	175.7 (3)
V(2)-O(32)	3.159 (5)		
B. Vanadium Atoms and Ligands 1 and 2			
V(1)-C(11)	2.217 (8)	O(13)-V(1)-C(21)	173.5 (2)
V(1)-C(21)	2.194 (8)	O(23)-V(1)-C(11)	173.3 (2)
V(2)-C(11)	2.199 (8)	O(12)-V(2)-C(21)	171.9 (2)
V(2)-C(21)	2.196 (8)	O(22)-V(2)-C(11)	172.0 (2)
V(1)-O(13)	2.217 (5)	C(11)-V(1)-C(21)	119.7 (3)
V(1)-O(23)	2.215 (5)	C(11)-V(2)-C(21)	120.4 (3)
V(2)-O(12)	2.222 (5)		
V(2)-O(22)	2.219 (5)	O(13)-V(1)-O(23)	113.5 (2)
		O(12)-V(2)-O(22)	112.8 (2)
O(13)-V(1)-C(11)	63.4 (3)		
O(23)-V(1)-C(21)	62.8 (2)	V(1)-C(11)-V(2)	59.8 (2)
O(12)-V(2)-C(11)	62.6 (3)	V(1)-C(21)-V(2)	60.2 (2)
O(22)-V(2)-C(21)	63.3 (2)		
C(11)-V(1)-V(2)	59.7 (2)		
C(21)-V(1)-V(2)	60.0 (2)		
C(11)-V(2)-V(1)	60.5 (2)		
C(21)-V(2)-V(1)	59.9 (2)		

Table III. Interatomic Distances (Å) and Bond Angles (deg) of Ligands[a,b]

	Ligand 1	Ligand 2	Ligand 3	Ligand 4
C(9)-O(2)	1.45 (1)	1.43 (1)	1.43 (1)	1.46 (1)
C(0)-O(3)	1.47 (1)	1.44 (1)	1.43 (1)	1.44 (1)
O(2)-C(8)	1.40 (1)	1.41 (1)	1.40 (1)	1.42 (1)
O(3)-C(4)	1.40 (1)	1.40 (1)	1.42 (1)	1.39 (1)
C(1)-C(4)	1.40 (1)	1.37 (1)	1.39 (1)	1.42 (1)
C(4)-C(5)	1.38 (1)	1.41 (1)	1.39 (1)	1.39 (1)
C(5)-C(6)	1.41 (1)	1.41 (1)	1.43 (1)	1.39 (1)
C(6)-C(7)	1.40 (1)	1.41 (1)	1.41 (1)	1.40 (1)
C(7)-C(8)	1.40 (1)	1.38 (1)	1.39 (1)	1.40 (1)
C(8)-C(1)	1.38 (1)	1.40 (1)	1.38 (1)	1.39 (1)
C(9)-O(2)-C(8)	119.2 (6)	119.1 (6)	119.3 (6)	117.3 (6)
C(0)-O(3)-C(4)	116.2 (6)	118.9 (6)	118.5 (6)	116.9 (7)
O(2)-C(8)-C(1)	111.8 (7)	111.5 (7)	113.3 (7)	112.8 (7)
O(3)-C(4)-C(1)	112.3 (7)	112.1 (7)	113.5 (6)	113.6 (7)
C(1)-C(4)-C(5)	124.7 (8)	125.9 (8)	126.8 (7)	123.5 (8)
C(4)-C(5)-C(6)	117.3 (8)	115.9 (8)	116.1 (8)	118.8 (8)
C(5)-C(6)-C(7)	121.0 (8)	121.8 (8)	121.1 (8)	122.2 (8)
C(6)-C(7)-C(8)	117.5 (7)	116.6 (8)	115.8 (8)	115.1 (8)
C(7)-C(8)-C(1)	124.5 (8)	126.0 (8)	127.4 (8)	127.1 (8)
C(8)-C(1)-C(4)	115.0 (7)	113.7 (7)	112.8 (7)	113.2 (7)

[a] Numbers in parentheses following each distance and angle are esd's occurring in the least significant digit. [b] For numbering scheme, see Figure 2. The first digit in each number in Figure 2, the ligand number, is omitted in column 1 of this table.

Discussion

The Ligand Arrangements. We have here, as in so many other cases,[10] a compound in which there is a strong metal-metal bond (vide infra) spanned by four bridging groups. However, in this case two of the bridging groups are of a novel type, for which, so far as we know, there is no close precedent. The two bidentate ligands are electronically and sterically akin to the carboxylate anion, the amidate ion, and others of this sort and their mode of attachment to the V_2 unit poses no new problem at the qualitative level. However, the mode of attachment, electronically, of the tridentate ligands is more complex and not directly analogous to any previously discussed case.

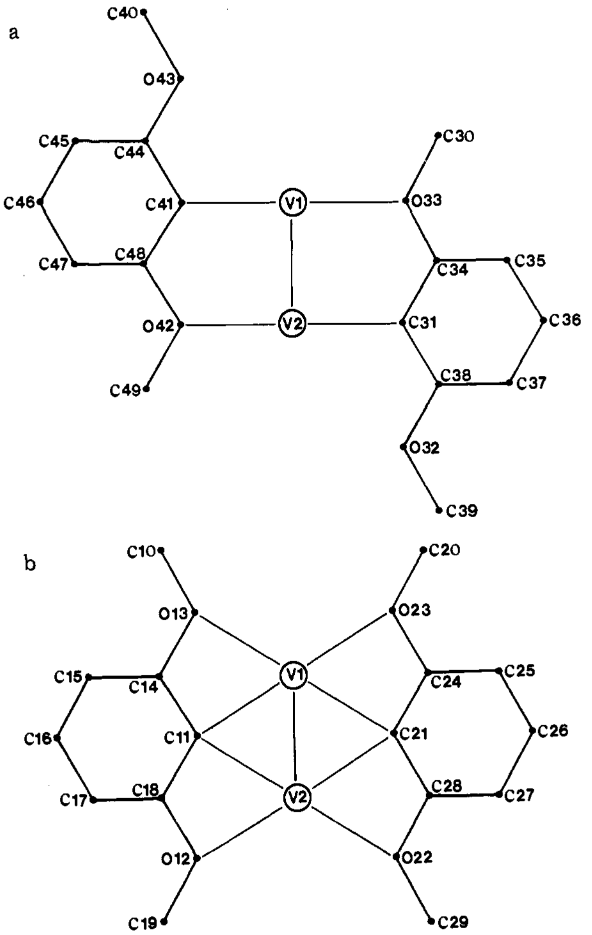


Figure 2. Diagrams of the two ligand arrangements. (a) The bidentate ligands. (b) The tridentate ligands. The numbering scheme used in the tables is defined.

The bridging phenyl group is in itself an oddity, since the plane (extended) of the phenyl ring *contains* the V-V bond. All previously reported cases of bridging phenyl groups, so far as we know, have the ring plane perpendicular to the metal-metal bond. These cases are found in several osmium cluster compounds,[16] several copper cluster compounds,[17] and in the bridged aluminum compounds, Al_2Ph_6[18] and $Al_2Ph_2(CH_3)_4$.[19]

The tridentate 2,6-dimethoxyphenyl ligand, considered as a neutral entity, is formally a five-electron donor. A number of the metal atom valence shell orbitals are potentially able to overlap with the filled orbitals of this ligand. However, the identification of some unique, or highly preferred, orbital set to accomplish the metal-ligand bonding is something that cannot be usefully discussed in the absence of some level of quantitative treatment, and we do not, therefore, propose to discuss the matter further at this time. Should this tridentate mode of bonding be found to occur in other compounds too, the effort to make a quantitative examination would then be worthwhile, but for the present, other calculations seem more imperative.

It is interesting to speculate on (a) the relative stabilities of the two ligand geometries, and (b) the ease with which they might interconvert. The first question could be framed more explicitly by asking how much less stable than the observed structure would be either of the two limiting ones in which all the ligands would be bidentate, or tridentate. Of course, we have no practical way to answer this directly. However, by changing the metal atoms, some sort of an indirect answer

Table IV. Least-Squares Planes for the Ligands[a]

Atom	Dev, Å	Atom	Dev, Å
Ligand 1 ($-0.4212X + 0.4367Y - 0.7949Z = 5.9709$)			
O(13)	−0.258	C(17)	0.064
O(12)	0.205	C(18)	0.079
C(11)	−0.023	C(19)	−0.066
C(14)	−0.122	C(10)	0.358
C(15)	−0.129	V(1)	−0.023
C(16)	−0.035	V(2)	−0.050
Ligand 2 ($-0.4424X + 0.4615Y - 0.7689Z = 5.9713$)			
O(23)	−0.209	C(27)	0.112
O(22)	0.185	C(28)	0.100
C(21)	0.007	C(29)	−0.297
C(24)	−0.082	C(20)	0.054
C(25)	−0.051	V(1)	0.089
C(26)	0.064	V(2)	0.028
Ligand 3 ($0.7707X - 0.3521Y - 0.5310Z = -2.0592$)			
O(33)	0.070	C(37)	−0.043
O(32)	0.020	C(38)	0.006
C(31)	0.057	C(39)	0.014
C(34)	0.048	C(30)	−0.059
C(35)	0.030	V(1)	−0.043
C(36)	−0.043	V(2)	−0.030
Ligand 4 ($0.7375X - 0.3713Y - 0.5642Z = -1.4214$)			
O(43)	−0.032	C(47)	−0.017
O(42)	−0.018	C(48)	−0.057
C(41)	−0.071	C(49)	0.018
C(44)	−0.035	C(40)	0.146
C(45)	−0.003	V(1)	−0.051
C(46)	−0.026	V(2)	0.048
Dihedral Angles between Planes (deg)			
Plane 1-plane 2			2.14
Plane 3-plane 4			2.9
Plane 1-plane 3			86.8
Plane 3-plane 2			95.5
Plane 2-plane 4			86.3
Plane 4-plane 1			91.4

[a] The equation for each plane is of the form $AX + BY + CZ = D$. where all 12 listed atoms were used to establish the plane, and the orthonormal coordinates, X, Y, Z, are related to the fractional coordinates, x. y, z, by

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cos\sigma & c\cos\beta \\ 0 & b\sin\gamma & \dfrac{c(\cos\alpha - \cos\beta\cos\gamma)}{\sin\gamma} \\ 0 & 0 & \dfrac{V}{ab\sin\gamma} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

and $V = abc(1 + 2\cos\alpha\cos\beta\cos\gamma - \cos\alpha^2\ \cos\beta^2\cos\gamma^2)^{1/2}$.

Table V. Distances (Å) and Angles (deg) in the Tetrahydrofuran Molecules[a]

Molecule 1			
O(1)-C(1)	1.48	C(3)-C(4)-O(1)	105
O(1)-C(4)	1.44	C(4)-O(1)-C(1)	106
C(1)-C(2)	1.51	O(1)-C(1)-C(2)	106
C(2)-C(3(	1.60	C(1)-C(2)-C(3)	105
C(3)-C(4)	1.51	C(2)-C(3)-C(4)	103
Molecule 2			
O(2)-C(8)	1.45	C(7)-C(8)-O(2)	105
O(2)-C(5)	1.42	C(8)-O(2)-C(5)	110
C(5)-C(6)	1.51	O(2)-C(5)-C(6)	107
C(6)-C(7)	1.49	C(5)-C(6)-C(7)	103
C(7)-C(8)	1.50	C(6)-C(7)-C(8)	109

[a] All distances have esd's of ca. 0.015 Å and all angles have esd's of ca. 1°.

might be sought. We are, in fact, in the process of preparing and structurally examining several other compounds of the same stoichiometry with other metal atoms. A related approach is to attempt the preparation of compounds containing the 2-methoxyphenyl ligand, in which case the compound, if formed at all, would have to contain entirely bidentate ligands.

The question of whether the two sorts of ligand geometries might participate in a concerted exchange process with a low activation energy is potentially answerable by NMR spectroscopy. Unfortunately, the compound is so insoluble that we have been unable to carry out this experiment.

The Metal-Metal Bond. It has long been recognized that the unambiguous assignment of bond orders to metal-metal bonds is only possible (though even then soemtimes subject to uncertainty) when there are no bridging groups spanning the M-M unit. When bridging groups are present, their possible contribution to, or direct participation in, the M-M interaction must always be considered. It is, therefore, with due caution that we undertake a discussion of the metal-metal bond order in this compound. This is especially true because of the complex and intimate association of the tridentate ligands with the V_2 unit.

We believe that it is reasonable to regard the V-V bond as a triple bond. From the point of view of the very short internuclear distance, 2.200 Å, this is credible. The only previous report[20] giving the length of a strong V-V bond concerns that in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$. In that case the V-V distance is 2.462 Å. The present distance of 2.200 Å is thus short enough to support the thesis that if a bond of order at least unity exists in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, then a multiple bond exists in the present case. The present distance also compares reasonably with the reported Cr-Cr triple bond distance of 2.280 Å.[6a] In view of the number of electrons available and the diamagnetism of the compound, we, in agreement with SKM, think that a triple bond is a very plausible proposal.

No attempt at a detailed description of this triple bond will be made because of the low symmetry of the molecule. However, as a heuristic argument we might begin by supposing the four 2,6-dimethoxyphenyl ligands to be equivalent, so that the axis of quantization for the problem would coincide with the V-V line. We are then in essentially the same position as we are with all of the more symmetrical cases of triple[5] and quadruple[10] bonds, and we can readily envision the formation of a V-V σ bond by overlap of two d_{z^2} orbitals and the formation of an axially symmetric, degenerate pair of π bonds by overlap of the matching pairs of d_{xz} and d_{yz} orbitals of the two metal atoms. The actual presence of two different arrangements of the ligands must, of course, perturb this symmetrical picture, but it should remain a useful approximation to the true situation.

It may be briefly noted, in conclusion, that the V_2 molecule has been detected in an argon matrix[21] and it has been suggested[22] that it contains a strong, multiple bond ($d_{VV} = 1.9$ Å) on the basis of an empirical MO calculation. A comparison of the V-V stretching frequencies in V_2 and V_2(2,6-dimethoxyphenyl)$_4$, if both could be measured, might afford an interesting test of this proposal.

Acknowledgments. We are grateful to the National Science Foundation for partial support of this work and to Dr. Stephen A. Koch for his interest and assistance.

Supplementary Material Available: A table of observed and final calculated structure factors (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966); *Proc. R. Soc. London, Ser. A*, **303**, 175 (1968).
(2) K. Waltersson, *Acta Crystallogr., Sect. B*, **32**, 1485 (1976).
(3) J. R. Ebner and R. A. Walton, *Inorg. Chem.*, **14**, 1987 (1975); F. A. Cotton,

B. A. Frenz, J. R. Ebner, and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, 4 (1974)., *Inorg. Chem.*, **15**, 1630 (1976).
(4) F. A. Cotton and G. G. Stanley, unpublished work.
(5) Cf. M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **16**, 603 (1977); M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *J. Am. Chem. Soc.*, **99**, 1652 (1977), and references cited therein.
(6) (a) J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, *Inorg. Chem.*, **13**, 2540 (1974); (b) for a review see R. B. King, *Coord. Chem. Rev.*, **20**, 155 (1976).
(7) S.-I. Murahashi, et al., *J. Chem. Soc., Chem. Commun.*, 563 (1974).
(8) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Am. Chem. Soc.*, **95**, 2021 (1973).
(9) F. A. Cotton and G. G. Stanley, *Inorg. Chem.*, **16**, 2668 (1977).
(10) F. A. Cotton, *Chem. Soc. Rev.*, 4, 27 (1975).
(11) W. Seidel, G. Kreisel, and H. Mennenga, *Z. Chem.*, **16**, 492 (1976).
(12) E. Kurras, *Naturwissenschaften*, **46**, 171 (1959).
(13) R. Levine and J. Sommers, *J. Org. Chem.*, **39**, 3559 (1974).
(14) Presumably $V(C_8H_9O_2)_3$. Cf. W. Seidel and G. Kreisel, *Z. Chem.*, **14**, 25 (1974).
(15) Crystallographic computer programs used were those of the Enraf-Nonius Structure Determination Package. These were used on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas.
(16) G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organomet. Chem.*, **40**, C70 (1972); C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 87 (1972).
(17) J. M. Guss, R. Mason, K. M. Thomas, G. Van Koten, and J. G. Noltes, *J. Organomet. Chem.*, **40**, C79 (1972); J. M. Guss, R. Mason, I. Sotofte, G. Van Koten, and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, **446** (1972).
(18) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2646 (1972).
(19) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2649 (1972).
(20) F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Am. Chem. Soc.*, **95**, 951 (1973).
(21) T. A. Ford, H. Huber, W. Klotzbücher, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Chem. Phys.*, **66**, 524 (1977).
(22) W. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, **16**, 984 (1977).

Intramolecular Electron Transfer. 3. Bis(4-pyridyl)methane as Bridging Group

K. Rieder and H. Taube*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received May 4, 1977*

Abstract: Attention is drawn to an ambiguity in the interpretation of so-called rates of intramolecular electron transfer for species in which Co(III) is the oxidizing agent, an ambiguity which raises questions about the relevance of the results thus far reported to the issue of whether the reactions are adiabatic. Measurements of the rate of intramolecular electron transfer for bis(4-pyridyl)methane bridging Co(III)–Ru(II) show the rate to be a factor of 21 slower than for the analogous system with 4,4′-bipyridine as bridging group. It appears that for this system at least the effects of nonadiabaticity are being felt, and this together with other arguments supports the conclusion that the ambiguity mentioned does not vitiate the inferences based on the related studies which have been done.

A number of recent studies[2-5] have been devoted to measuring rates of intramolecular electron transfer for systems in which the positions of the metal ions involved in the redox process are fixed. The most extensive measurements of this kind deal with species in which 4,4′-byridine and related molecules serve as the bridging groups. A striking result of these studies is that the rates of the so-called intramolecular electron transfer reactions differ only slightly for what would appear to be rather drastic changes in the electronic coupling between the two pyridine rings. The advantages of measuring the rates of reaction in the intramolecular mode have long been appreciated and have repeatedly been referred to. What has not been emphasized is that measurements of this kind themselves can suffer from a serious limitation. Consider the general reaction scheme:

$$(NH_3)_5Co^{III}L \ldots LRu^{II}(NH_3)_4H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NH_3)_3Co^{*II}L \ldots LRu^{III} \quad (1)$$

$$(NH_3)_5Co^{*II}L \ldots LRu^{III}(NH_3)_4H_2O \xrightarrow{k_2} \text{products} \quad (2)$$

In this mechanism, it is postulated that an intermediate species is produced in the net reduction of Co(III) to Co(II), an altogether reasonable possibility considering the fact that there is a spin change, and that substitution accompanies the net change in oxidation state. Reaction 2, in which the net change is consummated, may involve substitution, or a spin change,[16] or both. Should k_{-1} be substantially greater than k_2, the overall reaction rate is governed by the product K_1k_2, where K_1 is the equilibrium quotient for reaction 1. This limiting form of the general rate law would at once explain why the rates reported within the Co(III)–Ru(II) series (or within the Co(III)–Fe(II) series) are so nearly alike—since the immediate environment around the metal ions is the same within each series, both K_1 and k_2 are expected to be nearly constant. If this limit is applicable, the results have no bearing on the issue of whether the reactions are adiabatic.

By contrast, when the reactions are conducted in the intermolecular mode, the form of the rate law which has been observed ensures that the step analogous to (1) in the forward direction is solely rate determining. Cast into the intermolecular form, the mechanism becomes:

$$(NH_3)_5Co^{III}L + (NH_3)_5Ru^{II}L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (NH_3)_5{}^{*}Co^{II}L + (NH_3)_5Ru^{III}L \quad (3)$$

$$(NH_3)_5{}^{*}Co^{II}L \xrightarrow{k_4} \text{products} \quad (4)$$

and the general form of the rate law is

$$\frac{d[(\text{prod})]}{dt} = \frac{k_4k_3[\text{Co(III)}][\text{Ru(II)}]}{k_4 + k_{-3}[\text{Ru(III)}]}$$

Since the rates of reduction are not affected by the accumulation of the product of the oxidation of the reducing agent, it follows that $k_{-3}[\text{Ru(III)}] \ll k_4$ and the rate law reduces to $k_3[\text{Co(III)}][\text{Ru(II)}]$. Unfortunately, this outcome for the