The pH dependence of k_c/K_m below pH 8 stems from the dependence of k_c, not of K_m, on pH (Table II). This pH dependence of k_c, the pK value of 6.7, its shift to 7.35 by D_2O, and the one-unit slope of the log k_c/K_m function all match the data for chymotrypsin and are consistent with a requirement for a single, unprotonated imidazole group.[8] The isotope effect of 2.03 with D_2O is of the same magnitude as for chymotrypsin and is consistent with general basic catalysis by an imidazole group.[9] The constancy of k_c/K_m from pH 8 to 10.5 and the activity of the acetylated enzyme indicate that the binding of neutral substrates is completely independent of pH and is not influenced by ionizations of α- or ϵ-amino groups of the enzyme. This represents the only contrast with chymotrypsin, as the latter undergoes a change in conformation at alkaline pH values and loses its ability to bind substrates.[10]

The above comparison thus supports the indications of the direct kinetic evidence for chymotrypsin, *i.e.*, that its reaction mechanism involves only one histidine group.

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(8) M. L. Bender, G. E. Clement, F. J. Kezdy, and H. d'A. Heck, *J. Am. Chem. Soc.*, **86**, 3680 (1964); F. J. Kézdy, G. E. Clement, and M. L. Bender, *ibid.*, **86**, 3690 (1964).

(9) M. L. Bender, E. J. Pollock, and M. C. Neveu, *ibid.*, **84**, 595 (1962).

(10) H. L. Oppenheimer, B. Labouesse, and G. P. Hess. *J. Biol. Chem.*, **241**, 2720 (1966); M. L. Bender, M. J. Gibian, and D. J. Whelan, *Proc. Natl. Acad. Sci. U. S.*, **56**, 833 (1966).

(11) National Research Council of Canada Postdoctoral Fellow.

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Octahedral *vs.* Trigonal-Prismatic Coordination. The Structure of $(Me_4N)_2[V(mnt)_3]$[1]

Sir:

It has recently been shown that a large number of uncharged and monoanionic tris complexes of bidentate sulfur donor ligands possess trigonal-prismatic coordination and thus constitute the first examples of nonoctahedral six-coordinate complexes.[2-6] However, prior to this work there has been no unequivocal evidence relating to the structures of the more highly reduced species having charges 2− and 3−. It has in fact been suggested[3] that some of these complexes could be closer to the classical octahedral configuration. In this communication, we report the molecular structure of $V(mnt)_3^{2-}$, which exhibits the first nontrigonal-prismatic coordination geometry for this class of compounds.

Black monoclinic crystals of $(Me_4N)_2[V(mnt)_3]$[7-9] were grown from acetone–2-propanol solutions. Precession photography revealed systematic extinctions indicating the space group C2/c or C_c, with a cell of dimensions a = 20.53 A, b = 10.19 A, c = 16.98 A, β = 124° 15′ and vol. = 2935 A^3. The measured density of 1.37 ± 0.05 g cm^{-3} is consistent with four anions and eight cations in the unit cell of calculated density 1.40 g cm^{-3}. Assuming the space group C2/c, the four vanadium atoms are required to occupy the 4e special positions of the space group and thus the anion is required to have a twofold symmetry axis. This assumption is verified by the satisfactory agreement ultimately obtained.

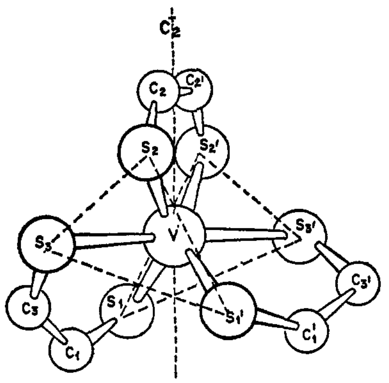

Figure 1. Perspective drawing of the molecular structure of the $V(mnt)_3^{2-}$ anion. The cyano groups are omitted.

The intensity data were collected by the multiple film equiinclination Weissenberg technique using Cu Kα radiation. Intensities were estimated visually and reduced to values of F_o by standard methods. The structure was solved by standard Patterson, least-squares, and Fourier methods. The R factor for 88 positional and thermal parameters (allowing the vanadium and three independent sulfurs to have anisotropic temperature factors) is currently 0.125 for 1187 independent nonzero reflections.

A perspective drawing of the coordination geometry is shown in Figure 1; some of the important bond distances are given in Table I. The vanadium lies on a twofold rotation axis which bisects one of the three ligands. The six sulfur donor atoms are located around the vanadium at an average distance of 2.36 ± 0.01 A. The polyhedron described by these sulfur atoms is by no means a regular one, but for some purposes it is usefully described as a very distorted octahedron (*vide supra*). The intraligand S–S dis-

Table I. Important Bond Lengths in the $V(mnt)_3^{2-}$ Anion[a]

Bond	Bond length, A	Bond	Bond length, A
$V-S_1$	2.36 ± 0.01	C_1-C_3	1.37 ± 0.02
$V-S_2$	2.35 ± 0.01	$C_2-C_{2'}$	1.29 ± 0.03
$V-S_3$	2.36 ± 0.01	$S_2-S_{2'}$	3.17 ± 0.01
S_1-C_1	1.72 ± 0.02	S_1-S_3	3.11 ± 0.01
S_2-C_2	1.74 ± 0.02	$S_{1'}-S_2$	3.43 ± 0.01
S_3-C_3	1.69 ± 0.02	S_2-S_3	2.98 ± 0.01
		$S_{1'}-S_3$	3.18 ± 0.01

[a] The prime denotes an atom related by the twofold axis.

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(1) Acknowledgment is made to the National Science Foundation for support of this research. We thank Professor R. Eisenberg of Brown University for several helpful discussions.

(2) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2956 (1966).

(3) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966).

(4) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).

(5) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).

(6) R. Eisenberg and H. B. Gray, to be published.

(7) The anion was first reported as the Ph_4As^+ salt by Davison and co-workers[8] and later isolated using a somewhat different procedure as the $Ph_3P(Me)^+$ salt.[9] The Me_4N^+, Et_4N^+, and Bu_4N^+ salts described in this study were prepared by a procedure only slightly modified from that given in ref 8.

(8) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).

(9) N. M. Atherton, J. Locke, and J. A. McCleverty, *Chem. Ind.* (London), **29**, 1300 (1965).

tances are longer than those of other dithiolate complexes, being 3.17 ± 0.01 (on twofold) and 3.11 ± 0.01 A for the other two ligands. Analogous distances have been found to be in the range 3.04–3.10 A in all other structures.[10]

A useful criterion for discussion of coordination geometry in the systems under consideration is the average S–M–S angle involving pairs of donor atoms that are farthest apart. This angle averages 136 ± 1° in the known trigonal-prismatic structures[2–6] and 180° for the perfect octahedron. However, we must first take into account the constraint imposed upon the idealized octahedron by the rigid nature of the maleonitriledithiolate ligands. Because of this constraint, the average for this angle in the chelated complex derived from an octahedron should be approximately 173°.[11] The average angle found for $V(mnt)_3^{2-}$ is 158.6°, which is somewhat closer to the "chelated octahedral structure." The observed distortion is not simply a solid-state phenomenon since the rich electronic spectrum of $V(mnt)_3^{2-}$ remains essentially identical for various cations (Me_4N^+, Et_4N^+, Bu_4N^+, and Ph_4As^+) in solid samples and in solutions. Furthermore, the infrared absorptions attributable to the anion are independent of the nature of the cation in solid samples. The distortion must then have an intramolecular electronic origin. We suggest that the two relatively short interligand S–S distances indicate some residual S–S bonding of the type which has been postulated as stabilizing the trigonal-prismatic structure in the uncharged complexes.[2] It is reasonable to expect the additional two electrons in the dianionic complex to cause the ligands to behave more like conventional dithiolates where a "classical" octahedral structure may be favored. Pitting these two effects against the geometric constants of the ligand, we can only say that nature has chosen an interesting compromise configuration; we have much work to do before we can begin to understand its subtleties.[12]

We have recently prepared the Ph_4As^+ salts of $M(mnt)_3^{2-}$ [13] for M = Ti, V,[8] Cr,[8] Mn,[14] Fe,[14] Mo,[14] W,[14] and Re. We find that the Ti, V, and Cr complexes have nearly identical X-ray powder patterns and thus appear isomorphous. It is also interesting to note the magnetic properties of these first-row complexes. If the ligands are considered to be dianions, then the central metal is in the formal IV oxidation state and the moments are found to be those typical of low-spin octahedral compounds (see Table II). Furthermore, spectral studies indicate a certain similarity in the electronic structures of the complex anions. In view of the evidence, then, we suggest that all the first-row $M(mnt)_3^{2-}$ complexes have distorted octahedral structures. Thus, the picture seems to be emerging that the more highly reduced species will approach the classical octahedral stereochemistry, while the oxidized forms will invariably possess the unusual trigonal-prismatic coordination.

Table II. Magnetic Properties of $M(mnt)_3^{n-}$ Complexes

Complex[a]	μ_{eff}, BM	Complex[a]	μ_{eff}, BM
$Ti(mnt)_3^{2-}$	Diamag[b]	$Fe(mnt)_3^{2-}$	3.00[b]
$V(mnt)_3^{2-}$	1.82[c]	$Cr(mnt)_3^{3-}$	3.90[c]
$Cr(mnt)_3^{2-}$	2.89[c]	$Co(mnt)_3^{3-}$	Diamag[b]
$Mn(mnt)_3^{2-}$	3.85[b]		

[a] Cation is Ph_4As^+. Magnetic moments are for solid samples at room temperature. [b] Details reported in ref 13. [c] From ref 8.

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(10) (a) This is true for the three prismatic structures,[2–6] the six square-planar structures,[10b–g] and the two dimeric structures[10h,i] which have been fully solved; (b) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965). (c) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1501 (1964); (d) *ibid.*, **3**, 1507 (1964); (e) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966); (f) D. Sartain and M. R. Truter, *Chem. Commun.*, **382**, (1966); (g) R. Eisenberg, Z. Dori, J. A. Ibers, and H. B. Gray, to be published; (h) J. M. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965); (i) M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, to be published.

(11) For comparison, in $Cr(C_2O_4)_3^{3-}$, where the average "bite" O–Cr–O angle is 82°, we have calculated the average (largest) O–Cr–O angle to be 172° [J. N. van Niekerk and F. R. L. Schoenig, *Acta Cryst.*, **5**, 499 (1952)].

(12) For example, the V atom lies significantly out of the planes determined by the ligands alone. Pertinent geometrical parameters (such as interligand dihedral angles) determined solely from the MS_6 framework tend toward octahedral structure whereas related parameters set by the ligand planes suggest structure closer to trigonal prismatic. This finding may indicate that the ligand unit "prefers" the prism structure whereas the metal is desirous of octahedral coordination. Another interesting result arises on comparison of the C–C bond lengths in this structure with corresponding parameters from the $V(S_2C_2Ph_2)_3$ structure.[3,6] The pertinent distances for $V(mnt)_3^{2-}$ are 1.37 ± 0.02 (two distances related by twofold axis) and 1.29 ± 0.03 A, whereas the corresponding distances for $V(S_2C_2Ph_2)_3$ are 1.38 ± 0.01 and 1.46 ± 0.02 A. The drastic shortening of one C–C bond (from 1.46 to 1.29 A) suggests that the ligands do not participate equally in the two-electron reduction described by $VL_3 + 2e \rightarrow VL_3^{2-}$.

(13) E. I. Stiefel, L. Bennett, Z. Dori, C. Simo, T. H. Crawford, and H. B. Gray, to be published.

(14) Salts of these anions have also been prepared by M. Gerlock, S. F. A. Kettle, J. Locke, and J. A. McCleverty, *Chem. Commun.*, 29 (1966). The magnetic results reported initially by these authors for the Mn and Fe compounds are apparently in error; our results are in agreement with their latest values (J. A. McCleverty, private communication).

(15) National Science Foundation Graduate Fellow, 1965–1967.

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Chronology in Photochemical Mechanisms. The Reaction of 6-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one. Mechanistic Organic Photochemistry. XXV[1]

Sir:

One of the most challenging questions in photochemistry concerns the chronology in photochemical reaction mechanisms. In particular, one would like to know at which point in a transformation electronic excitation is lost.

In the type B rearrangement[2] of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones the first step seems without doubt to be fission of bond 2–4 (cyclohexane numbering; see Chart I) of the triplet[3] excited state (**1***) of the bicyclic ketone; fission of this internal three-ring bond converts carbons 2 and 4 to valency-deficient centers to which aryl (or alkyl in nonaryl cases) migration might occur. However, the migration to C-2 and C-4 could occur immediately following bond 2–4 fission and therefore be a reaction of a triplet excited state (*e.g.*, **2***), or

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(1) For paper XXIV see H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Am. Chem. Soc.*, in press.

(2) See H. E. Zimmerman, *Science*, **153**, 837 (1966).

(3) Evidence for involvement of the triplet has been presented by H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966).