Frequencies attributable to the thiocarbamate ligand either remain unchanged or changed only slightly upon substitution of the disulfide ligand for the methoxide ligand in the parent compound. The characteristically strong infrared band assigned as the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ stretching frequency at 1510 cm^{-1} remains unchanged, while the ν(C–S) band diminished in intensity and increased in frequency by 10 cm^{-1} to a value of 680 cm^{-1}.

The uranium–oxygen (monothiocarbamate oxygen) band had been reported at 455 cm^{-1} in the infrared spectrum of $U((C_2H_5)_2NCOS)_4$,[33] comparing quite favorably with the 440 and 450-cm^{-1} values observed here for the uranyl thiocarbamate disulfide and its thiocarbamate alkoxide parent compound, respectively. The uranium–oxygen (alkoxide oxygen) stretching frequency is found at 388 cm^{-1} in the parent uranyl alkoxide compound, a value identical with that tabulated for terminal uranium–oxygen and bridging uranium–oxygen vibrations for uranium(IV) and uranium(VI) alkoxides, respectively.[34] This assignment is further corroborated when one replaces OCH_3^- in $[(n\text{-}C_3H_7)_2NH_2^+][UO_2((n\text{-}C_3H_7)_2NCOS)_2OCH_3^-]$ with the S_2^{2-} ligand; the band at 388 cm^{-1} in the original thiocarbamate alkoxide disappears, while all other bands in that region are left unchanged.

The sulfur–sulfur stretching frequency in other metal disulfide complexes has been reported to lie in the ~500–530-cm^{-1} region.[35] In the spectrum of the uranyl thiocarbamate disulfide described here, a triplet set of bands appears at 510, 520, and 530 cm^{-1}, which can be assigned as the ν(S–S) stretching frequencies. This assignment is in excellent agreement with the triplet set of bands assigned to the ν(S–S) of the $[Mo_4(NO)_4S_{13}]^{4-}$ anion.[21] This vibrational mode is often strongly coupled, as has been experimentally shown by Muller and co-workers using ^{92}Mo and ^{100}Mo isotopic substitution in the study of the $[Mo_3S(S_2)_6]^{2-}$ complex anion.[4]

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract Number W-7405-Eng-48. D.L.P. wishes to thank the Miller Research Institute, University of California, Berkeley, for a Miller Fellowship.

Registry No. I, 79483-32-2; II, 77535-75-2.

Supplementary Material Available: Listings of data processing formulas, anisotropic thermal parameters, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

---

(30) Ferraro, J. R.; Walker, A. *J. Chem. Phys.* **1966**, *45*, 550.

(31) Koglin, E.; Schenk, H. J.; Schwochau, K. *Appl. Spectrosc.* **1978**, *32*, 486.

(32) The position of the asymmetric UO_2^{2+} stretching frequency varies quite widely as a function of the presence and extent of hydrogen bonding. Compare, for example, the range of values tabulated in ref 31.

(33) Bagnall, K. W.; Yanir, E. *J. Inorg. Nucl. Chem.* **1974**, *36*, 777.

(34) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978; p 120.

(35) For a survey of the values of the sulfur–sulfur stretching frequency reported for metal–disulfur complexes, please see ref 4.

Contribution from the Department of Chemistry and Research Centre for Spectrochemistry,
Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

The Heteropolyvanadate of Phosphorus. Crystallographic and NMR Studies[1]

REIZO KATO, AKIKO KOBAYASHI, and YUKIYOSHI SASAKI*

Received May 6, 1981

The guanidinium salt of 14-vanadophosphate, $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$, was isolated by treating the mixture of $NaVO_3$ and H_3PO_4 (V:P ≈ 4, pH 2–3) with excess guanidine hydrochloride. Crystal data: tetragonal, space group $I\bar{4}$; $a = 13.058$ (2), $c = 18.431$ (6) Å; $Z = 2$. The structure was refined by using 2257 independent reflections to a conventional weighted R factor of 0.062. In the anion twelve V atoms form the usual Keggin structure and the remaining two V atoms occupy the pits on the Keggin molecule where a $\bar{4}$ axis is passing, forming trigonal-bipyramidal caps. Such a "bicapped Keggin" structure has never been observed in heteropolyanions of Mo and W. ^{31}P and ^{51}V NMR spectra of the aqueous solutions of the 1:14 bicapped Keggin anion showed a single ^{31}P resonance and two broad ^{51}V resonances with an intensity ratio of 2:12 (assigned to the capping 5-coordinated V atoms and the 6-coordinated V atoms in the Keggin units, respectively). The pH dependence of ^{31}P and ^{51}V chemical shift values could be explained by the protonation of the 1:14 anion. NMR studies of the NaH_2PO_4–$NaVO_3$–H_2SO_4 aqueous system ($^1/_2 \le$ V:P ≤ 14, $1 < \mathrm{pH} < 6$) at room temperature revealed that the 1:14 vanadophosphate anion exists in a wide range of V:P ratios as the only detectable heteropolyanion in this system.

Introduction

A number of heteropolymolybdates and -tungstates, including polyanions where some of the molybdenum or tungsten atoms are replaced by vanadium atoms, have been subjected to extensive studies. But, our knowledge about heteropolyvanadates, particularly those containing a tetrahedrally coordinated heteroatom(s), is still limited.[2] In the case of phosphorus as the heteroatoms(s), there have been several reports of the preparation of $PV_{12}O_{36}^{7-}$ anion and its protonated forms,[3] but the existence of this anion was doubted by Preuss and Schug. Instead, they claimed to have characterized 1:13 and 1:14 vanadophosphates by chemical analyses and the ultracentrifuge technique.[4] None of these previous works revealed the structure of these vanadophosphate anions and the equilibrium of solute species in the solution. In the present work, the vanadophosphate anion is investigated by X-ray crystallography and nuclear magnetic resonance spectroscopy.

---

(1) A preliminary report on this work was given in: Kato, R.; Kobayashi, A.; Sasaki, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6571.

(2) The structures of $Ni^{IV}V_{13}O_{38}^{7-}$, $Mn^{IV}V_{13}O_{38}^{7-}$, and $AlV^{V}_{12}V^{IV}_2O_{40}^{9-}$, which have octahedrally coordinated heteroatoms, were established: Flynn, C. M., Jr.; Pope, M. T. *J. Am. Chem. Soc.* **1970**, *92*, 85. Kobayashi, A.; Sasaki, Y. *Chem. Lett.* **1975**, 1123. Evans, H. T., Jr.; Konnert, J. A. *Am. Mineral.* **1978**, *63*, 863. Flynn and Pope also reported the preparation of $Mn^{IV}V_{11}O_{32}^{5-}$ and $HMn_3V_{12}O_{39}^{5-}$ anions: Flynn, C. M., Jr.; Pope, M. T. *Inorg. Chem.* **1970**, *9*, 2009. The only known example of heteropolyvanadates containing tetrahedrally coordinated heteroatoms was $H_6As_6V_4O_{30}^{4-}$: Durif, A.; Averbuch-Pouchot, M. T. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1441.

(3) Souchay, P.; Dubois, S. *Ann. Chim.* (*Paris*) **1948**, *3*, 88. Bekturov, A. B.; Il'yasova, A. K. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1964**, *10*, 130. Ripan, R.; Duca, A.; Cordis, V. *Rev. Roum. Chim.* **1967**, *12*, 375. Ripan, R.; Cordis, V. *Ibid.* **1969**, *14*, 197; **1970**, *15*, 559. Hagenbruch, R.; Hahn, H. *Z. Anorg. Allg. Chem.* **1978**, *438*, 273; **1980**, *467*, 126.

(4) Preuss, F.; Schug, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1585.

0020-1669/82/1321-0240$01.25/0

Table I. Fractional Atomic Coordinates ($\times 10^4$) and Anisotropic Temperature Parameters[a] ($Å^2 \times 10^4$ for P and V; $Å^2 \times 10^3$ for Others) with Their Estimated Standard Deviations for $(CN_3H_6)_8H[PV_{14}O_{42}]\cdot 7H_2O$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0	0	0	108 (25)	108	90 (20)	0	0	0
V(1)	−1581 (1)	−1105 (1)	−1306 (1)	238 (6)	188 (6)	218 (6)	−4 (5)	−91 (6)	−57 (5)
V(2)	−1252 (1)	1480 (1)	−1292 (1)	212 (6)	231 (6)	212 (6)	−20 (5)	−65 (5)	89 (6)
V(3)	−2644 (1)	331 (1)	−46 (1)	132 (5)	349 (7)	168 (5)	31 (5)	12 (6)	25 (7)
V(4A)	0	0	−2071 (1)	183 (14)	159 (14)	93 (10)	−1 (12)	0	0
V(4B)	−2252 (5)	−1859 (5)	−1 (5)	182 (28)	174 (28)	190 (29)	−52 (22)	−47 (36)	−34 (35)
OI	−952 (4)	110 (4)	−477 (3)	16 (2)	19 (2)	8 (2)	3 (2)	−2 (2)	2 (2)
OT(1)	−2099 (4)	−1798 (4)	−1926 (3)	20 (3)	19 (3)	23 (3)	−3 (2)	−7 (2)	−6 (2)
OT(2)	−1621 (4)	2266 (4)	−1918 (3)	28 (3)	21 (3)	19 (3)	−1 (2)	−6 (2)	10 (2)
OT(3)	−3864 (4)	440 (4)	93 (4)	21 (3)	27 (3)	23 (3)	4 (2)	−2 (2)	−3 (3)
OE(1)	−2714 (4)	−716 (4)	−789 (3)	20 (3)	24 (3)	20 (3)	−7 (2)	2 (2)	−9 (2)
OE(2)	−2486 (4)	1284 (4)	−805 (3)	14 (2)	23 (3)	23 (3)	9 (2)	0 (2)	1 (2)
OP(1)	−1235 (4)	−2124 (4)	−619 (3)	25 (3)	14 (2)	14 (2)	4 (2)	−1 (2)	2 (2)
OP(2)	−762 (4)	2352 (4)	−609 (3)	20 (2)	16 (2)	15 (2)	0 (2)	−2 (2)	−5 (2)
OP(C)	−141 (4)	−1246 (4)	−1630 (3)	17 (2)	18 (2)	17 (2)	−1 (2)	4 (2)	−2 (2)
OE(C)	−1480 (4)	171 (4)	−1821 (3)	34 (3)	23 (3)	8 (2)	−6 (2)	−6 (2)	1 (2)
OC(A)	0	0	−2983 (5)	38 (7)	88 (10)	44 (6)	−32 (7)	0	0
OC(B)	−3241 (9)	−2963 (12)	−61 (13)	69 (8)	172 (14)	107 (12)	−31 (8)	−9 (12)	18 (16)
C(1)	−4993 (8)	−1938 (9)	−1558 (6)	41 (6)	62 (7)	41 (6)	17 (5)	−1 (5)	−18 (5)
C(2)	1812 (11)	−5015 (7)	−1580 (7)	94 (10)	19 (4)	43 (7)	4 (5)	19 (7)	−3 (4)
N(1)	−4260 (8)	−2239 (10)	−1980 (7)	43 (6)	101 (9)	73 (8)	−9 (5)	22 (5)	−66 (7)
N(2)	−5996 (7)	−2232 (9)	−1634 (6)	24 (4)	87 (8)	62 (7)	−5 (4)	−4 (4)	−42 (6)
N(3)	−4777 (7)	−1288 (9)	−999 (6)	29 (4)	95 (8)	56 (6)	−9 (5)	1 (4)	−41 (6)
N(4)	2295 (9)	−4433 (7)	−2114 (6)	101 (9)	40 (5)	58 (6)	9 (5)	59 (6)	4 (5)
N(5)	1296 (10)	−4508 (8)	−1075 (6)	113 (9)	46 (6)	54 (6)	25 (6)	60 (7)	10 (5)
N(6)	1944 (10)	−5990 (8)	−1565 (6)	115 (10)	41 (6)	52 (7)	8 (6)	26 (7)	5 (5)
AQ(1)	−3639 (41)	−4983 (54)	−656 (26)	291 (65)	348 (80)	169 (44)	−92 (60)	−24 (43)	−50 (54)
AQ(2)	−4978 (74)	−4225 (40)	−508 (26)	366 (84)	353 (79)	240 (46)	98 (79)	−133 (76)	−39 (48)

[a] The parameters are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12} + ...)]$.

The former method established the structure of the polyanion in the solid state and the latter studied the structure and equilibrium in the solution under the preparative condition. Phosphorus-31 (heteroatom; $I = {}^1/_2$, 100%) and vanadium-51 (parent metal atom; $I = {}^7/_2$, 99.76%) are favorable nuclei for observation due to their natural abundance and high detection sensitivity.[5]

Experimental Section

Preparation of $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$. The guanidinium salt, which was easily obtained by the sodium salt metathesis, was well characterized[6] and the most suitable one for an X-ray study. In a typical preparation, 4.5 g of sodium metavanadate, $NaVO_3$ (37 mmol), was dissolved in 25 mL of hot water. To this vanadate solution was added with stirring 6.2 mL of 1.5 M H_3PO_4 at room temperature, and the pH value was adjusted to 3–2 by 3 M HNO_3. The resultant dark red solution was treated with an excess of an aqueous solution of guanidine hydrochloride (for example, 5.0 g) by gentle addition or by the diffusion method, which gave dark red distorted-octahedral crystals. This salt is insoluble in ethanol, nitromethane, acetonitrile, dioxane, and DMF and slightly soluble in water and Me_2SO.

All solutions having a starting V:P ratio >2 and <12 gave the same compound. When pH > 4, the yield of the guanidinium salt of decavanadate (orange yellow acicular crystal) increased. And the solution with pH <2 gave the lower yield of the desired compound.

Chemical Analyses. Vanadium was determined by two methods: ICP (inductively coupled argon Plasma Optical Emission Spectrography) and gravimetric determination using cupferron (the ammonium salt of nitrosylphenylhydroxylamine).[7] Phosphorus was determined by the ICP method. For the ICP method, a Jarrell-Ash Atomcomp MK II 975 instrument was used. The analyses of carbon, hydrogen, and nitrogen were carried out at the Analytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo. Anal. Calcd for $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$: C, 4.75; H, 3.14; N, 16.61; V, 35.2; P, 1.5. Found: C, 4.86; H, 3.28; N, 16.64; V, 35.3; P, 1.4.

Crystal Structure Determination of $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$. (a) Crystal Data and Intensity Measurements. Weissenberg photographs showed a tetragonal symmetry with Laue class $4/m$. Systematic extinctions ($h + k + l = 2n + 1$) indicated three possible space groups: the centrosymmetric $I4/m$ and the two noncentrosymmetric groups $I\bar{4}$ and $I4$. $I\bar{4}$ was chosen because the IR spectrum suggested the Keggin-like structure (which has a $\bar{4}$ axis) of the anion, which was confirmed by later success of the refinements. The lattice parameters were obtained from a least-squares refinement of the diffractometer angles of 14 strong reflections centered automatically on a four-circle diffractometer in the range $33° < 2\theta < 46°$; $a = 13.058$ (2), $c = 18.431$ (6) Å; $V = 3143$ (1) $Å^3$, $Z = 2$; d(calcd) = 2.14 g cm^{-3}, μ(Mo Kα) = 22.5 cm^{-1}. The c/a ratio was 1.412, which was very close to $2^{1/2}$. This suggested a pseudocubic packing of the anions.

The crystal selected for data collection had dimensions of 0.35 × 0.25 × 0.30 mm. A total of 3154 reflections ($2\theta \le 65°$) were recorded on a Rigaku automatic four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and the ω–2θ scan technique with a scan rate of 2° min^{-1}. Three reference reflections were monitored every 50 reflections and found to be constant.

---

(5) (a) Phosphorus-31 NMR study of heteropolyanions: Massart, R.; Contant, R.; Fruchart, J.-M.; Ciabrini, J.-P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916. Kazansky, L. P.; Chuvaev, V. R.; Spitsyn, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, *2*, 256. Levedeva, L. I.; Vanchikova, E. V. *Zh. Neorg. Khim.* **1974**, *19*, 3285. (b) Vanadium-51 NMR studies of the equilibrium in aqueous vanadate solution have proved that vanadium-51 NMR has been an excellent tool for the identification of the pH-dependent solute species: O'Donnell, S. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1976**, 2290. See also: Howarth, O. W.; Richards, R. E. *J. Chem. Soc.* **1965**, 864. Hatton, J. V.; Saito, Y.; Schneider, W. G. *Can. J. Chem.* **1965**, *43*, 47. Heath, E.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1981**, 1105. (c) Vanadium mixed molybdo- and tungstophosphate anions have aroused interest in view of the identification of the geometrical isomers with phosphorus-31 and vanadium-51 NMR: Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *J. Chem. Soc., Chem. Commun.* **1975**, 22. Pope, M. T.; Scully, T. F. *Inorg. Chem.* **1975**, *14*, 953. Pope, M. T.; O'Donnell, S. E.; Prados, R. A. *Adv. Chem. Ser.* **1976**, *No. 150*, 85. See also: Kazansky, L. P.; Spitsyn, V. K. *Dokl. Akad. Nauk SSSR* **1975**, *223*, 381. Kazansky, L. P.; Fedotov, M. A.; Ptushkina, M. N.; Spitsyn, V. I. *Ibid.* **1975**, *224*, 866. Maksimovskaya, R. I.; Fedotov, M. A.; Mastikhin, V. M.; Kuznetsova, L. I.; Matveev, K. I. *Ibid.* **1978**, *240*, 117.

(6) Other salts (sodium, potassium, ammonium, and tetraalkylammonium salts) were obtained only as powders or very efflorescent crystals and poorly characterized.

(7) Kolthoff, I. M., Elving, P. J., Eds. "Treatise on Analytical Chemistry"; Interscience: New York, 1963; Part II, Vol. 8, p 222.

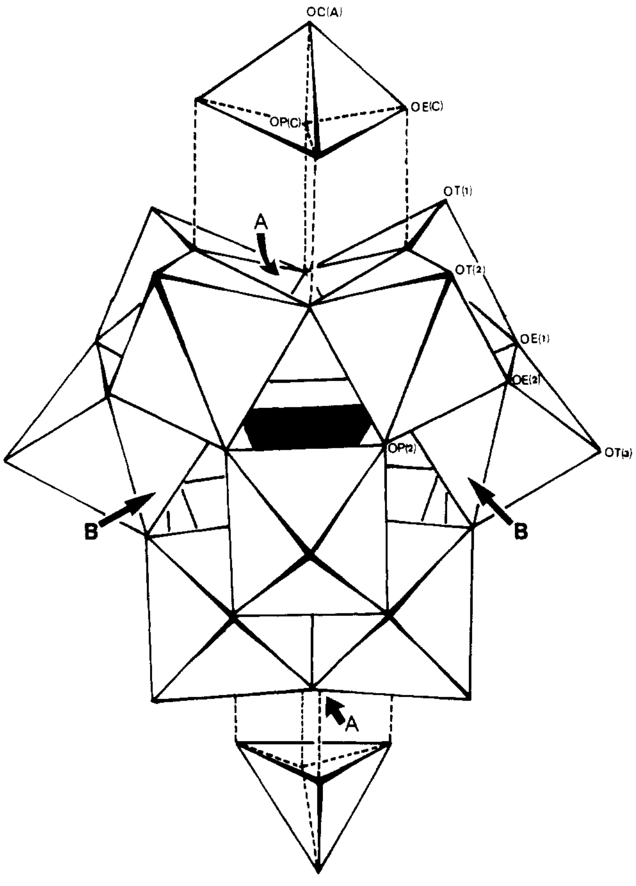


Figure 1. Polyhedral model of the $PV_{14}O_{42}^{9-}$ anion (idealized for clarity).

Background counts of 10 s were taken at each end of the scan. The intensities were corrected for Lorentz and polarization effects and not for absorption effects. For equivalent reflections a mean value was calculated and reflections with $|F_o| < 3\sigma$ were omitted, leaving 2257 independent reflections.

(b) Structure Solution and Refinement. P atoms were assigned to special positions at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$). The four unique V atoms were located by the solution of a Patterson map and the remaining nonhydrogen atoms from subsequent electron density Fourier syntheses. The structure was refined by the block-diagonal least-squares method, with use of anisotropic temperature factors for all the nonhydrogen atoms. Due to the disorder of the structure, the multipliers of the related atoms were treated with the full-matrix inversion in one of the final refinements.

All calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo, with use of standard programs.[8] Scattering factors were taken from ref 9, including $\Delta f'$ and $\Delta f''$. The agreement factors were defined by

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} \qquad R_w = \frac{\sum w||F_o| - |F_c||}{\sum w|F_o|}$$

The weighting scheme $w = 1/(\sigma^2 + 0.000625F^2)$ was employed. The final R and R_w values were 0.066 and 0.062, respectively. Atomic parameters with their estimated standard deviations are listed in Table I.

^{31}P and ^{51}V NMR. Unfortunately, the guanidinium salt of the 1:14 anion was not suitable for the NMR study because of the low solubility. Instead, the ammonium salt was used. This water-soluble salt, which was obtained as dark red octahedral efflorescent crystals,[10] is fairly stable and decomposes only slowly. The spectra were taken just after dissolving.

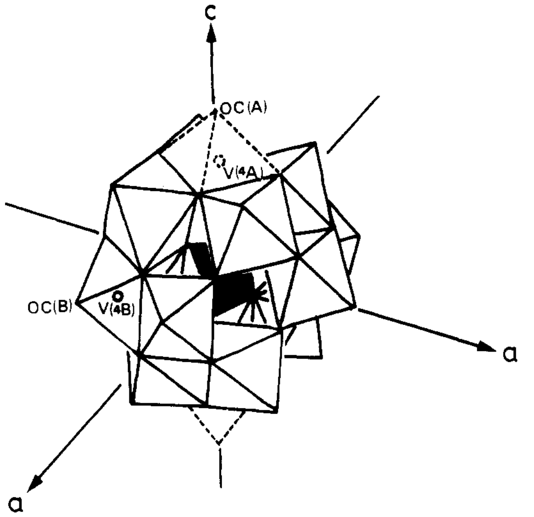


Figure 2. The overturned orientation of the anion. On the Keggin molecule there are two crystallographically independent sites A and B for the coordination of V atoms (see Figure 1). The occupancy of the capping V atoms (V(4A)) is 64 (1)%; instead, a Fourier map shows four symmetrically equivalent peaks at the B site with occupancy 18 (1)% for the V atom (named V(4B)) accompanied by another peak corresponding to the capping O atom (named OC(B)). This is interpreted as an indication of an "overturned" orientation of the anion with 36% probability in the crystal. Because there are two cases interrelated by the symmetry operation of $\bar{4}$ in the overturned orientation, the occupancy of V(4B) is 36/2 = 18%. Strictly speaking, the overturned orientation causes some displacement of the oxygen atoms, but this effect is small and does not appear on a Fourier map. It should be noted that since we are observing a weighted average structure, two independent VO_5 caps, which come from the orientational disorder, are not equivalent in size. Such site occupancies of V atoms can be explained only by the model having trans-located caps as an unique anion in the crystal and not by a cis configuration (capped at the A and B sites). Coexistence of trans and cis molecules is ruled out by NMR data.

The NaH_2PO_4–$NaVO_3$–H_2SO_4 aqueous solutions with various V:P ratios and pH values ($^1/_2 \leq$ V:P ≤ 14, $1 <$ pH < 6) were prepared by mixing 1 M NaH_2PO_4, 0.5 M (or 1.6 M) H_2SO_4, and 1 M $NaVO_3$ in this order at room temperature (1 M $NaVO_3$ solution was prepared by the reaction of V_2O_5 and $NaHCO_3$). The concentration of vanadium was 0.1–0.6 M. Serious change of the spectra was not observed within a month.

Vanadium-51 NMR spectra were obtained with a JEOL FX-90Q spectrometer (with a tunable probe) at 23.5 MHz with an internal deuterium lock. Samples were contained in 10-mm spinning-sample tubes with a sealed coaxial tube containing D_2O, which provided the lock signal. All spectra were obtained at approximately 25 °C and referenced externally to vanadium trichloride oxide (neat) by the sample replacement method, a spectral width of 20000 Hz being used. Free induction decay was obtained with use of a radio-frequency pulse

---

(8) The local versions of UNICS (Sakurai, 1967), ORTEP (Johnson, 1965), and LINUS (Coppens and Hamilton, 1970).

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

(10) The preparation was carried out as Preuss and Schug described.[4] Instead of their formulation $6(NH_4)_2O{\cdot}P_2O_5{\cdot}13V_2O_5{\cdot}aq$, i.e., 1:13 vanadophosphate, $(NH_4)_{6.5}H_{2.5}(PV_{14}O_{42}){\cdot}nH_2O$ was taken for this salt in the present work. It should be noted that IR and NMR (^{31}P and ^{51}V) spectra showed no structural difference between their two compounds reported as 1:13 and 1:14 vanadophosphates.
Weakly tried to determine the structure of this salt.[17] Crystal data: cubic, space group $F432$; a = 22.09 Å. The structure is based on a "KCl-like" array of Keggin molecules where each molecule differs from its six neighbors by a 90° rotation. Fourier and difference Fourier syntheses show six extra vanadium atoms per anion, lying on the diad axes——just where we have found them——each bonded to four Keggin oxygens and a terminal oxygen of its own. Refinement of the site occupancy factors implies an overall composition close to PV_{14}, in agreement with chemical analyses, which consistently give V:P ratios of ca. 14. Unfortunately, due to the disorder of the structure, his result was inconclusive.

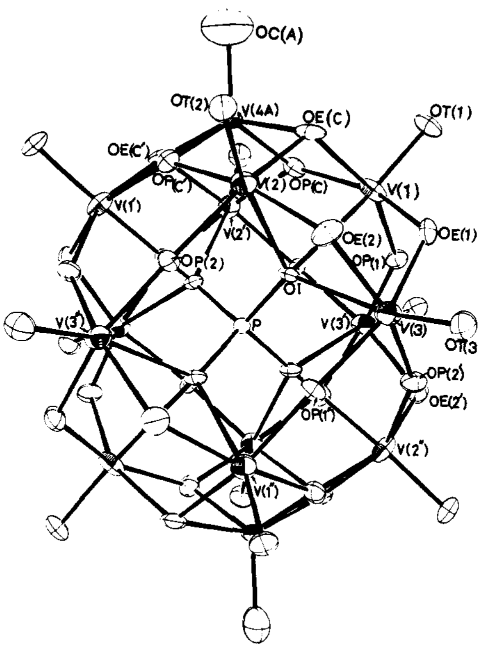


Figure 3. Structure of the $PV_{14}O_{42}^{9-}$ anion with labeling of the atoms.

of 25 μs (90° pulse) with a repetition time of 0.25 or 0.08 s. The data were accumulated as 8192 or 2048 data points in the time domain after a delay time of 50 μs.

Phosphorus-31 spectra were recorded in the pulse mode on a JEOL FX-60 spectrometer at 24.2 MHz using an internal deuterium lock. All spectra were obtained at approximately 25 °C and referenced externally to 85% H_3PO_4.

Phosphorus and vanadium chemical shifts to high field were calculated in parts per million as positive.

Results

Description of the Structure of $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$. The structure is built up from $PV_{14}O_{42}^{9-}$ anions (Figures 1 and 3), which are joined in a three-dimensional network by $(CN_3H_6)^+$ ions and water molecules. In the anion, the central PO_4 tetrahedron shares its oxygen atoms with four V_3O_{13} groups, each of which is made up of three edge-sharing VO_6 octahedra. These four V_3O_{13} groups are connected to each other by shared corners. This part is the well-known α-Keggin structure having T_d symmetry in an idealized form. There are two A sites and four B sites, which are "pits" on a Keggin molecule, for further coordination of vanadium atoms. The remaining VO units occupy two A sites through which a crystallographic $\bar{4}$ axis (*c* axis) is passing, forming trigonal-bipyramidal caps.

There is an orientational disorder of the anion (Figure 2).

The $PV_{14}O_{42}$ Group. Bond distances and angles within the anion are given in Table II. The metal–oxygen bonds in VO_6 octahedra are not equivalent. The variation of V–O bond lengths in VO_6 octahedra can be well correlated to the coordination number of oxygen atoms; the longest V–OI distances (ca. 2.36 Å) and the shortest V–OT distances (ca. 1.62 Å) are the typical case. All the V–O distances for 3-coordinated oxygen atoms (OE(C) and OP(C)) are longer than 1.92 Å, while those for 2-coordinated oxygen atoms (OE(1), OE(2), OP(1), and OP(2)) are between 1.81 and 1.94 Å.

The capping vanadium atom is bound to five oxygen atoms in a distorted trigonal-bipyramidal arrangement. The vanadium atom is in the same plane as the three equatorial oxygen atoms and the two apexes of the trigonal bipyramid are out of line with the vanadium atom (the OE(C)–V(4A)–OE(C') angle is 153.4°). The longer V(4A)–OE(C) distance shows the weakness of the V–O bond for the apical oxygen atoms.

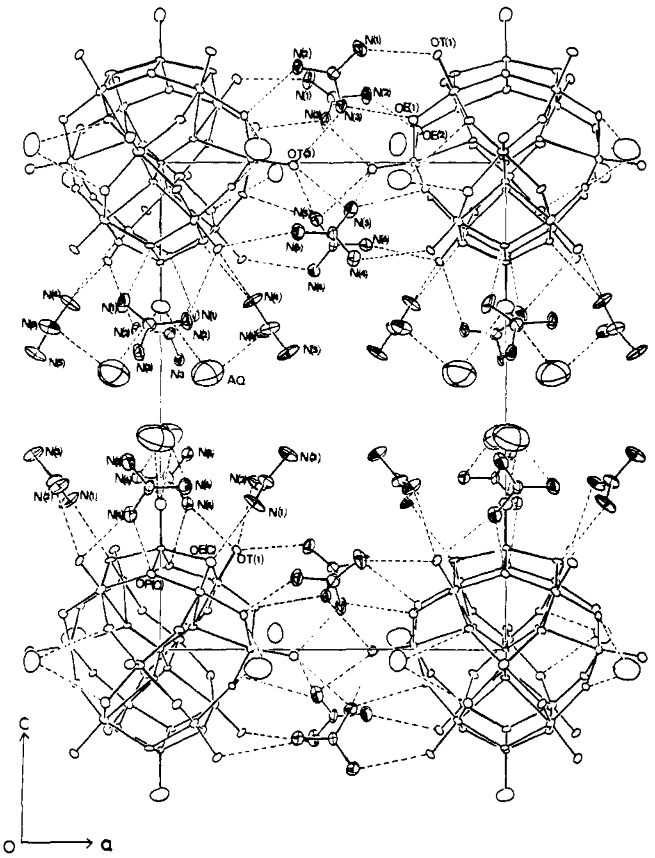


Figure 4. Hydrogen bonds (2.8–3.1 Å) in the structure projected along the *a* axis. For clarity the anion at the body center is omitted.

An oxygen framework of the anion approximately has point symmetry D_{2d} ($\bar{4}2m$). But a definite deviation of vanadium atoms from the ideal mirror plane lowers the point symmetry of the anion to *S*4 ($\bar{4}$).

Guanidinium Ion and Water Molecule. Water molecule AQ is disordered over two positions, 1 and 2, interrelated by ca. 90° rotation around the $\bar{4}$ axis with approximately equal occupancy.

The remaining three water molecules are found at the noncapped sites of the anion. The occupancies of OC(A) and OC(B) are 96 (3)% and 85 (3)%, respectively, indicating that OC(A) and OC(B) are the overlap of two capping O atoms and ca. three water molecules. Strictly speaking, the water molecule is distanced more apart from the anion than the capping O atom (compare V(4A)–OC(A) and V(4B)–OC(B) distances).

Figure 4 shows that the anions are connected through guanidinium cations and water molecules by hydrogen bonds, forming a three-dimensional network.

NMR Study. (a) 1:14 Vanadophosphate Anion in the Aqueous Solution. Phosphorus-31 and vanadium-51 NMR spectra of the aqueous solutions dissolving the ammonium salt of 1:14 vanadophosphate in (A) water and (B) CH_3COO-Na–HCl buffer (Figure 5) are well explained by the "bicapped Keggin" structure of the anion found in the crystal.

Phosphorus-31 NMR spectra show a single peak, which shifts downfield continuously as the pH value decreases.[11] Vanadium-51 NMR spectra show two broad peaks with a

---

(11) The phosphorus-31 NMR spectrum of $Na_7PV_{12}O_{36}$ (prepared by following the method of Souchay[3]) in H_2O was obtained by Massart et al. and Kazansky et al. They reported a single peak (−1, ca. 0 ppm, respectively).[5a] But they did not take notice of any pH dependence of the ^{31}P chemical shift. We believe that they were treating the sodium salt of the 1:14 anion.

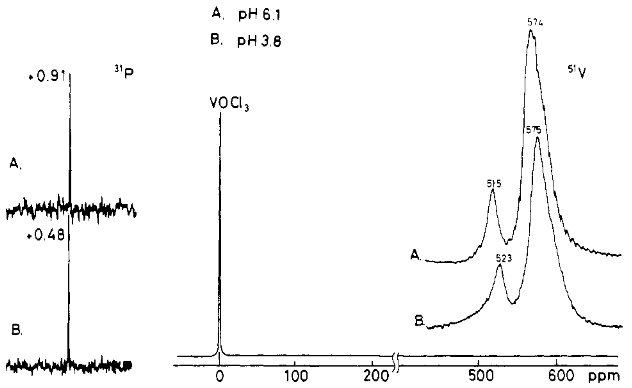


Figure 5. Phosphorus-31 and vanadium-51 NMR spectra of the ammonium salt of the 1:14 anion in the saturated aqueous solutions.

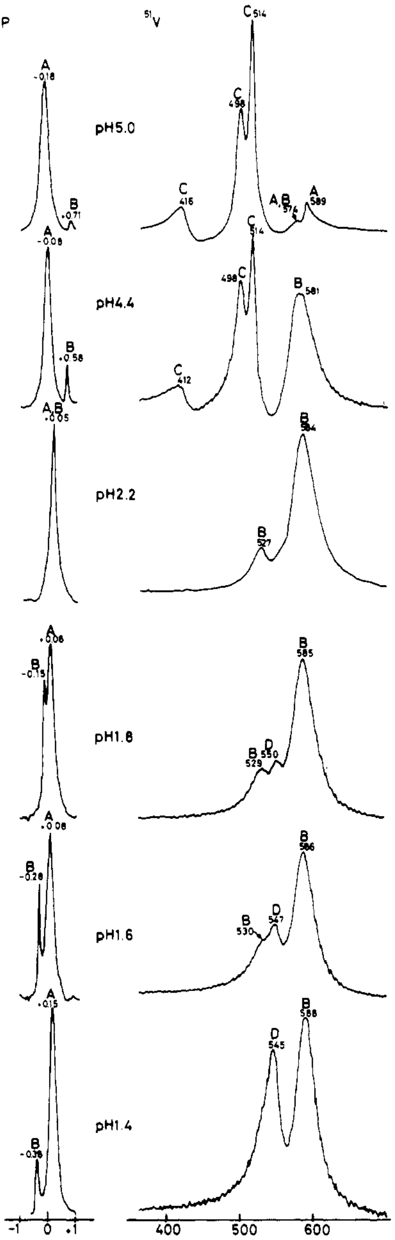


Figure 6. Phosphorus-31 and vanadium-51 NMR spectra of the NaH_2PO_4–$NaVO_3$–H_2SO_4 aqueous system (V:P 2:1) at room temperature. Peak assignment: ^{31}P (A) orthophosphate ion $H_nPO_4^{(3-n)-}$,[12] (B) 1:14 vanadophosphate anion $H_nPV_{14}O_{42}^{(9-n)-}$; ^{51}V (A) metavanadate ion $((VO_3)_x)^{x-}$ (the structure(s) in solution are still controversial[5b]), (B) 1:14 vanadophosphate anion, (C) decavanadate anion $H_nV_{10}O_{28}^{(6-n)-}$ [5b] (Figure 7), (D) vanadyl cation VO_2^+ (presumably a pseudooctahedral species $(VO_2(OH_2)_4)^+$) *cis*-dioxo structure.[5b]

relative intensity ratio of 2:12. The former one is assigned to the "capping" 5-coordinated vanadium, the latter one to the two nonequivalent 6-coordinated vanadiums in the Keggin unit (half-widths (Hz): 370, 670 at pH 6.1; 460, 770 at pH 3.8). Acidification of the solution causes the upfield shift and broadening of the two peaks but not the change of the intensity ratio or peak shape, indicating no serious structural change.

The pH-dependent behavior of ^{31}P and ^{51}V chemical shifts can be explained by the protonation of the 1:14 bicapped Keggin anion but not by the cis–trans isomerism of the 1:14 anion (figure caption for Figure 3) or by the coexistence of 1:12 noncapped or 1:13 monocapped Keggin anions, which are in fast chemical exchange with the 1:14 anion.

(b) NaH_2PO_4–$NaVO_3$–H_2SO_4 System. Figure 6 shows the phosphorus-31 and vanadium-51 NMR spectra of the V:P 2:1 solutions at six pH values between 5.0 and 1.4.

Phosphorus-31 NMR spectra consist of two pH-dependent signals corresponding to the orthophosphate ion and the 1:14 anion; the former is shifted upfield[12] and the latter downfield as the pH value decreases.

Vanadium-51 NMR spectra exhibit four groups of resonances, which have been assigned to the three oxovanadium ions——$((VO_3)_x)^{x-}$, $H_nV_{10}O_{28}^{(6-n)-}$, and VO_2^+——and the 1:14 bicapped Keggin anion $H_nPV_{14}O_{42}^{(9-n)-}$. The ^{51}V chemical shift values of the three oxovanadium ions agree with those in the results of Pope and O'Donnell.[5b]

These spectra give the following comprehensive picture of the solute species in the V:P 2:1 solution; at pH 5.0, the decavanadate anion and the orthophosphate anion are dominant. Acidification of the solution from pH 5.0 to 4.4 promotes the formation of the 1:14 anion. In the region of pH 2–3, almost all the vanadium ions form $H_nPV_{14}O_{42}^{(9-n)-}$ anions. Further acidification causes the decomposition of the 1:14 anion to the orthophosphate ion and the vanadyl cation.

The variation of the V:P ratio does not cause serious change of the solution equilibrium.

Although high V:P ratio and high acidity increase the yield of $V_2O_5{\cdot}xH_2O$ obtained as a sluggish dark brown precipitate,[13] phosphorus-31 NMR spectra of the liquid phase do not differ from those in the case of the V:P 2:1 system.

Low V:P ratio and high acidity prevent the formation of the 1:14 vanadophosphate anion (the orthophosphate ion and the vanadyl cation are dominant). This explains the color of the solution with low V:P ratio; in the V:P 1:2 system, the acidification of the solution changes its color from dark red to light orange.

Phosphorus-31 and vanadium-51 NMR spectra do not suggest the existence of any vanadophosphate anions other than 1:14 bicapped Keggin anions in the solution.

Discussion

X-ray structure analysis has established the new structural type of the polyanions, a "bicapped Keggin" structure. The Keggin structure with the capping 5-coordinated metal atoms has not been previously observed in the structures of heteropolyanions of molybdenum and tungsten.[14] This might come

---

(12) Crutchfield, M.; Callis, C.; Irani, R.; Roth, G. *Inorg. Chem.* **1962**, *1*, 813. Jones, R. A. Y.; Katritzky, A. R. *J. Inorg. Nucl. Chem.* **1960**, *15*, 193.

(13) Pletnev, R. N.; Ivakin, A. A.; Gorshkov, V. V.; Chirkov, A. K. *Dokl. Akad. Nauk SSSR* **1975**, *224*, 106. Ivakin, A. A.; Yatsenko, A. P.; Volkov, V. L. *Tr. Inst. Khim. Ural. Nauchn. Tsentr, Akad. Nauk SSSR* **1975**, *32*, 18. Fedorov, P. I.; Akulkina, L. M.; Razgon, E. S. *Zh. Neorg. Khim.* **1967**, *12*, 195.

Table II. Bond Lengths (Å) and Angles (Deg) within the $PV_{14}O_{42}$ Group

VO_6 Octahedra in Keggin Cage

	OI	OE(1)	OP(1)	OP(C)	OE(C)	OT(1)
V(1)-	2.350 (5)	1.831 (5)	1.891 (5)	1.981 (5)	1.922 (6)	1.608 (6)
OI-V(1)-		75.9 (2)	87.5 (2)	85.9 (2)	73.3 (2)	171.6 (2)

	OI	OE(2)	OP(2)	OP(C′)	OE(C)	OT(2)
V(2)-	2.368 (5)	1.862 (5)	1.813 (5)	1.947 (5)	1.990 (6)	1.618 (6)
OI-V(2)-		74.6 (2)	88.6 (2)	86.0 (2)	71.8 (2)	168.8 (3)

	OI	OE(1)	OE(2)	OP(1′)	OP(2′)	OT(3)
V(3)-	2.366 (5)	1.937 (6)	1.884 (6)	1.832 (5)	1.908 (5)	1.619 (5)
OI-V(3)-		73.8 (2)	74.3 (2)	87.5 (2)	86.2 (2)	169.2 (2)

Metal-Metal and Heteroatom-Metal Groups

	V(1)	V(2)	V(3)	V(4A)	V(4B)
P-	3.483 (1)	3.475 (1)	3.481 (1)	3.817 (2)	3.813 (6)
V(1)-		3.402 (2)	3.291 (2)	2.886 (2)	2.741 (9)
V(2)-			3.290 (2)	2.910 (2)	...
V(3)-				...	2.906 (6)

Corner Shared

V(1)-V(2′)	3.731 (2)	V(3)-V(2″)	3.558 (2)
V(3)-V(1″)	3.593 (2)		

Bridging Oxygen

V(1)-OE(1)-V(3)	121.7 (3)	V(1)-OE(C)-V(2)	120.8 (3)
V(2)-OE(2)-V(3)	122.9 (3)	V(1)-OP(C)-V(4A)	98.4 (2)
V(1)-OP(1)-V(3′)	149.6 (3)	V(1)-OE(C)-V(4A)	94.8 (3)
V(2)-OP(2)-V(3″)	146.0 (3)	V(2)-OE(C)-V(4A)	93.7 (2)
V(1)-OP(C)-V(2′)	143.6 (3)		

Capping VO_5 Unit

	OC(A)	OP(C)	OE(C)
V(4A)-	1.681 (10)	1.829 (5)	1.999 (6)
OC(A)-		2.984 (10)	2.893 (9)
OC(A)-V(4A)-		116.4 (4)	103.3 (4)
OP(C)-V(4A)-OP(C′)	127.2 (3)	OE(C)-V(4A)-OE(C′)	157.4 (3)

	OC(B)	OP(1)	OP(2′)	OE(1)	OE(2′)
V(4B)-	1.939 (15)	1.783 (10)	1.827 (9)	2.168 (10)	2.116 (10)
OC(B)-		3.020 (15)	3.338 (17)	3.299 (18)	3.076 (17)
OC(B)-V(4B)-		108.4 (6)	124.8 (6)	106.8 (6)	98.6 (5)
OP(1)-V(4B)-OP(2′)		126.8 (4)	OE(1)-V(4B)-OE(2′)		154.6 (4)

PO_4 Tetrahedron

P-OI	1.529 (5)	OI-OI	2.502 (9), 2.494 (10)

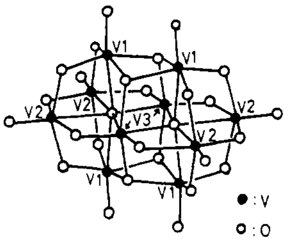


Figure 7. Structure of the decavanadate anion.

from the following reasons. (1) A high negative charge would prevent the formation of a normal Keggin anion $PV_{12}O_{40}^{15-}$ whereas the bicapped Keggin anion $PV_{14}O_{42}^{9-}$ is stabilized by the two capping VO^{3+} units. (2) The vanadium atom has the capability to take 5-coordination.

Several vanadium-containing molybdo- and tungstophosphate anions with the Keggin structure have been characterized.[15] It should be noted that these anions have a low V:M (M = Mo, W) ratio (V:M ≤ 6). The heteropolyanions with higher V:M ratios would be interesting cases in view of the conversion process from the noncapped to bicapped Keggin structure.

The NMR study has shown that the bicapped Keggin structure found in the crystal has been kept in the aqueous solution[16] and has ruled out the possibility of other capped Keggin ions (1:12 noncapped and 1:13 monocapped Keggin anions) in the aqueous $H^+-PO_4^{3-}-VO_3^-$ system. The important factor for the formation of the 1:14 bicapped Keggin anion is the pH value of the solution——the preparative and NMR studies show that the suitable pH value is 2–3——rather than

---

(14) Recently we have obtained a potassium salt of heteropolyvanadate containing arsenic as a heteroatom and determined its structure. This salt was obtained from the mixture of potassium metavanadate and arsenic acid (V:As ≈ 4, pH 2–3) as dark red cubic crystals. Anal. Calcd for $K_{4.5}H_{4.5}(AsV_{14}O_{42})\cdot 16H_2O$: K, 9.1; As, 3.9; V, 36.9. Found: K, 9.3; As, 4.1; V, 36.7. Crystal data: cubic, space group $P\bar{4}3m$; a = 10.728 (1) Å; V = 1234.9 (2) $Å^3$; Z = 1; d(calcd) = 2.60 g cm^{-3}; μ(Mo Kα) = 38.8 cm^{-1}. In spite of the fact that it has a highly disordered structure, it has been revealed that the anion also has a bicapped Keggin structure. But the larger size of the central AsO_4 tetrahedron (P–OI 1.529 (5) Å, As–OI 1.646 (11) Å) and the limited size of the surrounding V–O framework indicate structural instability. In fact, an aqueous solution of this salt changed its color from dark red to light yellow slowly. The vanadium-51 NMR spectrum showed that the anion entirely decomposed to decavanadate anion and (maybe) arsenate anion.

(15) Tsigdinos, G. A.; Hallada, C. J. *Inorg. Chem.* **1968**, *7*, 437. Smith, D. P.; Pope, M. T. *Ibid.* **1973**, *12*, 331.

(16) Very recently we have found that the phosphorus-31 NMR spectrum of the ammonium salt of the 1:14 anion in the mixture of dioxane and 1.7 M H_2SO_4 (6:1 v/v) shows two peaks at −3.13 and −1.71 ppm, which indicates the conversion of the 1:14 anion.

(17) Weakly, T. J. R., private communication, 1980.

the starting V:P ratio. As Preuss and Schug mentioned,[4] high temperature seems to promote the decomposition of the heteropolyvanadate anion.

Acknowledgment. We are grateful to Professor Yasukazu Saito, Mr. Hiroshi Moriyama, and Mr. Toshiya Aoki for help with ^{31}P and ^{51}V NMR measurements.

Registry No. $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$, 79482-68-1; $NaVO_3$, 13718-26-8; H_3PO_4, 7664-38-2.

Supplementary Material Available: The IR spectrum of $(CN_3H_6)_8H(PV_{14}O_{42})\cdot 7H_2O$, phosphorus-31 NMR spectra of the NaH_2PO_4–$NaVO_3$–H_2SO_4 aqueous system (V:P = $^1/_2$, 8, and 14), and a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, The University of Alberta,
Edmonton, Alberta, Canada T6G 2G2

Acetylene Activation in Binuclear Rhodium Complexes and the Structure of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(Ph_2PCH_2PPh_2)_2]$: A Complex Containing a Bridging Acetylene and a Ketonic Carbonyl Ligand

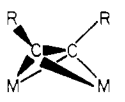
MARTIN COWIE* and TIMOTHY G. SOUTHERN

Received May 29, 1981

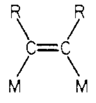
trans-[RhCl(CO)(DPM)]$_2$ and $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ react with DMA and HFB (DMA = $CH_3O_2CC_2CO_2CH_3$; HFB = $CF_3C_2CF_3$; DPM = $Ph_2PCH_2PPh_2$), yielding the complexes $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-acetylene})(DPM)_2]$. The bromo and iodo derivatives have also been prepared from $[Rh_2Br(CO)(\mu\text{-}CO)(DPM)_2][Br]$, $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$, $[Rh_2I(CO)(\mu\text{-}CO)(DPM)_2][I]$, and $[Rh_2I_2(\mu\text{-}CO)(DPM)_2]$. One member of this series, $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-DMA})(DPM)_2]$, has been structurally characterized by X-ray crystallography. This complex crystallizes in the space group $P4_12_12$ with a = 15.021 (2) Å, c = 25.738 (5) Å, and Z = 4. On the basis of 4566 unique observed reflections, the structure has been refined to R = 0.049 and R_w = 0.066. The molecule contains an acetylene ligand bound to both metals as a cis-dimetalated olefin, a bridging ketonic carbonyl ligand, and no metal–metal bond. All parameters about the acetylenic carbon atoms suggest sp^2 hybridization of these atoms. Similarly, the Rh–CO–Rh angle (116.0 (4)°) and the large metal–metal separation (3.3542 (9) Å) suggest that the carbonyl carbon atom is also sp^2 hybridized and bound to the metals by two localized electron-pair bonds. The ^{13}C NMR chemical shifts for these carbonyl carbons are at unusually high field compared to those for conventional carbonyl ligands, being more comparable to the values observed for organic carbonyl groups. The complex $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ catalyzes the cyclotrimerization of DMA but not its hydrogenation. In contrast, $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ catalyzes the hydrogenation of phenylacetylene to styrene but does not bring about its cyclotrimerization.

Introduction

As part of our continuing interest in binuclear complexes and their reactions with small molecules,[1-6] we undertook an investigation into the chemistry of several binuclear rhodium complexes with acetylene molecules. Of initial concern to us were the mode of acetylene binding and its relationship to the subsequent chemistry displayed by the acetylene molecule. In binuclear complexes, two acetylene bonding modes are most commonly observed: the tetrahedral μ_2-η^2 geometry (A) in



A



B

which the acetylene molecule sits perpendicular to the metal–metal axis[7-18] and the cis-dimetalated olefinic geometry (B) in which the acetylene molecule lies parallel to the metal–metal axis.[19-22]

It is anticipated that these acetylene coordination modes will give rise to different reactivity patterns. Not only are the steric environments of these groups different, but their electronic environments also differ significantly. In mode A each acetylenic carbon atom is bound to both metals whereas in structure B each carbon is bound to only one metal. Therefore, the acetylene in A functions as a two-electron donor to each metal whereas in B it donates one electron to each metal. As a corollary of this, complexes having the same metal and ancillary ligands but differing in the acetylene coordination mode (A or B) will differ with respect to metal–metal interactions. For example, if there is no metal–metal bond in A, there will be one in B (and vice versa).

---

(1) (a) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. (b) Cowie, M. *Inorg. Chem.* **1979**, *18*, 286.
(2) (a) Cowie, M.; Dwight, S. K.; Sanger, A. R. *Inorg. Chim. Acta* **1978**, *31*, L407. (b) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 209.
(3) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.
(4) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.
(5) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2508.
(6) (a) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1980**, *198*, C20. (b) Cowie, M.; Dwight, S. K. *Ibid.* **1981**, *214*, 233.
(7) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090.
(8) Day, V. W.; Abdel-Meguid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 8289.
(9) Bailey, W. I., Jr.; Collins, D. M.; Cotton, F. A., reported in ref 7.
(10) Bailey, W. I., Jr.; Cotton, F. A.; Jamerson, J. D.; Kolb, J. R. *J. Organomet. Chem.* **1976**, *121*, C23.
(11) Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774.
(12) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18.
(13) Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* **1976**, *15*, 97.
(14) Wang, Y.; Coppens, P. *Inorg. Chem.* **1976**, *15*, 1122.
(15) Mills, O. S.; Shaw, B. W. *J. Organomet. Chem.* **1968**, *11*, 595.
(16) Ban, E.; Cheng, P.-T.; Jack, T.; Nyburg, S. C.; Powell, J. *J. Chem. Soc., Chem. Commun.* **1973**, 368.
(17) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Stone, F. G. A.; Thomas, M. D. O.; Vincente, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 930.
(18) Dickson, R. S.; Pain, G. N.; Mackay, M. F. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2321.
(19) Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A. *J. Organomet. Chem.* **1972**, *46*, C47.
(20) Dickson, R. S.; Johnson, S. H.; Kirsch, H. P.; Lloyd, D. J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2057.
(21) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *177*, C22.
(22) Koie, Y.; Shinoda, S.; Saito, Y.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1980**, *19*, 770.

0020-1669/82/1321-0246$01.25/0