"$ReCl_3 \cdot B$," where B = 2,5-DTH, 2,2′-bipyridyl, or 1,10-phenanthroline, as described by Colton, *et al.*[11] Not only were we unable to repeat the preparative details (see Experimental Section), but the products isolated were not of this stoichiometry. Thus, although prolonged reaction of rhenium(III) chloride with 2,5-DTH *sometimes* yields a product of composition approaching $Re_3Cl_9(DTH)_3$, usually less than three molecules of ligand were coordinated. Also the assertion[11] that "$ReCl_3 \cdot B$" are five-coordinate is clearly incorrect. Their visible spectra are consistent in all cases with a trimeric species.

CONTRIBUTION FROM THE U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C., AND THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND

The Crystal Structures of Potassium and Cesium Trivanadates[1]

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Potassium and cesium trivanadates are monoclinic and isomorphous, space group $P2_1/m$, with the following dimensions ($Z = 2$): KV_3O_8, $a = 7.640$ A, $b = 8.380$ A, $c = 4.979$ A, $\beta = 96° 57'$; CsV_3O_8, $a = 8.176$ A, $b = 8.519$ A, $c = 4.988$ A, $\beta = 95° 32'$. The crystal structure of KV_3O_8 has been determined from *hk*0, 0*kl*, and *h*0*l* Weissenberg data with an *R* factor of 0.15. The structure of CsV_3O_8 has been refined with 1273 *hkl* Weissenberg data to an *R* factor of 0.089. The structures consist of corrugated sheets based on a linkage of distorted VO_6 octahedra. Two of the vanadium atoms lie in double, square-pyramid groups V_2O_8, which are linked through opposite basal corners into chains along the *b* axis. The chains are joined laterally along the *c* axis into sheets by the third vanadium atom in VO groups, also forming part of a square-pyramid coordination. Various aspects of these structures are compared with other known oxovanadate structures.

Introduction

A study of the crystal chemistry of vanadium in relation to the geochemistry of vanadium and uranium in the Colorado Plateau region has been carried on at the Geological Survey over the past decade. Several synthetic compounds have been analyzed by X-ray diffraction methods in order to learn more about the unusual coordination behavior of vanadium, especially in the higher valence states. Vanadium is deposited in the Colorado Plateau sandstones as lower valence oxides (for example, montroseite, VO(OH)), but under the influence of weathering conditions it is rapidly oxidized to the pentavalent state.[3] In this state readily soluble vanadates are formed, and many corresponding minerals have been found. Examples are the calcium metavanadate hydrate rossite, $Ca(VO_3)_2 \cdot 4H_2O$, the hexavanadate hewettite, $CaV_6O_{16} \cdot 9H_2O$, and the decavanadate pascoite, $Ca_3V_{10}O_{28} \cdot 17H_2O$. Alkali vanadate solutions also readily crystallize such compounds, but the natural products almost always contain an alkaline earth cation. Moderately acid potassium vanadate solutions produce crystals of decavanadates and hexavanadates but these are often accompanied, especially from warm solutions, by a light orange, crystalline phase of low solubility, potassium trivanadate KV_3O_8.[4] This seems to be a very stable phase but has not yet been found in nature.

As part of the general crystal chemical study the structure of KV_3O_8 was analyzed some time ago by Block.[5,6] Subsequently, considerably better data were obtained for the isomorphous compound cesium trivanadate CsV_3O_8, so that a more accurate description of the structure can now be presented. The present paper describes the study of both of these compounds.

Trivanadates and Vanadate Solutions

The complex behavior of vanadate solutions with respect to changes in pH has long been the subject of study by inorganic chemists, frequently with contradictory and inconclusive results. Jander and Jahr,[7] by means of diffusion-rate studies, were the first to delineate clearly the progressive condensation of vanadate anions into higher and higher molecular weight polyanions as the pH is lowered. More recently, careful studies by emf methods have been reported for sodium vanadate solutions over the pH range 7–10 by Brito and Ingri[8] and by Ingri and Brito,[9] and in the pH range 1–6.5 by Rossotti and Rossotti.[10] These authors have given reviews of previous work on these systems and no attempt will be made to give a comprehensive summary here.

According to Rossotti and Rossotti,[10] the main

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] (a) U. S. Geological Survey. (b) Johns Hopkins University; present address National Bureau of Standards, Washington, D. C.

[3] H. T. Evans, Jr., and R. M. Garrels, *Geochim. Cosmochim. Acta*, **15**, 131 (1958).

[4] For compounds with the O:V ratio <3, the names trivanadate, pentavanadate, hexavanadate, etc., are assigned arbitrarily according to the simplest formulation, except where a definite polyion is involved, such as decavanadate.

[5] S. Block, "Program and Abstracts of Pittsburgh Diffraction Conference and the American Crystallographic Association, Nov 3–5, 1954," p 15; Ph.D. Thesis, The Johns Hopkins University, Baltimore, Md., 1955.

[6] S. Block, *Nature*, **186**, 540 (1960). In Table 1 of this paper, *x* for O_4 is incorrectly given as 0.518 and should be 0.158.

[7] G. Jander and K. F. Jahr, *Z. Anorg. Allgem. Chem.*, **212**, 1 (1933).

[8] F. Brito and N. Ingri, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B56**, 165 (1960).

[9] N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).

[10] F. J. C. Rossotti and H. Rossotti, *ibid.*, **10**, 957 (1956).

vanadium components of sodium solutions in the pH range 2–6.5 are the decavanadates $V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$, and $H_2V_{10}O_{28}^{4-}$. These are bright orange in color and readily form well-crystallized, very soluble salts with various cations. The structure of the polyanion $V_{10}O_{28}^{6-}$ has only recently been determined through crystal structure analyses of $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$ and $Ca_3V_{10}O_{28}\cdot 17H_2O$.[11] Nevertheless, the equilibrium studies do not take into account certain less soluble solid phases which appear from the orange solutions containing cations other than sodium, especially when they are warmed. Potassium metavanadate KVO_3 can be dissolved in water and converted to the decavanadate by adding an appropriate amount of acid

$$10KVO_3 + 4H^+ \longrightarrow V_{10}O_{28}^{6-} + 10K^+ + 2H_2O$$

When less than this amount of acid is added and the solution is warmed to about 40°, dark red crystals of tripotassium pentavanadate $K_3V_5O_{14}$ occasionally appear. This material has no structural relationship to the decavanadate complex but has an unusual sheet structure.[12] When 0.4 equiv of acid has been added, the pentavanadate no longer appears, but light orange potassium trivanadate KV_3O_8 is precipitated at temperatures above 50–60°. This compound appears together with colorless KVO_3 at pH values near to neutrality (∼6) and also together with the pentavanadate when it is formed so that it is difficult to obtain the latter pure. The trivanadate is readily obtained pure at pH values below 5, where it appears to replace the more soluble decavanadate salts that may have crystallized previously. Even at room temperature, an orange decavanadate solution on standing for several weeks becomes nearly colorless, depositing small, platy, light orange crystals of the trivanadate. The compound is evidently formed by reaction of decavanadate with acid

$$10K^+ + 3V_{10}O_{28}^{6-} + 8H^+ \rightleftharpoons 10KV_3O_8 + 4H_2O$$

The reaction is very slow at room temperature but above 60° swings rapidly to the right. Thus, it has been suggested by Evans[13] that decavanadate solutions at room temperature are actually metastable in the presence of potassium and that the solid KV_3O_8 is the most stable phase in this system.

Potassium trivanadate KV_3O_8 was first prepared and described by Norblad[14] as forming a crust of brilliant orange crystals nearly insoluble in water. He also described $NH_4V_3O_8$ as forming golden yellow plates. These compounds have been rarely referred to in the literature since then until Kelmers[15,16] reported a detailed study of them in 1961. Kelmers found[16] that $NH_4V_3O_8$, KV_3O_8, RbV_3O_8, and CsV_3O_8 are all probably isostructural with the monoclinic KV_3O_8 as described by Block[5,6] and are all formed in a similar manner and have similar properties. Kelmers further found[15] that $NH_4V_3O_8$ is the stable phase with respect to the many other soluble, orange ammonium vanadates formed from the acidified solutions, analogous to Evans' observations[13] concerning KV_3O_8. Kelmers[16] was unable to synthesize analogous compounds of lithium and sodium from water solutions. Also, although Kelmers[17] found $K_3V_5O_{14}$ in the anhydrous system K_2O–V_2O_5, neither he nor Holtzberg, *et al.*,[18] nor Illavionov, *et al.*,[19] found KV_3O_8 at the temperatures studied (∼500–900°).

The isostructural phases γ-NaV_3O_8 and γ-$Li_{1+x}V_3O_8$ (x = 0–0.5) were prepared by Flood, *et al.*,[20] by slowly cooling melts of Li_2CO_3 and V_2O_5. Their structure as determined by Wadsley[21] is entirely different from that found for KV_3O_8 and CsV_3O_8 as described in this paper.

Experimental Section

Preparation and Characterization.—Crystals of KV_3O_8 and CsV_3O_8 were prepared by acidification of the corresponding metavanadate solutions at temperatures of about 60–80°, as described by Kelmers.[16] Optical data were determined with the polarizing microscope, and crystal morphology was studied on the two-circle goniometer. Densities were estimated by flotation and by means of the Berman balance. No piezoelectric response was found in either case on the Giebe–Scheibe apparatus. Debye–Scherrer X-ray diffraction patterns were in agreement with data reported by Kelmers.[16] Hägg–Guinier focused patterns were prepared at the Department of Chemistry of the Royal Institute of Technology in Stockholm, and these patterns provided 2θ data that were used to refine the unit cell parameters by a least-squares procedure (Table I).

TABLE I

CRYSTALLOGRAPHIC DATA FOR THE ALKALI TRIVANADATES[a]

	KV_3O_8[b]	CsV_2O_8[b]	$NH_4V_3O_8$[c]	RbV_3O_8[c]
Space group	$P2_1/m$	$P2_1/m$		
a, A	7.640 ± 2	8.176 ± 5	7.881 ± 4	7.859 ± 5
b, A	8.380 ± 3	8.519 ± 4	8.423 ± 6	8.439 ± 7
c, A	4.979 ± 2	4.988 ± 2	5.005 ± 5	4.972 ± 6
β	96° 57 ± 2′	95° 32 ± 3′	96° 28 ± 3′	96° 5 ± 3′
V, A^3	316.5 ± 1	345.8 ± 2	330.1 ± 3	327.9 ± 4
d(measd), g/cm³	3.33 ± 3	3.91 ± 7		
d(obsd), g/cm³	3.356	3.973		

[a] Estimated standard errors derived from least-squares analysis of indexed X-ray powder diffraction data are given in terms of the last significant figure. [b] Based on powder data measured from Hägg–Guinier patterns with KCl used as internal standard; Cu Kα radiation. [c] Based on powder data taken from Kelmers.[16]

Measurement of Diffraction Data.—The initial unit cells were determined from Buerger precession patterns. Diffraction intensities were measured by visual estimate from multiple-film Weissenberg patterns made with Cu Kα and Mo Kα radiation for KV_3O_8, giving 114 independent $h0l$ data, 68 $hk0$ data, and 54 $0kl$ data. The much better quality of the CsV_3O_8 crystals allowed the measurement of a complete set of three-dimensional data for this crystal, using hnl levels of multiple-film Weissenberg photographs made with Mo Kα radiation, for n = 0–11, inclusive. Thus, 1278 independent data were obtained, representing all reflections for which $(\sin\theta)/\lambda < 0.7$, of which 723

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TABLE II

*hk*0, 0*kl*, AND *h*0*l* STRUCTURE FACTORS FOR KV_3O_8 AND CsV_3O_8[a]

	KV_3O_8		CsV_3O_8	
hkl	F(obs)	F(cal)	F(obs)	F(cal)
1 0 0	54	-59	11.8	-13.5
2 0 0	32	-26	28.3	33.0
3 0 0	27	18	69.7	66.4
4 0 0	27	24	24.1	29.0
5 0 0	43	40	38.8	-44.5
6 0 0	15	-9		-0.3
7 0 0	29	32	25.7	-16.9
8 0 0	44	-37	79.5	-76.2
9 0 0		-6	14.0	-10.3
10 0 0		11	30.1	-22.1
11 0 0			35.3	-35.6
12 0 0				15.0
0 0 1	26	-25	36.1	38.1
1 0 1	30	25	95.0	103.4
2 0 1	71	82	132.0	129.4
3 0 1	51	-54		3.6
4 0 1	48	45	94.7	93.7
5 0 1	48	45	18.6	21.2
6 0 1	65	-59	66.8	-73.2
7 0 1		-6	20.6	21.7
8 0 1		6	26.5	-24.3
9 0 1		-6	40.5	-38.8
10 0 1	28	-25	29.8	-27.5
11 0 1				5.0
-1 0 1	10	-8	41.7	46.1
-2 0 1	80	79	125.5	116.8
-3 0 1	55	60	12.9	16.0
-4 0 1		-12	52.6	-63.3
-5 0 1	50	57	28.0	25.8
-6 0 1	58	-59	102.9	-101.2
-7 0 1		-7	23.8	-22.4
-8 0 1		5	28.2	-22.7
-9 0 1		-6	39.6	-38.4
-10 0 1	27	17	30.0	-29.0
-11 0 1				4.5
-12 0 1				-8.0
0 0 2	69	80	146.1	128.4
1 0 2		5	34.8	43.8
2 0 2	37	41	51.4	51.7
3 0 2	18	17	52.6	51.8
4 0 2	25	-18	24.1	29.6
5 0 2		-8	35.1	35.6
6 0 2	28	22	33.8	34.4
7 0 2		6	18.3	-19.4
8 0 2	61	-43	27.8	-27.7
9 0 2	43	34		18.3
10 0 2			63.9	-58.6
11 0 2			14.4	-6.0
-1 0 2	18	18	40.2	41.7
-2 0 2	85	-102	119.5	-98.3
-3 0 2	18	17	70.3	64.0
-4 0 2		-12	41.8	-44.9
-5 0 2	28	-27	64.4	-59.7
-6 0 2	33	-27	49.5	-48.9
-7 0 2	37	39		-2.5
-8 0 2	35	-22	81.9	-78.5
-9 0 2	46	-40	20.2	-22.3
-10 0 2	45	31	18.1	23.3
-11 0 2			23.1	-29.6
-12 0 2				9.4
0 0 3		-16		7.7
1 0 3	28	30	66.0	65.0
2 0 3	28	30	48.6	54.3
3 0 3	43	-51		4.6
4 0 3	62	72	129.5	127.6
5 0 3		4		-5.2
6 0 3		-15	15.5	13.5
7 0 3		4	19.7	22.2
8 0 3		3		-2.9
9 0 3		-14		-20.3
10 0 3				-0.9
-1 0 3	22	-18	22.8	-22.5
-2 0 3	47	49	39.2	38.7
-3 0 3	15	16	17.3	-19.5
-4 0 3	69	-73	122.0	-109.7
-5 0 3		8	11.5	-11.4
-6 0 3	27	12	31.7	-31.7
-7 0 3	47	-49	73.9	-70.9
-8 0 3	22	15		10.8
-9 0 3		7	17.7	-17.1
-10 0 3		4		-10.0
-11 0 3				-3.5
0 0 4	25	-20	29.5	-29.9
1 0 4		-18	16.3	16.0
2 0 4	53	58	87.2	76.0
3 0 4		15	14.7	14.3
4 0 4	18	-16	14.1	15.0
5 0 4		-12	45.7	47.7
6 0 4	55	44	57.2	48.3
7 0 4	35	-22	17.9	-24.1
8 0 4			26.9	29.2
9 0 4				9.2
-1 0 4	47	47	36.1	33.4
-2 0 4	53	-51	82.4	-75.4
-3 0 4		-7	27.9	-26.6
-4 0 4		6	24.4	-24.9
-5 0 4	22	-8	42.9	-46.4
-6 0 4		-16	37.8	-39.6
-7 0 4		5		-5.0
-8 0 4		5	14.9	-15.4
-9 0 4	40	-33	18.7	-23.5
-10 0 4			36.2	40.5
0 0 5	12	-10	15.6	-20.3
1 0 5	40	36	29.0	23.6
2 0 5	28	-33	32.3	-30.3
3 0 5		5	39.6	39.3
4 0 5	40	37	48.7	44.9
5 0 5		-11		-2.8
6 0 5		0	37.4	36.5
7 0 5			19.6	19.6
8 0 5				-2.3
-1 0 5		-1	20.1	-20.3
-2 0 5		-10	28.8	-33.8
-3 0 5	28	20		-8.2
-4 0 5	51	-42	71.2	-71.7
-5 0 5		-11	15.4	-18.0
-6 0 5	35	-27		9.7
-7 0 5	38	3	39.8	-42.4
-8 0 5			13.6	11.5
-9 0 5			18.2	18.4
0 0 6	40	-30	59.6	-55.4
1 0 6		-9		-0.5
2 0 6	35	24	25.8	24.5
3 0 6	20	11		-5.0
4 0 6		-10		0.0
5 0 6			33.3	30.8
6 0 6			20.5	18.8
-1 0 6	37	28		5.5
-2 0 6		-12	21.0	-22.0
-3 0 6	43	-36	60.2	-56.2
-4 0 6	33	25		8.6
-5 0 6		-1	13.7	-17.6
-6 0 6		-11	16.2	-16.6
-7 0 6				-7.2
-8 0 6			29.1	27.4
0 0 7				1.9
1 0 7			14.3	-13.1
2 0 7			34.1	-34.3
3 0 7			29.3	30.4
-1 0 7			19.7	-22.2
-2 0 7			28.0	-30.0
-3 0 7				-5.1
-4 0 7				-7.1
-5 0 7			29.1	-28.0
1 1 0	56	46	29.9	22.3
2 1 0	68	-66	106.0	-110.7
3 1 0	32	-33	73.5	-76.1
4 1 0	18	-18	55.0	-58.3
5 1 0		11	44.0	-43.2
6 1 0	25	23	69.2	-73.2
7 1 0		-6	24.6	-19.9
8 1 0		7	19.1	-12.6
9 1 0				-8.1
10 1 0			22.3	23.3
11 1 0				-0.8
12 1 0			27.7	20.0
0 2 0		1	79.0	-65.1
1 2 0	11	-3	77.0	-74.7
2 2 0	83	-79	128.0	-119.8
3 2 0	23	19		-8.6
4 2 0	16	11	16.2	-15.2
5 2 0	52	-52	26.2	-31.1
6 2 0	57	56	89.5	93.2
7 2 0	18	10		4.4
8 2 0		2	34.8	27.9
9 2 0			31.6	31.8
10 2 0			40.7	36.2
11 2 0				0.0
12 2 0			19.4	15.0
1 3 0	48	47	58.5	63.2
2 3 0	29	-22		4.0
3 3 0	34	-28	40.6	37.6
4 3 0	74	79	129.5	141.5
5 3 0		16	18.3	20.8
6 3 0	18	-19	26.5	28.9
7 3 0	25	28	53.2	50.6
8 3 0		-6		-1.5
9 3 0			20.6	-4.7
10 3 0				3.5
11 3 0				-3.3
0 4 0	53	55	108.8	108.0
1 4 0		-1	52.8	47.1
2 4 0	21	16	78.1	67.4
3 4 0	19	18	31.2	30.8
4 4 0	18	-18		-4.0
5 4 0		15	15.9	14.4
6 4 0	27	-28	42.0	-41.1
7 4 0		15	13.7	-11.9
8 4 0	29	-28	50.4	-50.3
9 4 0				-7.6
10 4 0			29.2	-31.1
11 4 0				-15.9
1 5 0	52	47		20.6
2 5 0	71	-66	106.0	-98.5
3 5 0	25	-30	42.4	-42.9
4 5 0	15	17	12.4	-20.5
5 5 0		4	47.0	-49.4
6 5 0	27	-31	67.8	-59.9
7 5 0	16	8		2.4
8 5 0			20.2	-23.9
9 5 0				-15.2
10 5 0			33.3	38.8
11 5 0				-8.8
0 6 0	88	-97	111.9	-140.3
1 6 0	31	22		-6.4
2 6 0		-1	35.3	-39.3
3 6 0		--	28.4	-30.9
4 6 0	18	-9	17.9	-16.0
5 6 0		9	20.2	19.3
6 6 0		16	16.1	13.6
7 6 0		-16	14.8	10.1
8 6 0			43.6	45.5
9 6 0			20.8	10.0
10 6 0				17.9
1 7 0		6		11.5
2 7 0		2	16.8	23.4
3 7 0		-7	29.3	32.6
4 7 0	34	46	68.2	69.3
5 7 0		10		5.8
6 7 0		-5	32.0	34.3
7 7 0	27	21	27.9	31.0
8 7 0				-6.9
9 7 0				-0.6
10 7 0				4.2
0 8 0		-2	29.9	27.1
1 8 0		-3	36.3	34.2
2 8 0	34	42	45.8	51.6
3 8 0	19	-19	9.3	-5.5
4 8 0		-2	16.5	14.6
5 8 0	27	32	10.9	19.3
6 8 0	27	-35	58.2	-58.7
7 8 0				4.6
8 8 0				-10.3
9 8 0			26.4	-25.6
1 9 0		3		-1.9
2 9 0		-13	20.9	-25.9
3 9 0		4	11.8	-16.5
4 9 0		-16	42.0	-42.4
5 9 0				-13.0
6 9 0			25.7	-24.6
7 9 0				-15.0
8 9 0				-3.2
0 10 0	62	-45	63.3	-65.4
1 10 0				-6.4
2 10 0				-13.4
3 10 0			26.5	-28.4
4 10 0				7.6
5 10 0				4.1
6 10 0				2.1
7 10 0				4.5
1 11 0				-8.9
2 11 0			30.7	35.9
3 11 0				10.0
4 11 0				13.8
5 11 0			19.2	18.3
6 11 0			25.0	23.7
0 1 1	22	18	*	-1.3
0 2 1	100	-116	*	-176.1
0 3 1	52	-45	*	-65.6
0 4 1	30	30	*	72.2
0 5 1		-8	*	18.9
0 6 1		-10	38.0	-43.2
0 7 1	26	-25	35.0	-36.3
0 8 1	55	56	69.7	68.8
0 9 1		10	12.9	17.0
0 10 1		9		-8.3
0 11 1		1		-10.8
0 1 2	24	20	64.1	64.2
0 2 2		2	39.3	-41.2
0 3 2		-3	42.6	-41.1
0 4 2	44	44	71.4	69.7
0 5 2	49	47	105.7	95.7
0 6 2	38	-32	76.5	-60.4
0 7 2	22	15		-6.7
0 8 2		10	11.3	14.7
0 9 2		17	37.2	32.8
0 10 2	44	-34	46.7	-43.3
0 11 2	24	-20	39.6	-38.8
0 1 3		13	56.6	53.5
0 2 3	30	-29	26.0	-25.4
0 3 3	87	90	145.4	-133.2
0 4 3		2		15.6
0 5 3	22	-12	15.8	21.0
0 6 3		3		-11.8
0 7 3	38	-39	76.3	-62.6
0 8 3		19	13.4	15.8
0 9 3	32	22	54.9	42.7
0 10 3		8		0.7
0 11 3			19.1	-15.9
0 1 4	53	50	79.7	76.6
0 2 4	22	13		6.7
0 3 4	33	22		-11.0
0 4 4		-8		-6.9
0 5 4	59	59	78.1	65.1
0 6 4		14	21.8	17.8
0 7 4		-4	17.4	-18.7
0 8 4		-10		-8.0
0 9 4		11	22.9	22.5
0 10 4				6.7
0 1 5	22	9	27.3	31.0
0 2 5	22	17	35.5	34.2
0 3 5	51	-43	64.4	-67.7
0 4 5		-4		-13.4
0 5 5		-12		-6.8
0 6 5		11	16.4	18.9
0 7 5	32	-31	40.1	-40.7
0 8 5	22	-16	27.2	-29.2
0 9 5			24.1	24.4
0 1 6	28	20	26.1	25.5
0 2 6		3	16.6	15.9
0 3 6		8		-2.0
0 4 6	28	-20	31.7	-31.8
0 5 6	49	30	23.3	27.1
0 6 6			30.8	34.8
0 7 6				-5.5
0 1 7				-4.3
0 2 7			41.2	30.4
0 3 7				1.9
0 4 7				-16.5

[a] Asterisk indicates reflections not measured.

were measurable above background. The data were corrected for Lorentz and polarization effects and scaled by conventional methods, but no corrections were made for absorption and extinction.

Structure Determination and Refinement.—The potassium and vanadium atoms in KV_3O_8 were found from Patterson syntheses and the oxygen atoms uniquely placed by spatial considerations. The three projections were refined by full-matrix, least-squares analysis of the data for the three projections. The observed F values were given unit weights. Because of the limited amount of data, the thermal parameters were held fixed at $B = 2.0$ A^2 for K, 0.7 A^2 for V, 1.0 A^2 for O_1 and O_2, and 1.5 A^2 for O_3, O_4, and O_5. The final conventional R factors (zero reflections excluded) were 0.14 for *hk*0, 0.15 for 0*kl*, and 0.16 for *h*0*l*.

The full-matrix, least-squares analysis of the three-dimensional data for CsV_3O_8 was started with parameters derived from the structure found for KV_3O_8. The data were weighted according to $\sqrt{w} = 4F_{\min}/F_{\text{obsd}}$ for $F_{\text{obsd}} > 4F_{\min}$ and $\sqrt{w} = F_{\text{obsd}}/4F_{\min}$ for $F_{\text{obsd}} < 4F_{\min}$, where $F_{\min}$ was set at 10.0 electrons. The isotropic thermal parameters were allowed to vary for each type of atom separately. The total number of parameters was 40 (20 structure parameters, 8 thermal parameters, 12 scale parameters). The final R factor excluding nonobserved reflections was 0.089, and the standard error of the observations F with weight unity was 2.8.

An attempt to refine CsV_3O_8 in the space group $P2_1$ failed because of the instability of the least-squares matrix, even though the atoms were artificially displaced from the mirror planes. A three-dimensional Fourier synthesis with ΔF values as amplitudes showed no evidence of displacement of any atoms from the mirror planes as would be expected if the structure were noncentrosymmetric. Therefore, there is no reason at present to believe that the structures of KV_3O_8 and CsV_3O_8 are not truly centrosymmetric.

Calculated and observed F values are listed for *hk*0, *h*0*l*, and 0*kl* for both crystals in Table II, and the complete *hkl* data for CsV_3O_8 are given in Table III. The final structure parameters for both KV_3O_8 and CsV_3O_8 are given in Table IV.

Description of the Crystals and the Crystal Structures

KV_3O_8 and CsV_3O_8 (and probably also $NH_4V_3O_8$ and RbV_3O_8) have the monoclinic space group $P2_1/m$ (C_{2h}^5, no. 11). Their unit cell parameters and other data are collected in Table I. Both KV_3O_8 and CsV_3O_8 form lathlike plates flattened on (100), but they are elongated along c for KV_3O_8 and along b for CsV_3O_8 (Figure 1). The habit of $NH_4V_3O_8$ is similar to that of KV_3O_8. The difference in crystal habit between KV_3O_8 and CsV_3O_8 is striking and unexplained. The former forms rosettes of tiny crystal plates making it difficult to obtain good specimens large enough for X-ray diffraction study, but the columnar habit and good quality of the crystals of CsV_3O_8 make them far better suited for this purpose.

Optical data were measured for KV_3O_8 as follows: n_α 1.77 ± 5 (lemon-yellow, nearly $\perp$(100)), $n_\beta = 2.27 \pm 5$ (orange, $\parallel b$), n_γ 2.34 ± 5 (orange), $2V = 26 \pm 3°$. The orientation of the strongly negative biaxial optical indicatrix is consistent with the layer structure found in the crystal structure analysis.

The structure is a clear-cut layer type as previously reported by Block,[6] consistent with the perfect (100) cleavage and large negative birefringence observed for these crystals. The layers consist of highly distorted VO_6 octahedra linked together by sharing corners and edges. The sheet as a whole has a corrugated appear-

TABLE III

hkl STRUCTURE FACTORS FOR CsV_3O_8[a]

H	K	L	F-OBS	F-CAL
1	1	0	29.9	22.3
2	1	0	110.0	-110.6
3	1	0	73.5	-76.1
4	1	0	55.0	-58.2
5	1	0	43.9	-43.2
6	1	0	69.2	-73.2
7	1	0	24.5	-19.8
8	1	0	19.1	-12.6
9	1	0		-8.4
10	1	0	22.3	23.2
11	1	0		-.7
12	1	0	27.6	20.0
0	1	1	*	41.2
1	1	1	20.9	-17.9
2	1	1	8.5	6.4
3	1	1	47.3	-52.3
4	1	1	75.8	-81.8
5	1	1	32.5	-34.2
6	1	1	71.7	-63.9
7	1	1	39.3	-39.0
8	1	1	19.6	-12.2
9	1	1	21.2	-15.3
10	1	1		-5.7
11	1	1		3.4
0	1	2	64.0	64.2
1	1	2	36.3	39.5
2	1	2	11.5	-7.2
3	1	2		-12.4
4	1	2	50.1	-48.3
5	1	2	27.4	-27.6
6	1	2	54.2	-50.3
7	1	2	26.7	-25.1
8	1	2	55.0	-51.7
9	1	2		-2.7
10	1	2		-4.6
11	1	2		-13.2
0	1	3	56.6	53.4
1	1	3	29.0	30.2
2	1	3	50.6	51.7
3	1	3		-9.5
4	1	3	20.0	-16.8
5	1	3		-7.2
6	1	3	59.2	-51.0
7	1	3	20.7	-19.6
8	1	3	28.3	-27.6
9	1	3		-14.5
10	1	3		-23.8
0	1	4	79.7	76.5
1	1	4		10.0
2	1	4	58.9	51.3
3	1	4	18.3	17.2
4	1	4		1.7
5	1	4		-17.3
6	1	4		-.5
7	1	4	22.4	-18.5
8	1	4	39.6	-39.0
9	1	4		-1.6
0	1	5	27.3	31.0
1	1	5	32.9	33.7
2	1	5	43.6	41.5
3	1	5		6.1
4	1	5	27.6	30.0
5	1	5		-1.4
6	1	5	23.4	-11.9
7	1	5		-2.0
8	1	5		-15.5
0	1	6	26.0	25.4
1	1	6		8.9
2	1	6	31.8	32.4
3	1	6	25.2	21.5
4	1	6	23.9	16.1
5	1	6		-1.0
6	1	6		16.1
0	1	7		4.2
1	1	7	20.8	21.9
2	1	7		11.8
3	1	7		6.9
-1	1	1	51.7	50.7
-2	1	1	101.0	101.7
-3	1	1	32.0	37.5
-4	1	1	122.5	113.7
-5	1	1	37.4	38.1
-6	1	1	26.7	30.5
-7	1	1	16.0	19.4
-8	1	1		-8.1
-9	1	1		-4.3
-10	1	1		-18.3
-11	1	1		-13.2
-12	1	1	32.7	-27.2
-1	1	2	35.1	40.6
-2	1	2	104.6	111.1
-3	1	2	67.2	71.3
-4	1	2	21.8	24.8
-5	1	2	43.5	39.8
-6	1	2	28.1	28.7
-7	1	2		1.1
-8	1	2	39.1	-37.2
-9	1	2		6.1
-10	1	2	37.9	-37.0
-11	1	2	20.3	-16.8
-12	1	2		-11.5
-1	1	3	56.6	61.0
-2	1	3	75.1	76.7
-3	1	3	19.7	25.1
-4	1	3	45.0	42.4
-5	1	3	33.9	32.0
-6	1	3	30.3	-34.6
-7	1	3		-.2
-8	1	3	26.6	-22.6
-9	1	3	22.1	-19.9
-10	1	3	30.2	-29.2
-11	1	3		-11.7
-1	1	4	39.7	38.7
-2	1	4	43.9	40.4
-3	1	4	24.4	26.2
-4	1	4		1.1
-5	1	4		3.6
-6	1	4		-15.0
-7	1	4		-15.8
-8	1	4	30.8	-38.5
-9	1	4		-12.1
-10	1	4		-14.5
-1	1	5	27.1	29.0
-2	1	5	23.0	19.7
-3	1	5		13.4
-4	1	5	16.9	-17.1
-5	1	5		7.7
-6	1	5	43.5	-42.8
-7	1	5		-14.7
-8	1	5		-12.6
-9	1	5		-23.9
-1	1	6	30.8	29.5
-2	1	6	22.1	-18.9
-3	1	6		8.3
-4	1	6		-15.0
-5	1	6		-12.1
-6	1	6	28.3	-25.5
-7	1	6		-11.7
-8	1	6		-17.5
-1	1	7		2.0
-2	1	7		-5.9
-3	1	7		2.7
-4	1	7	27.2	-25.3
-5	1	7		-11.8
0	2	0	79.0	-65.2
1	2	0	76.9	-74.6
2	2	0	128.0	-119.7
3	2	0		-8.9
4	2	0	16.2	-16.1
5	2	0	26.2	-31.0
6	2	0	89.5	90.1
7	2	0		4.3
8	2	0	34.8	27.9
9	2	0	31.6	31.7
10	2	0	40.6	36.1
11	2	0		.0
12	2	0	19.4	14.9
0	2	1	*	-176.1
1	2	1		-5.0
2	2	1	125.8	-120.8
3	2	1	51.4	-58.0
4	2	1		-10.2
5	2	1		-3.1
6	2	1	21.2	-26.4
7	2	1	19.5	18.1
8	2	1	60.0	61.4
9	2	1		-7.1
10	2	1	41.4	37.4
11	2	1	24.1	21.8
0	2	2	39.3	-41.1
1	2	2	55.7	-68.2
2	2	2	77.5	-96.4
3	2	2		-4.5
4	2	2	109.3	-110.3
5	2	2		-9.5
6	2	2	13.5	13.4
7	2	2		-14.5
8	2	2	18.9	16.2
9	2	2	20.2	20.1
10	2	2	25.5	18.9
11	2	2		5.4
0	2	3	26.0	-29.3
1	2	3		-7.6
2	2	3	90.8	-85.0
3	2	3	55.0	-49.5
4	2	3	25.8	-28.2
5	2	3	25.4	-25.2
6	2	3	54.1	-49.6
7	2	3		8.9
8	2	3		3.8
9	2	3		-8.2
10	2	3	45.2	37.5
0	2	4		8.6
1	2	4	40.4	-44.6
2	2	4		-5.0
3	2	4	23.4	-25.5
4	2	4	75.9	-76.9
5	2	4		.1
6	2	4	29.6	-33.0
7	2	4		-17.6
8	2	4		.1
9	2	4		3.7
0	2	5	35.4	34.1
1	2	5		-2.6
2	2	5	25.7	-27.7
3	2	5		-11.9
4	2	5		-19.4
5	2	5	24.1	-25.6
6	2	5	27.4	-30.7
7	2	5		5.9
8	2	5	38.8	-36.4
0	2	6	16.8	15.9
1	2	6		-8.6
2	2	6	26.7	31.3
3	2	6	25.1	-28.7
4	2	6	18.2	-14.1
5	2	6		-.4
6	2	6	32.6	-31.2
0	2	7	41.1	38.3
1	2	7		-6.8
2	2	7		7.3
-1	2	1	51.7	-50.0
-2	2	1		-5.1
-3	2	1	34.8	-33.5
-4	2	1	28.0	30.7
-5	2	1	22.1	23.4
-6	2	1	31.9	33.5
-7	2	1	22.5	24.4
-8	2	1	75.9	74.4
-9	2	1		11.5
-10	2	1		3.9
-11	2	1	30.5	35.1
-12	2	1		-14.3
-1	2	2	10.5	-14.1
-2	2	2	48.0	-46.1
-3	2	2		3.3
-4	2	2	73.2	77.3
-5	2	2		1.1
-6	2	2	56.7	75.2
-7	2	2	46.9	43.3
-8	2	2		4.5
-9	2	2	35.2	33.7
-10	2	2		18.8
-11	2	2		-1.1
-1	2	3	51.6	-59.5
-2	2	3	81.7	88.4
-3	2	3		6.4
-4	2	3	31.7	35.2
-5	2	3	36.8	38.6
-6	2	3	55.4	56.7
-7	2	3		15.6
-8	2	3	31.6	33.1
-9	2	3	23.8	22.1
-10	2	3	21.5	-25.4
-11	2	3		15.3
-1	2	4	18.2	16.8
-2	2	4	20.0	23.6
-3	2	4		6.8
-4	2	4	85.2	81.3
-5	2	4	22.2	27.8
-6	2	4		12.7
-7	2	4	45.1	44.4
-8	2	4		-9.6
-9	2	4		7.7
-10	2	4		-.4
-1	2	5		-13.1
-2	2	5	54.7	55.3
-3	2	5	42.8	41.4
-4	2	5		2.9
-5	2	5	33.1	34.9
-6	2	5	23.6	26.5
-7	2	5		8.6
-8	2	5		-14.4
-9	2	5		19.4
-1	2	6	23.7	24.5
-2	2	6	28.2	30.6
-3	2	6		6.0
-4	2	6	29.2	34.6
-5	2	6	27.4	28.0
-6	2	6	21.9	-23.6
-7	2	6		17.9
-1	2	7		9.4
-2	2	7		9.1
-3	2	7	29.2	33.8
-4	2	7		-7.2
1	3	0	58.4	63.2
2	3	0		3.9
3	3	0	40.5	37.5
4	3	0	129.5	141.5
5	3	0	18.3	20.7
6	3	0	26.4	28.8
7	3	0	53.2	50.6
8	3	0		-1.5
9	3	0	20.5	-4.7
10	3	0		3.4
11	3	0		-5.2
0	3	1	*	-66.6
1	3	1	12.2	-13.3
2	3	1	114.8	116.5
3	3	1	21.4	-17.3
4	3	1	37.5	36.5
5	3	1	70.4	68.5
6	3	1	65.2	63.8
7	3	1		-10.3
8	3	1	65.0	60.4
9	3	1		11.0
10	3	1	26.6	-25.6
11	3	1		10.0
0	3	2	42.5	-41.0
1	3	2		1.2
2	3	2	64.9	-66.6
3	3	2	35.3	40.9
4	3	2	49.7	52.0
5	3	2		11.0
6	3	2	66.1	61.2
7	3	2	31.7	33.9
8	3	2		7.8
9	3	2	25.8	24.2
10	3	2	23.3	19.3
11	3	2		-10.1
0	3	3	145.4	-133.2
1	3	3		-14.1
2	3	3	17.7	15.5
3	3	3	22.1	-24.3
4	3	3		-4.4
5	3	3	45.2	43.7
6	3	3	22.6	19.4
7	3	3		12.4
8	3	3	61.2	52.8
9	3	3		2.4
10	3	3		9.8
0	3	4		-11.0
1	3	4	56.7	-54.9
2	3	4	49.1	-52.8
3	3	4		12.9
4	3	4		-16.8
5	3	4		-9.2
6	3	4	49.7	49.9
7	3	4		-1.0
8	3	4		13.6
9	3	4		21.5
0	3	5	64.4	-67.6
1	3	5		-7.0
2	3	5	39.7	-36.9
3	3	5		-18.4
4	3	5		-10.9
5	3	5		3.0
6	3	5		-16.6
7	3	5	24.1	23.8
0	3	6		-1.9
1	3	6	33.8	-36.5
2	3	6	24.4	-27.3
3	3	6		4.5
4	3	6	39.4	-45.3
5	3	6		5.9
0	3	7		1.9
1	3	7		-5.6
-1	3	1	43.1	-41.5
-2	3	1	84.2	-80.9
-3	3	1	75.5	-72.6
-4	3	1	27.9	-30.2
-5	3	1	62.4	-61.7
-6	3	1	44.7	-42.7
-7	3	1		-.9
-8	3	1		3.5
-9	3	1		-18.8
-10	3	1	52.2	55.0
-11	3	1		1.3
-1	3	2	58.7	-56.6
-2	3	2	87.3	-85.3
-3	3	2		-16.4
-4	3	2	112.0	-110.1
-5	3	2	15.3	-16.5
-6	3	2	23.3	21.3
-7	3	2	23.2	-26.7
-8	3	2		12.4
-9	3	2	35.0	34.8
-10	3	2		9.2
-11	3	2		5.2
-1	3	3		-13.7
-2	3	3	40.5	-40.5
-3	3	3	71.2	-72.2
-4	3	3		-14.1
-5	3	3		3.9
-6	3	3	17.9	-17.2
-7	3	3		3.0
-8	3	3	57.6	49.4
-9	3	3		-.8
-10	3	3	29.9	28.1
-11	3	3	29.0	25.6
-1	3	4	39.4	-42.3
-2	3	4	56.4	-59.0
-3	3	4	20.4	-16.6
-4	3	4		6.0
-5	3	4	26.2	-30.9
-6	3	4	54.9	52.5
-7	3	4		3.7
-8	3	4	18.2	17.6
-9	3	4	23.1	25.8
-10	3	4		19.2
-1	3	5	16.0	-19.3
-2	3	5		9.3
-3	3	5	32.8	-33.5
-4	3	5		8.4
-5	3	5	26.7	27.6
-6	3	5		7.1
-7	3	5		5.5
-8	3	5	39.2	43.9
-9	3	5		14.2
-1	3	6		-5.0
-2	3	6	25.8	-25.7
-3	3	6		1.9
-4	3	6	37.5	38.7
-5	3	6		-11.8
-6	3	6	28.0	23.2
-7	3	6	34.3	34.9
-1	3	7	28.7	-29.0
-2	3	7	28.8	30.9
-3	3	7		-2.0
-4	3	7		8.0
0	4	0	108.8	107.8
1	4	0	51.8	47.1
2	4	0	78.1	67.4
3	4	0	31.2	30.7
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4	9	1	30.9	-35.4
5	9	1		-15.2
6	9	1	28.9	-34.9
7	9	1		-1.5
8	9	1		-20.2
0	9	2	37.1	32.5
1	9	2		.7
2	9	2	16.0	11.6
3	9	2		-11.5
4	9	2	22.2	-19.2
5	9	2		-10.2
6	9	2	26.1	-26.5
7	9	2		-11.7
0	9	3	54.9	42.7
1	9	3		5.8
2	9	3		13.3
3	9	3		-.3
4	9	3		-.9
5	9	3		-11.2
6	9	3	26.0	-20.8
0	9	4	22.8	22.3
1	9	4	17.8	14.6
2	9	4	26.0	22.7
3	9	4		1.8
4	9	4		3.4
5	9	4		-.1
0	9	5	24.0	24.5
1	9	5		8.3
2	9	5		23.5
-1	9	1	13.8	18.4
-2	9	1	26.9	32.4
-3	9	1	17.0	21.5
-4	9	1	32.5	33.4
-5	9	1	21.5	22.7
-6	9	1		10.4
-7	9	1		10.2
-8	9	1		-6.8
-1	9	2		11.6
-2	9	2	46.7	44.9
-3	9	2	15.0	14.1
-4	9	2	27.4	31.5
-5	9	2		9.3
-6	9	2		4.4
-7	9	2		6.9
-8	9	2		-13.7
-1	9	3		12.0
-2	9	3	25.6	28.4
-3	9	3	22.4	20.1
-4	9	3		14.2
-5	9	3		7.7
-6	9	3		-9.1
-7	9	3		3.4
-1	9	4	21.1	19.2
-2	9	4	19.4	18.1
-3	9	4	21.8	16.3
-4	9	4		-7.4
-5	9	4		12.5
-6	9	4		-19.6
-1	9	5		5.0
-2	9	5		4.6
-3	9	5	20.4	12.5
0	10	0	63.3	-66.2
1	10	0		-6.4
2	10	0		-13.4
3	10	0	26.4	-28.3
4	10	0		7.5
5	10	0		4.0
6	10	0		2.1
7	10	0		4.5
0	10	1		-8.3
1	10	1	15.0	-23.2
2	10	1	45.3	-52.9
3	10	1		9.6
4	10	1	27.5	-27.4
5	10	1		-10.2
6	10	1		23.5
7	10	1		-8.0
0	10	2	46.7	-43.2
1	10	2	17.3	10.6
2	10	2	36.6	-44.4
3	10	2		-21.0
4	10	2		-6.9
5	10	2		-4.0
6	10	2	33.0	-27.1
0	10	3		.6
1	10	3	27.1	-25.3
2	10	3		-11.9
3	10	3		-8.7
4	10	3	40.6	-46.9
5	10	3		8.8
0	10	4		6.7
1	10	4		2.9
2	10	4	32.8	-29.3
3	10	4		-8.1
-1	10	1		-16.6
-2	10	1	47.1	-43.4
-3	10	1	19.7	14.7
-4	10	1		15.7
-5	10	1	22.6	-22.5
-6	10	1	38.7	41.3
-7	10	1		15.5
-1	10	2	23.7	-20.3
-2	10	2	34.9	28.8
-3	10	2		-11.4
-4	10	2		7.4
-5	10	2		21.2
-6	10	2		22.2
-7	10	2		-.3
-1	10	3		-3.2
-2	10	3		-.2
-3	10	3		2.1
-4	10	3	45.8	44.3
-5	10	3		-10.2
-6	10	3		24.4
-1	10	4		-21.2
-2	10	4	44.4	39.7
-3	10	4		6.0
-4	10	4		.3
1	11	0		-8.9
2	11	0	30.7	35.9
3	11	0		9.9
4	11	0		13.7
5	11	0	19.2	18.5
6	11	0	25.0	23.5
0	11	1		-10.7
1	11	1	15.2	16.8
2	11	1	10.7	-8.6
3	11	1		6.4
4	11	1	39.2	36.4
5	11	1		.4
0	11	2	39.5	-36.9
1	11	2		-6.0
2	11	2	18.5	16.2
3	11	2		-7.8
4	11	2		8.8
0	11	3	19.1	-13.8
1	11	3		-7.4
2	11	3	25.3	-22.1
3	11	3		13.2
-1	11	1	17.4	-23.8
-2	11	1		-17.3
-3	11	1		2.3
-4	11	1	45.0	-50.5
-5	11	1		-5.4
-6	11	1		3.4
-1	11	2	14.1	4.9
-2	11	2	24.9	-28.0
-3	11	2	26.8	-27.1
-4	11	2		-3.7
-5	11	2		-7.5
-1	11	3	15.8	-16.8
-2	11	3	25.0	-24.6
-3	11	3		-.3
-4	11	3	12.9	-19.0

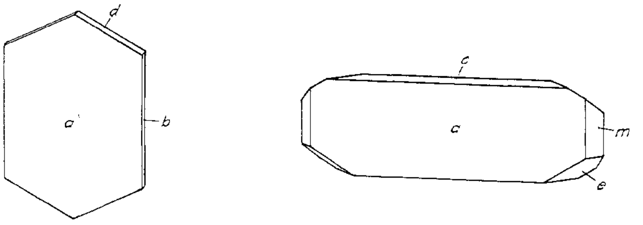
[a] Asterisk indicates reflections not measured. For *h0l* reflections, see Table II.

ance as shown in Figure 2. The cations occupy positions between the layers, in irregular 12-fold coordination with neighboring oxygen atoms. As shown in Table V, in KV_3O_8 the K–O distances vary from 2.70 to 3.55 A (average 3.11 A), and in CsV_3O_8 the Cs–O distances vary from 2.99 to 3.68 A (average 3.30 A). The marked increase in the average cation–oxygen distances in going from KV_3O_8 to CsV_3O_8 corresponds to the increase in the crystallographic *a* axis, as pointed out by Kelmers.[16] It is also apparent from Kelmers' observation[16] that sodium and lithium analogs cannot be prepared that the special layer structure found for the trivanadates probably requires the presence of relatively large interlayer cations to be stable.

TABLE IV
CRYSTAL STRUCTURE PARAMETERS FOR KV_3O_8 AND CsV_3O_8[a]

Atom	Parameter	KV_3O_8 Value	σ	CsV_3O_8 Value	σ
K, Cs in 2(e)	x	0.061	3	0.0553	2
	z	0.0951	6	0.9401	4
	B	2.0	...	1.88	4
V_1 in 2(e)	x	0.578	2	0.5674	5
	z	0.918	4	0.9105	8
	B	0.7	...	0.57	6
V_2 in 4(f)	x	0.693	1	0.6760	3
	y	0.055	2	0.0573	4
	z	0.441	2	0.4311	5
	B	0.7	...	0.61	5
O_1 in 2(e)	x	0.432	9	0.4229	24
	z	0.118	15	0.1124	39
	B	1.0	...	1.86	34
O_2 in 2(e)	x	0.758	8	0.7412	21
	z	0.609	13	0.5788	32
	B	1.0	...	1.05	24
O_3 in 4(f)	x	0.514	5	0.5029	14
	y	0.098	7	0.0841	16
	z	0.691	8	0.6807	22
	B	1.5	...	1.26	19
O_4 in 4(f)	x	0.156	5	0.1834	17
	y	0.062	8	0.0560	19
	z	0.437	8	0.4474	27
	B	1.5	...	1.97	25
O_5 in 4(f)	x	0.744	5	0.7188	14
	y	0.091	7	0.1048	16
	z	0.133	8	0.1074	23
	B	1.5	...	1.18	18

[a] Standard errors σ are given in terms of last significant figures. Thermal parameters B (A^2) for KV_3O_8 were held fixed in least-squares analysis.



a b

Figure 1.—Crystal habits of (a) KV_3O_8 and (b) CsV_3O_8. Crystal forms shown are: $a(100)$, $b(010)$, $c(001)$, $m(110)$, $d(011)$, $(e\bar{1}11)$.

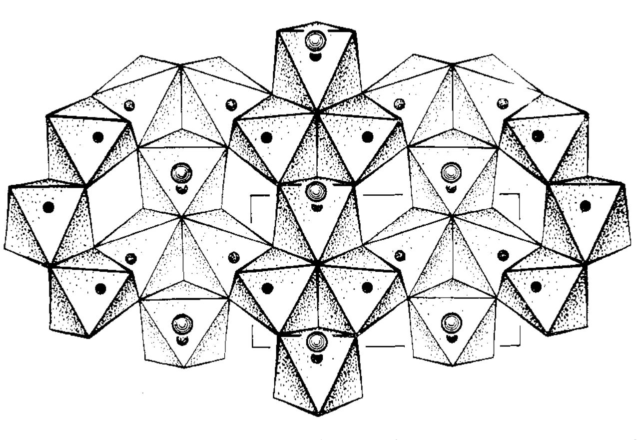


Figure 2.—View normal to (100) of the layer structure of CsV_3O_8, shown as linkages of distorted VO_6 octahedra: black circles, V atoms; large circles, Cs^- ions; rectangle shows trace of the unit cell at $x = {}^1/_2$.

TABLE V
INTERATOMIC DISTANCES AND ANGLES IN KV_3O_8 AND CsV_3O_8[a]

Atoms	Vectors	KV_3O_8	σ	CsV_3O_8	σ
Vanadium–oxygen coordination		Lengths, A			
V_1–O_1	A	1.58	8	1.624	20
V_1–O_3	B(2)	1.73	5	1.861	13
V_1–O_2	C	2.18	7	2.282	16
V_1–O_5	D(2)	2.05	5	1.945	13
V_2–O_4	E	1.58	5	1.575	15
V_2–O_1	F	2.91	6	2.973	17
V_2–O_2	G	1.88	3	1.855	8
V_2–O_3	H	1.99	4	1.986	11
V_2–O_3'	J	2.08	5	1.933	12
V_2–O_5	K	1.65	4	1.731	11
		Angles, deg			
O_1–V_1–O_3	$A \wedge B$	104	3	101.6	8
O_1–V_1–O_5	$A \wedge D$	96	3	98.8	8
O_2–V_1–O_3	$B \wedge C$	72	2	73.4	5
O_2–V_1–O_5	$C \wedge D$	88	2	87.4	6
O_3–V_1–O_5	$B \wedge D$	88	3	87.4	7
O_3–V_1–O_3^m	$B \wedge B^m$	95	3	98.7	7
O_5–V_1–O_5^m	$D \wedge D^m$	81	3	78.9	7
O_1–V_1–O_2	$A \wedge C$	174	5	171.9	12
O_3–V_1–O_5^m	$B \wedge D^m$	158	3	156.9	7
O_4–V_2–O_2	$E \wedge G$	103	3	102.6	7
O_4–V_2–O_3	$E \wedge H$	114	2	111.6	6
O_4–V_2–O_3'	$E \wedge J$	103	3	103.4	7
O_4–V_2–O_5	$E \wedge K$	103	3	107.1	8
O_1–V_2–O_2	$F \wedge G$	83	1	83.1	4
O_1–V_2–O_3	$F \wedge H$	76	2	76.7	5
O_1–V_2–O_3'	$F \wedge J$	74	1	73.9	4
O_1–V_2–O_5	$F \wedge K$	67	2	64.4	5
O_2–V_2–O_3	$G \wedge H$	74	3	81.0	7
O_3–V_2–O_3'	$H \wedge J$	76	2	71.8	6
O_3'–V_2–O_5	$J \wedge K$	94	2	95.4	7
O_2–V_2–O_5	$G \wedge K$	100	3	94.9	6
O_4–V_2–O_1	$E \wedge F$	169	2	170.4	6
O_2–V_2–O_3'	$G \wedge J$	146	2	147.6	6
O_3–V_2–O_5	$H \wedge K$	143	3	141.0	8
Oxygen–oxygen distances (<3.200 A)		Lengths, A			
O_1–O_3		2.62	8	2.706	21
O_1–O_5		2.73	7	2.717	21
O_2–O_3		2.34	7	2.498	18
O_2–O_5		2.94	8	2.930	19
O_3–O_5		2.64	5	2.631	16
O_3–O_3^m		2.56	12	2.825	27
O_5–O_5^m		2.68	11	2.472	26
O_4–O_2		2.72	7	2.683	17
O_4–O_3		2.99	6	2.953	18
O_4–O_3'		2.88	5	2.761	18
O_4–O_5		2.53	7	2.661	18
O_3–O_3'		2.50	10	2.297	24
O_3'–O_5		2.76	7	2.713	17
O_1'–O_3		3.12	8	3.173	21
O_1'–O_3'		3.09	6	3.065	15
O_1–O_4''		3.21	8	3.160	22
Cation–oxygen distances (M = K or Cs)					
M–O_1	L	2.85	7	3.042	20
M–O_2''	M	2.70	6	2.985	18
M–O_4''	N(2)	3.16	6	3.217	15
M–O_4'	O(2)	2.91	6	3.112	15
M–O_4'''	P(2)	3.55	6	3.684	16
M–O_5'	Q(2)	3.28	6	3.560	13
M–O_5''	R(2)	3.00	5	3.199	12
Vanadium–vanadium distances					
V_1–V_2		3.10	2	3.098	4
V_1–V_2'		3.62	2	3.695	4
V_2–V_2'		3.21	2	3.175	4

[a] Standard errors (σ) in terms of the last significant figures. Superscript m indicates mirror-equivalent atom or vector (see Figure 4).

The Vanadium Coordination

In these structures, both kinds of vanadium atoms are in square-pyramidal coordination with oxygen, with a sixth oxygen weakly coordinated through the base of the pyramid. This coordination is similar to that found in several other oxovanadate compounds with an O:V ratio <3, for example, LiV_3O_8,[21] V_2O_5,[22] $Na_3V_6O_{15}$,[23] AgV_2O_5,[24] $K_3V_5O_{14}$,[10] $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$,[9,25] $VO(OH)_2$,[26] $VO(acac)_2$,[27,28] and $VO(bzac)_2$.[28,29] Bachmann and Barnes[30] have given a comprehensive summary of available information concerning coordination and bond lengths in oxovanadium(V) compounds. They refer to all of the fivefold coordination configurations in these compounds as trigonal bipyramids. There is only a slight difference between the angular conformations of a trigonal bipyramid and a square pyramid. Nevertheless, in these structures we find that one vanadium–oxygen distance (bond type A) is always considerably shorter than the other four (bond type B) among the five ligands and that the latter four ligands usually lie very nearly in a plane perpendicular to the short V–O bond. This configuration is illustrated in Figure 3a, and the associated bond lengths are listed in Table VI for all well-refined structures containing this type of coordination. The only compounds in which the vanadium coordination approaches a true trigonal-bipyramid configuration are the closely related $KVO_3\cdot H_2O$,[31] $Ca(VO_3)_2\cdot 2H_2O$,[32] and $Ca(VO_3)_2\cdot 4H_2O$.[33] In the square-pyramid structures, the short V–O bond is so outstanding that Hanic[34] has suggested that the diatomic group should be regarded as a discrete VO^{3+} ion. Evans[26] has suggested that this bond is practically a pure double bond and that the four basal ligands each represent a three-quarters bond for vanadium(V) or one-half bond for vanadium(IV).

In KV_3O_8 and CsV_3O_8 (the structure of the latter is taken as the standard) the two kinds of vanadium both conform to a square pyramid but have rather different dimensions and surroundings. The V_2 atoms are in double pyramidal groups V_2O_8, in which the pyramids are joined by an edge with apices directed opposite to each other. These double groups are joined into zigzag chains along the *b* axis by sharing corners through O_2, and these chains are linked into sheets by VO groups represented by V_1 and O_1. The V_1–O_1 distance is somewhat shorter than the apical VO distance V_2–O_4, while the opposite V–O distances (C, F, Figure 4) through the pyramidal base are correspondingly longer and shorter.

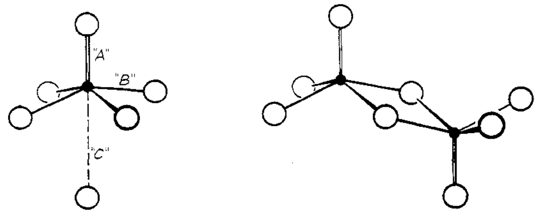


Figure 3—Vanadium–oxygen coordination configurations: (a) square-pyramid coordination found in many oxovanadates, as listed in Table VI; (b) double V_2O_8 group found in CsV_3O_8 and $Cs_2(UO_2)_2V_2O_8$.

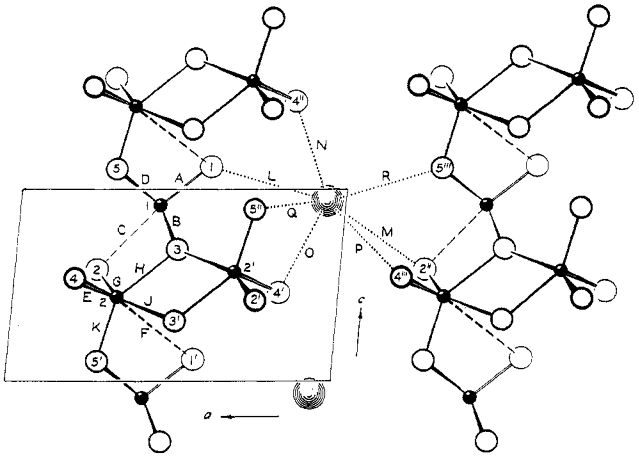


Figure 4.—Projection of the structure of CsV_3O_8 along the *b* axis. Numerals are serial numbers of atoms as given in Table IV; letters represent interatomic vectors as given in Table V. V_1O_1 groups and Cs^+ ions on the mirror plane at $y = {}^3/_4$ have been omitted to avoid confusion.

TABLE VI

BOND LENGTHS (A) IN SQUARE-PYRAMID VO_5 GROUPS IN VARIOUS OXO COMPOUNDS OF VANADIUM(IV) AND VANADIUM(V)

Compd	Ref	*A*	*B*	*C*	σ (estd)
CsV_3O_8		1.624	1.861–1.945	2.282	0.005
		1.575	1.731–1.986	2.973	0.005
KV_3O_8		1.58	1.73–2.05	2.18	0.05
		1.58	1.65–2.08	2.91	0.05
V_2O_5	18	1.585	1.780–2.021	2.785	0.004
LiV_3O_8	19	1.60	1.78–2.06	2.86	0.03
		1.64	1.72–2.10	2.36	0.03
		1.59	1.88–1.99	2.26	0.03
$Na_3V_6O_{15}$	20	1.56	1.89–2.01	2.32	0.03
		1.58	1.80–2.16	2.34	0.03
		1.56	1.78–2.00	2.68	0.03
AgV_2O_5	21	1.49	1.85–1.95	2.43	0.04
		1.54	1.78–2.09	2.35	0.04
$K_3V_5O_{14}$	10	1.60	1.85–1.97	...	0.02
$V_{10}O_{28}{}^{6-}$	9, 22	1.60	1.84–2.05	2.33	0.02
		1.61	1.83–1.98	2.23	0.02
$VO(OH)_2$	23	1.65	2.02	2.30	0.02
$VO(acac)_2$	24, 25	1.57	1.96–1.98	...	0.01
$VO(bzac)_2$	25, 26	1.612	1.946–1.986	...	0.08
Averages		1.60	1.91	(2.47)	

This confirms Evans' suggestion[35] that the strong apical bond is weakened somewhat if a sixth oxygen ligand approaches more closely at the base; however, there appears to be little basis, as yet, on which to dis-

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(22) H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Krist.*, **115**, 110 (1961).

(23) A. D. Wadsley, *Acta Cryst.*, **8**, 695 (1955).

(24) S. Anderson, *Acta Chem. Scand.*, **19**, 1371 (1965).

(25) H. T. Evans, Jr., *Inorg. Chem.*, **5**, 967 (1966).

(26) H. T. Evans, Jr., and M. E. Mrose, *Acta Cryst.*, **11**, 56 (1958).

(27) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961) (acac = acetylacetonate).

(28) P. K. Hon, R. L. Belford, and C. E. Pfluger, *ibid.*, **43**, 3111 (1965).

(29) P. K. Hon, R. L. Belford, and C. E. Pfluger, *ibid.*, **43**, 1323 (1965) [bzac = bis(2-phenyl-1,3-butanedionate)].

(30) H. G. Bachmann and W. H. Barnes, *Z. Krist.*, **115**, 215 (1961).

(31) C. L. Christ, J. R. Clark, and H. T. Evans, Jr., *Acta Cryst.*, **7**, 801 (1954); H. T. Evans, Jr., *Z. Krist.*, **114**, 257 (1960).

(32) C. H. Kelsey and W. H. Barnes, *Can. Mineralogist*, **6**, 448 (1960).

(33) F. R. Ahmed and W. H. Barnes, *ibid.*, **7**, 713 (1963).

(34) F. Hanic, *Chem. Zvesti*, **12**, 579 (1958).

(35) H. T. Evans, Jr., *Acta Cryst.*, **13**, 1019 (1960).

cuss such minor bond-length variations.[28] The V_2O_8 group in CsV_3O_8 is only slightly distorted from the ideal form shown in Figure 3b. If a plane is passed through the outer oxygen atoms numbered 2, 5′, 5″, and 2′ (Figure 4), the central oxygen atoms 3 and 3′ are displaced from the plane 0.15 A. The V_2 atoms lie 0.52 A from this plane, and the bonds V_2–O_4 make an angle of 87.5° with the plane.

The double V_2O_8 group illustrated in Figure 3b now appears to be a characteristic feature of many oxovanadium(V) structures. It can be clearly discerned in LiV_3O_8,[21] V_2O_5,[22] and $Na_3V_6O_{15}$.[23] Its discrete character is strikingly emphasized by its appearance in isolated form (but linked through UO_2^{2+} groups into a sheet structure) in the crystal structure of the carnotite analog $Cs_2(UO_2)V_2O_8$.[36] A binucleate ion $HV_2O_7^{3-}$ has been identified by Ingri and Brito[8,9] in alkaline vanadate solutions. This ion may be formulated $H_3V_2O_8^{3-}$, but of course it is not possible at this time to say whether it corresponds to the V_2O_8 group in the solid compounds. The V_2O_8 group is wholly lacking in the $V_{10}O_{28}^{6-}$ ion.[25] It is possible that the slow formation of KV_3O_8 from solutions of $V_{10}O_{28}^{6-}$ may be a result of some complex intermediate reactions in which the creation of the V_2O_8 group is involved.

A final detail worth noting is the close approach of the bridging oxygen atoms in the V_2O_8 group, namely, 2.30 ± 0.02 A in CsV_3O_8. This is fairly consistent with the distance of 2.35 ± 0.05 A found for the corresponding pair of atoms in $Cs_2(UO_2)V_2O_8$,[36] 2.42 ± 0.04 A found in LiV_3O_8,[21] 2.388 ± 0.003 A in V_2O_5,[22] and 2.43 ± 0.05 A in $Na_3V_6O_{15}$.[23] A pair of bridging oxygen atoms between two highly charged cations is frequently drawn quite close together. Between octahedrally coordinated aluminum in aluminosilicates, for example, this distance often lies between 2.4 and 2.5 A. The distances found in the V_2O_8 groups seem to be unusually short. Nevertheless, the shortest distance of this type that has been reported so far was found by Burnham and Buerger[37] in andalusite (Al_2SiO_5) for a pair of oxygen atoms bridging two aluminum atoms in fivefold coordination, namely, 2.247 ± 0.007 A.

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Notes

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Preliminary Crystallographic Studies on the Systems Calcium–Lanthanum–Hydrogen and Calcium–Yttrium–Hydrogen

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Solid solutions of yttrium trifluoride in calcium fluoride have been known since 1914[2] and have recently been definitely characterized by Short and Roy.[3] Up to 55 mole % YF_3 enters the fluorite lattice, the extra F^- of YF_3 entering the octahedral holes of CaF_2 until these are filled at a nominal 50%. The crystallographic analogy of hydride ion in saline hydrides to fluoride ion suggested the investigation of corresponding calcium–rare earth–hydrogen systems. Lanthanum and yttrium were chosen for first investigation by virtue of differing ionic size; the Zachariasen[4] ionic radii are: Ca^{2+}, 0.94 A; La^{3+}, 1.04 A; Y^{3+}, 0.88 A. CaH_2 is orthorhombic;[5] lanthanum forms an fcc fluorite phase from (approximately) LaH_2 through LaH_3;[6] YH_2 is fcc fluorite and YH_3 is hexagonal.[7] All of these are nonstoichiometric to some extent.

Experimental Section

The calcium metal was obtained from Dominion Magnesium, Ltd., Toronto, Canada, 99.9%. Lanthanum was obtained from Cerium Metals Division of Ronson Metals, Inc., Newark, N. J., 99+%. Yttrium was obtained from United Mineral and Chemical Co., New York, N. Y., 99+%.

The metals were weighed out into molybdenum boats in an argon glove box and allowed to react with catalytically purified hydrogen at elevated temperatures. The amount of hydrogen taken up was determined by *P–V–T* measurements. Each sample was ground to powder in an agate mortar in the argon drybox, and a sample was withdrawn for X-ray powder crystallography. The bulk of the sample was returned to the hydrogen reaction system, where it was further exposed to measured hy-

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