Crystal structure of $Cd(VO_3)_2 \cdot 4H_2O$ and its comparison with the structure of $Ca(VO_3)_2 \cdot 4H_2O$ and α-$Cd(VO_3)_2$

Ľ. ULICKÁ

*Department of Inorganic Chemistry, Faculty of Natural Sciences,
Comenius University, 842 15 Bratislava*

Crystals of $Cd(VO_3)_2 \cdot 4H_2O$ were prepared by the reaction between $Cd(CH_3COO)_2$ and NH_4VO_3 in aqueous solution. The compound crystallizes in the monoclinic system, the space group is Cc, $a = 1.3319(6)$ nm, $b = 1.0344(5)$ nm, $c = 0.7044(2)$ nm, $\beta = 111.51(3)°$ and there are four formula units in the unit cell. The structure was determined and refined by conventional methods using data measured on an automatic diffractometer. The final R value was 0.040 for 890 observed diffractions. Each vanadium atom is coordinated by five oxygen atoms forming a tetragonal pyramid which is connected with the others into the chain parallel to the c axis. The cadmium atom is coordinated octahedrally by four oxygen atoms and two water molecules. The relation between the structure of $Cd(VO_3)_2 \cdot 4H_2O$, $Ca(VO_3)_2 \cdot 4H_2O$, and α-$Cd(VO_3)_2$ is discussed.

Получены кристаллы $Cd(VO_3)_2 \cdot 4H_2O$ путем реакции между $Cd(CH_3COO)_2$ и NH_4VO_3 в водном растворе. Данное соединение кристаллизуется в моноклинной системе, пространственная группа симметрии Cc, $a = 1,3319(6)$ нм, $b = 1,0344(5)$ нм, $c = 0,7044(2)$ нм, $\beta = 111,51(3)°$, и в первичной ячейке находятся четыре формульные единицы. Строение было определено и уточнено с помощью обычных методов, используя данные, полученные на автоматическом дифрактометре. Конечное значение R было 0,040 для 890 наблюдаемых дифракций. Каждый атом ванадия координирован с пятью атомами кислорода, образуя тетрагональную пирамиду, связанную с остальными подобными в цепь, параллельную оси c. Атом кадмия координирован октаэдрически четырьмя атомами кислорода и двумя молекулами воды. Обсуждается взаимосвязь между строением $Cd(VO_3)_2 \cdot 4H_2O$, $Ca(VO_3)_2 \cdot 4H_2O$ и α-$Cd(VO_3)_2$.

Study of the structural aspects of metavanadates has been aimed in recent years at anhydrous salts of M^IVO_3 (M = NH$_4$, K, Li, Na, Tl) and $M^{II}(VO_3)_2$ (M = Zn, Cd, Cu, Mg, Pb) composition, prepared by reactions in solid state [1—14]. The small number of determined structures for hydrated metavanadates, *i.e.* $KVO_3 \cdot H_2O$, $Ca(VO_3)_2 \cdot 4H_2O$, $Ca(VO_3)_2 \cdot 2H_2O$, $Sr(VO_3)_2 \cdot 4H_2O$, and $Co(VO_3)_2 \cdot 4H_2O$ [15—19] is caused by problems connected with their synthesis.

The composition of vanadates which are obtained by reactions in aqueous solutions is influenced by several factors; the pH of the reaction solution is the most important of them. Its value is quite specific for the vanadate of each metal. Moreover, in the case of a few soluble compounds, the preparation of crystals with a size suitable for the application of monocrystal diffraction methods is a problem, too.

$Cd(VO_3)_2 \cdot 4H_2O$ monocrystals of a required size were obtained by taking into account the results of many reactions between NH_4VO_3 and $Cd(CH_3COO)_2$ under various conditions. Thus, the chance for a structural study of additional hydrated metavanadate as well as a comparison with the structures of analogous metavanadates was possible. From the point of mutual relationship between the structure and thermal reactivity of metavanadates, a comparison of the studied compound with hydrated calcium metavanadate appears to be important. For this reason the preliminary $Cd(VO_3)_2 \cdot 4H_2O$ structure [20] was refined and the results are presented in this paper.

Experimental

Preparation

Crystals of $Cd(VO_3)_2 \cdot 4H_2O$ were prepared by the reaction between ammonium metavanadate and cadmium acetate. The syntheses have been successful only when pH values of the used reaction solutions were in the range from 6.1 to 6.4. The best results were obtained by using the following procedure: 500 cm^3 of 0.040 molar solution of cadmium acetate was added to 1250 cm^3 of 0.027 molar solution of ammonium metavanadate. The solution was stirred until the fine precipitate was filtrable. The clear solution was kept in the refrigerator for 24 h. $Cd(VO_3)_2 \cdot 4H_2O$ crystals were obtained by a concentration of the solution using a vacuum evaporator. Analysis: ($M = 382.31 \text{ g mol}^{-1}$) w_i(calc.): 29.40 % Cd, 26.67 % V, 18.95 % H_2O; w_i(found): 29.14 % Cd, 26.65 % V, 18.56 % H_2O.

The cadmium content was determined complexometrically [21]. The vanadium content was found volumetrically using 0.1 molar solution of $FeSO_4$ [22] and water amount by drying the samples to 350 °C.

Collection of X-ray data

The $hk0$, $0kl$, and $h0l$ were recorded on Weissenberg photographs and used for a preliminary choice of unit cell dimensions as well as for the determination of the space group. Systematically absent diffractions with hkl and $h0l$ when $h + k = 2n + 1$, $l = 2n + 1$ pointed out the space group $C2/c$ or Cc. Comparing IR and Raman spectra of the prepared compound, the group Cc was considered as more probable. Nevertheless,

a model of the structure was refined in both groups, however, the results in the case of $C2/c$ group were much worse.

The accurate lattice parameters were determined and intensity data measured on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a graphite crystal monochromator, using $MoK\alpha$ radiation. A least-squares fit of the four position angles for fifteen reflections produced the orientation matrix required to control data collection and afforded the following unit cell dimensions: $a = 1.3319(6)$ nm, $b = = 1.0344(5)$ nm, $c = 0.7041(2)$ nm, $\beta = 111.51(3)°$. Assuming a value of Z equal to 4, the density 2.81 g cm^{-3} was calculated and 2.78 g cm^{-3} (flotation method) measured.

Data were collected in the range of $0° < 2\Theta \leq 55°$. The $\Theta - 2\Theta$ technique with a variable scan rate from 4.0 to 24.0 deg min^{-1} was used. The background counts were taken at each end of the range for a time equal to one half of the scan time. In order to check the stability of the measurement, two reflections were selected as standards and their intensities were recorded periodically throughout the data collection (every 320 reflections). Of the 1039 reflections which were collected, 890 reflections with $I > 3\sigma(I)$ were considered to be observed and used in the analysis. The intensities and their standard deviation were corrected for the Lorentz polarization factor and the polarization of the monochromator. The linear absorption coefficient was 44.9 cm^{-1} for $MoK\alpha$, $\mu R = 0.413$.

Refinement of X-ray data

The structure was determined by the standard heavy-atom method. The cadmium atom was located by means of a three-dimensional Patterson map. The solution and the

Table 1

Atomic and thermal parameters for $Cd(VO_3)_2 \cdot 4H_2O$ with standard deviation in parentheses

Atom	x	y	z	B_{eq}/B
Cd	0.0000	0.2503(3)	0.2500	0.99
V(1)	0.1447(5)	0.4741(5)	0.0522(8)	0.97
V(2)	0.3513(5)	0.5255(6)	0.4365(8)	1.00
O(1)	0.0867(12)	0.3338(13)	0.0498(21)	1.17(29)
O(2)	0.0398(13)	0.4318(16)	0.4448(25)	1.58(32)
O(3)	0.3102(9)	0.4538(10)	0.1726(17)	0.47(21)
O(4)	0.1908(11)	0.5142(11)	0.3369(19)	1.12(24)
O(5)	0.4488(12)	0.5836(14)	0.0300(22)	1.04(27)
O(6)	0.3959(11)	0.6725(14)	0.4184(21)	1.10(28)
O(7)	0.1392(12)	0.1230(14)	0.4657(22)	1.47(30)
O(8)	0.3545(13)	0.8525(15)	0.0147(24)	1.86(33)
O(9)	0.1316(15)	0.8743(20)	0.3500(31)	3.40(47)
O(10)	0.3465(13)	0.1246(17)	0.1294(25)	1.81(31)

$$B_{eq} = \frac{4}{3}\sum_i\sum_j B_{ij}a_ia_j.$$

refinement of the structure were carried out by the usual sequence of Fourier Syntheses and full-matrix least-squares refinements. The function minimized was: $\Sigma w(|F_o| - |F_c|)^2$ and $w = 1/\sigma_{F2}$, where $\sigma_{F2} = (F_o^2 + \sigma(I)/L_p)^{1/2} - F_o$. The final R values were $R = 0.040$ and $R_w = 0.046$. Parameter changes in the final cycle were all less than 0.25 times the ESD of 66 parameters. The refined atomic positions and temperature factors are listed in Table 1. The observed and calculated structure factors of $Cd(VO_3)_2 \cdot 4H_2O$ are available on request from the author.

All calculations were carried out on a Siemens 4004/151 computer using programs written by *P. Gautzel, R. Sparks, K. Trueblood*, and *A. Zalkin*. The mentioned programs were modified by *O. Lindgreen*.
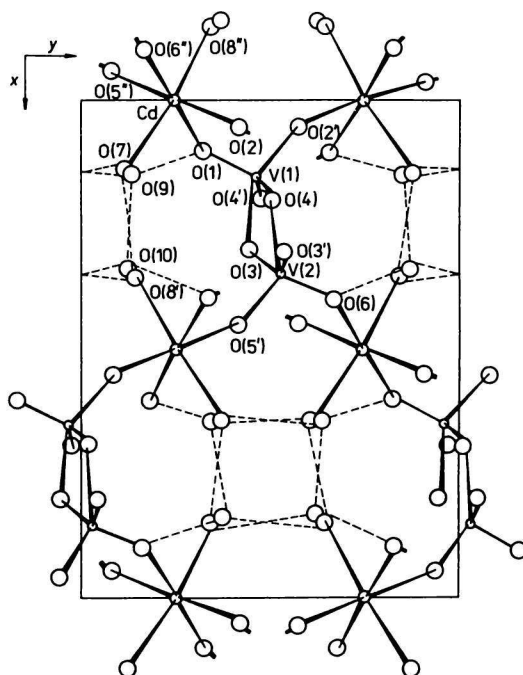

Fig. 1. Projection of the $Cd(VO_3)_2 \cdot 4H_2O$ structure on the (001) plane.

Results and discussion

The crystal structure of $Cd(VO_3)_2 \cdot 4H_2O$ in the (001) projection is shown in Fig. 1. With respect to the atomic positions and the procedure of their refinement, the given structure can be considered as pseudo-centrosymmetrical; pseudo-centrum of symmetry lies on the coordinates 0.250 0.500 0.250. The metavanadate anion is formed by VO_5 polyhedra which are connected into

14

Table 2

Interatomic distances and bond angles for $Cd(VO_3)_2 \cdot 4H_2O$ with standard deviations in parentheses

Atoms	d/nm	Atoms	$\varphi/°$
V(1)—O(1)	0.164(1)	O(4′)—V(1)—O(4)	140.7(8)
V(1)—O(2′)	0.164(1)	O(2′)—V(1)—O(3)	148.2(7)
V(1)—O(4)	0.183(1)	O(2′)—V(1)—O(4)	104.2(7)
V(1)—O(4′)	0.191(1)	O(1)—V(1)—O(2′)	101.6(8)
V(1)—O(3)	0.206(1)	O(3)—V(1)—O(4)	73.0(5)
		O(1)—V(1)—O(3)	110.0(6)
V(2)—O(6)	0.165(1)	O(3)—V(2)—O(3′)	144.6(7)
V(2)—O(5′)	0.166(1)	O(4)—V(2)—O(5′)	132.8(7)
V(2)—O(3)	0.188(1)	O(6)—V(2)—O(3′)	100.8(6)
V(2)—O(3′)	0.194(1)	O(6)—V(2)—O(4)	113.3(7)
V(2)—O(4)	0.199(1)	O(4)—V(2)—O(3)	75.1(5)
		O(5′)—V(2)—O(6)	113.8(8)
V(1)—V(2)	0.311(0)		
Cd—O(1)	0.229(1)	O(1)—Cd—O(2)	90.0(5)
Cd—O(2)	0.227(1)	O(5″)—Cd—O(6″)	89.9(5)
Cd—O(5″)	0.225(1)	O(6″)—Cd—O(2)	91.7(5)
Cd—O(6″)	0.227(1)	O(7)—Cd—O(8″)	172.8(5)
Cd—O(7)	0.232(1)	O(1)—Cd—O(5″)	87.6(5)
Cd—O(8″)	0.229(1)		
O(7)—O(8′)	0.277(2)		
O(1)—O(9′)	0.275(2)	O(1)—O(9′)—O(7′)*	127.1(9)
O(7)—O(9′)	0.274(2)	O(9′)—O(7)—O(8′)	106.6(7)
O(7)—O(9)*	0.268(2)	O(9′)—O(7)—O(9)*	107.2(7)
O(10)—O(9′)	0.281(2)	O(7)—O(9′)—O(10)	107.0(8)

* Neighbouring unit cell.

infinite chains along the *c* axis. Interatomic V—O distances as well as the O—V—O bond angles point out two sorts of differently deformed polyhedra (Table 2). With respect to the bond angles, these polyhedra should be better considered as tetragonal pyramids than trigonal bipyramids. Repulsive forces between V(1) and V(2) atoms cause considerable differences in the interatomic V—O distances (terminal and bridged bonds). The values near 0.16 nm can be assigned to predominantly double covalent bonds and values above 0.18 nm to simple covalent bonds with some ionic contribution [23].

Cadmium atoms in the structure are coordinated octahedrally. Equatorial positions are occupied by four oxygen atoms which are shared with neighbouring vanadium atoms (atoms O(1), O(2), O(5), and O(6)), in the axial positions of the octahedron there are two water molecules (represented by oxygen atoms O(7) and O(8)). The greater distortion of the $CdO_4(H_2O)_2$ octahedron in the

Table 3

Interatomic distances

Cd(VO$_3$)$_2$·4H$_2$O		α-Cd(VO$_3$)$_2$ [9]		Ca(VO$_3$)$_2$·4H$_2$O [16]	
Atoms	d/nm	Atoms	d/nm	Atoms	d/nm
V(1)—O(1)	0.164			V(2)—O(4)	0.1632
V(1)—O(2')	0.164			V(2)—O(7)	0.1660
V(1)—O(4)	0.183			V(2)—O(2)	0.1862
V(1)—O(3)	0.206			V(2)—O(2')	0.2198
V(2)—O(6)	0.165	V—O(1)	0.171	V(1)—O(5)	0.1636
V(2)—O(5')	0.166	V—O(2)	0.169	V(1)—O(6)	0.1648
V(2)—O(3)	0.188	V—O(3')	0.188	V(1)—O(2)	0.1898
V(2)—O(4)	0.199	V—O(3)	0.198	V(1)—O(1')	0.1984

axial direction (Table 2) could be caused by additional H bonds. Water molecules in the axial positions join neighbouring octahedra CdO$_4$(H$_2$O)$_2$ by means of H bonds and moreover, they are bound to the remaining two molecules of water (represented by O(9) and O(10)) located in the free cavities of the crystal structure.

The above facts prove the existence of two kinds of water molecules in the Cd(VO$_3$)$_2$·4H$_2$O crystal structure: *a*) water molecules coordinated to the cadmium atoms; each of them participates in one donor—acceptor bond and three H bonds, *b*) water molecules occupying cavities in the structure; they are bound by means of H bonds to the three neighbouring water molecules and to one terminal oxygen atom of VO$_5$ pyramid. Interatomic distances O $\cdots$ O are given in Table 2.

The structure of Cd(VO$_3$)$_2$·4H$_2$O described herein differs from that of Ca(VO$_3$)$_2$·4H$_2$O [16] above all in the shape of cadmium and calcium coordination polyhedron. While in the cadmium salt octahedral CdO$_4$(H$_2$O)$_2$ has been found, the calcium atom is eight-fold coordinated in the form of a square antiprism of CaO$_3$(H$_2$O)$_5$ composition. Given coordination number differences could be explained by different bonding properties of both elements. With respect to the electron configuration and low electronegativity, calcium atom has a tendency to the formation of predominantly ionic bonds. In addition, the Ca^{2+} cation belongs to hard acids and shows affinity to water as a hard base. The coordination number of calcium atom in Ca(VO$_3$)$_2$·4H$_2$O is therefore allowed by the radius ratio r_C/r_A, *i.e.* 6—8 and all of the water molecules take part in its coordination. On the other hand, cadmium ions form bonds of more covalent character (are softer) so that charge neutralization occurs with fewer oxygen donors than is the case with calcium ions. This effect coupled with a

slightly smaller size of the calcium ions, provides six-coordinate cadmium in this salt.

Vanadium atoms have five-fold oxygen coordination in both discussed compounds. Interatomic V—O distances in $Cd(VO_3)_2 \cdot 4H_2O$ differ from those in $Ca(VO_3)_2 \cdot 4H_2O$ only slightly, with the exception of the longest bond. The value of this bond in the case of calcium salt is 0.219 nm and in cadmium metavanadate 0.206 nm (Table 3).

Specific features of the structure of metavanadate discussed manifest themselves in its thermal properties, above all in the manner of dehydration. The dehydration of $Ca(VO_3)_2 \cdot 4H_2O$ takes place in two steps with intermediate $Ca(VO_3)_2 \cdot 2H_2O$ [24]. The two-step dehydration is enabled by the different manner by which water molecules are bound in the structure. The crystal structure of $Ca(VO_3)_2 \cdot 2H_2O$ [17] formed after the loss of the two water molecules with the least number of bonds is close to that of $Ca(VO_3)_2 \cdot 4H_2O$. The coordination number of calcium is again 8 and the composition of the coordination sphere is $CaO_5(H_2O)_3$.
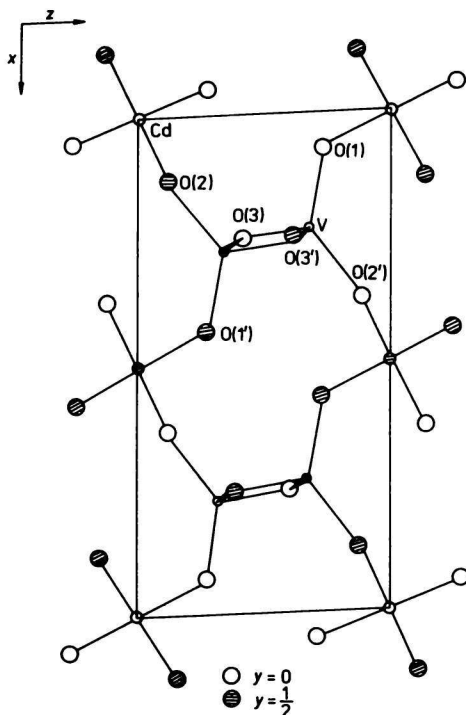

Fig. 2. Projection of the α-$Cd(VO_3)_2$ structure on the (010) plane [9].

In contrast to the Ca salt, the dehydration of $Cd(VO_3)_2 \cdot 4H_2O$ is continual without formation of an intermediate dihydrate [25]. This fact is rather surprising with respect to the presence of two kinds of water molecules in the structure of given compound. It is thus obvious that in the process of dehydration not only the number and strength of water molecule bonds must be taken into account, but also the destabilization of the structure caused by partial dehydration. Considering the temperature factors of the oxygen atoms (Table 1), the high value of this factor for O(9) could indicate that the dehydration of $Cd(VO_3)_2 \cdot 4H_2O$ starts with water molecules localized in the cavities of the structure. This presumption is sustained also by the fact that these molecules are bound in the structure by weak H bonds only. It is probable that the original stability of the structure is brought down to such an extent that the structural changes which should follow the partial dehydration are energetically less advantageous than the total dehydration. This concept is in agreement with the found one-step dehydration of the compound in question [25].

The tendency of cadmium atom to octahedral coordination manifests itself in the anhydrous metavanadate, too. However, the octahedral CdO_6 could form only at the expense of a marked rearrangement of the atoms in the structure of α-$Cd(VO_3)_2$ [9] (Fig. 2) which is stable at lower temperature than β-$Cd(VO_3)_2$ [8]. Interatomic distances for V—O_{term} in the α-$Cd(VO_3)_2$ are a bit longer than in $Cd(VO_3)_2 \cdot 4H_2O$ (Table 3). On the other hand, the Cd—O distances are shorter in the anhydrous salt. This phenomenon could be explained by increased polarization of the Cd-O bonds with the temperature increase.

References

1. Petrášová, M., Maďar, J., and Hanic, F., *Chem. Zvesti 12*, 410 (1958).
2. Syneček, V. and Hanic, F., *Czechoslov. J. Phys. 4*, 120 (1954).
3. Evans, H. T., Jr., *Z. Kristallogr. 114*, 257 (1960).
4. Shannon, R. D. and Calvo, C., *Can. J. Chem. 51*, 265 (1973).
5. Marumo, F., Isobe, M., and Iwai, S., *Acta Crystallogr. B30*, 1628 (1974).
6. Ganne, M., Piffard, Y., and Touroux, M., *Can. J. Chem. 52*, 3539 (1974).
7. Angenault, J. and Rimsky, A., *C. R. Acad. Sci.* (Paris) *t267*, 227 (1968).
8. Bouloux, J. C. and Galy, J., *Bull. Soc. Chim. Fr. 3*, 736 (1969).
9. Bouloux, J. C., Perez, G., and Galy, J., *Bull. Soc. Fr. Mineral. Cristallogr. 95*, 130 (1972).

10. Lavaud, D. and Galy, J., *Bull. Soc. Fr. Mineral. Cristallogr. 95*, 134 (1972).
11. Hok Nam Ng and Calvo, C., *Can. J. Chem. 50*, 3619 (1972).
12. Jordan, B. D. and Calvo, C., *Can. J. Chem. 52*, 2701 (1974).
13. Calestani, G., Andreetti, G. D., and Montenero, A., *Acta Crystallogr. C41*, 177 (1985).
14. Calestani, G., Andreetti, G. D., and Montenero, A., *Acta Crystallogr. C41*, 179 (1985).
15. Christ, C. L., Clark, J. R., and Evans, H. T., Jr., *Acta Crystallogr. 7*, 801 (1954).
16. Ahmed, F. R. and Barnes, W. H., *Can. Mineralogist 7*, 713 (1963).
17. Kelsey, C. H. and Barnes, W. H., *Can. Mineralogist 6*, 448 (1962).
18. Sedlacek, P. and Dornberger-Schiff, K., *Acta Crystallogr. 18*, 407 (1965).
19. Safiyanov, Yu. N., Bochkova, P. I., Kuzmin, E. A., and Belov, N. V., *Dokl. Akad. Nauk SSSR 226*, 574 (1976).
20. Ulická, Ľ., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia) 28*, 153 (1980).
21. Sajó, I., *Komplexometria*. Technical Publishing House, Budapest, 1973.
22. Tomíček, O., *Kvantitativní analysa*. (Quantitative Analysis) P. 278. Státní zdravotnické nakladatelství. (State Publishing House of Public Health.) Prague, 1958.
23. Bachman, H. G. and Barnes, W. H., *Z. Kristallogr. 115*, 215 (1961).
24. Gőczeová, Č., unpublished results.
25. Ulická, Ľ., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia) 20*, 11 (1974).

Translated by Ľ. Ulická