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Revised Space Groups for Three Molybdenum(V) Phosphate Compounds

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The space groups of three previously described Mo(V) phosphate structures are revised. (1) δ-$KMo_2P_3O_{13}$, originally reported as triclinic, $P\bar{1}$, is revised to monoclinic, $C2/c$; it is identical to the compound previously identified as $K_4Mo_8P_{12}O_{52}$. (2) The compound formulated as $[Mo_{12}CdP_8O_{50}(OH)_{12}]Cd[N(CH_3)_4]_2(H_3O)_6\cdot 5H_2O$, originally described as monoclinic, Pn, is revised to $P2_1/n$ (also monoclinic). (3) $Rb_3O_2(MoO)_4(PO_4)_4$, originally reported as orthorhombic, $C222_1$, is revised to tetragonal, $P4_32_12$. The general descriptions of the structures are unchanged; however, for compound 2 the revision involves the addition of a center of symmetry and, as a result, there are significant changes in the interatomic distances and angles. © 2001 Academic Press

INTRODUCTION

It is the purpose of this paper to point out that the crystal structures of three Mo(V) phosphate cluster compounds are better described in space groups of symmetry higher than that of those originally reported. For compound **1**, δ-$KMo_2P_3O_{13}$, which was reported (1) in space group $P\bar{1}$, the revised structure in space group $C2/c$ is identical to that previously reported (2) for $K_4Mo_8P_{12}O_{52}$. For compound **2**, $[Mo_{12}CdP_8O_{50}(OH)_{12}]Cd[N(CH_3)_4]_2(H_3O)_6\cdot 5H_2O$, originally described (3) in the noncentrosymmetric space group Pn, re-refinement in the centrosymmetric $P2_1/n$ leads to more reasonable interatomic distances. Revision of compound **3**, $Rb_3O_2(MoO)_4(PO_4)_4$, is from space group $C222_1$ to $P4_32_12$.

EXPERIMENTAL

For compound **1**, the transformation matrix $(1, 1, -1)$, $(1, -1, -1)$, $(-1, 0, 0)$, when applied to the original triclinic cell dimensions (1), leads to a C-centered monoclinic cell. The 5243 reflections used in the triclinic refinement ($I \geq 3\sigma$) were similarly transformed and averaged according to $2/m$ Laue symmetry; the value of R(merge) was 0.0125. There were no reflections that violated the extinction requirement for the c-glide plane in $C2/c$. Least-squares refinement in $C2/c$ was straightforward, leading to an R of 0.020 for 2828 reflections compared to the R of 0.022 for the $P\bar{1}$ refinement. Final coordinates and cell dimensions are effectively identical to those in Ref. (2). We note that the cell reduction software associated with the diffractometer used in the original investigation was not able to find the correct cell transformation.

For compound **2**, the first step was to shift the y coordinates by 0.25, in order to place the center of symmetry at a conventional origin in $P2_1/n$; pairs of equivalent atoms could then be matched across this symmetry center within an *rms* deviation of about 0.08 Å. Refinement in $P2_1/n$ proceeded smoothly to an R of 0.038 for 271 parameters (Cd, Mo, and P anisotropic; O, C, and N isotropic; Hs of $N(CH_3)_4$ group in assumed positions, other Hs ignored) compared to the R of 0.036 for 442 parameters in the earlier Pn description (3). Coordinates are in Table 1.

For compound **3** (4), the transformation matrix $(\frac{1}{2}, -\frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, 0, 1)$ generates a tetragonal cell; transforming and averaging the F values according to point symmetry 422 led to an R(merge) of 0.014. After transforming and averaging the coordinates, refinement in $P4_32_12$ resulted in no significant coordinate shifts and in an R of 0.030 for 2362 reflections—effectively identical to the R of 0.029 for 2523 reflections reported previously for space group $C222_1$. Coordinates for space group $P4_32_12$ are in Table 2.

DISCUSSION

For compound **1**, the revised cell dimensions and atom coordinates are in nearly exact agreement with the values

TABLE 1

$[Mo_{12}CdP_8O_{50}(OH)_{12}]$ $[Cd(H_3O)_6]$ $[N(CH_3)_4]_2 \cdot 5H_2O$: Coordinates, Space Group $P2_1/n$ (Cell Dimensions: $a = 15.123(1)$ Å, $b = 12.305(1)$ Å, $c = 19.264(2)$ Å, $\beta = 98.620(8)°$)

Atom	*x*	*y*	*z*	U_{eq}[a] or U_{iso}
Cd1	0	0	0	0.0114(2)
Cd2	0	0	0.5	0.0119(2)
Mo1	0.4836(1)	0.6464(1)	0.6761(1)	0.0114(2)
Mo2	0.3807(1)	0.7462(1)	0.5754(1)	0.0120(2)
Mo3	0.2534(1)	0.5910(1)	0.4410(1)	0.0120(2)
Mo4	0.2635(1)	0.3805(1)	0.4424(1)	0.0114(2)
Mo5	0.4033(1)	0.2456(1)	0.5799(1)	0.0113(2)
Mo6	0.4956(1)	0.3591(1)	0.6794(1)	0.0116(2)
P1	0.3023(2)	0.4896(3)	0.6076(1)	0.0107(4)
P2	0.4658(2)	0.5034(3)	0.8226(1)	0.0143(5)
P3	0.1613(3)	0.7684(3)	0.5399(2)	0.0184(6)
P4	0.1864(3)	0.1980(3)	0.5443(2)	0.0164(5)
O1	0.5625(7)	0.7401(8)	0.6990(6)	0.0211(18)[b]
O2	0.3710(7)	0.7218(7)	0.6733(6)	0.0134(15)[b]
O3	0.4778(7)	0.6390(7)	0.5735(6)	0.0119(16)[b]
O4	0.4760(10)	0.6046(7)	0.7797(8)	0.0188(21)[b]
O5	0.5653(5)	0.5088(8)	0.6803(4)	0.0119(13)[b]
O6	0.3916(5)	0.4954(9)	0.6580(4)	0.0130(13)[b]
O7	0.4347(7)	0.8654(8)	0.5725(6)	0.0220(18)[b]
O8	0.3489(7)	0.7172(7)	0.4669(6)	0.0119(15)[b]
O9	0.2535(7)	0.8121(7)	0.5668(6)	0.0189(18)[b]
O10	0.2971(7)	0.5910(7)	0.5597(6)	0.0114(15)[b]
O11	0.2242(7)	0.6181(7)	0.3557(5)	0.0195(18)[b]
O12	0.3572(5)	0.4924(8)	0.4426(4)	0.0119(13)[b]
O13	0.1723(5)	0.4798(6)	0.4635(5)	0.0150(15)[b]
O14	0.1643(7)	0.7008(7)	0.4734(5)	0.0182(16)[b]
O15	0.2365(7)	0.3521(7)	0.3562(6)	0.0186(16)[b]
O16	0.3067(7)	0.3892(6)	0.5599(6)	0.0115(16)[b]
O17	0.1832(6)	0.2577(7)	0.4743(5)	0.0181(16)[b]
O18	0.3677(7)	0.2682(7)	0.4696(6)	0.0140(16)[b]
O19	0.3913(7)	0.2686(7)	0.6787(6)	0.0148(16)[b]
O20	0.2824(7)	0.1663(7)	0.5736(6)	0.0175(18)[b]
O21	0.4671(7)	0.1347(8)	0.5771(6)	0.0199(18)[b]
O22	0.4910(7)	0.3624(8)	0.5765(6)	0.0130(16)[b]
O23	0.4766(10)	0.4008(7)	0.7793(8)	0.0179(20)[b]
O24	0.5832(7)	0.2775(7)	0.7052(6)	0.0199(19)[b]
O25	0.2204(6)	0.4808(7)	0.6435(5)	0.0180(16)[b]
O26	0.5292(5)	0.5069(9)	0.8899(4)	0.0182(14)[b]
O27	0.3652(5)	0.5008(11)	0.8378(5)	0.0204(14)[b]
O28	0.1363(8)	0.6880(8)	0.5978(7)	0.0280(21)[b]
O29	0.0879(7)	0.8491(8)	0.5296(6)	0.0241(19)[b]
O30	0.1266(7)	0.1010(7)	0.5397(6)	0.0220(18)[b]
O31	0.1512(8)	0.2779(8)	0.6000(6)	0.0241(20)[b]
H_2O1	0.4754(12)	0.2079(12)	0.1416(9)	0.0510(38)[b]
H_2O2	−0.0344(12)	0.7200(12)	0.6306(10)	0.0519(38)[b]
H_2O3	0.8597(8)	0.4989(19)	0.1816(7)	0.0588(29)[b]
H_2O4	−0.0382(9)	0.4945(19)	0.3128(7)	0.0692(34)[b]
H_2O5	0.2594(9)	0.3318(9)	0.7629(7)	0.0431(28)[b]
H_2O6[c]	−0.0200(23)	0.5293(28)	0.4634(16)	0.0836(100)[b]
N	0.7860(8)	0.5065(14)	0.8486(6)	0.0325(22)[b]
C1	0.7339(18)	0.4113(18)	0.8187(14)	0.0520(54)[b]
C2	0.7355(18)	0.6064(17)	0.8310(14)	0.0509(55)[b]
C3	0.8662(13)	0.5044(28)	0.8127(10)	0.0621(45)[b]
C4	0.8136(16)	0.5057(35)	0.9255(12)	0.0830(81)[b]

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j [U_{ij}(a_i^*, a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$.

[b] U_{iso}.

[c] Population = 0.5.

TABLE 2

$Rb_3O_2(MoO)_4(PO_4)_4$: Coordinates, Space Group $P4_32_12$ (Cell Dimensions: $a = 10.057(1)$ Å, $c = 19.227(4)$ Å)

Atom	*x*	*y*	*z*
Rb1	−0.3877	0.4948	0.1265
Rb2	0.2918	0.7082	0.25
Mo1	−0.0162	0.3643	0.0603
Mo2	0.2446	0.6056	0.0637
P1	0.2387	0.3443	0.1696
P2	−0.0446	0.6455	0.1600
O1	0.0234	0.2294	0.0136
O2	0.1210	0.4772	0.0368
O3	0.0970	0.3166	0.1448
O4	−0.1396	0.4518	−0.0096
O5	−0.1719	0.2663	0.1074
O6	−0.0906	0.5154	0.1274
O7	0.3726	0.5652	0.0128
O8	0.1574	0.7403	0.0003
O9	0.3544	0.7464	0.1137
O10	0.2922	0.4814	0.1466
O11	0.0951	0.6840	0.1376

reported (2) for $K_4Mo_8P_{12}O_{52}$, and there can be no doubt that the crystals were effectively identical; the description of the structure is unchanged. Similarly, the re-refinement of compound **3** in the higher Laue symmetry has led to no significant change in the description of the structure.

But the situation is quite different for compound **2**, where re-refinement in the centrosymmetric space group $P2_1/n$ has led to highly significant changes in the atom coordinates and, hence, in the interatomic distances. The distances we obtain for the $P2_1/n$ results are, in general, considerably more reasonable. For example, within the tetramethylammonium cation the C–N distances calculated from the *Pn* coordinates ranged from 1.48 to 1.64 Å and the C–N–C angles from 87° to 133°, whereas the $P2_1/n$ refinement leads to much more sensible values: 1.46–1.48 Å and 106–113°. In the groupings of the different types of Mo–O bonds (see Table 4, Ref. 3), the scatter of individual values is reduced by a factor of approximately 5. Such differences are typical of the centrosymmetric–noncentrosymmetric dilemma and usually (as in the present case) lead to the conclusion that the centrosymmetric choice is to be preferred.

In view of the improvements in the positions of the heavier atoms, we had hoped that the details of the extensive hydrogen-bonding network might become apparent. We were, for the most part, disappointed; while some of the largest peaks in a final difference map were in reasonable sites for hydrogen atoms, most were not, and we were unable to arrive at a definitive pattern of hydrogen bonding. The geometry of the MoO_6 octahedra is characteristic of Mo(V) (5) and the bond valence sums (BVS) associated with the Mo atoms, as calculated with the general formula of Zocchi (6), also agree with Mo(V). The BVS values determined as in Ref. (3) show that the large, centrosymmetric cluster of Mo–O octahedra and P–O tetrahedra has the composition $CdMo_{12}P_8O_{62}H_{12}$. Of the six H atoms in the asymmetric unit of this cluster, three are parts of P–OH groups and are easily identified as attached to O27, O28, and O31 (P–O = 1.59(1) Å and BVS = 1.07 vu). The remaining three are attached to O5, O8, and O18 as parts of OH bridges linking pairs of Mo octahedra (Mo–O = 2.12(2) Å and BVS = 1.10 vu); the nonprotonated bridging atoms O2, O13, and O19 have shorter Mo–O distances, 1.94(1) Å, and BVS values close to the expected value of 2. With this composition and an oxidation state of $+5$ for Mo, the cluster would have a formal charge of -10, which would require that six of the water molecules (three per asymmetric unit) be protonated. However, none of the O---O distances associated with potential hydrogen bonds is shorter than 2.75 Å, much too long to represent symmetric O--H--O bonds and also too long to suggest the strong hydrogen bonds that are usually associated with H_3O^+ ions. Perhaps the six hydrogen atoms are randomly spread over the 11 available water molecules, and the O--O distances observed for the potential hydrogen bonds are in fact mean values between short H_3O^+---H_2O bonds and longer distances corresponding to H_2O---H_2O bonds. The large U_{eq} values for these 11 oxygen atoms seem to support this point of view.

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