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New triple molybdates $Cs_3LiCo_2(MoO_4)_4$ and $Rb_3LiZn_2(MoO_4)_4$, filled derivatives of the $Cs_6Zn_5(MoO_4)_8$ type

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Two new isotypic triple molybdates, namely tricesium lithium dicobalt tetrakis(tetraoxomolybdate), $Cs_3LiCo_2(MoO_4)_4$, and trirubidium lithium dizinc tetrakis(tetraoxomolybdate), $Rb_3LiZn_2(MoO_4)_4$, crystallize in the non-centrosymmetric cubic space group $I\bar{4}3d$ and adopt the $Cs_6Zn_5(MoO_4)_8$ structure type. In the parent structure, the Zn positions have 5/6 occupancy, while they are fully occupied by statistically distributed M^{2+} and Li^+ cations in the title compounds. In both structures, all corners of the $(M_{2/3}Li_{1/3})O_4$ tetrahedra (M = Co and Zn), having point symmetry $\bar{4}$, are shared with the MoO_4 tetrahedra, which lie on threefold axes and share corners with three $(M,Li)O_4$ tetrahedra to form open mixed frameworks. Large alkaline cations occupy distorted cuboctahedral cavities with $\bar{4}$ symmetry. The mixed tetrahedral frameworks in the structures are close to those of mayenite ($12CaO{\cdot}7Al_2O_3$) and the related compounds $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$, wadalite ($Ca_6Al_5Si_2O_{16}Cl_3$) and $Na_6Zn_3(AsO_4)_4{\cdot}3H_2O$, but the terminal vertices of the MoO_4 tetrahedra are directed in opposite directions along the threefold axes compared with the configurations of $Al(Si)O_4$ or AsO_4 tetrahedra. The cation arrangements in $Cs_3LiCo_2(MoO_4)_4$, $Rb_3LiZn_2(MoO_4)_4$ and $Cs_6Zn_5(MoO_4)_8$ repeat the structure of $Y_3Au_3Sb_4$, being stuffed derivatives of the Th_3P_4 type.

Comment

Double molybdates of alkaline and bivalent ions formed in the A_2MoO_4–$MMoO_4$ systems (A = Li, Na, K, Rb and Cs, and M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and Ba) have been well known for at least three decades, and some of them, such as $K_4Zn(MoO_4)_3$ and $A_2Pb(MoO_4)_2$ (A = K, Rb and Cs), may be used as ferroelastic and other inorganic materials (Solodovnikov *et al.*, 1994). Most of the studied structures of these molybdates, for example, $Li_2Ni_2(MoO_4)_3$ (Ozima & Sato, 1977), $K_2Zn_2(MoO_4)_3$ (Gicquel-Mayer & Perez, 1975), $K_2Ni(MoO_4)_2$ (Klevtsova & Klevtsov, 1978) and $Rb_2Cu_2(MoO_4)_3$ (Solodovnikov & Solodovnikova, 1997), contain MO_6 octahedra and MoO_4 tetrahedra linked by the corners. Other O-atom coordinations of bivalent cations were found in the structures of $Rb_4Mn(MoO_4)_3$ and $Cs_4Cu(MoO_4)_3$ (Solodovnikov *et al.*, 1988), which contain trigonal bipyramids around M^{2+} ions (M = Mn and Cu), and in $K_4Zn(MoO_4)_3$ (Gicquel-Mayer *et al.*, 1980) and $Cs_6Zn_5(MoO_4)_8$ (Solodovnikov *et al.*, 1987; Mueller *et al.*, 1987), which contain ZnO_4 tetrahedra. The latter structure is unique among double salts with tetrahedral oxoanions and has an incomplete Zn position (site-occupation factor 5/6), leading to the formula $Cs_3(Zn_{5/6}\square_{1/6})_3(MoO_4)_4$, where □ denotes a cationic vacancy. The only triple molybdate known to date, which contains two monovalent cations along with a bivalent cation, *viz.* $AgKCu_3(MoO_4)_4$ (Szillat & Müller-Buschbaum, 1995), has a crystal structure very close to that of $K_2Cu_3(MoO_4)_4$ (Glinskaya *et al.*, 1980), with highly distorted CuO_6 octahedra. The present paper presents the crystal structure determination of two new triple molybdates, *viz.* $Cs_3LiCo_2(MoO_4)_4$, (I), and $Rb_3LiZn_2(MoO_4)_4$, (II), isolated upon studying the phase formation in the systems Cs_2MoO_4–Li_2MoO_4–$CoMoO_4$ and Rb_2MoO_4–Li_2MoO_4–$ZnMoO_4$.

In the title structures, the Li^+ and M^{2+} (M = Co and Zn) cations are statistically distributed in the 12a Wyckoff position (site symmetry $\bar{4}$), whereas the Cs and Mo atoms occupy the 12b (site symmetry $\bar{4}$) and 16c (site symmetry 3) positions, respectively. Atoms O1 and O2 are in the special 16c and general 48e positions, respectively, forming tetrahedral environments around the M,Li position and Mo atoms. Tetrahedral coordination of Co^{2+} is found for the first time among molybdates. Metal–oxygen distances in the $(M_{2/3}Li_{1/3})O_4$ tetrahedra (M = Co and Zn; Table 1) are in a good agreement with the Co—O (1.967–1.980 Å) and Li—O (1.774–2.092 Å) bond lengths in β_{II}-Li_2CoSiO_4 (Yamaguchi *et al.*, 1979), and the Zn—O (1.858–2.038 Å) bond lengths in $K_4Zn(MoO_4)_3$ (Gicquel-Mayer *et al.*, 1980). In the $Cs_6Zn_5(MoO_4)_8$ structure (Solodovnikov *et al.*, 1987; Mueller *et al.*, 1987), the slightly increased Zn—O distances (1.98–2.00 Å) could be caused by the presence of vacancies in the Zn positions.

In the structures of (I) and (II), the $(M_{2/3}Li_{1/3})O_4$ tetrahedra (M = Co and Zn) share all corners with the MoO_4 tetrahedra, which share three corners with adjacent $(M,Li)O_4$ tetrahedra to form open mixed frameworks (Fig. 1). Characteristic details of the frameworks are the eight-membered rings of alternating $(M_{2/3}Li_{1/3})O_4$ and MoO_4 tetrahedra (1–8 in Fig. 2). Each $(M_{2/3}Li_{1/3})O_4$ tetrahedron takes part in four rings, whereas the MoO_4 tetrahedron connects three rings. The eight-membered ring, together with four terminal MoO_4 tetrahedra (9–12 in Fig. 2) attached to the $(M_{2/3}Li_{1/3})O_4$ tetrahedra, form a cage around the large Cs^+ or Rb^+ cations, which have a distorted 12-fold cuboctahedral coordination.

Both compounds adopt the $Cs_6Zn_5(MoO_4)_8$ structure type (Solodovnikov *et al.*, 1987; Mueller *et al.*, 1987). Thus, (I) and (II) may be considered as completely filled derivatives of the $Cs_6Zn_5(MoO_4)_8$ structure following the scheme $5Zn^{2+} + \square \rightarrow 4M^{2+} + 2Li^+$. The cation arrangements in these three

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compounds repeat the atomic arrangement of the $Y_3Au_3Sb_4$ structure (Dwight, 1977), being stuffed derivatives of the Th_3P_4 type.

The mixed tetrahedral frameworks in (I), (II) and $Cs_6Zn_5(MoO_4)_8$ are close to those of mayenite ($12CaO\cdot 7Al_2O_3$; Bartl & Scheller, 1970) and the related compounds $11CaO\cdot 7Al_2O_3\cdot CaF_2$ (Williams, 1973), wadalite ($Ca_6Al_5Si_2O_{16}Cl_3$; Tsukimura *et al.*, 1993) and $Na_6Zn_3(AsO_4)_4\cdot 3H_2O$ (Grey *et al.*, 1989). However, there is an important difference: the terminal vertices of the MoO_4 tetrahedra are oppositely directed along the threefold axes compared with the $Al(Si)O_4$ or AsO_4 tetrahedra. The latter arrangement substantially changes the configuration of the tetrahedral cage around the out-of-framework ions, instead providing three new inner sites occupied by two Ca^{2+} or Na^+ cations, and O^{2-}, F^- or Cl^- anions or water molecules.

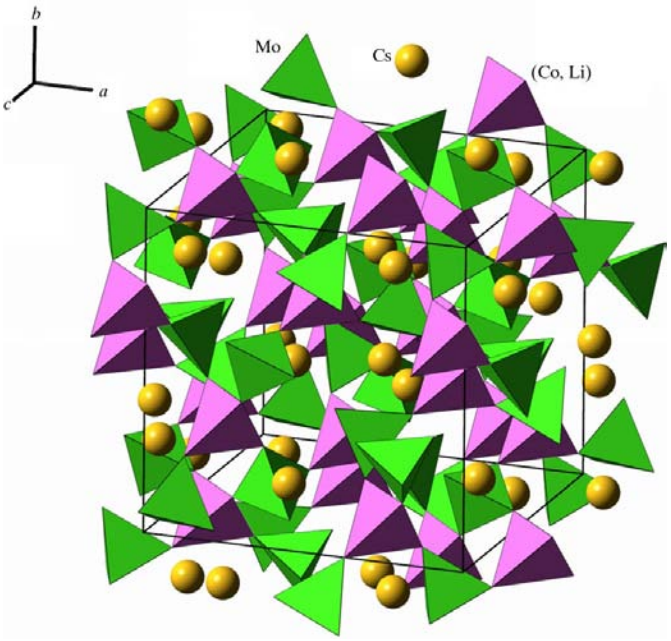

Figure 1
A general view of the $Cs_3LiCo_2(MoO_4)_4$ structure.

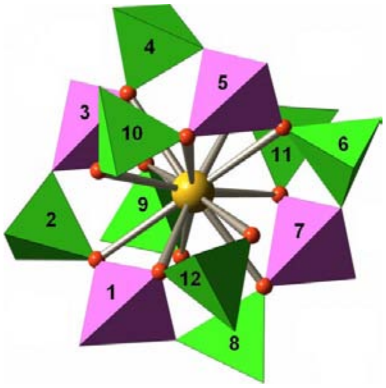

Figure 2
The tetrahedral cage around the Cs atom in the $Cs_3LiCo_2(MoO_4)_4$ structure. An eight-membered ring is indicated by the tetrahedra labelled 1–8; attached tetrahedra are numbered 9–12.

Experimental

Compounds (I) and (II) were revealed upon studying the systems Cs_2MoO_4–Li_2MoO_4–$CoMoO_4$ and Rb_2MoO_4–Li_2MoO_4–$ZnMoO_4$, respectively. Polycrystalline samples of the compounds were prepared by solid-state reactions from simple molybdates at 773 K for 150 h. Single crystals were grown by spontaneous crystallization of melted mixtures of Li_2MoO_4, Cs_2MoO_4, $2CoMoO_4$ and $2Cs_2Mo_2O_7$, and sintered $Rb_3LiZn_2(MoO_4)_4$ and $3Rb_2Mo_2O_7$, upon slow cooling at rates of 3 K h^{-1} in the ranges 873–673 and 793–673 K, respectively. X-ray powder diffraction patterns of ground crystals of both compounds were consistent with their calculated powder diffractograms, experimental X-ray diffraction data for corresponding sintered samples and the powder pattern reported for $Cs_6Zn_5(MoO_4)_8$ (Solodovnikov *et al.*, 1987). The crystals have the shapes of partly faceted fragments of a cubic habit with maximum dimensions of 2 mm.

Compound (I)

Crystal data

$Cs_3LiCo_2(MoO_4)_4$
$M_r = 1163.34$
Cubic, $I\bar{4}3d$
$a = 12.2239$ (2) Å
$V = 1826.54$ (5) Å^3
$Z = 4$
$D_x = 4.231$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2582 reflections
$\theta = 4.1$–$29.0°$
$\mu = 10.40$ mm^{-1}
$T = 293$ (2) K
Fragment, blue
0.11 × 0.10 × 0.01 mm

Data collection

Bruker–Nonius X8 APEX CCD diffractometer
φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.394$, $T_{max} = 0.903$
8959 measured reflections
705 independent reflections
615 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 35.9°$
$h = -19 \rightarrow 11$
$k = -19 \rightarrow 19$
$l = -19 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.038$
$S = 0.99$
705 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-3}
Absolute structure: Flack (1983), 303 Friedel pairs
Flack parameter: −0.002 (17)

Compound (II)

Crystal data

$Rb_3LiZn_2(MoO_4)_4$
$M_r = 1033.95$
Cubic, $I\bar{4}3d$
$a = 11.9018$ (14) Å
$V = 1685.9$ (3) Å^3
$Z = 4$
$D_x = 4.074$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5301 reflections
$\theta = 2.4$–$34.5°$
$\mu = 14.37$ mm^{-1}
$T = 293$ (2) K
Fragment, colourless
0.10 × 0.10 × 0.08 mm

Data collection

Bruker–Nonius X8 APEX CCD diffractometer
φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.264$, $T_{max} = 0.317$
7827 measured reflections
643 independent reflections
617 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 35.7°$
$h = -14 \rightarrow 18$
$k = -10 \rightarrow 19$
$l = -19 \rightarrow 17$

Acta Cryst. (2006). C**62**, i6–i8 Solodovnikova *et al.* • $Cs_3LiCo_2(MoO_4)_4$ and $Rb_3LiZn_2(MoO_4)_4$ **i7**

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.011$
$wR(F^2) = 0.026$
$S = 1.07$
643 reflections
21 parameters
$w = 1/[\sigma^2(F_o^2) + (0.009P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00099 (7)
Absolute structure: Flack (1983), 365 Friedel pairs
Flack parameter: 0.004 (6)

Table 1
Selected interatomic distances (Å) for (I) and (II).

	AM = CsCo	*AM* = RbZn
A—O1^{i}	3.350 (2)	3.2339 (19)
A—O2^{ii}	3.262 (2)	3.0307 (12)
A—O2^{iii}	3.361 (2)	3.3270 (13)
M,Li—O2^{i}	1.9338 (19)	1.9345 (12)
Mo—O1	1.719 (4)	1.721 (2)
Mo—O2	1.7715 (18)	1.7780 (10)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $z+\frac{3}{4}, y-\frac{1}{4}, x-\frac{1}{4}$; (iii) $y+\frac{1}{2}, z-\frac{1}{2}, x-\frac{1}{2}$.

In both structures, the contents of the M,Li positions (M = Co and Zn) were accepted as $2M/3 + \mathrm{Li}/3$, taking into account their complete occupations and electroneutrality requirements in accordance with X-ray diffraction data for corresponding sintered samples.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1066). Services for accessing these data are described at the back of the journal.

References

Bartl, H. & Scheller, Th. (1970). *Neues Jahrb. Mineral. Monatsch.* pp. 547–552.
Bruker (2004). *APEX2* (Version 1.08), *SAINT* (Version 7.03) and *SADABS* (Version 2.11). Bruker AXS Inc., Madison, Wisconsin, USA.
Dwight, A. E. (1977). *Acta Cryst.* B**33**, 1579–1581.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gicquel-Mayer, C., Mayer, M. & Perez, G. (1980). *Rev. Chim. Miner.* **17**, 445–457.
Gicquel-Mayer, C. & Perez, G. (1975). *Rev. Chim. Miner.* **12**, 537–545.
Glinskaya, L. A., Klevtsova, R. F., Kim, V. G. & Klevtsov, P. V. (1980). *Dokl. Akad. Nauk SSSR*, **254**, 1122–1126.
Grey, I. E., Madsen, I. C., Jones, D. J. & Smith, P. W. (1989). *J. Solid State Chem.* **82**, 52–59.
Klevtsova, R. F. & Klevtsov, P. V. (1978). *Kristallografiya*, **23**, 261–265.
Mueller, M., Hildmann, B. O. & Hahn, Th. (1987). *Acta Cryst.* C**43**, 184–186.
Ozawa, T. C. & Kang, S. J. (2004). *Balls & Sticks* (*BS*). Version 1.51. URL: http://www.softbug.com/toycrate/bs.
Ozima, M. & Sato, S. (1977). *Acta Cryst.* B**33**, 2175–2181.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Solodovnikov, S. F., Klevtsov, P. V., Glinskaya, L. A. & Klevtsova, R. F. (1987). *Kristallografiya*, **32**, 618–622.
Solodovnikov, S. F., Klevtsova, R. F., Glinskaya, L. A. & Klevtsov, P. V. (1988). *Kristallografiya*, **33**, 1380–1386.
Solodovnikov, S. F., Klevtsova, R. F. & Klevtsov, P. V. (1994). *Zh. Strukt. Khim.* **35**, 145–157.
Solodovnikov, S. F. & Solodovnikova, Z. A. (1997). *Zh. Strukt. Khim.* **38**, 914–921.
Szillat, H. & Müller-Buschbaum, Hk. (1995). *Z. Naturforsch. Teil B*, **50**, 253–256.
Tsukimura, K., Kanazawa, Y., Aoki, M. & Bunno, M. (1993). *Acta Cryst.* C**49**, 205–207.
Williams, P. P. (1973). *Acta Cryst.* B**29**, 1550–1551.
Yamaguchi, H., Akatsuka, K., Setoguchi, M. & Takaki, Y. (1979). *Acta Cryst.* B**35**, 2680–2682.

i8 Solodovnikova *et al.* • $Cs_3LiCo_2(MoO_4)_4$ and $Rb_3LiZn_2(MoO_4)_4$ *Acta Cryst.* (2006). C**62**, i6–i8