The $K_{2n}CoMo_{2+n}O_{7+4n}$ family of structures, with n = 2, 3 or 5

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The compounds $K_4CoMo_4O_{15}$ (tetrapotassium cobalt tetra-molybdate), $K_6CoMo_5O_{19}$ (hexapotassium cobalt pentamolybdate) and $K_{10}CoMo_7O_{27}$ (decapotassium cobalt heptamolybdate) belong to a series of compounds with closely related crystal structures. In $K_4CoMo_4O_{15}$, the Co atom and one of the two unique Mo atoms are at sites with threefold symmetry; two of the three unique K atoms lie at sites with $\bar{3}$ symmetry. $K_6CoMo_5O_{19}$ crystallizes in a new monoclinic structure type. Each $[CoO_6]$ octahedron is surrounded by one face-sharing $[MoO_6]$ octahedron and six corner-sharing $[MoO_4]$ tetrahedra. All three compounds have this structural unit in common, but differ in the degree of connectivity between these units. They form layers in $K_4CoMo_4O_{15}$ and zigzag chains in $K_6CoMo_5O_{19}$, both by sharing $[MoO_4]$ tetrahedra. In $K_{10}CoMo_7O_{27}$, the structural units are isolated from each other.

Comment

Quarternary compounds of alkali metals (A), 3d transition metals (T), molybdenum and oxygen exist with a rich variety of crystal structures. The most common types are orthomol-ybdates $A_xT_y(MoO_4)_z$ with networks of $[TO_6]$ octahedra and $[MoO_4]$ tetrahedra. In the course of a systematic investigation of crystalline phases in the Na–Fe–Mo–O system, four orthomolybdate structures, namely α-NaFe$_2$(MoO$_4$)$_3$, β-NaFe$_2$(MoO$_4$)$_3$, Na$_3$Fe$_2$(MoO$_4$)$_3$ and NaFe$_4$(MoO$_4$)$_5$, were established (Muessig *et al.*, 2003) and only one phase, Na$_3$Fe$_2$Mo$_5$O$_{16}$, with both $[MoO_4]$ tetrahedra and $[MoO_6]$ octahedra (Bramnik *et al.*, 2003). This study has now been extended to the K–Co–Mo–O system. To date, only one orthomolybdate, $K_2Co_2(MoO_4)_3$, has been reported for this system in full detail (Klevtsova *et al.*, 1980). Furthermore, a second orthomolybdate, $K_4Co(MoO_4)_3$, is described as isostructural with $K_4Mn(MoO_4)_3$ (Solodovnikov *et al.*, 1998). For two other compounds, $K_4TMo_4O_{15}$ and $K_{10}TMo_7O_{27}$, crystal structures with both $[MoO_4]$ tetrahedra and $[MoO_6]$ octahedra have been established for T = Mn from single-crystal X-ray diffraction and are reported as isostructural for T = Co, but based on powder diffraction data only (Solo-

dovnikov, Klevtsova *et al.*, 1997; Solodovnikov, Zolotova *et al.*, 1997). In this contribution, we present structural data for $K_4CoMo_4O_{15}$ and for a new compound, $K_6CoMo_5O_{19}$, both from single-crystal X-ray diffraction studies. The crystal structures of $K_4CoMo_4O_{15}$, $K_6CoMo_5O_{19}$, and $K_{10}CoMo_7O_{27}$ are closely related to each other and can be considered as three members of one structural family of compounds $K_{2n}CoMo_{2+n}O_{7+4n}$, with n = 2, 3 and 5.

The present results confirm the proposed structure model for $K_4CoMo_4O_{15}$ (Solodovnikov, Zolotova *et al.*, 1997), while the crystal structure of the new compound, $K_6CoMo_5O_{19}$, has been solved and refined. It is now evident from its crystal structure that $K_6CoMo_5O_{19}$ fits into a series of structures of compounds with the general formula $K_{2n}CoMo_{2+n}O_{7+4n}$ with n = 3. Other representatives are known for n = 2 ($K_4CoMo_4O_{15}$; Solodovnikov, Zolotova *et al.*, 1997) and n = 5
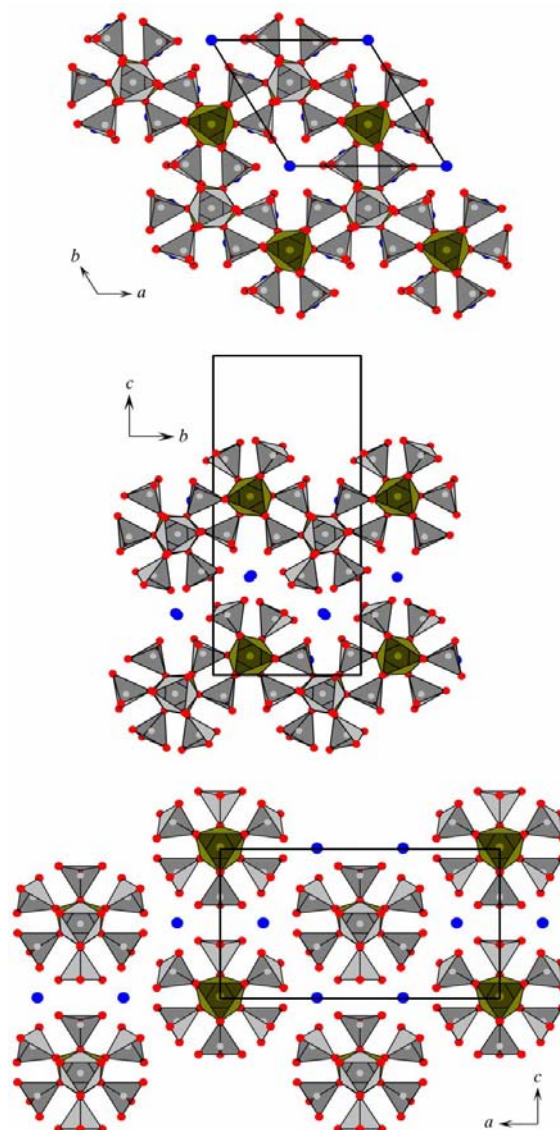

Figure 1
Different connectivity schemes for the same basic structural units in $K_{2n}CoMo_{2+n}O_{7+4n}$ compounds for n = 2, 3 and 5 (from top to bottom, respectively). $[MoO_4]$ and $[MoO_6]$ polyhedra are shown in light grey, while the K$^+$ ions are shown as isolated dark circles.

inorganic compounds

($K_{10}CoMo_7O_{27}$; Solodovnikov, Klevtsova *et al.*, 1997). Bond lengths and charge balances are in agreement with the formal oxidation states of Co^{2+} and Mo^{6+} for all compounds. The structures have one motif in common: $[CoO_6]$ and $[MoO_6]$ octahedra share faces and, in addition, each $[CoO_6]$ octahedron is further connected with six $[MoO_4]$ tetrahedra by sharing corners. The difference between these structures is the connectivity of the CoO_6 octahedra with each other. If m is the number of neighbouring octahedral units linked by sharing of $[MoO_4]$ tetrahedra, the equation $m + n = 5$ holds for all three representatives.

A comparison of the different connectivity schemes is shown in Fig. 1. In all structures, the orientations of the face-sharing $[MoO_6]$ and $[CoO_6]$ pairs of octahedra alternate. Note that in Fig. 1 the smaller $[MoO_6]$ octahedra behind the $[CoO_6]$ octahedra cannot be seen.

In terms of the structural systematics outlined here, dimers of face-sharing octahedra ($m = 1$) linked by $[MoO_4]$ tetrahedra should be observed for the hypothetical compound $K_8CoMo_6O_{23}$ ($n = 4$). This proposed member of the structure family has not yet been found.

Experimental

All samples were prepared from K_2MoO_4 (Aldrich, 98%), CoO (Alfa Aesar, 99.999%) and MoO_3 (Sigma–Aldrich, 99.5+%). Different ratios with a fixed K:Co ratio of 4:1 were mixed in an agate mortar, pressed into pellets and placed in silica tubes, which were then sealed with an ambient air atmosphere inside. The samples were heated to temperatures between 773 and 923 K for 48 h and then cooled to room temperature. The samples thus obtained consist of several K–Mo–O and Co–Mo–O ternary and K–Co–Mo–O quarternary phases.

Compound (I)

Crystal data

$K_4CoMo_4O_{15}$	Mo $K\alpha$ radiation
$M_r = 839.09$	Cell parameters from 2013
Trigonal, $P\bar{3}$	reflections
$a = 10.2920$ (10) Å	$\theta = 2.3$–$30.1°$
$c = 8.1271$ (8) Å	$\mu = 5.55$ mm^{-1}
$V = 745.53$ (13) Å^3	$T = 298$ (2) K
$Z = 2$	Prism, blue
$D_x = 3.738$ Mg m^{-3}	$0.04 \times 0.04 \times 0.03$ mm

Data collection

Oxford Xcalibur diffractometer with Sapphire CCD area detector	derived by Clark & Reid (1995)] $T_{min} = 0.771$, $T_{max} = 0.835$
ω and φ scans	3620 measured reflections
Absorption correction: numerical [*CrysAlis RED* (Oxford Diffraction, 2003); analytical numerical absorption correction using a multifaceted crystal model based on expressions	1318 independent reflections
	1041 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.047$
	$\theta_{max} = 30.0°$
	$h = -13 \rightarrow 14$
	$k = -14 \rightarrow 14$
	$l = -10 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 3.9972P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
1318 reflections	$\Delta\rho_{max} = 1.72$ e Å^{-3}
75 parameters	$\Delta\rho_{min} = -1.09$ e Å^{-3}
	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0009 (4)

Compound (II)

Crystal data

$K_6CoMo_5O_{19}$	$D_x = 3.523$ Mg m^{-3}
$M_r = 1077.23$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6106
$a = 8.0804$ (6) Å	reflections
$b = 10.3856$ (4) Å	$\theta = 3.3$–$30.3°$
$c = 24.2048$ (11) Å	$\mu = 5.11$ mm^{-1}
$\beta = 90.728$ (5)°	$T = 298$ (2) K
$V = 2031.10$ (19) Å^3	Prism, blue
$Z = 4$	$0.08 \times 0.07 \times 0.06$ mm

Data collection

Oxford Xcalibur diffractometer with Sapphire CCD area detector	derived by Clark & Reid (1995)] $T_{min} = 0.640$, $T_{max} = 0.772$
ω and φ scans	27463 measured reflections
Absorption correction: numerical [*CrysAlis RED* (Oxford Diffraction, 2003); analytical numerical absorption correction using a multifaceted crystal model based on expressions	5522 independent reflections
	4488 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.042$
	$\theta_{max} = 30.1°$
	$h = -10 \rightarrow 11$
	$k = -14 \rightarrow 14$
	$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 23.4209P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.35$	$(\Delta/\sigma)_{max} < 0.001$
5522 reflections	$\Delta\rho_{max} = 1.76$ e Å^{-3}
281 parameters	$\Delta\rho_{min} = -1.36$ e Å^{-3}
	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.00024 (5)

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1222). Services for accessing these data are described at the back of the journal.

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