Giglio, M. (1958). *Acta Cryst.* **11**, 789–793.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Nozik, Y. Z. & Fykin, L. E. (1980). Eur. Crystallogr. Meet., p. 109.

Rumanova, I. M. & Malitskaja, G. I. (1959). *Kristallografiya*, **4**, 510–525.

Sheldrick, G. M. (1993). *SHELX93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1980). *The XRAY80 System*. Computer Science Center, University of Maryland, College Park, Maryland, USA.

Vizcayno, C., Garcia-Gonzalez, M. T., Gutierrez, M. & Rodriguez, R. (1995). *Geoderma*, **68**, 193–210.

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Cobalt(II) trisodium hexamolybdoperiodate tetradecahydrate

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Abstract

In the title salt, $CoNa_3[IMo_6O_{24}]\cdot 14H_2O$, the anion has the Anderson structure with crystallographic $\bar{3}m$ symmetry. The unique cation site is occupied by disordered Na^+ and Co^{2+} ions. The I—O bond length is 1.890 (4) Å. There are three types of Mo—O distances at 1.711 (4), 1.933 (2) and 2.352 (3) Å, corresponding to terminal O atoms, O atoms bridging to other Mo^{6+} ions and those bridging to I^{7+} ions, respectively. The anions form layers perpendicular to the *c* axis which are separated by double layers of cations.

Comment

The present study was undertaken as part of an investigation of the interaction of transition metals with polyoxometalate anions. Elemental analysis indicated one Co atom per six Mo atoms and the structure determination was performed to elucidate the role of cobalt in the salt.

The resulting structure (Fig. 1) reveals $[IMo_6O_{24}]^{5-}$ anions with crystallographic $\bar{3}m$ symmetry. The anion has the well known Anderson structure (Pope, 1983), consisting of a central octahedron surrounded in a planar fashion by six additional octahedra. The anion is surrounded by cations above and below the plane of the anion. The anion structure was originally proposed for $[IMo_6O_{24}]^{5-}$ and similar hexametalates (Anderson, 1937) and later confirmed for $[TeMo_6O_{24}]^{6-}$ (Evans, 1948). For a review of the history of these and other polyoxometalates, see Baker & Glick (1998). Recent structural determinations of similar salts include $[NH_4]_4[Zn(OH)_6Mo_6O_{18}]\cdot 6H_2O$ (Allen *et al.*, 1997) and $[Ga(H_2O)_6][Co(OH)_6Mo_6O_{18}]$ (Panneerselvam *et al.*, 1996). These salts contain protons on the triply bridging O atoms, which is typical for Anderson ions with central atoms having a charge of +3 or +2.

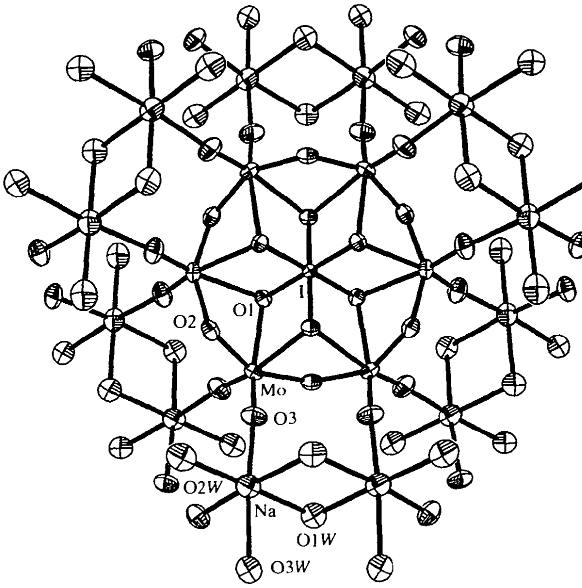

Fig. 1. View of the title compound, perpendicular to the *c* axis, showing the numbering scheme. Anisotropic displacement ellipsoids are shown at the 50% probability level.

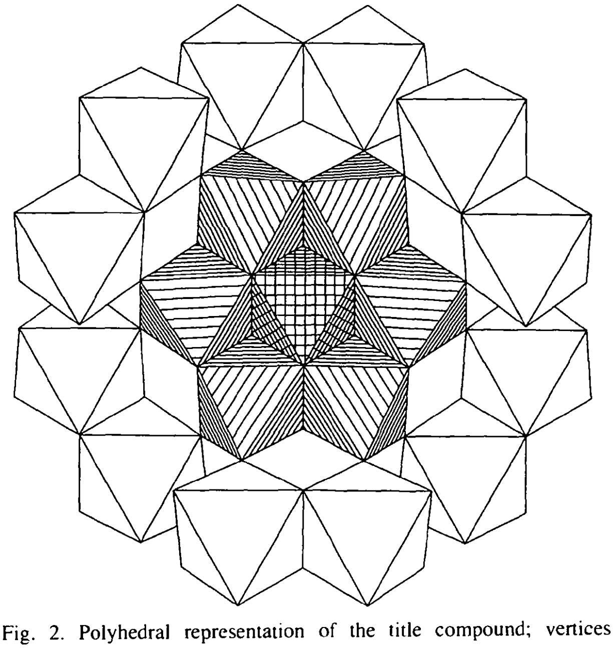

Fig. 2. Polyhedral representation of the title compound; vertices represent O atoms.

The structure of $K_5[IMo_6O_{24}]\cdot5H_2O$ has been reported previously (Kondo *et al.*, 1980). The interatomic distances and angles for the anion are essentially the same as reported here. Two other Anderson structures have been reported in the $R\bar{3}m$ space group: $K_6Na_2[Mn^{IV}W_6O_{24}]\cdot12H_2O$ (Sergienko *et al.*, 1979) and $K_6Na_2[Pt^{IV}W_6O_{24}]\cdot12H_2O$ (Lee *et al.*, 1984). These structures have two crystallographically distinct cation sites in contrast to the present structure which contains a unique cation site. The elemental analysis and charge-balance requirements suggest that, on average, the cation site is two thirds occupied by both sodium and cobalt in a 3:1 ratio. Refinement of this model was successful. The packing of the structure consists of $[IMo_6O_{24}]^{5-}$ anions in layers perpendicular to the *c* axis. These layers are separated by double layers of cations to form a *BABBAB* pattern.

Experimental

MoO_3 (43.2 g, 0.3 mol) and Na_2CO_3 (10.6 g, 0.1 mol) were added quickly with stirring to a slurry of $NaIO_4$ (10.7 g, 0.05 mol) in 50 ml water. Most of the solid dissolved and the final pH was 6. The solution was filtered and allowed to evaporate. After two days, 41 g of $Na_5[IMo_6O_{24}]\cdot16.5H_2O$ was collected. The sodium salt was recrystallized twice from hot water. To a fresh slurry of this material (7.5 g, 5 mmol) in 20 ml water was added $CoCl_2\cdot6H_2O$ (1.19 g, 5 mmol). The mixture was adjusted to pH 6 with acetic acid, stirred for 5 min and then refluxed for about 30 min. The solution was filtered while hot and allowed to evaporate. After two days, 6.2 g (78.8% yield) of crystals were collected, some of which were suitable for structural analysis. Elemental analysis (%) found (calculated) for $Na_3Co[IMo_6O_{24}]\cdot14H_2O$: Na 4.3 (4.7), Co 3.1 (4.0), Mo 38.5 (39.3), H_2O 18.1% (17.2%).

Crystal data

$CoNa_3[IMo_6O_{24}]\cdot14H_2O$
$M_r = 1466.66$
Trigonal
$R\bar{3}m$
$a = 11.8769\,(1)$ Å
$c = 23.0394\,(4)$ Å
$V = 2814.54\,(6)$ Å^3
$Z = 3$
$D_x = 2.596$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8108 reflections
$\theta = 2.17$–$28.23°$
$\mu = 3.34$ mm^{-1}
$T = 228\,(2)$ K
Rhomboid
0.32 × 0.26 × 0.20 mm
Pink

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: semi-empirical from equivalents (Blessing, 1995)
$T_{min} = 0.40$, $T_{max} = 0.51$
9368 measured reflections

854 independent reflections
795 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 28.23°$
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -30 \rightarrow 30$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.102$
$S = 1.17$
854 reflections
50 parameters
H atoms were not included in the refinement model

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 32.80P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -1.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
I	0	0	0	0.0165 (2)
Mo	0.28020 (4)	0	0	0.0256 (2)
Na†	0.56784 (15)	0.1357 (3)	0.11689 (14)	0.0432 (7)
Co‡	0.56784 (15)	0.1357 (3)	0.11689 (14)	0.0432 (7)
O1	0.0769 (2)	$-x$	−0.0449 (2)	0.0233 (8)
O2	0.1580 (2)	$-x$	0.0396 (2)	0.0295 (9)
O3	0.3956 (4)	0.0611 (4)	0.0534 (2)	0.0424 (10)
O1*W*	2/3	1/3	0.0548 (4)	0.049 (2)
O2*W*	0.4733 (3)	−0.0534 (6)	0.1767 (2)	0.0521 (14)
O3*W*	0.7638 (2)	$1 - x$	0.1694 (2)	0.0410 (13)

† Site occupancy = 0.50. ‡ Site occupancy = 0.17.

Table 2. *Selected geometric parameters (Å, °)*

I—O1	1.890 (4)	Na—O3	2.301 (4)
Mo—O3	1.711 (4)	Na O3*W*	2.352 (4)
Mo—O2	1.933 (2)	Na—O2*W*	2.383 (7)
Mo—O1	2.352 (3)	Na—O1*W*	2.485 (7)
$O1^i$—I—O1	87.1 (2)	$O3^{iv}$—Mo—O1	92.9 (2)
$O1^{ii}$—I—O1	92.9 (2)	O2—Mo—O1	72.80 (12)
O1—I—$O1^{iii}$	180.0	O2—Mo—$O1^v$	81.58 (15)
O3—Mo—$O3^{iv}$	107.8 (2)	O1—Mo—$O1^v$	67.3 (2)
O3—Mo—O2	97.2 (2)	I—O1—Mo	102.80 (13)
$O3^{iv}$—Mo—O2	100.8 (2)	Mo—O1—Mo^i	90.06 (14)
O2—Mo—$O2^v$	149.2 (2)	Mo^i—O2—Mo	118.8 (2)
O3—Mo—O1	158.6 (2)		

Symmetry codes: (i) $y, -x+y, -z$; (ii) $-y, x-y, z$; (iii) $-x, -y, -z$; (iv) $x-y, -y, -z$; (v) $x-y, x, -z$.

Crystal decay was monitored by recollection of the first 50 frames after data collection was complete. The data were corrected for absorption and other systematic errors (Blessing, 1995). Three peaks had absolute values greater than 1.0 e Å^{-3} in the final difference Fourier synthesis, with values of 1.74, 1.19 and −1.21 e Å^{-3}. The first two were 1.42 and 2.66 Å from O2*W*, respectively, and the last (negative) peak was 0.84 Å from the I atom.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1375). Services for accessing these data are described at the back of the journal.

References

Allen, C. C., Burns, R. C., Lawrance, G. A., Turner, P. & Hambley, T. W. (1997). *Acta Cryst.* **C53**, 7–9.

Anderson, J. S. (1937). *Nature*, **140**, 850.

Baker, L. C. W. & Glick, D. C. (1998). *Chem. Rev.* **98**, 3–49.

Blessing, R. (1995). *Acta Cryst.* **A51**, 33–38.

Evans, H. T. Jr (1948). *J. Am. Chem. Soc.* **70**, 1291–1292.

Kondo, H., Kobayashi, A. & Sasaki, Y. (1980). *Acta Cryst.* **B36**, 661–664.

Lee, U., Ichida, H., Kobayashi, A. & Sasaki, Y. (1984). *Acta Cryst.* **C40**, 5–7.

Panneerselvam, K., Soriano-García, M., Holguin-Quiñones, S. & Holt, E. M. (1996). *Acta Cryst.* **C52**, 1605–1607.

Pope, M. T. (1983). In *Heteropoly and Isopoly Oxometalates*. Berlin: Springer.

Sergienko, V. S., Molchanov, V. N., Porai-Koshits, M. A. & Torchenkova, E. A. (1979). *Koord. Khim.* **5**, 936–942.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1995). *SAINT*. Version 4.050. *Data Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART User's Manual*. Version 4.050. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Potassium tetrabromoaurate(III)

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Abstract

The structure of $KAuBr_4$, previously reported to be an isotype of $KAuCl_4$, has been determined in the centrosymmetric space group $P2_1/c$. The monoclinic cell contains four Au atoms (two Au1 and two Au2). The $AuBr_4^-$ anions are nearly square planar, with Au1—Br bond lengths of 2.4096 (15) and 2.4146 (15) Å, Au2—Br bond lengths of 2.4016 (17) and 2.4172 (15) Å, and Br—Au—Br angles of 90.31 (5) and 90.87 (6)° for Au1 and Au2, respectively.

Comment

X-ray powder diffraction studies of anhydrous $KAuCl_{4-x}Br_x$ $(0 < x < 4)$ solid solutions (Omrani, 1979) have demonstrated that these compounds are isotypes of potassium tetrachloroaurate(III) and potassium tetrabromoaurate(III). For anhydrous $KAuCl_4$, the space group ($P2_1/c$) and cell parameters were originally reported by Cox & Webster (1936). A complete crystal structure determination of the $KAuCl_4$ compounds was recently published by Jones & Bembenek (1992). In the present work, we report the crystal structure determination of the $KAuBr_4$ compound. $KAuBr_4$ crystallizes in the monoclinic system in the $P2_1/c$ space group. Both Au atoms lie on centres of symmetry (Fig. 1). The $AuBr_4^-$ anions are thus exactly planar. There is only one independent K atom; it is coordinated by nine Br atoms at distances in the range 3.274 (4)–3.756 (4) Å.

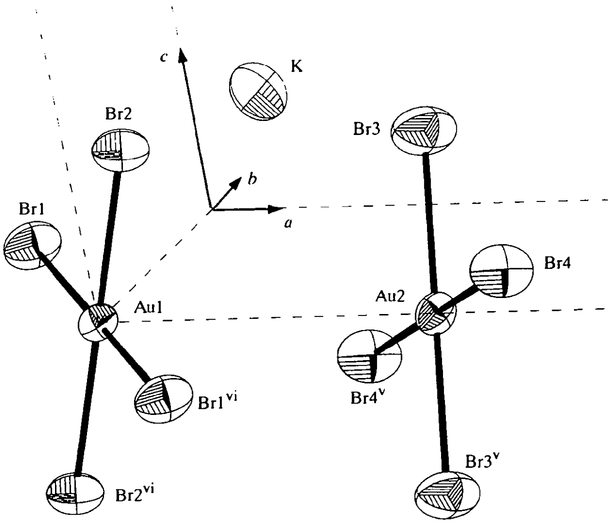

Fig. 1. View of $KAuBr_4$, with displacement ellipsoids shown at 50% probability levels.

Experimental

Crystals of $KAuBr_4$ were prepared by dissolving commercial powders of $KAuBr_4$ (Fluka 'purissiumum') in aqueous HCl (M/10). The solution concentration was 0.005 mol l^{-1} in $KAuBr_4$ and the solution was slowly evaporated in a furnace at 353 K. After complete crystallization, dark brick-red crystals were obtained and were kept in a desiccator over P_4O_{10}. A single crystal was then sealed in a Lindemann glass capillary.

Crystal data

$KAuBr_4$
$M_r = 555.71$
Ag $K\alpha$ radiation
$\lambda = 0.5608$ Å