

Fig. 2. Projection of the  $N_2H_6^{2+}$  ion down the N-N bond, and hydrogen bonds.

In the  $[TiF_6]^{2-}$  ion the F atoms are octahedrally disposed round the Ti atom. The Ti-F bond lengths (Table 2) are close to reported values (Kojić-Prodić, Matković & Ščavničar, 1971; Weiss, Fischer & Chevrier, 1966; Fischer, de Cian & Weiss, 1967).

We thank Professor Dr J. Slivnik for the crystals and the Research Council of Slovenia for financial support.

### References

- ANDERSON, M. R., VILMINOT, S. & BROWN, I. D. (1973). *Acta Cryst.* B29, 2961-2962.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891-1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321-324.
- FISCHER, J., DE CIAN, A. & WEISS, R. (1967). *Acta Cryst.* 22, 338-343.
- GOLIČ, L. & LAZARINI, F. (1974). *Monatsh. Chem.* 105, 735-741.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOJIĆ-PRODIĆ, B., MATKOVIĆ, B. & ŠČAVNIČAR, S. (1971). *Acta Cryst.* B27, 635-637.
- KOJIĆ-PRODIĆ, B., ŠČAVNIČAR, S. & MATKOVIĆ, B. (1971). *Acta Cryst.* B27, 638-644.
- SLIVNIK, J., MAČEK, J., OREL, B. & SEDEJ, B. (1973). *Monatsh. Chem.* 104, 624-632.
- SLIVNIK, J., ŠMALC, A., SEDEJ, B. & VILHAR, M. (1964). NIJS Report R-430. Nuclear Institute 'Jožef Stefan', Ljubljana, Yugoslavia.
- SLIVNIK, J. & VOLAVŠEK, B. (1968). NIJS Report R-548. Nuclear Institute 'Jožef Stefan', Ljubljana, Yugoslavia.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system - version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175-3187.
- WEISS, R., FISCHER, J. & CHEVRIER, B. (1966). *Acta Cryst.* 20, 534-537.

*Acta Cryst.* (1980). B36, 661-664

## The Structure of the Hexamolybdoperiodate Anion in Its Potassium Salt

BY HIDETAKA KONDO, AKIKO KOBAYASHI AND YUKIYOSHI SASAKI

Department of Chemistry and The Research Centre for Spectrochemistry, Faculty of Science,  
The University of Tokyo, Hongo, Tokyo 113, Japan

(Received 6 September 1979; accepted 6 November 1979)

**Abstract.**  $K_5[IMo_6O_{24}] \cdot 5H_2O$ ,  $P\bar{1}$ ,  $a = 10.084$  (1),  $b = 17.593$  (2),  $c = 7.692$  (1) Å,  $\alpha = 95.07$  (1),  $\beta = 91.38$  (1),  $\gamma = 82.45$  (1)°,  $U = 1347.5$  (2) Å<sup>3</sup>,  $FW = 1372.10$ ,  $Z = 2$ ,  $D_m = 3.37$ ,  $D_x = 3.42$  Mg m<sup>-3</sup>,  $\mu = 4.375$  mm<sup>-1</sup> (for Mo  $K\alpha$ ). The  $[IMo_6O_{24}]^{5-}$  anion has been found to be a typical Anderson-type heteropolyanion and has approximate  $\bar{3}m$  symmetry. The metal-oxygen bond lengths in this anion and in  $[TeMo_6O_{24}]^{6-}$  show the difference between the  $I^{7+}-O$  and  $Te^{6+}-O$  bond strengths.

**Introduction.** Many Keggin-type heteropolyanions have been studied; there is also another group of heteropolyanions called the Anderson type (Anderson, 1937). The latter type of polyanion consists of seven octahedra sharing edges with one another. Six Mo octahedra are arranged hexagonally around the octahedron containing the heteroatom.

A number of examples of the preparations of Anderson-type polyanions have been reported (*Gmelins Handbuch der Anorganischen Chemie*,

1935), but fewer structural studies have been carried out (Evans, 1974; Perloff, 1970). The present structure was originally proposed by Anderson (1937) for this  $[\text{IMo}_6\text{O}_{24}]^{5-}$  anion. This paper reports its structure determination and the structure is compared with that of  $[\text{TeMo}_6\text{O}_{24}]^{6-}$ .

Preparations of the periodatomolybdates have been described by Blomstrand (1892). The intensities of the reflections were measured with a Rigaku automatic four-circle diffractometer (graphite monochromator, Mo  $K\alpha$  radiation,  $\omega$ - $2\theta$  scan technique) up to  $2\theta = 65^\circ$ . The intensities of 6627 observed independent reflections, with  $|F_o| > 3\sigma(|F_o|)$ , were used for the structure determination. The dimensions of the crystal were  $0.3 \times 0.1 \times 0.05$  mm. The structure was solved by the heavy-atom method, except for the H atoms, and refined by the block-diagonal least-squares method.

Table 1. Fractional coordinates ( $\times 10^4$ )

	x	y	z
I	2574 (1)	2564 (1)	2477 (1)
Mo(1)	4607 (1)	3901 (1)	2991 (1)
Mo(2)	5765 (1)	2091 (1)	3419 (1)
Mo(3)	3749 (1)	756 (1)	3120 (1)
Mo(4)	567 (1)	1223 (1)	1962 (1)
Mo(5)	-595 (1)	3029 (1)	1319 (1)
Mo(6)	1429 (1)	4363 (1)	1822 (1)
O <sub>i</sub> (1a)	5379 (6)	4126 (3)	4938 (7)
O <sub>i</sub> (1b)	5104 (6)	4498 (3)	1540 (8)
O <sub>i</sub> (2a)	6654 (6)	2375 (4)	5222 (9)
O <sub>i</sub> (2b)	6806 (6)	1457 (3)	2116 (9)
O <sub>i</sub> (3a)	3166 (6)	244 (3)	4662 (7)
O <sub>i</sub> (3b)	4940 (6)	141 (3)	1963 (8)
O <sub>i</sub> (4a)	89 (6)	707 (3)	3575 (9)
O <sub>i</sub> (4b)	-222 (6)	915 (4)	67 (9)
O <sub>i</sub> (5a)	-1741 (5)	3674 (3)	2451 (8)
O <sub>i</sub> (5b)	-1386 (6)	2715 (3)	-549 (7)
O <sub>i</sub> (6a)	197 (5)	4954 (3)	2979 (7)
O <sub>i</sub> (6b)	2012 (6)	4900 (3)	329 (7)
O <sub>c</sub> (12)	3773 (4)	2893 (3)	4200 (6)
O <sub>c</sub> (23)	3988 (5)	1830 (3)	1606 (6)
O <sub>c</sub> (34)	2068 (5)	1805 (3)	3817 (6)
O <sub>c</sub> (45)	1391 (4)	2229 (3)	716 (6)
O <sub>c</sub> (56)	1136 (4)	3296 (3)	3293 (6)
O <sub>c</sub> (61)	3062 (5)	3334 (3)	1137 (6)
O <sub>b</sub> (12)	5690 (5)	2976 (3)	2131 (7)
O <sub>b</sub> (23)	4822 (5)	1371 (3)	4548 (7)
O <sub>b</sub> (34)	2294 (5)	694 (3)	1408 (7)
O <sub>b</sub> (45)	-576 (5)	2171 (3)	2666 (6)
O <sub>b</sub> (56)	389 (5)	3748 (3)	295 (6)
O <sub>b</sub> (61)	2857 (5)	4424 (3)	3535 (6)
K(1)	9346 (2)	2083 (1)	6191 (2)
K(2)	2705 (2)	4776 (1)	6963 (2)
K(3)	2163 (2)	65 (1)	7929 (2)
K(4)	5302 (3)	1487 (1)	8257 (3)
K(5)	6485 (2)	3867 (1)	8419 (3)
Aq(1)	-2055 (8)	1017 (4)	7368 (10)
Aq(2)	-1443 (7)	3669 (4)	6117 (8)
Aq(3)	1565 (8)	3308 (5)	7041 (8)
Aq(4)	2332 (9)	1556 (4)	7509 (9)
Aq(5)	4377 (7)	3073 (4)	7975 (8)

Calculations were performed with a local version of UNICS (Sakurai, 1967) on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo. Anisotropic temperature factors were used for all the non-hydrogen atoms. Atomic scattering factors and corrections for anomalous scattering were taken from *International Tables for X-ray Crystallography* (1974). No absorption correction was made. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/(a + |F_o| + c|F_o|^2)$  with  $a = 43.03$  and  $c = 0.00469$  estimated experimentally according to Cruickshank (1970), for  $|F_o| > 21.0$ , and  $w = 0.122$  for others. The final  $R$  values are  $R_w(F) = 0.050$  and  $R(F) = 0.047$ , where  $R_w(F) = \sum w||F_o| - |F_c||/\sum w|F_o|$  and  $R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$ .

Atomic fractional coordinates and averaged bond distances and angles are listed in Tables 1 and 2.\*

**Discussion.** The  $[\text{IMo}_6\text{O}_{24}]^{5-}$  anion has approximate  $D_{3d}$  ( $\bar{3}m$ ) symmetry, analogous to that found in  $[\text{TeMo}_6\text{O}_{24}]^{6-}$  (Evans, 1974) and in  $[\text{CrMo}_6\text{O}_{24}\text{H}_6]^{3-}$  (Perloff, 1970). The anion is illustrated in Fig. 1.

The I atom and the six Mo atoms are coplanar and these Mo atoms form a nearly regular hexagon around the I atom. All the I and Mo atoms are octahedrally surrounded by O atoms.

The hexagon containing the six Mo atoms is approximately parallel to the (001) plane. The  $\text{K}^+$  ions and the water molecules form a network coordinated to the anions by hydrogen bonds and ion-dipole interactions.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34892 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

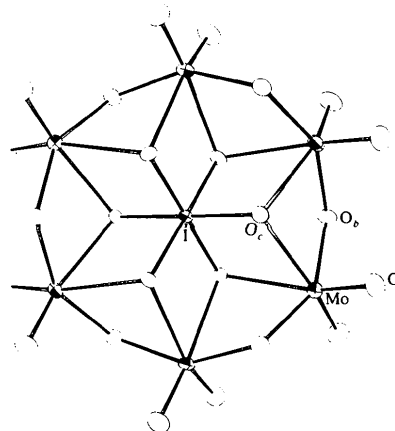


Fig. 1. Structure of the  $[\text{IMo}_6\text{O}_{24}]^{5-}$  Anderson-type polyanion viewed perpendicular to the hexagon of the six Mo atoms. The thermal-vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

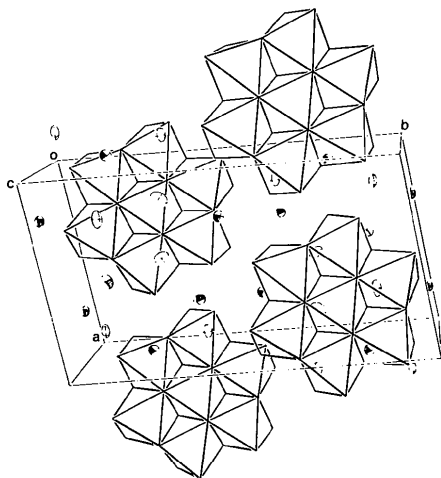
Table 2. Average bond distances (Å) and bond angles (°) in  $[\text{IMo}_6\text{O}_{24}]^{5-}$  and  $[\text{TeMo}_6\text{O}_{24}]^{6-}$  (Evans, 1974)Estimated standard deviations are given in parentheses; X indicates  $\text{I}^{7+}$  or  $\text{Te}^{6+}$ .

## (a) Bond distances

	$[\text{IMo}_6\text{O}_{24}]^{5-}$		$[\text{TeMo}_6\text{O}_{24}]^{6-}$	
	Average distance	Range	Average distance	Range
X—Mo	3.307 (1)	3.296–3.322	3.291 (5)	3.282–3.300
Mo—Mo	3.307 (1)	3.287–3.327	3.291 (5)	3.275–3.312
X—O <sub>c</sub>	1.887 (5)	1.877–1.893	1.934 (10)	1.930–1.938
Mo—O <sub>c</sub>	2.338 (5)	2.314–2.369	2.294 (10)	2.282–2.316
Mo—O <sub>b</sub>	1.923 (5)	1.894–1.955	1.939 (10)	1.913–1.957
Mo—O <sub>t</sub>	1.713 (5)	1.702–1.724	1.711 (10)	1.693–1.723

(b) Bond angles (*anti* indicates that the two O atoms are on opposite sides of the Mo<sub>6</sub> plane, *syn* indicates that they are on the same side)

	$[\text{IMo}_6\text{O}_{24}]^{5-}$		$[\text{TeMo}_6\text{O}_{24}]^{6-}$	
	Average angle	Range	Average angle	Range
O <sub>c</sub> —X—O <sub>c</sub> ( <i>syn</i> )	92.7 (2)	91.6–93.8	94.0 (4)	93.6–94.2
O <sub>c</sub> —X—O <sub>c</sub> ( <i>anti</i> )	87.3 (2)	86.7–87.8	86.0 (4)	85.8–86.4
O <sub>c</sub> —Mo—O <sub>c</sub> ( <i>anti</i> )	67.7 (2)	67.3–68.0	70.2 (4)	70.1–70.3
O <sub>c</sub> —Mo—O <sub>b</sub> ( <i>syn</i> )	81.4 (2)	79.7–82.9	83.1 (5)	82.4–84.1
O <sub>c</sub> —Mo—O <sub>t</sub> ( <i>anti</i> )	72.9 (2)	71.9–73.8	73.8 (5)	73.2–74.7
O <sub>c</sub> —Mo—O <sub>t</sub> ( <i>syn</i> )	93.0 (3)	89.4–97.3	92.1 (5)	90.1–93.3
O <sub>c</sub> —Mo—O <sub>b</sub> ( <i>anti</i> )	159.3 (3)	155.8–163.3	160.4 (5)	158.0–162.0
O <sub>b</sub> —Mo—O <sub>b</sub> ( <i>anti</i> )	148.9 (2)	148.3–149.8	151.7 (5)	151.3–152.0
O <sub>b</sub> —Mo—O <sub>t</sub> ( <i>syn</i> )	97.9 (3)	96.1–100.0	96.4 (6)	94.7–97.3
O <sub>b</sub> —Mo—O <sub>t</sub> ( <i>anti</i> )	100.4 (3)	97.9–102.1	100.4 (6)	98.2–102.1
O <sub>t</sub> —Mo—O <sub>t</sub> ( <i>anti</i> )	106.9 (3)	106.3–108.1	106.6 (6)	106.2–107.3
Mo—O <sub>c</sub> —Mo	90.0 (2)	89.0–90.9	91.7 (4)	91.1–92.4
Mo—O <sub>c</sub> —X	102.5 (2)	101.7–103.3	101.9 (5)	101.5–102.1
Mo—O <sub>b</sub> —Mo	118.6 (3)	117.7–119.2	116.1 (5)	114.9–117.3

Fig. 2. Crystal structure looking from the direction perpendicular to the Mo<sub>6</sub> hexagon. The partially shaded ellipsoids represent the K<sup>+</sup> ions; other ellipsoids are water molecules. Anions are shown by the polyhedral model.

There are three types of O atoms denoted as O<sub>t</sub>, O<sub>b</sub> and O<sub>c</sub>, which were described as O<sub>c</sub>, O<sub>b</sub> and O<sub>a</sub>, respectively by Evans (1974). O<sub>t</sub> represents a terminal O atom bonding to a Mo atom, O<sub>b</sub> a bridging atom

between two Mo atoms and O<sub>c</sub> an atom coordinating to the I and to two Mo atoms, which make up the central octahedron.

Compared with Te<sup>6+</sup> in  $[\text{TeMo}_6\text{O}_{24}]^{6-}$ , the small ionic radius (0.67 Å) and the higher formal oxidation state of I<sup>7+</sup> in  $[\text{IMo}_6\text{O}_{24}]^{5-}$  require that the bond order of I—O<sub>c</sub> be greater than that of Te—O<sub>c</sub>. This may result in loose Mo—O<sub>c</sub> bonding in the case of the  $[\text{IMo}_6\text{O}_{24}]^{5-}$  anion. Table 2 clearly shows that this is indeed the case. As a result, the size of the Mo<sub>6</sub> hexagons does not vary significantly with differences in the ionic radii of the heteroatoms. It has been found in many Keggin-type polyanions that different heteroatoms affect only the lengths and angles of neighboring bonds, and the size of the polyanion is not so sensitive to the radius of the heteroatom.

Fig. 2 shows the crystal structure.

## References

- ANDERSON, J. S. (1937). *Nature (London)*, **140**, 850.  
 BLOMSTRAND, C. W. (1892). *Z. Anorg. Chem.* **1**, 10–50.  
 CRUICKSHANK, D. W. J. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 187–197. Copenhagen: Munksgaard.

EVANS, H. T. JR (1974). *Acta Cryst.* B30, 2095–2100.

*Gmelins Handbuch der Anorganischen Chemie* (1935). Part 53, Molybdän. Berlin: Verlag Chemie.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

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

PERLOFF, A. (1970). *Inorg. Chem.* 9, 2228–2239.

SAKURAI, T. (1967). *UNICS. The Universal Crystallographic Program System*. Tokyo: The Crystallographic Society of Japan.

*Acta Cryst.* (1980). B36, 664–666

## Structure du Fluorure de Thallium(I) et d'Uranium(IV)

PAR D. AVIGNANT, I. MANSOURI, R. SABATIER ET J. C. COUSSEINS

Laboratoire de Chimie des Solides, Université de Clermont-Ferrand II, BP 45, 63170 Aubière, France

ET R. CHEVALIER

Laboratoire de Cristallographie et Physico-Chimie des Matériaux, Université de Clermont-Ferrand II, BP 45, 63170 Aubière, France

(Reçu le 7 mai 1979, accepté le 12 novembre 1979)

**Abstract.**  $\text{TiUF}_5$ ,  $M_r = 518.39$ , monoclinic,  $P2_1/c$ ,  $a = 8.222$  (2),  $b = 13.821$  (4),  $c = 8.317$  (5) Å,  $\beta = 102.53$  (3)°,  $D_m = 7.42$  (5),  $D_c = 7.46$  Mg m<sup>-3</sup>,  $Z = 8$ . The structure was refined by full-matrix least-squares techniques using data measured on a Nonius CAD-4 automatic diffractometer to an  $R$  value of 0.055 for 1171 independent reflections. The structure consists of sheets perpendicular to the  $b$  axis in which each of the two crystallographically independent U ions is nine-coordinated by F atoms in a tricapped trigonal prism arrangement. Ti atoms bind the sheets together. The Ti ions have nine nearest-neighbour F ions.

**Introduction.** Dans le cadre d'une étude générale des systèmes  $\text{TlF}-M'\text{F}_4$  ( $M' = \text{Th}, \text{U}, \text{Zr}, \text{Hf}$ ), celle du système  $\text{TlF}-\text{UF}_4$  (Avignant & Cousseins, 1971) effectuée par analyse thermique différentielle et radio-cristallographie nous avait permis de caractériser le composé  $\text{TiUF}_5$ .

Parmi les nombreux composés de formule  $MM'\text{F}_5$  ( $M = \text{alcalin}, \text{NH}_4^+$ ;  $M' = \text{Th}, \text{U}, \text{Zr}, \text{Hf}$ ), connus jusqu'à présent, seuls  $\text{LiUF}_5$  (Brunton, 1966) et  $\text{NH}_4\text{UF}_5\beta$  (Penneman, Ryan & Rosenzweig, 1974) ont fait l'objet d'une étude structurale complète. Cependant malgré l'analogie de taille entre  $\text{Ti}^+$  et  $\text{NH}_4^+$  il n'existe pas d'isotypie entre  $\text{TiUF}_5$  et  $\text{NH}_4\text{UF}_5\beta$ . Par conséquent, nous avons synthétisé  $\text{TiUF}_5$  sous forme de monocristaux afin d'en déterminer la structure.

Les monocristaux ont été préparés par la méthode des flux selon un processus décrit précédemment

(Avignant, Vêdrine & Cousseins, 1977). Les paramètres cristallins ont été affinés par moindres carrés à partir de 15 réflexions centrées sur diffractomètre Nonius CAD-4. La densité expérimentale a été déterminée par pycnométrie dans l'*o*-xylène.

Les intensités diffractées ont été mesurées sur diffractomètre automatique dans les conditions suivantes: dimensions du cristal:  $0,028 \times 0,022 \times 0,304$  mm, anticathode de molybdène, monochromateur au graphite; balayage  $\omega-2\theta$ ; angle de balayage:  $(1,00 + 0,30 \text{ tg } \theta)^\circ$ ; ouverture du compteur:  $(2,00 + 1,00 \text{ tg } \theta)$  mm.

Tableau 1. Coordonnées atomiques ( $\times 10^4$ ) et facteurs de température équivalents ou isotropes (Å<sup>2</sup>)

Les écarts types figurent entre parenthèses.					$B_{\text{eq}}$ ou $B_{\text{iso}}$
Site	$x$	$y$	$z$		
Tl(1)	4(e) 2330 (3)	4791 (2)	2242 (3)		1,2
Tl(2)	4(e) 2778 (3)	176 (2)	2016 (3)		1,9
U(1)	4(e) 148 (2)	7456 (2)	921 (2)		0,4
U(2)	4(e) 4459 (2)	7545 (2)	4616 (2)		0,3
F(1)	4(e) 4659 (31)	1963 (21)	2665 (36)		0,9 (0,5)
F(2)	4(e) 812 (41)	2904 (25)	1804 (44)		2,2 (0,5)
F(3)	4(e) 2685 (36)	2632 (20)	4710 (38)		1,5 (0,4)
F(4)	4(e) 2250 (31)	6491 (17)	111 (34)		0,7 (0,4)
F(5)	4(e) 4848 (36)	6019 (23)	5127 (39)		1,4 (0,5)
F(6)	4(e) 1733 (36)	6845 (23)	3634 (40)		1,4 (0,5)
F(7)	4(e) 2840 (32)	-1907 (20)	1902 (35)		1,0 (0,5)
F(8)	4(e) 650 (36)	985 (23)	3903 (41)		1,3 (0,5)
F(9)	4(e) 4701 (40)	3949 (26)	763 (44)		2,0 (0,6)
F(10)	4(e) 159 (39)	3993 (26)	4299 (44)		1,9 (0,6)