A Novel Type of Heteropolynuclear Complex Anion: *X*-Ray Crystal Structure of the Polymeric Complex Anion $[Th(H_2O)_3UMo_{12}O_{42}]_n^{4n-}$

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Summary The interaction of the $[UMo_{12}O_{42}]^{8-}$ anion with Th^{4+} results in the formation of an infinite chain complex $[Th(H_2O)_3UMo_{12}O_{42}]_n^{4n-}$, in which the Th atom has tricapped trigonal-prismatic geometry.

IN a series of solution studies of the interaction between heteropolyanions of the type $[XMo_{12}O_{42}]^{8-}$ ($X = Ce^{4+}$, Th^{4+}, and U^{4+}) with d- and f-block elements it was shown that the heteropolyanion acts as a polydentate ligand.[1] Complexes of various stoicheiometries were isolated as solids and some of them were examined by *X*-ray crystallography.[2]

By adding thorium nitrate solution to a freshly prepared solution of 12-molybdouranic acid with successive introduction of ammonium nitrate crystals, a salt was precipitated and examined by single-crystal *X*-ray diffraction. Analysis indicated the formula $(NH_4)_3HThUMo_{12}O_{42}$, $15H_2O$.

Crystal data: hexagonal, space group $R\bar{3}c$, $a = 18{\cdot}699(4)$, $c = 24{\cdot}381(9)$ Å, $D_c = 3{\cdot}53$ g cm^{-3}, $U = 7380$ A^3. Data were collected using Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å) with a Syntex P1 automatic diffractometer. All calculations were performed using the programs Kristall.[3]

From analysis of the Patterson maps the positions of the heavy atoms (U, Th, and 2 Mo) were determined. Least-squares refinement using isotropic temperature factors for all non-hydrogen atoms resulted in $R = 5{\cdot}5\%$. The final structure refinement using 1201 independent reflexions with anisotropic temperature factors for U, Th, and Mo reduced R to $4{\cdot}9\%$.†

The *X*-ray structure determination has shown that it is impossible to consider the separate molecules of the complex in isolation because it is a polymer of the 'core-link' type (Figure). The $[UMo_{12}O_{42}]^{8-}$ heteropolyanion, which is isostructural with the $[CeMo_{12}O_{42}]^{8-}$ anion[4] and has similar

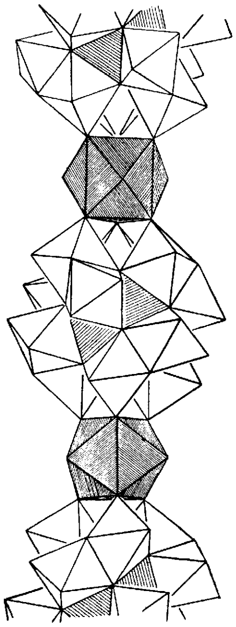

FIGURE. General polyhedral representation of the structure of the chain complex $[Th(H_2O)_3UMo_{12}O_{42}]_n^{4n-}$.

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk.-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

dimensions to those found in $CuH_6UMo_{12}O_{42}$, $12H_2O$,[5] acts as a hexadentate ligand forming two co-ordination sets by the three terminal oxygen atoms of the three adjacent MoO_6 octahedra for the co-ordination of the thorium atom.

From eight possible positions, two in *trans*-positions along the C_3 axis are occupied by thorium atoms forming 'core-link' or polymer chains. Molybdenum–oxygen distances as expected are divided in four groups: molybdenum–terminal oxygen bonded only to one molybdenum, 1·687 Å; molybdenum–oxygen shared with thorium, 1·760 Å; molybdenum–bridging oxygen in Mo_2O_9 face-shared groups, 1·898 and 1·961 Å in the MoO_6 octahedra disturbed and undisturbed by complex formation, respectively; molybdenum–internal oxygen common to three molybdenum atoms, 1·922 and 2·289 Å. Six pairs of Mo_2O_9 groups each formed by two face-shared octahedra are linked by 12 oxygen atoms by corner-sharing. These twelve internal oxygen atoms form an icosahedron around uranium(IV) with a mean U–O distance 2·501 Å.

Thorium(IV) has a co-ordination number of 9 and is in the centre of a tricapped trigonal prism formed by three terminal oxygen atoms from two $[UMo_{12}O_{42}]^{8-}$ anions (Th–O 2·402 Å) and by three water molecules (Th–OH_2 2·537 Å). In the crystal the polymer chains $[Th(H_2O)_3UMo_{12}O_{42}]_n^{4n-}$ have no direct contact with each other and are linked by a complicated system of hydrogen bonds.

Comparison of structural parameters of the previously reported compounds $CuH_6UMo_{12}O_{42}$[5] and $(NH_4)_2Er_2UMo_{12}O_{42}$[2] with those found in this study shows unambiguously that the protonation in the acid salt takes place at the bridging oxygen atoms of the Mo–O–Mo bonds and not at the terminal ones.

It should be noted that the complex formation of d- and f-block elements with the heteropolyanions $[XMo_{12}O_{42}]^{8-}$ proceeds readily without destruction of the MoO_6 octahedron owing to the high negative charge and the presence of suitable oxygen atoms. This is in contrast with the Keggin molecule $[ZM_{12}O_{40}]^{n-}$ or the related $[P_2W_{18}O_{62}]^{6-}$ which gain higher charge after the removal of M=O groups from the structure leaving 4 or 5 oxygen atoms acting as donor atoms to the introduced element. f-Block elements co-ordinate two such 'defect' anions forming a complex XL_2[6] with X placed in the square antiprism.[7]

We are grateful to V. E. Zavodnik and V. K. Bel'skii for the *X*-ray diffraction results.

(*Received*, 28*th August* 1980; *Com.* 944.)

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