

## A Novel Type of Heteropolynuclear Complex Anion: X-Ray Crystal Structure of the Polymeric Complex Anion $[\text{Th}(\text{H}_2\text{O})_3\text{UMo}_{12}\text{O}_{42}]_n^{4n-}$

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**Summary** The interaction of the  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$  anion with  $\text{Th}^{4+}$  results in the formation of an infinite chain complex  $[\text{Th}(\text{H}_2\text{O})_3\text{UMo}_{12}\text{O}_{42}]_n^{4n-}$ , in which the Th atom has tricapped trigonal-prismatic geometry.

in isolation because it is a polymer of the 'core-link' type (Figure). The  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$  heteropolyanion, which is isostructural with the  $[\text{CeMo}_{12}\text{O}_{42}]^{8-}$  anion<sup>4</sup> and has similar

In a series of solution studies of the interaction between heteropolyanions of the type  $[\text{XMo}_{12}\text{O}_{42}]^{8-}$  ( $\text{X} = \text{Ce}^{4+}$ ,  $\text{Th}^{4+}$ , and  $\text{U}^{4+}$ ) with d- and f-block elements it was shown that the heteropolyanion acts as a polydentate ligand.<sup>1</sup> Complexes of various stoichiometries were isolated as solids and some of them were examined by X-ray crystallography.<sup>2</sup>

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  $(\text{NH}_4)_3\text{HThUMo}_{12}\text{O}_{42} \cdot 15\text{H}_2\text{O}$ .

**Crystal data:** hexagonal, space group  $R\bar{3}c$ ,  $a = 18.699(4)$ ,  $c = 24.381(9)$  Å,  $D_c = 3.53$  g cm<sup>-3</sup>,  $U = 7380$  Å<sup>3</sup>. Data were collected using Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$  Å) with a Syntex P1 automatic diffractometer. All calculations were performed using the programs Kristall.<sup>3</sup>

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  $R = 5.5\%$ . The final structure refinement using 1201 independent reflexions with anisotropic temperature factors for U, Th, and Mo reduced  $R$  to 4.9%.†

The X-ray structure determination has shown that it is impossible to consider the separate molecules of the complex

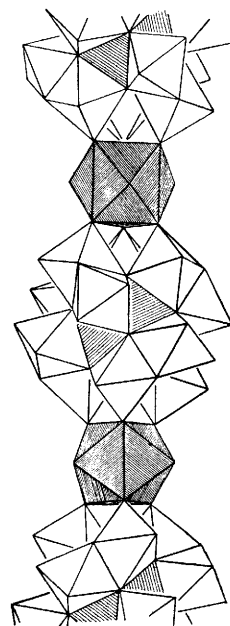


FIGURE. General polyhedral representation of the structure of the chain complex  $[\text{Th}(\text{H}_2\text{O})_3\text{UMo}_{12}\text{O}_{42}]_n^{4n-}$ .

† 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  $\text{CuH}_6\text{UMo}_{12}\text{O}_{42} \cdot 12\text{H}_2\text{O}$ ,<sup>5</sup> acts as a hexadentate ligand forming two co-ordination sets by the three terminal oxygen atoms of the three adjacent  $\text{MoO}_6$  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  $\text{Mo}_2\text{O}_9$  face-shared groups, 1.898 and 1.961 Å in the  $\text{MoO}_6$  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  $\text{Mo}_2\text{O}_9$  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  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$  anions (Th-O 2.402 Å) and by three water molecules (Th-OH<sub>2</sub> 2.537 Å). In the crystal the polymer chains  $[\text{Th}(\text{H}_2\text{O})_3-$

$\text{UMo}_{12}\text{O}_{42}]_n^{4n-}$  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  $\text{CuH}_6\text{UMo}_{12}\text{O}_{42}$ <sup>5</sup> and  $(\text{NH}_4)_2\text{Er}_2\text{UMo}_{12}\text{O}_{42}$ <sup>2</sup> 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  $[\text{XMo}_{12}\text{O}_{42}]^{8-}$  proceeds readily without destruction of the  $\text{MoO}_6$  octahedron owing to the high negative charge and the presence of suitable oxygen atoms. This is in contrast with the Keggin molecule  $[\text{ZM}_{12}\text{O}_{40}]^{n-}$  or the related  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  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  $\text{XL}_2$ <sup>6</sup> with X placed in the square antiprism.<sup>7</sup>

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