The Novel Heteropolyoxo-metallate Anion $[Te_6Mo_{12}O_{60}]^{12-}$ in $(NH_4)_{12}[Te_6Mo_{12}O_{60}]\cdot8H_2O$

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The novel cyclic heteropolyoxo-metallate anion $[Te_6Mo_{12}O_{60}]^{12-}$ representing the first inorganic derivative of a hitherto unknown cyclic hexatelluric acid has been synthesized in aqueous solution and characterized by X-ray structure analysis of a single crystal of $(NH_4)_{12}[Te_6Mo_{12}O_{60}]\cdot8H_2O$.

Various polyoxo-metallate anions, the derivatives of the so-called heteropoly acids, with the general formula $[A_xB_yO_z]^{n-}$ (A = Te, P, Si, Se, etc., B = V, Nb, Mo etc.), are known in great number, the first of them having been described more than a century ago.[1] Compared to the variability of their chemical composition, the number of different anion structure types is rather small. A few types of anions are favoured because of their particular stability and are known as, e.g., Keggin, Anderson–Evans, Dexter–Silverton and Dawson structures.[2] However, it must be assumed that further anion types occur during the various intermediate steps of condensation on the way to the well known heteropoly anions like the Anderson–Evans type anion.

The Anderson–Evans type anion $[TeMo_6O_{24}]^{6-}$, which is composed of six edge-sharing MoO_6 coordination octahedra linked to a central TeO_6 octahedron by common edges, predominates in aqueous solution even in the presence of an excess of telluric acid. Thus compounds are formed entrapping $Te(OH)_6$ molecules in the crystalline state such as $(NH_4)_6[TeMo_6O_{24}]\cdot Te(OH)_6\cdot7H_2O$[3] and $Cs_6[TeMo_6O_{24}]\cdot2Te(OH)_6\cdot4H_2O$.[4] Recently we succeeded in isolating a novel heteropolyanion containing Te and Mo in the stoichiometric ratio of 1:2.

An aqueous suspension of $Te(OH)_6$ and MoO_3 in the molar ratio of 1:1.8 was heated to 60 °C and adjusted to pH 7.5 by dropwise addition of aqueous NH_3 (25%). The mixture was concentrated to one-sixth of its initial volume and allowed to cool slowly. Rhombic plate-like crystals of $(NH_4)_{12}[Te_6Mo_{12}O_{60}]\cdot8H_2O$ appeared within a few hours and were removed from the mother liquor in order to prevent their

conversion to compounds containing the Anderson–Evans type anion which were found to be the final products.

A single-crystal structure analysis† showed a puckered ring composed of six corner-sharing distorted TeO_6 octahedra to be the dominant structural feature of the $[Te_6Mo_{12}O_{60}]^{12-}$ anion (Fig. 1). A pair of face-sharing, considerably distorted, MoO_6 octahedra is attached to each TeO_6 octahedron via common corners and common edges, respectively (Fig. 2), thus yielding the cyclic heteropoly anion with crystallographic $\bar{3}$ symmetry shown in Fig. 3.

Hence we have found the first example of a heteropoly anion derived from the hypothetical cyclic hexatelluric acid $[TeO(OH)_4]_6$. Oligomeric condensation products of telluric
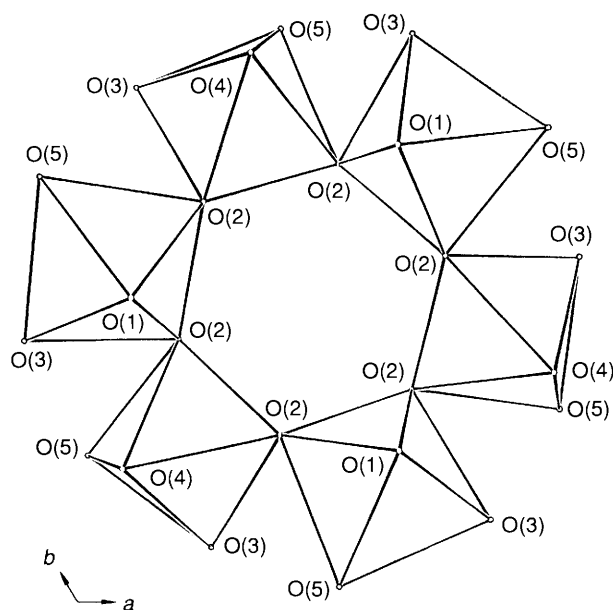
Fig. 1 The distorted coordination octahedra around Te are connected by common corners [O(2)] to form a six-membered puckered ring. The Te atoms lie alternately 41 pm above and below the mean plane of the six Te atoms of the ring.
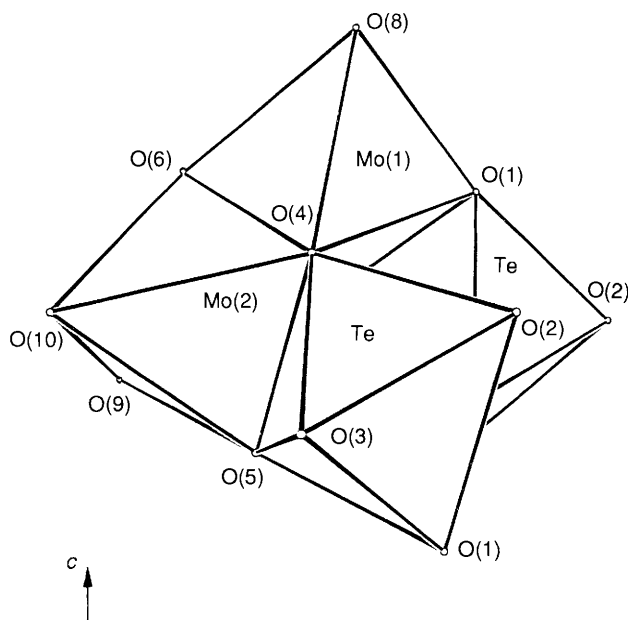

Fig. 2 A fragment of the novel cyclic heteropoly anion showing two coordination octahedra around Te and both the coordination octahedra around Mo(1) and Mo(2). The MoO_6 octahedra are linked by a common face [O(3), O(4) and O(6)]. The Mo coordination octahedra share common edges [Mo(1): O(1)–O(3), Mo(2): O(4)–O(5)] and common corners [Mo(1): O(4), Mo(2): O(3)] with the TeO_6 octahedra. Face-sharing MoO_6 octahedra are rare in heteropoly-anions. One example is provided in the Dexter–Silverton anion $[CeMo_{12}O_{42}]^{8-}$.

acid have been assumed to occur in concentrated aqueous solutions of $Te(OH)_6$;[5] however, only few oligo-tellurates have been described hitherto. The $[Te_2O_6(OH)_4]^{4-}$ anion in $K_4[Te_2O_6(OH)_4]\cdot7.3H_2O$ consists of two edge-sharing tellurium–oxygen coordination octahedra with Te–O bond lengths ranging from 186.1(10) to 202.9(10) pm.[6] Chains of corner-sharing TeO_6 octahedra have been found in the crystal structure of tellurium(IV, VI) oxide hydroxide, $H_2Te_2O_6$, with Te^{VI}–O bonds in the range between 186.4(5) and 195.2(5) pm.[7]
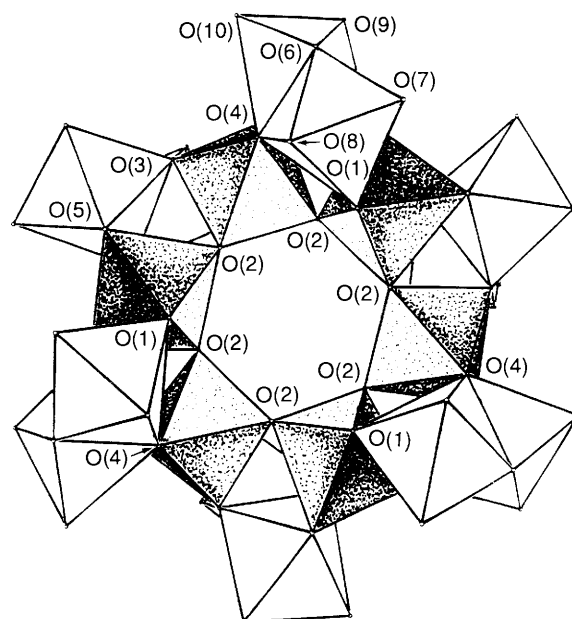

Fig. 3 The entire $[Te_6Mo_{12}O_{60}]^{12-}$ anion viewed from the [001] direction. (The coordination octahedra around Te are shaded.) Adjacent pairs of MoO_6 octahedra do not share oxygen atoms with one another, but only with the TeO_6 octahedra to which they are attached. Hence, the anion lacks a continuous –O–Mo–O–Mo–O– pathway and may be formulated alternatively as $[Te_6O_6(Mo_2O_9)_6]^{12-}$.

Table 1 Bond distances (pm) in the $[Te_6Mo_{12}O_{60}]^{12-}$ anion

Te–O(4)	189.0(2)	Mo(1)–O(7)	169.9(3)	Mo(2)–O(10)	170.7(2)
Te–O(3)	191.0(2)	Mo(1)–O(8)	172.5(3)	Mo(2)–O(9)	171.2(3)
Te–O(2)	192.0(3)	Mo(1)–O(6)	190.8(2)	Mo(2)–O(6)	193.1(2)
Te–O(1)	192.7(2)	Mo(1)–O(1)	197.0(2)	Mo(2)–O(5)	196.4(3)
Te–O(2')	193.3(2)	Mo(1)–O(3)	220.9(2)	Mo(2)–O(4)	222.2(3)
Te–O(5)	193.8(3)	Mo(1)–O(4)	249.0(3)	Mo(2)–O(3)	240.2(2)

Table 2 Mean M–O bond distances (pm) of the $[Te_6Mo_{12}O_{60}]^{12-}$ anion compared to those of the Anderson–Evans-Type anion $[TeMo_6O_{24}]^{6-}$ in $Cs_6[TeMo_6O_{24}]\cdot2Te(OH)_6\cdot4H_2O$ (M = Te, Mo)[a]

No. M atoms bound to O	$[Te_6Mo_{12}O_{60}]^{12-}$			$[TeMo_6O_{24}]^{6-}$		
	min	max	mean	min	max	mean
1	169.9	172.5	171.1	169.3	173.1	171.3
2	190.8	197.0	193.6	190.4	197.3	193.7
3	189.0	249.0	218.7	192.3	233.2	218.0

[a] Ref. 4.

Table 1 gives bond distances of the $[Te_6Mo_{12}O_{60}]^{12-}$ anion. The Te–O bond lengths are spread over the narrow range between 189.0 and 193.8 pm, resembling the values known for Te–OH bonds [190.7(1)–191.4(1) pm] in $Te(OH)_6$.[8] The Mo–O bond lengths vary considerably according to the number of atoms bound to O. The mean bond distances (Table 2) of the $[Te_6Mo_{12}O_{60}]^{12-}$ anion correspond well with those found in the Anderson–Evans type anion $[TeMo_6O_{24}]^{6-}$.[4] The same is true for the range of M–O distances, except those with oxygen atoms bound to three atoms. Correspondingly the mean bonding order of the Te and Mo atoms calculated according to the method of Brown[9] is 5.8 in both compounds, close to the expected value of 6.0.

Close metal–metal‡ contacts may be regarded as a charac-

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‡ Te is regarded as a metal in this context.

teristic feature of the $[Te_6Mo_{12}O_{60}]^{12-}$ anion [Mo(1)–Mo(2) 314.9(2), Te–Mo(1) 313.9(2), Te–Mo(2) 312.7(3) pm]. The metal atoms of $[TeMo_6O_{24}]^{6-}$ are more remote from each other [Te–Mo 330.0(1)–330.4(1), Mo–Mo 328.3(1)–331.3(1) pm].[4] This may be responsible for the dominance of the $[TeMo_6O_{24}]^{6-}$ anion even in solution with a considerable excess of telluric acid.

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