Synthesis and Structure of a Novel Polymolybdate which contains Five-coordinated Molybdenum(VI)

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The reaction of $Te(OH)_6$ with $[Bu^n{}_4N]_4[\alpha\text{-}Mo_8O_{26}]$ yields a novel heteropolymolybdate, $[Bu^n{}_4N]_4[TeMo_8O_{29}(OH_2)]$, which, according to X-ray structural analysis, contains a five-coordinated molybdenum(VI) atom.

Polyoxometallates have been studied mainly in aqueous systems.[1] Recent studies,[2–4] however, implied the existence of new kinds of polyoxoanions in non-aqueous systems which have structures totally different from those of aqueous polyoxometallates. Here we report the synthesis and structure of a new non-aqueous polymolybdate which has an unprecedented type of structure.

Compound **1**, $[Bu^n{}_4N]_4[TeMo_8O_{29}(OH_2)]$, was prepared as follows. A mixture of $Te(OH)_6$ (4.4×10^{-4} mol) and $[Bu^n{}_4N]_4[\alpha\text{-}Mo_8O_{26}]$[5] ($4.4 \times 10^{-4}$ mol) in MeCN (30 ml) was heated at reflux for 3 h. After filtration, the pale yellow solution was evaporated to dryness, and the residue was washed with Et_2O (2×30 ml) to yield 0.83 g (81%) of crude material. This material was dissolved in acetone (12 ml) and precipitated by the addition of Et_2O (10 ml) to give 0.55 g (54%) of compound **1** as an analytically pure white powder.†

X-Ray structure analysis of crystalline compound **1**, obtained from acetone–ethyl acetate solution, revealed the presence of discrete $[TeMo_8O_{29}(OH_2)]^{4-}$ anions.‡ As can be seen from Fig. 1, the $[TeMo_8O_{29}(OH_2)]^{4-}$ anion contains a five-coordinated Mo^{VI} atom, Mo(7). The coordination around Mo(7) atom is best approximated by a distorted square pyramid. Four basal oxygen atoms O(6), O(11), O(13) and O(26) are coplanar to within 0.05 Å, and Mo(7) is displaced from this plane towards O(27) by 0.45 Å. This contrasts with the trigonal bipyramidal coordination around Mo observed in $MoO_2[C_5H_3N(CH_2CPh_2S)_2]$,[6] the only other structurally

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† Satisfactory elemental analyses (C, H, N, Mo, Te) were obtained; IR: ν/cm^{-1} (mineral oil) 950m, 924s, 900m, 806s, 732s, 732s, 670w, 644m, 570m, 536w, 498w, 422w and 382m.

‡ *Crystal data* for **1**: $C_{64}H_{146}N_4TeMo_8O_{30}$, $M = 2347.0$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 16.738(4)$, $b = 34.709(9)$, $c = 16.291(4)$ Å; $U = 9464(4)$ Å^3; $Z = 4$; $D_c = 1.65$ g cm^{-3}; λ(Mo-Kα) = 0.71069 Å, $\mu = 13.7$ cm^{-1}, crystal size $0.29 \times 0.14 \times 0.16$ mm, $T = 25$ °C, $F(000) = 4744$, $6 \leq 2\theta \leq 55°$, R (R_w) = 0.069 (0.069), for 3066 unique reflections with $I > 3.0\sigma(I)$. The structure was solved by analysing the Patterson function and refined by full-matrix least-squares. Metal atoms (Mo and Te) were refined anisotropically. All other non-hydrogen atoms were refined isotropically. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Date Centre. See Notice to Authors, Issue No. 1.

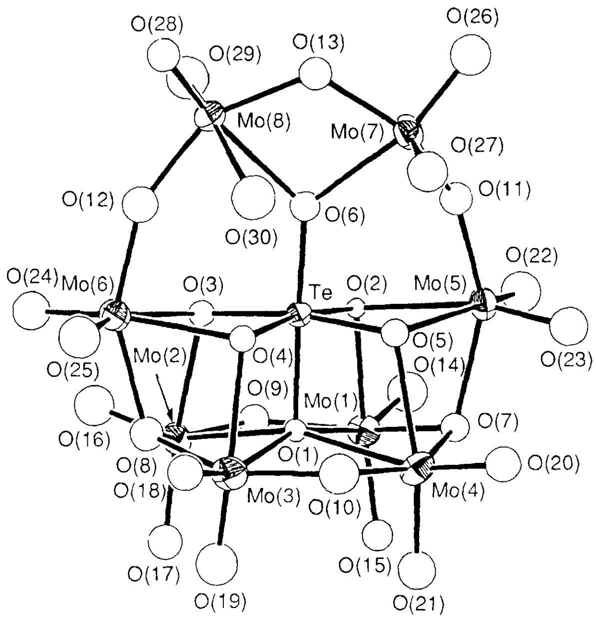

Fig. 1 The structure of $[TeMo_8O_{29}(OH_2)]^{4-}$. Ellipsoids and spheres are drawn to encompass 30% of the electron density. O(30) is the oxygen atom of a water molecule. Selected distances (Å): Te–O(1) 1.98(2), Te–O(2) 1.90(2), Te–O(3) 1.85(2), Te–O(4) 1.88(2), Te–O(5) 1.84(2), Te–O(6) 1.85(2), Mo(1)–O(1) 2.40(2), Mo(1)–O(2) 2.22(2), Mo(1)–O(7) 2.08(2), Mo(1)–O(9) 1.91(2), Mo(1)–O(14) 1.68(3), Mo(1)–O(15) 1.76(2), Mo(2)–O(1) 2.36(2), Mo(2)–O(3) 2.26(2), Mo(2)–O(8) 2.05(3), Mo(2)–O(9) 1.83(2), Mo(2)–O(16) 1.70(3), Mo(2)–O(17) 1.73(3), Mo(3)–O(1) 2.42(2), Mo(3)–O(4) 2.26(2), Mo(3)–O(8) 1.97(2), Mo(3)–O(10) 1.90(3), Mo(3)–O(18) 1.67(3), Mo(3)–O(19) 1.62(3), Mo(4)–O(5) 2.29(2), Mo(4)–O(7) 2.02(2), Mo(4)–O(10) 1.86(3), Mo(4)–O(20) 1.71(3), Mo(4)–O(21) 1.77(3), Mo(5)–O(2) 2.29(2), Mo(5)–O(5) 2.24(2), Mo(5)–O(7) 2.13(2), Mo(5)–O(11) 1.89(3), Mo(5)–O(22) 1.66(3), Mo(5)–O(23) 1.80(3), Mo(6)–O(3) 2.22(2), Mo(6)–O(4) 2.32(2), Mo(6)–O(8) 2.09(2), Mo(6)–O(12) 1.90(3), Mo(6)–O(24) 1.73(3), Mo(6)–O(25) 1.69(3), Mo(7)–O(6) 2.20(2), Mo(7)–O(11) 1.88(3), Mo(7)–O(13) 1.87(2), Mo(7)–O(26) 1.66(3), Mo(7)–O(27) 1.72(3), Mo(8)–O(6) 2.29(2), Mo(8)–O(12) 1.89(3), Mo(8)–O(13) 1.95(3), Mo(8)–O(28) 1.67(3), Mo(8)–O(29) 1.68(3), Mo(8)–O(30) 2.64(3).

characterized five-coordinated Mo^{VI} complex to our knowledge. The oxgen atoms O(6), O(12), O(13), O(28) and O(29) form a distorted square pyramid around Mo(8). The basal oxygen atoms [O(6), O(12), O(13), O(28)] are coplanar to within 0.04 Å, and Mo(8) is displaced from this plane towards O(29) by 0.35 Å. A water molecule is weakly bound to the Mo atom from the other side of the apical O(29) to complete an elongated octahedron. Square pyramidal and elongated octahedral coordinations around the metal atom are often encountered in polyoxovanadate chemistry,[1,7] but are rare in Mo^{VI} compounds and have never been reported for discrete polymolybdates before.§

Unlike that in $[TeMo_6O_{24}]^{6-}$,[9] the TeO_6 octahedron in **1** is highly distorted. The Te–O(1) distance (1.98 Å) is significantly longer than the other five Te–O bonds which average 1.86 Å.

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§ The infinite $([Mo_3O_{10}]^{2-})_\infty$ chain in $K_2Mo_3O_{10}$ contains five-coordinated Mo^{VI}.[8]