Synthesis and *X*-Ray Structure of a Mixed Oxidation State Tetrameric Molybdenum(III,IV) Complex Di-μ-oxo-bis[μ-oxo-μ-hydroxo-μ(*NN*′)-ethylenediaminetetra-acetatomolybdate(III,IV)]

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Summary The title complex, obtained by azide oxidation of a dimeric molybdenum(III,III) complex, is diamagnetic; it has four identical Mo's in a rectangular planar arrangement with alternate μ-oxo-μ-hydroxo (Mo–Mo 2·41 Å) and μ-oxo bridges.

Dimeric molybdenum(III,III),[1] -(V,V),[2] and -(VI,VI)[3] complexes, each having a single sexadentate ethylenediaminetetra-acetate (edta) ligand, have been prepared previously. Studies on the reaction of azide (and less extensively hydrazine) with the green molybdenum(III,III) dimer μ-acetato-di-μ-hydroxo-μ(*NN*′)ethylenediaminetetra-acetatobis[molybdate(III)], K[$Mo_2(OH)_2(O_2CMe)$(edta)], (A), under rigorous air-free conditions (N_2 or Ar) have shown that a maroon molybdenum(III,IV) species (C) is formed. No reaction is observed in sodium acetate–acetic acid buffer, pH 4·7 (pK_a 4·68 for HN_3 acid dissociation at 20 °C).[4] At pH 8 however, using either acetate or triethanolamine as buffer, the reaction occurs within 2 h at 20 °C. Acid dissociation of one of the μ-hydroxo ligands of (A) was detected spectrophotometrically (green → brown) and a pK_a of 7·73 at 25 °C was determined by pH titration of a 0·01M solution. The pK_a (7·29) of the di-μ-hydroxo-μ(*NN'*)ethylenediaminetetra-acetato-bis[thiocyanatomolybdate(III)] complex, $K_2[Mo_2(OH)_2(NCS)_2(edta)].3H_2O$, (B),[1] was also determined. On addition of acid both reactions were instantly reversible; no second acid dissociation was detected on addition of NaOH to pH $\leqslant$ 11·8. It is concluded therefore that the conjugate-base form of (A) is redox active. The non-reactivity of (B) under similar conditions suggests that in the reaction with (A) N_3^- partially displaces acetate (and subsequently oxidises the Mo), but is unable to displace thiocyanate. Other products which predominate with increasing amounts of azide are a molybdenum(IV) species, the nature of which is at present uncertain, and the molybdenum(V,V) dimer $[Mo_2O_4(edta)]^{2-}$. A maximum build-up (*ca.* 40%) of the molybdenum(III,IV) complex (C) is observed for a 1:1 azide to dimer reactant ratio. The amounts of nitrogen (volume of gas) and ammonia (micro-Kjeldahl method) evolved are consistent with the reaction: $N_3^- + 2e^- + 3H^+ \rightarrow NH_3 + N_2$.

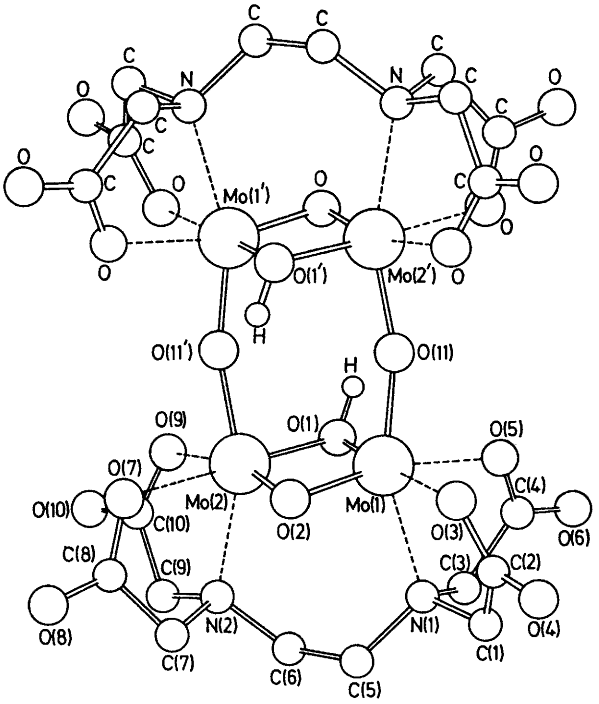

FIGURE. *X*-Ray structure of the molybdenum(III,IV) tetramer, (C) (title complex).

To isolate the sodium salt of (C) an aqueous solution of (A) and NaN_3 (both *ca.* 0·023M) was allowed to react for *ca.* 10 h at 20 °C. Solid sodium acetate (*ca.* 1·0M) was added and the solution kept at 0 °C for 2 days. Crystals, which analysed for $Na_4[Mo_4O_4(OH)_2(edta)_2].12H_2O$, were obtained (yield 32%). To isolate the potassium salt approximately twice the concentration of reactants was required and *ca.* 2 weeks allowed for crystallisation after addition of KN_3 (yield 27%).‡ The oxidation state of Mo in (C) was found to be 3·5 by addition of iron(III) and back titration with cerium(IV).

The *X*-ray crystal structure of the potassium salt of (C), (see Figure) was determined by Patterson and Fourier synthesis and refined by a full-matrix least-squares method to a final *R* index of 0·046.[5] The analysis was based on 4560 reflections collected on an Enraf-Nonius CAD-4 diffractometer at room temperature using graphite crystal-monochromatised Cu-$K_{\alpha 1}$ radiation (λ = 1·5405 Å) to θ = 70° with the ω—2θ scan technique. The data were corrected for absorption by assuming a spherical crystal with μR = 2·62. The complex crystallises in the triclinic system, space group $P\bar{1}$ with cell dimensions a = 9·893, b = 11·603, c = 12·129 Å, α = 115·65, β = 99·16, γ = 77·50° and Z = 2. Four Mo atoms lie in a plane containing a centre of symmetry and each is co-ordinated by six ligands in a distorted octahedral environment similar to the molybdenum(III,III) complex. In this case, however, the double oxygen bridge is not symmetrical O(1) being a hydroxy-group (position of the H-atom determined). The Mo(1)–O(1) and Mo(2)–O(1) (2·08 Å), and the Mo(1)–O(2) and Mo(2)–O(2) (1·93 Å) distances are identical (± 0·6%). The Mo(1)–Mo(2) distance is short (2·41 Å), and the single oxygen bridge has Mo–O distances of 1·90 Å and an Mo(1)–O(11)–Mo(2') angle of 164°. The latter is similar to values found in the molybdenum(VI) complexes $[Mo_2O_7]^{2-}$,[6] and $[\{MoO(O_2)_2(H_2O)\}_2O]^{2-}$.[7] Angles subtended at the Mo's differ by amounts between −18 and +16° from those for an idealized octahedral arrangement.

The u.v.-visible spectrum of (C) gives λ_{max}, nm (ϵ, l mol^{-1} cm^{-1}) as follows: 325 (3200), 300 (2380), 473 (3800), 536 (3520) and 730 (1650). The complex is diamagnetic and is stable for > 2 h at pH 7—10. Further reaction of (C) with azide is extremely slow. It is not clear whether formation of (C) proceeds *via* molybdenum(IV) which then reacts further with molybdenum(III,III), or molybdenum(III,IV) which is highly reactive and subsequently forms the tetramer. Evidence for a tetrameric molybdenum(IV,V) species in electrochemical studies involving dimeric complexes has been reported.[8]

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‡ Satisfactory elemental analytical data were obtained.

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