Synthesis and Crystal Structure Determination of a Novel α-Dawson Mixed-valence Octadecatungstoperchlorate

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The 'heteropoly-blue' species, $[NBu^n{}_4]_3[Cl_2W^VW^{VI}{}_{17}O_{62}]$, prepared by exposure to UV light, has been structurally determined by X-ray diffraction; the anion contains randomly distributed W^V and W^{VI} in a 1:17 ratio and is the first reported mixed-valence heterotungstate which contains two chlorine heteroatoms.

To date, the blue species of the Keggin ($XM_{12}O_{40}$), hexametalate (M_6O_{19}), decatungstate ($W_{10}O_{32}$) and Dawson ($X_2M_{18}O_{62}$) structures have been investigated.[1-5] Pope[6] pointed out that heteropoly-blue formation is a rapid and reversible reduction process accompanied by only minor structural changes if the MO_6 octahedra each have one terminal oxygen atom (Type I anion). We have previously studied the photochemical properties of polyoxometalates in both solution and solid states[7-9] and here we report on the photosynthesis and structure of an α-Dawson[10] mixed-valence tungstoperchlorate with unusual redox properties.

The compound $[NBu^n{}_4]_3[Cl_2W^VW^{VI}{}_{17}O_{62}]$ was prepared by dissolving $Na_2WO_4{\cdot}2H_2O$ (10 g, 30.3 mmol) in acetic anhydride–dimethylformamide (dmf)–HCl (35%) (15 cm^3:10 cm^3:5 cm^3) and irradiating the stirred refluxing solution with a 250 W superhigh-pressure mercury lamp for 10 h. A blue precipitate was obtained upon adition of an aqueous methanol solution (20 cm^3) of tetrabutylammonium bromide (5 g). The precipitate was washed with ethanol and diethyl ether and then recrystallized from dimethyl sulfoxide. Blue crystals (4.3 g, 50.1% yield) were formed after a week, turning increasingly dark blue on exposure to air. This observation implies an *irreversible* reduction of W^{VI} to W^V, in contrast to Pope's argument stated above,[6] and his observations upon $[P_2W_{18}O_{62}]^{6-}$.[11]

Elemental analysis was in accord with the proposed formulation (Found: C, 11.90; H, 2.20; N, 1.00; WO_3, 81.35. $C_{48}H_{108}Cl_2N_3O_{62}W_{18}$ requires C, 11.30; H, 2.10; N, 0.80; WO_3, 81.85%). Quantitative analysis of W^V by titration with $KMnO_4$ under a nitrogen atmosphere confirmed the one-electron reduced nature of the species. IR (KBr, cm^{-1}): 1091.3 [$\nu(Cl^{VII}O_4)$]; 987.5, 965.6 [$\nu(W{-}O_d)$]; 906.2 [$\nu(W{-}O_b{-}W)$]; 803.1, 512.5, 487.5 [$\nu(W{-}O_c{-}W)$]. UV (λ/nm, in MeCN): 213, 250, 295. Cyclic voltammetry of the compound in dmf (10^{-3} mol dm^{-3}) with NBu_4BF_4 (0.1 mol dm^{-3}) as supporting electrolyte, utilising platinum electrodes and a scan rate of 100 mV s^{-1}, showed three irreversible two-electron reduction peaks at −0.55, −0.68 and −1.17 V relative to Ag–AgCl. The mechanism of the formal oxidation of Cl^- to Cl^{7+} is as yet uncertain.

The single-crystal X-ray diffraction study † indicated an α-Dawson structure consisting of two ClW_9O_{31} half-units with $3/m$ pseudo-symmetry (Fig. 1). Each half-unit has a central distorted ClO_4 tetrahedron sharing corners with three edge-shared polar WO_6 octahedra and six alternately edge- and corner-shared equatorial ones. An alternative description of the anion frame can be made in terms of the fusion of two Keggin structures $[XW_{12}O_{40}]^{n-}$ with the removal of a W_3O_{12} ring formed by three corner-shared WO_6 octahedra from each $[XW_{12}O_{40}]^{n-}$ unit and connection of the two residues *via* six oxygen atoms which lie on an approximate mirror plane.

Three kinds of oxygen atoms are found in the structure: O_d (unshared terminal), O_b (shared by two neighbouring WO_6 octahedra) and O_c (belonging to ClO_4 tetrahedra) with W–O_d 1.59–1.80 Å, W–O_b 1.82–2.01 Å and W–O_c 2.41–2.54 Å. These values can be compared with the corresponding bond lengths for $[P_2W_{18}O_{62}]^{6-}$ (ref. 10) of *ca.* 1.85, 2.00 and 2.35 Å respectively, indicating considerable displacement of individual WO_6 octahedra and structural distortion of the present anion framework. We can speculate that the introduction of the paramagnetic electron may lead to this distortion (absent in $[P_2W_{18}O_{62}]^{6-}$).

The oxygen atoms in the ClO_4 tetrahedra can be further divided into two types: those shared by two neighbouring equatorial WO_6 octahedra with Cl–O bond lengths (1.42–1.47 Å) in the range for unbound perchlorate (Cl–O 1.41–1.48 Å)[13] and those shared by three polar WO_6 octahedra with Cl–O distances (1.49 and 1.55 Å) somewhat longer due to their higher effective co-ordination number.

The powder ESR spectrum of $[NBu^n{}_4]_3[Cl_2W^VW^{VI}{}_{17}O_{62}]$ indicates the presence of W^V. The only signal at 100 K is a singlet [$\Delta H = 28$ G (0.0028T)], with the isotropic *g* factor of 1.841 being a little lower than those of α-$[P_2W_{18}O_{62}]^{7-}$ ($\langle g \rangle = 1.858$) and α-$[As_2W_{18}O_{62}]^{7-}$ ($\langle g \rangle = 1.854$).[14] Because of the limitation of our experimental equipment, the temperature could not be lowered further to enable the

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† Crystal data. $[NBu^n{}_4]_3[Cl_2W^VW^{VI}{}_{17}O_{62}]$, $C_{48}H_{108}Cl_2N_3O_{62}W_{18}$, $M = 5099.6$, crystal dimensions 2.5 × 3.0 × 2.5 mm, triclinic, space group $P1$, $a = 15.676(3)$, $b = 16.315(4)$, $c = 15.062(2)$ Å, $\alpha = 62.26(1)$, $\beta = 121.35(2)$, $\gamma = 118.74(2)°$, $U = 2762.5$ Å^3, $Z = 1$, $D_c = 3.065$ g cm^{-3}, μ(Mo-Kα) = 191.934 cm^{-1}, $F(000) = 2279$, Enraf–Nonius CAD4 diffractometer, Micro-VAX II computer, graphite-monochromated Mo-Kα radiation (λ = 0.709 30 Å), scan range $0 \leqslant \theta \leqslant 25°$. A total of 10 093 reflections were obtained, of which 6384 with $I > 3\sigma(I)$ were considered observed and to which unit weights were applied ($w = 1$). The structure was solved by direct methods with the SDP program[12] and refined anisotropically to give $R = 0.039$ and $R' = 0.048$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

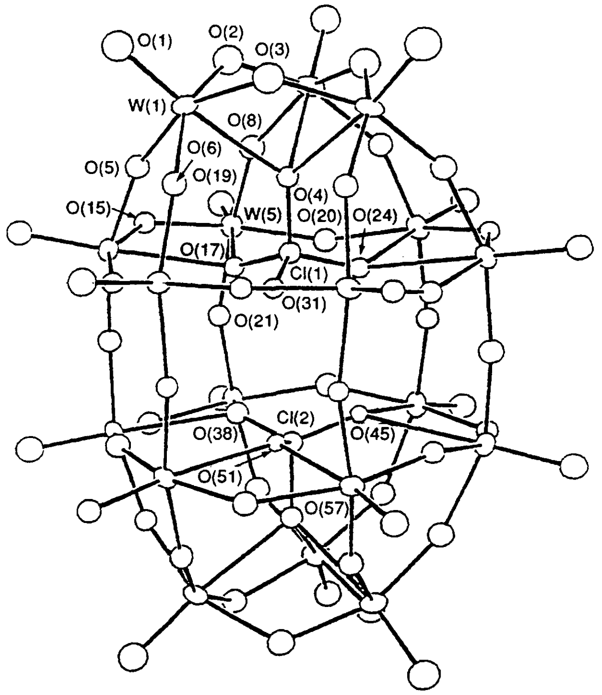

Fig. 1 Structure of the anion in $[NBu^n{}_4]_3[Cl_2W^VW^{VI}{}_{17}O_{62}]$. Selected bond lengths (Å): W(1)–O(1) 1.73(1), W(1)–O(2) 1.86(1), W(1)–O(3) 1.89(1), W(1)–O(4) 2.46(2), W(1)–O(5) 1.89(2), W(1)–O(6) 1.93(1), W(5)–O(8) 1.88(1), W(5)–O(15) 1.91(2), W(5)–O(17) 2.516(9), W(5)–O(19) 1.59(1), W(5)–O(20) 1.86(2), W(5)–O(21) 1.89(2), Cl(1)–O(4) 1.49(1), Cl(1)–O(17) 1.47(2), Cl(1)–O(24) 1.42(2), Cl(1)–O(31) 1.46(2), Cl(2)–O(38) 1.44(2), Cl(2)–O(45) 1.433(9), Cl(2)–O(51) 1.43(1), Cl(2)–O(57) 1.55(1)

observation of possible hyperfine structure which may arise from a trapped paramagnetic electron at low temperature. The absence of hyperfine structure at 100 K and above suggests that the unpaired electron may be somewhat delocalized over the W atoms in the anion network due to thermally activated electron hopping.

Further investigation of the redox properties and possible utilization of this kind of heteropoly-blue would be of interest.

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