COMMUNICATION

ChemComm
www.rsc.org/chemcomm

The three-electron heteropoly blue $[P_6Mo_{18}O_{73}]^{11-}$ with a basket-shaped skeleton†

Xian-Ming Zhang,*[a,b] Hai-Shun Wu,[a] Fu-Qiang Zhang,[a] Alexander Prikhod'ko,[b] Shigemasa Kuwata[b] and Peter Comba*[b]

[a] *School of Chemistry & Material Science, Shanxi Normal University, Linfen 041004, Shanxi, P. R. China. E-mail: zhangxm@dns.sxtu.edu.cn*

[b] *Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. E-mail: peter.comba@aci.uni-heidelberg.de*

Received (in Cambridge, UK) 20th April 2004, Accepted 1st July 2004
First published as an Advance Article on the web 13th August 2004

The novel basket-shaped three-electron-reduced heteropoly blue $[H_2dmpip]_5[K \subset P_6Mo_{18}O_{73}]$ was prepared and characterized; it shows reversible one-electron redox properties.

The continuing interest in heteropoly metallates results from their aesthetically pleasing structures, their interesting host–guest chemistry and manifold applications in catalysis and medicine.[1] Heteropoly blues are an interesting subclass which are deep blue mixed-valence molybdates or tungstates and are obtained by one- or more-electron reduction of the corresponding Mo^{VI} and W^{VI} polyoxo anions. They have been intensely studied with respect to inter- and intramolecular electron transfer, mixed metal oxide conductivity, various types, mechanisms and pathways for mixed-valence electron delocalization, electron spin coupling and the properties of isolated, paramagnetic spin-coupled systems. Furthermore, the heteropoly blues have potential as specific reducing agents since they can release a defined number of their "blue" electrons at well specified redox potentials.[1a] Most applications are based on few small to medium classical heteropoly metallates, particularly the Anderson–Evans structure $[XM_6O_{24}]^{x-}$ (X = heteroatom, M = Mo, W), the Keggin structure $[XM_{12}O_{40}]^{x-}$ (M = V, Mo, W), the Wells–Dawson structure $[X_2M_{18}O_{62}]^{x-}$ (M = V, Mo, W), the Pope–Jeannin–Preyssler structure $[X_5M_{30}O_{110}]^{x-}$ (M = W) and derivatives, such as monovacant, divacant and trivacant clusters. A range of spectacular giant polymolybdate structures have been reported recently[2a] and various new applications are emerging.[2b] For both a better understanding of the fundamental principles and the development of new applications, it is of interest to extend the range of non-classical heteropoly clusters.[3] We have a continuing interest in polyoxometallates[4] and mixed-valence compounds in general,[5] and here we report the structure and properties of the heteropoly blue $[H_2dmpip]_5[K \subset P_6Mo_{18}O_{73}]$ **1**, which can reversibly release and recapture its three "blue" electrons.

Compound **1** was obtained by hydrothermal synthesis as dark blue block-like single crystals (70% yield based on Mo) as a single phase, from a mixture of MoO_3, Mo, 2,5-dimethylpiperazine (dmpip), KH_2PO_4, H_3PO_4 and distilled water in the molar ratio of 2 : 0.5 : 1 : 1 : 3 : 666, heated for 5 days at 150 °C under autogenous pressure.‡ Compound **1** is soluble in DMSO and DMSO–H_2O mixtures. The IR spectrum of **1** (KBr pellet) displays one intense band at 938 cm^{-1}, attributed to the Mo–O vibration, and the typical bands for phosphate (1077, 1049, and 1006 cm^{-1}), the H_2dmpip^{2+} cation (3121, 3002, 2987, 2903, and 1587 cm^{-1}), as well as some skeletal vibrations (817, 763, 702, and 590 cm^{-1}). The UV–visible spectrum of **1** has two transitions centered at 619 (sh, $\varepsilon \approx$ 5130 L $mol^{-1}cm^{-1}$) and 745 nm ($\varepsilon \approx$ 7100 L $mol^{-1}cm^{-1}$), attributed to the typical intervalence charge-transfer optical absorption of heteropoly blues (Fig. S1†).

X-Ray single crystal diffraction reveals **1** to consist of isolated $[K \subset P_6Mo_{18}O_{73}]^{10-}$ cryptands and protonated dmpip cations.§ The asymmetric unit consists of nine molybdenum atoms, three phosphorus atoms, the potassium cation, 38 oxygen atoms, 2.5 H_2dmpip cations and some water molecules. O(15) and K(1) lie on the crystallographic two-fold axis and have a site occupancy of 0.5. All nine molybdenum atoms are part of distorted MoO_6 octahedra, the Mo–O bond lengths are in the range of 1.678(3)–2.460(3) Å, and the *cis*-O–Mo–O angles are in the range of 68.21(13)–105.92(15)°. The phosphorus atoms are tetrahedrally coordinated by oxygen, and the P–O bond lengths are in the range of 1.506(3)–1.580(3) Å, the O–P–O angles are in the range of 106.01(17)–112.15(17)°.

There are 2 μ_4, 6 μ_3, 43 μ_2 and 22 terminal oxo groups in the anionic $[P_6Mo_{18}O_{73}]^{11-}$ cluster. The six phosphorus atoms of the cluster belong to two distinct types: two phosphorus atoms are inside the cluster and can be regarded as interstitial heteroatoms, similar to the phosphorus atoms in the Wells–Dawson structure $[P_2M_{18}O_{62}]^{x-}$; the other four phosphorus atoms function as addenda, sharing vertexes with MoO_6 octahedra. The resulting $[P_6Mo_{18}O_{73}]^{11-}$ cluster has approximate C_{2v} symmetry, and is built from two crystallographically equivalent $[P_3Mo_9O_{39}]$ fragments which are linked by 5 oxygen atoms, shared by the two fragments, to result in a basket-shaped cluster, as shown in Fig. 1. Alternately, $[P_6Mo_{18}O_{73}]^{11-}$ can be divided into a lower and an upper part: the

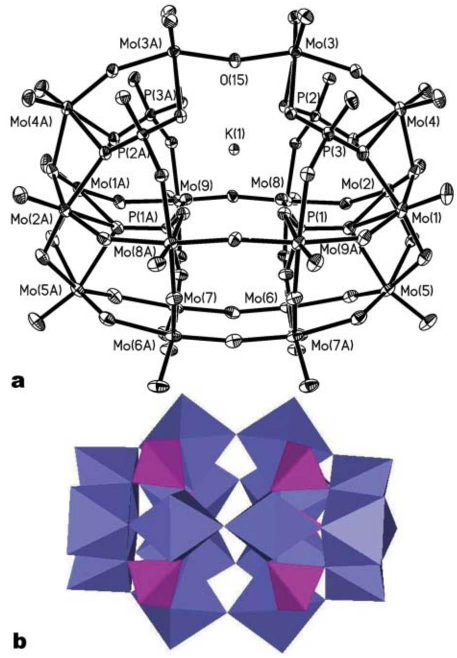

Fig. 1 ORTEP (a) and polyhedral (b) plots of the basket-shaped $[P_6Mo_{18}O_{73}]^{11-}$ cluster (encapsulated K^+ ion included in (a); the polyhedral plot is a top view with respect to the ORTEP plot).

---

† Electronic supplementary information (ESI) available: UV-vis and EPR spectra, magnetic data, and plot of the arrays of clusters of **1**. See http://www.rsc.org/suppdata/cc/b4/b405931j/

DOI: 10.1039/b405931j

lower part is a tetravacant, lacunary derivative of the α-Wells–Dawson structure, formed by removal of four "belt" Mo octahedra; the upper part is the handle of the basket, formed by four MoO_6 octahedra and four PO_4 tetrahedra. Each of the 14 Mo atoms in the lower part of the cluster has only one terminal, double-bonded oxygen atom [Mo–O distances 1.678(3)–1.697(3) Å]. Each of the four Mo atoms in the upper part of the cluster has two terminal, double-bonded oxygen atoms [Mo–O distances 1.697(3)–1.712(3) Å].

The result is a cluster with a void, and this is filled by the guest potassium cation with K···O distances of 2.477–2.768 Å. The H_2dmpip cations are hydrogen bonded to crystal lattice water molecules and oxygen atoms from the $[P_6Mo_{18}O_{73}]^{11-}$ cluster anions (see Fig. S4†). The formation of **1** relies on the presence of K^+, and a similar reaction but without KH_2PO_4 resulted in $[C_6N_2H_{16}]_2[Mo_5O_{15}(HPO_4)]$.[6] This indicates that the K^+ ion is necessary as a template for the formation of $[P_6Mo_{18}O_{73}]^{11-}$. It is interesting to compare **1** with the classical Wells–Dawson $[P_2Mo_{18}O_{62}]^{x-}$ cluster because both contain 18 molybdenum and interstitial phosphorus atoms. The Wells–Dawson structure has 6 oxygen atoms which are shared between two $[PMo_9O_{34}]$ fragments; $[P_6Mo_{18}O_{73}]^{11-}$ has 5 oxygen atoms, shared between two equivalent $[P_3Mo_9O_{39}]$ fragments. Our new cluster has lower symmetry and, in contrast to the Wells–Dawson cluster, a void filled with K^+.

Electronically, the polyanion is remarkable because it is directly obtained as a partially reduced cluster. The $Mo^V : Mo^{VI}$ ratio of 1 : 5, determined from cerimetric titration of a DMSO–H_2O solution, indicates that $[P_6Mo_{18}O_{73}]^{11-}$ is the three-electron-reduced polyanion. Based on the structural properties it is reasonable to assume that the "blue" electrons are located on the Mo atoms of the lower part since only these Mo atoms meet the criteria for receiving "blue" electrons, *i.e.*, double-bonded d^0 addendum atoms in octahedral geometry and a single terminal oxygen atom.[1a]

The magnetic properties of **1** suggest that only one electron is unpaired, the other two "blue" electrons are antiferromagnetically coupled (Fig. S4).† Similar behavior in a heteropolyanion has been observed before.[7] The effective magnetic moment of 1.75 μ_B per cluster anion at room temperature, which is slightly higher than the spin-only value of 1.73 μ_B, may partly be due to a positive, temperature-independent contribution from the coupling of ground and excited state levels through Zeeman perturbation, and to orbital contributions of the Mo^V d^1 ion. The temperature-dependent magnetic measurements show a non-Curie-type behavior, which may be due to second-order Zeeman coefficients. The EPR spectrum of **1** (undiluted powder) also shows that at low temperature (77 K) the single unpaired electron is trapped on a single molybdenum center (Fig. S3,† $g_{1,2,3} \approx 1.86, 1.91, 1.95$; computer simulation). This emerges from the anisotropic hyperfine structure. At elevated temperatures there is a considerable broadening of the signals, indicating that delocalization occurs. Such behavior is typical for class II mixed-valence compounds.

The cyclic voltammogram of **1** in aqueous DMSO, with and without added HCl shows three redox couples between +320 and −149 mV (Fig. 2). In the absence of HCl, the peak-to-peak separations of the three couples are approx. 120, 94 and 81 mV, indicating irreversible and quasi-reversible redox processes. In the presence of HCl (5×10^{-5} M) the three couples are fully reversible, and the peak positions are shifted to more positive potentials. The three well resolved waves ($\Delta E_p \approx 56 \pm 4$ mV) suggest that the three redox couples are sequential one-electron transfer processes. This is confirmed by controlled potential electrolysis. When **1** is further reduced, irreversible peaks emerge at a more negative potential, where **1** decomposes. The electrochemical behavior of three-electron-reduced **1** indicates that it is a good candidate for a specific reducing agent since it can release its three blue electrons at specific and well separated potentials.

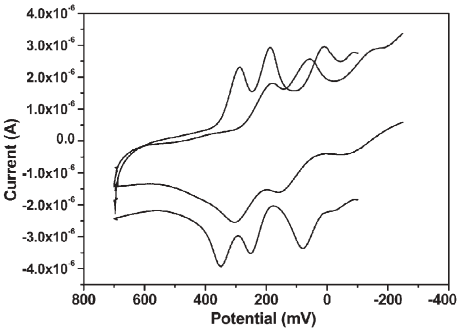

Fig. 2 Cyclic voltammograms of 2.5×10^{-4} M solutions of **1** in aqueous DMSO (1 : 1) without HCl (a) and with HCl (5×10^{-5} M) (b), scan rate 100 mV s^{-1}, potentials measured *versus* Ag/AgCl.

This work is financially supported by the Youth Foundation of Shanxi No. 20041009. Dr X.-M. Zhang thanks Professor Xiao-Ming Chen and Seik Weng Ng for structural solution and refinement and the Alexander von Humboldt Foundation for support during his stay in Germany.

Notes and references

‡ Anal: Calc. For **1** $C_{30}H_{108}N_{10}O_{88}KP_6Mo_{18}$: C, 9.08; H, 2.77; N, 3.54. Found: C, 9.13; H, 2.68; N, 3.54%. IR (KBr, cm^{-1}) for **1**: 3507sb, 3121w, 3002w, 2987w, 2903w, 2826w, 2756w, 2513m, 2322w, 1601s, 1452s, 1384m, 1343w, 1291w, 1124m,, 1072s, 993m, 938s, 898m, 817s,763m, 702m, 590m, 519w.

§ *Crystal data for 1*: monoclinic, space group C2/c, M_r =3925, a = 25.375(4), b = 20.003(3), c = 19.700(3) Å, β = 96.261(2), V = 9940(3) $Å^3$, Z = 4, D_c = 2.658 g cm^{-3}. Data collection $1.61 \leqslant \theta \leqslant 27.55$ for *1* was performed at 293 K on a Bruker Apex CCD diffractometer (Mo-Kα, λ = 0.71073 Å). The structure was solved with direct methods (SHELXS-97[8]) and refined with the full-matrix least-squares technique (SHELXL-97[9]), leading to a final R_1 value of 0.0363 for 695 parameters and 9529 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.0874 for all 10380 reflections. CCDC reference number 237041. See http://www.rsc.org/suppdata/cc/b4/b405931j/ for crystallographic data in .cif format.

1 (*a*) L. C. W. Baker and D. C. Glick, *Chem. Rev.*, 1998, **98**, 3; (*b*) I. V. Kozhevnikow, *Chem. Rev.*, 1998, **98**, 171; (*c*) I. A. Weinstock, *Chem. Rev.*, 1998, **98**, 113; (*d*) N. Mizuno and M. Misono, *Chem. Rev.*, 1998, **98**, 199; (*e*) E. Coronado and C. J. G. Garcia, *Chem. Rev.*, 1998, **98**, 273; (*f*) W. G. Klemperer and C. G. Wall, *Chem. Rev.*, 1998, **98**, 297; (*g*) T. Yamase, *Chem. Rev.*, 1998, **98**, 307; (*h*) J. T. Rhule, C. L. Hill, D. A. Judd and R. F. Schinazi, *Chem. Rev.*, 1998, **98**, 327.

2 (*a*) A. Müller and C. Serain, *Acc. Chem. Res.*, 2000, **33**, 2; (*b*) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, B. Botar and M. O. Talismanova, *Angew. Chem., Int. Ed.*, 2003, **42**, 2085.

3 (*a*) D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4180; (*b*) D.-L. Long, P. Kögerler and L. Cronin, *Angew. Chem., Int. Ed.*, 2004, **43**, 1817.

4 X.-M Zhang, M.-L. Tong and X.-M. Chen, *Chem. Commun.*, 2000, 1817; J. Tao, X.-M. Zhang, M.-L. Tong and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 770.

5 X.-M. Zhang, M.-L. Tong and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1029; X.-M. Zhang, M.-L. Tong, M.-L. Gong, H.-K. Lee, L. Luo, J.-H. Li, Y.-X. Tong and X.-M. Chen, *Chem. Eur. J.*, 2002, **8**, 3187; X.-M. Zhang and X.-M. Chen, *Eur. J. Inorg. Chem.*, 2003, 413.

6 X.-M. Zhang, R.-Q. Fang, H.-S. Wu and S. W. Ng, *Acta Crystallogr., Sect. E*, 2004, **E60**, m171.

7 D. C. Duncan and C. L. Hill, *Inorg. Chem.*, 1996, **35**, 5828; E. Dumas, C. Debiemme-Chouvy and S. C. Sevov, *J. Am. Chem. Soc.*, 2002, **124**, 908.

8 G. M. Sheldrick, SHELXS-97, *Program for Crystal Structure Solution*, Göttingen University, Germany, 1997.

9 G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, Göttingen University, Germany, 1997.