Synthesis and characterization of a Mo/Ag/Rb heterotrimetallic cluster with double-cage architecture

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The first Mo/Ag/Rb heterotrimetallic cluster has been synthesised by a self-assembly reaction involving [Mo₂O₂S₂edt]²⁻, Ag⁺, Rb⁺, S²⁻ and dibenzo-18-crown-6 (DB18C6); the structure consists of two [[Mo₆Ag₆O₆S₇edt]₆][Rb(DB18C6)]⁻ units linked by Rb–C contacts.

Polynuclear metallo-clusters on the one hand, and complexes with extended 3D assemblies on the other, are two quite different types of inorganic compounds which exhibit unusual physical properties and chemical reactivity. We are developing methods to produce extended 3D assemblies of clusters, in the expectation that such materials will have unprecedented structures, properties and reactivity.

The thioanions of molybdenum(VI) and tungsten(VI), [MXS₃]ⁿ⁻ (X = O, S, n = 2; X = HB(C₃H₃N₂)₃ or C₅Me₅, n = 1) have been used to prepare a structurally diverse range of heterometallic sulfido clusters.¹–⁶ Many of these clusters are of interest because of their relevance to biological systems or potential applications in conductive and non-linear optical materials.⁷–⁹

Previous studies¹⁰ have demonstrated that a series of heterobimetallic dodecanuclear M(Ⅴ)/M′(Ⅰ) single cage-like clusters (M = Mo, W; M′ = Cu, Ag) can be isolated from the reactions of [Et₄N][M₂O₂S₂edt] (H₂edt = 1,2-ethanedithiol) with M⁺ cations and [NH₄]Y (Y = S, S₂ and Se₂). The thiolato and sulfur ligands in these clusters function as η¹-, η³- and η⁶- bridging ligands to metal centres. A feature of these clusters which we have exploited is that the Mo sites contain terminal oxo-ligands. Herein, we report the synthesis† and X-ray crystal structure‡ of a new type of cluster formed by alkali metal cations {in the presence of dibenzo-18-crown-6 (DB18C6)} coordinating to the terminal oxo-ligands of the known [Mo₂Ag₂O₂S₆edt]²⁻ to form [[Mo₆Ag₆O₆S₇edt]₆][Rb(DB18C6)]⁻ (Scheme 1). Furthermore, two such units link through Rb–C contacts to produce the cluster shown in Fig. 1.

![Scheme 1](image)

![Fig. 1](image)
The crystalline solid isolated has been identified as
\[
\{[\text{Rb}](DB18C6)\}(\text{NCMe})_2\cdot\text{t}-\text{C6H6}\cdot0.5\text{C6H6},\ (1) \text{ by X-ray crystallography. However, one of these ions must be}
\]
protonated for charge balance. We cannot identify the position of protonation from the structure but it seems likely that a
terminal oxo-ligand on the cluster or one of the oxygen atoms of the

The dimensions of this cluster are identical to those reported earlier.\(^{11}\) The Rb is contained within the

Two \([\{\text{Mo},\text{Ag},\text{O},\text{S,edt}_1,\}^{\text{Rb}(\text{DB18C6})]\] units combine through Rb–C contacts, in which each Rb interacts with two carbon atoms of an aryl group of the

The structure of \([\text{Rb}(\text{DB18C6}(\text{NCMe})(\text{H}2\text{O}))_2\]^+ contains a centre of symmetry coincident with the centre of the middle DB18C6. The two outer Rb ions are 9-coordinate, being bound to an acetonitrile

The middle portion of \([\text{Rb}(\text{DB18C6}(\text{NCMe})(\text{H}2\text{O}))_2\] ligand adopts a centrosymmetric ‘chair’ conformation with the six Ocrown atoms essentially coplanar (largest deviation from the mean O crown plane being less than 0.15 Å). The central Rb is also 9-coordinate, and is disordered between two sites. In each site the Rb is coordinated by six Ocrown atoms of the macrocycle with Rb(4)–Ocrown distances ranging from 2.549(8) to 3.174(7) Å. The remainder of the coordination sphere of the central Rb is made up of one acetone ligand (Rb(4)–O(34) = 3.128(18) Å) and one water ligand (Rb(4)–O(34) = 3.128(18) Å), both of which bridge to a terminal Rb, and a terminally coordinated water molecule (Rb(4)–O(35) = 2.96(2) Å).

The structure of \([\text{Rb}(\text{DB18C6}(\text{NCMe})(\text{H}2\text{O}))_2\]^+ is unusual. Ocrown atoms bridging with alkali metals is rare, but some examples have been reported with lithium,\(^{15}\) sodium\(^{14}\) and potassium.\(^{15}\) In these examples, aggregates containing four alkali metals and two crown ethers have been described. \([\text{Rb}(\text{DB18C6})\] (NCMe)(H2O))\(^+\) is also quite different from complexes with a 2 : 4 crown ether : alkali phenoxy ratio in which the two inner alkali ions are bridged by two phenoxy ligands.\(^{15,14,15}\) It is also different from the 2 : 1 “sandwich”\(^{16}\) or the 3 : 2 “club sandwich” of [NaA(15-crown-5),]([C6H4(H2))n in which each sodium resides between two neighbouring crown ether molecules and forms links via crown–Na–crown interactions.

Whilst polyoxomolybdenum clusters have been explored extensively for a wide range of applications, the use of molybdenum–sulfur clusters, and metal–sulfur clusters in general,
has been relatively little exploited. The main reason for this difference is that metal–sulfur clusters are more difficult to synthesise due to their sensitivity to acid conditions and high temperature. The approach described in this communication, whereby extended arrays of metal–sulfur clusters linked through metal-crown ether complexes, can be formed, introduces a method for synthesising a new type of metal–sulfur-based clusters under mild conditions. In the synthesis described herein, we have shown how pre-formed clusters can be coupled together using the terminal oxo-ligands on the cluster. The approach we have employed is sufficiently general that the synthesis of other new extended arrays of metallo-clusters can be anticipated using the same method.

Acknowledgements

We thank the EPSRC (UK) for equipment funding. P.L. acknowledges studentship from the University of Newcastle. The crystallographic data were obtained with synchrotron facilities (1) and additional disorder of one Rb+ cation, one acetonitrile 18-crown-6 molecule was resolved and successfully modelled in a 4:1 ratio, in addition to disorder of one EDTA cation, one acetonitrile and two water molecules across an inversion centre. CCDC reference number 263038. See http://www.ccdc.cam.ac.uk/ for crystallographic data in CIF or other electronic format.

18 G. M. Sheldrick, SADABS: Siemens Area Detector Absorption Correction Software, University of Göttingen, Germany, 1996.
20 (NH4)2[Na4(Mo6O19S5)2(S2O7)2] was prepared as follows. H2S (gas) was bubbled into a 20 mL aqueous solution of Na2MoO4 (8.48g, 20 mmol). After approximately 3 minutes, the solution turned red and was then heated to 85 °C and then Na2S2O7 (0.574g, 3.3 mmol) and H2EDTA (1.6 mL, 20 mmol) added. After being stirred for 2 h, the solution was cooled to room temperature and NH4Cl (1.06g, 20 mmol) was added with vigorous stirring. The isolated microcrystalline precipitate was collected and washed with ethanol and Et2O (yield 3.2 g; 62%). Elemental analyses are in agreement with the formula.