Synthesis and characterization of $[NBu_4]_4[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$, a novel polyoxomolybdate complex with a short $Ag^{I}\cdots Ag^{I}$ distance

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In methanol, the defect nitrosylpolyoxomolybdate $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ reacts with Ag^+ to give the complex $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ which displays attractive interactions between the two square-planar closed-shell Ag^I cations.

The molecular building block approach, *i.e.* the linking of preorganized units, has proved efficient in the synthesis of polyoxometalates with increasing complexity.[1–6] Whereas the structures of large polyoxomolybdates are mainly based on $\{Mo_7\}$, $\{Mo_8\}$ and $\{Mo_{17}\}$ units, those of polyoxotungstates are mainly based on defect $\{XW_{11}\}$ and $\{XW_9\}$ Keggin subunits but also may include defect $\{W_5\}$ Lindqvist subunits.[1] While the defect anion $\{W_5O_{18}\}^{6-}$ has been characterized in lanthanide[7,8] and actinide[9] complexes and in a palladium complex,[10] complexes of the related $\{Mo_5O_{18}\}^{6-}$ have not yet been reported. However, a derivatized Lindqvist-type $\{Mo_5\}$ unit, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, has been characterized,[11] and its coordination chemistry has been investigated. We report herein the synthesis and characterization of $[NBu_4]_4[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$, the anion of which displays several unusual features.

To the best of our knowledge, silver complexes of polyoxometalates have not been previously reported, with the exception of the cyclic $[As_4W_{40}O_{140}]^{28-}$ anion where each of the four lacunary sites S_2 may be occupied by Ag^I.[12] The compound $[NBu_4]_4[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ **2** was obtained by reacting $[NBu_4]_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ **1**[11] with $AgNO_3$ in methanol.§ Compound **2** was characterized by elemental analysis, spectroscopic methods (IR and UV–VIS)¶ and single-crystal X-ray structure analysis.‖ The structure of **2** consists of discrete centrosymmetrical $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ anions (Fig. 1) and of tetrabutylammonium cations. The silver complex $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ appears to be roughly similar to the palladium complex $[Pd_2\{W_5O_{18}\}_2]^{8-}$.[10] In both cases, each defect polyoxoanion bridges between two cations in slightly distorted square-planar environments. The Ag–O distances range from 2.342 to 2.477 Å (av. 2.381 Å) and the O–Ag–O angles range from 76.1(2) to 102.0(2)°, the larger angles occurring between two oxygen atoms of the same Mo_5 unit. The silver atom is displaced inside by 0.23 Å from the mean plane of its surrounding oxygen atoms. Square-planar coordination is precedented for Ag^I cations, *e.g.* in $[\{(NH_3)_4Pt_2(C_5H_5N_2O_2)_2\}_2Ag]^{5+}$ where Ag^+ is coordinated to four oxygen atoms of 1-methyluracil ligands.[13] The average Ag–O distance of 2.381 Å in $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ is close to the average Ag–O distance of 2.39 Å in the Pt_4Ag complex. In contrast to $[Pd_2\{W_5O_{18}\}_2]^{8-}$ in which the symmetry of the overall anion approaches D_{2h},[10] the Ag···Ag vector deviates by 40.5° from the normal to the mean coordination planes of the silver cations. Another unexpected feature of the molecular structure of $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ is the short distance between the two Ag^I cations. Indeed the Ag···Ag distance of 2.873(2) Å in $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ is less than the Ag···Ag distance in the metal, which suggests significant Ag···Ag bonding interaction. Closed-shell interactions in inorganic chemistry are well documented, especially for Au^I which has a strong tendency for metallophilic attraction.[14,15] Although the shortest $Ag^I\cdots Ag^I$ contacts have been observed for ligand-supported metal pairs, *e.g.* in $[Ag_2(PhNNNPh)_2]$,[16a] $[Ag_2(ArNCHNAr)_2]$ (Ar = *p*-tolyl,[16b] *o*-methoxyphenyl[16c]), $[Ag_2(1,8\text{-naphthyridine})_2][ClO_4]_2$,[16d] and in $[Ag_3(1,8\text{-diisocyano-}p\text{-menthane})_2I_3]$,[16e] attractive Ag···Ag interactions do exist in the absence of any bridging ligand.[17] The bridging polyoxoanions most probably play a role in the Ag···Ag separation; however, it is noteworthy that the Ag···Ag distance is significantly shorter than the ligand bite distance of *ca.* 3.15 Å. In contrast, the $Pd^{II}\cdots Pd^{I}$ distance in $[Pd_2\{W_5O_{18}\}_2]^{8-}$ is longer (3.034 Å)[10] than it would be expected in case of a significant direct interaction.[18] Altogether, these features support the view that attractive $Ag^I\cdots Ag^I$ interactions exist in $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$.

The reason for the difference between $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ and $[Pd_2\{W_5O_{18}\}_2]^{8-}$ with respect to metal–metal interaction is not straightforward. It should be pointed out that there are some systematic differences between $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ and $[W_5O_{18}]^{6-}$, according to the molecular structures of their respective complexes.[7b,8,10,11,19] In particular, the Mo–O distances involving the coordinated axial oxygen atoms (O_a, av. 1.717 Å in **2**) are comparable with those to equatorial oxygen atoms [O_e, av. 1.698(7) Å in **2**), while the $W–O_a$ distances {av. 1.805(5) Å in $[Pd_2\{W_5O_{18}\}_2]^{8-}$}[10] are significantly lengthened by comparison with $W–O_e$ {av. 1.718(6) Å in $[Pd_2\{W_5O_{18}\}_2]^{3-}$}.[10] In addition, the central oxygen atom is much more displaced from the plane of the four basal M atoms toward the apical M atom in the complexes of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ (*e.g.* 0.41 Å in **2**) than in those of $[W_5O_{18}]^{6-}$ {*e.g.* 0.14 Å in $[Pd_2\{W_5O_{18}\}_2]^{8-}$}. Therefore the

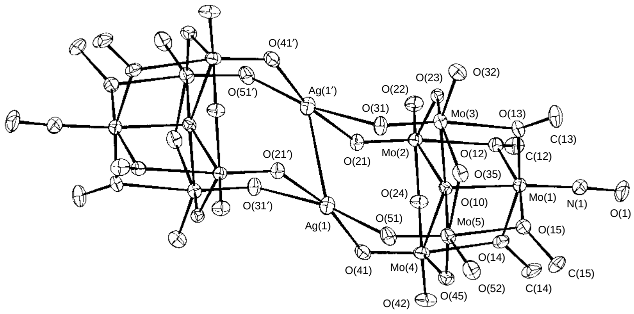

Fig. 1 Molecular drawing of $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ in **2**.[21] Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.746(9), N(1)–O(1) 1.22(1), Mo(2)–O(21) 1.720(7), Mo(2)–O(22) 1.698(6), Mo(3)–O(31) 1.716(6), Mo(3)–O(32) 1.704(7), Mo(4)–O(41) 1.717(7), Mo(4)–O(42) 1.700(7), Mo(5)–O(51) 1.717(7), Mo(5)–O(52) 1.692(7), Ag(1)–O(41) 2.342(8), Ag(1)–O(51) 2.346(7), Ag(1′)–O(21) 2.361(7), Ag(1′)–O(31) 2.477(7), Ag(1)–Ag(1′) 2.873(2); O(41)–Ag(1)–O(51) 82.3(3), O(41)–Ag(1)–O(21′) 167.4(2), O(51)–Ag(1)–O(31′) 169.1(2), O(21)–Ag(1′)–O(31) 76.1(2), O(41)–Ag(1)–Ag(1′) 121.4(2), O(51)–Ag(1)–Ag(1′) 126.5(2), O(21′)–Ag(1)–Ag(1′) 65.6(2), O(31′)–Ag(1)–Ag(1′) 62.8(2). The coordinates of the halves of the anion are related *via* the transformation [*x*′, *y*′, *z*′] = [−*x*, −*y*, −*z*].

comparison of $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$ with $[Pd_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{2-}$ should have been more appropriate. Unfortunately, our efforts to obtain the palladium analogue of **2**, *i.e.* $[NBu_4]_2[Pd_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ by reaction of **1** with either $PdCl_2$ or $Na_2[PdCl_4]$ have failed up to now. Only nitrosyl reduced decamolybdates[20] were obtained in these reactions. The behaviour of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ towards other main-group cations has been investigated. Both Ba^{2+} and Bi^{3+} form eight-coordinate complexes of the type $[M\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{n-}$ (M = Ba, n = 4; M = Bi, n = 3). However, these complexes differ in the geometry of the coordination polyhedron which is best described as an elongated cube for Ba and a tetragonal antiprism for Bi.[19]

Notes and References

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§ An equimolar mixture of $[NBu_4]_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ **1** (0.34 g, 0.25 mmol) and $AgNO_3$ (0.042 g, 0.25 mmol) in MeOH (10 ml) was stirred for 4 h at room temperature. After separation of the yellow precipitate of $[NBu_4]_2[Mo_6O_{19}]$, purple crystals of $[NBu_4]_4[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ **2** were obtained in 56% yield by keeping the filtrate overnight at −30 °C.

¶ IR (KBr pellet, ν/cm^{-1}): 1605 (NO), 924, 906, 885, 865, 698. UV–VIS [MeOH, λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 540 (148) $\{Mo^{II}(NO)\}$.

‖ *Crystal data*: **2**: orthorhombic, space group *Pbca*, a = 18.439(2), b = 24.354(3), c = 24.739(3) Å, U = 11 109(3) Å^3, Z = 4, D_c = 1.715 g cm^{-3}; structure solution and refinement based on 5522 reflections with $I > 3\sigma(I)$ [λ(Mo-Kα) = 0.710 69 Å] converged at R = 0.043 and R_w = 0.047 (w = 1.0). CCDC 182/898.

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