

Synthesis and characterization of $[\text{NBu}_4]_4[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$, a novel polyoxomolybdate complex with a short $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ distance

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In methanol, the defect nitrosylpolyoxomolybdate $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ reacts with Ag^+ to give the complex $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ 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 $\{\text{Mo}_7\}$, $\{\text{Mo}_8\}$ and $\{\text{Mo}_{17}\}$ units, those of polyoxotungstates are mainly based on defect $\{\text{XW}_{11}\}$ and $\{\text{XW}_9\}$ Keggin subunits but also may include defect $\{\text{W}_5\}$ Lindqvist subunits.¹ While the defect anion $\{\text{W}_5\text{O}_{18}\}^{6-}$ has been characterized in lanthanide^{7,8} and actinide⁹ complexes and in a palladium complex,¹⁰ complexes of the related $\{\text{Mo}_5\text{O}_{18}\}^{6-}$ have not yet been reported. However, a derivatized Lindqvist-type $\{\text{Mo}_5\}$ unit, $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$, has been characterized,¹¹ and its coordination chemistry has been investigated. We report herein the synthesis and characterization of $[\text{NBu}_4]_4[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$, 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 $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ anion where each of the four lacunary sites S_2 may be occupied by Ag^{I} .¹² The compound $[\text{NBu}_4]_4[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$ **2** was obtained by reacting $[\text{NBu}_4]_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]\{\text{Na}(\text{MeOH})\} \cdot 3\text{MeOH}$ **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 $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ anions (Fig. 1) and of tetrabutylammonium cations. The silver complex $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ appears to be roughly similar to the palladium complex $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{8-}$.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 unprecedented for Ag^{I} cations, *e.g.* in $[(\text{NH}_3)_4\text{Pt}_2(\text{C}_5\text{H}_5\text{N}_2\text{O}_2)_2]_2\text{Ag}^{5+}$ where Ag^+ is coordinated to four oxygen atoms of 1-methyluracil ligands.¹³ The average Ag–O distance of 2.381 Å in $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ is close to the average Ag–O distance of 2.39 Å in the Pt_4Ag complex. In contrast to $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{8-}$ in which the symmetry of the overall anion approaches D_{2h} ,¹⁰ the Ag \cdots 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 $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ is the short distance between the two Ag^{I} cations. Indeed the Ag \cdots Ag distance of 2.873(2) Å in $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ is less than the Ag \cdots Ag distance in the metal, which suggests significant Ag \cdots Ag bonding inter-

action. 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 $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ contacts have been observed for ligand-supported metal pairs, *e.g.* in $[\text{Ag}_2(\text{PhNNPh})_2]$,^{16a} $[\text{Ag}_2(\text{ArNCHNAr})_2]$ (Ar = *p*-tolyl,^{16b} *o*-methoxyphenyl^{16c}), $[\text{Ag}_2(1,8\text{-naphthyridine})_2]\text{[ClO}_4\text{]}_2$,^{16d} and in $[\text{Ag}_3(1,8\text{-diisocyanop-menthane})_2\text{I}_3]$,^{16e} attractive Ag \cdots Ag interactions do exist in the absence of any bridging ligand.¹⁷ The bridging polyoxoanions most probably play a role in the Ag \cdots Ag separation; however, it is noteworthy that the Ag \cdots Ag distance is significantly shorter than the ligand bite distance of *ca.* 3.15 Å. In contrast, the $\text{Pd}^{\text{II}}\cdots\text{Pd}^{\text{II}}$ distance in $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{8-}$ 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 $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions exist in $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$.

The reason for the difference between $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ and $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{8-}$ with respect to metal–metal interaction is not straightforward. It should be pointed out that there are some systematic differences between $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ and $[\text{W}_5\text{O}_{18}]^{6-}$, 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 $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{8-}$ }¹⁰ are significantly lengthened by comparison with W– O_e {av. 1.718(6) Å in $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{3-}$ }.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 $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ (*e.g.* 0.41 Å in **2**) than in those of $[\text{W}_5\text{O}_{18}]^{6-}$ (*e.g.* 0.14 Å in $[\text{Pd}_2\{\text{W}_5\text{O}_{18}\}_2]^{8-}$). Therefore the

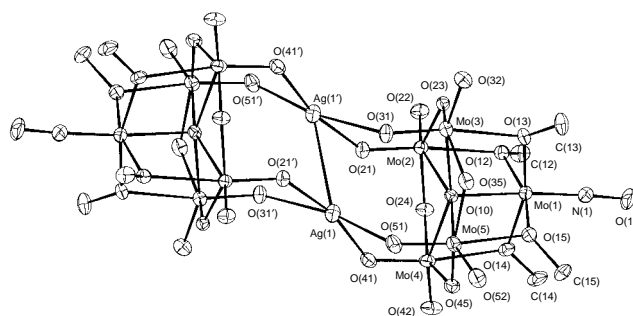


Fig. 1 Molecular drawing of $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ in **2**.²¹ Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.746(9), N(1)–O(1) 1.22(1), Mo(2)–O(21) 1.720(7), Mo(2)–O(22) 1.698(6), Mo(3)–O(31) 1.716(6), Mo(3)–O(32) 1.704(7), Mo(4)–O(41) 1.717(7), 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 $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ with $[\text{Pd}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{2-}$ should have been more appropriate. Unfortunately, our efforts to obtain the palladium analogue of **2**, i.e. $[\text{NBu}_4]_2[\text{Pd}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$ by reaction of **1** with either PdCl_2 or $\text{Na}_2[\text{PdCl}_4]$ have failed up to now. Only nitrosyl reduced decamolybdates²⁰ were obtained in these reactions. The behaviour of $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ towards other main-group cations has been investigated. Both Ba^{2+} and Bi^{3+} form eight-coordinate complexes of the type $[\text{M}\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{n-}$ ($\text{M} = \text{Ba}$, $n = 4$; $\text{M} = \text{Bi}$, $n = 3$). 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 $[\text{NBu}_4]_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}(\text{MeOH})\}_3\text{MeOH}]$ **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 $[\text{NBu}_4]_2[\text{Mo}_6\text{O}_{19}]$, purple crystals of $[\text{NBu}_4]_4[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$ **2** were obtained in 56% yield by keeping the filtrate overnight at -30°C .

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

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

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