‘Adding’ stable functional complementary, nucleophilic and electrophilic clusters: a synthetic route to $[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]^{10-}$ and $[\{(P_2W_{17}O_{61})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]^{14-}$ as examples

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Stable functional complementary clusters, *i.e.* of the electrophilic and nucleophilic type, can be ‘added’ resulting in the planned formation of the related reaction products: the high-yield synthesis of the crystalline compounds $[Me_2NH_2]_{10}[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]\cdot 20H_2O$ 1 and $[Me_2NH_2]_{14}[\{(P_2W_{17}O_{61})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]\cdot 25H_2O$ 2 containing the related $\{Mo_3S_4\}^{4+}$ as well as $\{W_{11}O_{39}\}^{8-}$ and $\{W_{17}O_{61}\}^{10-}$ clusters as constituents, respectively, is a good example.

The deliberate synthesis of large clusters by ‘adding’ or ‘linking’ smaller ones, which are stable in solution under certain reaction conditions, is a challenge for the inorganic chemist. The aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ can for instance be regarded as an archetypical electrophilic building block in this respect since the H_2O ligands are labile and can be easily substituted by nucleophilic cluster anions with donor functions and therefore act formally as ligands. Here, we report the deliberate high-yield synthesis of the title species and provide two examples of the potentially large class of compounds having complementary functional polyoxometalate[1] and chalcogenide clusters as constituents.[2]

In an acidic medium two electrophilic $[Mo_3S_4(H_2O)_9]^{4+}$ [3] aqua cations react with two monovacant lacunary anions $\{[SiW_{11}O_{39}]^{8-}$ [4] or $[P_2W_{17}O_{61}]^{10-}$ [5]$\}$ to yield the cluster species $[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]^{10-}$ **1a** and $[\{(P_2W_{17}O_{61})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]^{14-}$ **2a** respectively, which were isolated as the Me_2NH_2 salts **1** and **2** in high yield.†‡ It is important to note that the structure of the reaction products of the complementary educts can be predicted by considering (a) the preferred octahedral coordination of molybdenum, (b) the easily removable H_2O ligands of the $[Mo_3S_4(H_2O)_9]^{4+}$ aqua ion, and (c) the number of oxygen atoms in the lacunary-type anions $[SiW_{11}O_{39}]^{8-}/[P_2W_{17}O_{61}]^{10-}$ acting as strong donors. Under the same conditions, other products should (preferably) not be formed.

Single crystal X-ray structure determinations have revealed that the yellow–brown diamagnetic compounds $[Me_2NH_2]_{10}[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]\cdot 20H_2O$ **1** and $[Me_2NH_2]_{14}[\{(P_2W_{17}O_{61})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]\cdot 25H_2O$ **2** contain the discrete cluster anions **1a** and **2a**, $[Me_2NH_2]^+$ cations, and crystal water molecules in their lattices.§ Fig. 1 and 2 show perspective views of the structures of **1a** and **2a** both having a central core built up by two $\{Mo_3S_4(H_2O)_3\}^{4+}$ fragments connected through two hydroxo bridging groups which are *cis* to the μ_3-S core atoms. [Note that in $[Mo_3S_4(H_2O)_9]^{4+}$, the H_2O ligands in *cis* position to the μ_3-S atom are more acidic than the c-H_2O ligands in *trans* position;[6] the protonation of the bridging oxygen atoms clearly follows from bond valence sum (BVS) calculations.[7]]

The two nucleophilic lacunary anions, of the Keggin type $\{[SiW_{11}O_{39}]^{8-}\}$ and of the Dawson type $\{[P_2W_{17}O_{61}]^{10-}\}$, can be considered as negatively charged ligands which replace coordinated H_2O ligands of the electrophilic educt (during the reaction). In this respect the monovacant lacunary anions with four oxygen donor atoms can be regarded as inorganic equivalents of a porphyrin ligand.[1c] In agreement with our

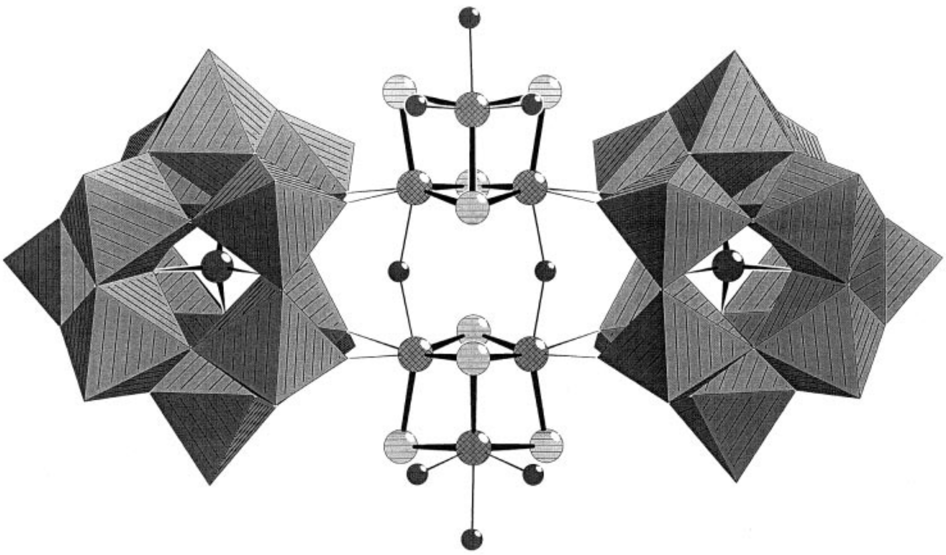

Fig. 1 Structure of the cluster anion **1a** distinguishing between the building units or constituents: $\{Mo_3S_4\}$ fragments in ball-and-stick and $\{W_9\}$ fragments in polyhedral representation.

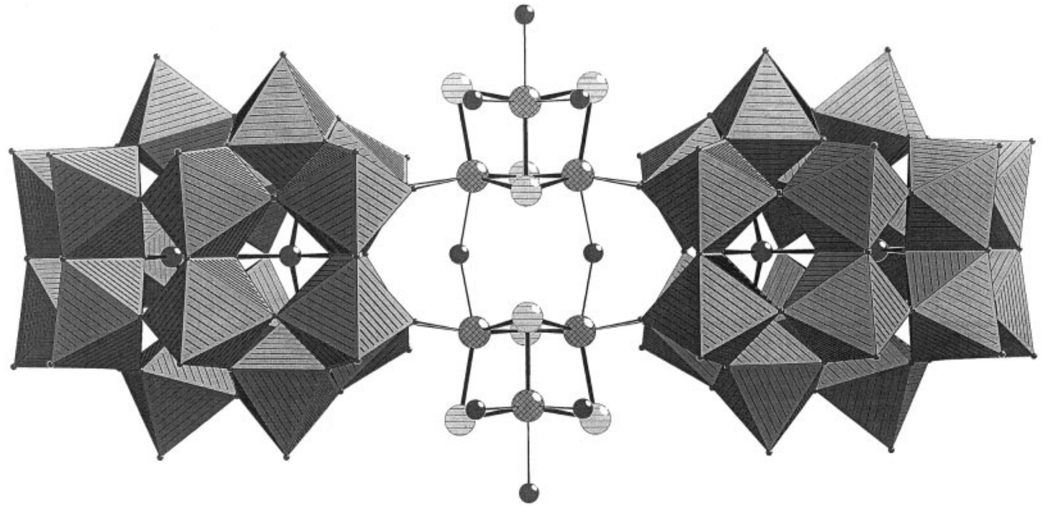

Fig. 2 Structure of the cluster anion **2a** showing the $\{Mo_3S_4\}$ and $\{W_{17}\}$ fragments as building units or constituents.

concept—the addition of stable clusters—the geometrical parameters of the constituents of the anions **1a** and **2a** are practically identical to those of the cluster educts.[8–10]

Compounds **1** and **2** are stable in air and in aqueous solutions (pH = 1–7). Heating **1** or **2** in concentrated hydrochloric acid leads to the reverse reaction, *i.e.* to the reformation of the $[Mo_3S_4(H_2O)_9]^{4+}$ cluster in quantitative yields.

The relative abundance of the different cluster constituents of **1a** and **2a** is also confirmed by the IR, Raman, UV–VIS and ^{31}P NMR spectra. The characteristic UV–VIS spectra indicate not only the presence of $\{Mo_3S_4\}^{4+}$ units possessing a d^6 electron configuration[2a] but also that these are almost electronically uncoupled. The characteristic vibrational spectra show bands due to the almost uncoupled vibrations of the constituents, while the ^{31}P NMR spectrum of **2a** [in a buffered aqueous solution (0.5 M $MeCO_2Na$–0.05 M $MeCO_2H$)] shows, consistent with the solid-state structure of **2**, signals in the intensity ratio 1 : 1.

We believe that the strategy of reacting appropriate stable nucleophilic and electrophilic, *i.e.* functional complementary, clusters may be of general importance for the synthesis of this type of compound.

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Notes and references

† *Synthesis* of $[Me_2NH_2]_{10}[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]\cdot 20H_2O$ **1**: to an aqueous acetate buffered (0.5 M $MeCO_2Na$–0.05 M $MeCO_2H$) solution (30 ml) of $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$ (1.65 g; 0.51 mmol), 3.55 ml of a solution of 0.144 M $[Mo_3S_4(H_2O)_9]^{4+}$ (0.51 mmol) in 2 M HCl was added under vigorous stirring. The pH of the solution was adjusted to 1.8 by adding 6 M HCl dropwise. After stirring the yellow–brown solution for 15 min, Me_2NH_2Cl (2.0 g) was added and the reaction mixture was heated (80 °C) for 20 min. The solution was cooled to room temp. and allowed to stand for 3–5 days. The yellow–brown crystals which precipitated were filtered off, washed with water (5 °C) and dried over $CaCl_2$. Yield: 1.48 g of **1** (81%). Correct elemental analysis for C, H, N, S and H_2O. UV–VIS data [0.5 M $MeCO_2Na$–0.05 M $MeCO_2H$ buffer, absorption, λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 380 (16000), 450 (sh), 630 (800). IR (solid, KBr pellet, ν/cm^{-1}): 1612m [$\delta(H_2O)$], 1461m, 1411w, 1162w, 1016 (sh), 999m/950s/889s [ν(W=O)], 818m, 761s, 522m. FT-Raman (solid, λ = 1064nm, ν/cm^{-1}): 970s/913m/889m [ν(W=O)], 830m, 522w, 437s, $\{\nu_s[Mo_3\text{-}(\mu_3\text{-}S)]\}$, 360w, 335w, 282m, 236m, 198w.

‡ *Synthesis* of $[Me_2NH_2]_{14}[\{(P_2W_{17}O_{61})Mo_3S_4(H_2O)_3(\mu\text{-}OH)\}_2]\cdot 25H_2O$ **2**. The same method was applied for the preparation of **2** using $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ (1.50 g; 0.305 mmol) and 2.13 ml of 0.144 M $[Mo_3S_4(H_2O)_9]^{4+}$ (0.305 mmol) in 2 M HCl. Yield: 1.34 g of **2** (86%). Correct elemental analysis for C, H, N and H_2O. UV–VIS data (0.5 M $MeCO_2Na$–0.05 M $MeCO_2H$ buffer, absorption, λ/nm): 365 (sh), 465 (sh), 620 (sh). IR (solid, KBr pellet, ν/cm^{-1}): 1612m [$\delta(H_2O)$], 1461m, 1412w, 1085s, 1053m, 1017m, 942s/913s [ν(W=O)], 768s, 522m. FT-Raman (solid, λ = 1064 nm, ν/cm^{-1}): 1015w, 974vs, 883s, 519w, 437s $\{\nu_s[Mo_3\text{-}(\mu_3\text{-}S)]\}$, 365m, 337w, 284w, 232m, 170w. ^{31}P NMR (0.5 M $MeCO_2Na$–0.05 M $MeCO_2H$ buffer solution, 85% H_3PO_4 as external reference): δ −6.58 (1P), −13.22 (1P).

§ *Crystal data*: $C_{20}H_{134}Mo_6N_{10}O_{106}S_8Si_2W_{22}$ **1**: M = 7144.37, monoclinic, space group $C2/m$, a = 24.820(5), b = 20.980(4), c = 26.870(5) Å, β = 97.24(3)°, U = 13880(5) Å^3, Z = 4, D_c = 3.419 g cm^{-3}, $2\theta_{max}$ = 54°, T = 200(2) K, μ = 18.91 mm^{-1}, R = 0.051 for 9300 reflections with $I > 2\sigma(I)$; STOE IPDS Image Plate diffractometer, Mo-Kα radiation, graphite monochromator. The structure was solved using direct methods and refined with the programs SHELXS-86 and SHELXL-97.

$C_{28}H_{176}Mo_6N_{14}O_{155}P_4S_8W_{34}$ **2**: M = 10396.73, orthorhombic, space group $Cmcm$, a = 22.419(5), b = 15.110(3), c = 56.036(11) Å, U = 18983(7) Å^3, Z = 4, D_c = 3.638 g cm^{-3}, $2\theta_{max}$ = 54°, T = 183(2) K, μ = 21.11 mm^{-1}, R = 0.123 for 8616 reflections with $I > 2\sigma(I)$; AXS SMART diffractometer, Mo-Kα radiation, graphite monochromator. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-97 (all programs from G. M. Sheldrick, University of Göttingen). The structure was also refined in several lower symmetrical space groups, which lead to up to 2% lower R values. However, as no significant deviations from the higher symmetry were observed, $Cmcm$ was chosen for the final refinements. In both compounds not all cations could be located due to Me_2NH_2/H_2O disorder problems.

The figures were prepared with the program DIAMOND (K. Brandenburg, *Diamond-Informationssystem für Kristallstrukturen*, Crystal Impact GbR, Germany).

CCDC 182/1262. See http://www.rsc.org/suppdata/cc/1999/1189/ for crystallographic files in .cif format.

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