Assembling nanosized ring-shaped synthons to an anionic layer structure based on the synergetically induced functional complementarity of their surface-sites: $Na_{21}[Mo^{VI}{}_{126}Mo^{V}{}_{28}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]\cdot xH_2O$ ($x \approx 300$)

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The reaction of an aqueous solution of sodium molybdate with hypophosphorous (phosphinic) acid acting both as reducing agent and ligand at low pH values (≈ 1) results in the formation of nanosized ring-shaped cluster units which assemble to form layers of the compound $Na_{21}[Mo^{VI}{}_{126}Mo^{V}{}_{28}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]\cdot xH_2O$ 1 ($x \approx 300$); the assemblage is based on the synergetically induced functional complementarity of amphiphilic O=MoL (L = H_2O, $H_2PO_2^-$) groups and corresponds to the replacement of H_2O ligands of rings by related terminal Mo=O groups of other rings (and *vice versa*) the nucleophilicity of which is induced by coordinated $H_2PO_2^-$ ligands.

One of the great challenges of modern chemistry is to create multifunctional structures which have well defined cavities and surfaces with sites or areas of different reactivity by linking preorganized robust building blocks/synthons.[1,2] Here we report the synthesis of a related metal–oxide based electron-rich compound built up by nanosized ring-shaped cluster units using a type of crystal engineering.

If an aqueous acidified solution of Na_2MoO_4 is reduced with hypophosphorous acid (H_3PO_2) in the presence of a rather high electrolyte (salt) concentration, blue crystals of **1** precipitate after a few days.† Compound **1** was characterized by elemental analysis, thermogravimetric analysis (to determine the crystal water content), cerimetric titrations [for the determination of the (formal) number of the (28) Mo^V centres], bond valence sum (BVS) calculations (to determine the number and positions of H_2O ligands and OH groups as well as the number of Mo^V centres), [3] spectroscopic methods (IR, resonance-Raman, VIS–NIR) ‡ and single-crystal X-ray structure analysis.§

$$Na_{21}[Mo^{VI}{}_{126}Mo^{V}{}_{28}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]\cdot xH_2O \ \mathbf{1} \equiv Na_{21}\mathbf{1a}\cdot xH_2O \ (x \approx 300)$$

The crystal structure of **1** (space group *Cmca*)§ shows the abundance of nanosized ring-shaped units (crystallographic site symmetry $2/m$) which are linked through covalent Mo–O–Mo bonds to give a layered structure (Fig. 1). In the crystallographic *ac* plane, each cluster ring is surrounded by four rings such that the anionic layer structure **1a** with condensed ring-shaped units parallel to the *ac* plane results. The packing of these layers gives rise to nanosized channels (Fig. 1) with 'encapsulated' $H_2PO_2^-$ ligands, while 7 of the 14 $\{Mo_2\}$-type groups of the 'parent' layer system [with only H_2O ligands (see **2a**)] show the coordination of 7 bidentate $H_2PO_2^-$ ions (which are statistically distributed over the ring system but always with one ligand per bridge). Since the corresponding discrete (non–condensed) ring-shaped cluster with only H_2O ligands, which is known as the Na^+ salt, has the stoichiometry[4] $[\{(O)_2{=}Mo^{VI}(H_2O)(\mu_2\text{-}O)(H_2O)Mo^{VI} = (O)_2\}^{2+}{}_{14}\{Mo^{VI/V}{}_8O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}^{3-}{}_{14}]^{14-}$ ($\equiv [\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}]^{14-}$) **2a**, the building-block description for the corresponding hypothetical discrete unit of **1a**, with 14 H_2O ligands replaced by 7 bidentate $H_2PO_2^-$ ligands, is $[\{(O)_2{=}Mo^{VI}(\mu_2\text{-}H_2PO_2^-)_{0.5}(\mu_2\text{-}O)(H_2O)Mo^{VI} = (O)_2\}^{1.5+}{}_{14}\{Mo^{VI/V}\text{ir8}O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}^{3-}{}_{14}]^{21-}$ **3a**.

It can be assumed that the formation of the ring system **1a** based on the reducing power of the hypophosphorous acid constitutes the initial step of the reaction considered here. This is a reasonable assumption as the characteristic spectrum of the

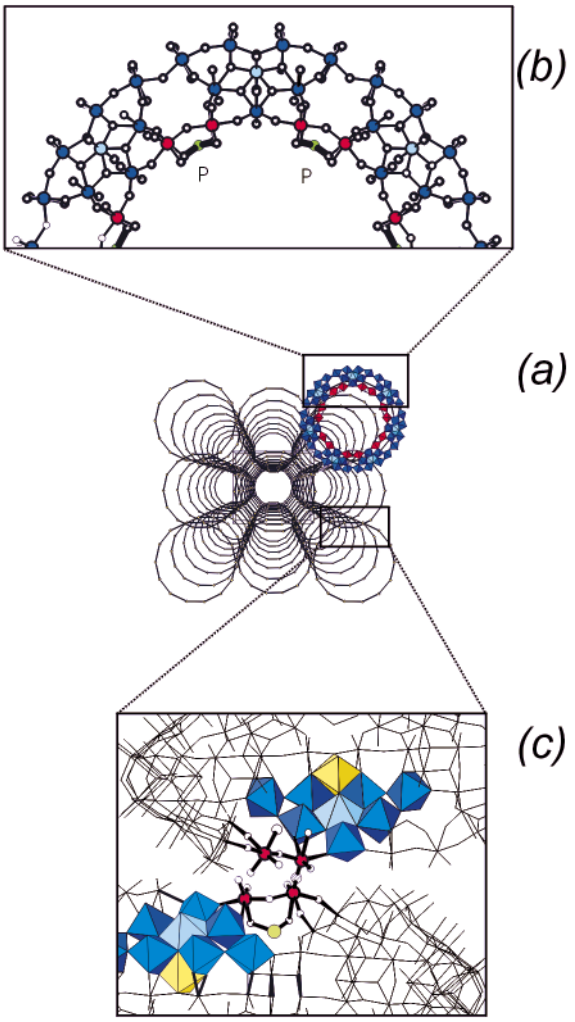

Fig. 1 (*a*) Perspective view of the cluster framework of **1** along the crystallographic *c* axis, showing the abundance of nanotubes and cavities. For clarity, only one complete ring (without the P ligands) is shown in polyhedral representation. With respect to the other rings, only the centres of the $\{Mo_1\}$ units are given and connected. (*b*) Ball-and-stick representation of the upper half of a ring segment showing the principal positions of the $H_2PO_2^-$ ligands. (*c*) Detailed view [perpendicular to (*a*) and (*b*)] of the bridging region between two cluster rings of **1** emphasizing one $\{Mo_8\}$, one $\{Mo_1\}$ unit (in polyhedral representation) as well as one $\{Mo_2\}^{2+}$ unit and one $H_2PO_2^-$ ligand (in ball-and-stick representation). The bridging (disordered) oxygen centre is depicted as a large hatched circle [colour code: $\{Mo_2\}$, red; $\{Mo_8\}$, blue (central MoO_7 pentagonal-bipyramid, light blue); $\{Mo_1\}$, yellow; P, green].

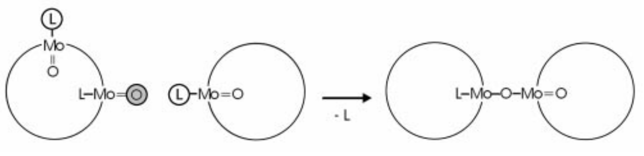

Fig. 2 Schematic presentation of the basic assembly principles of ring-shaped cluster units forming the layers of **1a** which are based on the synergetically induced functional complementarity of the {Mo_2}-type O=MoL (L = H_2O, $H_2PO_2^-$) sites of their surfaces: each precursor ring contains the corresponding virtual functional complementary O=Mo(H_2O) groups (becoming 'donors' due to the electron-donating $H_2PO_2^-$ replacing H_2O ligands and 'acceptors' without $H_2PO_2^-$ ligands).

discrete ring is observed after a few minutes, independent of the type of reducing agent used. The value accepted now for the charge of **1a** and all related compounds is in accord with the results of numerous Na analyses [4,5] and also with the analysis of the hydrogen-bond situation[5,6] in respect of the constant BVS values for the μ_3-O atoms of the equatorial (μ_3-O) · · · H · · · (μ_3-O) units.[4,5] Not only for the 'parent' system **2a** with only H_2O ligands but also for all known tetradecameric ring-shaped clusters without defects, the charge of 14− corresponds to the difference between the (formal) number of Mo^V centres and the number of protons at equatorial μ_3-O atoms.

The main difference between the discrete cluster **3a** and **1a** with the condensed clusters is that **1a** contains two {Mo_2}-type H_2O ligands less per formula unit. This is caused by the substitution of {Mo_2}-type H_2O ligands by terminal {Mo_2}-type Mo=O groups of neighbouring rings formally acting as ligands which results in the linkage of the rings (see formulae **2a** and **3a**). This means that each of the four connections of one ring unit corresponds to 0.5 H_2O molecules less per formula unit in **1a**. As the same {Mo_2}-type O=MoL group (L = H_2O, $H_2PO_2^-$) of the 'ring unit precursor' is involved in the present case, the linking procedure is based on a type of synergetically induced functional complementarity at the O=MoL sites of the cluster surfaces (see **2a** and **3a** as well as Fig. 2). In the crystal lattice the O=MoL groups are found for L = H_2O disordered in the sense that the O and L ligands can change their positions and the O=MoL group can thus act as 'donor' or 'acceptor'.

Because of the increased electron density (or the nucleophilicity/donor properties) of the considered Mo=O groups (when pointing to the outside of the ring), caused by the coordinated $H_2PO_2^-$ ligand, the related ring formally acts as a ligand due to a synergetic process resulting in the substitution of the H_2O ligand of a corresponding {Mo_2}-type Mo=O group of the adjacent ring which has no coordinated $H_2PO_2^-$ ligands (Fig. 2). In this context, it should be noted that in order to form the layer structure, not all H_2O ligands of the 14 {Mo_2} groups have of course to be replaced by the abundant $H_2PO_2^-$ ligands.

The interesting aspects of this work are: (1) Giant robust ring-shaped building blocks can be linked together to form a well-defined layered network based on a type of crystal engineering, *i.e.* in this case based especially on the synergetically induced functional complementarity of relevant sites of the surfaces. (2) It is possible to place molecules/replace ligands at different sites of the surface of a giant cluster or within its cavity and subsequently change the properties of well defined regions of its surface (*e.g.* increase the nucleophilicity). (3) The investigation of reactions between molecules inside the cavity is in principle possible. (In this context, it is important to note that the system is metal–oxide based and electron rich, which allows activation of ligands.) The anion of the hypophosphorous acid, which is involved in each ring connection and coordinates as a bidentate ligand to the {Mo_2} groups of **2a** by substituting two H_2O ligands of the 'parent' ring, can in principle be replaced by several other bidentate ligands, too.

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Notes and references

† To a solution of $Na_2MoO_4 \cdot 2H_2O$ (3.04 g, 12.56 mmol) and NaCl (1.0 g, 17.11 mmol) in 25 mL of water which was acidified with 2.5 mL of hydrochloric acid (32%), hypophosphorous acid (0.2 mL, 50%, 1.93 mmol) was added as reducing agent. After stirring for 15 min under bubbling argon gas, the resulting solution was kept in a closed flask at room temperature. After 4 days the precipitated blue bipyramidal-shaped crystals were filtered, washed quickly with a small amount of cold water and dried at room temperature under argon. Yield: 0.38 g (16% based on Mo). (Note: the crystals should be separated out from the reaction mixture after 4 days, to avoid the coprecipitation of amorphous materials as after effect).

‡ *Selected data* for **1**: VIS–NIR (water) [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 745 (1.59×10^5), 1070 (1.15×10^5). VIS/NIR (KBr pellet, in transmission) (λ_{max}/nm): 750 (IVCT), 1050 (IVCT). IR (KBr pellet, prepared under argon) (ν/cm^{-1}): 1616 m {$\delta(H_2O)$}, 1124w/1076vw/1039vw [$\tau(PH_2)$, $\gamma(PH_2)$, $\nu(PO_2)$], 991m/974m/910m {ν(M=O)}, 858m, 820sh, 740sh, 710sh, 631s, 558s, 482w. Resonance-Raman (KBr matrix, λ_e = 1064 nm) (ν/cm^{-1}): 806s, 535s, 462s, 325s, 215s. Anal. Calc. for $H_{736}Mo_{154}$-$Na_{21}O_{830}P_7$ (*M* 29 496.23): Na, 1.6; Mo^V, 28; P, 0.73; crystal water (not coordinated), 18.3. Found: Na, 1.64; Mo^V, 28; P, 0.65; crystal water (not coordinated), 18.5% (thermogravimetry). The formal ε value of the layer is a rough measure for the number of Mo^V centres.

§ *Crystal data* for **1**: $H_{736}Mo_{154}Na_{21}O_{830}P_7$, M = 29 496.23, orthorhombic, space group *Cmca*, a = 50.075(3), b = 56.049(4), c = 30.302(2) Å; U = 85 048(10) Å^3, Z = 4, D_c = 2.304 g cm^{-3}, μ = 2.33 mm^{-1}, $F(000)$ = 56720, crystal size = 0.30 x 0.30 x 0.15 mm^3. Crystals of **1** were taken directly out of the mother liquor and measured immediately (to prevent weathering through loss of water) at 183(2) K on a Bruker AXS SMART diffractometer (Mo-Kα radiation graphite monochromator). A total of 248 836 reflections ($1.53 < \theta < 26.99°$) were collected of which 46 660 unique reflections (R_{int} = 0.0983) were used. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-97 to R = 0.0735 for 25 500 reflections with $I > 2\sigma(I)$. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD 410795. CCDC 182/1228. See http://www.rsc.org/suppdata/cc/1999/1035/ for crystallographic files in .cif format.

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