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42. POLYOXOMOLYBDATE CLUSTERS: GIANT WHEELS AND BALLS

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The syntheses of aesthetically beautiful nanoscaled polyoxomolybdates of the type $\{Mo_{11}\}_n$, which have spherical-/ball- ($n = 12$) or wheel-shaped ($n = 14$) anions (see Figs. 1–3) and are interesting not only for inorganic chemistry, are reported. In spite of their completely different overall structure, they have similar building blocks[1,2] (see also Refs. 3, 4) (Fig. 1), resulting in the remarkable equivalent stoichiometry.[1] Important in this context is that the species can probably be considered as belonging to the class of the most complex discrete inorganic species and consequently, their characterization was correspondingly complex.

A formulation of the discrete wheel-type species (Fig. 2), which is useful for reactivity studies, corresponds to $[\{Mo_2^{VI}O_4\ (\mu_2\text{-}O)\ L_2\}^{2+}_{n-x}\ \{Mo_8^{VI/V}O_{26}\ (\mu_3\text{-}O)_2\ H(H_2O)_3\ Mo^{VI/V}\}^{3-}_n]^{(n+2x)-} \equiv [\{Mo_2\}_{n-x}\ \{Mo_8\}_n\ \{Mo_1\}_n]^{(n+2x)-}$ ($L = H_2O$ or other ligands), where x refers to the number of defects or missing $\{Mo_2\}$ groups introduced into the system, $n = 14$ corresponds to a tetradecameric, and $n = 16$ corresponds to a hexadecameric species.[1,2,5] Here we report the synthesis of a relevant mixed-crystal compound C, which contains the tetradecameric ring ($n = 14$) both as a complete entity and as one with a missing $\{Mo_2\}$ group in the ratio 1 : 1, as well as the compound D with the rings linked to layers. It should be mentioned that it is a difficult task to determine the formula of a compound belonging to class II or III of the Robin–Day classification with a

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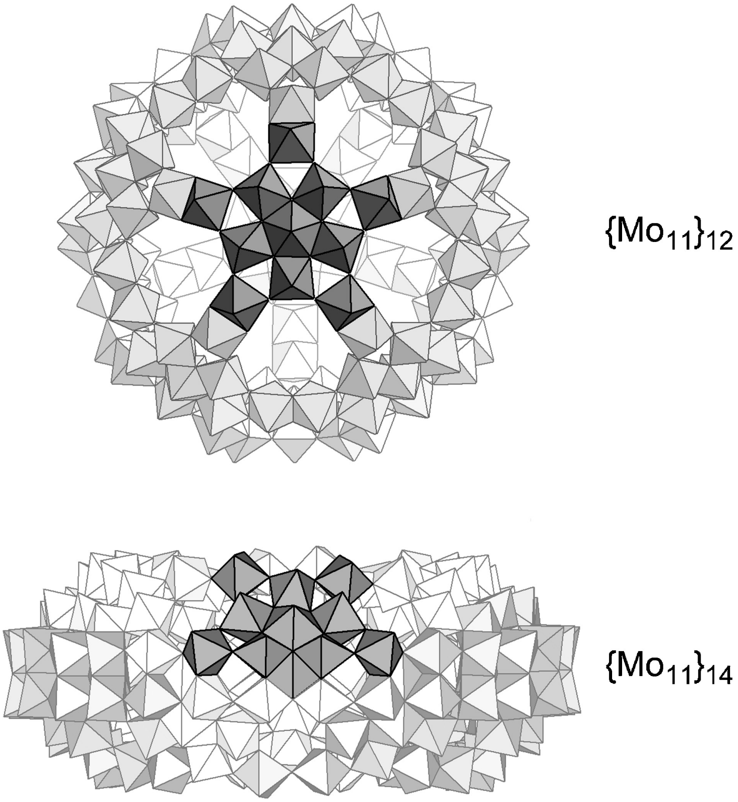

Figure 1. Schematic comparison of the pentagonal C_5- and C_s-type $\{Mo_{11}\}$ motifs (dark gray) as present, for example, in the ball-shaped $\{Mo_{11}\}_{12}$-(above; corresponding to the anion of compound A) and in the $\{Mo_{11}\}_{14}$-type cluster with view perpendicular to that of Fig. 2 (below; corresponding to an anion of compound C without defect).

protonated, mixed-valence anionic species with a very high relative molecular mass, especially if a very low concentration of disordered cations in the lattice complicates the determination of the anion charge.[5]

In the case of giant wheel (molybdenum blue) compounds, the general synthetic strategy involves the acidification (pH ~ 1) and reduction of an aqueous molybdate(VI) solution [possible reducing agents: iron powder, tin(II) chloride, molybdenum(V) chloride, ascorbic acid, cysteine, hydroxylamine, hypophosphorous acid, sodium dithionite, or hydrazine sulfate].[2–5] On the other hand, an icosahedral ball-shaped cluster can be formed in an aqueous Mo(VI)

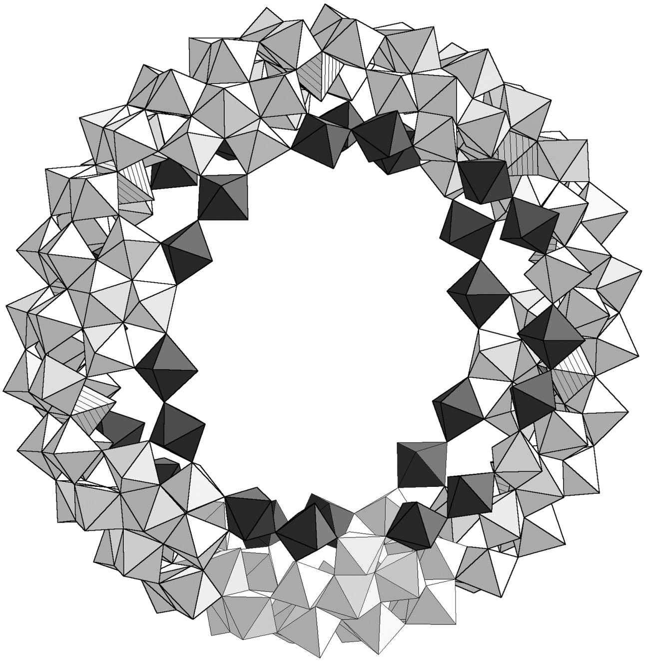

Figure 2. Polyhedral representation of the $\{Mo_{11}\}_{14}$-type cluster ($\equiv[\{Mo_2\}\ \{Mo_8\}\ \{Mo_1\}]_{14}{}^{14-}$) with one $\{Mo_8\}$ group more pale at the bottom ($\{Mo_1\}$ units: hatched; $\{Mo_2\}$ groups: dark gray).

containing solution at relatively higher pH values (ranging from 2 to 4) in the presence of an appropriate bidentate bridging ligand L, for instance, acetate, stabilizing the dinuclear $\{Mo_2^{V}\}$ units formed in the presence of a reducing agent.

The formula for the discrete ball-shaped species described here is $[\{Mo^{VI}(Mo_5^{VI}O_{21})(H_2O)_6\}_{12}\ \{Mo_2^{V}O_4L\}_{30}]^{42-}$ ($\equiv P_{12}S_{30}$) ($L = CH_3COO^-$, $PO_2H_2^-$). In agreement with the formula, 30 dinuclear spacer groups S for 12 pentagonal units P (spanning an icosahedron) are positioned on the corners of a (distorted) truncated icosahedron (Fig. 3).[1,2,6,7]

The compounds have been characterized by elemental analyses, spectroscopy [electronic absorption, IR, Raman (or resonance Raman for the blue compounds with $\lambda_e = 1064$ nm)], redox titration [for the determination of the (formal) number of Mo^V centers], thermal gravimetric analyses (TGA), and single-crystal X-ray structure analyses (see Refs. 2, 5 and literature cited therein). Mainly the crystals of the compounds that contain discrete wheel-shaped anions lose lattice water rapidly on removal from the mother liquor even at room temperature,[2,5] a

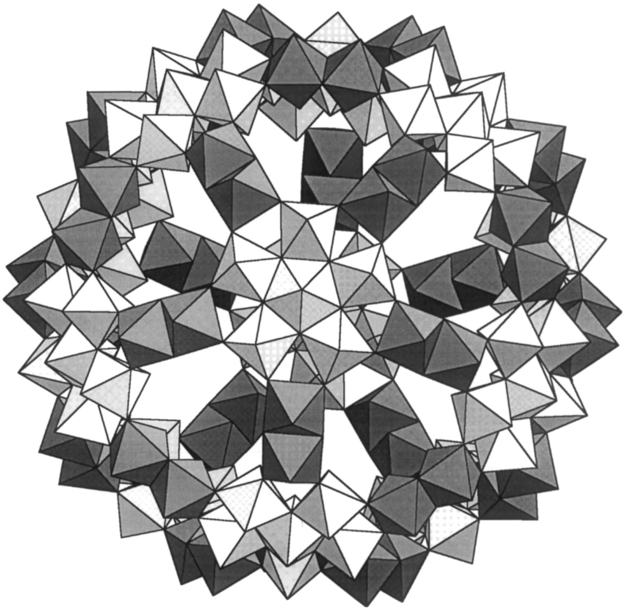

Figure 3. Polyhedral representation of the ball-shaped cluster anion of compound A highlighting the binuclear spacer units (see Fig. 1 highlighting the pentagons).

fact that complicates the analyses. (In particular, the crystal water content[*] is difficult to determine, especially for species where the cluster units are loosely packed in the crystal lattice, e.g., in the case of C.) As the above mentioned spectra and most values of the elementary analyses of different molybdenum blue compounds (e.g., with and without defects or with linked and nonlinked units) are necessarily almost identical, it is practically impossible to distinguish the compounds alone on the basis of such data. Therefore, in order to ensure their purity, it is essential to determine in addition the characteristic unit cell dimensions of several crystals of each type of compound, and thus these values are included here. For the syntheses of related compounds other than those described here, see papers cited in Refs. 1, 2, and 5.

Materials and Hazards

All chemicals used are obtained commercially and are of analytical grade. No further purification is done prior to use. Concentrated acids, such as hydrochloric

[*] The theoretical number of crystal water molecules is calculated from the residual volume of the unit cell not occupied by the refined lattice components.

or acetic acid, are corrosive. Sodium molybdate is harmful if swallowed in small doses. Hydrazinium sulfate is toxic and corrosive and harmful on inhalation, contact with the skin, or if swallowed. Sodium dithionite is harmful if swallowed, and in contact with acids produces toxic SO_2. Both reducing agents used have to be fresh, stored cool, dry, and airtight.

A. $(NH_4)_{42}$ $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}$ $(CH_3COO)_{30}$ $(H_2O)_{72}]$ · HYDRATE

$$132\,MoO_4^{2-} + 15\,N_2H_6^{2+} + 30\,CH_3COOH + 192\,H^+ \longrightarrow$$

$$[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-} + 15\,N_2 + 84\,H_2O$$

Procedure

After adding $N_2H_6 \cdot SO_4$ (0.8 g, 6.1 mmol) to a solution of $(NH_4)_6\,Mo_7O_{24} \cdot 4H_2O$ (5.6 g, 4.5 mmol) and CH_3COONH_4 (12.5 g, 162.2 mmol) in H_2O (250 mL) and stirring for 10 min (color change to blue-green), 50% (v/v) CH_3COOH (83 mL) is added. The reaction solution, now green, is stored in an open 500-mL Erlenmeyer flask at 20°C without further stirring (slow color change to dark brown). After 4 days the precipitated red-brown crystals are filtered off through a glass frit (D2), washed with 90% ethanol and diethyl ether, and finally dried in air. Yield: 3.3 g (52% based on Mo). (*Note*: Compound A can in principle be recrystallized from a very concentrated aqueous solution by adding additional NH_4Cl.)

Anal. Calcd. for $(NH_4)_{42}$ $[Mo^{VI}_{72}Mo^{V}{}_{60}O_{372}$ $(CH_3COO)_{30}$ $(H_2O)_{72}] \cdot \sim 300$ $H_2O \cdot \sim 10$ CH_3COONH_4: C, 3.4; H, 3.8; N, 2.6; Mo, 44.3 (Mo^V, 20.1); crystal H_2O, 18.9. Found: C, 3.4; H, 3.2; N, 2.7; Mo, 45.8 (Mo^V, 20.2; cerimetric titration); crystal H_2O, 18.0 (TGA value).

Properties

The water-soluble red-brown compound crystallizes in a cubic space group [$a = 46.0576$ (14) Å]^6 and forms octahedral crystals (including related truncated ones). The IR spectrum (Fig. 4) shows main peaks at 1626 (m) (δ_{H_2O}), 1546 (m) ($\nu_{as,COO}$), 1440 (sh), 1407 (m) (δ_{CH_3}, $\nu_{s,COO}$, δ_{as,NH_4^+}) 969 (m), 936 (w-m) ($\nu_{Mo=O}$), 853 (m), 792 (s), 723 (s), 567 (s) cm^{-1}, while the electronic absorption spectrum (H_2O/CH_3COOH, pH = 4) shows an intense band at 450 nm ($\varepsilon = 3.5 \cdot 10^5\ M^{-1}cm^{-1}$). Because of the high symmetry, relatively

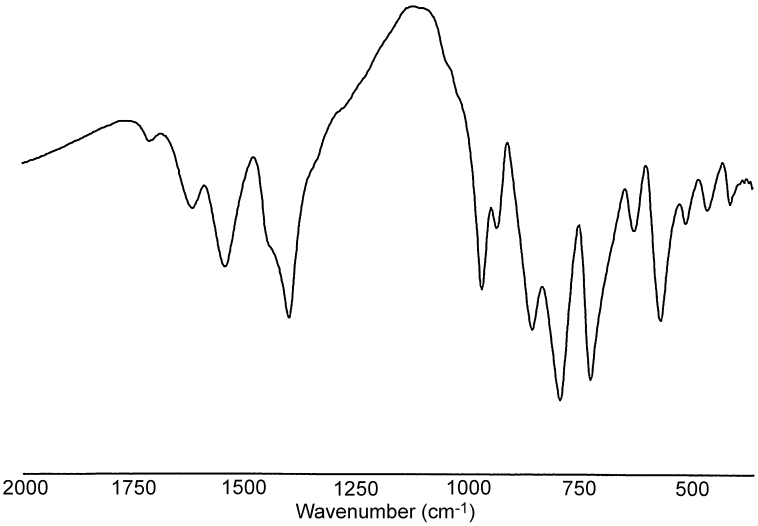

Figure 4. IR spectrum of $(NH_4)_{42}[\mathrm{Mo}^{VI}_{72}\mathrm{Mo}^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot{\sim}300\ H_2O\cdot{\sim}10\ CH_3COONH_4$ (compound A) (KBr disk).

few characteristic Raman bands [953 (m), 935 (m), 875 (s) ($\nu_{\mathrm{Mo=O}}$), ~845 (sh), 374 (m-s), 314 (m), 212 (w) cm^{-1}] are observed that are assignable to the irreducible representations H_g and A_{1g} (bands with highest intensity).

B. $(NH_4)_{42}$ $[\mathrm{Mo}^{VI}_{72}\mathrm{Mo}^{V}_{60}O_{372}$ $(H_2PO_2)_{30}$ $(H_2O)_{72}]$ HYDRATE

$$[\mathrm{Mo}^{VI}_{72}\mathrm{Mo}^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-} + 30\,H_3PO_2 \longrightarrow$$
$$[\mathrm{Mo}^{VI}_{72}\mathrm{Mo}^{V}_{60}O_{372}(H_2PO_2)_{30}(H_2O)_{72}]^{42-} + 30\,CH_3COOH$$

Procedure

A stirred solution of compound A (1.0 g, 0.04 mmol) in H_2O (50 mL) is treated with $NaH_2PO_2\cdot H_2O$ (1.0 g, 9.4 mmol) and subsequently 3 mL of 1 M HCl is added dropwise, giving a pH value of ~2. After stirring for 24 h in a closed flask at 20°C and addition of NH_4Cl (2.0 g, 37.4 mmol), the mixture is kept at 15°C without further stirring. The dark brown crystals of $(NH_4)_{42}$ $[\mathrm{Mo}^{VI}_{72}\mathrm{Mo}^{V}_{60}O_{372}$ $(H_2PO_2)_{30}$ $(H_2O)_{72}]\cdot{\sim}300\ H_2O$, which slowly precipitate from the dark brown solution over a period of 4 days, are filtered through a glass frit (D2), washed with 10 mL of ice-cooled 98% 2-propanol, and dried in air. Yield: 0.8 g (81% based on compound A).

Anal. Calcd. for $(NH_4)_{42}$ $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}$ $(H_2PO_2)_{30}$ $(H_2O)_{72}] \cdot \sim 300$ H_2O: H, 3.5; N, 2.1; P, 3.3; Mo, 45.2 (Mo^V, 20.5); crystal H_2O, 19.3. Found: H, 3.2; N, 2.1; P, 3.4; Mo, 45.5 (Mo^V, 20.8; cerimetric titration); crystal H_2O, 18.5 (TGA value).

Properties

The compound [space group $R\bar{3}$, $a = 32.719$ (1), $c = 73.567$ (2) Å][7] is obtained by a ligand exchange (30 CH_3COO^- by 30 $H_2PO_2^-$) reaction. The IR spectrum is practically identical to that of compound A except for the appearance of $H_2PO_2^-$ bands [1118 (m), 1075 (w), 1033 (m) cm^{-1}] instead of CH_3COO^- bands. Also the Raman and electronic absorption spectra are almost identical to those of compound A.

C. $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5}$ HYDRATE

$$154\,MoO_4^{2-} + 14\,S_2O_4^{2-} + 322\,H^+ \longrightarrow$$

$$[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-} + 28\,SO_2 + 84\,H_2O$$

■ **Caution.** *This reaction evolves SO_2; hence, it should be carried out in a good fume hood.*

Procedure

To a solution of $Na_2MoO_4 \cdot 2H_2O$ (3.0 g, 12.4 mmol) in 10 mL of water, freshly powdered* $Na_2S_2O_4$ (0.2 g, 1.15 mmol) is added (light yellow coloration). Immediately afterward, under continuous stirring, 30 mL of hydrochloric acid (1 M) is rushed into the solution (color changes to deep blue). The solution is stirred in an open 100-mL Erlenmeyer flask for a further 10 min and then stored undisturbed in a closed flask at 20°C (not higher!) for 3 days.† The precipitated blue crystals (plate crystal aggregation may occur because of the high concentrations used) are removed by filtration, washed quickly with a small amount of cold water (note the rather high solubility!), and dried at room temperature over $CaCl_2$. Yield: 0.7 g (28% based on Mo).

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*Sodium dithionite should be fresh. The stability of $S_2O_4^{2-}$ ions in acidic media has not been considered for the formulation of the equation (formulated for the non-defect cluster). It is used as it gives the best results as reducing agent.

†Crystals filtered off after less than 3 days might be too small to be identified by X-ray diffraction. On standing much longer than 3 days (e.g., 2 weeks), other types of crystals (Mo_{176}) are found. (The checkers found these after 2 weeks, also.)

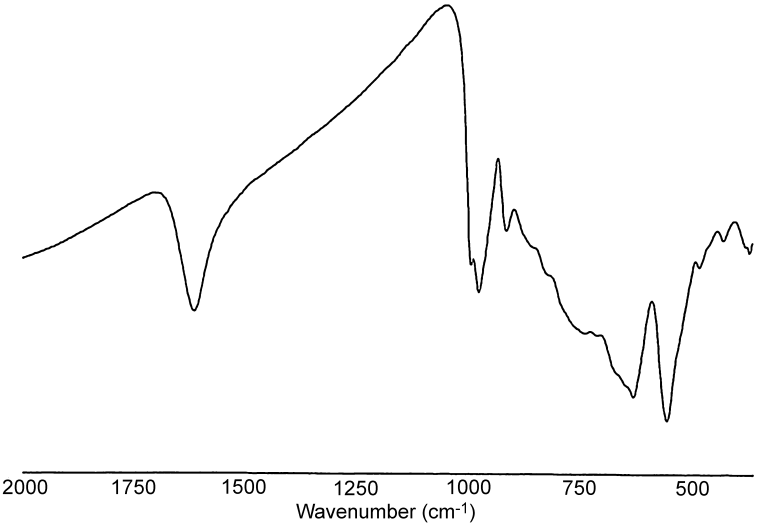

Figure 5. IR spectrum of $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5} \cdot \sim 400\ H_2O$ (compound C) (KBr disk).

Anal. Calcd. for $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5} \cdot \sim 400\ H_2O$: Na, 1.1; Mo, 47.6 ($Mo^V$, 8.7); crystal H_2O, 23.4. Found: Na, 1.2; Mo, 49.0 (Mo^V, 8.9; cerimetric titration); crystal H_2O, 23.0 (TGA value).

Properties

The molybdenum blue compound C crystallizes in the form of deep blue plates, which are extremely soluble at room temperature in water and even in low-molecular-weight alcohols. When removed from the mother liquor, a type of fast weathering process is observed associated with the loss of crystal water and crystallinity* [space group $P\bar{1}$ with $a = 30.785$ (2), $b = 32.958$ (2), $c = 47.318$ (3) Å; $\alpha = 90.53$ (1), $\beta = 89.86$ (1), $\gamma = 96.85$ (1)°].[8] The IR spectrum (Fig. 5) shows peaks at 1616 (m) (δ_{H_2O}), 975 (m), 913 (w-m) ($\nu_{Mo=O}$), 820 (sh), 750 (s), 630 (s), 555 (s) cm^{-1}. The electronic absorption spectrum is dominated by two bands characteristic for all molybdenum blue species [H_2O/HCl, pH = 1: λmax, nm (ε, $M^{-1}cm^{-1}$) = 745 (1.8×10^5), 1070 (1.4×10^5)] that have to be assigned to intervalence (Mo^V/Mo^{VI}) charge transfer transitions

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*For the same reason the single crystals taken from the mother liquor were immediately cooled to liquid nitrogen temperature for data collection within the process of single-crystal X-ray structure determination.

(IVCT). The second ε value corresponds to the abundance of 28 Mo^V centers (see Ref. 5). Using an excitation line within the contour of the 1070-nm band gives rise to a resonance–Raman spectrum showing five bands in the region between 900 and 200 cm^{-1} very characteristic for all molybdenum blue species [802 (s), 535 (m), 462 (s), 326 (s), 215 (s) cm^{-1}].

D. Na_{21} $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}$ $(H_2O)_{54}$ $(H_2PO_2)_7]$ HYDRATE

$$154\,MoO_4^{2-} + 21\,H_2PO_2^- + 294\,H^+ \longrightarrow$$
$$[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]^{21-} + 14\,H_2PO_3^- + 86\,H_2O^{\dagger}$$

Procedure

To a solution of $Na_2MoO_4 \cdot 2H_2O$ (3.0 g, 12.4 mmol) and NaCl (1.0 g, 17.1 mmol) in 25 mL hydrochloric acid (1.1 M), $NaH_2PO_2 \cdot H_2O$[*] (0.212 g, 2.0 mmol) is added. After stirring for 15 min under bubbling nitrogen gas, the resulting solution is kept undisturbed in a closed flask at room temperature. After 3 days[‡] the precipitated, blue bipyramid-shaped crystals are filtered, washed quickly with a small amount of cold water, and dried at room temperature under argon. Yield: 0.43 g (18% based on Mo).

Anal. Calcd. for Na_{21} $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}$ $(H_2O)_{54}$ $(H_2PO_2)_7] \cdot \sim 300$ H_2O: Na, 1.6; Mo, 50.1 (Mo^V, 9.1); P, 0.7; crystal H_2O, 18.3. Found: Na, 1.7; Mo, 50.9 (Mo^V, 9.5; cerimetric titration); P, 0.7; crystal H_2O, 18.5 (TGA value).

Properties

The compound crystallizes mainly in the form of blue square bipyramidal crystals. The IR spectrum is practically identical to that of C except for the additional IR bands at 1124 (w)/1076 (vw)/1039 (vw) (τ_{PH_2}, γ_{PH_2}, δ_{PO_2}) showing nicely the presence of the $H_2PO_2^-$ ligand. Also, the resonance Raman and electronic absorption spectra are almost identical to those of compound C. The crystal structure[9] [space group *Cmca*, $a = 50.075$ (3), $b = 56.049$ (4), $c = 30.302$ (2) Å] shows the abundance of nanosized ring-shaped units (crystallographic site symmetry $2/m$), which are linked through covalent Mo–O–Mo bonds: each cluster ring is surrounded by four rings, resulting in a layer structure with condensed

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[*] The quality of the NaH_2PO_2 used strongly affects this reaction. The checkers found material from Aldrich to be best.

[†] Equation formulated by the checkers.

[‡] Disturbance of the reaction mixture might result in the precipitation of a less crystalline material. The crystals should be separated out from the reaction mixture not later than 3 days, to avoid the coprecipitation of amorphous materials as aftereffect.

ring-shaped units parallel to the *ac* plane. The packing of the layers gives rise to the formation of a type of nanosized channel with the "encapsulated" $H_2PO_2^-$ ligands, which are coordinated at the well-defined sites of $\{Mo_2\}$ groups, replacing the H_2O ligands.

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43. TETRAKIS-{(η^6-1-ISOPROPYL-4-METHYLBENZENE) RUTHENIUM(II)TETRAOXOMOLYBDATE(VI)}

Submitted by BRUNO THERRIEN,[*] LAURENT PLASSERAUD,[*]
and GEORG SÜSS-FINK[*]
Checked by DANIELLE LAURENCIN[†] AND ANNA PROUST[†]

$$2(\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2\text{Cl}_4 + 4\text{Na}_2\text{MoO}_4 \longrightarrow (\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16} + 8\text{NaCl}$$

Since the early 1980s there has been a steadily growing interest in molecules containing both organometallic groups and oxometallic entities,[1] particularly since they provide molecular models for heterogeneous catalysts derived from

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