Polyoxometalates

A Supramolecular Tetradecanuclear Copper(II) Polyoxotungstate

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Polyoxometalates (POMs) can be perceived as discrete fragments of extended metal oxide lattices.[1] They continue to attract much attention with respect to their widespread applications.[2] To date, the two most studied POM types have been the so-called Keggin and Dawson–Wells families, which can be formulated $[XM_{12}O_{40}]^{n-}$ and $[X_2M_{18}O_{62}]^{n-}$ ($X = P^{V}$, Si^{IV}; $M = W^{VI,V}$, $Mo^{VI,V}$, $V^{IV,V}$) respectively. These species are diamagnetic when the metals M are in their highest oxidation state. Mono, di and trivacant species of the Keggin type polyoxotungstates can be easily prepared,[3] and then act as nucleophilic ligands for transition-metal (TM) or rare-earth cations. Such inclusions can then lead to the formation of magnetic clusters. Trivacant POMs are the best candidates to obtain compounds with the largest number of interacting magnetic cations. Recently, compounds with a number (from one to nine) of paramagnetic TM centers of the first row ranging were reported.[4] Among the numerous complexes reported to date, the most often encountered contain three or four M^{II} or M^{III} centers. Trimeric M^{II} or M^{III} compounds consist of either complexes in which the TM centers complete the free sites of the POMs to form $[XW_9O_{37}M_3(H_2O)_3]^{n-}$ ($X = Si^{IV}$, $M = Cr^{III}$, Co^{II}, Ni^{II}, Cu^{II}),[5] or sandwich complexes of general formula $[(XW_9O_m)_2M_3(H_2O)_3]^{n-}$ ($m = 37$, $X = P^{V}$, $M = Mn^{II}$, Fe^{II}, Ni^{II}, Cu^{II}, Zn^{II}; $m = 33$, $X = As^{III}$, $M = Mn^{II}$, Ni^{II}, Cu^{II}).[6] Similarly, complexes containing four paramagnetic TM centers have been characterized: the $[H_2PW_9O_{34}Ni_4(OH)_3(H_2O)_6]^{2-}$ POM, in which a nickel cubane caps the $\{PW_9O_{34}\}$ entity,[7] and the sandwich complexes $[(XW_9O_{34})_2M_4(H_2O)_2]^{n-}$ ($X = P^{V}$, $M = Mn^{II,III}$, $Fe^{II,III}$, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}; $X = Si^{IV}$, $M = Cr^{III}$, Mn^{II}, Cu^{II}, Zn^{II}).[8] In 1995, the hexameric Cr^{III} complex $[\{SiW_9O_{34}Cr_3(OH)_3\}_2(OH)_3]^{11-}$ was isolated,[9] and finally, Clemente-Juan et al. reported in 1999 the nonanuclear Ni^{II} complex $[(PW_9O_{34}Ni_3)_3(H_2O)_6(HPO_4)_2(OH)_3]^{16-}$.[10] An increase in the number of magnetic centers encapsulated in diamagnetic polyoxometalate matrices remains a challenge. We report herein the characterization of tetradecanuclear Cu^{II} com-

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351486

pounds, constructed through supramolecular assembly: $Na_{19}K_4[(SiW_9O_{34})(SiW_9O_{33}(OH))(Cu(OH))_6Cu]_2X\cdot nH_2O$ ($X = Cl$, $n = 160$ **2Cl** ; $X = Cl$, $n = 90$ $\mathbf{2\,Cl_{dhyd}}$; $X = Br$, $n = 160$ **2Br** ; $X = Br$, $n = 90$ $\mathbf{2\,Br_{dhyd}}$; $\mathbf{2\,Cl_{dhyd}}$ and $\mathbf{2\,Br_{hdyd}}$ are the dehydrated forms of **2Cl** and **2Br**, respectively).

These compounds represent, to the best of our knowledge, the molecular POMs with the greatest number of di or trivalent TM ions of the first row.

Compounds **2Cl** and **2Br** were synthesized in good yield starting from the same crude precursor **1**. Compound **1** is an azido complex of general formula $H_5K_6[(SiW_9O_{37})Cu_3N_3]\cdot 19H_2O$ obtained by mixing in water at room temperature stoichiometric amounts of $[A,\alpha\text{-}SiW_9O_{34}]^{10-}$, $CuCl_2$, and NaN_3. The addition of an excess of azide has no influence on the composition of the final product. The IR spectrum of the product shows the presence of two single bands relative to the $\tilde{\nu}_{as(N=N)}$ vibration at 2082 and 1282 cm^{-1}, thus indicating that the azido group acts as an end-on bridging ligand.[11] Huge efforts were made to obtain single crystals of this compound suitable for X-Ray diffraction without success. A solution of **1** dissolved in molar NaCl or NaBr aqueous media turns from yellow to green upon heating, and crystals of **2Cl** or **2Br,** respectively, appear after cooling to room temperature within minutes. This phenomenon was not observed when the precursor was dissolved in a 1 M NaF solution, and reduction followed by the decomposition of the POM occurs when a NaI solution was used. Similarly, the dissolution in nonhalide sodium salt solutions (Na_2SO_4, Na_2SO_3, $NaNO_3$) did not lead to the formation of the expected Cu^{II} complex, and compound **1** was systematically recovered. Even if **2Cl** or **2Br** do not contain any azido ligand, its presence during the synthetic process seems crucial since it has not been possible to obtain the title compound in absence of this reactant. The role of this bridging ligand remains unclear. Sodium azide may act as a base, as a preassembling agent, or may simply favor the crystallization process.

Single-crystal X-ray diffraction analyses were performed on compounds **2Cl** and **2Br**.[12] The protonated oxo bridges were localized by valence bound summations.[13] Complex **2Cl** is formed from two $[(SiW_9O_{34})(Cu(OH))_3]^{7-}$ subunits (denoted $\{Cu_3\}$), and two $[(SiW_9O_{33}(OH))(Cu(OH))_3Cu]^{4-}$ subunits (denoted $\{Cu_4\}$; Figure 1). Each subunit contains a Cu^{II} center in a square pyramidal environment, the remaining Cu^{II} centers are in a highly distorted octahedral geometry. Within the tetradecanuclear Cu^{II} subunit, the four divalent metals capping the $[SiW_9O_{34}]^{10-}$ entity form a distorted trigonal pyramid. Connections between the subunits inside the tetradecanuclear Cu^{II} complex occur a) between one Cu^{II} cation of each subunit and an oxygen atom of an adjacent subunit (Figure 1 a), and b) through bridging OH ligands shared by the copper centers (Figure 2). Finally, a Cl^- anion is locked in the center of the cluster, surrounded by six Cu^{II} cations with long Cu–Cl distances ($d_{Cu-Cl} = 2.834(11)$–$3.003(11)$ Å). Compound **2Cl** approaches C_2 symmetry. The C_2 pseudo-axis passes through the chloride anion and is associated with the plane defined by the four Cu^{II} centers of two $\{Cu_4\}$ units linked to the central halide. Assembly of trivacant POMs through Y^{III}[14] or Nb^{V}[15] centers leading to diamagnetic tetrameric species were recently reported. The connecting modes inside the yttrium, niobium and copper tetramers are radically different. In the first case, a $[Y_8W_7O_{30}]^{6+}$ cluster connects the subunits, while a $Nb_4O_6^{8-}$ unit ensures the connection in the second case. In **2Cl**, the formation of the high nuclearity cluster is driven by supramolecular assembly around a templating halide. The structure of **2Br** is similar to that of **2Cl**, the Br^- replacing the Cl^- ion,

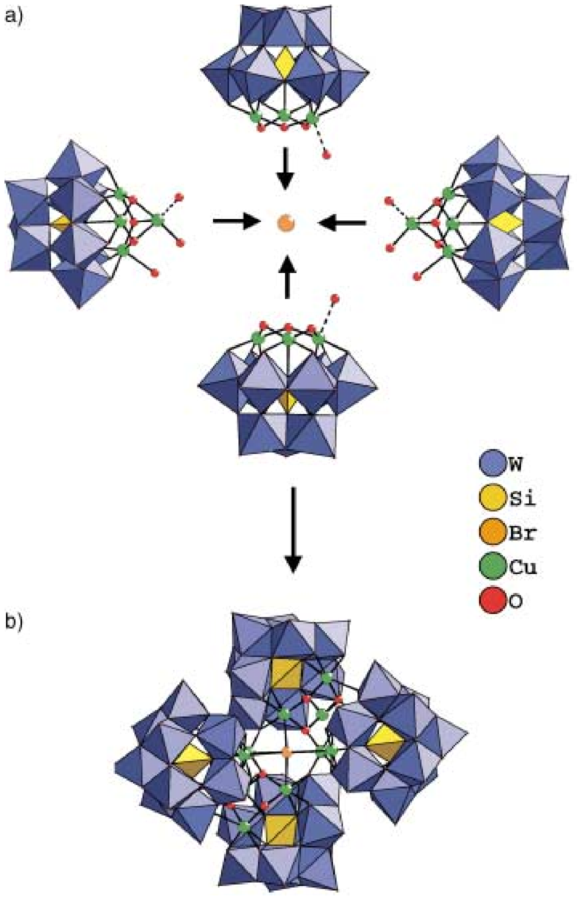

Figure 1. Polyhedral representation showing a) the four building blocks constituting the tetradecanuclear Cu^{II} cluster b) complex $[\{(SiW_9O_{34})\text{-}\{SiW_9O_{33}(OH)\}(Cu(OH))_6Cu\}_2X]^{23-}$ ($X = Cl$ in **2Cl**; $X = Br$ in **2Br,** depicted). Bounds between Cu^{II} centers and oxygen atoms from another $\{SiW_9O_{34}\}$ subunit are shown as dashed lines.

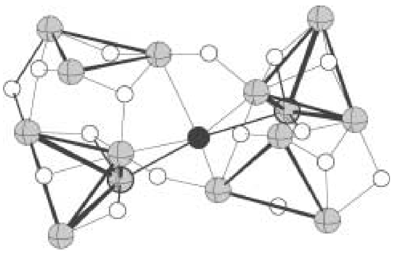

Figure 2. Ball-and-stick structural representation of the $\{Cu_{14}\}$ cluster. Cu = Gray crosshatched circles, O = white circles, X = black circles, (X = Cl in **2Cl**; X = Br in **2Br**). For clarity, only oxygen atoms linking the Cu^{II} ions are represented. Edges of the $\{Cu_3\}$ and $\{Cu_4\}$ sub-units are shown as bold lines.

with, as expected, longer metal–halide distances (d_{Cu-Br} = 2.918(15)–3.071(9) Å).

The well defined experimental X-ray diffraction powder pattern performed in air on crystals of **2Cl** is not similar to the simulated powder pattern calculated from the data obtained by single-crystal analysis performed on the same compound in a Lindeman tube. Complexes **2Cl** and **2Br** are highly hydrated; exposure to air of these compounds lead to a spontaneous loss of water molecules of crystallization. Single-crystal X-ray diffraction analysis was performed on a dehydrated crystal of **2Cl** (i.e. **2Cl**$_{\mathbf{dhyd}}$). Surprisingly, despite the poor quality of the crystal, it has been possible to refine the diffraction data to obtain an acceptable structural model for **2Cl**$_{\mathbf{dhyd}}$,[12] thus showing that dehydration lead to a large compression along the *a* axis of the lattice (Figure 3).[16] Simulated and experimental powder patterns of **2Cl**$_{\mathbf{dhyd}}$ are in good agreement. Even in the dehydrated form, the magnetic clusters are well isolated from each other in **2Cl**$_{\mathbf{dhyd}}$, with the shortest Cu–Cu distances of 7.439 Å (d_{Cu-Cu} = 9.119 Å in **2Cl**).

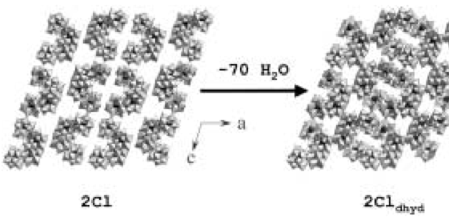

Figure 3. Polyhedral representation of **2Cl** and **2Cl**$_{\mathbf{dhyd}}$ showing the contraction of the *a* axis when dehydration occurs.

The magnetic behavior of a microcrystalline sample of compound **2Br**$_{\mathbf{dhyd}}$ has been studied in the range of 2 to 300 K, and the result is shown in Figure 4 under the form $\chi_M T$ versus T (χ_M = molar magnetic susceptibility). Due to the topological complexity of the {Cu_{14}} cluster, it is not possible to fit the magnetic behavior of **2Br**$_{\mathbf{dhyd}}$ with a current theory. Indeed, by using reasonable approximations, up to nine exchange parameters would be required.[17] Nevertheless, the continuous decrease of the $\chi_M T = f(T)$ curve and the $\chi_M T$ value at 300 K ($\chi_M T$ = 4.33 cm^{3}mol^{-1} K for a calculated $\chi_M T$ value of 5.79 K cm^{3}mol^{-1} for fourteen noninteracting $S = ^1/_2$ centers assuming g = 2.1; S = spin angular momentum, g = Landé factor) clearly indicates that antiferromagnetic interactions are predominant in 2 Br$_{dhyd}$. The magnetization study at 2 K showed that M tends to a value of 3 MB at high field (M = magnetization). As a half-spin ground state is excluded, this indicates that excited states are populated at 2 K. In the absence of data at very low temperature, the strong decrease observed under 4 K (Figure 4, inset) cannot be interpreted unambiguously. It can be attributed to the presence of a singlet ground state, but also to a triplet, the decrease being then a consequence of the zero-field splitting effect on the S = 1 state.

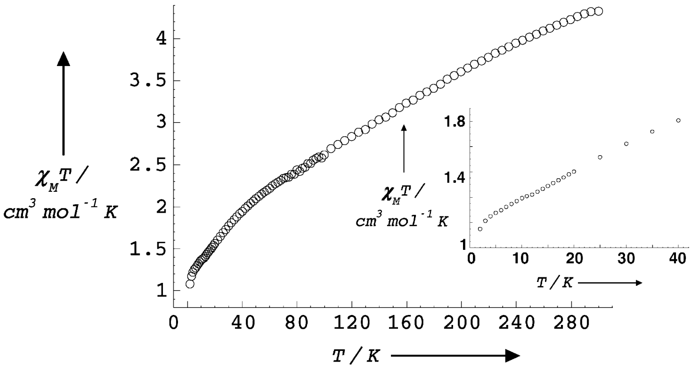

Figure 4. Thermal dependence of $\chi_M T$ for **2Br**$_{\mathbf{dhyd}}$ a) in the 2–300 K range, (B = 10 kG) b) in the 2–40 K range (B = 1 kG) (inset).

In conclusion, tetradecanuclear Cu^{II} polyoxometalates have been synthesized and characterized. The role of the N_3^- ligand during the synthetic process is not clearly understood but seems crucial. Structural characterization of azido–POM complexes must be performed. The recrystallization of the POM in high halide concentration allowed the formation of a supramolecular assembly. Now, it has to be checked whether the synthetic strategy described herein can be extended to other divalent metals and/or trivacant POMs systems. This work is in progress.

Experimental Section

1: A sample of Na_{10}[A,α-SiW_9O_{34}]·20H_2O[3] (2.8 g, 1 mmol) was dissolved at room temperature in stirring water (40 mL) by adding solid $CuCl_2$·2H_2O (0.5 g, 3 mmol). After 5 minutes, NaN_3 (0.2 g, 3 mmol) in water (20 mL) was added dropwise to the reaction mixture, and the green solution turned instantaneously to yellow. Solid potassium chloride (1.5 g, 20 mmol) was then added. After 2 h, the resulting yellow precipitate was filtered, washed with a KCl solution (20 mL, 1 M), dried with ethanol and diethyl ether. Yield: 2.4 g (80 %, based on Cu). Elemental analysis calcd (%) for $H_5K_6[(SiW_9O_{37})Cu_3N_3]\cdot 19H_2O$: W 54.41, Cu 6.27, K 7.71, N 1.38; found: W 55.11, Cu 6.11, K 7.56, N 1.58, Na 0.08. IR (KBr pellet): $\tilde{\nu}$ = 2082(s), 1282(w), 1001(m), 940(s), 905(s), 887(s), 783(s), 682(s), 548(m), 527(m), 364(m), 328(m)cm^{-1}. UV/Vis (H_2O): $\lambda_{max}(\varepsilon)$ = 747 (90).

2Cl and **2Br**: Compound **1** (0.3 g) was dissolved in a hot (80 °C) aqueous solution of NaCl (1 M, 5 mL). The green solution was cooled down to room temperature, and after one hour, large and long green needles of **2Cl** were obtained. Isolation of the product by filtration led to the dehydrated complex **2Cl**$_{\mathbf{dhyd}}$. Yield: 190 mg, 55 % based on Cu. IR (KBr pellet): $\tilde{\nu}$ = 1006(m), 943(s), 910(s), 894(s), 774(s), 735(s), 670(s), 525(m), 357(m) cm^{-1}. UV/Vis (NaCl 1 M): $\lambda_{max}(\varepsilon)$ = 757 (310). Elemental analysis calcd (%) for $H_{194}ClCu_{14}W_{36}O_{238}Si_4Na_{19}K_4$: W 54.09, Cu 7.27, Na 3.76, K 0.96, Cl 0.29; found: W 53.98, Cu 7.32, Na 4.08, K 1.26, Cl 0.55.

2Br and **2Br**$_{\mathbf{dhyd}}$ were obtained following the procedure described for **2Cl** and **2Cl**$_{\mathbf{dhyd}}$ in the same yield, but dissolving **1** in a 1 M NaBr solution instead of a 1 M NaCl solution. Infrared and UV/Vis spectra are similar to that found for compound **2Cl**$_{\mathbf{dhyd}}$. Elemental analysis calcd (%) for $H_{194}BrCu_{14}W_{36}O_{238}Si_4Na_{19}K_4$: W 53.83, Cu 7.24, Na 3.55, K 1.27, Br 0.65; found: W 53.53, Cu 7.26, Na 3.78, K 1.57, Br 1.06.

X-ray powder diffraction data were collected in air on a Siemens D5000 diffractometer (Cu Kα radiation).

TGA was carried out on compounds **2Cl**$_{\mathbf{dhyd}}$ and **2Br**$_{\mathbf{dhyd}}$ under nitrogen flow (60 mL min^{-1}) with a Perkin-Elmer electrobalance TGA-7 at a heating rate of 1 °C min^{-1} up to 600 °C, confirming the degree of hydration of these compounds.

Magnetic susceptibility measurements were carried out with a Quantum Design SQUID Magnetometer with an applied field of 1000 and 10000 G. The independence of the susceptibility value with respect to the applied field was checked at room temperature. The susceptibility data were corrected from the diamagnetic contributions of **2Br**$_{\mathbf{dhyd}}$ as deduced by using Pascal's constant tables. The $\boldsymbol{M} = f(B)$ curve at 2 K is given as supplementary material.

Received: March 26, 2003 [Z51486]

Keywords: copper · magnetism · polyanions · solid-state structures · tungsten

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[12] Crystal data and structure refinements for **2Cl**: a large green needle (0.35 × 0.15 × 0.07 mm) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector with $\mathrm{Mo_{K\alpha}}$ monochromatized radiation ($\lambda = 0.71073$ Å). Monoclinic, space group $C2/c$, $a = 63.5191(16)$ Å, $b = 18.5238(5)$ Å, $c = 41.1156(10)$ Å, $\beta = 107.395(1)°$, $V = 46165.2(2)$ Å^3, $Z = 8$, $\rho_{\text{calc}} = 3.273$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 19.353$ mm^{-1}, $F(000) = 39920$, 100177 reflections measured, of which 32701 were independent, 2343 refined parameters, $R_1 = 0.0772$, $wR_2 = 0.1863$. Crystal data and structure refinements for **2Br**: a green large needle crystal (0.25 × 0.08 × 0.06 mm) was analysed. Monoclinic, space group $C2/c$, $a = 63.4405(9)$ Å, $b = 18.4975(4)$ Å, $c = 41.3627(9)$ Å, $\beta = 107.514(1)°$, $V = 46288.6(16)$ Å^3, $Z = 8$, $\rho_{\text{calc}} = 3.270$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 19.462$ mm^{-1}, $F(000) = 39968$, 103640 reflections measured, of which 33148 were independent, 2379 refined parameters, $R_1 = 0.0649$, $wR_2 = 0.1443$. Crystal data and structure refinements for **2Cl**$_{\mathbf{dhyd}}$: a green large needle crystal (0.440 × 0.08 × 0.04 mm) was analyzed. Monoclinic, space group $C2/c$, $a = 52.5809(10)$, $b = 18.2519(2)$, $c = 39.89370(10)$ Å, $\beta = 110.35(1)°$, $V = 35897.6(8)$ Å^3, $Z = 8$, $\rho_{\text{calc}} = 3.805$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 24.748$ mm^{-1}, $F(000) = 35612$, 80012 reflections measured, of which 25916 were independent, 1135 refined parameters, $R = 0.1816$, $wR_2 = 0.4297$. For **2Cl, 2Br** and **2Cl**$_{\mathbf{dhyd}}$, data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set by using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares by using the SHELX-TL package. Crystallographic data for the structure reported in this paper have been deposited at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number numbers CSD-413064 (**2Cl**) and -413063 (**2Br**).

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[16] The number of crystallization water molecules have been determined for **2Cl** by considering the difference in cell volume between **2Cl** and **2Cl**$_{\mathbf{dhyd}}$.

[17] Considering the overall pseudo C_2 symmetry of the magnetic cluster, $\{\mathrm{Cu_{14}}\}$ can be viewed as the adjunction of two $\{\mathrm{Cu_7}\}$ clusters, formed by a $\{\mathrm{Cu_4}\}$ and a $\{\mathrm{Cu_3}\}$ subunits. If only one J constant can be considered for the modeling of the magnetic interactions inside the $\{\mathrm{Cu_3}\}$ part, four are needed for the $\{\mathrm{Cu_4}\}$ subunit. Three additional exchange parameters have to be considered for taking into account the interaction between the $\{\mathrm{Cu_3}\}$ and the $\{\mathrm{Cu_4}\}$ subunits. Finally, another J constant is needed, related to the interaction between the $\{\mathrm{Cu_7}\}$ parts.