Functionalization of Polyoxometalates by a Negatively Charged Bridging Ligand: The Dimeric $[(SiW_{11}O_{39}Ln)_2(\mu\text{-}CH_3COO)_2]^{12-}$ (Ln = Gd^{III}, Yb^{III}) Complexes

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The possibility of coupling lacunary polyoxometalates through a cationic center present in the vacancy by negatively charged organic ligands is demonstrated for the first time by single-crystal X-ray diffraction. The structure of the dimeric $K_{12}[\{Yb(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ complex, where two acetato ligands connect the ytterbium centers in a (η^2, μ-1,1) fashion, is reported. Using gadolinium instead of ytterbium, both the isostructural dimeric compound $K_{12}[\{Gd(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ and the mononuclear sandwich complex $[Gd(SiW_{11}O_{39})_2]^{13-}$ can be selectively isolated, depending on the synthetic conditions. The magnetic properties of the dimeric gadolinium complex are presented. The influence of the nature of the rare-earth metal on the final compound is further highlighted by the fact that when praseodymium is used as the rare-earth element, only the sandwich compound can be obtained.

Introduction

Polyoxometalates (POMs) have definite sizes and shapes and resemble discrete fragments of metal-oxide structures.[1] They are especially valuable for studies in diverse areas of current interest, which include medicine, catalysis and magnetism.[2] Among the wide variety of POMs, the Keggin series has been the most studied. These complexes have the general formula $\{XM_{12}O_{40}\}$, where X is the central atom (X = Si^{4+}, P^{5+}, As^{5+}, etc.) and M is a metal in a high oxidation state (M = $W^{5+/6+}$, $Mo^{5+/6+}$, $V^{4+/5+}$, etc.). They are usually synthesized in acidic aqueous media. The mono-, di- and trivacant species, corresponding to the formal removal of one, two or three metal centers, respectively, are successively obtained when the pH of the solution is increased. The resulting vacancies can be filled by addition of rare-earth or transition-metal cations. The vacant POM acts, for each atom incorporated in the vacancies, as a tetradentate ligand for rare-earth metals or a pentadentate ligand for transition metals. While the coupling of transition-metal or rare-earth centers coordinated to polydentate organic ligands through negatively charged bridging species (such as acetate, oxalate, squarate, phenolate, etc.) has been widely explored and has led to one of the largest family of inorganic compounds, analogous connection through either Ln^{3+} or transition-metal cations$^{2+/3+}$ present in the vacancies of POMs has not been observed. Polymeric polyoxometalate complexes have then been mainly obtained by acid-base condensation.[3] More recently, connections of the tetracapped $[\varepsilon\text{-}H_4PMo_{12}O_{40}\{La(H_2O)_4\}_4]^{5+}$ polyoxocations by carboxylates, affording multidimensional materials, have been made successfully.[4]

This lack of reactivity of polyoxoanions toward negatively charged organic ligands is mainly due to the following three characteristics of these species: (1) rare-earth- or transition-metal- substituted POMs are generally highly negatively charged, and then connection to bridging anionic ligands is not favored; (2) when a transition metal is used, as the POM acts as a pentadentate ligand, only one coordination site is available, preventing reactivity with chelating ligands; (3) due to the steric hindrance of POMs, bridging of subunits by relatively large ligands is unlikely. Nevertheless, we have developed a synthetic approach which has allowed us to overcome these difficulties. First, as the negative charge of a POM decreases with the number of vacancies, we have started our study considering a monovacant POM. Secondly, rare-earth cations have been preferred to transition-metal cations. Indeed, considering that the lanthanides have higher coordination numbers than transition metal cations, linkage to organic ligands must be facilitated. Finally, acetate has been chosen as the bridging agent, considering both its small size and its high affinity for rare-earth centers. We present here the structural characterization of compound $K_{12}[\{Yb(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}$

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$CH_3COO)_2]\cdot 38H_2O$, a unique di-μ-acetato polyoxometalate complex. The influence of the size of the rare-earth metal and of the nature of the synthetic media is discussed. Magnetic properties of the isostructural $K_{12}[\{Gd(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ complex are presented.

Results and Discussion

It has been shown recently that $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ {written below as $[SiW_{11}O_{39}]^{8-}$} reacts with rare-earth metals to afford solid-state one- or two-dimensional compounds.[5] These compounds dissociate in water leading to molecular species, of general formula $[Ln(SiW_{11}O_{39})(H_2O)_x]^{5-}$. Dissolution with heating of the precursor $K_5[Yb(SiW_{11}O_{39})(H_2O)_2]\cdot 24H_2O$ in 2 M acetate buffer has afforded crystals of the dimeric complex $K_{12}[\{Yb(SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ (**1**; Figure 1). In **1**, each ytterbium ion is eight-coordinate, adopting a distorted Archimedean antiprism geometry (pseudo-D_{4d}), with one $[SiW_{11}O_{39}]^{8-}$ entity acting as a tetradentate ligand and with a terminal water molecule. The remaining three coordination sites are occupied by two oxygen atoms of the bidentate-bridging acetate and one acetato-oxygen atom from the other $\{(Yb(SiW_{11}O_{39})(H_2O))(\mu\text{-}CH_3COO)_2\}$ subunits. The ytterbium ions are therefore doubly bridged by two (η^2, μ-1,1)-acetate ligands, separated by a distance of 4.085(18) Å. This connection mode has been previously encountered for two ytterbium dimers where each rare-earth center is coordinated to two cyclopentadienyl ligands, with intramolecular Yb−Yb lengths similar to that found in **1** (d_{Yb-Yb} = 3.905 and 3.930 Å).[6] The Yb−O lengths are divided into three groups, corresponding to the three different types of oxygen atoms present in the coordination sphere of the rare-earth metal [$d_{Yb-O(POM)}$ = 2.255(2)−2.289(1) Å; d_{Yb-OH_2} = 2.342(14) Å; $d_{Yb-O(Ac)}$ = 2.420(7)−2.448(4) Å]. The structure of complex **1** can be compared to the two previously reported dimeric Dawson polyoxometalates $[Ln^{III}(\alpha\text{-}n\text{-}P_2W_{17}O_{61})]^{7-}$ (Ln = Ce, n = 1; Ln = Eu, n = 2).[7] In both cases, the absence of exogenous ligands provokes the connection of each lanthanide center to the two $[P_2W_{17}O_{61}]$ subunits. Moreover, the rare-earth cations are not directly bridged with long Ln−Ln lengths [d_{Ce-Ce} = 6.0803(4) and d_{Eu-Eu} = 6.600(1) Å].

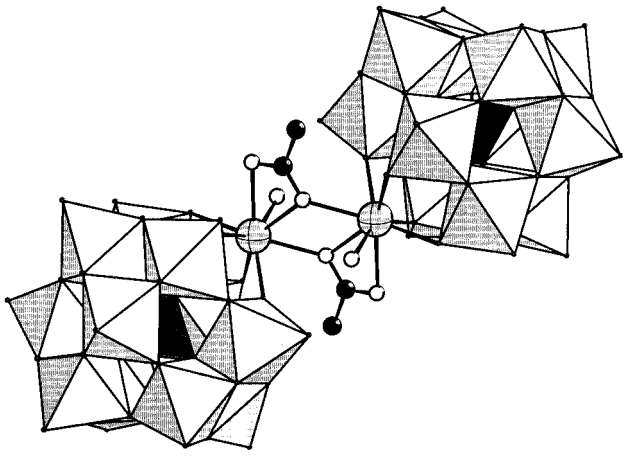

Figure 1. Polyhedral representation of complex $[\{Yb(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]^{12-}$ in **1**; grey crosshatched circles, Yb; white circles, O; light gray octahedra, $\{WO_6\}$; black tetrahedra, $\{SiO_4\}$

Syntheses in similar conditions have been performed replacing the ytterbium precursor by the related praseodymium complex **2a**. The IR spectrum of the obtained compound **2b** indicates the absence of an acetato ligand. A single-crystal X-ray diffraction study revealed that compound **2b** is the sandwich complex $K_{13}[Pr(SiW_{11}O_{39})_2]\cdot 35H_2O$, which structure has been previously postulated by Blasse et al.[8] by analogy with the known structure of $Cs_{12}[U(GeW_{11}O_{39})_2]$.[9] In **2b**, the Pr^{3+} cation is in an antiprismatic environment, coordinated to four oxygen atoms of each $[SiW_{11}O_{39}]^{8-}$ subunit [$d_{Pr-O(POM)}$ = 2.421(1)−2.518(2) Å]. Analogously, anion $[Gd(SiW_{11}O_{39})_2]^{13-}$ was obtained from heating a solution of $K_5[Gd(SiW_{11}O_{39})]\cdot 25H_2O$ in a 2 M acetate buffer. An alternative synthetic pathway was conducted to obtain the gadolinium acetato species. A concentrated acetate buffering solution was added to a solution of the gadolinium precursor dissolved in hot water and cooled to room temperature, until a 1 M acetate buffer solution was obtained. A microcrystalline compound **3** containing acetato ligands as shown by IR spectroscopy was isolated after slow evaporation. Comparison of the simulated diffraction powder pattern of **1** with the experimental X-ray diffraction powder pattern of **3** showed that **1** and **3** are isostructural. If the buffer concentration is adjusted to 2 M, the sandwich gadolinium complex $[Gd(SiW_{11}O_{39})_2]^{13-}$ is recovered. It must be noted that it has not been possible to isolate the praseodymium dimeric compound, while the ytterbium sandwich complex has never been obtained even in highly concentrated buffer solutions. It can then be concluded that as the atomic radius of the rare-earth metal decreases, the dimeric $[\{Ln(SiW_{11}O_{39})\}_2(\mu\text{-}CH_3COO)_2]^{12-}$ is preferentially formed, while an increase of the acetato buffer concentration favors the formation of the sandwich $[Ln(SiW_{11}O_{39})_2]^{13-}$ complex. It is not possible at this stage to rationalize the two observed tendencies, but clearly, this indicates that considerations on the affinity of rare-earth cations for carboxylato ligands, which increases when the size of the lanthanide decreases, are not sufficient to elucidate the reaction pathway.

The magnetic properties of $K_{12}[\{Gd(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ have been studied. The thermal dependence (χ_{MT}) of **3** is shown in Figure 2. The $\chi_M T$ curve follows a Curie law from 300 K ($\chi_M T$ = 16.2 $cm^3\cdot mol^{-1}\cdot K$) to 50 K, and then decreases from 50 K to 2 K ($\chi_M T$ = 14.6 $cm^3\cdot mol^{-1}\cdot K$). This behavior is characteristic of an antiferromagnetic coupling, in agreement with the previously reported homopolynuclear gadolinium complexes, with the exception of the dimeric Gd^{3+} salicylic complex reported by Costes et al., where the lanthanide centers were found to be ferromagnetically coupled.[10] As Gd^{3+} has an $^8S_{7/2}$ ground state, the $\chi_M T = f(T)$ curve can be fitted considering the HDVV isotropic spin Hamiltonian

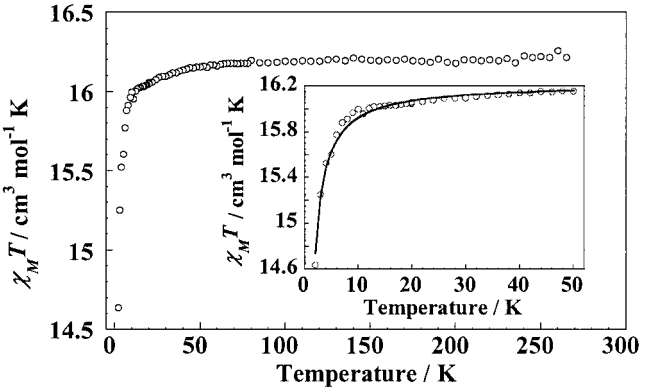

Figure 2. $\chi_M T$ per mol of compound $K_{12}[\{Gd(\alpha\text{-}SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ (**2**) as a function of temperature between 300 and 2 K; inset: $\chi_M T = f(T)$ between 300 and 2 K; the solid line was generated from the best fit parameters given in the text

$H = -JS_{Gd1}\cdot S_{Gd2}$, with $S_{Gd1} = S_{Gd2} = 7/2$. An excellent fit is found (Figure 2) for $J = -0.02\ cm^{-1}$ and $g = 2.02$, with an agreement factor R equal to 2.0×10^{-6} $\{R = [\Sigma(\chi_M T_{calcd.} - \chi_M T_{obsd.})^2/\Sigma(\chi_M T_{obsd.})^2]\}$. This J value is close but slightly lower than for the two previously reported dinuclear gadolinium complexes ($J = -0.05$ and $-0.21\ cm^{-1}$).[11] Nevertheless, due to the lack of structural and magnetic data, it is not possible to propose magneto-structural correlations at the moment.

Connection through Ln^{3+} or transition-metal cations$^{2+/3+}$ located in the POM vacancies has therefore been achieved. It should be noted that such dimeric lanthanide polyoxometalate compounds allow a highly accurate determination of the magnetic exchange parameters, as the Ln_2 cores are well isolated from each other due to the steric hindrance of the diamagnetic POM ligands. The magnetic study of dimeric analogous lanthanide complexes with rare-earth metals possessing a ground state with first-order orbital momentum must be performed. The reactivity of $[Ln(\alpha\text{-}SiW_{11}O_{39})(H_2O)_2]^{5-}$ ($Ln = Gd^{3+}$, Yb^{3+}) precursors with more sophisticated negatively charged organic ligands is under investigation.

Experimental Section

Synthesis: Compounds $K_5[Yb(SiW_{11}O_{39})(H_2O)_2]\cdot 24H_2O$ and $K_5[Gd(SiW_{11}O_{39})]\cdot 25H_2O$ have been prepared as described previously, for the preparation of the cesium salt[5b] but using KCl instead of CsCl. $K_5[Pr(SiW_{11}O_{39})]\cdot 26H_2O$ **2a** was prepared following the procedure described for the ytterbium compound, but using $PrCl_3\cdot 6H_2O$ instead of $YbCl_3\cdot 6H_2O$. The degree of hydration for the three precursors was determined by TGA.

$K_{12}[\{Yb(SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ (1): $K_5[Yb(SiW_{11}O_{39})(H_2O)_2]\cdot 24H_2O$ (350 mg, 0.1 mmol) is dissolved in potassium acetate buffer (10 mL, 2 M) and stirred at 60 °C for 1 h. After cooling to room temperature, the solution was left to evaporate. After a few days, colorless parallelopipedes of **1** were obtained. Yield: 220 mg (68 %). $C_4H_{86}K_{12}O_{122}Si_2W_{22}Yb_2$ (7002.16): calcd. Yb 4.94, W 57.76, K 6.70, C 0.68; found Yb 4.95, W 57.78, K 6.90, C 0.86. IR: $\tilde{\nu}$ = 1618 cm^{-1} (m), 1537 (m), 1453 (m), 1007 (m), 951 (s), 915 (s), 884 (s), 820 (s), 790 (s), 703 (s), 681 (s), 541 (m), 523 (m).

$K_{13}[Pr(SiW_{11}O_{39})_2]\cdot 35H_2O$ (2b): Compound **2b** was synthesized following the procedure described for **1** but with $K_5[Pr(SiW_{11}O_{39})]\cdot 26H_2O$ instead of $K_5[Yb(SiW_{11}O_{39})(H_2O)_2]\cdot 24H_2O$. After a few days, large pale green parallelepipedes of **2b** were obtained. Yield: 130 mg. $H_{70}K_{13}O_{113}PrSi_2W_{22}$ (6628.09): calcd. Pr 2.11, W 60.69, K 7.63; found Pr 1.90, W 60.77, K 7.53. IR: $\tilde{\nu}$ = 1619 cm^{-1} (m), 1005 (m), 948 (s), 906 (s), 891 (s), 827 (s), 765 (s), 720 (s), 545 (m), 526 (m), 482 (m).

$K_{12}[\{Gd(SiW_{11}O_{39})(H_2O)\}_2(\mu\text{-}CH_3COO)_2]\cdot 38H_2O$ (3): $K_5[Gd(SiW_{11}O_{39})(H_2O)_2]\cdot 24H_2O$ (350 mg, 0.1 mmol) was dissolved in water (5 mL) and heated to 60 °C. The resulting solution was cooled to room temperature. Potassium acetate buffer (5 mL, 2 M) was added and the solution left to evaporate. After a few days, colorless parallelepipedes of **3** were obtained. Yield: 170 mg (52 %). $C_4H_{86}Gd_2K_{12}O_{83}W_{22}$ (6290.40): calcd. Gd 4.50, W 57.90, K 6.72, C 0.69; found Gd 4.48, W 57.38, K 7.23, C 0.90. IR: $\tilde{\nu}$ = 1624 cm^{-1} (m), 1530 (m), 1453 (m), 999 (m), 955 (s), 906 (s), 889 (s), 812 (s), 790 (s), 755 (m), 703 (m), 693 (m), 678 (m), 543 (m), 523 (m).

X-ray Crystallography: Crystal data for **1**: monoclinic, $P2_1/c$, a = 20.0744(3), b = 12.5270(1), c = 21.1311(4) Å; β = 111.239(1)°, V = 4952.95(13) Å^3, T = 296 K, Z = 2, μ = 27.943 mm^{-1}, 34256 reflections measured, 12968 unique (R_{int} = 0.0641) which were used in all calculations. Final R indices were R_1 = 0.0430, $wR2$ = 0.0834 [$I > 2\sigma(I)$], R_1 = 0.0830, $wR2$ = 0.0960 (all data). CCDC-213782 contain the supplementary crystallographic data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Crystal data for **2**: triclinic, $P\bar{1}$, a = 13.7261(3), b = 19.6025(3), c = 20.6635(1) Å; α = 111.341(1), β = 105.380(1), γ = 97.683(1)°; V = 4826.31(13) Å^3, T = 296 K, Z = 2, μ = 27.282 mm^{-1}, 22578 reflections measured, 13859 unique (R_{int} = 0.0628) which were used in all calculations. Final R indices were R_1 = 0.0497, $wR2$ = 0.1081 [$I > 2\sigma(I)$], R_1 = 0.1086, $wR2$ = 0.1271 (all data). Crystallographic data for **2** have been deposited at the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [Fax: (internat.) + 49-7247-808-666; E-mail: crystdata@fiz-karlsruhe.de] on quoting the depository number CSD-413215.

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