Polyoxometalate Hybrids

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Terbium Polyoxometalate Organic Complexes: Correlation of Structure with Luminescence Properties**

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The investigation of polyoxometalates (POMs) continues to provide interesting new molecules with properties relevant to a wide variety of applications.[1] Of particular interest to us is the ability of lacunary POMs to act as ligands to other metals, affording complexes with novel electronic and magnetic behavior.[2] Lacunary POMs offer useful features as ligands, including their size, solubility, diamagnetic nature, arrangement of coordination sites, flexibility of coordination modes, and ability to rearrange.[3] Oxophilic trivalent lanthanoid (Ln) metal centers are particularly well-suited for binding to lacunary POMs, and examples of POM-ligated lanthanoid complexes with one or more lanthanoid metal are known.[4] Lanthanoid complexes of organic ligands are more numerous and have relevance as luminescent molecular materials and as contrast agents for magnetic resonance imaging.[5] However, complexes with both organic and POM ligands bound simultaneously to lanthanoid centers are rare,[6,7] despite their potential as novel hybrid molecules that can combine the useful properties conveyed by both types of ligand.

We recently utilized the lacunary POM $[As_2W_{19}O_{67}(H_2O)]^{14-}$ as a precursor for new POM-ligated lanthanoid complexes.[7] The $\{WO(H_2O)\}$ linker between the two $[B\text{-}\alpha\text{-}AsW_9O_{33}]^{9-}$ subunits is critical to the reactivity of this precursor, as it serves as a starting point for apparent free rotation and dissociation of the $\{AsW_9\}$ groups. This dissociation facilitates the generation of a number of POM-based building blocks in solution. Combining this property with the stereodirecting influence of the lone pair on the As^{III} heteroatom[8] has enabled the stabilization of rare POM architectures and the inclusion of unprecedented structural features.

Typically, highly luminescent complexes of trivalent lanthanoid ions employ multidentate organic ligands as chromophores, which act as antennae to sensitize the otherwise weakly luminescent metal centers.[9] In these cases, multidentate topologies also ensure solution stability and the exclusion of inner-sphere water molecules that otherwise quench the metal-centered emission. The observation of luminescence for POM complexes of Ln^{III} ions, especially Eu^{III}, has generally been restricted to examples in which the POM acts as the antenna.[10] In these compounds, sensitization occurs by energy transfer from ligand-to-metal charge-transfer (LMCT) excited states centered on the POM, with subsequent lanthanoid emission. More recently, organic chromophores have been reported to act as light-harvesting antennae in Eu-POM containing materials, although the luminescent species were not structurally characterized.[11] To our knowledge, the only structurally characterized luminescent lanthanoid complex with both POM and organic ligands is the polymeric $K_2Na[Eu_3(H_2O)_{14}(HNA)_3\{Eu(H_2O)P_5W_{30}O_{110}\}]\cdot 3H_2O$ (HNA = nicotinic acid). However, the photophysical properties of this compound were not studied in detail, and neither a site-specific determination of the luminescence properties of the Eu^{III} centers nor a delineation of the function of the organic ligand was possible.[12]

We rationalized that the lacunary site provided by $[As_2W_{19}O_{67}(H_2O)]^{14-}$ or the products of its structural rearrangement may prove effective in shielding a Ln^{III} cation from solvent-induced nonradiative deactivation, after trapping of one or more {LnL} units (L = organic ligand). As a model system we chose the 2-picolinate ligand (pic$^-$), because the photophysics of its lanthanoid complexes are well understood.[13] Herein we report for the first time the synthesis, single-crystal X-ray structures (Figure 1), and magnetic and luminescence properties of two structurally related polynuclear Tb^{III} complexes that contain both organic and POM ligands, with the luminescence sensitized by the organic ligands. These compounds are $H_{0.5}K_{8.5}Na[\mathbf{1}]\cdot 30H_2O$ ($\mathbf{1}=[Tb_2(pic)(H_2O)_2(B\text{-}\beta\text{-}AsW_8O_{30})_2(WO_2(pic))_3]^{10-}$) and $K_4Li_4H_4[\mathbf{2}]\cdot 58H_2O$ ($\mathbf{2}=[Tb_8(pic)_6(H_2O)_{22}(B\text{-}\beta\text{-}AsW_8O_{30})_4(WO_2(pic))_6]^{12-}$).

Under acidic conditions (pH 3.6–3.9), the reaction of $[As_2W_{19}O_{67}(H_2O)]^{14-}$ with picH and LnX_3 (X = OAc or NO_3) in the respective stoichiometric ratios of 1:4:2 resulted in the controlled crystallization of either **1** or **2** in yields of 31 and 18%, respectively. Selective crystallization of **1** or **2** was achieved by varying the lanthanoid salt employed as a starting material and the cations available for crystallization. The use of $Tb(OAc)_3$ results in the formation of **1**, while **2** is obtained when $Tb(NO_3)_3$ is used and an excess of Li^+ is included in the reaction mixture. The presence of Li^+ appears to promote the formation of **2**, probably as a consequence of the increased solubility of the polyanion building blocks compared to the typically less soluble K^+ salts. Instances of similar structural dependence on the cation have been reported for POMs.[14]

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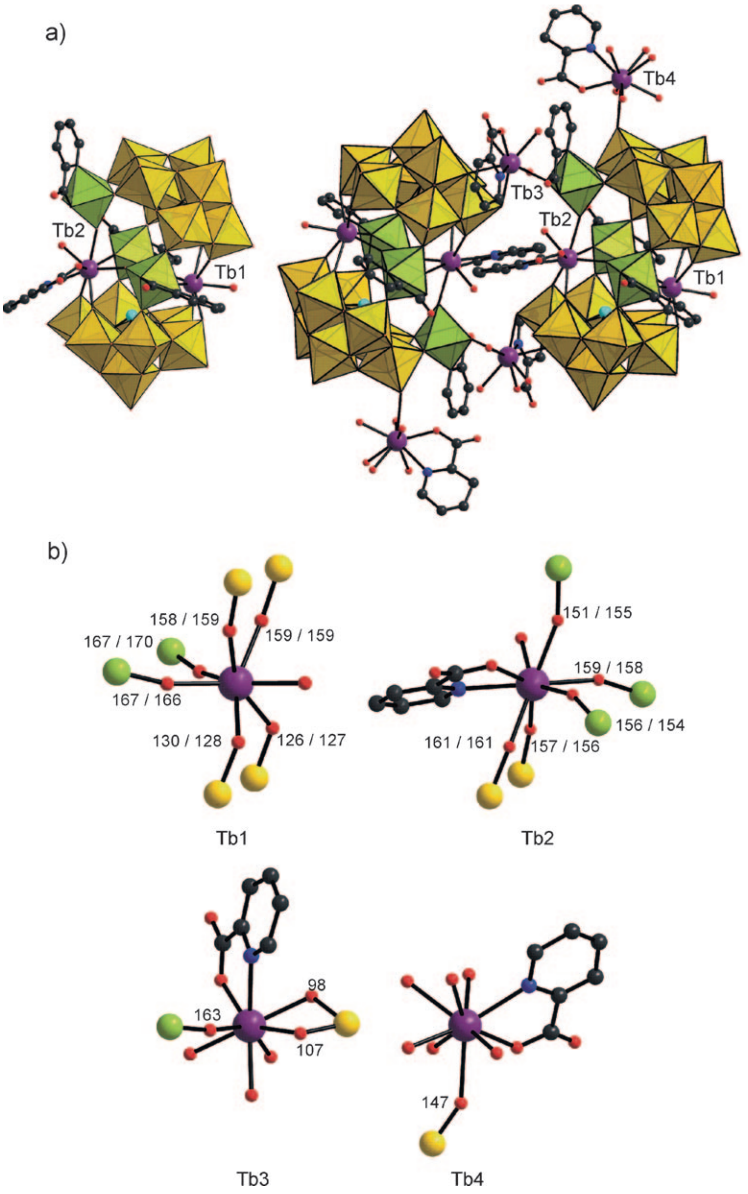

Figure 1. a) Structures of complexes **1** (left) and **2** (right). b) Coordination environments and Tb-O-W bond angles for Tb centers in **1** and **2**, bond angles [°] given as angle for complex **1**/angle for complex **2** for Tb1 and Tb2. Tb purple, W yellow and green, As pale blue, C black, O red, N blue.

Single crystals of compounds $H_{0.5}K_{8.5}Na[\mathbf{1}]\cdot 30\,H_2O$ and $K_4Li_4H_4[\mathbf{2}]\cdot 58\,H_2O$ were characterized by X-ray diffraction. The structures of **1** and **2** are unprecedented and feature rare POM ligands bound to mononuclear pic⁻ complexes of terbium, with additional tungstate linkers. The molecular arrangement of complex **1** can be described as two $[B\text{-}\beta\text{-}AsW_8O_{30}]^{9-}$ units oriented at 180° with respect to each other. Three $\{WO_2(pic)\}$ moieties and two Tb^{III} centers are sandwiched between these two units. The seven-coordinate center Tb1 can be considered as a $\{Tb(H_2O)\}$ hinge between the two $[AsW_8O_{30}]^{9-}$ subunits, with six corner-sharing Tb–O(W) bonds and distorted capped trigonal-prismatic coordination geometry. In contrast, eight-coordinate Tb2 binds as a $\{Tb(pic)(H_2O)\}$ unit with five corner-sharing Tb–O(W) bonds and a distorted square antiprismatic coordination geometry. Notably, coordination of the pic⁻ ligands to the W^{VI} centers observed herein represents the first report of a W^{VI} to N coordination bond (av. W–N 2.303 Å) within a POM.

Structurally, complex **2** can be considered to be based on two molecules of **1** linked by two crystallographically equivalent $\{Tb(pic)(H_2O)_3\}$ moieties (Tb3). These sites possess distorted square antiprismatic coordination environments, with three Tb–O(W) bonds. Two of these bonds are involved in an edge-shared link to the polyoxotungstate portion of the complex, with associated Tb-O-W bond angles of 98° and 107°. These angles are smaller than those observed for corner-shared linkages and appear to be essential for minimizing quenching of the Tb^{III} emission (see below). Complex **2** also incorporates two further $\{Tb(pic)(H_2O)_6\}$ units (Tb4), each with distorted nine-coordinate capped trigonal-prismatic coordination geometries and a single corner-shared Tb–O(W) bond.

Multiple well-defined intramolecular hydrogen bonds within each molecule stabilize the structures, and further stabilization occurs through the coordination of K^+ ions to the POMs (Figure S1–S3 in the Supporting Information). This stabilization is particularly important for complex **1**, where these K^+ ions appear to prevent agglomeration to the larger species **2**.

Isolation of pure, bulk samples of both $H_{0.5}K_{8.5}Na[\mathbf{1}]\cdot 30\,H_2O$ and $K_4Li_4H_4[\mathbf{2}]\cdot 58\,H_2O$ has enabled us to interpret the luminescence behavior of the four unique Tb^{III} sites in **2**, which would not have been possible if **1** had not also been accessible. Upon irradiation with a standard UV lamp ($\lambda_{ex} = 254$ nm), intense green luminescence was observed for a solid sample of $K_4Li_4H_4[\mathbf{2}]\cdot 58\,H_2O$ but not for $H_{0.5}K_{8.5}Na[\mathbf{1}]\cdot 30\,H_2O$. The corresponding emission spectrum for $K_4Li_4H_4[\mathbf{2}]\cdot 58\,H_2O$ is shown in Figure 2. Characteristic transitions from the $^5D_4$ excited state of Tb^{III} to the ground-state ^7F_J manifold are evident. The apparent peak maxima are at approximately 492, 544, 583, and 622 nm for the $J = 6, 5, 4$, and 3 transitions, respectively. By monitoring Tb^{III} emission at 490 nm, the excitation spectrum was also collected, which shows a peak maximum at approximately 276 nm and a smaller shoulder to slightly higher energy, both of which we attribute to absorption by the coordinated pic⁻ ligands, resulting in subsequent metal-centered emission. The absence of any other excitation peaks in the UV region indicates that sensitization of the Tb^{III} cations proceeds through the organic chromophores and does not involve POM-centered LMCT states. This finding is in accordance with results from Yamase, who has shown that room-temperature sensitization by the latter pathway is not efficient for Tb^{III}, owing to radiationless deactivation involving Tb^{IV}–W^{V} charge-transfer (CT) states.[15]

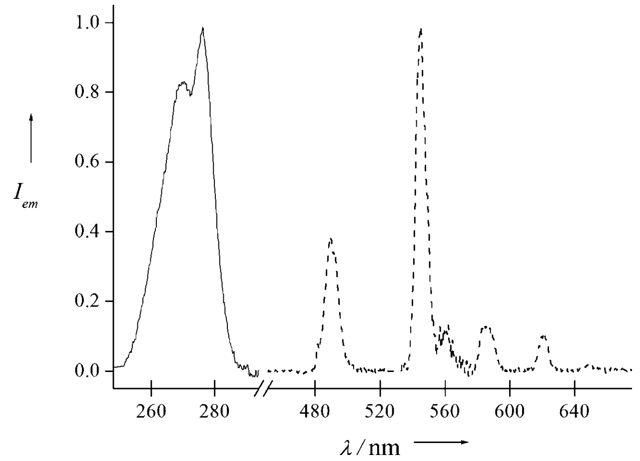

Figure 2. Emission spectrum ($\lambda_{ex}=275$ nm) of $K_4Li_4H_4[\mathbf{2}]\cdot58\,H_2O$ (dashed line) showing characteristic Tb^{III} emission. Excitation spectrum ($\lambda_{em}=490$ nm) of $K_4Li_4H_4[\mathbf{2}]\cdot58\,H_2O$ (solid line) showing pic$^-$-centered absorption that results in Tb^{III} emission.

The time-resolved emission profile at 490 nm was also collected for $K_4Li_4H_4[\mathbf{2}]\cdot58\,H_2O$ ($\lambda_{ex}=280$ nm) in the solid state, and it demonstrated multiexponential decay behavior, which was not surprising given the presence of four different Tb^{III} centers in the complex. Fitting the decay profile gave satisfactory agreement to a biexponential function, with lifetime values of $\tau_1=(58\pm2)$ μs (51%) and $\tau_2=(274\pm10)$ μs (49%), respectively (Figure S4 in the Supporting Information), consistent with expected values for hydrated complexes of Tb^{III}.[16]

As no sensitized Tb^{III} emission was detected for **1**, we are able to deduce the contribution to the observed luminescence from each metal center in **2**. The lack of luminescence for **1** suggests that metal centers Tb1 and Tb2, which are present in both **1** and **2**, do not contribute to the luminescence observed for **2**. Tb1 has no pic$^-$ ligands, and since the excitation spectrum has shown that sensitization proceeds through the organic chromophore, we conclude that this metal center is not sensitized and does not contribute to the luminescence. A similar conclusion can be made for Tb2, although a pic$^-$ ligand is coordinated. To understand this effect, we have undertaken an analysis of bond angles and coordination geometries for each of the Tb^{III} metal centers (Table S1 in the Supporting Information). Previous work from Yamase has shown that for Eu^{III} the efficiency of emission is strongly temperature-dependent in POM complexes that contain Ln-O-W bond angles of approximately 150°, as this angle allows for effective d^1 hopping through fπ–pπ–dπ orbital mixing.[17] The presence of five such (corner-sharing) bond angles to Tb2 (151–161°) in both **1** and **2** facilitates efficient quenching of the emission, through involvement of the aforementioned Tb^{IV}–W^{V} CT states.

For compound **2**, we therefore assign the observed biexponential decay components to Tb3 and Tb4. For Tb3, two of the three Tb-O-W bonds are involved in an edge-shared linkage with smaller Tb-O-W bond angles of 107° and 98°, which will be less efficient for quenching the Tb^{III} luminescence. Similarly, for Tb4, there is a single Tb-O-W bond with an angle of 147°, but this is evidently insufficient to completely quench the emission sensitized by the organic ligand. On the basis of the luminescent lifetimes, we assign the long- and short-lived components to Tb3 and Tb4, respectively, owing to the presence of three and six inner-sphere water molecules and to the well-known nonradiative quenching of emissive Ln^{III} complexes by coordinated water molecules, which shorten luminescence lifetimes by coupling with proximal OH oscillators.[18]

Variable-temperature magnetic susceptibility data for $H_{0.5}K_{8.5}Na[\mathbf{1}]\cdot30\,H_2O$ and $K_4Li_4H_4[\mathbf{2}]\cdot58\,H_2O$ (2–290 K, 0.1 T) approach room-temperature $\chi_M T$ values of 11.7 and 11.6 $cm^3\,K\,mol^{-1}$ per Tb^{III} ion (Figures S5 and S6 in the Supporting Information), respectively, in agreement with the corresponding value of 11.8 $cm^3\,K\,mol^{-1}$ for single a Tb^{III} ion in a noncubic ligand environment. The observed decrease of $\chi_M T$ with decreasing temperature, virtually identical for both compounds, is due to the thermal population of multiplet states and is primarily of single-ion origin. Both the temperature-dependent and the field-dependent susceptibilities of **1** and **2** can be modeled using a single-ion Hamiltonian that incorporates interelectronic repulsion, ligand-field effects, spin–orbit coupling, and Zeeman splitting by an external field.[19] Approximating the Tb^{III} environments as square antiprismatic, we find ligand-field parameters $B^2{}_0=56\ cm^{-1}$, $B^4{}_0=-1250\ cm^{-1}$, and $B^6{}_0=-340\ cm^{-1}$ for a spin–orbit coupling constant of $\zeta=1704\ cm^{-1}$. Note that this results in an $m_J=6$ ground state for both **1** and **2**. The overall ligand-field splitting of the ligand-field ground term of 200 cm^{-1} is in good agreement with other Tb POM complexes.[20] Very weak antiferromagnetic coupling, modeled using a molecular-field approach, likely indicates dipole–dipole interactions between the Tb^{III} centers ($\lambda_{MF}=-6.3\times10^{-2}\ cm^{-3}\,mol$). Alternating-current magnetic susceptibility measurements do not display frequency-dependent peaks in the out-of-phase response, thus indicating that complexes **1** and **2** do not exhibit single-molecule characteristics above 2 K.

In conclusion, careful synthetic control using a structure-directed approach has afforded two structurally related complexes in which multiple Tb^{III} centers are bound to both organic pic$^-$ and inorganic tungstoarsenate ligands. The two polyanions follow a structural hierarchy that imparts differential luminescence behavior, and the isolation of both compounds has allowed the elucidation of the luminescence properties of the four terbium coordination environments. Compound **2** is the first structurally characterized discrete terbium complex with both organic and POM ligands to display luminescence. A detailed analysis of the photophysical properties of this complex has revealed the importance of the smaller Tb-O-W angles provided by edge- rather than corner-sharing in limiting the quenching of the organic-ligand-sensitized terbium luminescence by the POM ligands. Thus, the required design principles have been elucidated for future luminescent lanthanoid organic POM compounds, which represent a new class of hybrid materials linking classical inorganic lanthanoid phosphors with molecular lanthanoid complexes of organic ligands.

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