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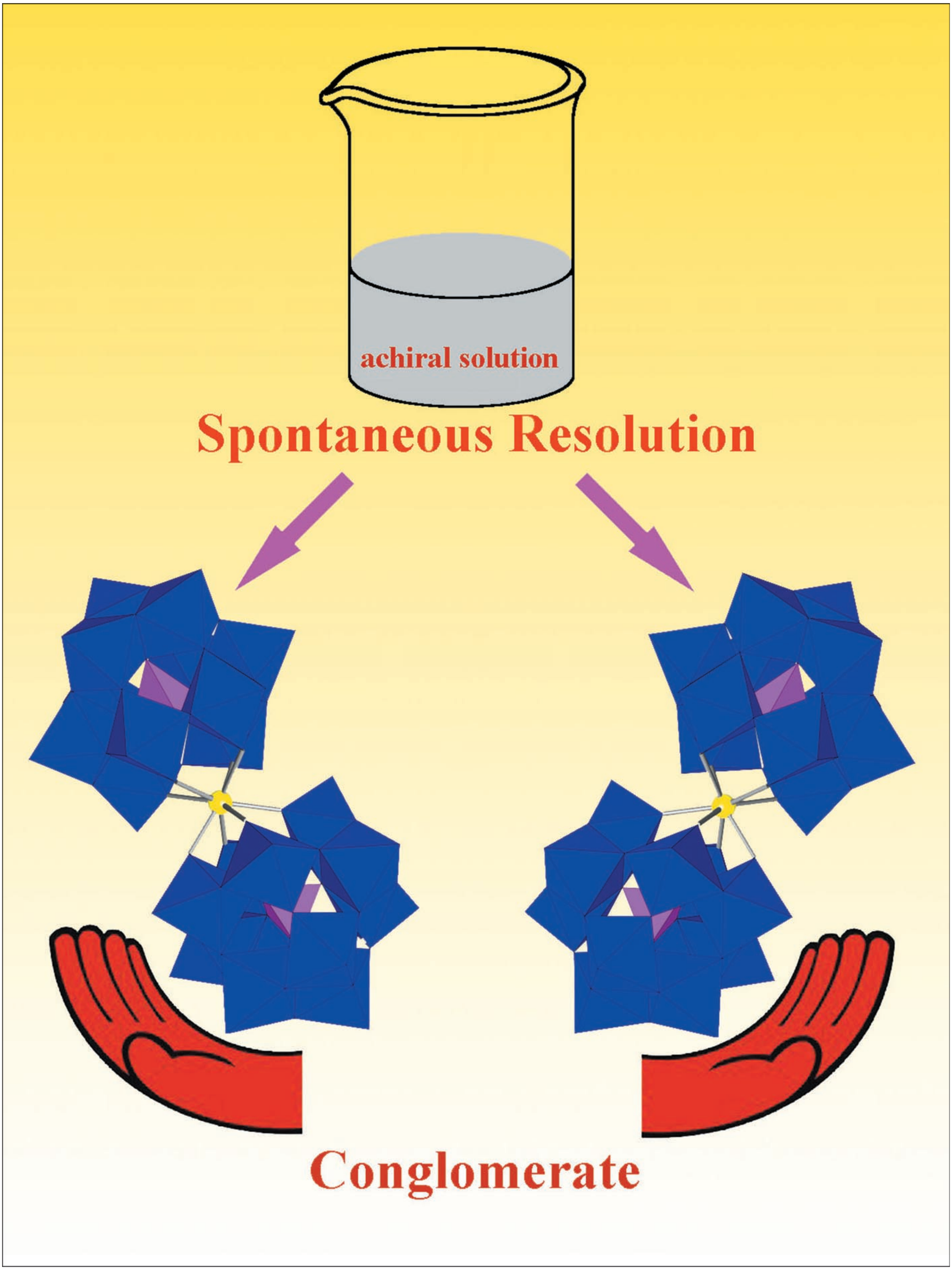

Breaking Symmetry: Spontaneous Resolution of a Polyoxometalate

Yu Hou, Xikui Fang, and Craig L. Hill*[a]

Abstract: A chiral polyoxometalate $[Hf(PW_{11}O_{39})_2]^{10-}$ (**1**) has been prepared and structurally characterized. It crystallizes in the chiral space group $P2_12_12$, as a conglomerate of two enantiomerically pure crystals in the absence of any chiral source. The absolute configuration of **1** was determined from the Flack parameter by X-ray crystallography. The structure of **1** comprises two lacunary $[PW_{11}O_{39}]^{7-}$ units, each functioning as a tetra-dentate ligand sandwiching an 8-coordinate Hf^{IV} centre in a distorted square antiprismatic geometry. Optically active crystals of both enantiomers were spectroscopically distinguishable by means of solid state circular dichroism spectroscopy. This hafnium-substituted polyoxometalate (POM), **1**, shows that spontaneous chiral resolution, a rare phenomenon, can be operable in POM systems.

Keywords: chirality · hafnium · polyoxometalates · spontaneous resolution · tungsten

Introduction

Spontaneous resolution, known as the segregation of enantiomers upon crystallization, was first reported by Louis Pasteur in 1848 when he manually separated left-handed from right-handed crystals of sodium ammonium tartrate.[1] When mixtures of mirror-image configurations of a compound aggregate or crystallize, they can form a racemic compound, a racemic solid solution, or a conglomerate (racemic mixture of chiral crystallites). Only the latter category, the conglomerate, involves spontaneous resolution.[2] Spontaneous chiral resolution upon crystallization in the absence of any chiral source is of considerable interest in context with homochirality in life[3] and absolute asymmetric synthesis in the solid state.[4] Statistically, between 5 % and 10 % of all racemates form conglomerate crystals,[5] this would indicate that heterochiral interactions are prevalent and more facile than homochiral interactions in the formation of crystalline racemates.[6]

To date, the concept of spontaneous resolution has not been documented for polyoxometalate (POM)[7] systems to the best of our knowledge, although the resolution of chiral POMs is highly sought after, given the potential applications of these compounds in asymmetric catalysis, sensing, and medicine.[8,9] Enantiomerically pure chiral POM crystals have been obtained in the presence of chiral organic ligands,[10] chiral metal-organic moieties[11] and other chiral cluster-based building blocks.[12,13] The major challenge remains to achieve even partial resolution of the two enantiomers of racemic POMs in the absence of chiral influence (solute, solvent, or counterion). It is more challenging to realize spontaneous resolution in some cluster systems including POMs than in most other classes of compounds, because the multiple metal domains in POMs can undergo facile racemization by means of water exchange, partial hydrolysis, or fluxional behavior. These collective processes frequently lead to crystals with both enantiomers in a same unit cell. For example, sandwich-type complexes, the most promising class of POMs as homogeneous catalysts based on rates, selectivities, and tunabability (synthetic alterability),[14] occasionally crystallize as chiral structures, but in racemic (most frequently centrosymmetric) space groups. Such chiral POMs based on both monovacant Keggin[15] or Wells–Dawson POM ligands[9b] are known.

While the vast majority of POM crystals in the Cambridge Crystallographic (CCDC) and Fachinformationszentrum (FIZ) databases involve crystallization in achiral space groups, there are several examples of enantiopure crystallites of POMs and other cluster molecules with a large number of metal centers. In other words, there are several examples of POMs that crystallize in chiral space groups in the absence of a chiral influence. Examination of these

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cases, however, reveals that enantiomeric purity derives from one of two phenomena, neither of which involves significant chirality manifested in the cluster structure itself as quantified by circular dichroism spectra. The first manifestation of chirality in POMs is bond length alteration,[16] a general feature not only of large metal oxide clusters, but also metal oxides themselves, dating back to the early work of Pauling.[17] The second manifestation of chirality in POMs and related large clusters derives from the asymmetry inherent in the association of organic[18] or organometallic[19] groups with the POM. Some of these composite compounds can potentially afford significant opportunity for chirality transfer from the POM derivative to other molecules in stoichiometric or catalytic reactions. However, these compounds do not really involve enantiopure POM units themselves; rather the chirality derives from the spacial arrangement and association between the two units.

We report here the spontaneous resolution of a POM whose chirality is not a result of bound groups, bond length alteration, or other subtle packing effects. Thus, this compound exhibits major circular dichroism, because the chirality is derived from significant spacial structural asymmetry. This complex is a Hf-containing cluster that affords large isolable enantiopure crystals. There is only one other report of a crystallographically characterized POM containing the element Hf,[20] despite the fact that Hf centers should offer a rich landscape of stereochemical possibilities with cluster ligands. We chose Hf for this exploratory study because the charge (4+) and large ionic radius (0.85 Å) of Hf should facilitate strong and multidentate binding of POM ligands, with each POM to occupy only one coordination hemisphere of the Hf ion. The other structurally characterized Hf-containing POM, which appeared a few months ago,[20] is a conventional achiral structure.

Results and Discussion

Addition of powdered $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 16\,H_2O$ to an aqueous solution of $HfCl_2O\cdot 8\,H_2O$ adjusted to $pH \approx 1.5$ with 1 M HCl, followed by addition of the hydrogen bonding counterion dimethylammonium (DMA^+) yields $[(CH_3)_2NH_2]_{10}[Hf(PW_{11}O_{39})_2]\cdot 8\,H_2O$, the DMA^+ salt of $[Hf(PW_{11}O_{39})_2]^{10-}$ (**1**) (henceforth DMA**1**). No crystal was obtained when DMA^+ was replaced with another counter cation (K^+ or Na^+). Maintenance of the acidic pH is necessary for production of **1**; it keeps the polytungstates in solution, while converting $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ to $[PW_{11}O_{39}]^{7-}$ in situ.

Single crystal X-ray diffraction shows that **1** is a sandwich-type POM with no crystallographically imposed symmetry. The absolute configuration of **1** is determined from the Flack parameter, which is 0.015(13).[21] The R_1 and wR_2 values and the statistics on DMA**1** are unusually good for a polytungstate. This polyoxoanion contains an 8-coordinate hafnium cation sandwiched between two lacunary anions, $[PW_{11}O_{39}]^{7-}$, in a distorted square antiprismatic geometry (Figure 1). The Hf^{IV} center is coordinated by four unsaturated oxygen atoms of each lacunary anion. Compound DMA**1** crystallizes in the chiral orthorhombic space group $P2_12_12$, with only one enantiomer present in the unit cell ($Z=2$, Figure 2). There are extensive hydrogen-bonding interactions between **1**, dimethylammonium cations and H_2O molecules in the unit cell; donor-acceptor distances in key hydrogen bonds are 2.933 Å (N3S···O32), 2.941 Å (N2S···O39) and 2.838 Å (N4S···O4W).

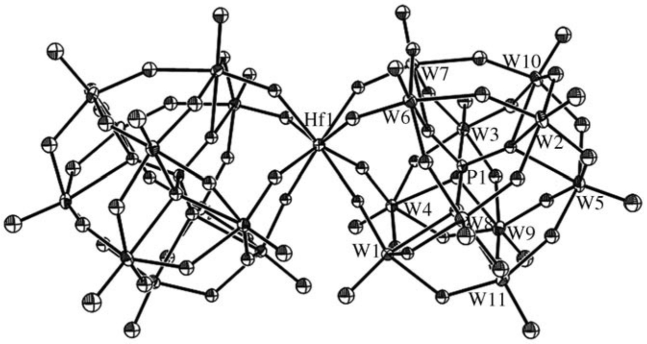

Figure 1. An ORTEP plot (50% probability ellipsoids) of $[Hf(PW_{11}O_{39})_2]^{10-}$, **1**, in $[(CH_3)_2NH_2]_{10}[Hf(PW_{11}O_{39})_2]\cdot 8\,H_2O$.

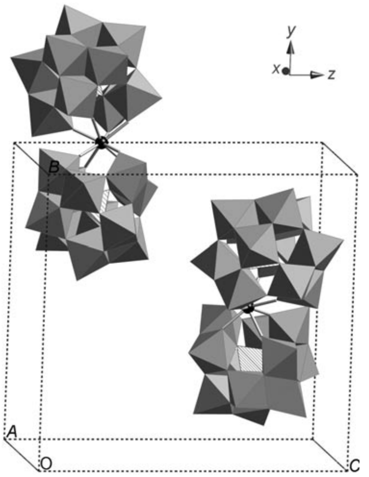

Figure 2. Packing of enantiopure $[Hf(PW_{11}O_{39})_2]^{10-}$, **1**, in the unit cell. Space group, $P2_12_12$, $Z=2$. The $PW_{11}O_{39}{}^{7-}$ units are in polyhedral notation (WO_6 octahedra, gray; central PO_4 tetrahedra, striped). The coordination of Hf^{IV} is in ball-and-stick notation (Hf, black).

Although a series of lanthanide-substituted compounds, $[Ln(PW_{11}O_{39})_2]^{11-}$, were characterized by ^{31}P and ^{183}W NMR 35 years ago,[22] crystallographically well characterized sandwich-type polyoxometalates based on $PW_{11}O_{39}{}^{7-}$ are rare. The complex $Cs_{11}Eu(PW_{11}O_{39})_2\cdot 28\,H_2O$ is typical: it crystallizes in a centrosymmetric space group in which the two enantiomers are related by an inversion center.[23] Thus, each independent polyoxoanion unit is chiral, but the unit cell is racemic. Usually, chiral sandwich-type POMs are racemic compounds both in the solid state or in solution. In contrast, **1** is chiral and was obtained by spontaneous resolution on crystallization in the absence of any outside chiral influence.

The chirality of the two enantiomers derives from the two configurations of **1** in which the two PW_{11} units are staggered relative to one another around a rotational axis through the center of the two ligating O_4 approximate planes of each PW_{11} group and the Hf atom. The antiprismatic orientation of the two O_4 ligand sets from each PW_{11} unit is neither eclipsing nor perfectly staggered as would define local idealized D_{4h} or D_{4d} $Hf(O_4)_2$ coordination polyhedra, respectively, but at an intermediate stagger (dihedral) angle of ≈38° (Scheme S1 in the Supporting Information). Such chiral POMs have not been noted to crystallize as a conglomerate, that is, one containing enantiopure crystallites.

As solid-state circular dichroism has emerged as a very useful technique in stereochemistry in recent years, the formation of a conglomerate of DMA**1** was examined by using solid state circular dichroism spectroscopy by incorporating individual crystals into KBr matrices. The two enantiomers show considerable optical activity in the solid state and afford approximately mirror-image CD spectra of each other (Figure 3). The crystals are designated as (+) and (−) based on the sign of the ellipticity at $\lambda \approx 242$ nm. Significantly, the circular dichroism is large, and it extends throughout the chromophore (adsorption) range of d^0 polytungstates. These two findings are consistent with those from the X-ray crystal structure that the chirality in **1** is largely manifested in asymmetry of the entire cluster polyanion and not in the $Hf(O_4)_2$ coordination polyhedron. To the best of our knowledge, this is the first time that solid state circular dichroism has been used to characterize a chiral polyoxometalate.

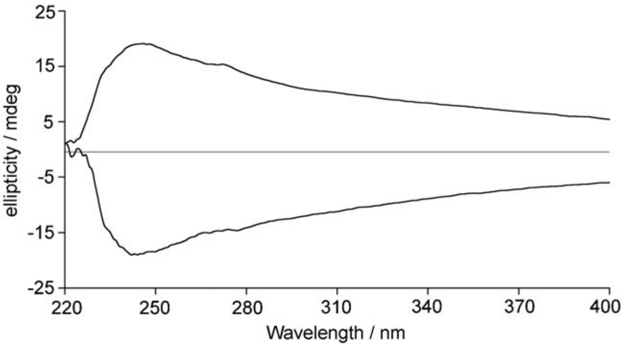

Figure 3. Solid state CD spectra of two enantiomeric crystals of $[Hf(PW_{11}O_{39})_2]^{10-}$, **1**, in KBr. A mixture of ≈150 µg of each crystal and 100 mg of KBr was ground well and compacted into a transparent disk with a radius of 13 mm.

The solid state cross-polarization magic-angle spinning (CP-MAS) ^{31}P NMR of DMA**1** (Figure 4) shows a single peak at $\delta = -15.6$ ppm that is indicative of a pure compound with a single phosphorus center by symmetry. This is consistent with the asymmetric unit in Figure 1 and the C_2 symmetry of polyanion **1**.

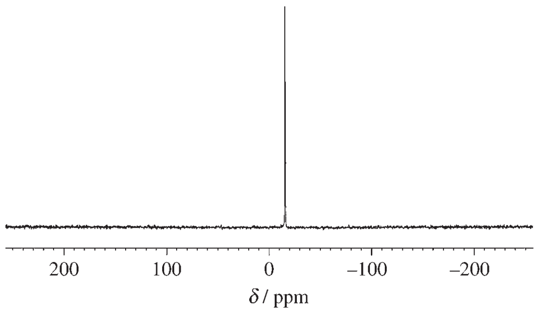

Figure 4. The solid state ^{31}P NMR spectra of DMA**1**.

The tetraheptylammonium salt of **1** (THA**1**) was obtained via cation exchange from DMA**1** in chloroform solvent. The ^{31}P NMR spectrum of THA**1** in $CDCl_3$ solution also shows one peak at $\delta = -16.7$ ppm (Figure 5). In addition, the IR spectrum of THA**1** (Figure S2) is very similar to that of DMA**1** (Figure S1), which indicates that cation exchange does not change the polyoxoanion structure.

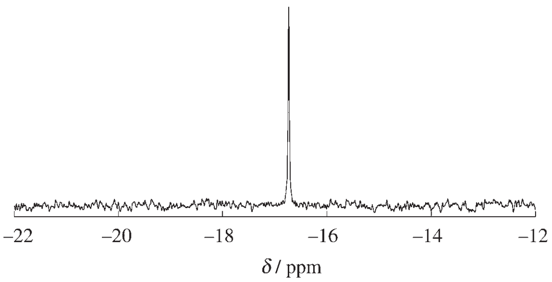

Figure 5. The ^{31}P NMR spectra of THA**1** in $CDCl_3$ solution.

In contrast, dissolution of DMA**1** in D_2O followed by immediate (< 15 min) analysis by ^{31}P NMR shows two peaks at −14.3 and −14.2 ppm (Figure 6). To assess this spectrum, it is necessary to examine the results recently reported by Nomiya and co-workers on very similar, but conventional racemic complexes $(Et_2NH_2)_{10}[M(\alpha\text{-}PW_{11}O_{39})_2]$, $M = Zr^{IV}$ and Hf^{IV} and the corresponding racemic Wells–Dawson Zr^{IV} and Hf^{IV} analogues, $K_{15}H[Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ and $K_{16}[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]$.[20] The Keggin derivatives, $(Et_2NH_2)_{10}[M(\alpha\text{-}PW_{11}O_{39})_2]$, $M = Zr^{IV}$ and Hf^{IV}, crystallize with two enantiomeric pairs of C_2-symmetry diastereomers in the unit cell. The diastereomers have slightly different orientations of

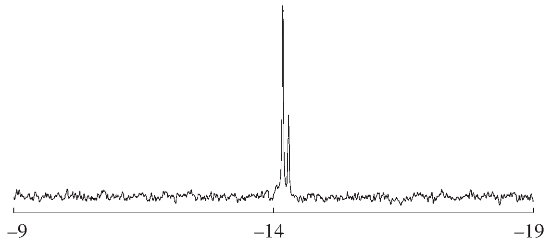

Figure 6. The ^{31}P NMR spectra of DMA**1** in D_2O solution.

their two O4 tetradentate ligands on the Zr and Hf centers. The Wells–Dawson derivatives crystallize with only one pair of C_2-symmetry enantiomers in the unit cell. The ^{31}P NMR spectra of the former conventional racemic complexes show 2 peaks with nearly identical chemical shifts (α-$PW_{11}O_{39}^{7-}$ alone, a control spectrum, shows one peak). The ^{31}P NMR spectra of the latter racemic Wells–Dawson analogues show 2 peaks (as did the α_2-$P_2W_{17}O_{61}$ alone). The authors, inferred, without discussion, that all four racemic sandwich complexes were maintaining their structures in solution.

This inference is reasonable based on two arguments. 1) The rates of aqua ligand exchange on metal centers with formal 4+ oxidation states and commensurately high local positive charges such as Hf^{IV}, in aqueous solution is very slow. 2) Chelation, as in the case of the tetradentate ligand $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$, further stabilizes the complex thermodynamically and kinetically. Therefore, the two peaks in the ^{31}P NMR spectrum of DMA**1** (Figure 6) most likely arise from protonation isomers (different protonation states). To evaluate this possibility, addition of ≈2 equivalents of HCl (0.05 M) to the DMA**1** in D_2O produces a single broadened peak at $\delta = -14.2$ ppm. The chemical shift difference between $\delta = -14.3$ and -14.2 ppm is quite small, so it is reasonable to suggest that both species have nearly the same POM framework. In addition, the product recrystallized from the solution of DMA**1** in H_2O is also pure DMA**1** as confirmed by FT-IR. The results are consistent with a structurally nondisruptive reversible deprotonation of DMA**1** when it is dissolved in H/D_2O and that the two peaks in Figure 6 arise from two different protonation states of the same complex, DMA**1**.

Conclusion

In summary, a chiral cluster compound, a POM, $[Hf(PW_{11}O_{39})_2]^{10-}$ (**1**) has been obtained by spontaneous resolution upon crystallization in the absence of any chiral source. Optically active crystals of both enantiomers were isolable and spectroscopically distinguishable. The solid state CD spectrum and X-ray crystal structure of enantiopure crystals indicate significant chirality manifested throughout the entire polyanion structure.

Experimental Section

General methods and materials: All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 16H_2O$ was obtained by the published procedure[24] and its purity was confirmed by infrared spectroscopy. Elemental analyses for C, H, and N were performed by Atlantic Microlabs (Atlanta, Georgia); those for P, Hf, and W were performed by Desert Analytics (Tucson, Arizona). Infrared spectra (2% sample in KBr) were recorded by using a Nicolet 510 instrument. Solid-state CD spectra for the two enantiomers of **1** were recorded by using a Jasco J-810 spectropolarimeter. Thermogravimetric data were collected by using a TGA 1000 instrument. Solution ^{31}P NMR spectra were obtained by using a Varian INOVA 400 MHz spectrometer, referenced to 85% H_3PO_4 as an internal standard. Solid-state ^{31}P NMR spectra were obtained by using Bruker DSX400 solid state NMR spectrometer (Bruker–Biospin, Rheinstetten/Germany).

Solid-state CD spectroscopy: Solid-state CD spectra for the two enantiomers of **1** were recorded by means of a Jasco J-810 spectropolarimeter, using KBr disks of thickness of ≈0.25 mm and diameter of 13 mm. The disc was prepared by mixing about 100 mg of KBr (Aldrich, 98%, heated at 100 °C) and about 150 µg of DMA**1** single crystals with a Perkin–Elmer vibrating mill for 5 min. The mixture then was pressed at 10 tons with a Perkin–Elmer press to obtain a transparent disc, which was placed between two quartz slides in the sample compartment in a fixed position. An initial CD spectrum was run, the sample rotated 60–80° and another spectrum recorded; about five rotations were performed for each sample and the corresponding spectra recorded. The final CD spectrum is an average of several individual CD spectra recorded for the compound. In order to verify that the crystals were high-quality and single, they were carefully inspected under a microscope before use. Spectra were collected between 200 and 400 nm, with a step size of 1.0 nm and at a speed of 100 nm min^{-1}.

Preparation of $[(CH_3)_2NH_2]_{10}[Hf(PW_{11}O_{39})_2]\cdot 8H_2O$ (DMA1): $HfCl_2O\cdot 8H_2O$ (0.143 g, 0.35 mmol) was dissolved in H_2O (20 mL), and the pH was adjusted to ≈1.5 with 1 M HCl solution. Solid $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 16H_2O$ (1.00 g, 0.39 mmol) was added to the mixture all at once with vigorous stirring. The solution was heated at 50 °C for 30 min and cooled to room temperature. Dimethylamine hydrochloride (0.25 g, 3.125 mmol) was added to the solution, and then the solution was heated at 50 °C for 5 min. The final pH of the reaction solution is about 5.0. Slow evaporation of the solution produced rod-like crystals after three days (yield, 0.48 g, 49.5% based on W). The numbers of counter-cations and crystal water molecules were determined by both elemental analysis and thermogravimetric analysis (TGA) (Figure S3). FT-IR data (KBr): 3452 (m), 3149(m), 2923(w), 2852(w), 1600(W), 1464(s), 1122(s), 1056(s), 1018(w), 957(s), 886(s), 816(s), 746(s), 514 cm^{-1} (s); elemental analysis calcd (%) for $[(CH_3)_2NH_2]_{10}[Hf(PW_{11}O_{39})_2]\cdot 8H_2O$: C 3.9, H 1.6, N 2.3, Hf 2.9, P 1.0, W 65.9; found: C 4.0, H 1.7, N 2.4, Hf 2.8, P 1.1, W 65.2.

Single X-ray Crystallography: X-ray analysis and crystal data for DMA**1** at 173 K, $[(CH_3)_2NH_2]_{10}[Hf(PW_{11}O_{39})_2]\cdot 8H_2O$: colorless rods, crystal size $0.25 \times 0.08 \times 0.05$ mm, $C_{20}H_{96}HfN_{10}O_{86}P_2W_{22}$, orthorhombic, space group $P2_12_12$, $a = 12.1687(13)$, $b = 19.764(2)$, $c = 20.598(2)$ Å, $V = 4953.9(9)$ Å^3, $Z = 2$, $M_r = 6138.20$, $\rho_{calcd} = 4.115$ g·cm^{-3}; $\mu(Mo_{K\alpha}) = 26.609$ mm^{-1}; $1.43 \leq \theta \leq 28.30°$. The Flack parameter = 0.015(13) indicates the correct absolute configuration of DMA**1**. The refinement converged to $R(F_0) = 0.0325$, $wR(F_0^2) = 0.0804$, and GOF = 1.173, for 12290 reflections with $I > 2\sigma(I)$. Data were collected by means of a Bruker SMART-APEX CCD sealed tube diffractometer with graphite monochromated $Mo_{K\alpha}$ (0.71073 Å) radiation. Data were measured by using a series of combinations of φ and ω scans with 30 s frame exposures and 0.3° frame widths. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of all data using SHELXTL software. Hydrogen atoms, except for the water hydrogen atoms, were included in calculated positions and assigned isotropic thermal parameters. The refinement converged with $R_1 = 0.0325$ and $wR_2 = 0.0804$ for 12290 reflections with $I > 2\sigma(I)$. Max/min residual electron density is $3.099/-1.245$ e Å^{-3}. The highest residual peaks are all associated with W atoms. CCDC 653386 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] **Flack parameter**: The Flack parameter = 0.015(13) indicates the correct absolute configuration of **1**. Flack parameter, x, is defined from the equation, $I(hkl) = (1-x)\ |F(hkl)|^2 + x|F(-h-k-l)|^2$ and it is used to estimate the absolute configuration of a structural model. The physically meaningful range of x is between 0 and 1. The ideal value of 0 indicates the correctness of the absolute structure given by the structural refinement. In the experimental data, $x(\mu)$ represents the Flack parameter and its standard uncertainty. When $x(\mu)$ is within the reasonable statistical fluctuation $|X| = 3\mu$, its value will be near to 0 which helps certify the correctness of the structure.

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