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Communication

Incorporation of Cr^{III} into a Keggin Polyoxometalate as a Chemical Strategy to Stabilize a Labile $\{Cr^{III}O_4\}$ Tetrahedral Conformation and Promote Unattended Single-Ion Magnet Properties

Nadiia I. Gumerova, Alexander Roller, Gerald Giester, J. Krzystek, Joan Cano, and Annette Rompel*

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ABSTRACT: Polyoxometalates (POMs) provide rigid and highly symmetric coordination sites and can be used as a strategy for the stabilization of magnetic ions. Herein, we report a new member of the Keggin archetype, the Cr-centered Keggin anion $[\alpha\text{-}CrW_{12}O_{40}]^{5-}$ (CrW_{12}), with the unusual tetrahedral coordination of Cr^{III} reported for the first time in POMs conferring unattended magnetic properties. POM chemistry has recently presented excellent examples of single-molecule and single-ion magnets (SMMs and SIMs) as well as molecular spin qubits; however, the majority of POM-based SIMs reported to date contain lanthanoid ions. CrW_{12}, as the first example of a chromium(III) SIM, exhibits slow relaxation of magnetization and quantum tunneling with a single-ion magnetic behavior even above 10 K with an energy barrier for the reversal of the magnetization of 3.0 K. The first 3d-metal SIM based on a nonlacunary Keggin anion is the foundation for a new research area in POM chemistry.

Chromium(III) ions in inorganic compounds exhibit a strong tendency to adopt an octahedral coordination[1] owing to high ligand field stabilization energy (LFSE) for a 3d^3 ion with a $^4A_2$ ground state. The equivalent tetrahedral complexes, which have a ground state that is degenerate, are not stable, and the tetrahedral coordination has been confirmed only in blue-colored diopsides and $Cr^{III}[\mu_3\text{-}O_4]$ cubanes.[2] The confinement of Cr^{III} inside certain molecular cages, such as polyoxometalates (POMs), can help to stabilize a tetrahedral coordination geometry. A handful of chromium-containing POMs are known to date, with all exhibiting an octahedral coordination of Cr^{III}.[3−5] In 1962, Brown reported the preparation of 12-tungstochromic(III) acid $H_5[\alpha\text{-}CrW_{12}O_{40}]\cdot nH_2O$ with Cr^{III} ions in a tetrahedral ligand field.[6] The conclusion of the formation of $[\alpha\text{-}CrW_{12}O_{40}]^{5-}$ was solely based on the appearance of a weak band assigned to $(Cr{-}O)_{Td}$ at 8300 cm^{-1} in the near-infrared spectrum of $[\alpha\text{-}CrW_{12}O_{40}]^{5-}$ and was subsequently questioned.[7] To the best of our knowledge, the crystal structure of $[\alpha\text{-}CrW_{12}O_{40}]^{5-}$ with a tetrahedral $\{CrO_4\}$ unit in POMs has not been documented yet.

The incorporation of magnetic units into the POM architectures is of considerable interest, since POMs as ligands may shield the magnetic core from interaction with other molecules, creating a single-molecule magnet (SMM).[8] SMMs based on POMs reported so far can be divided into three groups, representing: (1) a number of 3d-transition metal ions, which can be connected through oxo-bridges forming magnetic clusters of variable nuclearities and high symmetries;[9] (2) a number of lanthanoid ions giving rise to lanthanoid complexes in which 4f-magnetic ions are submitted to the crystal field created by POM ligands;[8] (3) a mixed-valence framework hosting a number of electrons that are usually delocalized over all the framework structure.[10] The possibility of constructing nanomagnets using a single lanthanoid ion has been demonstrated for both polyoxotungstates ($[Ln(W_5O_{18})_2]^{9-}$,[11] $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$,[12] $[LnW_{30}O_{110}]^{12-}$[13]) and polyoxomolybdates ($[Ln(\beta\text{-}Mo_8O_{26})_2]^{5-}$,[14] $[Ln\{Mo_5O_{13}(OMe)_4NNC_6H_4\text{-}p\text{-}NO_2\}_2]^{3-}$[14]). Although a growing number of first-row d-block single-ion magnets (SIMs) has been reported,[15] d-block SIMs based on POMs are particularly rare.[16,17] Even though there are a few examples of heteropolynuclear SMMs containing chromium(III) centers,[18] there are no reported chromium(III) SIMs.

Herein, we report the first Cr^{III}-centered Keggin-type anion $[\alpha\text{-}CrW_{12}O_{40}]^{5-}$ (CrW_{12}), representing a new member of the Keggin ($[XM_{12}O_{40}]^{n-}$, better represented as $[XO_4M_{12}O_{36}]^{n-}$, X: heteroatom; M: Mo, W, V, or Nb) POM family. CrW_{12} was characterized by elemental analysis, single-crystal and powder X-ray diffraction analysis, IR spectroscopy, thermogravimetric analysis, electrospray ionization mass spectrometry, cyclic voltammetry, X-ray absorption and photoelectron spectroscopy, UV−vis−NIR electronic spectroscopy, high-frequency and -field electron paramagnetic resonance, magnetic susceptibility measurements, and DFT calculations (see the SI, Figures S1−S14, Tables S1−S5). The $\{Cr^{III}O_4\}$ unit is stabilized inside the Keggin cavity, which causes a slow relaxation of magnetization. This type of system, where a POM cavity isolates the SIM unit from the environment, is an interesting approach to acquire direct and explicit information about the mechanisms that govern the SIM behavior.

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CrW_{12} was isolated as the double salt $Na_{2.4}(TMA)_3[\alpha\text{-}CrW_{12}O_{40}]_{0.6}[\alpha\text{-}H_2W_{12}O_{40}]_{0.4}\cdot 37H_2O$ (TMA: tetramethylammonium, $(CH_3)_4N^+$) from the system $Cr^{III}-WO_4^{2-}$ (c = 0.04 M)$-H^+-$Tris-NH_2 with a molar ratio of 1 Cr^{III}:10 W^{VI}:12 H^+:5 Tris-NH_2 (Tris-NH_2: tris(hydroxymethyl)-aminomethane, $H_2NC(CH_2OH)_3$) at the final pH of 7.5. Interestingly, when the pH was adjusted to 7.5 with NaOH instead of Tris-NH_2 or with a phosphate buffer, CrW_{12} could not be isolated (Scheme S1). The use of phosphate buffer most likely leads to the formation of lacunary forms of $[\alpha\text{-}PW_{12}O_{40}]^{3-}$. The failure to crystallize the target product with NaOH indicates the importance of buffering during the CrW_{12} synthesis due to the complex hydrolysis equilibria in POT solution. The formation of monolacunary anions in the unbuffered system was also shown by ESI-MS (Figure S2).

CrW_{12} possesses a typical disordered α-Keggin structure (CCDC 1913668, Figure 1). The central cation Cr^{III} is surrounded by eight half-occupied oxygen atoms (Figure 1A), thus reducing its effective coordination number to four. This disorder of the oxygen atoms in the Keggin ion was first mentioned in 1984[19] and reported for many Keggin structures with different heteroatoms, e.g., Si^{4+}[20] or P^{5+}.[21] The cubic environment around the central heteroatom X can be formed from the superimposition of one tetrahedrally coordinated X in one unit cell with another X tetrahedron (just oppositely oriented) in the neighboring unit cell.

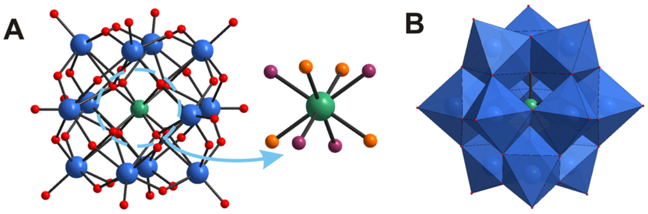

Figure 1. CrW_{12} anion. (A) Ball-and-stick representation including the crystallographic disorder in $\{CrO_4\}$. (B) Polyhedral representation. Color code: W, blue; Cr, green; O, red, orange, and purple.

The Cr^{III} site occupancy amounts up to 60% based on the X-ray data, which indicates that an alternative population of the central Keggin tetrahedron with Cr^{III} or two protons is most likely. The synthesized compound can be described as a double salt of CrW_{12} and the metatungstate anion $[\alpha\text{-}H_2W_{12}O_{40}]^{6-}$ (H_2W_{12}). The alternating occupancy with two hetero ions in a Keggin anion was previously described for Cu^{II} and two protons in $[\alpha\text{-}Cu_{0.4}(H_2)_{0.6}W_{12}O_{40}]^{6-}$.[22]

The direct current (dc) magnetic behavior of CrW_{12} is shown in Figure 2 as a plot of $\chi_M T$ against T, where $\chi_M T$ is the molar magnetic susceptibility, and of the magnetization (M) versus H/T at different applied dc fields. At room temperature, $\chi_M T$ of CrW_{12} amounts to 0.65 $cm^3\cdot mol^{-1}\cdot K$ and remains constant by cooling down to 50 K. This value is distinctly lower than the spin-only value (1.874 $cm^3\cdot mol^{-1}\cdot K$) for a high-spin d^3 ion supporting the partial occupancy of Cr^{III} site in CrW_{12}.

Since the paramagnetic Cr^{III} in CrW_{12} is kept isolated from other neighbors inside the polyoxotungstate, the decrease of $\chi_M T$ below 12 K and the non-superposition of the curves of the reduced magnetization can be attributed only to zero-field splitting (zfs). The simultaneous analysis of all data through the spin Hamiltonian, $\hat{H} = D(\hat{S}_z^2 - S(S+1)/3) + E(\hat{S}_x^2 - \hat{S}_y^2) + g\beta H\hat{S}$, provided a good agreement between experimental and simulated curves with the best-fit parameters: $|D|$ = +0.98 cm^{-1}, E/D = 0.095, and g = 2.005. Although there is no doubt about the presence of a zfs in CrW_{12}, the sign of the axial component (D) is uncertain.

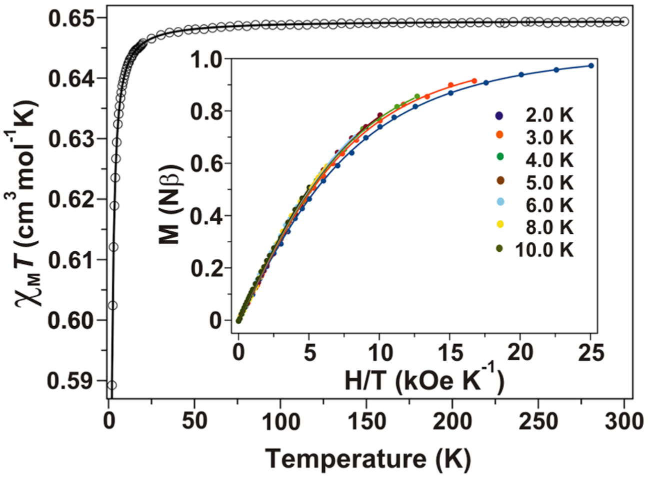

Figure 2. Magnetometry of CrW_{12}. Temperature dependence of $\chi_M T$ and the magnetization curves (inset) for CrW_{12}: (○, ●) experimental; (−) best-fit curves to the experimental data using the parameters provided in the text. The $\chi_M T$ value supports a partial (36%) occupancy of Cr^{III}.

In order to more accurately determine zfs in CrW_{12}, we used high-frequency and -field electron paramagnetic resonance (HFEPR). Although the spectral quality was moderate at best, a low-temperature, multifrequency experiment in the V-band range (Figure 3) delivered a direct measure of zfs by observing a near-zero field absorption between the ±1/2 and ±3/2 Kramers doublets at 65 ± 1 GHz = 2.16(3) cm^{-1}. This value represents the parameter $\Delta = 2[(D^2 + 3E^2)^{1/2}]$ for an S = 3/2 spin state. In order to deconvolute Δ into D and E we

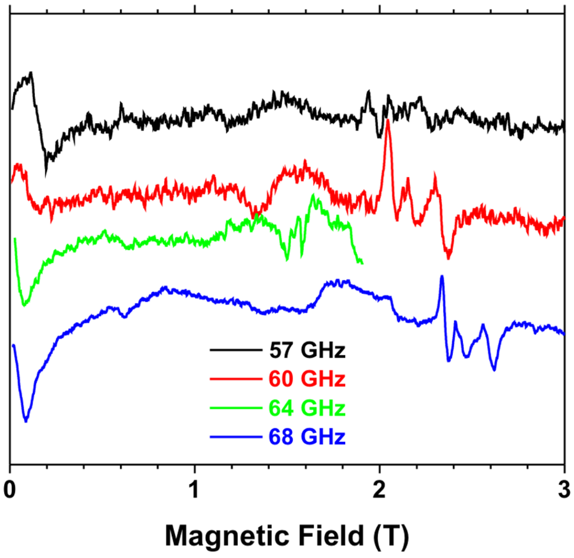

Figure 3. HFEPR spectra of CrW_{12} at 4.5 K and indicated frequencies in the vicinity of the zero-field transition between the ±1/2 and ±3/2 Kramers doublets. The resonances appearing between 2 and 3 T depending on frequency ($g \sim 1.95$) belong to a different spin species, which has a much lower anisotropy (about 0.1 cm^{-1}) and thus represents a small fraction of total absorption despite its amplitude, signifying low abundance.

performed standard X-band EPR (Figure S6), which resulted in spectra originating from the ±1/2 Kramers doublet only, and typical for the case $|D| > h\nu$ where h is Planck's constant and ν is the EPR operating frequency (9.47 GHz = ∼ 0.3 cm^{-1}). The spectra could be satisfactorily simulated using $|D| = 1.07$ and $|E| = 0.07$ cm^{-1} (rhombicity factor $E/D = 0.07$). Both zfs parameters are in excellent agreement with the magnetometric result. These parameters were then used in plotting the field vs frequency (or energy) dependence of the EPR turning points, confirming their accuracy (Figure S7). Given the modest zfs magnitude and the relatively low EPR frequencies employed, it was not possible to unequivocally determine the sign of D. A perfect cancellation of large contributions to zfs in an ideal tetrahedral high-spin d^3 system is broken due to small distortions and a partial charge transfer in the ground state from the highly charged oxo-groups bound to Cr^{III} ion, which can accept electrons, with an unstable geometry that facilitates this electronic drain (see SI text and Table S4). The UV−vis−NIR solid reflectance spectrum of CrW_{12} also supports a moderate charge-transfer from the oxo groups to the Cr^{III} ion and the presence of a high-spin d^3 Cr^{III} ion in a tetrahedral coordination environment (see SI text and Figure S14). Alternating current (ac) magnetic susceptibility measurements below 10 K did not show out-of-phase magnetic susceptibility χ_M'' signals at frequencies up to 10 000 Hz in the absence of an applied dc field. However, the suppression of fast tunneling of the magnetization (QTM) by the application of an external dc field (H_{dc}, 1000 and 2500 G) resulted in a set of frequency-dependent signals in plots of χ_M'' vs T (Figure S8). This slow relaxation of the magnetization in mononuclear complexes is characteristic for SIMs. The relaxation times (τ) at each temperature were extracted from χ_M'' vs frequencies (ν) plots, in which χ_M'' reaches its highest value (Figure S9). The obtained data in the form of $\{T, \nu\}$ pairs was used to build Arrhenius plots (Figure S10), showing a linear dependence that can only be described by a unique relaxation process following an Arrhenius law, $\tau^{-1} = \tau_0^{-1} \exp(-E_a/kT)$, where k is the Boltzmann constant and E_a is the energy barrier governing the spin reversal. The E_a and τ_0 values calculated for CrW_{12} (Table S3) are in the range of those found in octahedral and tetrahedral complexes with first-row transition metal ions. In both magnetic fields, the E_a values are about 3.0 cm^{-1}, which is the energy barrier calculated from $|D| = 1.5$ cm^{-1}, a value close to those derived from the EPR study and magnetometry. However, an energy barrier for the spin reversal governed by an Orbach mechanism is only possible for a negative value of D, which could not be experimentally confirmed. SIMs with positive D values or even with an $S = 1/2$ ground state are increasingly common; however, the relaxation mechanism governing their spin dynamics is still under discussion.[15,23−25]

Only two cases of POM-based d-block (Fe^{III} and Co^{II}) SIMs have been described in literature.[16,17] The single-ion magnet behavior is unusual in high-spin Fe^{III} complexes and rarely encountered for the systems based on POMs; however, this effect is well-known for Fe^{III} porphyrin complexes.[26] In contrast, in CrW_{12}, the zfs is induced through a unique tetrahedral geometry for a d^3 ion. Compared with other SIMs based on third-row transition metal ions (Table S5), the energy barrier for CrW_{12} is small, but more importantly, the magnetic blocking temperature is above 10 K, which places it in the same range or better than other analogs. The chemical surrounding can hamper, randomly modify or even abolish the slow relaxation of magnetization. In our case, the use of POMs as shielding ligands is a strategy to avoid these unwanted interactions. Moreover, tetrahedral high-spin Cr^{III} complexes with a small zfs, as in CrW_{12}, feature both allowed and forbidden transitions and can therefore be applied as qubits.[27]

The existence of CrW_{12} demonstrates that Cr^{III} can adopt a tetrahedral coordination in the Keggin cavity and opens a new perspective for Cr-centered lacunary POMs. The Keggin cavity is capable of stabilizing an a priori unstable tetrahedral geometry for a high-spin d^3 ion, which results in a single-ion magnet behavior. These novel properties of POMs enhance the relevance of these inorganic compounds in molecular magnetism because a variety of a new series of 3d-metal SIMs can be foreseen by a suitable choice of POM ligands.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b12797.

Synthesis details and spectroscopic data along with structural characterizations of the new compound (PDF)

Crystallographic data for CrW_{12} (CIF)

■ AUTHOR INFORMATION

Corresponding Author

Annette Rompel − *Universität Wien, Fakultät für Chemie, Institut für Biophysikalische Chemie, 1090 Vienna, Austria;* orcid.org/0000-0002-5919-0553;
Email: annette.rompel@univie.ac.at; www.bpc.univie.ac.at

Authors

Nadiia I. Gumerova − *Universität Wien, Fakultät für Chemie, Institut für Biophysikalische Chemie, 1090 Vienna, Austria*

Alexander Roller − *Universität Wien, Fakultät für Chemie, Zentrum für Röntgenstrukturanalyse, 1090 Vienna, Austria*

Gerald Giester − *Universität Wien, Fakultät für Geowissenschaften, Geographie und Astronomie, Institut für Mineralogie und Kristallographie, 1090 Vienna, Austria*

J. Krzystek − *National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, United States;* orcid.org/0000-0001-6088-1936

Joan Cano − *Department of Quimica Inorgànica/Instituto de Ciencia Molecular (ICMol), Facultat de Quimica, Universitat de València, 46980 Paterna, València, Spain;* orcid.org/0000-0002-7382-7135

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

CCDC 1913668 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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