Effect of Heteroatoms on Field-Induced Slow Magnetic Relaxation of Mononuclear Fe-III (S=5/2) Ions within Polyoxometalates.

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**ABSTRACT**

In this paper, synthesis and magnetic properties of mononuclear Fe\textsuperscript{III}-containing polyoxometalates (POMs) TBA\textsubscript{2}H\textsubscript{10}[(A-\(\alpha\)-XW\textsubscript{9}O\textsubscript{34})\textsubscript{2}]Fe\textsuperscript{II} (IIX, X = Ge, Si; TBA = tetra-n-butylammonium) with heteroatoms are reported. In these POMs, Fe\textsuperscript{III} ion coordinates to two trivacant lacunary units [A-\(\alpha\)-XW\textsubscript{9}O\textsubscript{34}]\textsuperscript{2-} (X = Ge, Si) and shows a highly distorted six-coordinate octahedral geometry. These POMs exhibit field-induced single-molecule magnet properties based on the single high-spin Fe\textsuperscript{III} magnetic center (S = 5/2). Combining experiment and ab initio calculations, we investigated the effect of heteroatoms of the lacunary units on the single-molecule magnet properties of these POMs. By changing the heteroatoms from Si (IISi) to Ge (IIGe), the coordination geometry around the Fe\textsuperscript{III} ion is mildly changed. Concretely, the axial Fe–O bond length of IIGe is shortened compared with that of IISi, and consequently the distortion from the ideal octahedral coordination geometry of IIGe is larger than that of IISi. The effective demagnetization barrier of IIGe (11.4 K) is slightly larger than that of IISi (9.2 K). Multireference ab initio calculations predict zero-field splitting parameters in good agreement with experiment. Although the differences in the coordination geometries and magnetic properties of IIGe and IISi are quite small, ab initio calculations indicate subtle changes in the magnetic anisotropy which are in line with the observed magnetic relaxation properties.

**INTRODUCTION**

Polyoxometalates (POMs) are a class of anionic metal oxide clusters that exhibit large structural diversity, and their properties can be controlled by selecting structures, constituent elements, and charges. Various types of metal cations can be introduced into the structurally well-defined vacant sites of lacunary POMs, where precise structural design of metal oxo clusters is possible; i.e., numbers, arrangements, and coordination geometries of metal cations can be designed within the vacant sites. Therefore, lacunary POMs are useful ligands for the rational investigation of catalytic, redox, and magnetic properties of metal oxo clusters. In particular, since the coordination geometries of metal cations directly affect their electron configurations, rigid multidentate lacunary POM ligands are useful to design and control their magnetic properties. We have recently reported that various mononuclear and multinuclear metal oxo clusters can be selectively synthesized using lacunary POMs in organic solvents. In particular, a mononuclear Fe\textsuperscript{III} ion possessing an unusually distorted six-coordinate octahedral geometry within a trivacant lacunary POM exhibited a unique field-induced single-molecule magnet (SMM) property for a high spin Fe\textsuperscript{III} ion. Ab initio calculations showed that the axial ligand elongations of the octahedrally coordinated [FeO\textsubscript{6}]\textsuperscript{9-} unit destabilized the \(d_{\perp,2}\) orbital, which lowered the sextet–quartet gap, resulting in a large magnetic anisotropy of the Fe\textsuperscript{III} ion required
for SMMs. It is noteworthy that although a number of reports of mononuclear SMMs consisted of 3d transition metals have been reported, there have been only two reports on mononuclear Fe(III)-POM, to the best of our knowledge: i.e., Mossin, Mindiola, and coworkers reported [(PNP)FeCl₂] (PNP = N[2-P(CHMe₂)₂-4-methylphenyl]₂), and Nocera and coworkers reported (PR₃)₂FeCl₃ (R = Me or Me₂Ph). Both examples are associated with intermediate spin Fe(III) (S = 3/2), in contrast with our compound that is based on high spin Fe(III) (S = 5/2).

To date, several experimental and theoretical studies have revealed that heteroatoms of POMs play important roles in controlling the catalytic and redox properties because the anion charges and/or the coordination geometries of POMs depend on the heteroatoms. In magnetic molecules, a few comparative studies on POM-based SMMs with different heteroatoms have been reported, e.g., {Mn₆} clusters in [B-α-XW₉O₃₄]₀ (X = Si, Ge) and {Co₁₆} clusters in [A-α-XW₉O₃₄]₀ (X = P, Si, Ge). However, theoretical studies about the effect of heteroatoms on the magnetic properties are lacking. Herein, we synthesized octahedrally coordinated mononuclear Fe(III)-containing POMs with different heteroatoms, TBA₄H₁₀[(A-α-XW₉O₃₄)₂Fe] (IIₓ, X = Ge, Si; TBA = tetra-n-butylammonium). These POMs showed field-induced slow magnetic relaxation characteristic for SMMs. Experimental and theoretical investigations revealed that by changing the heteroatom from Si to Ge, the coordination geometries of Fe(III) ions in IIₓ and their electronic structures were slightly changed, engendering a small enhancement of the SMM properties.

EXPERIMENTAL SECTION

Materials. Acetone (Kanto Chemical), 1,2-dichloroethane (Kanto Chemical), diethyl ether (Kanto Chemical), and Fe(acac)₃ (Aldrich) were used as received. TBA₄[A-α-GeW₉O₃₄(OCH₃)₆] (IₓGe) and TBA₄H₁₀[(A-α-SiW₉O₃₄)₂Fe] (IIₙSi) were synthesized according to reported procedures.

Instruments. IR spectra were measured on JASCO FT/IR-4100 using KBr disks. UV/vis spectra were measured on JASCO V-570. Cold-spray ionization (CSI) mass spectra were recorded on JEOL JMS-T100CS. Thermogravimetric and differential thermal analyses (TG-DTA) were performed on Rigaku Thermo Plus TG 8120. ICP-AES analyses for Fe, Ge, and W were performed on Shimadzu ICPS-8100. Elemental analyses were performed on Elemental vario MICRO cube (for C, H, and N) at the Elemental Analysis Center of School of Science of the University of Tokyo.

X-ray Crystallography. Diffraction measurements were made on a Rigaku MicroMax-007 Saturn 724 CCD detector with graphic monochromated Mo Kα radiation (λ = 0.71069 Å, 50 kV, 24 mA) at 123 K. The data were collected and processed using CrystalClear and HKL2000. Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization
corrections were made. The structural analyses were performed using CrystalStructure and WinGX. All structures were solved by SHELXS-97 (direct methods) and refined by SHELXL-2014. The metal atoms (Fe, Ge, and W) and oxygen atoms in the POM frameworks were refined anisotropically. CCDC-1824491 (II₆Ge) and CCDC-1035329 (II₆Si) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**Bond Valence Sum (BVS) Calculations.** The BVS values were calculated by the expression for the variation of the length $r_{ij}$ of a bond between two atoms $i$ and $j$ in observed crystal with valence $V_i$.

$$V_i = \sum_j \exp\left(\frac{r_0' - r_{ij}}{B}\right)$$

where $B$ is constant equal to 0.37 Å, $r_0'$ is bond valence parameter for a given atom pair.

**Magnetic Susceptibilities.** Magnetic susceptibilities of polycrystalline samples were measured on Quantum Design MPMS-XL7. Direct current (dc) magnetic susceptibility measurements were carried out between 1.9 and 300 K under 0.1 T magnetic field. Diamagnetic corrections were applied by the diamagnetisms of the sample holder and I₂Ge. Alternating current (ac) magnetic susceptibility measurements were carried out under 0.1 T dc field and 3.96 × 10⁻⁴ T ac oscillating field. Variable-field (1–7 T) magnetization measurements were carried out in the temperature range of 1.9–10 K.

**Synthesis of TBA₇H₁₀[(A-α-Ge₇W₉O₃₄)₂Fe]·3H₂O (II₆Ge).** To Fe(acac)₃ (5.2 mg, 14.8 μmol) in mixture of acetone and water (24:1, v/v, 3 mL, I₂Ge (100 mg, 29.5 μmol, 2.0 equiv. with respect to Fe(acac)₃) was added, and the resulting solution was stirred for 5 h at room temperature (ca. 20°C). Then, diethyl ether (50 mL) was added. Pale yellow precipitates formed were filtered off, followed by recrystallization from a mixture of 1,2-dichloroethane and diethyl ether. Pale yellow crystals of II₆Ge suitable for X-ray crystallographic analysis were obtained (33.8 mg, 36% yield based on I₂Ge).

Positive-ion MS (CSI, 1,2-dichloroethane): $m/z$ 3350 (calcd. 3350.2) [TBA₉Ge₂W₁₈O₆₃Fe]²⁺, 6458 (calcd. 6457.9) [TBA₉Ge₂W₁₈O₆₃Fe]⁻. IR (KBr pellet): 1635, 1380, 1152, 1107, 1061, 1014, 992, 954, 889, 814, 772, 737, 683, 561, 524, 360, 338, 321 cm⁻¹. Elemental analysis, calcd (%) for C₁₁₄H₂₇₀Cl₃FeGe₂N₇'O₇W₁₈: C, 21.15; H, 4.25; N, 1.54; Ge, 2.28; Fe, 0.88; W, 52.03. Found: C, 21.24; H, 4.23; N, 1.52; Ge, 2.29; Fe, 0.89; W, 53.05.

**Computational Details.** Electronic structure calculations were performed by means of the ORCA 4.0.1.2 program. Complete active space self-consistent field (CASSCF) calculations were converged for two different active spaces: (i) a (5,5) model including all 3d orbitals of the Fe(III) center and (ii) a (9,7) model that also includes the five 3d orbitals but also considers the bonding combinations between the e₅ d orbitals and the adequate linear combinations of ligand orbitals.
yielding an essentially σ-type metal-ligand interaction. N-electron valence state perturbation theory (NEVPT2) correction to CASSCF energies was included to account for dynamic correlation. Scalar relativistic effects were described by the second order Douglas-Kroll-Hess Hamiltonian (DKH2). Spin-orbit-coupling (SOC) mixing was considered by state interaction between converged CASSCF states (Quasi degenerate perturbation theory method). CASSCF(5,5) calculations included 1 sextet, 24 quartets and 75 doublets. CASSCF(9,7) calculations included 11 sextets and 24 quartets. To construct the model, atoms connected the FeIII center by three bonds or less were kept their position determined by X-ray diffraction. Dangling bonds were completed with hydrogen atoms, which were optimized using the BP86 density functional. Multireference calculations were carried out using the recontracted versions of the def2-TZVP all electron basis set available in ORCA. DFT optimizations were performed using the def2-TZVP basis set. To speed up calculations, resolution of the identity (RI) approximation was considered in conjunction with their corresponding auxiliary basis sets. The splitting of d-orbitals for CASSCF(5,5) calculations was derived from ab initio ligand filed theory (AILFT). This method employs the configuration interaction matrix to map each matrix element to the corresponding ligand field matrix. In this way, interelectronic repulsion and ligand field parameters can be obtained by least-squares minimization.

RESULTS AND DISCUSSION

Synthesis of FeIII-Containing POMs. We have recently synthesized an organic-solvent soluble Ge-centered trivacant lacunary POM and isolated it as a methoxide form (TBA4[A-\(\alpha\)-GeW5O28(OCH3)6], \(\text{I}_{\text{Ge}}\)). As mentioned in our previous report, the methoxy groups of TBA4[A-\(\alpha\)-SiW5O28(OCH3)6] (\(\text{I}_{\text{Si}}\)) were easily hydrolyzed in organic media even by the presence of trace amounts of water, showing that \(\text{I}_{\text{Si}}\) could be used as a precursor of metal substituted POMs. Based on these results, a mononuclear FeIII-containing germanotungstate (\(\text{II}_{\text{Ge}}\)) was synthesized by reacting \(\text{I}_{\text{Ge}}\) with 0.5 equivalents of Fe(acac)3 in a mixture of acetone and water (96:4, v/v) (Figure 1). Single crystals of \(\text{II}_{\text{Ge}}\) suitable for X-ray crystallographic analysis were obtained from a mixture of 1,2-dichloroethane and diethyl ether. The crystallographic analysis revealed that the anion structure of \(\text{II}_{\text{Ge}}\) was a mononuclear Fe-containing S-shaped dimer possessing vacant sites and essentially isostructural with that of TBA4[H10\(\{\text{A-}\(\alpha\)-SiW5O28}\}\text{2Fe}\]} (\(\text{II}_{\text{Si}}\)) except for the heteroatom (Ge; \(\text{I}_{\text{Ge}}\), \(\text{II}_{\text{Ge}}\), Ge; \(\text{II}_{\text{Si}}\), Si) (Figures 1, S1, Table 1). Seven TBA cations were observed in the crystallographic analysis in agreement with the results of the elemental analyses. The bond valence sum values of \(\text{II}_{\text{Ge}}\) for W (5.93–6.61), Ge (4.12), and Fe (2.83) indicate that the respective valences are +6, +4, and +3 (Table S1). These values are similar to those of \(\text{II}_{\text{Si}}\) for W (6.02–6.19), Si (3.97), and Fe (2.90).
Table 1. Crystallographic data for II\textsubscript{Ge} and II\textsubscript{Si}

| Compound | II\textsubscript{Ge} | II\textsubscript{Si} |
|----------|---------------------|---------------------|
| formula  | C\textsubscript{116}Cl\textsubscript{4}FeGe\textsubscript{2}N\textsubscript{7}O\textsubscript{72}W\textsubscript{18} | C\textsubscript{116}Cl\textsubscript{4}FeN\textsubscript{7}O\textsubscript{72}Si\textsubscript{2}W\textsubscript{18} |
| \(F_w\) (g mol\(^{-1}\)) | 6295.36 | 6206.36 |
| crystal system | monoclinic | monoclinic |
| space group | C\textsubscript{2}/\textsubscript{c} (#15) | C\textsubscript{2}/\textsubscript{c} (#15) |
| \(a\) (Å) | 35.7121(3) | 35.5945(2) |
| \(b\) (Å) | 14.5597(2) | 14.48620(10) |
| \(c\) (Å) | 38.5030(3) | 38.2599(2) |
| \(\alpha\) (deg) | 90 | 90 |
| \(\beta\) (deg) | 114.0479(2) | 113.9049(3) |
| \(\gamma\) (deg) | 90 | 90 |
| \(V\) (Å\(^3\)) | 18282.3(3) | 18035.63(19) |
| \(Z\) | 4 | 4 |
| temp (K) | 123(2) | 123(2) |
| \(\rho_{\text{calcd}}\) (g cm\(^{-3}\)) | 2.287 | 2.286 |
| GOF | 1.121 | 1.115 |
| \(R_1[I>2\sigma(I)]\) | 0.0768 | 0.0424 |
| \(wR_2\) | 0.2221 | 0.0994 |

\(a\) \(R_1 = \sum[|F_o|−|F_c|]/\sum|F_o|\), \(wR_2 = \{\sum[w(F_{o2}−F_{c2})^2]/\sum[w(F_{o2})^2]\}^{1/2}\).
Figure 1. Schematic of the synthesis of II\textsubscript{Ge} by reacting I\textsubscript{Ge} with Fe(acac)\textsubscript{3}. Light green, gray, and orange polyhedra represent [WO\textsubscript{6}]\textsuperscript{6–}, [GeO\textsubscript{4}]\textsuperscript{4–}, and [FeO\textsubscript{6}]\textsuperscript{3–}, respectively. Red, purple, blue, black, and orange spheres represent O, OH, OH\textsubscript{2}, C, and Fe, respectively.

The coordination geometry of the introduced Fe\textsuperscript{III} ion was six-coordinate distorted octahedral:
\textit{i.e.}, the Fe\textsuperscript{III} ion was coordinated by four equatorial oxygen atoms (O1, O1\textsuperscript{*}, O2, O2\textsuperscript{*}) and two axial oxygen atoms (O19, O19\textsuperscript{*}). Notably, the coordination geometries of II\textsubscript{Ge} were slightly different from those of II\textsubscript{Si}: By changing the heteroatom (X) from Si to Ge, the X–O bond lengths (II\textsubscript{Ge}, 1.720–1.749 Å; II\textsubscript{Si}, 1.610–1.645 Å) were elongated owing to the larger ionic radius of Ge\textsuperscript{IV} (Table 2), which was the same trend as those of IX.\textsuperscript{11} The axial Fe–O bond lengths (Fe1–O19; II\textsubscript{Ge}, 2.058 Å; II\textsubscript{Si}, 2.099 Å) were shortened while the equatorial Fe–O bond lengths (Fe1–O1, Fe1–O2; II\textsubscript{Ge}, 2.020, 2.033 Å; II\textsubscript{Si}, 1.991, 2.003 Å) were moderately elongated (Table 2). The distortion angles of the axial ligands against the equatorial planes (\(\phi\) II\textsubscript{Ge}, 74.5°; II\textsubscript{Si}, 75.8°) decreased slightly (Table 2), thus showing that the distortion of the Fe\textsuperscript{III} ion from the ideal six-coordinate octahedral geometry in II\textsubscript{Ge} was larger than that in II\textsubscript{Si}. In the case of II\textsubscript{Ge}, The intermolecular shortest Fe···Fe distance of II\textsubscript{Ge} was 14.560 Å (Figure S2a), and this value was similar to that of II\textsubscript{Si} (14.486 Å, Figure S2b), showing that each paramagnetic Fe\textsuperscript{III} ion was separated. The CSI mass spectrum of II\textsubscript{Ge} in acetonitrile showed signal sets centered at \(m/z\) 3350 and 6458 assignable to [TBA\textsubscript{5}Ge\textsubscript{2}W\textsubscript{18}O\textsubscript{63}Fe\textsubscript{2+}] and [TBA\textsubscript{5}Ge\textsubscript{2}W\textsubscript{18}O\textsubscript{63}Fe\textsubscript{3+}], respectively (Figure S3), supporting that II\textsubscript{Ge} was selectively synthesized and stable in this solvent. The UV/vis absorption spectrum of II\textsubscript{Ge} in acetonitrile showed a broad band at 350 nm assignable to LMCT transition of the [FeO\textsubscript{6}]\textsuperscript{3–} unit. The LMCT absorption band was observed a slight shorter
wavelength in the case of II\textsubscript{Si} (345 nm) (Figure S4). All the above mentioned results, the elemental analyses, and TG-DTA data showed that the formula of II\textsubscript{Ge} is TBA\textsubscript{7}H\textsubscript{10}[(A-\alpha-GeW\textsubscript{9}O\textsubscript{34})\textsubscript{2}Fe]\cdot3H\textsubscript{2}O.

Table 2. Selected bond lengths (Å) and distortion angles (°) for II\textsubscript{Ge} and II\textsubscript{Si}

|       | II\textsubscript{Ge} | II\textsubscript{Si} |
|-------|-----------------------|----------------------|
| Fe1–O1| 2.033                 | 2.003                |
| Fe1–O2| 2.020                 | 1.991                |
| Fe1–O19| 2.058               | 2.099                |
| X1–O19| 1.745                 | 1.638                |
| X1–O20| 1.737                 | 1.617                |
| X1–O21| 1.720                 | 1.610                |
| X1–O22| 1.749                 | 1.645                |
| distortion angle (\(\phi\)) | 74.5 | 75.8 |

Magnetic Properties of Mononuclear Fe\textsuperscript{III}-Containing POMs. DC magnetic susceptibility of the polycrystalline samples under 0.1 T showed that \(\chi\) values of II\textsubscript{Ge} and II\textsubscript{Si} at 300 K were 4.15 and 4.35 cm\textsuperscript{3} K mol\textsuperscript{-1}, respectively (Figure S5).\textsuperscript{4} These values are close to the spin-only value for a high-spin Fe\textsuperscript{III} ion (4.37 cm\textsuperscript{3} K mol\textsuperscript{-1}; \(S = 5/2, g = 2.00\)), supporting the valence of Fe\textsuperscript{III}. The \(M\) vs. \(HT\) data showed the presence of magnetic anisotropy in II\textsubscript{Ge} and II\textsubscript{Si} (Figure 3). The \(M\) vs. \(HT\) data was fitted by using the PHI program\textsuperscript{27} adopting the anisotropic Hamiltonian \((H)\) given by the following equation with the parameters of the axial \((D)\) and transverse \((E)\) magnetic anisotropies and Landé \(g\)-factor:

\[
H = D(S_z^2 - S(S + 1)/3) + E(S_x^2 - S_z^2) + \mu_B g S H
\]

The best fitting parameters for II\textsubscript{Ge} and II\textsubscript{Si} were obtained as follows: \(D = -1.26\) cm\textsuperscript{-1}, \(E = -4.76 \times 10^{-1}\) cm\textsuperscript{-1}, \(g_x = g_y = 1.58, g_z = 2.53\) for II\textsubscript{Ge} (Figure 3a) and \(D = -1.22\) cm\textsuperscript{-1}, \(E = -2.48 \times 10^{-1}\) cm\textsuperscript{-1}, \(g_x = g_y = 1.80, g_z = 2.05\) for II\textsubscript{Si} (Figure 3b). The axial magnetic anisotropy parameter \(|D|\) of II\textsubscript{Ge} was slightly larger than that of II\textsubscript{Si}, indicating that the change of coordination geometries of Fe\textsuperscript{III} ions affects the magnetic properties. From a phenomenological point of view, these parameters accurately reproduce magnetization data. However, the large anisotropy of the \(g\)-values appears unlikely for an Fe\textsuperscript{III} ion. We attempted to fit the magnetization curves using an isotropic \(g\)-values and found a reasonable match with experiment, although not as accurate as the former fit due to the lower number of fitting variables.
The ac magnetic susceptibility of II\textsubscript{Ge} under the external dc magnetic field of 0.1 T showed temperature- and frequency-dependence of $\chi'$ and $\chi''$, indicating the field-induced slow relaxation of magnetization characteristic for SMMs (Figures 2a and S6). The Cole–Cole plots for II\textsubscript{Ge} in the form of $\chi''$ versus $\chi'$ were fitted by means of the generalized Debye model,\textsuperscript{28} which showed the small $\alpha$ values in the range of 0.06–0.09, thus indicating a single relaxation process (Figure S7). According to the Arrhenius plot, the energy barrier for the magnetization reversal of II\textsubscript{Ge} was 11.4 K ($\tau_0 = 1.3 \times 10^{-6}$ s). This value was slightly higher than that of II\textsubscript{Si} (9.2 K, $\tau_0 = 3.3 \times 10^{-6}$ s) presumably owing to the larger $D$ value of II\textsubscript{Ge} (Figure 2b).\textsuperscript{4}

![Figure 2.](image)

(a) Frequency dependences of $\chi''$ for II\textsubscript{Ge} under 0.1 T external dc field. (b) Plots of relaxation time ($\tau$) versus $T^{-1}$ for II\textsubscript{Ge}. The solid lines represent the best fit with the Arrhenius law ($\ln \tau$ ($\tau = \tau_0 \exp(\frac{U_{\text{eff}}}{k_B T})$) vs. $T^{-1}$) at the thermally activated regime.
**Figure 3.** Low temperature magnetization data for (a) II\textsubscript{Ge} and (b) II\textsubscript{Si}. Solid lines represent the best fits obtained by PHI program.

*Ab initio* calculations. Next, to investigate the electronic structures of II\textsubscript{Ge} and II\textsubscript{Si}, multireference *ab initio* calculations were carried out. Since the size of the lacunary POM ligands prevented the calculation of the full complexes, model structures were constructed for both molecules (Figure 4a), where atomic positions were obtained from the corresponding crystallographic structures (Figure S1). The Fe\textsuperscript{III} ions and all atoms at a distance equal or under three covalent bonds from the Fe\textsuperscript{III} ions were retained in the model structure. Dangling bonds for atoms at the frontier of the model were completed with hydrogens, which positions were optimized. CASSCF(5,5) and CASSCF(9,7) calculations were performed for II\textsubscript{Ge} and II\textsubscript{Si}, where the smaller active space corresponds to the five 3d orbitals of the Fe\textsuperscript{III} ions and the extended model incorporates the bonding counterparts of the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals. Dynamical correlation was taken into account by the NEVPT2 method and spin-orbit effects were considered by a quasi-degenerate perturbation theory (QDPT) step for state interaction due to the electronic spin-orbit coupling operator (see Computational Details section for further
Ab initio ligand field theory analysis pictures a qualitatively similar d-orbital splitting for \( \text{II}_{\text{Ge}} \) and \( \text{II}_{\text{Si}} \) (Figure 4b). From the CASSCF(5,5) energies and wave functions, AILFT yields d-orbital energies which are more consistent with a square planar coordination than with an octahedral geometry. This is in line with the axially elongated Fe–O distance associated to the more exposed position of equatorial oxygen donor atoms in comparison to the axial oxygen atoms (Table 2).\(^2\) Given the more pronounced axial elongation of \( \text{II}_{\text{Si}} \), the total orbital energy splitting for this complex is larger than \( \text{II}_{\text{Ge}} \). In both cases, \( d_{xy} \) and \( d_{yz} \) orbitals are lower in energy and almost degenerate, with an energy separation of \( 397.7 \text{ cm}^{-1} \) (\( \text{II}_{\text{Ge}} \)) and \( 239.3 \text{ cm}^{-1} \) (\( \text{II}_{\text{Si}} \)). The third orbital is mainly \( d_{z^2} \), with an energy of \( 4316.9 \text{ cm}^{-1} \) (\( \text{II}_{\text{Ge}} \)) and \( 4382.8 \text{ cm}^{-1} \) (\( \text{II}_{\text{Si}} \)). The \( d_{z^2} \) orbitals are the most differing, as they appear at \( 9211.9 \text{ cm}^{-1} \) (\( \text{II}_{\text{Ge}} \)) and \( 7962.3 \text{ cm}^{-1} \) (\( \text{II}_{\text{Si}} \)). Finally, the antibonding \( d_{x^2-y^2} \) orbitals are at \( 17733.9 \text{ cm}^{-1} \) (\( \text{II}_{\text{Ge}} \)) and \( 18771.3 \text{ cm}^{-1} \) (\( \text{II}_{\text{Si}} \)) (Figure 4b). As noted in our previous theoretical investigations, zero-field splitting parameters of high spin d\(_5\) complexes tend to be underestimated by CASSCF calculations as they chiefly depend on the sextet-quartet energy gap, which is overestimated under this methodology. As expected, NEVPT2 calculations tend to improve results, although their correction is only partial.

Figure 4. (a) Calculated model structure of \( \text{II}_{\text{Ge}} \), the model for \( \text{II}_{\text{Si}} \) is analogous. Color code: W: dark blue, Fe: orange, Ge: blue, O: red, H: pink. (b) AILFT d-orbital splitting obtained from NEVPT2 energies on top of a CASSCF(5,5) calculation.

To account for these limitations, CASSCF(9,7) calculations were performed including the bonding complement of the antibonding \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals. 11 sextet and 24 quartet roots where included in the state average orbital optimization. In this way, 10 of the sextet roots are LMCT states, which will give a higher weight of charge transfer configurations and lower the sextet-quartet gap. Of course, the inclusion of more LMCT roots will increasingly bias the result in this direction, potentially leading to calculation artifacts. To prevent from this possibility, LMCT transitions were calculated, which are in
reasonable agreement with experimental UV/vis spectra (Figure S4, Table S2). Considering NEVPT2 energies, the sextet-quartet gaps are 8784 cm$^{-1}$ and 8478 cm$^{-1}$, while the zero-field splitting parameters ($D$) are $-1.07$ cm$^{-1}$ and $-1.01$ cm$^{-1}$ for $\text{II}_{\text{Ge}}$ and $\text{II}_{\text{Si}}$, respectively (Table S3). These values are in close agreement with the experimental fit for $\text{II}_{\text{Ge}}$ ($-1.26$ cm$^{-1}$) and $\text{II}_{\text{Si}}$ ($-1.22$ cm$^{-1}$). Then, axial magnetic anisotropy is slightly smaller for $\text{II}_{\text{Si}}$ in comparison to $\text{II}_{\text{Ge}}$. In addition, calculations indicate that $E/D$ is lower for $\text{II}_{\text{Ge}}$ (0.056) in comparison to $\text{II}_{\text{Si}}$ (0.083), in line with the observed enhancement of SMM properties for $\text{II}_{\text{Ge}}$ (Figure 2b). Although the differences in spin Hamiltonian parameters are small for both complexes, the trend of a higher axiality for $\text{II}_{\text{Ge}}$ shows up independently of the active space (5,5 or 9,7) for both CASSCF and NEVPT2 energies.

The orientation of the anisotropy axis matches the vector connecting the axial donor atoms (Figure 5). The alignment with the z-axis can be rationalized if we consider the sextet-quartet excitations which are responsible for magnetic anisotropy in a high spin $d^5$ ion. In the free ion limit, the ground $eS$ term mixes with the $4P$ excited term by the SOC operator. Under a square planar ligand field, the $4P$ term will split in $4A_2$ and $4E$ states and mix with levels stemming from the other quartet terms. Spin-orbit coupling mixing to the $4A_2$ level will be related with $l_z$ and $4E$ state interaction will be related to $l_{x,y}$ (see Figure 6). Thus, the difference in the $x$ and $y$ directions due to the structural distortion will be related with the presence of a nonzero component for the rhombic zero-field splitting parameter ($E$). This rhombic contribution favors the quantum tunneling contribution resulting in a faster magnetic relaxation worsening SMM properties. In the case of $\text{II}_{\text{Si}}$ and $\text{II}_{\text{Ge}}$, several excitations contribute to $D$ and $E$, given their departure from square planar geometry. As expected, sextet-quartet excitations contribute more than sextet-sextet transitions to zero-field splitting parameters, especially for $E$ (Tables S3). Table S4 shows the contribution of all quartet and sextet states to $D$ and $E$ for $\text{II}_{\text{Si}}$ and $\text{II}_{\text{Ge}}$. Although the final $D$ and $E$ parameters results for the sum (or cancellation) of many contributions, it is possible to appreciate how cancellation of contributions to $E$ is less effective in $\text{II}_{\text{Si}}$ when comparing with $\text{II}_{\text{Ge}}$. Finally, we stress that the relatively good agreement between the calculated magnetic anisotropy properties with the experimental data does not guarantee a quantitative prediction due to the small energy differences involves for these systems.
Figure 5. Orientation of the z-axis of the zero-field splitting tensor of II_{Ge} and II_{Si}. Color code: W: dark blue, Fe: orange, Ge: blue, Si: light blue, O: red, H: pink. Values are based on NEVPT2 energies on top of a CASSCF(9,7) calculation. D tensor was obtained by the second order perturbation theory approach.

\[ \begin{align*}
4F & \rightarrow 4A_{2g} + 2 4E_{g} + 4B_{1g} + 4B_{2g} \\
4D & \rightarrow 4A_{1g} + 4B_{2g} + 4E_{g} + 4B_{1g} \\
4P & \rightarrow 4A_{2g} + 4E_{g} \\
4G & \rightarrow 2 4A_{1g} + 4B_{2g} + 4A_{2g} + 2 4E_{g} + 4B_{1g} \\
6S & \rightarrow 6A_{1g}
\end{align*} \]

free ion \quad \text{square planar (D}_{4h}\text{)}

Figure 6. Free ion terms and their splitting under \text{D}_{4h} symmetry for a high-spin \text{d}_5 configuration. The excited states involved in SOC contribution are highlighted in color, blue for the \text{E}_g states (through the \text{l}_x and \text{l}_y operators) and red for the \text{A}_{2g} states (\text{l}_z operator).
CONCLUSION

We synthesized Fe$$^{III}$$-containing POMs TBA$$^+$H$$^{10}$$[(A-$$\alpha$$-XW$$^{9}$$O$$^{34}$$)Fe] (II$$^x$$, X = Ge, Si) and investigated the effect of heteroatoms on their magnetic properties. These POMs possessed mononuclear Fe$$^{III}$$ ions with distorted six-coordinate octahedral coordination geometries and showed field-induced SMM properties. By changing the heteroatoms from Si to Ge in II$$^x$$, the coordination geometries of Fe$$^{III}$$ ions were mildly changed; the axial Fe–O bond length of II$$^x$$Ge was shortened compared with that of II$$^x$$Si and the distortion from the ideal octahedral coordination geometry of II$$^x$$Ge was larger than that of II$$^x$$Si. Changes in the coordination geometries engendered the slightly larger magnetic anisotropy for II$$^x$$Ge, likely resulting in the increase in the energy barrier of the magnetization reversal. Although the difference in coordination geometries and the magnetic properties of II$$^x$$Ge and II$$^x$$Si were small, the small changes of magnetic properties were consistent with that of the theoretical results. Multi-reference calculations provide similar values of the zero-field splitting parameters for both compounds, with II$$^x$$Ge presenting moderately larger and more axial parameters. E/D ratio shows to be sensitive to the deviation of the coordination environment from the ideal elongated octahedral geometry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Crystallographic data, CSI mass spectrum, UV/vis spectra, magnetic data, and cartesian coordinates of molecular models for electronic structure calculations (PDF)

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Notes

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The effect of heteroatoms on single-molecule magnet properties of mononuclear high-spin Fe$^{III}$ magnetic center within lacunary polyoxometalates was investigated by combining experiment and multireference \textit{ab initio} calculations. By changing the heteroatoms from Si to Ge, the coordination geometry around the Fe$^{III}$ ion is mildly changed, which engendered the slightly larger magnetic anisotropy, likely resulting in a small enhancement of the single-molecule magnet properties.