Magnetic Properties

Pentagonal Bipyramid Fe\(^{II}\) Complexes: Robust Ising-Spin Units towards Heteropolynuclear Nanomagnets

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Abstract: Pentagonal bipyramid Fe\(^{II}\) complexes have been investigated to evaluate their potential as Ising-spin building units for the preparation of heteropolynuclear complexes that are likely to behave as single-molecule magnets (SMMs). The considered mononuclear complexes were prepared from the association of a divalent metal ion with pentadentate ligands that have a 2,6-diacetylpyridine bis(hydrazzone) core (H\(_4\)L\(^{2+}\)). Their magnetic anisotropy was established by magnetometry to reveal their zero-field splitting (ZFS) parameter \(D\), which ranged between \(-4\) and \(-13\) cm\(^{-1}\) and was found to be modulated by the apical ligands (ROH versus Cl\(^{-}\)). The alteration of the \(D\) value by N-bound axial CN ligands, upon association with cyanometallates, was also assessed for heptacoordinated Fe\(^{II}\) as well as for related Ni\(^{II}\) and Co\(^{II}\) derivatives. In all cases, N-coordinated cyanide ligands led to large magnetic anisotropy (i.e., \(-8\) to \(-18\) cm\(^{-1}\) for Fe and Ni, \(+33\) cm\(^{-1}\) for Co). Ab initio calculations were performed on three Fe\(^{II}\) complexes, which enabled one to rationalize the role of the ligand on the nature and magnitude of the magnetic anisotropy. Starting from the pre-existing heptacoordinated complexes, a series of pentanuclear compounds were obtained by reactions with paramagnetic [W(CN)\(_6\)]\(^{3-}\). Magnetic studies revealed the occurrence of ferromagnetic interactions between the spin carriers in all the heterometallic systems. Field-induced slow magnetic relaxation was observed for mononuclear Fe\(^{II}\) complexes (\(U_{\text{eff}}/k_B\) up to 53 K (37 cm\(^{-1}\)), \(\tau_B = 5 \times 10^{-9}\) s), and SMM behavior was evidenced for a heteronuclear [Fe\(_3\)W\(_2\)]\(^{6-}\) derivative (\(U_{\text{eff}}/k_B = 35\) K and \(\tau_B = 4.6 \times 10^{-10}\) s), which confirmed that the parent complexes were robust Ising-type building units. High-field EPR spectroscopic investigation of the ZFS parameters for a Ni derivative is also reported.

Introduction

The discovery of Single-Molecule Magnets (SMMs)\(^{[1]}\) and Single-Chain Magnets (SCMs)\(^{[2]}\) triggered an active research in the field of molecular magnetism owing to their remarkable physical properties. These encompass slow relaxation of the magnetization, which results in magnetization hysteresis, quantum tunneling of the magnetization (QTM), quantum phase interference, etc.\(^{[3]}\) Such physical properties have raised interests not only for fundamental reasons, but also because of the potential importance of such materials in fields such as information storage,\(^{[4]}\) quantum computing,\(^{[5,6]}\) spintronics,\(^{[7]}\) etc. From a chemical point of view, they have stimulated an intense activity that is aimed at improving the physical features of these species. The energy barrier (\(U_{\text{eff}}\), which controls the characteristic slow relaxation of the magnetization in such molecular magnets, inherently depends on the axial zero-field splitting parameter \(D\) and the spin ground state \(S\).\(^{[8]}\) Enormous efforts have been made during the last decade to understand the chemical factors that govern the magnetic anisotropy and attain control over both the strength and the sign of the \(D\) value by chemical design.\(^{[9]}\) The subsequent challenge is to take advantage of a controlled anisotropy to rationally construct nanomagnets with enhanced \(U_{\text{eff}}\) and consequently, to increase their blocking temperatures (\(T_B\)).
Metal coordination that deviates from the common hexacoordinate can induce significant magnetic anisotropy in mononuclear transition-metal complexes. In this regard, 3d metal complexes with various coordination environments, such as linear two-coordinated, trigonal planar, tetrahedral, trigonal pyramidal, trigonal bipyramidal, square pyramidal, hexacoordinated nonoctahedral, heptacoordinated pentagonal bipyramidal and octacoordinated square-antiprismatic complexes, were carefully selected to study the effect of weak ligand-field environments and geometry distortions on the magnetic anisotropy. These ligand-field symmetries are indeed appropriate for two main reasons: 1) in 3d complexes they may avoid the quenching of the orbital contribution, and favor emergence of a first-order spin-orbit coupling (SOC) contribution, and 2) they reduce the orbital splitting between the ground state and the excited states and thus strengthen second-order SOC. The latter contributes to the zero-field splitting (ZFS) which is characterized by axial (D) and transverse (E) magnetic anisotropy parameters. These two effects work in concert to enhance magnetic anisotropy.

The pentagonal bipyramid (D5h) exhibited in heptacoordinated complexes has been among the first nonconventional geometry for which a significant increase of the magnetic anisotropy has been demonstrated and quantified for a 3d metal ion. Notably, in this environment, FeIII (with a high-spin d5 electron configuration) and NiII have been found to exhibit Ising-type anisotropy with negative D parameters in the order of about −15 cm−1, whereas for CoII (with a high-spin d7 electron configuration) positive D values that range between 13 and 40 cm−1, have been reported. Interestingly, such complexes with the equatorial positions occupied by a pentadentate ligand can be structurally robust enough to allow substitutions of the apical positions, and hence, they can be involved in the formation of polynuclear compounds. With NiII, we have illustrated the possibility of employing such an anisotropic complex as building units towards heteronuclear SMMs.

The aim of the present investigation was to identify novel heptacoordinated complexes based on a 3d ion possessing both a large-spin ground state and a significant Ising-type anisotropy, and to evaluate their potential as building units towards heterometallic systems with SMM properties. High-spin FeIII complexes (S = 2) with a pentagonal bipyramid environment imposed by a pentadentate [N1O2]2− ligand were selected for this purpose (Scheme 1). The effect of the ligand set on the anisotropy was investigated for a series of derivatives, and a negative D parameter was found for all complexes, which is modulated by the nature of the ligands in the apical positions. The alteration of the magnitude of D by N-bound CN ligands in the axial positions upon association with cyanometallate was also assessed. Ab initio calculations enable one to rationalize the role of the ligand on the nature and magnitude of the magnetic anisotropy. Interestingly, two complexes were found to exhibit slow relaxation of the magnetization above 2 K, a premiere for FeIII in this coordination environment. Finally, pentanuclear complexes that were formed by association with paramagnetic connector [W(CN)3]2− demonstrated the potential of these heptacoordinated complexes to be used as Ising-spin building units towards molecular nanomagnets. As a matter of comparison, related systems with CoII and NiII have also been considered.

Results and Discussion

The series of seven-coordinated mononuclear complexes that we have investigated are based on pentadentate [N1O2]2− ligands derived from 2,6-diacylpyridine-bis(R-hydrazone), H3L010(2H3O) (Scheme 1). Preliminary results for an FeII complex with H3L010 established that FeII exhibits a significant magnetic anisotropy that is characterized by a negative D parameter of −16 cm−1. To obtain a more general trend on the magnetic behavior of FeII in such a coordination environment and to evaluate the possible effect of ligand alteration, we prepared related complexes with different R substituents, namely R = Ph, MeOH (H3L010Ph), and NH2 (H3L010NH2) (Scheme 1). Such ligand modification was considered as a means to control possible intermolecular contacts that often impede a strictly single-molecule magnet behavior.

All the compounds investigated are summarized in Table 1 with their respective labeling. The mononuclear FeIII, CoIII, and NiIII derivatives considered were [Fe(HL010Ph)(Cl)]·0.5 MeOH (1a), [Fe(HL010Ph)(MeOH)(H2O)]·2 BF4·2 MeOH (1b), [Fe(HL010Ph)(MeOH)(Cl)]·MeOH (2), [Fe(HL010NH2)(Cl)]·3 [CoHL010NH2(PhMeOH)(NO3)]·(NO3)·MeOH (4), and [Ni(HL010NH2)(H2O)2]·H2O (5). The compounds used to assess the effect of the N-bound cyano ligand on the D value were 1D coordination polymers [FeHL010NH2(Ni(CN))6]·x MeOH (6a), [FeHL010NH2(Ni(CN))6]·x MeOH (6b), [CoHL010NH2(Ni(CN))6]·x MeOH (7), and [NiHL010NH2(Ni(CN))6]·x MeOH (8), which were formed with diamagnetic [Ni(CN)3]2−. The exchange-coupled pentanuclear complexes assembled with [W(CN)3]2− were
The ZFS parameters of complexes 1–8 have been deduced from magnetic investigations. These parameters for the Ni derivative 5 were confirmed by high-field EPR (HFEPR). The occurrence of slow relaxation of the magnetization was systematically investigated by AC susceptibility experiments.

Synthesis and characterization

All complexes that involve FeⅢ were synthesized under strictly anaerobic conditions by using standard Schlenk technique and solvents that had been distilled under N2. The complexes 2 and 3 were synthesized by following the synthetic conditions reported for 1a.18 Treatment of the inorganic divalent hydrated metal salt FeCl2·4H2O in methanol with one equivalent of the corresponding pentadentate organic ligands (H2L3) for 2 and H2L4 for 3) suspended in methanol (slurry suspension) resulted in the formation of the respective mononuclear heptacoordinated complexes. The progress of the reactions was evidenced by the immediate color change from white to dark blue with concomitant consumption of the suspended ligand, and the reactions were completed in around 6 h at room temperature. Both the complexes 2 and 3 were isolated as microcrystalline materials upon diffusion of diethyl ether into the alcohol solutions of the respective complexes. The Ni derivative 4 was formed upon reacting H2L3 and Co(NO3)2, whereas [Ni(H2L3)2(NO3)2]·H2O (5)19b was obtained by a reported procedure. The 1D polymeric complex [Fe(H2L3)2] [(CN)2] (6a) was obtained as a pale green crystalline material by reacting a solution of complex 3 with K2[Fe(CN)4]. Upon using substrates 4 and 5, the same procedure resulted in [Co(H2L3)2][Ni(CN)4] (7), [Ni(H2L3)2][Ni(CN)4] (8), respectively. The association of ising-type magnetic building units with paramagnetic connectors could lead to ferrimagnetic systems with a resulting easy-axis magnetic anisotropy. The strength of the magnetic exchange interaction is a key parameter that determines the stability of the magnetic ground state in SMMs and also contributes to the energy barrier in SCM.6 However, it remains a challenge to synthetic chemists to achieve the association of such anisotropic building units through strong exchange interactions to form stable high-spin systems that are characterized by large magnetic anisotropy. Herein, octacyanotungstate [W12(CN)12]3– was used as an assembling spin-connector of the heptacoordinated Ising-spin units. [W12(CN)12]3– was chosen owing to the strong magnetic exchange interactions that take place with 3d transition metals that are connected through the cyanide ligands.21 The FeⅢ, WⅤ, or ⅤⅢ pentanuclear complexes, [(FeH2L4)2(H2O)2(W2(CN)8)] (9) and [(FeH2L4)2(H2O)2(W2(CN)8)] (10), were formed from complexes 1a and 2, respectively. The related (CoⅢ, WⅤ, or ⅤⅢ) complexes, [(CoH2L4)2(H2O)2(W2(CN)8)]·13H2O (11) and [(CoH2L4)2(H2O)2(W2(CN)8)] (12), were obtained by adapting the synthetic conditions used for the preparation of complex 9. Details for the synthesis of all derivatives are given in the Experimental Section.

Solid-state FTIR spectroscopic analyses of the mononuclear complexes showed significantly large shifts in stretching frequencies that correspond to the amide carbonyl groups (νC=O) as well as the imine bonds (υC=N) compared with the corresponding free ligands (see the Supporting Information, Table S1), which indicated the metal–ligand coordination. In the case of the complexes 6–8, the FTIR spectra showed a large shift of the stretching frequency that corresponded to the cyanide bond (νC≡N = 2153 and 2133 cm−1 for 6a, 2147 and 2133 cm−1 for 7, and 2162 and 2134 cm−1 for 8) compared to the K2[Fe(CN)4] (νC≡N = 2119 cm−1), which confirms the coordination of cyanide nitrogen atoms. Moreover, a significant shift of the stretching frequency that corresponds to the amide carbonyl bond in the products compared with the corresponding precursors indicated modifications of the ligand field around the metal centers (see the Supporting Information, Table S1). For complexes 9–12, the characteristic C≡N stretching bands were detected in the 2000–2200 cm−1 region (νC≡N = 2117–2072, 2136–2068, 2148, and 2144 cm−1, respectively) and were shifted noticeably compared with those of [nBu4N]2[W12(CN)12]. In addition, a shift of the amido carbonyl bond (νC=O = 1605 and 1572, 1605 and 1579, 1573 and 1617, 1580 and 1606 cm−1, respectively) and the imino bond (νC=N = 1532, 1520, 1525, and 1563 cm−1, respectively) stretching bands for complex 9–12 (see the Supporting Information, Table S1) indicated the formation of heterometallic products.

Crystallographic studies

Single-crystal X-ray diffraction structure analyses were performed for all the complexes. Crystallographic data and refinement parameters are summarized in Tables 1, 2, and 3. Extended sets of selected bond parameters are gathered in the Supporting Information.

The molecular structures of the monometallic complexes 2 and 3 are portrayed in Figure 1, the others are shown in Figures S3–S4 (see the Supporting Information). Complex 2 crystallizes as the cationic complex [FeH2L4Cl2] [(ROH)Cl]2+ together with one MeOH molecule and one chloride anion located in the lattice. Owing to the crystallization conditions (see the Experimental Section), either MeOH or EtOH (with a ratio 0.65:0.35) were found as the apical ligand in a crystal. [FeH2L4Cl2]2+ is neutral and crystallizes without any interstitial solvent molecule. Notably, the crystal structure22 reported for the complex formed from FeCl3 and H2L3 was different from that found for complex 3, even though the preparation procedure was the same except for the strictly anaerobic conditions applied for complex 3. For the related derivatives 4 and 5,21 the axial positions were occupied by one methanol and one nitrate, and by two water molecules, respectively (see the Supporting Information, Figure S3 and Figure S4). These complexes co-crystallized along with one solvent molecule (methanol and water, respectively) per formula unit. In all the complexes, the coordinating sites of the penta-
dentate ligands chelate five equatorial positions of the metal centers in almost a coplanar fashion. In complex 2, the length of the equatorial bonds ranged between 2.161 and 2.264 Å, and the axial bond distances were 2.186 Å with the oxygen and 2.443 Å with Cl atoms. These bond distances lie within

standard metal–ligand coordination bond lengths, which confirms the seven-coordinate geometry around the Fe⁹ center.
Table 3. Selected crystallographic data and refinement parameters of the complexes 9–12.

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[a] Including co-crystallized solvent molecules for complex 9. [b] \( R = \sum([F_o] - |F_c|)/\sum[F_o] \). [c] \( wR = \sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2) \), in which \( w = 1/(a^2(F_o^2) + b^2 + c^2) \) with \( P = (2F_c^2 + \max(F_o^2,0))/3 \).

Similar bond parameters were observed for complexes 3–5 (see the Supporting Information, Tables S4–S11).

Solid-state packing diagrams of complex 2 (see the Supporting Information, Figure S1), 3 (Figure S2), and 5 (Figure S4) showed that molecules are mutually parallel with the apical bond axis pointing in the same directions. In the case of complex 4, the apical Co–O axis was tilted with respect to the ones of the nearest neighbor molecules, and thus, the complexes were arranged in a zig-zag fashion within the crystal packing (see the Supporting Information, Figure S3). For all compounds, the shortest intermetallic distances are rather large: 6.8305(4), 7.1061(6), 6.7684(4), 6.8136(3) Å for complexes 2 (Fe(I-x,1-x,1'), 3 (Fe(I-x,1-x,1'), 4 (Co(I-x,1-x,1'), 5 (Ni(I-x,1-x,1'). Intermolecular linkages by H bonds that involve atoms from the first coordination sphere of the metal center may provide pathways for exchange interactions. Such intermolecular bonding was not found for complex 2; some were observed in complex 3, which take place between the NH groups of the hydrazide or amine units and the Cl and O atoms coordinated to the Fe center. However, the corresponding NH–Cl/O bond distances were rather long, which suggests weak interactions (see the Supporting Information, Figure S2).

The 1D coordination polymers constructed with [Ni(CN)₃]²⁻ crystallized without any interstitial solvent molecules; the molecular arrangement for [Fe(H₄L₆(NO₂)₄)Ni(CN)₃]₉ (6a) is shown in Figure 2, and those for complexes 7 and 8 are given in Figures S6 and S7 (see the Supporting Information). The axial positions of the seven-coordinated metal centers are occupied by two cyanide nitrogen atoms from two [Ni(CN)₃]²⁻ units, and each metal–ligand is linked to two (MH₄L₆(NO₂)₄) moieties by trans-cyanide groups to generate polymeric chains. The equatorial coordination features of the heptacoordinated centers were almost identical when compared to the parent complexes (Figure 2; caption; see the Supporting Information), whereas the two N–M bonds with the coordinated cyanide groups were nearly perpendicular to the equatorial plane. In the chains, the metal centers were not positioned to be collinear, but the axes that are defined by the apical bond directions of the paramagnetic moieties were mutually parallel along the chain (see the Supporting Information, Figures S5–S7). The shortest interchain distances between the paramagnetic centers were found to be 7.3985(4), 8.4101(3), and 7.9591(9) Å for

Figure 2. Molecular structure of [Fe(H₄L₆(NO₂)₄)Ni(CN)₃]₉ (6a). The coordinating atoms are highlighted by a ball-and-stick representation. Selected bond distances [Å] and angles [°]: Fe–Ni, 2.119(1); Fe–N3, 2.220(2); Fe–N4, 2.242(1); Fe–O1, 2.208(1) Å; C1–N1–Fe1, 164.1(1); N1–Fe–N1`, 176.74(5); N1–Fe–N3, 91.63(4).
complexes \(6a\) (Fe\(^{1-x,y,z} - \text{Fe}^{1-x,y,z}\) and Fe\(^{1-x,y,z} - \text{Fe}^{1-x,y,z}\)), 7 (Co\(^{1-x,y,z} - \text{Co}^{1-x,y,z}\) and Co\(^{1-x,y,z} - \text{Co}^{1-x,y,z}\)), and \(8\) (Ni\(^{1-x,y,z} - \text{Ni}^{1-x,y,z}\)), respectively, and the shortest distances between the intrachain paramagnetic centers were 10.1423(3), 10.2130(4), and 10.0588(9) \(\text{Å}\) for complexes \(6a\), 7, and 8, respectively (see the Supporting Information, Figures S5–S7). In all these 1D coordination polymers, both the intra and interchain distances between the magnetic centers were larger than the shortest distances between the magnetic centers in the solid-state packing diagrams of the corresponding monometallic parent complexes. In complex \(6a\), weak H-bond interactions were found to take place between the semicarbazide NH\(_2\) groups and the coordinated N atoms of the cyano-metalate moieties (N–N, 3.296 \(\text{Å}\); see the Supporting Information, Figure S5). For complexes 7–8, solid-state packing diagrams revealed that there were no significant interchain interactions through any direct H bonding or short contacts between the paramagnetic centers. Hence, the paramagnetic units can be considered as quite well isolated. Powder X-ray diffraction patterns collected on the synthesized polycrystalline materials \(6a\) and 8 confirmed the formation of single phases (see the Supporting Information, Figure S12).

The molecular structures of the discrete pentanuclear [Fe\(_2\)W\(_4\)] complexes 9 and 10 are depicted in Figure 3. They consist of three Fe\(^{8}\) moieties that are bridged by two (W(CN)\(_4\)) units each linked to two 3d centers. For the central Fe\(^{8}\) unit, the two axial positions are occupied by nitrogen atoms from the bridging CN linker, and for the terminal Fe centers, one apical site is occupied by cyanide nitrogen atoms of the cyano-metalates and the other apical site is occupied by a water molecule. In complex 9, the terminal Fe\(^{1}\) centers are crystallographically equivalent, whereas the three iron moieties in complex 10 are nonequivalent. Although the Fe centers were almost collinear along the molecular backbone in complex 9, they formed a bent geometry in complex 10 (Figure 3). Both complexes crystallized with several solvent molecules. Based on single-crystal X-ray diffraction analyses, complex 9 accommodated nine water molecules per formula unit, whereas eight water and two methanol molecules were detected in the unit cell for complex 10, but these were not included in the final refinement. Structural analyses for complexes 11 and 12 (see the Supporting Information, Figures S10 and S11) revealed complexes that were isosctructural to 9 and 10, respectively, with Co instead of Fe centers.

The polyhedral shape around the metal centers for all the complexes 1–12 was examined by continuous-shape analyses carried out with SHAPE.\(^{24}\) Distorted pentagonal bipyramid geometry was confirmed for all the heptacoordinated metal centers, whereas the octacoordinated W metal ions adopted distorted square antiprism geometries (see the Supporting Information, Tables S22 and 23).

Mössbauer spectroscopy

\(^{57}\)Fe Mössbauer spectroscopy was used to confirm the oxidation state of the Fe centers and the purity of the bulk samples for Fe-containing derivatives. Mössbauer spectra of complexes 2 and 3 (Figure 4) that were recorded at 80 K showed a unique sharp doublet defined by chemical shifts of 1.26 and 1.24 mm s\(^{-1}\) and quadrupole splittings of 2.91 and 1.11 mm s\(^{-1}\), respectively, which is characteristic of high-spin Fe\(^{2}\) ions in a pentagonal bipyramid geometry.\(^{15a,25}\) Their respective quadrupole splitting provides information on the nature of the ligands located in the apical positions, such that a smaller value is characteristic for the complex with two Cl ligands in the axial positions with respect to the ROH-substituted species (R = H, Me).\(^{15g}\) In compliance with this, the spectrum of the pentanuclear compound 9 exhibited two symmetric doublets that correspond to two high-spin Fe\(^{3}\) sites with site populations of 69 and 31% for two terminal and one central Fe\(^{3}\) centers, respectively (see the Supporting Information, Figure S14).
Magnetic properties

The magnetic behaviors of all the compounds were recorded on freshly isolated polycrystalline samples restrained in grease. For the Fe derivatives, the same batches were used to collect the Mössbauer spectra and PRXD patterns given herein. Both the static field (DC) and AC susceptibility behaviors have been systematically investigated; they are discussed in separate sections. The DC data mostly committed to the assessment of the magnetic anisotropy.

Mononuclear complexes 2–5

The temperature dependence of the molar susceptibilities ($\chi_mT$) for complexes 2–5 between 2–300 K is plotted as $\chi_mT$ versus $T$ in Figure S15 (see the Supporting Information). The experimental $\chi_mT$ values at room temperature are 3.43 (2), 3.55 (3), 2.57 (4), and 1.28 (5) cm$^3$ K mol$^{-1}$ K, which correspond to the expected values for one high-spin paramagnetic metal center with g factors of 2.14 (2), 2.17 (3), 2.21 (4), and 2.26 (5), respectively.

Upon cooling, the above $\chi_mT$ values remained constant down to around 20 K (2), 50 K (3), 65 K (4), and 12 K (5) followed by a rapid decrease to 1.61 (2), 1.89 (3), 1.35 (4), and 0.56 (5) cm$^3$ K mol$^{-1}$ at 2 K. Field-dependent magnetization studies revealed that the $M$ versus $H$ isotherms at 2 K did not reach saturations, even at 50 kOe (see the Supporting Information, Figure S16). The magnetization values observed for the highest fields investigated were 3.15 (2), 2.46 (3), 2.01 (4), and 1.74 $\mu_B$ (5), which are significantly lower than the expected values at saturation given by $M_\text{sat} = g \times S$ (with $S = 2$ for 2 and 3, 3/2 for 4, and 1 for 5) with the aforementioned g factors. The reduced magnetization $M$ versus $H/T$ plots are not superimposed, and thus, confirm the presence of significant magnetic anisotropy (Figure 5).

To quantify the magnetic anisotropy in these compounds, the PHI code was employed to fit the magnetic data by taking into account ZFS contributions; the results are gathered in Table 4. For compounds 3–5, concomitant fitting of $M$ versus $H$ and the $\chi_mT$ versus $T$ curves resulted in excellent agreement with the experimental data (Figure 5; see the Supporting Information, Figure S15). For complex 2, fitting of the magnetization isotherms at several temperatures with ZFS parameters $D, E$, and an isotropic g factor ($g_{\text{iso}}$) resulted in good fits; however, the experimental $\chi_mT$ versus $T$ behavior at lower $T$ was poorly reproduced. This, in addition to the dubious $|E/D|$ ratio, suggested an intermolecular contribution to the magnetic behavior. The latter was assessed by fitting the $\chi_mT$ versus $T$ plots that included a mean field contribution ($zJ$) and by using the value of $D$ that was obtained for the $M$ versus $H$ analysis as first-guess values. The same analysis was applied for complex 1b. This resulted in an excellent fit between the calculated and experimental behaviors (see the Supporting Information, Figure S15). However, it must be noted that the strong correlation between the parameters $E$ and $zJ$ leads to a large uncertainty in their values (Table 4).

| Table 4. ZFS parameters deduced from the magnetic behaviors of compounds 1–8. |
|---|---|---|---|
| $D$ [cm$^{-1}$] | $E$ [cm$^{-1}$] | $g$ | $g^*$ [cm$^{-1}$] |
| 1a$^{[a]}$ | $-13.3^{[h]}$ | 0.02$^{[e]}$ | 2.30 | $- $ |
| 1b | $-4.0 \pm 0.5^{[i]}$ | 0.02 $\pm 0.7^{[j]}$ | 2.28 | $-0.04 \pm 0.4^{[k]}$ |
| 2 | $-6.3 \pm 0.5^{[l]}$ | 0.16 $\pm 0.7^{[m]}$ | 2.14 | $-0.06 \pm 0.1^{[n]}$ |
| 3 | $-13.0^{[o]}$ | 3.3$^{[p]}$ | 2.16 | $-$ |
| 4 | $+33.4^{[q]}$ | 4.7$^{[r]}$ | 2.22 | $-$ |
| 5 | $-13.5^{[s]}$ | 1.7$^{[t]}$ | 2.26 | $-$ |
| 6a$^{[u]}$ | $-8.3^{[v]}$ | 1.8$^{[w]}$ | 2.18 | $-$ |
| 6b$^{[x]}$ | $-10.7^{[y]}$ | 0.12$^{[z]}$ | 2.22 | $-$ |
| 7 | $-16.3^{[a]}$ | 0.05$^{[b]}$ | 2.29 | $-$ |
| 8 | $-17.7^{[c]}$ | 1.0$^{[d]}$ | 2.18 | $-$ |

[a] From concomitant fit of $M=f(H)$ and $\chi_mT=f(T)$ data. [b] From fit of $\chi_mT=f(T)$ with first-guess values for $D$ and $E$, which were deduced from $M=f(H)$ data. [c] From HFEPR. [d] From fit of $M=f(H)$. 

---

For all the FeII complexes 1–3, the axial anisotropy parameter was found to be negative, which is in agreement with our earlier results,[15a, g] but obviously, D is modulated by the ligands located in apical positions. D is about $-13 \text{ cm}^{-1}$ with two Cl ligands coordinated to the Fe center (1a and 3), whereas its magnitude decreases to $-6 \text{ cm}^{-1}$ (2) and further to $-4 \text{ cm}^{-1}$ (1b) upon replacing the axially bound Cl atoms with O ligands (i.e., ROH, H$_2$O). Notably, the difference in the D parameter that was found for the Cl- and O-coordinated FeII complexes is reminiscent to the different quadrupole splitting of their Mössbauer spectra, which suggests that there is a significant effect imparted on the metal center by the apical ligand; this was further confirmed by ab initio calculations (see below). For the Co and Ni derivatives 4 and 5, the order of magnitude of the D parameters was very similar to those reported for related complexes.[1b, 15b, d, f] The accuracy, both in sign and magnitude, of these ZFS parameters was further verified by HFEPR spectroscopic studies for complex 5. The spectra, which were obtained at 5 K in the 0–16 T field range with several frequencies starting from 190 to 575 GHz, are shown in Figure S17 (see the Supporting Information). Resonance signals are rather broad, which may be due to the effect of strain on the ZFS parameters. The spectra were simulated at all frequencies to yield $D = -15.6 \text{ cm}^{-1}$, $E = 1.9 \text{ cm}^{-1}$, and $g_x = 2.3$, $g_y = g_z = 2.2$, which are in good agreement with the parameters deduced from the magnetic behaviors.

The results obtained for complexes 1–5 suggest little effect of the R substituent from the equatorial H$_2$L$_{N3O2R}$ ligand on the D value, whereas the ligands in apical positions are likely to more significantly alter the D value in such heptacoordinated species. Subsequently, it appeared important to assess the anisotropy of these metal centers when N-bonded cyanides were involved as axial ligands. This was undertaken with derivatives 6–8.

1D-[M(H$_2$L$_{N3O2R}$)Ni(CN)$_4$], 6a, 7, and 8

The temperature dependence of the magnetic susceptibility of these complexes is displayed as a $\chi_M T$ versus T plot in Figure S18 (see the Supporting Information). The $\chi_M T$ behaviors were very similar to that of the mononuclear parent complexes with room-temperature $\chi_M T$ values of 3.56 (6a Fe), 2.28 (7 Co), and 1.18 cm$^3$Kmol$^{-1}$ (8 Ni), which are coherent with ground spin states $S = 2$, 3/2, and 1 with $g_{\text{iso}} = 2.18, 2.19$, and 2.18, respectively. The $1/\chi_M$ versus T behaviors for these compounds obeyed the Curie–Weiss law with Curie constants (C) 5.56, 2.34, and 1.18 cm$^3$mol$^{-1}$K, respectively, and very small $\theta$ values (see the Supporting Information, Figure S18). Such small Weiss tem-
temperatures are indicative of the absence of magnetic exchange interactions between the paramagnetic centers through the diamagnetic Ni\textsuperscript{II} linkers. The ZFS parameters D deduced from magnetization studies were of the same order of magnitude as the heptacoordinated parent complexes that incorporate the respective metal ions (Table 4; see the Supporting Information, Figure S18). Interestingly, N-bound cyanide in apical positions of Fe\textsuperscript{II} led to a |D| value close to that found for a Cl-substituted complex, but it clearly increased with respect to H\textsubscript{2}O-coordinated centers. This trend was confirmed by Ni derivative 8 with |D| = -17.7 cm\textsuperscript{-1}, whereas a value of -13.9 cm\textsuperscript{-1} was reported for [NiH\textsubscript{2}L\textsuperscript{NIO2Ph}(H\textsubscript{2}O)]\textsuperscript{2+}. For the Co derivative, the value of D was hardly changed.\textsuperscript{[13b,d]}

\[ [(\text{MH}_L\text{NIO2Ph})_2(H\textsubscript{2}O)_2(W(CN))_2] \text{ 9–12} \]

All pentanuclear [M\textsubscript{4}W\textsubscript{1}] compounds were characterized by ferromagnetic interaction between the 3d and 5d metal centers. The magnetic behaviors for the complexes 9 and 10 (M = Fe) are plotted in Figures 6 and S19 (see the Supporting Information). Starting from 300 K, the $\chi_M T$ values for complexes 9 (11.26 cm\textsuperscript{3}Kmol\textsuperscript{-1}) and 10 (11.41 cm\textsuperscript{3}Kmol\textsuperscript{-1}) gradually increased as the temperature was lowered to reach a maximum (16.35 cm\textsuperscript{3}Kmol\textsuperscript{-1} at 24 K for 9; 19.0 cm\textsuperscript{3}Kmol\textsuperscript{-1} at 14 K for 10) followed by a rapid decrease to 9.3 and 14.2 cm\textsuperscript{3}Kmol\textsuperscript{-1} for complexes 9 and 10 at 2 K, respectively. Curie–Weiss analysis of the magnetic susceptibility confirmed the ferromagnetic Fe–W interactions with Curie constants of 9.9 and 10.1 cm\textsuperscript{3}Kmol\textsuperscript{-1} and Weiss constants of +33.7 and +30.3 K for complexes 9 and 10, respectively (see the Supporting Information, Figure S19). Magnetization isotherms measured between 2 and 10 K were characterized by a fast increase of the magnetization for low fields followed by a more gradual but steady increase for higher fields (Figure 7; see the Supporting Information). The spins at sites 1, 3, and 5 correspond to Fe\textsuperscript{II}, whereas sites 2 and 4 relate to the $W^{IV}$ ions, $\vec{D}_i$ is the local single-ion anisotropy tensor, $\vec{H}$ is the applied magnetic field, $J$ is the intermolecular exchange interaction, which is treated in the mean field ap-

\[
\begin{align*}
\chi_M T &= J \sum_{i=1}^{4} \sum_{i=1}^{4} \frac{\delta_i \cdot \delta_{i+1} + \sum_{j=13}^{15} \delta_j \cdot \vec{D}_j \cdot \delta_j}{2} - zJ < S > \sum_{i=1}^{5} \delta_i \\
\mu_B \vec{H} &= \sum_{i=1}^{5} g_i \delta_i - zJ < S > \sum_{i=1}^{5} \delta_i
\end{align*}
\]

Figure 7. $r$ versus $T^{-1}$ plot for complex 3 with the fit (solid line) of the data above 5 K to an Arrhenius law.

\[ y = 4.9142c^{-9} \cdot e^{c' \cdot (35.558c)} \quad R^2 = 0.99914 \]
proximation. In the above Hamiltonian, a positive exchange value implies a ferromagnetic interaction.

The magnetic axis of the Fe\(^{2+}\) site is chosen such that the \(z\)-axis is along the Fe–N (cyano) bond and the \(x\) and \(y\) axes are in the perpendicular planes along the Fe–O bonds. Hence, the orientation of the local magnetic axes of all the spins is not the same for the three Fe\(^{3+}\) ions. We considered the laboratory axis as the magnetic axis for one of the terminal Fe\(^{3+}\) ions. The only non-zero component of the local \(D\) tensor was taken to be the component \(D_{zz}\) in which \(z\) is the local magnetic \(z\) axis. To solve the above Hamiltonian, we first rotated the local anisotropy operator \(D_{zz}\) along the local \(z\) axis to the laboratory axis. This was achieved by obtaining the rotation matrix for the local axis to be rotated to the laboratory frame from the direction cosines between the local axis and the laboratory axis. The angles between the axes were provided by the X-ray crystal structure. From the rotation matrix of an ion, the three Euler angles \(\psi\), \(\theta\), and \(\varphi\) were obtained. From the Euler angles, the spin rotation matrices were obtained, and the transformation led to the matrix representation of the anisotropy term in the Hamiltonian, which is given by Equation (2):

\[
H_{\text{aniso}} = D_{zz}e^{i\varphi}e^{i\theta}e^{i\psi} S_z^2 e^{-i\psi} e^{-i\theta} e^{-i\varphi} \otimes I_2 \\
\otimes D_{xx} e^{i\varphi} e^{i\theta} e^{i\psi} S_x^2 e^{-i\psi} e^{-i\theta} e^{-i\varphi} \otimes I_4 \\
\otimes D_{yy} e^{i\varphi} e^{i\theta} e^{i\psi} S_y^2 e^{-i\psi} e^{-i\theta} e^{-i\varphi} \otimes I_4
\]

where \(D_{zz}, D_{xx}, D_{yy}\) are the non-zero components of the local \(D\) tensor in the laboratory axis. \(S_x, S_y, S_z\) are the spin matrices for \(s = 2\) spin of the Fe\(^{3+}\) ions. The full basis of the system was taken to be \([I \ M_{\alpha} M_{\beta} M_{\gamma} M_{\delta} M_{\epsilon} M_{\zeta} >]\) with the \(M_{\alpha}\) values ranging from \(-s\) to \(+s\). The full basis consists of all possible orientations of the site spins, and the dimensionality of the space is given by \(5\times 2^5 = 500\).

The magnetic Hamiltonian we have considered does not conserve either total spin \(S^z\) or the \(z\) component of the total spin \(S_z\). Hence, in the above discussion, we diagonalized the matrix representation of the Hamiltonian without the intermolecular interactions and obtained all five hundred eigenvalues and eigenvectors. We considered the intermolecular term as a perturbation and treated it in the mean field approximation. We computed expectation values \(\langle S_x \rangle_n, \langle S_y \rangle_n, \langle S_z \rangle_n\) for all the eigenstates \(|n\rangle\) of the Hamiltonian. The temperature-dependent expectation values of the total spin components at any finite temperature \(T\) was given by Equation (3):

\[
\langle S_\alpha \rangle_n = \frac{\sum_n \langle S_\alpha \rangle_n e^{-\beta E_n}}{\sum_n \langle S_\alpha \rangle_n e^{-\beta E_n}}
\]

The exponent of the partition function was expanded to retain only the first-order term in \(1/T\) for computing \(\langle S_\alpha \rangle_n\). By knowing \(\langle S_\alpha >\), the components of the magnetization of the system were evaluated by using Equation (4):

\[
M_\alpha = \sum_n \langle S_\alpha \rangle_n e^{-\beta E_n} \left[ \frac{1}{\sum_n \langle S_\alpha \rangle_n e^{-\beta E_n}} \right]
\]

The average magnetization was given by Equation (5):

\[
M_{av} = \sqrt{M_x^2 + M_y^2 + M_z^2}
\]

The components of the magnetic susceptibility tensor were given by Equation (6):

\[
\chi_{\alpha\beta} = -N\alpha g \frac{\partial M_\alpha}{\partial H_{\beta}}
\]

The isotropic susceptibility \(\chi\) was given by \((\chi_{xx} + \chi_{yy} + \chi_{zz})/3\).

For the calculations, we considered distinct \(D\) parameters for the central and terminal Fe\(^{3+}\) sites that were based on the values found experimentally for the complexes with two N-bound NC ligands or one H\(_2\)O ligand in apical positions (Table 4). All the parameters were then refined to reach good agreement between calculated and experimental \(M_{av}\) versus \(H\) behavior for complex 10. We found that the best fit was obtained for parameters \(J_1 = 30\ \text{cm}^{-1}\), \(D_{zz}\) (Fe central) = \(-11.0\ \text{cm}^{-1}\), \(D_{zz}\) (Fe terminal) = \(-4.5\ \text{cm}^{-1}\), \(g_{av} = 2.07\), \(g_{av} = 2.0\), \(zJ = -0.04\ \text{cm}^{-1}\). The resulting set of parameters was used to calculate the \(\chi_{av} T\) versus \(T\) behavior (Figure 6). Values of \(D\) that were obtained for both central and terminal Fe atoms for complex 10 were in good agreement with those that were obtained for the model complexes (Table 4), which confirms the reliability of the anisotropy of Fe\(^{3+}\) in an octahedrally coordinated environment. Furthermore, the modeling revealed a rather large ferromagnetic \(W\) and Fe interaction. Based on the \(M\) versus \(H\) behavior, intermolecular exchange interactions are very weak, but the discrepancy found at lower \(T\) in the \(\chi_{av} T\) behavior suggested that the actual \(J^0\) contribution might be slightly larger. Increasing this parameter indeed improved the fit to low-temperature \(\chi_{av} T\) behavior, but it also led to an \(S\)-shaped magnetization curve in the low-field domain, which is not observed experimentally.

The same approach was employed for Co derivative 12 by using a single \(D\) value for all Co centers, because of its invariance with H\(_2\)O or cyanometallate ligands (see above). The best agreement between calculated and experimental behaviors for complex 12 was obtained for the parameters \(J_1 = 19\ \text{cm}^{-1}\), \(D_{zz} = +33.0\ \text{cm}^{-1}\), \(g_{av} = 2.25\), \(g_{av} = 2.0\), and \(zJ = 0.35\ \text{cm}^{-1}\) (see the Supporting Information, Figure S20), which confirmed the constancy of the magnetic anisotropy for Co\(^{3+}\) in this coordination geometry.

**AC susceptibility behaviors**

Alternating current (AC) magnetic susceptibility measurements were carried out for all compounds in the absence and with an applied static magnetic field to reveal the possible slow re-
laxation of their magnetization. In the series of mononuclear complexes, the Fe⁶ derivatives 1a and 3 were found to exhibit an out-of-phase component of the susceptibility (χ_m'') when a static field was applied. The frequency dependence of χ_m'' for complex 3 under 3 kOe (see the Supporting Information, Figure S21) was used to estimate the relaxation time τ at different temperatures; they are reported in log scale as a function of T⁻¹ in Figure 7. Below 4.5 K, the feeble temperature dependence of τ suggests a significant contribution of quantum tunneling of the magnetization (QTM) to the relaxation process with τ_QTM = 4 × 10⁻⁸ s, whereas a linear variation was found for higher T. The latter dependence was analyzed by considering a thermally activated (Orbach) process, and fitting with the Arrhenius equation τ = τ_0 exp(U_0/k_B T) gave an effective energy barrier U_0/k_B = 53 K (37 cm⁻¹) with a pre-exponential relaxation time constant τ_0 = 5 × 10⁻⁸ s. This effective barrier is smaller than the anticipated barrier defined by |D|S² (52 cm⁻¹). However, U_0 matches quite well with the energy splitting between the ground state (S = 2) and the first excited state (S = 1) that corresponds to 3D (i.e., 39 cm⁻¹ or 56 K), which suggests an Orbach relaxation mechanism through the S = 1 excited state. Further information can be found in the Supporting Information, Figure S21. Compound 3 and the earlier communicated derivative 1a were characterized by a very similar energy barrier for magnetization reversal; they are the first examples of mononuclear Fe⁶ in a pentagonal bipyramid surrounding to exhibit slow relaxation of the magnetization.

None of the 1D-[M(H₅L₃N₃O₂R)] compounds exhibited slow relaxation of magnetization, even under applied DC magnetic fields. For the Fe³ derivative 6a, this is a striking contrast with the magnetic dynamics found for the parent complex 3 and the homologous system [FeH₅L₃N₃O₂Ph] (6b). The most likely origin for this situation are the hydrogen bonds that connect the coordination spheres of Fe³ centers of adjacent chains in complex 6a (see the Supporting Information, Figure S55). The spin-density mapping for complex 3, obtained by DFT calculations, clearly shows that the NH₃ group carries some spin (see the Supporting Information, Figure S25); thus, its H-bonding with the cyanonickelate Na atoms that are coordinated to the Fe center provides a pathway for weak magnetic interactions between the Fe centers at very low temperature. Therefore, even if the Fe centers are more than 7 Å apart, they may communicate by means of these supramolecular connections, which affect the magnetic dynamics of complex 6a. Such supramolecular pathways do not exist in complex 6b, in which the NH₃ groups are exchanged for Ph groups, and slow relaxation of the magnetization was indeed observed for this compound. Of course, the bulkier Ph group also slightly increases the interchain Fe···Fe separation from 7.398 (in 6a) to 7.995 Å (in 6b), which reduces further possible dipolar interactions.

The pentanuclear complexes 9 and 10 present χ_m'' signals, even in the absence of an applied magnetic field (see the Supporting Information, Figures S21 and S22), but no maxima on the χ_m'' versus T plots were seen above 2 K at 1000 Hz. For complex 10, well-defined maxima appeared under an applied DC field; data recorded with H_DC = 3 kOe are shown in Figure 8. The plot of the resulting relaxation times (τ) in log scale highlights a linear variation with T⁻¹ that was fitted with an Arrhenius law to afford U_0/k_B = 35 K with a pre-exponential time constant τ_0 = 4.6 × 10⁻¹⁸ s, which confirms SMM-type behavior for complex 10. Such a thermally activated relaxation process was not observed for complex 9, even in the presence of a static magnetic field (see the Supporting Information, Figure S22); obviously the relaxation of the magnetization for this compound is driven by QTM. The presence of magnetic dynamics was investigated for complexes 11 and 12, but no contribution for the out-of-phase part of the magnetic susceptibility (χ_m'') was detected, either with or without an applied magnetic field. A related pentanuclear compound based on hepta-coordinated Ni⁶ was previously reported to also exhibit slow relaxation of the magnetization. A rationale for the distinct magnetic behavior observed for the Fe and Co derivatives is provided by the magnetic anisotropy characteristics of the building units. In the present exchange-coupled supramolecular arrangements, metal centers with Ising anisotropy, such as...
Fe$^3$ or Ni$^{3+}$, lead to slow relaxation of the magnetization for the polynuclear species, whereas the Co derivatives with planar anisotropy do not.

**Theoretical calculations**

Calculations have been performed to determine the structural factors that control the magnetic anisotropy in this family of complexes. In particular, we were interested in understanding how the apical ligand modulates the magnetic anisotropy. For this purpose, we focused on three iron-based complexes, namely $1a$, $1b$, and $6b$, because complexes $1a$ and $6b$ exhibit a large axial anisotropy parameter, whereas the anisotropy is significantly reduced for complex $1b$ in which O ligands (i.e., ROH, H$_2$O) are incorporated. The method to extract the $D$ and $E$ parameters$^{[12b, 15d, 31]}$ from the computed spectrum and wave-functions of low energy was successfully used to study the anisotropic properties of various mono- and binuclear complexes.$^{[32]}$ It proceeds in two steps: Firstly, the electronic energies and wave-functions of the lowest states are computed by using the Complete Active Space Self-Consistent Field (CASSCF) method and the second-order CASPT2$^{[33]}$ and NEVPT2$^{[34]}$ corrections to the energies. Secondly, the spin-orbit coupling (SOC) between the $M_i$ components of the corresponding states of spin $S$ are calculated using the State Interaction Spin-Orbit (SISO) method.$^{[35]}$ The use of the effective Hamiltonian theory$^{[36]}$ enabled one to extract the components $D_{xx}, D_{xy}, D_{yx}, D_{yy}$, and $D_{zz}$ of the ZFS tensor in a rigorous manner from the computed energies and wave-functions of the spin-orbit states. Finally, the diagonalization of the ZFS tensor gave the $D$ and $E$ values (by using the conventions $|D| > |E|$ and $E > 0$) and allowed the determination of the magnetic axes. The computed $D$ and $E$ values are reported in Table 5. They were obtained at both CAS(6/10)PT2 level by considering 5 quintet and CAS(6/5) + NEVPT2 level by considering 5 quintet and 11 triplet states. The magnetic axes extracted from the ab initio calculations were very similar in the three complexes (Figure 9; see the Supporting Information), the $z$ axis being perpendicular to the pentadentate ligand.

For all complexes, ab initio calculations largely overestimated the axial anisotropy parameters in comparison to the values that were deduced from magnetic measurements. However, one should note the similarity of the NEVPT2 and CASPT2 values, despite the change in the active space and number of excited states. As it will be explained later, this overestimation may have two origins: 1) A lack of dynamic electron correlation owing to the use of perturbative corrections of the electronic energies. Unfortunately, better methods, such as difference dedicated configuration interactions$^{[37]}$ cannot be used here as the size of the complexes is by far too large. 2) A difference in the geometrical structure between 100 K, for which the X-ray structure that is used in the ab initio calculation has been determined, and 2–10 K, at which the magnetic measurements were performed. Owing to vibrational excitations, the geometry around the metal ion is probably more symmetric at 100 K, which in the present case, would result in an overestimation of the $D$ values (see below). Nevertheless, the obtained qualitative agreement in the trend was sufficient to use calculations as a tool for the rationalization of the magnetic anisotropy properties of these complexes.

The ORCA code allows one to have access to the contributions of each excited state to the ZFS parameters. Notably, the main contribution to the $D$ parameter is brought by a single excited quintet state for the three complexes (Table 5). Therefore, this peculiar state can be selected for the rationalization of the nature and magnitude of the magnetic anisotropy. The energy difference between this state and the ground state is also reported in Table 5, and it shows that the two states are very close in energy. Even if the ab initio calculation of the SOC is variational in the SOSI method (and in the present case, SOC must be treated variationally due to the quasidegeneracy of the ground state), we can use perturbative arguments to recall that ZFS is inversely proportional to the energy differ-

---

**Table 5.** Values of $D$ and $E$ parameters obtained from wave-functions theory (WFT) calculations, the contribution of the first excited quintet state to the ZFS parameters, the energy difference $\Delta E(d_{xx} - d_{yy})$ between the lowest 3d orbitals, and the energy difference $\Delta E(Q_1 - Q_2)$ between the two lowest quintet states, $Q_1$ and $Q_2$.

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b</th>
<th>6b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ [cm$^{-1}$]</td>
<td>$E$ [cm$^{-1}$]</td>
<td>$D$ [cm$^{-1}$]</td>
<td>$E$ [cm$^{-1}$]</td>
</tr>
<tr>
<td>CAS(6/10)PT2 5 quintets</td>
<td>$-23.23$</td>
<td>$0.29$</td>
<td>$-14.38$</td>
</tr>
<tr>
<td>CAS(6/5)NEVPT2 5 quintets: 11 triplets</td>
<td>$-21.64$</td>
<td>$0.85$</td>
<td>$-12.32$</td>
</tr>
<tr>
<td>first excited quintet contribution NEVPT2</td>
<td>$-28.30$</td>
<td>$-0.03$</td>
<td>$-18.95$</td>
</tr>
<tr>
<td>$\Delta E(d_{xx} - d_{yy})$ [cm$^{-1}$] CAS/6/5SCF</td>
<td>$169$</td>
<td>$411$</td>
<td>$206$</td>
</tr>
<tr>
<td>$\Delta E(Q_1 - Q_2)$ [cm$^{-1}$] NEVPT2</td>
<td>$233$</td>
<td>$405$</td>
<td>$286$</td>
</tr>
</tbody>
</table>
ence between the ground and the excited states at the second order. Consequently, any uncertainty on the electronic spectrum (either due to the structure or a lack of electron correlation) has dramatic consequences on the values of the $D$ and $E$ parameters. In the present case, this energy difference is underestimated for all complexes, which induces an overestimation of the axial ZFS parameters. However, it is larger in complex 1b, which rationalizes the smaller value of $|D|$ in this complex than in complexes 1a and 6b.

The analysis of the theoretical results is very instructive. By looking at the wave-functions of these two states, the energy difference between the lowest 3d orbitals, and their shape (Table 5 and Figure 10), we came to several conclusions:

1) The two states are strongly mono-determinantal and the main Slater determinants were $|d_x^0 d_y^0 d_z^0|$, $|d_x d_y d_z|$, and $|d_y d_z d_x|$, respectively, for the ground state and $|d_x^0 d_y^0 d_z^0|$, $|d_x d_y d_z|$, and $|d_y d_z d_x|$, respectively, for the first excited state. They only differ by the occupation of the $d_{xz}$ and $d_{yz}$ orbitals.

2) The energy difference between the two lowest quintet states can directly be related to the energy difference between the $d_{xz}$ and $d_{yz}$ orbitals. These orbitals as well as the two lowest states were very close in energy.

3) The $d_{xz}$ and $d_{yz}$ orbitals are linear combinations of the $d_{x^2}$ and $d_{y^2}$ spherical harmonics. Therefore, it is the $l_z d_z$ part of the Hamiltonian that couple these two states and leads to a negative contribution to the $D$ value, as already explained in previous work.$^{[15d]}$

4) Notably, the energy of the $d_{x^2}$ orbital increases when going from Cl to O (H$_2$O, MeOH) and CN ligands as the ligand field increases.

5) Finally, by considering the shape of the $d_{xz}$ and $d_{yz}$ orbitals, one may see that two $\pi$ interactions occur between the Fe$^{2+}$ and both the apical Cl and CN ligands in the $x$ and $y$ directions; only a single $\pi$ interaction exists with O ligands (H$_2$O, MeOH), which differentiates the $d_{xz}$ and $d_{yz}$ orbitals. As a consequence, the energy difference between these orbitals is larger in complex 1b than in 1a and 6b, and this is also the case for the energy difference between the ground and excited states, which results in a smaller $|D|$ value.

This last conclusion also shows that, as the value of $D$ in this series of complexes is governed by the differential $\pi$ interactions between the $x$ and $y$ directions, any effect (such as temperature) that would contribute to symmetrize the structure in the $x$ and $y$ directions would lead to a smaller energy difference between the two lowest states and therefore to an over-estimation of $|D|$.

Conclusions

The results gathered herein show that Fe$^{2+}$ in a heptacoordinated pentagonal bipyramid surrounding imposed by a pentadentate equatorial N$_2$O$_2$ ligand exhibits a magnetic anisotropy that is characterized by a negative ZFS parameter $D$. However, the anisotropy is modulated by the nature of the ligands in the apical positions, with values of $D$ in the order of $-15$ cm$^{-1}$ for weak-field ligands. This effect can be understood by considering that magnetic anisotropy arises from the spin-orbit coupling with the first excited quintet states, which differ from the ground state by the occupation of the $d_{xz}$ and $d_{yz}$ orbitals. When the apical ligands generate similar $\pi$ interactions in the $x$ and $y$ directions with the Fe$^{2+}$ atom (two $\pi$ interactions), the energy difference between the $d_{xz}$ and $d_{yz}$ orbitals is very small. As a consequence, the ground and excited states become quasi-degenerate, which induces strong anisotropic effects that result in a more negative $D$ value in the case of N-bound cyanometallates, whereas O-coordinated ligands have dissymmetric interactions, which result in reduced anisotropy.

The suitability of the Fe complexes to be used as building units towards heterometallic species is illustrated by the assemblegals realized with cyanometallates. During these associations, the pentagonal bipyramid environment of the 3d centers is unchanged and the magnetic anisotropy remains preserved. Moreover, the weak ligand field from N-bound cyanides contributes to maintain a large $|D|$ value. Therefore, it becomes possible to rationally design the magnetic features of a poly-nuclear derivative. This is highlighted by the series of pentanuclear compounds that were obtained with $[\text{W(CN)}_6]^{3-}$ for which blocking of the magnetization was observed when Ising-spin building units were involved. In this context, pentag-
X-ray crystallographic studies

Single crystals that were suitable for X-ray diffraction were coated with paratone oil and mounted onto the goniometer. The X-ray crystallographic data were obtained from a Gemini Oxford Diffraction or an Apex II Bruker diffractometer by using MoKα radiation source and equipped with an Oxford Cryosystem. The structures were solved by direct methods by using SIR2002 or Superflip and refined by means of least-square procedures on F by using the PC version of the program CRYSTALS. The scattering factors for all the atoms were used as listed in the International Tables for X-ray Crystallography. Absorption correction was performed by using a multiscan procedure. When it was possible, the H atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry and Uiso(H) (in the range 1.2–1.5 times Ueq of the parent atom), after which the positions were refined with riding constraints. All non-hydrogen atoms were refined anisotropically except for 10 and for 12 (for the latter, the metal centers were refined anisotropically). For these two structures, the quality of the data could not give rise to an anisotropic refinement despite a large number of data, and no twin could be detected either by inspecting the reciprocal lattice or by using crystallographic software. Solvent molecules were squeezed for complexes 7, 10–12: disordered water and methylol molecules in partial occupancy for 7, two methanol and eight water molecules for 10, four water molecules for 11, and thirteen water molecules for 12 as a symmetric unit. The squeezed molecules were not included in the given formula. Crystallographic data and refinement parameters for the single-crystal X-ray data analyses for the complexes 2–12 are summarized in Tables 1–3, and selected bond parameters are gathered in the Supporting Information.\[45\]\[46\] The structures were refined with a PhasFit24 program.\[46\] Isothermal magnetization curves have been computed with PHI.\[24\] Mössbauer measurements were recorded at 80 K by using an MD 306 Oxford cryostat on a constant acceleration conventional spectrometer with a 50 mCi source of 57Fe (Rh matrix). The absorber was a powder sample enclosed in a 20 mm diameter cylindrical, plastic sample holder, the size of which had been determined to optimize the absorption. A least-squares computer program was used to fit the Mössbauer parameters and determine their standard deviations (given in parentheses). Isomer shift values (δ) are relative to iron foil at 293 K.

High-frequency EPR spectra were recorded at the Laboratoire National des Champs Magnétiques Intenses in Grenoble on a home-built spectrometer working in double-pass mode, at 5 and 15 K.\[24\] Gun diodes operating at 95 or 115 GHz and equipped with a frequency doubler, a frequency tripler or a frequency quintuplet, were used as an excitation source. A Quasi-Optical table propagated the exciting light outside the cryostat, whereas a corrugated waveguide is used for this purpose inside the cryostat. A small modulating field is added to the main magnetic field (maximum field 16 T) to measure the derivative of the light transmitted through the sample. The detection was performed with a hot electron InSb bolometer.

Computational studies

Ab initio calculations were performed by using both the ORCA\[46\] and MOLCAS 8.0\[47\] packages. X-ray geometrical structures of complexes 1 a, 1 b, and 6b\[15d\] were used in the calculations. Complex 6b was truncated to the first Ni atom surrounded by CN ligands. The CAS(6,5) contains 6 electrons in 5 active d orbitals that were essentially located on the iron ion, whereas CAS(6/10) contained an additional set of diffuse d orbitals, which has also been included in the active space, as such a procedure has shown to provide better results.\[13e\] In Molcas calculations, ANO-pace atomic basis sets are used.\[46\] 6s5p3d1f for Fe, 4s3p1d for Cl, 3s2p1d for C, N, and O, and 2s for H. Orca calculations were performed by using cc-pVQZ Dunning atomic basis sets.\[29\] 6s5p3d1f for Fe, 4s3p1d for Cl, 3s2p1d for C, N, and O, and 2s for H.

Synthetic procedures

[Fe(H3NO22PPh)2(MeOH)][Cl·MeOH] (2): The reaction was carried out at room temperature under a N2 atmosphere by using standard Schlenk line technique. In a 50 mL round bottom Schlenk flask, FeCl3·H2O (397.7 mg, 2 mmol) was dissolved in MeOH (20 mL) to yield a green-yellow solution. In a 100 mL Schlenk tube, H3L022PPh (1.10 g, 2 mmol) in MeOH (60 mL) gave a milky slurry to which the methanol solution of FeCl3 was slowly added by syringe.
The deep blue solution that was formed was stirred at room temperature for 6 h then filtered through a frit under N₂ atmosphere into a 250 mL Schlenk tube. The filtrate was concentrated under vacuum to about 15 mL, and diethyl ether (25 mL) was added into it and the corresponding complex precipitated under stirring for 5 min. The crystalline solid was then isolated by filtration through a frit and quickly dried under vacuum to yield complex 2 as a green crystalline solid (988 mg, 68 %). IR: ν = 1607 (vs) and 1580 (s); δ = 2.9146(52) mm s⁻¹, Δ = 2.9146(52) mm s⁻¹.

[Fe(H₃L¹²O₂N₂P)Cl₂] (3): Complex 3 was synthesized by following the synthetic procedure for complex 2 by using H₃L¹²O₂N₂P (556 mg, 2 mmol). Complex 3 is less soluble in MeOH, which resulted in the formation of a blue precipitate in suspension in the dark blue solution at the end of the reaction. Additional MeOH (100 mL) was added, and the reaction mixture was heated to dissolve the precipitate and filtered while still hot through a frit under N₂ atmosphere for complexes 6a and 7, respectively. The whole set-up was kept undisturbed (under a N₂ atmosphere for complexes 9 and 10) in darkness. Interdiffusion of the solutions yielded needle-shaped crystals after 3 days. The mother liquor was removed by filtration through a frit under a N₂ atmosphere, and the product was washed with H₂O (2 x 5 mL) and MeOH (2 x 5 mL). The product was quickly dried under vacuum to obtain a crystalline solid.

\[ \text{Co(H₃L¹²O₂N₂P)[MeOH][NO₃][NO₃]} \] (1): A suspension of H₃L¹²O₂N₂P (1.0 g, 2 mmol) in water (25 mL) was heated at 60 °C to obtain a milky slurry. Co(NO₃)₂·6H₂O (582 mg, 2 mmol) was dissolved in ethanol (25 mL) by warming, and this solution was added slowly into the slurry of the ligand. The reaction mixture was stirred at 60 °C for 30 min to obtain a clear brown solution. The reaction mixture was purified by hot filtration, and the filtrate was left to evaporate slowly at room temperature, which resulted in block-shaped orange crystals of complex 4 after few days. The crystals were isolated by filtration, washed with acetone, and dried under vacuum to obtain crystals of complex 4 (910 mg, 57 %). IR: ν = 1629 (vs) and 1607 (s); δ = 1540 cm⁻¹ (vs); δ = 1530 cm⁻¹ (vs); δ = 1520 cm⁻¹ (vs); δ = 2177 (br) and 2072 cm⁻¹ (br); elemental analysis calc (%) for C₅H₈N₂O₃FeW (2348); δ = 43.48, H 3.65, 18.49; found: C 43.82, H 3.79, N 18.22; Mössbauer: two symmetric doublets; site 1: site population 11(2) %, δ = 1.268(16) mm s⁻¹, Δ = 2.9271(17) mm s⁻¹; site 2: site population 29(11) %, δ = 1.077(18) mm s⁻¹, Δ = 2.8262(22) mm s⁻¹.

[Fe(H₃L¹²O₂N₂P)[H₂O][W(CN)₆]] (10): Crystalline blue solid, yield: 420 mg, 80 %. IR: ν = 1605 (vs) and 1579 (s); δ = 2068–2136 cm⁻¹ (br); elemental analysis calc (%) for C₅H₈N₂O₃FeW (2642.44): C 55.00, H 3.47, N 16.43; found: C 55.27, H 3.59, N 16.72.

\[ \text{Co(H₃L¹²O₂N₂P)[H₂O][W(CN)₆]} \] (11): Crystalline brown solid, yield: 695 mg, 80 %. IR: ν = 1617 (vs) and 1573 (s); δ = 1525 (vs); δ = 2148 cm⁻¹ (w); elemental analysis calc (%) for C₅H₈N₂O₃CoW₄·8H₂O (2339.27): C 43.64, H 3.58, N 18.56; found: C 43.82, H 3.79, N 18.22.

\[ \text{Co(H₃L¹²O₂N₂P)[H₂O][W(CN)₆]} \] (12): Crystalline brown solid, yield: 695 mg, ≈ 80 %. IR: ν = 1606 (vs) and 1580 (s); δ = 1534 (s); δ = 2148 cm⁻¹ (w); elemental analysis calc (%) for C₅H₈N₂O₃CoW₄·19H₂O: δ = 48.54, H 4.34, N 14.50; found: C 48.6, H 3.9, N 14.2.

Acknowledgements

This work was supported by CEFIPRA/IFCPAR (Indo-French Center for the Promotion of Advanced Research). The authors are grateful to L. Rechnat, J.-F. Meunier (LCC), and Dr. M. Re- spaud (INSA Toulouse) for technical assistance in SQUID and Mössbauer measurements. Ab initio calculations have been performed by using HPC resources from CALMIP (Toulouse University Grant 2016-1517).

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Keywords: ab initio calculations, bipyramidal pentagonal coordination, chemistry, iron, magnetic properties


[50] The sample was dried in vacuo before analysis.

Manuscript received: November 28, 2016
Accepted Article published: January 24, 2017
Final Article published: March 6, 2017