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Analysis of the Uniaxial Magnetic Properties of High-Spin d^6 Ions at Trigonal Prism and Linear Two-Coordinate Sites: Uniaxial Magnetic Properties of $Ca_3Co_2O_6$ and $Fe[C(SiMe_3)_3]_2$

Dadi Dai and Myung-Hwan Whangbo*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

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It was shown that high-spin d^6 ions at trigonal prism and linear two coordinate sites have uniaxial magnetic properties by calculating their low-lying eigenstates under the influence of crystal field and spin–orbit coupling and then determining their *g*-factors for the parallel and perpendicular directions. On the basis of our theoretical findings, we interpreted the uniaxial magnetic properties of $Ca_3Co_2O_6$ with high-spin Co^{3+} (d^6) ions at the trigonal prism sites and those of $Fe[C(SiMe_3)_3]_2$ with high-spin Fe^{2+} (d^6) ions at linear two-coordinate sites, and discussed why compounds with high-spin d^6 ions at octahedral sites cannot have uniaxial magnetic properties.

1. Introduction

A hexagonal perovskite-type oxide $Ca_3Co_2O_6$ consists of $(Co_2O_6)_\infty$ chains separated by Ca^{2+} cations, and each $(Co_2O_6)_\infty$ chain has CoO_6 octahedra alternating with CoO_6 trigonal prisms by sharing their triangular faces.[1] The magnetic properties of $Ca_3Co_2O_6$ are uniaxial[2,3] with its magnetic moment reaching 4.8 μ_B per formula unit when the magnetic field is applied along the chain direction ($\mu_{\parallel} = 4.8\ \mu_B$),[4] and are described by an Ising spin Hamiltonian. Recent experimental[5,6] and theoretical studies[7,8] established that each octahedral-site cobalt is essentially nonmagnetic with a low-spin Co^{3+} (d^6) ion, and each trigonal prism cobalt has a high-spin Co^{3+} (d^6) ion with four unpaired spins. Consequently, the highly anisotropic magnetic properties of $Ca_3Co_2O_6$ originate from the high-spin d^6 ions at the trigonal prism sites. This implies that the magnetic moment of a high-spin d^6 ion at each trigonal prism site is parallel to its 3-fold rotational axis. (Hereafter, the directions parallel and perpendicular to the *n*-fold rotational axis of a coordination site with $n \geq 3$ will be referred to as the parallel and perpendicular directions, respectively.) Indeed, the powder neutron diffraction study[9] of $Ca_3Co_2O_6$ showed this to be the case. Thus, the magnetic moment is zero along the perpendicular direction ($\mu_\perp = 0$), and hence so is the *g*-factor along the perpendicular direction ($g_\perp = 0$).

The ground electronic state of a free high-spin d^6 ion is ^5D (i.e., $L = 2$, $S = 2$). When such an ion is placed at a coordinate site, the associated symmetry lowering splits the ^5D state into a number of levels by the effects of crystal field and spin−orbit coupling. Under an external magnetic field, these split levels may split further by the Zeeman effect. In understanding the magnetic properties of a high-spin d^6 ion system, it is essential to know the nature of the ground and low-lying excited states under the influence of crystal field and spin−orbit coupling. Kageyama et al. [2] interpreted the highly anisotropic magnetic properties of $Ca_3Co_2O_6$ by considering the ground state of a trigonal prism site Co^{3+} ion in terms of pseudo-spin with $\tilde{S} = 1$ and assuming that this pseudo-triplet is split into a “doublet-below-singlet” pattern. From the magnetization and magnetic susceptibility study of oriented $Ca_3Co_2O_6$ samples, Kageyama et al. reported $\mu_{\parallel} = 4\ \mu_B$ per formula unit and the *g*-factor of 4.5 for the parallel direction ($g_{\parallel} = 4.5$), which are consistent with their assumption that the ground state of a trigonal prism

* To whom correspondence should be addressed. E-mail: mike_whangbo@ncsu.edu.

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site Co^{3+} ion is a doublet. However, the $\mu_{||}$ and $g_{||}$ values observed by Maignan et al.[4] from the study of a single-crystal $Ca_3Co_2O_6$ are considerably different (i.e., $g_{||} = 2.55$ and $\mu_{||} = 4.8\ \mu_B$).

High-spin Fe^{2+} (d^6) ions in other coordinate environments also exhibit interesting magnetic properties. From their Mössbauer and EPR measurements of planar three-coordinate high-spin Fe^{2+} complexes (with Fe^{2+} ions at sites with C_{2v} symmetry), Andres et al.[10] showed that these complexes possess uniaxial magnetization properties arising from a quasi-doublet with $S_z = \pm 2$, and have an effective g value much greater than the spin-only value 8 (i.e., 10.9, 11.4). In the high-spin Fe^{2+} complex $Fe[C(SiMe_3)_3]_2$,[11] linear two-coordinate Fe^{2+} ions are located at sites with D_{3d} symmetry. The Mössbauer study of Reiff et al.[12a] showed that this compound has an internal hyperfine field much stronger than observed for the planar three-coordinate high-spin Fe^{2+} complexes of Andres et al., and the contribution of the orbital moment to the internal field is equivalent to adding two full spins relative to spin only $S = 2$ behavior. Furthermore, their analysis of the electric field gradient tensor and the direction of the internal hyperfine fields shows[12b] that the magnetic properties of $Fe[C(SiMe_3)_3]_2$ are uniaxial. In contrast, high-spin Fe^{2+} ions at octahedral sites are not known to exhibit uniaxial magnetic properties. High-spin Fe^{2+} octahedral complexes with trigonal or tetragonal distortion exhibit effective moments that are greater than the spin-only value for $S = 2$.[13] The magnetic solid $RbFeCl_3$ consists of linear chains made up of face-sharing $FeCl_6$ octahedra with trigonal distortion,[14] and $FeCl_2{\cdot}2H_2O$ consists of isolated $FeCl_6$ octahedra with tetragonal distortion.[15] Both $RbFeCl_3$ and $FeCl_2{\cdot}2H_2O$ exhibit only weakly anisotropic magnetic properties.[14,15]

In the present work we probe the origin of the uniaxial magnetic magnetic properties of compounds containing high-spin d^6 ions at trigonal prism and linear two-coordinate sites by calculating their g-factors for the parallel and perpendicular directions ($g_{||}$ and $g_{\perp}$, respectively) using the method of Abragam and Pryce.[16] On the basis of our theoretical findings, we then interpret the uniaxial magnetic properties of $Ca_3Co_2O_6$ and $Fe[C(SiMe_3)_3]_2$. Given the J_z and $g_{||}$ values for a state of a given magnetic ion, its magnetic moment $\mu_{||}$ is given by[17]

$$\mu_{||} = -g_{||}J_z\mu_B \tag{1}$$

To calculate g-factors of high-spin d^6 ions at trigonal prism and linear two-coordinate sites, it is necessary to determine the electronic structures of these ions under the influence of crystal field and spin−orbit coupling and then examine how the resulting doublet states of these ions are split by an external magnetic field. To our knowledge, no such theoretical study has been carried out for a high-spin d^6 ion at trigonal prism and linear two-coordinate sites. However, the magnetic properties of a high-spin Fe^{2+} (d^6) ion at an octahedral site were examined more than three and one-half decades ago.[13−15] For our discussion, it is important to recognize the low-energy electron configurations for high-spin d^6 ions at trigonal prism and linear two-coordinate sites. For a trigonal prism coordination, the energy difference between the nondegenerate configuration (Figure 1a) and the two degenerate configurations (Figure 1b,c) plays an important role in determining the nature of the ground electronic state. For a linear two-coordinate ion, the ground electronic state should be expressed as linear combinations of two degenerate electron configurations (Figure 2). Under the effect of crystal field and spin−orbit coupling, doubly degenerate electron configurations of high-spin d^6 ions at trigonal prism and linear two-coordinate sites give rise to doublet states, which are crucial in determining the anisotropy of magnetic properties.

Our work is organized as follows: In section 2 we examine the low-lying eigenstates of a high-spin d^6 ion at a trigonal prism and at a linear two-coordinate site under the combined effect of crystal field and spin−orbit coupling. In section 3 we calculate the parallel and perpendicular g-factors for a

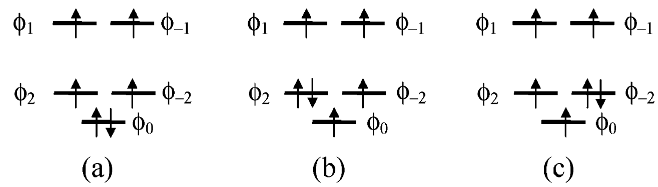

Figure 1. Three low-energy electron configurations expected for a high-spin d^6 ion at a trigonal prism site. It is assumed that the high-spin d^6 ion of a transition metal M forms a trigonal prism ML_6 with six surrounding main group elements L, and the electron configurations are described in terms of the molecular orbitals ϕ_n ($n = 0, \pm 1, \pm 2$) of ML_6. The d-orbital of M with magnetic quantum number $m_l = n$ is the major component of the molecular orbital ϕ_n, namely, the d_{z^2} orbital in ϕ_0, the $\{d_{xz}, d_{yz}\}$ orbitals in the set $\{\phi_{+1}, \phi_{-1}\}$, and the $\{d_{xy}, d_{x^2-y^2}\}$ orbitals in the set $\{\phi_{+2}, \phi_{-2}\}$.

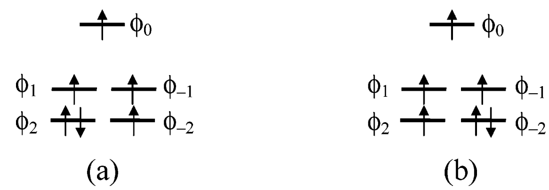

Figure 2. Two low-energy electron configurations expected for a high-spin d^6 ion at a linear two-coordinate site. It is assumed that the high-spin d^6 ion of a transition metal M forms a linear two-coordinate complex ML_2 with two main group elements L, and the electron configurations are described in terms of the molecular orbitals ϕ_n ($n = 0, \pm 1, \pm 2$) of ML_2. The d-orbital of M with magnetic quantum number $m_l = n$ is the major component of the molecular orbital ϕ_n, namely, the d_{z^2} orbital in ϕ_0 and the $\{d_{xz}, d_{yz}\}$ orbitals in the set $\{\phi_{+1}, \phi_{-1}\}$. In linear ML_2 the ligand s/p orbitals cannot mix with the $\{d_{xy}, d_{x^2-y^2}\}$ orbitals of M, so that the molecular orbitals $\{\phi_{+2}, \phi_{-2}\}$ are composed solely of the $\{d_{xy}, d_{x^2-y^2}\}$ orbitals.

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high-spin d^6 ion at a trigonal prism and at a linear two-coordinate site. In section 4 we discuss the uniaxial magnetic properties of $Ca_3Co_2O_6$ and $Fe[C(SiMe_3)_3]_2$ on the basis of our results in sections 2 and 3, and then comment on why a high-spin d^6 ion at an octahedral site exhibits only weakly anisotropic magnetic properties. Our conclusions are briefly summarized in Section 5.

2. Eigenstates under Crystal Field and Spin−Orbit Coupling

To calculate the *g*-factors of a magnetic system, one needs to determine the eigenstates of its Hamiltonian $\hat{H}$,

$$\hat{H} = \hat{H}_{CF} + \hat{H}_{SO} + \hat{H}_{Z} \tag{2}$$

where $\hat{H}_{CF}$, $\hat{H}_{SO}$, and $\hat{H}_{Z}$ are the crystal field, spin−orbit, and Zeeman operators, respectively. The crystal field Hamiltonian $\hat{H}_{CF}$ for a d-electron system with D_3 symmetry (e.g., an octahedral or a trigonal prism coordination) is expressed in terms of the spherical harmonics Y_k^q as[18,19]

$$\hat{H}_{CF} = B_2^0Y_2^0 + B_4^0Y_4^0 + B_4^3(Y_4^3 - Y_4^{-3}) \tag{3}$$

where B_2^0, B_4^0, and B_4^3 are adjustable parameters. In terms of the ladder operators,[20] the spin−orbit Hamiltonian $\hat{H}_{SO} = \lambda\hat{S}\cdot\hat{L}$ is written as

$$\hat{H}_{SO} = \lambda(\hat{S}_+\hat{L}_- + \hat{S}_-\hat{L}_+)/2 + \lambda\hat{S}_z\hat{L}_z \tag{4}$$

where λ is the spin−orbit coupling parameter. For a high-spin d^6 ion, $\lambda < 0$, since the d-shell is more than half-filled. The Zeeman operator is given by

$$\hat{H}_Z = \mu_B(\hat{L} + 2\hat{S})\cdot\vec{H} \tag{5}$$

where $\vec{H}$ is the external magnetic field. The magnitude of $\vec{H}$ will be denoted by $H_{\parallel}$ and $H_{\perp}$ when $\vec{H}$ is parallel and perpendicular to the *n*-fold rotational axis, respectively. In addition, the magnetic field $\vec{H}$ parallel and perpendicular to the *n*-fold rotational axis will be referred to as the parallel and perpendicular magnetic field, respectively.

To determine the eigenstates of the Hamiltonian $\hat{H}$, eq 2, one needs to construct its matrix representation using suitable basis functions (e.g., $|L\ L_z\rangle|S\ S_z\rangle$) and diagonalize the resulting matrix. The ground electronic state of a high-spin d^6 transition metal ion is ^{5}D. By neglecting the excited electronic states of this system, we describe the ground state ^{5}D using $(2L + 1)(2S + 1) = (2 \times 2 + 1)(2 \times 2 + 1) = 25$ basis functions $|L\ L_z\rangle|S\ S_z\rangle$. In general, the energy splitting induced by crystal field and spin−orbit coupling is of the order of 10^{-2} to 10^{-1} eV, while that induced by an external magnetic field is much smaller (e.g., $\mu_B H = 5.8 \times 10^{-5}$ eV for $H = 1$ T).[21] Consequently, we determine the eigenstates of $\hat{H}$ using perturbation theory with $\hat{H}_{CF} + \hat{H}_{SO}$ as the unperturbed Hamiltonian and $\hat{H}_Z$ as the perturbation Hamiltonian.

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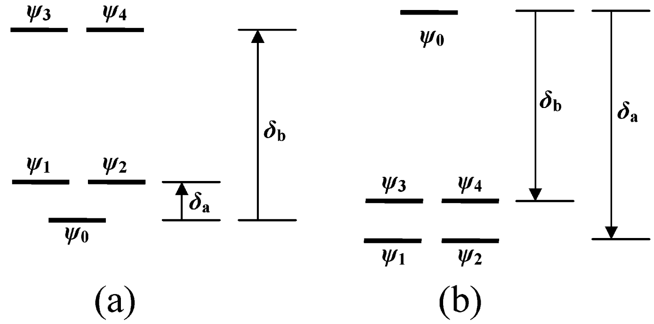

Figure 3. Crystal-field eigenstates resulting from the ^{5}D state of a high-spin d^6 ion at (a) a trigonal prism and (b) a linear two-coordinate site. The signs of the δ_a and δ_b values are positive when their arrows are pointed upward, but negative when their arrows are pointed downward.

In Appendix A of the Supporting Information, the basis function $|L\ L_z\rangle$ was shown to be an eigenfunction of $\hat{H}_{CF}$ for a trigonal prism. Thus L_z is a good quantum number for a trigonal prism. As shown in Figure 3, we define δ_a as the energy difference between the $L_z = 0$ and $L_z = \pm2$ levels, and δ_b as the energy difference between the $L_z = 0$ and $L_z = \pm1$ levels. For the ^{5}D state, the matrix representation of $\hat{H}_{CF} + \hat{H}_{SO}$ using the basis functions $|L\ L_z\rangle|S\ S_z\rangle$ is block-diagonalized in terms of the values of $J_z = L_z + S_z$. Since $L = 2$ and $S = 2$ for the ^{5}D state, there are nine such blocks classified by $J_z = 0, \pm1, \pm2, \pm3,$ and ±4. Using the simplified notations $|L_z\ S_z\rangle \equiv |L\ L_z\rangle|S\ S_z\rangle$, the matrix elements $\langle L_z\ S_z|\hat{H}_{CF} + \hat{H}_{SO}|L'_z\ S'_z\rangle$ are summarized in Table 1. By diagonalizing these blocks, we obtain the eigenfunctions of $\hat{H}_{CF} + \hat{H}_{SO}$, which can be written as

$$\begin{aligned}
&J_z = 0:\\
&\Phi_0 = a_1(|2\ {-2}\rangle + |{-2}\ 2\rangle) + a_2(|1\ {-1}\rangle + |{-1}\ 1\rangle) + a_3|0\ 0\rangle\\
&J_z = \pm1:\\
&\quad\Phi_{+1} = b_1|{+2}\ {-1}\rangle + b_2|{+1}\ 0\rangle + b_3|0\ {+1}\rangle + b_4|{-1}\ {+2}\rangle\\
&\quad\Phi_{-1} = b_1|{-2}\ {+1}\rangle + b_2|{-1}\ 0\rangle + b_3|0\ {-1}\rangle + b_4|{+1}\ {-2}\rangle\\
&J_z = \pm2:\\
&\quad\Phi_{+2} = c_1|{+2}\ 0\rangle + c_2|{+1}\ {+1}\rangle + c_3|0\ {+2}\rangle\\
&\quad\Phi_{-2} = c_1|{-2}\ 0\rangle + c_2|{-1}\ {-1}> + c_3|0\ {-2}\rangle\\
&J_z = \pm3:\\
&\quad\Phi_{+3} = d_1|{+2}\ {+1}\rangle + d_2|{+1}\ {+2}\rangle\\
&\quad\Phi_{-3} = d_1|{-2}\ {-1}\rangle + d_2|{-1}\ {-2}\rangle\\
&J_z = \pm4:\\
&\quad\Phi_{+4} = |{+2}\ {+2}\rangle\\
&\quad\Phi_{-4} = |{-2}\ {-2}\rangle
\end{aligned} \tag{6}$$

where a_i, b_i, c_i, and d_i ($i = 1, 2, 3, 4$) are coefficients that depend on the three parameters δ_a, δ_b, and λ. The state Φ_0 is a singlet, and the states $\Phi_{\pm n}$ ($n = 1-4$) are doublets. The

Table 1. Matrix Elements of $\hat{H}_{CF} + \hat{H}_{SO}$ for a Trigonal Prism in Terms of the Basis Functions $|L_z\ S_z\rangle \equiv |2\ L_z\rangle|2\ S_z\rangle$

(1) $J_z = 0$ Block

	$|2\ {-2}\rangle$	$|1\ {-1}\rangle$	$|0\ 0\rangle$	$|{-1}\ 1\rangle$	$|{-2}\ 2\rangle$
$|2\ {-2}\rangle$	$\delta_a - 4\lambda$	2λ	0	0	0
$|1\ {-1}\rangle$	2λ	$\delta_b - \lambda$	3λ	0	0
$|0\ 0\rangle$	0	3λ	0	3λ	0
$|{-1}\ 1\rangle$	0	0	3λ	$\delta_b - \lambda$	2λ
$|{-2}\ 2\rangle$	0	0	0	2λ	$\delta_a - 4\lambda$

(2) $J_z = 1$ Block[a]

	$|2\ {-1}\rangle$	$|1\ 0\rangle$	$|0\ 1\rangle$	$|{-1}\ 2\rangle$
$|2\ {-1}\rangle$	$\delta_a - 2\lambda$	$\sqrt{6}\,\lambda$	0	0
$|1\ 0\rangle$	$\sqrt{6}\,\lambda$	δ_b	3λ	0
$|0\ 1\rangle$	0	3λ	0	$\sqrt{6}\,\lambda$
$|{-1}\ 2\rangle$	0	0	$\sqrt{6}\,\lambda$	$\delta_b - 2\lambda$

(3) $J_z = 2$ Block[a]

	$|2\ 0\rangle$	$|1\ 1\rangle$	$|0\ 2\rangle$
$|2\ 0\rangle$	δ_a	$\sqrt{6}\,\lambda$	0
$|1\ 1\rangle$	$\sqrt{6}\,\lambda$	$\delta_b + \lambda$	$\sqrt{6}\,\lambda$
$|0\ 2\rangle$	0	$\sqrt{6}\,\lambda$	0

(4) $J_z = 3$ Block[a]

	$|2\ 1\rangle$	$|1\ 2\rangle$
$|2\ 1\rangle$	$\delta_a + 2\lambda$	2λ
$|1\ 2\rangle$	2λ	$\delta_b + 2\lambda$

(5) $J_z = 4$ Block[a]

	$|2\ 2\rangle$
$|2\ 2\rangle$	$\delta_a + 4\lambda$

[a] The elements in the $J_z = -1, -2, -3$, and -4 blocks are the same as those in the $J_z = 1, 2, 3$, and 4 blocks, respectively, except that the basis changes from $|L_z\ S_z\rangle$ to $|{-L_z}\ {-S_z}\rangle$.

eigenvalues E_0 and $E_{\pm n}$ ($n = 1-4$) associated with these eigenstates also depend on the three parameters δ_a, δ_b, and λ.

For numerical calculations, it is convenient to express the state energies E_i ($i = 0, \pm n$) and one crystal field parameter (e.g., δ_b) in units of $|\lambda|$. Then, for a certain δ_a/δ_b ratio appropriate for a given crystal field, the energies $E_i/|\lambda|$ can be readily calculated and plotted as a function of $\delta_b/|\lambda|$. Results of our calculations for a representative case of a trigonal prism (i.e., $\delta_a/\delta_b = 0.2$ and $\delta_b > 0$) are summarized in Figure 4a.

The crystal field Hamiltonian for a linear two-coordinate system has the same expression as does that for a trigonal prism. Therefore, our description for a trigonal prism is also valid for a linear two-coordinate system. The only difference between the two lies in the ranges of the parameters δ_a, δ_b, and λ. Results of our calculations for a representative linear system (i.e., $\delta_a/\delta_b = 1.2$ and $\delta_b < 0$) are summarized in Figure 5a.

3. Calculations of Parallel and Perpendicular *g*-Factors

3.1. Perturbation Treatment. Our discussion of the previous section shows that the eigenstates of a high-spin d^6 ion at a trigonal prism or a linear two-coordinate site under the zero-field Hamiltonian $\hat{H}_{CF} + \hat{H}_{SO}$ are either a singlet Φ_0 with $J_z = 0$ or a doublet $\Phi_{\pm n}$ with $J_z = \pm n$. For the singlet Φ_0, the Zeeman operator $\hat{H}_Z$ does not induce any splitting so that $g_{||} = g_\perp = 0$ for the singlet state. Each doublet state of $\hat{H}_{CF} + \hat{H}_{SO}$ can be split under the action of $\hat{H}_Z$. Each doublet state, described by two functions Φ_{+n} and Φ_{-n}, is doubly degenerate so that the energy split, ΔE_n, between the two under the action of $\hat{H}_Z$ can be determined by employing first-order perturbation theory. We denote the ΔE_n values for the parallel and perpendicular magnetic fields by $\Delta E_{n(||)}$ and $\Delta E_{n(\perp)}$, respectively. Then, the associated parallel and perpendicular *g*-factors are expressed as[22]

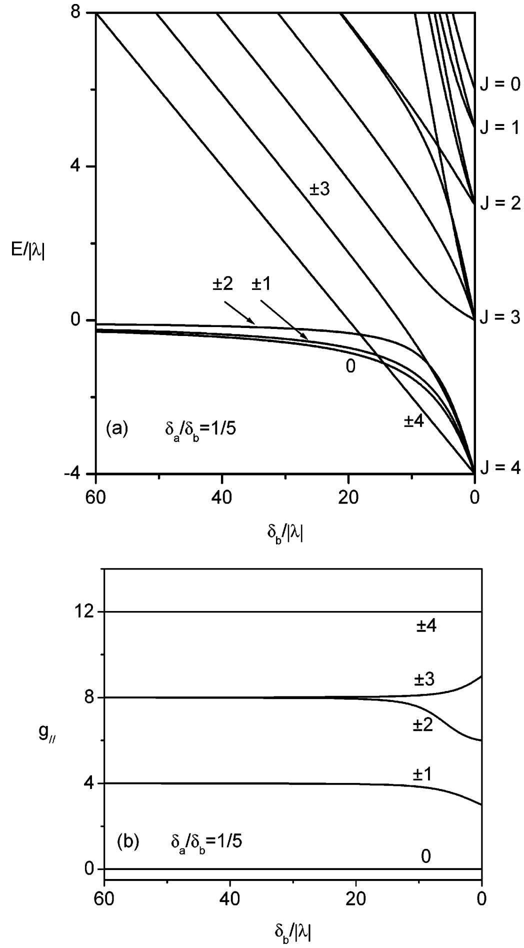

Figure 4. Energies and parallel *g*-factors of a high-spin d^6 ion at a trigonal prism site. (a) The energies $E_i/|\lambda|$ of the low-lying eigenstates of $\hat{H}_{CF} + \hat{H}_{SO}$ as a function of $\delta_b/|\lambda|$ and (b) their $g_{||}$ values as a function of $\delta_b/|\lambda|$. The J values at $\delta_b/|\lambda| = 0$ refer to the quantum numbers of a high-spin d^6 ion under the influence of spin−orbit coupling in the absence of crystal field.

$$g_{n(||)} = \Delta E_{n(||)}/\mu_B H_{||} = 2\langle\Phi_{+n}|\hat{L}_z + 2\hat{S}_z|\Phi_{+n}\rangle \tag{7}$$

$$g_{n(\perp)} = \Delta E_{n(\perp)}/\mu_B H_\perp = \langle\Phi_{+n}|(\hat{L}_+ + \hat{L}_-) + 2(\hat{S}_+ + \hat{S}_-)|\Phi_{-n}\rangle \tag{8}$$

For the derivation of these expressions, see Appendix B of the Supporting Information.

3.2. Perpendicular *g*-Factors of Doublet States. The doublet states $\Phi_{\pm n}$ ($n = 1-4$) of a high-spin d^6 ion at a trigonal prism or a linear two-coordinate site are specified in eq 6. It is found that $g_{n(\perp)} = 0$ for all these doublet states,

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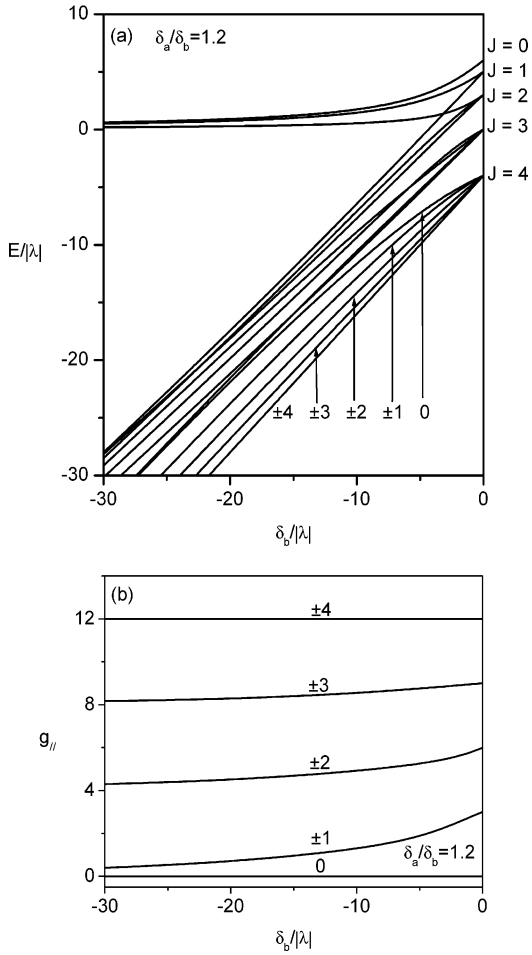

Figure 5. Energies and parallel g-factors of a high-spin d^6 ion at a linear two-coordinate site. (a) The energies $E_i/|\lambda|$ of the low-lying eigenstates of $\hat{H}_{CF} + \hat{H}_{SO}$ as a function of $\delta_b/|\lambda|$ and (b) their $g_{\|}$ values as a function of $\delta_b/|\lambda|$. The J values at $\delta_b/|\lambda| = 0$ refer to the quantum numbers of a high-spin d^6 ion under the influence of spin−orbit coupling in the absence of crystal field.

because each basis function of Φ_{-n} changed by $(\hat{L}_+ + \hat{L}_-) + 2(\hat{S}_+ + \hat{S}_-)$ does not match with any basis function of Φ_{+n}. It is important to understand the reason for this observation. The J_z value for each doublet state $\Phi_{\pm n}$ is given by $\pm n$, where n is an integer greater than zero. Therefore, the J_z value for each basis function of Φ_{+n} is greater than that for each basis function of Φ_{-n} by $2n$ (= 2, 4, 6, etc). However, for each basis function of Φ_{-n}, the operators $\hat{L}_+$ and $\hat{S}_+$ change its J_z value by +1, while the operators $\hat{L}_-$ and $\hat{S}_-$ change it by −1. Consequently, the integral $\langle\Phi_{+n}|(\hat{L}_+ + \hat{L}_-) + 2(\hat{S}_+ + \hat{S}_-)|\Phi_{-n}\rangle$ vanishes, so that $g_{n(\perp)} = 0$.

It is clear from the above discussion that the eigenstates of the zero-field Hamiltonian, $\hat{H}_{CF} + \hat{H}_{SO}$, can interact under the Zeeman Hamiltonian

$$\hat{H}_{Z(\perp)} = \mu_B H_\perp[(\hat{L}_+ + \hat{L}_-) + 2(\hat{S}_+ + \hat{S}_-)]/2 \qquad (9)$$

if their J_z values differ by ±1 (i.e., if $\Delta J_z = \pm 1$), e.g., Φ_0 and $\Phi_{\pm 1}$, $\Phi_{\pm 1}$ and $\Phi_{\pm 2}$, and so on. Such interactions give rise to second-order perturbation energy corrections. However, if the energy separation between such pairs of zero-field eigenstates is large compared with the maximum available magnetic energy $\mu_B H_{max}$ in a given experiment (i.e., magnetization, EPR, or magnetic susceptibility measurements), the associated second-order energy corrections are negligible, and so is their effect on the perpendicular g-factor, $g_\perp$. As already pointed out in section 2, the energy splitting induced by an external magnetic field can be several orders of magnitude smaller than that induced by crystal field and spin−orbit coupling.

3.3. Parallel *g*-Factors of Doublet States. For the doublet states of a trigonal prism, the $g_{n(\|)}$ values are calculated from eqs 6 and 7. Each basis function $|L_z\, S_z\rangle$ of eq 6 gives rise to the $g_{\|}$ value of $2(L_z + 2S_z)$. Therefore, we obtain

$$J_z = \pm 1: \quad g_{1(\|)} = 2b_2^2 + 4b_3^2 + 6b_4^2$$

$$J_z = \pm 2: \quad g_{2(\|)} = 4c_1^2 + 6c_2^2 + 8c_3^2$$

$$J_z = \pm 3: \quad g_{3(\|)} = 8d_1^2 + 10d_2^2$$

$$J_z = \pm 4: \quad g_{4(\|)} = 12 \qquad (10)$$

The $g_{n(\|)}$ values calculated for a trigonal prism crystal field ($\delta_a/\delta_b = 0.2$ and $\delta_b > 0$) as a function of $\delta_b/|\lambda|$ by using eq 10 are plotted in Figure 4b. The $g_{n(\|)}$ values calculated for a linear crystal field ($\delta_a/\delta_b = 1.2$ and $\delta_b < 0$) as a function of $\delta_b/|\lambda|$ by using eq 10 are plotted in Figure 5b.

4. Discussion

4.1. Uniaxial Magnetic Property High-Spin d⁶ Ions at Trigonal Prism and Linear Two-Coordinate Sites. The g-factor for the excitation $\Phi_{-n} \rightarrow \Phi_{+n}$ of each doublet can be determined from EPR experiments when the excitation is allowed, i.e., if the J_z values of Φ_{-n} and Φ_{+n} differ by ±1 (i.e., if $|\Delta J_z| = 1$).[23] For a high-spin d^6 ion at a trigonal prism or a linear two-coordinate site, the transition between the two split levels Φ_{-n} and Φ_{+n} for any of their doublets is forbidden because the $|\Delta J_z|$ value is $2n > 1$. However, the transition can become weakly allowed if the site symmetry of a high-spin d^6 ion is lowered such that the n-fold rotational axis disappears, as found for the three-coordinate high-spin Fe^{2+} complexes with site symmetry C_{2v}.[9] Such a system cannot possess doubly degenerate levels (i.e., doublets), but can have quasi-doublets made up of slightly different singlets.

For each doublet state $\Phi_{\pm n}$ of a high-spin d^6 ion at a trigonal prism or a linear two-coordinate site, the perpendicular g-factor, $g_{n(\perp)}$, is zero because the J_z values of their doublet states $\Phi_{\pm n}$ are $\pm n$, where n is a positive integer and hence the energy of the doublet is not split under an external magnetic field. Thus, the magnetic moment for the perpendicular direction is zero. This gives rise to uniaxial magnetic properties for compounds containing a high-spin d^6 ion at a trigonal prism or a linear two-coordinate site.

As mentioned above, in EPR experiments, excitations are allowed between Φ_0 and $\Phi_{\pm 1}$, between $\Phi_{\pm 1}$ and $\Phi_{\pm 2}$, and so on. Nevertheless, such an allowed transition cannot be observed if the associated energy separation is much greater than the maximum available magnetic energy $\mu_B H_{max}$. In such

(23) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; Chapman and Hall, NY, 1986.

a case, the associated g-factors cannot be detected in EPR measurements.

The positive integer value n of each doublet state $\Phi_{\pm n}$ of a high-spin d^6 ion originates from the fact that it has an even number of unpaired spins and hence the total spin S is an integer (i.e., $S = 2$). Doublet states $\Phi_{\pm n}$ of any magnetic ion with integer total spin S should have an integer n value greater than zero and hence $g_{n(\perp)} = 0$. In this context, it is of interest to consider an archetypal Ising system $LiTbF_4$,[24] which has high-spin Tb^{3+} (f^8) ions at sites with point group S_4. The ground state of a high-spin Tb^{3+} (f^8) ion, arising from the ^7F state ($L = 3$, $S = 3$), is characterized by a quasi-doublet consisting of two singlets with the zero-field splitting of 1 cm^{-1}.[24] The wave functions of this quasi-doublet state are made up mainly of $|J_z = \pm 6\rangle$ states with some admixture of $|J_z = \pm 2\rangle$.[25] The $g_{\|}$ value of $LiTbF_4$ with the field parallel to the 4-fold axis is approximately 17.7, slightly smaller than the maximum possible value of $18 = 2(3 + 2 \times 3)$. The ground state is not a true doublet because the $|J_z = \pm 6\rangle$ states do not belong to the E-representation of the S_4 point group.

For a doublet state $\Phi_{\pm n}$ to have a nonzero $g_{n(\perp)}$ value, the n value should be $^1/_2$ because the integral $\langle \Phi_{+n}|\hat{H}_{Z(\perp)}|\Phi_{-n}\rangle$ can be nonzero in such a case. This condition can be satisfied only if a magnetic ion has an odd number of unpaired spins so that the total spin S becomes a half integer, and hence the $J_z = L_z + S_z$ values for doublet states can be $\pm^1/_2$, $\pm^3/_2$, etc.

4.2. Trigonal Prism Site Co^{3+} Ion in $Ca_3Co_2O_6$. For a high-spin d^6 ion at a trigonal prism site, Figure 4a shows that the magnetic ground state is a singlet ($J_z = 0$). The first excited state is a doublet $\Phi_{\pm 1}$ with $J_z = \pm 1$, and the second excited state is a doublet $\Phi_{\pm 2}$ with $J_z = \pm 2$. For a trigonal prism, a large $\delta_b/|\lambda|$ value is appropriate. With increasing the $\delta_b/|\lambda|$ value, the first excited state becomes almost degenerate with the ground state while the second excited state becomes close to the first excited state. As shown in Figure 4b, the singlet ground state contributes zero to $g_{\|}$, the first excited state contributes 4 to $g_{\|}$, and the second excited state contributes 8 to $g_{\|}$. Thus, the parallel magnetic moment $\mu_{\|} = g_{\|}|J_z|\mu_B$ is zero from the singlet Φ_0, $4\mu_B$ from the doublet $\Phi_{\pm 1}$, and $16\mu_B$ from the doublet $\Phi_{\pm 2}$.

On the basis of the above observations, we discuss the $g_{\|}$ and $\mu_{\|}$ values observed for $Ca_3Co_2O_6$, whose trigonal prism sites contain high-spin Co^{3+} ions. Maignan et al. obtained $\mu_{\|} = 4.8$ μ_B at 2 K when $H > 8$ T.[4] At such a low temperature, thermal occupation of first and second excited states should be zero. To explain $\mu_{\|} = 4.8$ μ_B at 2 K, therefore, the singlet state Φ_0 cannot be the ground state, and the doublet state $\Phi_{\pm 1}$ should be the ground state as depicted in Figure 6. Even in this case, the $\mu_{\|}$ value is predicted to be 4 μ_B, still smaller than 4.8 μ_B. At this point we recall that the CoO_6 trigonal prisms of $Ca_3Co_2O_6$ are not an ideal trigonal prism with $\theta = 0°$ but a trigonal prism with D_3 symmetry in which $\theta \approx 15°$. As discussed in Appendix

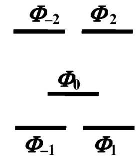

Figure 6. Schematic diagram expected for the low-lying energy states of a trigonal prism site Co^{3+} ion in $Ca_3Co_2O_6$.

A of the Supporting Information, this rotation leads to a slight mixing between the crystal-field eigenstates of a trigonal prism, which in turn leads to a slight mixing between the eigenstates of $\hat{H}_{CF} + \hat{H}_{SO}$. Namely, due to the slight rotation, the doublet function $\Phi_{\pm 2}$ mixes slightly into the doublet function $\Phi_{\pm 1}$, so that the $\mu_{\|}$ value can become greater than 4 μ_B.

Maignan et al.[4] deduced $g_{\|} = 2.55$ from the magnetic susceptibility data in the temperature region $T > 150$ K at $H = 3 \times 10^{-4}$ T. This is readily explained in terms of the eigenvalue structure of a high-spin trigonal prism site Co^{3+} ion depicted in Figure 6. As the temperature is raised, the population of the ground state $\Phi_{\pm 1}$ becomes reduced while the population of the first excited state Φ_0 is increased. As the $g_{\|}$ values for the states $\Phi_{\pm 1}$ and Φ_0 and are 4 and 0, respectively, the thermally averaged $g_{\|}$ value in the region of $T > 150$ K can be considerably smaller than 4 if the Φ_0 state is close enough in energy to $\Phi_{\pm 1}$.

The key point of the above discussion is that the doublet state $\Phi_{\pm 1}$ lies lower in energy than the singlet state Φ_0, as suggested by Kageyama et al.[2] From the viewpoint of the electron configurations of Figure 1, this implies that the nondegenerate configuration (Figure 1a) is quite close in energy to the degenerate configurations (Figure 1b,c), unlike the case of a high-spin d^6 ion in an isolated trigonal prism. In the $(Co_2O_6)_\infty$ chains of $Ca_3Co_2O_6$, however, each CoO_6 trigonal prism shares its triangular faces with adjacent CoO_6 octahedra with a short Co−Co distance (2.595 Å).[1] Thus, the d_{z^2} orbital of a CoO_6 trigonal prism (the major orbital component of its lowest-lying d-block level, Figure 1) overlaps strongly with the d_{z^2} orbital of an adjacent CoO_6 octahedron (the major orbital component of one of its t_{2g} levels). Then, from the viewpoint of one-electron orbital picture, one might consider that the resulting overlap-repulsion (i.e., two-orbital four-electron repulsion)[26] raises the energy of the nondegenerate electron configuration (Figure 1a) toward the degenerate electron configurations (Figure 1b,c). This eventually would be responsible for raising the singlet state Φ_0 level slightly above the doublet level $\Phi_{\pm 1}$.

Finally, we comment on why the $g_{\|}$ value of $Ca_3Co_2O_6$ obtained by Kageyama et al.[2] for oriented samples deviates strongly from that obtained by Maignan et al.[4] for a single-crystal sample (i.e., 4.5 vs 2.55). In deducing $g_{\|} = 4.5$, Kageyama et al. fitted the parallel magnetic susceptibility data with the magnetic susceptibility expression of Achiwa.[14] However, this expression was derived for a high-spin d^6 ion at an octahedral site with tetragonal distortion, and hence

(24) Romanova, I. V.; Malkin, B. Z.; Mukhamedshin, I. R.; Suzuki, H.; Tagirov, M. S. *Phys. Solid State* **2002**, *44*, 1544.
(25) Laursen, I.; Holmes, L. M. *J. Phys. C: Solid State Phys*. **1974**, *7*, 3765.
(26) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: NY, 1985.

would not be quite adequate for describing a high-spin d^6 ion at a trigonal prism site.

4.3. Linear Two-Coordinate Fe^{2+} Ion in $Fe[C(SiMe_3)_3]_2$. For a high-spin d^6 ion at a linear two-coordinate site, Figure 5a shows that the magnetic ground state is a doublet with $J_z = \pm 4$, the first excited state is a doublet with $J_z = \pm 3$, and the second excited state is a doublet with $J_z = \pm 2$, and so on. For a linear two-coordinate system, a large negative $\delta_b/|\lambda|$ value is appropriate. As the $\delta_b/|\lambda|$ value becomes more strongly negative, the energy differences between the ground state and the excited states become larger. Then the magnetic properties of a high-spin d^6 ion at a linear two-coordinate site should be governed by the ground state. This conclusion is supported by the uniaxial magnetic properties of $Fe[C(SiMe_3)_3]_2$.[12] Figure 5b shows that the $g_{\parallel}$ value of the ground state (i.e., the doublet with $J_z = \pm 4$) is 12. Our findings for a high-spin d^6 ion in a linear two-coordinate system (i.e., $J_z = \pm 4$, $g_{\parallel} = 12$, and $g_{\perp} = 0$ for the ground state) are consistent with the experimental observations for $Fe[C(SiMe_3)_3]_2$ by Reiff et al.[12]

4.4. Weakly Anisotropic Magnetic Properties of High-Spin d^6 Ions at Octahedral Sites. For the sake of completeness, we briefly discuss why a high-spin d^6 ion at an octahedral site exhibits only weakly anisotropic magnetic properties.[14,15] The eigenfunctions of an octahedral crystal field Hamiltonian are

$$\begin{cases} \psi'_0 = |0\rangle \\ \psi'_1 = \sqrt{2/3}|2\rangle - \sqrt{1/3}|-1\rangle \\ \psi'_2 = -\sqrt{2/3}|-2\rangle - \sqrt{1/3}|1\rangle \end{cases} \quad \mathrm{T_{2g}}$$

$$\begin{cases} \psi'_3 = \sqrt{1/3}|2\rangle + \sqrt{2/3}|-1\rangle \\ \psi'_4 = \sqrt{1/3}|-2\rangle - \sqrt{2/3}|1\rangle \end{cases} \quad \mathrm{E_g} \tag{11}$$

In the eigenstates ψ'_n ($n = 1-4$), the basis functions $|+2\rangle$ and $|-1\rangle$ mix, and so do the basis functions $|-2\rangle$ and $|+1\rangle$. Therefore, the eigenstates ψ'_n ($n = 0-4$) of $\hat{H}_{CF}$ are not eigenfunctions of the operator $\hat{L}_z$, and hence L_z is not a good quantum number. For such an ion, the low-lying eigenstates of the zero-field Hamiltonian $\hat{H}_{CF} + \hat{H}_{SO}$ arise mainly from the T_{2g} levels ψ'_0, ψ'_1, and ψ'_2. Thus, the truncated basis functions $|\psi'_n\rangle|S\ S_z\rangle$ ($n = 0-2$) may be employed to determine the eigenstates of $\hat{H}_{CF} + \hat{H}_{SO}$. This approximation gives rise to the pseudo-orbital method[22] (see Appendix C of the Supporting Information for details). This approximation has also been used for a high-spin d^6 ion at an octahedral site with trigonal or tetragonal distortion when the extent of distortion is small, e.g., if $|\delta_a|$ is small in Figure 3. Only the two parameters δ_a and λ are needed in the pseudo-orbital description of an octahedral system, so that the parameter δ_a may be referred to as δ.

For the pseudo-orbital angular momentum $\tilde{L} = 1$, the $\tilde{L}_z$ components are $-\tilde{1}$, $\tilde{0}$, and $+\tilde{1}$. As described in Appendix C of the Supporting Information, the functions ψ'_1, ψ'_0, and ψ'_2 behave as the pseudo-orbital functions $|\tilde{1},-\tilde{1}\rangle$, $|\tilde{1},\tilde{0}\rangle$, and $|\tilde{1},+\tilde{1}\rangle$, respectively, in the pseudo-orbital approximation. The matrix representation of $\hat{H}_{CF} + \hat{H}_{SO}$ for the ^5D state using the basis functions $|\tilde{L}\ \tilde{L}_z\rangle|S\ S_z\rangle$ is block-diagonalized with respect to the values of $\tilde{J}_z = \tilde{L}_z + S_z$, namely, $\tilde{J}_z = 0, \pm 1, \pm 2$, and ± 3. The state Φ_0 is a singlet, and the states $\Phi_{\pm n}$ ($n = 1-3$) are doublets. The eigenvalues E_0 and $E_{\pm n}$ ($n = 1-3$) associated with these eigenfunctions are functions of the parameters δ and λ. The state energies $E_i/|\lambda|$ ($i = 0, \pm n$) can be readily calculated as a function of the crystal field parameter $\delta/|\lambda|$. Results of our calculations for a representative range of $\delta/|\lambda|$ are summarized in Figure 7.

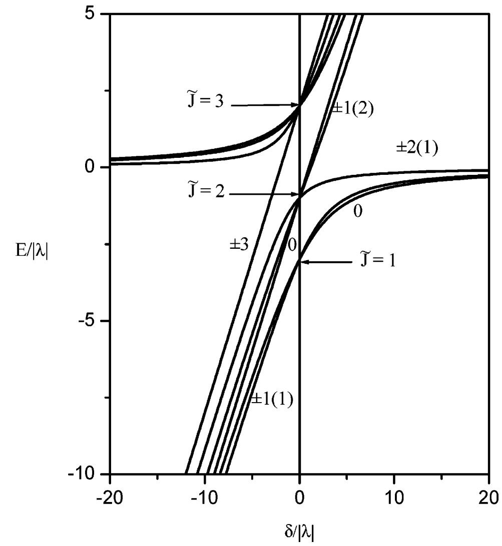

Figure 7. Energies $E_i/|\lambda|$ of a high-spin d^6 ion at an octahedral site with or without trigonal distortion as a function of $\delta/|\lambda|$. The $\tilde{J}$ values at $\delta/|\lambda| = 0$ refer to the pseudo-quantum numbers of a high-spin d^6 ion at an octahedral site under the influence of spin−orbit coupling in the absence of a trigonal distortion. It should be noted that our definition of δ differs from that employed in refs 14, 15, and 22.

It is noted from Figure 7 that the singlet state Φ_0 and the doublet state $\Phi_{\pm 1}$ are close in energy and are well separated from the remaining excited states, as found by Inomata and Oguchi.[15] When $\delta = 0$, the Φ_0 and $\Phi_{\pm 1}$ states are degenerate, which leads to isotropic magnetic properties. (Note that the orbital set $\{\Phi_{-1}, \Phi_0, \Phi_{+1}\}$ behaves like the set $\{P_{-1}, P_0, P_{+1}\}$ of an atomic P state.) For an octahedron with weakly trigonal distortion, small $|\delta/\lambda|$ values are appropriate, and weakly anisotropic magnetic properties set in. As already discussed, $\langle\Phi_{+1}|\hat{H}_{Z(\perp)}|\Phi_{-1}\rangle = 0$ but $\langle\Phi_0|\hat{H}_{Z(\perp)}|\Phi_{-1}\rangle \neq 0$ and $\langle\Phi_0|\hat{H}_{Z(\perp)}|\Phi_{+1}\rangle \neq 0$. Consequently, $g_{\perp} \neq 0$ and $\mu_{\perp} \neq 0$ because, for an octahedron with weakly trigonal distortion, the energy difference δ between Φ_0 and $\Phi_{\pm 1}$ is small compared with the maximum available magnetic energy $\mu_B H_{max}$. This makes the transition between Φ_0 and $\Phi_{\pm 1}$ observable in EPR experiments. Obviously, a nonzero δ means the presence of a zero-field splitting of the triply degenerate T_{2g} levels. The latter gives rise to weakly anisotropic magnetic properties.[17]

5. Concluding Remarks

The low-energy eigenstates of a high-spin d^6 ion at a trigonal prism or a linear two-coordinate site under the influence of crystal field and spin−orbit coupling are either a singlet Φ_0 with $J_z = 0$ or a doublet $\Phi_{\pm n}$ with $J_z = \pm n$, where n is a positive integer. The perpendicular g-factor $g_{n(\perp)}$

is zero for each doublet $\Phi_{\pm n}$ because its energy is not split by an external magnetic field due to the fact that the difference in the J_z values of Φ_{-n} and Φ_{+n} is greater than 1 (i.e., $|\Delta J_z| = 2n > 1$). Thus, when the maximum available magnetic energy $\mu_B H_{max}$ is very small compared with the energy separation between any two states whose J_z values differ by ± 1, the perpendicular magnetic moment ($\mu_\perp$) and the perpendicular g-factor ($g_\perp$) become zero. This gives rise to uniaxial magnetic properties of high-spin d^6 ions at trigonal prism and linear two-coordinate sites. The magnetic properties of high-spin d^6 ions at octahedral sites cannot be uniaxial because the J_z values of the ground and the first excited states differ by ± 1 and the energy separation between the two (i.e., δ) is small compared with $\mu_B H_{max}$.

The $\mu_{||} = 4.8\,\mu_B$ and $g_{||} = 2.55$ values of $Ca_3Co_2O_6$ derived by Maignan et al.[4] from the magnetization and magnetic susceptibility measurements of a single-crystal sample are well explained if the ground and the first two excited states of the high-spin Co^{3+} (d^6) ions at the trigonal prism sites have the energy ordering depicted in Figure 6, where the doublet $\Phi_{\pm 1}$ ($J_z = \pm 1$) and the singlet Φ_0 ($J_z = 0$) are the ground and the first excited states, respectively. The singlet state Φ_0 is higher in energy than the doublet state $\Phi_{\pm 1}$ due probably to the overlap repulsion between the d_{z^2} orbitals of adjacent trigonal prism and octahedral sites. A high-spin d^6 ion at a linear two-coordinate site has the ground state with $J_z = \pm 4$, $g_{||} = 12$, and $g_\perp = 0$, and the first excited state with $J_z = \pm 3$, $g_{||} \approx 8$, and $g_\perp = 0$. The uniaxial magnetic properties [12] of $Fe[C(SiMe_3)_3]_2$ means that the energy separation between the ground and first excited states of the high-spin Fe^{2+} (d^6) ions is significantly greater than $\mu_B H_{max}$, which in turn predicts that $Fe[C(SiMe_3)_3]_2$ should give no resonance signal in EPR measurements.

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Supporting Information Available: Appendix A for the derivation of the eigenstates of $\hat{H}_{CF}$ for a transition metal ion at a D_3 symmetry site with Table S.1 and Figures S.1 and S.2, Appendix B for the derivation of the expressions for the parallel and perpendicular g-factors, and Appendix C for the pseudo-orbital description of the low-lying eigenstates of a high-spin d^6 ion at an octahedral site with Tables S.2, S.3, and S.4. This material is available free of charge via the Internet at http://pubs.acs.org.

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