Polyhedron 64 (2013) 209-217

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Slow magnetic relaxation in the tetrahedral cobalt(II) complexes $[Co(EPh)_4]^{2-}$ (E=O, S, Se)

Joseph M. Zadrozny^a, Joshua Telser^b, Jeffrey R. Long^{a,*}

^a Department of Chemistry, University of California, Berkeley, CA 94720-1460, United States
^b Department of Biological, Chemical and Physical Sciences, Roosevelt University, Chicago, IL 60605, United States

ARTICLE INFO

Article history: Available online 10 April 2013

Dedicated to Prof. George Christou on the occasion of his 60th birthday.

Keywords: Single-molecule magnets Zero-field splitting Ligand field theory

ABSTRACT

Salts of the homoleptic cobalt(II) complexes $[Co(EPh)_4]^{2-}$ (E = O, S, Se) were isolated as $(Ph_4P)_2[Co(OPh)_4$ (CH₃CN) (1), K(Ph₄P)[Co(OPh)₄] (2), (Ph₄P)₂[Co(SPh)₄] (3), and (Ph₄P)₂[Co(SePh)₄] (4) from reactions of CoCl₂ or Col₂ with excess amounts of K(EPh) and (Ph₄P)Br in acetonitrile. Single-crystal Xray structural studies show all four compounds to contain mononuclear $[Co(EPh)_4]^{2-}$ complexes with structures conforming to or approaching D_{2d} symmetry. Magnetic susceptibility data for 1-4 indicate anisotropic S = 3/2 spin ground states, with axial zero-field splitting parameters ranging from $D = -11.1(3) \text{ cm}^{-1}$ in **1** to $-83(1) \text{ cm}^{-1}$ in **4**. Ac susceptibility measurements reveal slow magnetic relaxation at zero dc field for 2-4, while a bias dc field is required to see this effect in 1. Arrhenius plots of the data indicate spin reversal barriers of U_{eff} = 21(1), 21(1), and 19(1) cm⁻¹ for **1**, **3**, and **4**, respectively, while the plot for **2** shows substantial curvature, indicative of strong intermolecular interactions. For **2**, dilution with $[Zn(OPh)_4]^{2-}$ was necessary to observe thermally-activated magnetic relaxation, with $U_{eff} = 34.0(5)$ cm^{-1} . The trend in U_{eff} for 1–4 does not follow the trend in D values, possibly indicating that magnetic relaxation in 2-4 is not fully thermally activated under the conditions probed. Solid-state diffuse-reflectance spectra display d-d excitations that follow the general trend of D values. An analysis of 1-4 within the framework of ligand field theory shows that the increase in |D| occurs in concert with an decrease in the Racah *B* parameter, highlighting the importance of soft donor ligands in the pursuit of systems with a large magnetic anisotropy.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Mononuclear lanthanide complexes have been known for a decade to display single-molecule magnet behavior as a result of highly axial magnetic moments [1–4]. In such systems, the characteristic strong spin–orbit couplings of the constituent lanthanide ions work in concert with unquenched orbital angular momenta to produce magnetic moments that prefer to align up or down relative to a molecular axis. Implicit in this property is an energy barrier for inversion of the magnetic moment between the two orientations. If the barrier is appropriately large, slow magnetic relaxation and even magnetic hysteresis of a molecular nature can be observed. This property of single-molecule magnets has elicited proposals for applications as information storage media [5] or qubits for quantum computing [6–8].

Three years ago, slow magnetic relaxation was observed for a series of trigonal pyramidal complexes of iron(II) [9,10], extending the field of single-molecule magnet research to mononuclear transition metal complexes. In these complexes, the coordination

geometries enforced by the picketed tris(pyrrolyl- α -methyl)amine (tpa^R) ligands were found to give rise to large, negative values for the axial zero-field splitting parameters, *D*, and large spin reversal barriers, U_{eff} . For example, the complex [(tpa^{Rb})Fe]⁻ was found to exhibit $D = -48 \text{ cm}^{-1}$ and $U_{\text{eff}} = 65 \text{ cm}^{-1}$ [10]. Further studies [11–14] have since revealed slow magnetic relaxation for iron(II) in a variety of other coordination environments, most notably two-coordinate linear geometries, for which U_{eff} values as large as 181 cm⁻¹ can arise as a result of unquenched orbital angular momentum [11]. Importantly, however, in all of these cases, the observation of magnetic susceptibility experiment (<1500 Hz) requires the application of a bias dc magnetic field to disrupt ground-state tunneling between the ground M_s (or M_I) levels.

The direct observation of slow magnetic relaxation for a mononuclear transition metal complex without a requisite bias dc field was achieved for the first time in the tetraphenylphosphonium salt of the tetrahedral cobalt(II) complex [Co(SPh)₄]^{2–} [15]. Prior characterization of this species [16–18] via EPR spectroscopy and magnetic susceptometry revealed a substantial, negative zero-field splitting ($D \approx -70$ cm⁻¹). In accordance with Kramers' theorem [19], ground state magnetization tunneling between the





^{*} Corresponding author. Tel.: +1 510 642 0860; fax: +1 510 643 3546. *E-mail address:* jrlong@berkeley.edu (J.R. Long).

^{0277-5387/\$ -} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2013.04.008

 $M_S = \pm 3/2$ sublevels is weakened due to the half-integer spin, and consequently this complex displays slow relaxation of the magnetization with $U_{\text{eff}} = 21(1) \text{ cm}^{-1}$ in zero applied dc field. Independently, a trigonal bipyramidal S = 3/2 iron(III) complex was also discovered to demonstrate slow magnetic relaxation without an applied dc field at low temperature [20].

The magnitude of the relaxation barrier observed for $[Co(SPh)_4]^{2-}$ is modest when compared to many of the aforementioned mononuclear single-molecule magnets, but could potentially be increased through manipulation of the ligand field. Previous studies of other pseudotetrahedral cobalt(II) complexes with four S-donor ligands revealed a strong dependence of D on the relative arrangements of the donor atoms within the coordination sphere of the cobalt(II) center [16,21,22]. In particular, these studies showed that a distortion away from ideal T_d symmetry via a tetragonal elongation enforces a large, negative D value. Zero-field splitting is a second order effect, and thus within the tetragonally-elongated coordination geometry, D will hypothetically be enhanced for weak-field ligands, as such ligands may lower the d-d excitation energies responsible for the magnitude of D. Further, the relation between *D* and *U* for an S = 3/2 complex, U = 2D, suggests that the observed spin reversal barriers will increase linearly with an increase in D. Herein, we report the preparation and structural, magnetic, and spectral characterization of a series of homoleptic cobalt(II) complexes of phenylchalcogenide ligands: (Ph₄P)₂[Co(OPh)₄]·(CH₃CN) (1), (Ph₄P)K[Co(OPh)₄] (2), (Ph₄-P)₂[Co(SPh)₄] (**3**) [23–25], and (Ph₄P)₂[Co(SePh)₄] (**4**) [26]. We demonstrate that the increasing softness of the heavier phenylchalcogenide ligands leads to larger *D* values among 1–4, but that this does not necessarily afford larger $U_{\rm eff}$ values.

2. Experimental

2.1. General considerations

All manipulations were performed in an inert atmosphere box under N₂. Acetonitrile (MeCN), diethylether (Et₂O), and tetrahydrofuran (THF) were dried using a commercial solvent purification system designed by JC Meyer Solvent Systems. The compounds KOPh [27], KSPh [28], and KSePh [29] were prepared employing previously reported methods. Anhydrous CoCl₂, CoI₂, ZnI₂, and (Ph₄P)Br were purchased from Aldrich and used as received. Diatomaceous earth (Celite[®] 545) was dried under vacuum prior to use.

2.2. (*Ph*₄*P*)₂[*Co*(*OPh*)₄]·(*CH*₃*CN*) (**1**)

A solution of (Ph₄P)Br (0.45 g, 1.1 mmol) in 4 mL of MeCN was added to a slurry of KOPh (0.14 g, 1.1 mmol) in 2 mL of MeCN with vigorous stirring to afford a yellow solution and a white precipitate. The yellow solution was filtered through diatomaceous earth. A solution of CoCl₂ (16 mg, 0.12 mmol) in 2 mL of MeCN was added to the filtrate, stirred briefly, and allowed to stand overnight. Dark blue, block-shaped crystals suitable for X-ray analysis formed from this solution, accompanied by a white precipitate. The large blue triangular-block-shaped crystals were separated from the mixture mechanically, washed with 2 mL of MeCN, and briefly dried in the atmosphere of the glovebox to yield 64 mg (46%) of product. IR (neat): 3053 (m), 3019 (w), 1921 (w), 1841 (w), 1580 (vs), 1560 (w), 1474 (vs), 1468 (vs), 1299 (vs), 1277 (w), 1190 (m), 1158 (m), 1105 (vs), 1088 (w), 1026 (w), 985 (s), 870 (m), 848 (m), 829 (m), 756 (vs), 720 (vs), 685 (vs), 617 (m), 569 (s), and 522 (vs) cm⁻¹. Anal. Calc. for C₇₀H₆₀CoO₄P₂·CH₃CN: C, 77.21; H, 5.52; N, 1.22. Found: C, 77.28; H, 5.34; N, 1.36%.

2.3. $K(Ph_4P)[Co(OPh)_4]$ (2)

A solution of (Ph₄P)Br (0.41 g, 0.97 mmol) in 2 mL of MeCN was added to a slurry of KOPh (0.13 g, 0.98 mmol) in 2 mL of MeCN with vigorous stirring to afford a yellow solution and a white precipitate. The yellow solution was filtered through diatomaceous earth. A solution of Col₂ (60 mg, 0.19 mmol) in 2 mL of MeCN was added to the filtrate, stirred briefly, and allowed to stand overnight to afford purple, block-shaped crystals suitable for X-ray analysis. The crystals were collected via filtration, washed with 1 mL of MeCN, and dried briefly to yield 80 mg (40%) of product. IR (neat): 3082 (m), 3066 (m), 3048 (m), 3014 (m), 2982 (m), 1584 (vs), 1560 (m), 1475 (vs), 1436 (s), 1337 (m), 1316 (m), 1290 (vs), 1266 (w), 1186 (m), 1165 (s), 1146 (m), 1107 (vs), 1069 (m), 1020 (m), 996 (w), 986 (vs), 932 (m), 865 (s), 841 (s), 826 (s), 756 (vs), 722 (vs), 689 (vs), 620 (s), 563 (s), 527 (m), and 518 (vs) cm⁻¹. Anal. Calc. for C₄₈H₄₀CoKO₄P: C, 71.19; H, 4.98; N, 0.00. Found: C, 70.91; H, 5.18; N, 0.02%.

2.4. $(Ph_4P)_2[Co(SPh)_4]$ (3)

This compound was prepared by an alternative method to the reported procedure [25]. A solution of (Ph₄P)Br (0.37 g, 0.87 mmol) in 2 mL of MeCN was added with stirring to a slurry of KSPh (0.13 g, 0.88 mmol) in 2 mL of MeCN, affording a yellow-orange solution and a white precipitate. The solution was filtered through diatomaceous earth, and a solution of CoCl₂ (16 mg, 0.12 mmol) in 2 mL of MeCN was added to the filtrate to afford a dark green solution. This solution was stirred briefly, then allowed to sit undisturbed for 24 h to yield 0.11 g (76%) of product as large green, block-shaped crystals of product with a unit cell matching that previously reported [16]. IR (neat): 3054 (w), 3039 (w), 3001 (w), 2984 (w), 1569 (vs), 1469 (vs), 1436 (vs), 1342 (w), 1319 (m), 1264 (w), 1188 (m), 1162 (m), 1105 (vs), 1079 (vs), 1020 (s0, 994 (s), 899 (m), 849 (m), 745 (vs), 719 (vs), 688 (vs), 631 (w), 522 (vs), 479 (s), and 416 (m) cm⁻¹. Anal. Calc. for C₇₂H₆₀CoP₂S₄: C. 73.64: H. 5.15: N. 0.00. Found: C. 73.64: H. 5.30: N. 0.02%.

2.5. (Ph₄P)₂[Co(SePh)₄] (4)

This compound was prepared by an alternative method to the reported procedure [26]. A solution of (Ph₄P)Br (0.86 g, 2.1 mmol) in 5 mL of MeCN was added with stirring to a slurry of KSePh (0.40 g, 2.0 mmol) in 2 mL of THF, forming a deep orange solution and a white precipitate. The solution was filtered, and the white solid was washed with an additional 3 mL of MeCN. A solution of CoCl₂ (68 mg, 0.54 mmol) in 2 mL of MeCN, was added to the filtrate, forming a blue, then green solution and a brown precipitate. This mixture was filtered to collect the brown precipitate, which was then washed with 2×3 mL aliquots of MeCN. The solid was then redissolved in 100 mL of MeCN, and diffusion of Et₂O vapor into the resulting solution produced 0.52 g (70%) of dark brown, block-shaped crystals suitable for X-ray analysis. IR (neat): 3056 (m), 3035 (m), 1583 (s), 1568 (vs), 1482 (s), 1467 (vs), 1433 (vs), 1340 (m), 1314 (vs), 1264 (w), 1183 (m), 1164 (m), 1104 (vs), 1063 (s), 1019 (s), 995 (s), 933 (m), 899 (m), 847 (m), 756 (vs), 740 (vs), 719 (vs), 687 (vs), 661 (vs), 615 (s), 522 (vs), and 467 (s) cm⁻¹. Anal. Calc. for C₇₂H₆₀CoP₂Se₄: C, 63.49; H, 4.44; N, 0.00. Found: C, 63.47; H, 4.63; N, 0.00%.

2.6. K(Ph₄P)[Co_{0.06}Zn_{0.94}(OPh)₄] (**5**)

A solution of $(Ph_4P)Br$ (0.69 g, 1.6 mmol) in 2 mL of MeCN was added to a slurry of KOPh (0.22 g, 1.7 mmol) in 2 mL of MeCN with vigorous stirring to afford a yellow solution and a white precipitate. The yellow solution was filtered through diatomaceous earth. A solution of Col₂ (9 mg, 0.03 mmol) and Znl₂ (94 mg, 0.29 mmol) in 2 mL of MeCN was added to the filtrate, stirred briefly, and allowed to stand overnight to afford light-purple, block-shaped crystals. The crystals were collected via filtration, washed with 1 mL of MeCN, and dried briefly to yield 0.5 g of product with the same unit cell as **2**. Successful dilution, and the relative transition metal ion composition, was confirmed by the consistent unit cell, magnetization, and solution UV–Vis data, as was done previously for **3** [15] to yield a ratio of 1 cobalt to 17(2) zinc ions. The transition metal composition listed for **5** is taken from the magnetization data.

2.7. Magnetic measurements

Polycrystalline samples were loaded into guartz tubes and coated with eicosane in a glove box. To avoid possible desolvation in **1**, which contains cocrystallized MeCN in the crystal structure. the crystals were removed from mother liquor immediately prior to placement in the sample quartz tubes. The quartz tubes were then fixed to a sealable hose-adapter, evacuated briefly with a Schlenk line outside of the glove box, frozen in liquid N₂, and flame sealed. Samples were measured from 2 to 300 K at dc fields ranging from 0 to 7 T with a Quantum Design MPMS-XL SQUID magnetometer. Dc susceptibility and magnetization data were fit or simulated, respectively, with the Van Vleck equation for an S = 3/2system with axial zero-field splitting using Excel[®]. Ac magnetic susceptibility data measurements were performed using a 4-Oe switching field. Ac magnetic relaxation data were fitted using formulae describing χ' and χ'' in terms of frequency, constant temperature susceptibility (χ_T), adiabatic susceptibility (χ_S), relaxation time (τ) , and a variable to represent a distribution of relaxation times (α) [30]. All data were corrected for diamagnetic contributions from the eicosane restraint, sample holder, and the compound itself (estimated with Pascal's constants [31]). The errors in all fitted magnetic parameters were determined from a nonlinear least-squares analysis using the program solveraid [32].

2.8. X-ray data collection, structure solution and refinement

Data collections were performed on single crystals coated in paratone oil and mounted on Kaptan loops under a freezing stream of N₂. Data were collected using a Bruker QUAZAR diffractometer (1, 4) equipped with a Bruker MICROSTAR X-ray source of Mo Ka $(\lambda = 0.71073 \text{ Å})$ radiation and a APEX-II detector, or a Bruker MICROSTAR-H diffractometer (2) equipped with a Microfocus rotating anode X-ray source of Cu K α (λ = 1.54178 Å) radiation and a APEX-II detector. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker Apex2 v. 2009.1 [33]. Absorption corrections were applied using sADABS [34]. The space group was determined by examination of systematic absences, E-statistics, and successive refinement of the structure. The crystal structures were solved with siR-97 [35] and further refined with SHELXTL [36] operated with the WIN-GX interface [37]. The crystals did not show significant decay during data collection. Thermal parameters were refined anisotropically for all nonhydrogen atoms or ions in 1, 2, and 4. Hydrogen atoms were placed in ideal positions and refined using a riding model for all structures. Twinning in 1 required application of the twin law [001010 – 100] and yielded a final BASF of 0.245. Full crystal tables are located in the ESI.

2.9. Ligand field analysis

Ligand field theory (LFT) analyses of the electronic structure of the cobalt(II) complexes in **1–4** were performed with two approaches. The first approach used a crystal-field parameterization described by Ballhausen [38], while the second approach employed

the angular overlap model (AOM) [39-41]. Two programs were used for the computations resulting from these two approaches. Ligfield, written by Bendix et al. [42] (University of Copenhagen, Denmark) and DDN, available from Telser, were chosen because both programs use the complete d⁷ weak-field basis set including interelectron repulsions (Racah parameters B and C), spin-orbit coupling (SOC), and either crystal-field (for DDN, the parameters Dq, Ds, and Dt, [38]) or AOM ligand-field bonding parameters $(\varepsilon(\sigma) \varepsilon(\pi))$ [39,43]. DDN allowed input of single-electron d orbital energies, while Ligfield allowed the identification of the orbital occupancy and spin progeny of a given energy level (eigenstate). The two programs gave identical results when directly compared. An additional version of DDN, DDNFIT, was used to fit the experimental electronic absorption band positions to single-electron d orbital energy values calculated by iteration of Racah and either crystal-field (first approach) or AOM bonding parameters (second approach). Assignments were made as discussed in the manuscript (see also the ESI) and input into DDNFIT, along with the transition energies, for fitting. Definitive values of Racah parameters for free d-block ions are given by Brorson and Schäffer [44] and those of SOC constants by Bendix et al. [42]. Free-ion Racah and SOC parameters (in cm⁻¹) for Co(II) are $B = 988.6 \text{ cm}^{-1}$, $C = 4214 \text{ cm}^{-1}$ (C/B = 4.26) and $\zeta = 533$ cm⁻¹, respectively.

2.10. Other physical measurements

UV–Vis-NIR diffuse reflectance spectroscopy over the range of 4000–20000 cm⁻¹ was performed on pulverized microcrystalline samples using a CARY 5000 spectrophotometer interfaced to VARIAN WINUV software. Elemental (C, H, and N) analyses were performed at the Microanalytical Laboratory of the University of California, Berkeley.

3. Results and discussion

3.1. Syntheses and structures

Preparations of **1–4** proceeded via the addition of acetonitrile solutions of $CoCl_2$ (**1**, **3**, **4**) or Col_2 (**2**) to acetonitrile solutions containing excess amounts of the Ph_4P^+ salts of the respective phenyl-chalcogenide ligands. Upon work-up, high-quality crystals of **1–4** were obtained, allowing for the determination of the crystal structures of **1**, **2**, and **4** by single-crystal X-ray diffraction analysis.

All compounds possess pseudotetrahedral environments around the cobalt(II) centers with tetragonal distortions to give exactly or approximately D_{2d} symmetry (see Fig. 1). For **1**, a tetragonal compression of the cobalt(II) coordination sphere is observed, and the local CoO_4 symmetry is D_{2d} . The overall molecular symmetry for $[Co(OPh)_4]^{2-}$ in **1**, however, is actually lower than D_{2d} due to significant twisting of the phenyl rings about the Co-O bonds, which leads to C₁ molecular symmetry. In **2–4**, tetragonal elongations are instead observed in the cobalt(II) coordination spheres, but local symmetries of the cobalt(II) ions are D_{2d} , as in **1**. Of note here is that the K^+ cation in the structure of **2** appears to enforce the tetragonal elongation via $K^+ \cdots O$ interactions along the *c* axis of the crystal (see Fig. 2). For 2, the molecular symmetry assignment of D_{2d} for $[Co(OPh)_4]^{2-}$ is exact because the molecule resides on a crystallographic site of D_{2d} symmetry. In **3** and **4**, this same assignment is in contrast only approximate due to slight variations in the positions of the phenyl rings, though these variations are significantly less pronounced than in 1. Selected interatomic bond distances and angles are reported in Table 1. The average Co-O distances for 1 and 2 (1.963(8) and 1.959(2) Å respectively) are longer than calculated using the sum of ionic radii (Co-O: 1.93 Å) [45], possibly indicating relatively more ionic Co-E interactions than



Fig. 1. Observed structures of the $[Co(EPh)_4]^{2-}$ complexes in **1–4**. The molecules are viewed approximately down the S_4 molecular axis for **2–4**, but perpendicular to the S_4 axis for **1**. Counterions and hydrogen atoms have been omitted for clarity. Purple, orange, yellow, red, and gray spheres represent cobalt, selenium, sulfur, oxygen, and carbon atoms, respectively. (Color online.)

for **3** and **4**, where the average Co–S and Co–Se bond distances, 2.323(8) and 2.432(6) Å, respectively, are shorter than those predicted by the sums of their respective ionic radii (2.42 and 2.56 Å).

Surprisingly, the crystal structures of the homoleptic $[Co(OPh)_4]^{2-}$ complexes in **1** and **2** represent the first crystallographic characterization of this moiety as a mononuclear species. The first published preparations of Li₂Co(OPh)₄·4(THF), Na₂₋ Co(OPh)₄·5THF and K₂Co(OPh)₄·0.75 THF were reported in 1991, but the lack of structural characterization left in doubt whether the authors truly obtained isolated $[Co(OPh)_4]^{2-}$ moieties [46]. Some thirteen years later, it was questioned whether these mononuclear complexes were really even isolable, due to the tendency of the phenoxy oxygen to bridge cobalt(II) ions [47] and produce multinuclear structures [48]. Preparations of the related mononuclear complexes $[Co(OAr')_4]^{2-}$ and $[Co(OAr^F)_4]^{2-}$ (OAr' = 3,5-bis(tri-fluoromethyl)phenoxide; OAr^F = pentafluorophenoxide) were reported and their accessibility was attributed to the strongly electron-withdrawing substituents on the phenoxide ligands, which were argued to reduce the electron density around the phenoxide oxygen and prevent the formation of multinuclear assemblies [47]. The observation that in solution, low ratios of free PhS⁻ ligand to Co²⁺ ion favor multinuclear species rather than mononuclear $[Co(SPh)_4]^{2-}$ complexes [25] inspired the syntheses employed here with large ligand:cobalt molar ratios. The resulting compounds therefore suggest that the difficulties in isolating mononuclear $[Co(OPh)_4]^{2-}$ and related species can be circumvented by adjusting the reaction conditions.

3.2. Magnetic properties

Investigation of the magnetic properties of **1–4** first proceeded via the analysis of variable-temperature dc magnetic susceptibility data (see Fig. 3). At 300 K, the values of $\chi_{\rm M}T$ for **1–4** are 2.18, 3.67,



Fig. 2. Packing arrangement of $[Co(OPh)_4]^{2-}$ moieties in **2**. (a) Chain-like extended structure observed in **2**. The molecules are viewed along the crystallographic *a* axis, which is perpendicular to the coincident molecular S_4 and crystallographic *c* axes. Hydrogen atoms and Ph₄P⁺ counterions are omitted. Purple, dark red, light red, and gray spheres represent cobalt, potassium, oxygen, and carbon atoms, respectively. (b) Packing arrangement of chains and Ph₄P⁺ counterions, as viewed along the crystallographic *b* axis. Crystallographic axes are denoted. Note that the chains are aligned parallel. Hydrogen atoms are omitted for clarity. (Color online.)

3.11, and 2.99 cm³ K/mol, respectively, and are significantly greater than the expected value of 1.875 cm^3 K/mol for an isotropic S = 3/2 center. With decreasing temperature, $\chi_M T$ stays relatively constant down to 100 K, when $\chi_M T$ begins to drop, ultimately reaching 1.50, 2.55, 2.46, and 2.45 cm³ K/mol at 2 K for 1–4, respectively. For a system with one spin center, the temperature dependence of the $\chi_M T$ plot reflects the fluctuating populations of the M_S levels for the spin ground state. Anisotropic spins possess energy separations between their M_S levels that are often within an order of magnitude of $k_B T$ (k_B = Boltzmann constant), leading to a temperature dependence. Thus, the temperature dependent $\chi_M T$ values for 1–4 likely highlight the presence of an appreciable magnetic anisotropy.

To quantitate the axial zero-field splitting parameter *D*, the variable-temperature $\chi_M T$ data were fit to the following two-term Hamiltonian for a perfect powder of randomly oriented magnetic moments: $\hat{H} = D\hat{S}_z^2 + \mu_B g S \cdot H$. Here, *D* is the zero-field splitting, μ_B is the Bohr magneton, *g* is the Landé *g*-factor, \hat{S}_z the spin operator, *S* the spin, and *H* the magnetic field. Our model employs only these axial *D* and *g*-tensors ($g_z \neq g_x = g_y$), and ignores any transverse anisotropy (*E*) (see the Supplementary information for additional details regarding this choice of Hamiltonian). The best fits

Table 1 Selected interatomic distances (Å) and angles (°) for 1–4.

	1	2 ^a	3 ^b	4
Co-E	1.957(3)	1.959(2)	2.326(4)	2.436(1)
	1.957(3)	-	2.342(4)	2.429(1)
	1.967(3)	-	2.316(4)	2.425(1)
	1.970(3)	-	2.328(4)	2.437(1)
E-Co-E	111.4(2)	94.3(1)	95.6(2)	97.74(3)
	122.9(2)	-	97.0(2)	94.25(3)
	104.1(2)	117.5(1)	121.3(2)	116.89(3)
	106.9(2)	-	116.1(2)	114.95(3)
	104.4(2)	-	114.8(2)	113.55(3)
	105.9(2)	-	113.5(2)	120.96(3)
Co-E-C ^c	128(4)	125(1)	110(2)	108(2)
Co···Co ^d	12.10(1)	6.99(1)	10.46(1)	10.68(1)

In 2 this distance is along the chainlike structure.

^a D_{2d} site symmetry at Co(II) ion in this structure.

^b Taken from [25].

^c Average value.

^d Shortest Co...Co distance.



Fig. 3. Variable temperature dc magnetic susceptibility data for **1–4**. Data were collected on microcrystalline samples of **1–4** under a static 1000 Oe applied magnetic field. Black lines represent the best fits to the Hamiltonian $\hat{H} = D\hat{S}_z^2 + \mu_B g \boldsymbol{S} \cdot \boldsymbol{H}$, as decribed in the main body of the report.

 Table 2

 Spin Hamiltonian and Orbach relaxation parameters for 1–4.

-			-		
	gz	$g_{x,y}$	$D(cm^{-1})$	$U_{\rm eff}({ m cm}^{-1})$	$\tau_0(s)$
1 ^a	2.222(9)	2.118(6)	-11.1(3)	21(1)	$7(1) imes 10^{-10}$
2 ^b	2.958(3)	2.701(2)	-23.8(2)	-	-
3	2.960(3)	2.285(4)	-62(1)	21(1)	$1.0(3) imes 10^{-6c}$
4	2.953(3)	2.165(5)	-83(1)	19(1)	$3(1) imes 10^{-6}$
5 ^d	-		-	34.0(5)	$1.0(1) imes 10^{-9}$

^a Ac data obtained under 1400 Oe applied dc field.

^b Determination of $U_{\rm eff}$ and τ_0 ruled out by nonlinearity of Arrhenius plot.

^c Erroneously reported as $1.0(3) \times 10^{-7}$ s in Ref. [15].

^d Diamagnetic dilution of composition (Ph₄P)K[Co_{0.06}Zn_{0.94}(OPh)₄].

produced g_z , g_x , g_y , and *D* values for **1–4** as given in Table 2 (see Fig. 3 and SI for fitting details). The resulting *D* values show a marked dependence upon both the donor atom of the ligand, as well as the coordination environment. For $[Co(OPh)_4]^{2-}$ in **1**, the best fits afford $D = -11.1(3) \text{ cm}^{-1}$, indicating a $2D = 22.2 \text{ cm}^{-1}$ splitting between the ground $M_S = \pm 3/2$ levels and the excited $M_S = \pm 1/2$ levels. In contrast, for the more symmetric complex in **2**, a *D* value of $-23.8(2) \text{ cm}^{-1}$ was obtained. For the $[Co(EPh)_4]^{2-}$ complexes in **3** and **4**, with softer ligand donor atoms (E = S, Se,

respectively), a substantial increase in the magnitude of *D* is apparent, with the best fits revealing D = -62(1) and -83(1) cm⁻¹, respectively. These values suggest very large splittings between the $\pm 3/2$ and $\pm 1/2$ M_S levels, and therefore predict substantial energy barriers of 124 and 166 cm⁻¹ for spin inversion from $M_S = \pm 3/2$ to -3/2 and vice versa. We note that the *D* value obtained here is slightly lower in magnitude than those determined before [15–18]. The discrepancy may originate from the difficulty that ANISOFIT [49] has with spin systems possessing highly anisotropic *g*-tensors. Good agreement was observed between the isofield lines in the experimental magnetization data for **3** and simulations performed with the spin Hamiltonian parameters obtained from fitting the $\chi_M T$ plot (see Fig. S1).

Ac magnetic susceptibility measurements were conducted to check for the slow magnetic relaxation predicted by the derived negative *D* values of the *S* = 3/2 centers in **1–4** (see Figs. S2–S5 and Ref. [15]). For **1**, no slow magnetic relaxation is observed from 1 to 1500 Hz at 2 K under zero applied field, as evidenced by a featureless plot of the out-of-phase susceptibility (χ''_M) versus applied ac field frequency (see Fig. S2). Upon an application of a small dc field, however, a peak emerges for **1** that moves to lower frequency with increasing field, eventually plateauing at 65 Hz under a 1400 Oe dc field. In contrast, **2–4** exhibit slow magnetic relaxation at 2 K under zero applied field, with χ''_M peak maxima observed at 267, 28, and 3 Hz, respectively (see Figs. S3–S5 and [15]).

The ac field frequency at which peak maxima occur provides the magnetic relaxation time via the fitting of the variable-frequency ac susceptibility data to a Debye model [30] (see Figs. S7-S10). Further, the temperature dependence of the resulting relaxation times, when used to construct Arrhenius plots (see Fig. 4), allows for the determination of the magnitudes of the spin-reversal barriers giving rise to the slow magnetic relaxation. Here, a linear regime in the Arrhenius plot corresponds to a temperature range where the spin system relaxes via an Orbach process [50], whereas other relaxation processes, such as Raman and direct processes, produce curvature in the plot [50]. Further, when relaxation via quantum tunneling is operative, temperature independent regimes are observed in the Arrhenius plots, as the absorption or emission of phonons is not required. These latter relaxation mechanisms are predominantly encouraged by nuclear spin, intermolecular dipolar interactions, and transverse anisotropy [51]. For compound 1, a linear regime is observed in the Arrhenius plot over the entire temperature range of investigation at H_{dc} = 1400 Oe, corresponding to dominant Orbach relaxation with $U_{\rm eff} = 21 \, {\rm cm}^{-1}$ and $\tau_0 = 7 \times 10^{-10}$ s. In contrast, **2** and **4** display both temperaturedependent and temperature-independent regimes for τ , as also previously observed for **3** [15]. For **2**, however, τ appears to become strongly temperature dependent only after the peak has moved to a frequency above the range of our instrument. In contrast, for 4, the peak is temperature dependent within the frequency range accessible by the magnetometer, yielding $U_{\rm eff} = 19(1) \, {\rm cm}^{-1}$ and $\tau_0 = 3(1) \times 10^{-6}$ s.

The temperature independent regimes of the data collected for **2** and **4** are likely attributable to dipolar interactions between adjacent cobalt centers, as was discovered for **3**. Of note here is that the relaxation times for the temperature independent regimes of **2–4** follow the trend in the nearest Co—Co contacts determined for the crystalline phase (see Table 1). Additionally, the dipolar interactions appear to be strong enough in **2** that an estimation of the magnitude of U_{eff} from the high temperature regime of the Arrhenius plot is unfeasible. To achieve a better estimation of U_{eff} for this system, $K(Ph_4P)[Co_{0.06}Zn_{0.94}(OPh)_4]$ (**5**) was prepared by performing the synthesis of **2** starting from a 1:10 mixture of Col₂ and Znl₂ in a manner similar to that accomplished for **3** [15]. This magnetically dilute sample was then subjected to ac susceptibility measurements (see Figs. S6 and S10). The Arrhenius plot derived



Fig. 4. Arrhenius plots of the natural log of the relaxation time, τ , vs. the inverse temperature. (a) Data for **1-4**: relaxation time data for **2-4** were collected under zero applied dc field; data for **1** were collected under a 1400 Oe applied dc field. Black lines represent fits to Orbach relaxation processes, as described in the main body of the report. (b) Data for **2** and the 1:18 Co:Zn diluted compound, **5**, both collected under zero applied dc field, with Arrhenius fit to five highest-temperature data points.

from the $\chi_M^{"}$ data for **5** is comparatively temperature dependent over the entire temperature range of investigation (see Fig. 4b). At the highest temperatures, a linear fit to the Arrhenius plot affords $U_{\text{eff}} = 34.0(5) \text{ cm}^{-1}$ and $\tau_0 = 1.0(1) \times 10^{-9} \text{ s}$. Furthermore, the remnant curvature of the Arrhenius plot for **5** indicates relaxation processes other than the Orbach process are operative, even upon dilution of the complex, as was also observed for previously reported (Ph₄P)₂[Co_{0.09}Zn_{0.91}(SPh)₄] [15].

3.3. Solid-state electronic absorption spectra

To facilitate a ligand field theory analysis, UV–Vis-NIR diffuse reflectance spectra were collected at room temperature on pulverized crystals of **1–4** in the energy range 4000 to 20000 cm⁻¹ (see Fig. 5). There are two main features of each spectrum. Some relatively weak absorption bands appear below 6000 cm⁻¹ and three stronger, overlaid bands are found from 10000 to 20000 cm⁻¹ (see also Tables S3 and S4). Based on the previous work of Fukui et al. [16–18] these peaks result from d-d excitations. Thus, the general decrease in the energies of the transitions from **1** and **2** to **3** to **4**, suggests a decreasing ligand-field strength in the order of PhO⁻ > PhS⁻ > PhS⁻. Notably, despite having the same CoO₄ chromophore, the spectra for **1** and **2** are significantly different. The spectrum of **2** appears to be blue-shifted relative to that of **1** by \sim 300 cm⁻¹, except at the lowest edge of the set of peaks at \sim 6000 cm⁻¹. The contrast in the spectra for **1** and **2** is likely due to the two distinct types of tetragonal distortion in the structures of these complexes. A more quantitative analysis of the spectra is given in the following section to account for such distortions.

3.4. Ligand field analysis of solid state absorption spectra

The analyses of the spectra begin within an idealized T_d symmetry reference frame. The d^7 cobalt(II) center in T_d symmetry gives a ⁴A ground state and ⁴T₂, ⁴T₁(⁴F), and ⁴T₁(⁴P) excited states, listed in order of increasing energy, which can produce three strong absorptions in the UV-Vis-NIR spectra. In order to perform an analysis of the transitions of 1, 2, and 4, the observed transitions were assigned assuming idealized T_d symmetry and input along with transition energies to DDNFIT (see the ESI for details). Approximate values of 10Dq obtained for 1-4 via this method are -4350, -4656, -4200, and -5130 cm⁻¹, respectively, leading to the T_d d-orbital splittings depicted in Fig. 6a. Further, the Racah B parameters obtained from the best fits to the spectra for 1-4 are 763.3, 768.9, 590, and 408 cm⁻¹, respectively, suggesting considerable Co-E covalency on account of the deviations from the free cobalt(II) ion value of B (956 cm^{-1} [44]). Indeed, the trend also appears to follow the increasing softness of the PhE⁻ ligands, suggesting more Co-E covalency in 3 and 4 than 1 and 2. The presence of the K⁺ cation in the structure of **2** possibly engenders a more ionic Co–O interaction than 1 and thus a slightly larger B value. The analysis of the 10Dq values here would benefit from the accuracy afforded by knowledge of the energy of the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transition, which was not observed (see SI for more details regarding transition assignments). Note that tetragonal distortions of the coordination geometries of the cobalt(II) centers are observed in the crystal structures of these complexes. Such distortions necessitated the exploration of lower symmetry models for more realistic insight into the electronic structures of 1-4.

The structures of **1–4** undergo tetragonal distortions such that the local symmetries around the cobalt(II) centers are lowered from T_d to D_{2d} , or possibly even C_{2v} . Such a symmetry lowering splits the T_d d–d excitations into multiple transitions, yielding the heavily-featured peaks observed in Fig. 5. Given the overall similarities among the diffuse reflectance spectra, the transitions observed for **1**, **2**, and **4** were assigned in accord with the interpre-



Fig. 5. Solid-state diffuse reflectance spectrum for pulverized crystals of **1–4**. Data were collected at 298 K and 2 cm⁻¹ resolution. The absorption intensity is given in terms of the Kubelka–Munk transform of the % reflectance data.



Fig. 6. Relative energy diagrams for the 3d orbitals of the $[Co(EPh)_4]^{2-}$ complexes in **1–4**, as extracted from diffuse reflectance data. (a) Splitting of the 3d-orbitals for **1–4** assuming a simple T_d symmetry model. (b) Relative energies of the 3d orbitals assuming a reduced symmetry. Orbitals for **1** were determined from C_{2v} symmetry, while those for **2** were from D_{2d} symmetry and incorporating an estimated ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transition; orbitals for **3** correspond to those obtained by Fukui et al. [17]. Energies for **4** were determined in D_{2d} symmetry and incorporating an estimated ${}^{4}A_2 \rightarrow {}^{4}T_2$ transition. For **2**, **3**, and **4**, the d_{xz} and d_{yz} orbitals are degenerate, but depicted separately for ease of viewing.

tation by Fukui et al. of the polarized single-crystal UV–Vis absorption data obtained for **3** [17]. Two separate geometric models, assuming D_{2d} and C_{2v} symmetry, respectively, were applied to determine spectral assignments for the fitting (see the ESI for details). Observed absorption energies, their assignments, and calculated values from DDNFIT are listed in Tables S4 and S5. The fitted d-orbital splittings giving rise to the calculated excitation energies for **1–4** are listed in Table S6, while selected results are depicted in Fig. 6.

For 1–4, all models found the d_{7^2} orbitals to be lowest in energy. The next lowest energy orbitals tended to be the d_{xy} and $d_{x^2-y^2}$ orbitals, with d_{xz} and d_{yz} orbitals at higher energy. In particular, the energies of the d_{xy} and $d_{x^2-y^2}$ orbitals are very sensitive to the assignment and energy of the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transition (see ESI), which may not be observed in Fig. 5. The fitted energies of the two sets of $(d_{xy}, d_{x^2-y^2})$ and (d_{xz}, d_{yz}) orbitals may be split depending upon the use of D_{2d} or C_{2v} symmetry, with the D_{2d} symmetry model tending to produce the best fits, but with unrealistic degeneracies of the $(d_{xy}, d_{x^2-y^2})$ orbitals. Degeneracies of the (d_{xz}, d_{yz}) orbitals also result, but these are reasonable within an idealized D_{2d} symmetry, as closely approximated by 3 and 4 and crystallographically exact for 2. The averaged B values for 1-4 are 786(2), 841(12), 584(1) and 508(30) cm⁻¹, respectively, and follow the same trend observed for the simple T_d model. The current values, however, suggest a much stronger influence for the K⁺ ion in the Co-E interactions in 2 as compared to 1.

Application of the angular overlap model (AOM) to the interpretation of the above spectra was also performed, as this allowed the incorporation of the crystal structures in the analyses of the ligand fields in **1–4**. We applied two separate bonding models with metrical parameters determined from the crystal structures and summarized in Tables S7–S9. Each model assumed that the AOM parameters ($\varepsilon(\sigma)$, $\varepsilon(\pi)$) were equal for all four phenylchalcogenide ligands; a more detailed discussion of the models employed is given in the ESI. These parameters, once defined, were then adjusted to fit the diffuse reflectance and polarized absorption spectra [17]. The results are summarized in Tables S9 and S10. These fits, like those from DDNFIT, would benefit from definitive observations of the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transitions. Note, however, that the Racah *B* parameters obtained by AOM follow those obtained from the model using single electron d-orbitals. Here, values averaged over the two models utilized are $B \approx 770 \text{ cm}^{-1}$ for **1**, 550 cm⁻¹ for **3**, and 480 cm⁻¹ for **4**. For **1**–**4**, fits utilizing -only Co–E interactions were of significantly lower quality than those incorporating π -interactions, as dramatically demonstrated in **2**, for which a successful fit of the transitions was impossible using the -only model.

3.5. Impact of electronic structure on anisotropy and magnetization dynamics

The magnetic anisotropy of a given spin center without any first-order orbital angular momentum is determined by a secondorder interaction between the electronic ground state and excited states with anisotropy [52]. This interaction is responsible for whether or not the sign of D is positive or negative [53]. The magnitude of D is determined by two factors: it is inversely proportional to the energy separation between the electronic ground state and the anisotropic excited states contributing to D, and it is proportional to the square of the effective spin-orbit coupling constant, ζ , for the spin center. The earlier-highlighted ambiguity regarding the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transition precluded definitive determination of the energies of the d orbitals and of the excited states involved in the generation of the magnetic anisotropy for 1-4. In principle, the expected weaker ligand-fields induced by the diffuse PhS⁻ and PhSe⁻ ligands should ensure lower energy d-d excitations compared to 1 and 2, and this is indeed evidenced by the diffuse reflectance data

The results of our analyses of the d-orbital splittings for 1-4, though approximate, consistently suggest $(d_{x^2-v^2}, d_{xy})$ orbitals that are lower in energy than the (d_{xz}, d_{yz}) orbitals. Thus, it stands to reason that the lowest electronic excited state is likely an excitation between the nondegenerate $d_{x^2-y^2}$ and d_{xy} orbitals. This excitation, which connects two orbitals linked by the \hat{l}_z operator, would interact strictly with the \hat{S}_z spin components of the S = 3/2 moment and generate a negative contribution to the axial anisotropy [53,54]. Thus, weaker field ligands can be envisioned to ensure a lower energy splitting of the $d_{x^2-v^2}$ and d_{xv} orbitals, and produce lower-energy excited states, which would result in the increasing trend of |D| for **2–4**. That this correlation is not observed with our fitted parameters is likely attributable to the lack of direct observation of the lowest energy transition, which is crucial for the definitive evaluation of the relative energies of the d_{xy} and $d_{x^2-v^2}$ orbitals. However, the trend in *D* values for **1–4** follows the *B* parameters obtained, highlighting the importance of soft donor-atom ligands in the design of molecules with large magnetic anisotropies. Highly covalent systems may also potentially increase the anisotropy via a spin-orbit coupling enhancement mechanism from heavy diamagnetic ligand donor atoms, as has been observed in the past for chromium(III) complexes [55] and investigated on theoretical grounds for pseudotetrahedral complexes of nickel(II) [56]. The factors that affect the magnetic anisotropy of the cobalt(II) center in 1-4 are not limited to the influences of the ligand-field strength and/or donor atom spin-orbit coupling constants. As demonstrated by the difference in the anisotropies of 1 and 2, as well as previous studies of the anisotropies of the Me_4N^+ , Et_4N^+ , and Ph_4P^+ salts of $[Co(SPh)_4]^{2-}$ [18], the geometric arrangement of the ligands is very important for generating the appropriate d-orbital splitting necessary for large, negative D values.

The differing low-temperature zero-field magnetization dynamics for **1** and **2** could be attributed to two factors. The first difference, which would explain why **1** requires an applied field for slow magnetic relaxation to be observed, is that *D* is in fact positive for **1** but negative for **2**. In this case, the slow magnetic relaxation process for **1** under nonzero dc field could be an Orbach process made favorable by a bottlenecked direct relaxation process, as was suggested for the *D* > 0 complex [(3G)CoCI]⁺ [57]. The second difference between **1** and **2** of import to the generation of slow magnetic relaxation is the relatively lower-symmetry ligand field around the cobalt(II) center of **1** compared to **2**, which may open pathways for ground state magnetic tunneling at zero dc field that are not present for the rigorously D_{2d} -symmetric [Co(OPh)₄]^{2–} complex in **2**.

The ac magnetic susceptibility data for compounds **1–4** revealed a surprising independence of U_{eff} on *D*. Here, the relatively large τ_0 values for **3** and **4** suggest that pure thermal relaxation may not be observed in the temperature ranges of our investigations. If this is true, then the magnitudes of U_{eff} determined for **3** and **4** may in fact be lower estimates of the true values.

4. Conclusions and outlook

Slow magnetic relaxation at zero field has been demonstrated in the series of cobalt(II) complexes of the phenylchalcogenato ligands PhE^{-} (E = O, S, Se). Zero-field splittings in 1–4, determined by the fitting of variable-temperature magnetic susceptibility data, appear to be highly sensitive to the donor atoms of the ligand, as exemplified by significant increase in D along the nearly isostructural series of **2**, **3**, and **4**. Inspection of the electronic absorption spectra and d-orbital splittings highlight the importance of soft ligands in generating weak ligand fields with significant covalency (those with small Dq and small B) and thus larger zero-field splitting parameters. Indeed, this relationship in 1–4 is currently under investigation by *ab initio* methods [59]. However, the arrangement of the ligands around the metal ion is also clearly influential, as underlined by the differences in the magnetic properties of **1** and 2. The arrangements are also important to the low temperature magnetization dynamics, as 2 displays slow magnetic relaxation at zero field while **1** requires a modest applied field to observe a peak in the out-of-phase ac susceptibility. Further, the magnitudes of the relaxation barriers for **1–4** do not appear to follow the trend in *D* values, implying that there may be other factors that influence the low temperature magnetization dynamics. As suggested by the relatively large τ_0 values for **3** and **4**, the magnetic relaxation in **3** and 4 may not approach a completely thermally activated relaxation over the temperature range of our investigations, a possibility that we are currently studying. Also of particular interest is the role of vibronic coupling in reducing the magnitude of the effective barrier, as has been suggested for iron(II) complexes with both trigonal pyramidal and linear geometries [11,12,58]. Notably, the large magnetic anisotropies observed in the present complexes suggest that large barriers may also be obtained in single-chain magnets or even multinuclear single-molecule magnets which incorporate exchange-coupled four-coordinate cobalt(II) ions in D_{2d} coordination environments.

Acknowledgments

This research was funded by the National Science Foundation through Grant CHE-1111900.

Appendix A. Supplementary data

CCDC 919744, 919745, and 919746 contains the supplementary crystallographic data for $(Ph_4P)_2[Co(OPh)_4]\cdot(CH_3CN)$ (1), $K(Ph_4-P)[Co(OPh)_4]$ (2), and $(Ph4P)_2[Co(SePh)_4]$ (4). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.04.008.

References

- [1] N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, Y. Kaizu, J. Am. Chem. Soc. 125 (2003) 8694.
- [2] N. Ishikawa, Struct. Bond. 135 (2010) 211.
- [3] J.D. Rinehart, J.R. Long, Chem. Sci. 2 (2011) 2078.
- [4] J. Luzon, R. Sessoli, Dalton Trans. 41 (2012) 13556.
- [5] M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A.M. Talarico, M.-A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, Nat. Mater. 8 (2009) 194.
- [6] M.N. Leuenberger, D. Loss, Nature 410 (2001) 789.
- [7] A. Ardavan, O. Rival, J.J.L. Morton, S.J. Blundell, A.M. Tyryshkin, G.A. Timco, R.E.P. Winpenny, Phys. Rev. Lett. 98 (2007) 057201.
- [8] P.C.E. Stamp, A. Gaita-Ariño, J. Mater. Chem. 19 (2009) 1718.
- [9] D.E. Freedman, W.H. Harman, T.D. Harris, G.J. Long, C.J. Chang, J.R. Long, J. Am. Chem. Soc. 132 (2010) 1224.
- [10] W.H. Harman, T.D. Harris, D.E. Freedman, H. Fong, A. Chang, J.D. Rinehart, A. Ozarowski, M.T. Sougrati, F. Grandjean, G.J. Long, J.R. Long, C.J. Chang, J. Am. Chem. Soc. 132 (2010) 18115.
- [11] J.M. Zadrozny, M. Atanasov, A.M. Bryan, C.-Y. Lin, B.D. Rekken, P.P. Power, F. Neese, J.R. Long, Chem. Sci. 4 (2013) 125.
- [12] M. Atanasov, J.M. Zadrozny, J.R. Long, F. Neese, Chem. Sci. 4 (2013) 139.
- [13] P.-H. Lin, N.C. Smythe, S.I. Gorelsky, S. Maguire, N.J. Henson, I. Korobkov, B.L. Scott, J.C. Gordon, R.T. Baker, M. Murugesu, J. Am. Chem. Soc. 133 (2011) 15806.
- [14] D. Weismann, Y. Sun, Y. Lan, G. Wolmershauser, A.K. Powell, H. Sitzmann, Chem. Eur. J. 17 (2011) 4700.
- [15] J.M. Zadrozny, J.R. Long, J. Am. Chem. Soc. 133 (2011) 20732.
- [16] K. Fukui, H. Ohya-Nishiguchi, N. Hirota, Bull. Chem. Soc. Jpn. 64 (1991) 1205.
 [17] K. Fukui, N. Kojima, H. Ohya-Nishiguchi, N. Hirota, Inorg. Chem. 31 (1992) 1338
- [18] K. Fukui, H. Masuda, H. Ohya-Nishiguchi, H. Kamada, Inorg. Chim. Acta 238 (1995) 73.
- [19] H.A. Kramers, Proc. R. Acad. Sci. Amsterdam 33 (1930) 959.
- [20] S. Mossin, B.L. Tran, D. Adikari, M. Pink, F.W. Heinemann, J. Sutter, R.K. Szilagyi, K. Meyer, D.J. Mindiola, J. Am. Chem. Soc. 134 (2012) 13651.
- [21] D. Maganas, S. Milikisyants, J.M.A. Rijnbeek, S. Sottini, N. Levesanos, P. Kyritsis, E.J.J. Groenen, Inorg. Chem. 49 (2010) 595.
- [22] D. Maganas, S. Sottini, P. Kyritsis, E.J.J. Groenen, F. Neese, Inorg. Chem. 50 (2011) 8741.
- [23] D.G. Holah, D. Coucouvanis, J. Am. Chem. Soc. 97 (1975) 6917.
- [24] D. Swenson, N.C. Baenziger, D. Coucouvanis, J. Am. Chem. Soc. 100 (1978) 1932.
- [25] I.G. Dance, J. Am. Chem. Soc. 101 (1979) 6264.
- [26] J.M. McConnachie, J.A. Ibers, Inorg. Chem. 308 (1991) 1771.
- [27] M. Hatano, E. Takagi, K. Ishihara, Org. Lett. 9 (2008) 4527.
- [28] C.D. Baumgarner, A.H. Malen, S.D. Pastor, M.A. NabiRahni, Helv. Chim. Acta 75 (1992) 480.
- [29] P. Dowd, P. Kennedy, Synth. Commun. 11 (1981) 935.
- [30] K.S. Cole, R.H. Cole, J. Chem. Phys. 9 (1941) 341.
- [31] G.A. Bain, J.F. Berry, J. Chem. Educ. 85 (2008) 532.
- [32] R. de Levie, solveraid (Version 7), [Microsoft Excel Macro], 2007.
- [33] APEX2, v. 2009, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2009.
- [34] G.M. Sheldrick, saDaBs, Version 2.03, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2000.
- [35] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
- [36] G.M. Sheldrick, SHELXTL, Version 6.12, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2000.
- [37] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
- [38] C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962.
- [39] C.E. Schäffer, Struct. Bonding 5 (1968) 68.
- [40] C.K. Jørgensen, R. Pappalardo, H.-H. Schmidtke, J. Chem. Phys. 39 (1963) 1422.
- [41] C.E. Schäffer, C.K. Jørgensen, Mol. Phys. 9 (1965) 401.
- [42] J. Bendix, M. Brorson, C.E. Schäffer, Inorg. Chem. 32 (1993) 2838.
- [43] B.N. Figgis, M.A. Hitchman, Ligand Field Theory and its Applications, John Wiley & Sons, New York, 2000.
- [44] M. Brorson, C.E. Schäffer, Inorg. Chem. 27 (1988) 2522.

- [45] R.D. Shannon, Acta Crystallogr., Sect. A 32 (1976) 751.
- [46] A.I. Ibrahim, W. Gaube, W. Kalies, B. Witt, J. Prakt. Chem. 333 (1991) 397.
 [47] M.C. Buzzeo, A.H. Iqbal, C.M. Long, D. Millar, S. Patel, M.A. Pellow, S.A. [47] M.C. DUZZO, A.H. HQAI, C.M. DUIG, D. MIMAI, S. Fatci, M. Fellow, S.A. Saddoughi, A.L. Smenton, J.F.C. Turner, J.D. Wadhawan, R.G. Compton, J.A. Golen, A.L. Rheingold, L.H. Doerrer, Inorg. Chem. 43 (2004) 7709.
 [48] D.C. Bradley, R.C. Mehrotra, I.P. Rothwell, A. Singh, Alkoxo and Aryloxo Derivatives of Metals, Academic Press, New York, 2001.
 [40] M.D. G. B. Statistical Statistics of Metals, Academic Press, New York, 2001.
- [49] M.P. Shores, J.J. Sokol, J.R. Long, J. Am. Chem. Soc. 124 (2002) 2279.
- [50] R.L. Carlin, Magnetochemistry, Springer, New York, 1986.
- [51] D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268.
- [52] B.R. McGarvey, J. Telser, Inorg. Chem. 51 (2012) 6000.

- [53] D. Dai, H. Xiang, M.-H. Whangbo, J. Comput. Chem. 29 (2008) 2187.
- [54] R. Ruamps, L.J. Batchelor, R. Maurice, N. Gogoi, P. Jiménez-Lozano, N. Guihéry, C. de Graaf, A.-L. Barra, J.-P. Sutter, T. Mallah, Chem. Eur. J. 19 (2013) 950. [55] H.I. Karunadasa, K.D. Arquero, L.A. Berben, J.R. Long, Inorg. Chem. 49 (2010) 4738.
- [56] S. Ye, F. Neese, J. Chem. Theory Comput. 8 (2012) 2344.
- [57] J.M. Zadrozny, J. Liu, N.A. Piro, C.J. Chang, S. Hill, J.R. Long, Chem. Commun. 48 (2012) 3927.
- [58] M. Atanasov, D. Ganyushin, D.A. Pantazis, K. Sivalingam, F. Neese, Inorg. Chem. 50 (2011) 7460.
- [59] M. Atanasov, F. Neese, manuscript in preparation.