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The search for cobalt single-molecule magnets: A disk-like $Co^{III}Co^{II}_6$ cluster with a ligand derived from a novel transformation of 2-acetylpyridine

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ABSTRACT

The initial employment of 2-acetylpyridine, (py)(Me)CO, in Co cluster chemistry is reported, and the synthesis, crystal structure, and full magnetic study of $[Co_7(OH)_6(L)_6](ClO_4)_3 \cdot 1.6H_2O$ (**1**·$1.6H_2O$) are described; L^- is the anion of 2-(pyridine-2-yl)pentane-2-ol-4-one, $(py)(Me)C(CH_2COCH_3)(O)^-$, formed in situ through a crossed-aldol reaction in acetone under strongly basic conditions. The reaction of $Co(ClO_4)_2 \cdot 6H_2O$, (py)(Me)CO and NBu^n_4OMe (1:1:1.2) in acetone at room temperature under aerobic conditions affords **1**·$1.6H_2O$ in 35% yield. The mixed-valent cation possesses a wheel-shaped (or disk-like) structural motif comprising a central octahedral Co^{III} atom linked to six peripheral distorted octahedral Co^{II} atoms by six μ_3-OH^- groups; the six Co^{II} atoms on the rim are held together by six $\eta^1:\eta^1:\eta^1:\mu_2 \cdot L^-$ ligands and the oxygen atoms of the hydroxo groups. Variable-temperature, solid-state dc and ac magnetic susceptibility studies were carried out on **1**. The dc magnetic study of **1** shows a decline in the product $\chi_M T$ with decreasing T. The observation of out-of phase (χ''_M) ac susceptibility signals below ~4 K suggests that the $Co^{III}Co^{II}_6$ complex may be a single molecule magnet, and this was confirmed by single-crystal magnetization vs. dc field sweeps down to 0.04 K that exhibited hysteresis. The study reveals that each complex cation is a weak single-molecule magnet, but that there are also intermolecular interactions (also confirmed crystallographically) to create a 3D ordered lattice; this still gives some hysteresis at 5 K.

1. Introduction

Molecular 3d-metal cluster chemistry has been attracting intense interest from many groups around the world [1]. There are diverse reasons for this, including the esthetically pleasing structures that many such molecular clusters possess [2]. However, the two main reasons are the relevance of this area to bioinorganic chemistry [3] and to nanoscale magnetic materials. Restricting further discussion to the latter, the field involves the synthesis, among other compounds, of single-molecule magnets (SMMs) [4], also referred to occasionally as molecular nanomagnets. SMMs are molecular transition metal and/or lanthanide clusters that retain their magnetization below a blocking temperature in the absence of an applied magnetic field. This area thus represents a molecular, "bottom-up" approach to nanoscale magnets, complementary to the standard "top-down" approaches to nanoparticles of traditional magnetic materials, e.g. Fe, Fe_3O_4, CrO_2, which are atom based with d- (or f-) spin sites and with extended network bonding on the three dimensions. Due to their small size, SMMs straddle the classical/quantum interface in also displaying quantum tunneling of magnetization (QTM) [5], quantum phase interference [6] and exchange biasing [7], which are properties of the microscale. SMMs have been proposed for several potential applications [8]. The magnetic behavior of SMMs results from the combination of two intramolecular properties, a large ground spin state (S) with a large and negative Ising (or easy-axis) type of magnetoanisotropy, as measured by the axial zero-field splitting parameter D [4]. Many different classes of 3d-metal based SMMs are now known [4], and the majority continue to be in Mn polynuclear complexes containing at least some Mn^{III} centers, since the Jahn–Teller distortion of this high-spin $3d^4$ ion in octahedral geometry is a source of significant single-ion anisotropy of the easy axis type and thus of resulting anisotropy for the molecular cluster; in addition, Mn

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clusters will often possess large ground state *S* values, the other requirement for a SMM.

In the weak-exchange limit [9], the magnetic anisotropies on metal sites are much stronger than the exchange interactions between the sites. In this limit, the below equation is not applicable to the description of the energy barrier for reversal of magnetization, since it involves the total spin of the molecule, which is no longer a good quantum number. Such a situation is encountered in complexes involving 3d-metal ions with strong magnetic anisotropies, such as Co^{II}. In such complexes, the single-ion anisotropy and the exchange interaction can both contribute to the height of the barrier for reversal of magnetization [10]. Generally, however, the origin of SMM behavior of complexes in the weak-exchange limit is difficult to elucidate. *Thus, octahedrally coordinated* Co^{II}*, which has a large single ion anisotropy due to the orbitally degenerate* $^4T_{1g}$ *ground state, may potentially be a promising candidate for preparing SMMs,* and there are few reports in the literature of Co^{II}-based SMMs [11,12]. However, some examples demonstrate the difficulty in proving the SMM behavior as they do not show all the features observed in more clear-cut SMMs.

$$U = |D|S^2$$

As a result of the interest in SMMs, there is continuing demand for new synthetic methods that can yield new 3d-metal clusters and new SMMs with improved properties [13]. In the development of new synthetic routes to metal clusters, the choice of the ligands is always a key issue [14]. We and others have explored a wide variety of ligands that can simultaneously bridge and chelate, and might foster the formation of high nuclearity products. A popular such ligand is di-2-pyridyl ketone, $(py)_2CO$ (Scheme 1) [15]. There is a chemical characteristic that makes this molecule special as ligand; this is its carbonyl group. Water and alcohols (ROH), among other [16] nucleophiles, have been shown to add to the carbonyl group *upon coordination* of the carbonyl oxygen and/or the 2-pyridyl rings, forming the ligands $(py)_2C(OH)_2$ [the *gem*-diol form of $(py)_2CO$] and $(py)_2C(OR)(OH)$ [the hemiketal form of $(py)_2CO$], respectively (Scheme 1). The immense structural diversity displayed by the hundreds of clusters reported stems, in part, from the ability of $(py)_2CO_2^{2-}$, $(py)_2C(OH)(O)^-$ and $(py)_2C(OR)(O)^-$ to exhibit no less than ten distinct bridging modes ranging from μ_2 to μ_5 [15]. Employment of carboxylates and/or inorganic anions (Cl^-, NO_3^-, N_3^-, NCO^-, SO_4^{2-}, …) as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the synthesis of a variety of 3d-metal clusters with nuclearities ranging from 3 to 26 [15,17] and with interesting magnetic properties, including SMM behavior [17c,f].

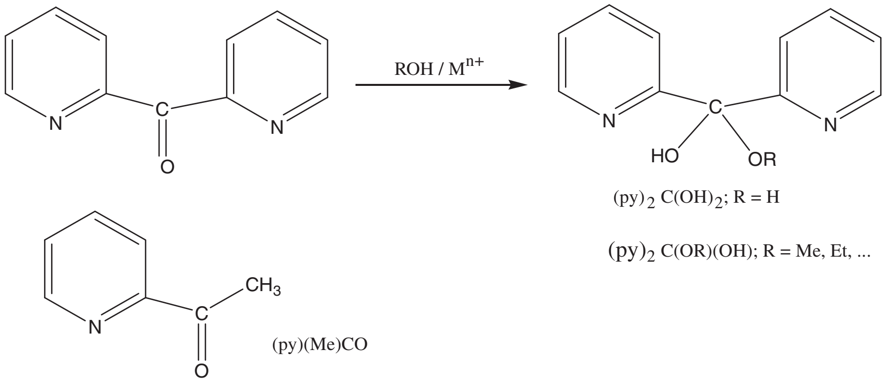
As part of our continuing search for new preparative routes to polynuclear species, we have recently turned our attention to polydentate ligands that present a structural similarity to $(py)_2CO$. Our goals are to investigate to what extent the use of such ligands might affect the identity of the obtained products compared with $(py)_2CO$ and to what extent this might thus prove to be a route to new cluster types. We have decided to start our efforts with the simple ligand 2-acetylpyridine, (py)(Me)CO (Scheme 1). This ligand, which has been widely used in coordination chemistry [18], is less bulky than $(py)_2CO$ and it lacks the second nitrogen atom. *We were particularly interested in investigating whether (py)(Me)CO would be capable of undergoing reactivity towards nucleophiles in the presence of metal ions.* For example, nucleophilic attack of H_2O and alcohols on the carbonyl carbon in the presence of metal ions could generate the anionic ligands $(py)(Me)CO_2^{2-}$, $(py)(Me)C(OH)(O)^-$ and $(py)(Me)C(OR)(O)^-$ [analogous to well explored ligands $(py)_2CO_2^{2-}$, $(py)_2C(OH)(O)^-$ and $(py)_2C(OR)(O)^-$, respectively] and yield clusters with new structural motifs. We were skeptical about this possibility. The reason is that there is electron attraction from one side of the carbonyl group by the 2-pyridyl heterocycle, but simultaneously there is electron release from the other side of the carbonyl group by the methyl group. The high reactivity of coordinated $(py)_2CO$ is generally attributed [15] to the electron-withdrawing character of both substituents on the carbonyl C atom, and thus the polarization of the C–C σ bonds connecting the 2-pyridyl groups to the central C atom is sufficient to increase its electrophilic nature and activate it for further reaction.

We herein report our first results on a new project which can be considered as an amalgamation of the two above discussed, italicized aspects. We describe the synthesis, crystal structure and physical characterization of a $Co^{III}Co^{II}_6$ SMM possessing an organic ligand that has derived from an impressive transformation of the initially used (py)(Me)CO. This work is a part of our continuing efforts on Co cluster chemistry [17i,19] and in the area of reactivity of coordinated ligands [15c,20].

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. *Warning*: Although no such behavior was observed during the present work, perchlorate salts are potentially explosive; such compounds should be used in small quantities, and treated with utmost care at all times.



Scheme 1. Some of the ligands discussed in the text. Note that $(py)_2C(OH)_2$, $(py)_2C(OR)(OH)$ and their anions do not exist as free species but exist only in their respective metal complexes. The ligand used in this work is (py)(Me)CO. M^{n+} is a metal ion and n is normally 2 or 3.

Microanalyses (C, H, N) were performed by the in-house facilities of the Chemistry Department at the University of Florida. IR spectra (4000–400 cm^{-1}) were recorded on a Perkin–Elmer 16 PC FT-spectrometer with the sample prepared as KBr pellet. Variable-temperature dc and ac magnetic susceptibility data were collected on an air dried sample of the $Co^{III}Co^{II}_6$ cluster (vide infra) using a Quantum Design MPMS-XL SQUID susceptometer equipped with a 7 T magnet and operating in the 1.8–300 K range (University of Florida). The sample was embedded in solid eicosane to prevent torquing. Pascal's constants [21] were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar susceptibility. Low-temperature (<1.8 K) hysteresis studies were performed at Grenoble using an array of micro-SQUIDs [22]. The high sensitivity of this magnetometer allows the study of single crystals of SMMs of the order of 10–500 μm. The field can be applied in any direction by separately driving three orthogonal coils. Crystals were maintained in mother liquor to avoid possible degradation and were covered with grease for protection during transfer to the micro-SQUID and subsequent cooling.

2.2. Compound preparation

2.2.1. $[Co_7(OH)_6(L)_6](ClO_4)_3{\cdot}1.6H_2O$ (**1**·$1.6H_2O$), where L^- is the anion of 2-(pyridine-2-yl)pentane-2-ol-4-one

To a stirred solution of (py)(Me)CO (0.056 mL, 0.5 mmol) in acetone (15 mL) was added a 20% (w/v) solution of NBu^n_4OMe in MeOH (0.84 mL, 0.6 mmol). The obtained solution was stirred for 15 min to obtain a pale yellow color and then solid $Co(ClO_4)_2{\cdot}6H_2O$ (0.183 g, 0.5 mmol) was added under vigorous stirring, which caused a color change to brown. The solution was stirred for a further 1 h, filtered and the filtrate was left undisturbed in an open flask. Slow evaporation of the solvent at room temperature gave pale green crystals of the product which were collected by filtration, washed with cold Me_2CO (3 × 2 mL) and dried in air. Yield: ∼35%. The solid analyzed as **1**·$3Me_2CO$. *Anal.* Calc. for $C_{69}H_{96}N_6Co_7O_{31}Cl_3$ (2056.42): C, 40.29; H, 4.71; N, 4.09. Found: C, 40.58; H, 4.25; N, 4.32%. IR (KBr pellet): ν = 3454sb, 2970w, 2923w,1678s, 1636m, 1602m, 1570m, 1508sh, 1436m, 1366m, 1298w, 1238w, 1144sh, 1120s, 1090sb, 1008w, 950w, 776m, 690m, 626m, 576m, 536m, 453w cm^{-1}.

2.3. Single-crystal X-ray crystallography

A crystal of **1**·$1.6H_2O$ with appropriate dimensions 0.14 × 0.13 × 0.08 mm was attached to a glass fiber using silicone grease. Data were collected on an Oxford Diffraction Xcalibur-3 diffractometer, equipped with a Sapphire CCD area detector, at 100 K using a graphite monochromated Mo Kα radiation. Complete crystal data and parameters for data collection and processing are listed in Table 1.

Several crystals of the compound were tested on the X-rays at 100 K. The diffraction quality of the crystals has proven to be moderate and structure determination was eventually carried out by means of the best data set collected. As a necessary compromise between resolution and data completeness we have used data up to 50° with a completeness of 99.4%.

The structure was solved by direct methods using SIR92 [23] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [24]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms (including the hydrogen atoms of the OH^- ligands) were located from a difference Fourier map and refined isotropically, while the remaining were placed in calculated ideal positions and refined as riding on their respective carbon atoms. The C(20) methyl group is disordered and has been modeled over two orientations with a domain ratio of 65:35 after competitive refinement. The Cl(2)O(14)O(15)O(16)O(17) perchlorate counterion exhibits orientational disorder; the Cl(2) atom lies on an inversion center, and the ion is distributed over two orientations (50:50) sharing a common center of gravity. The programs used were CrysAlis CCD [25] for data collection, CrysAlis RED [25] for cell and data refinement, WINGX [26] for crystallographic calculations, and MERCURY [27] and DIAMOND [28] for molecular graphics.

Table 1
Crystallographic data for complex **1**·$1.6H_2O$.

Formula	$C_{60}H_{81.20}N_6Co_7O_{31.60}Cl_3$
Formula weight	1910.97
Color, habit	pale green prisms
Crystal system	triclinic
Space group	*P*-1
a (Å)	12.687(2)
b (Å)	13.1673(17)
c (Å)	13.733(2)
α (°)	92.069(11)
β (°)	98.328(13)
γ (°)	109.218(13)
V (Å^3)	2134.7(5)
Z	1
ρ_{calc} (g cm^{-3})	1.486
Radiation, λ (Å)	Mo Kα, 0.71073
μ (mm^{-1})	1.499
T (K)	100(2)
Ranges h	−15 → 15
k	−15 → 15
l	−16 → 16
Measured reflections	28385
Unique reflections (R_{int})	7495 (0.161)
Reflections used ($I > 2\sigma(I)$)	2532
Parameters refined	534
Goodness-of-fit (GOF) (on F^2)	0.820
R_1[a] ($I > 2\sigma(I)$)	0.0595
wR_2[b] ($I > 2\sigma(I)$)	0.1058
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	1.054/−0.529

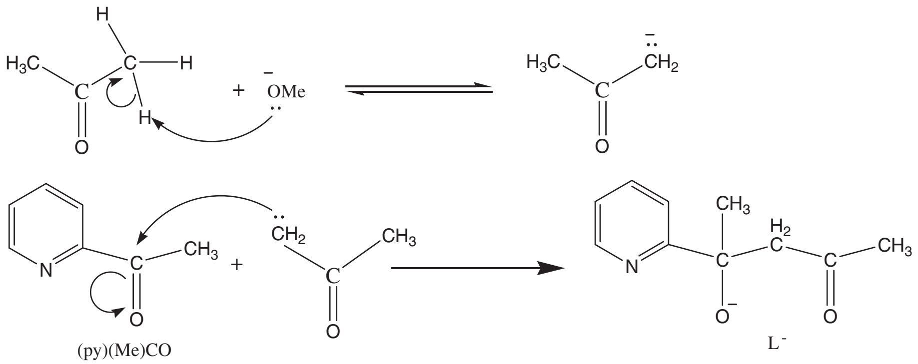
[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

3. Results and discussion

3.1. Synthetic comments and IR spectrum

One of our synthetic approaches to activate the proligand 2-acetylpyridine, (py)(Me)CO (Scheme 1), for further reactivity in cluster chemistry was to treat a cobalt(II) salt with (py)(Me)CO *under strongly basic conditions* in a protic solvent (H_2O or alcohols). We believed that the nucleophile (OH^- or RO^-) would add to the partially positive carbonyl C atom to eventually give one or possibly more of the coordinated ligands $(py)(Me)CO_2^{2-}$, $(py)(Me)C(OH)(O)^-$ or/and $(py)(Me)C(OR)(O)^-$. The results of this investigation will be reported in a forthcoming paper [29]. What we describe here is a product from this reaction system in *acetone*. This solvent was previously responsible for an impressive reactivity of coordinated $(py)_2CO$ that has led to structurally and magnetically interesting Ni^{II}_4 and Ni^{II}_5 clusters [15c].

Treatment of $Co(ClO_4)_2{\cdot}H_2O$ with a pale yellow solution containing (py)(Me)CO and NBu^n_4OMe (1:1:1.2) in Me_2CO at room temperature under aerobic conditions gave a brown solution from which the pale green cluster $[Co_7(OH)_6(L)_6](ClO_4)_3$ (**1**) was subsequently isolated in moderate yield. We were happy to see that a structurally interesting mixed-valent $Co^{III}Co^{II}_6$ complex had been isolated. At the same time we were surprised to realize that the ligand involved in the cluster was not one of the anticipated $(py)(Me)CO_2^{2-}$ or $(py)(Me)C(OH)(O)^-$, but instead the anion of 2-(pyridine-2-yl)pentane-2-ol-4-one, $(py)(Me)C(CH_2COCH_3)(O)^-$, abbreviated as L^- (Scheme 2). Assuming that the only product from



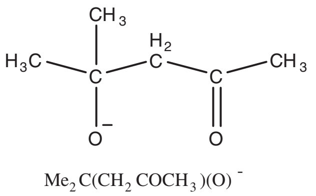
Scheme 2. The proposed simplified mechanism that leads to L$^-$, which is present as a ligand in cluster **1**.

this reaction system (most probably this is not the case here) is the Co^{III}Co^{II}$_6$, the formation of **1** can be summarized in Eq. (1).

$$\begin{aligned}&14Co(ClO_4)_2\cdot 6H_2O + 12(py)(Me)CO + 1/2O_2\\&\quad + 22NBu^n_4OMe + 12CH_3COCH_3\\&\quad \rightarrow 2[Co^{III}Co^{II}_6\{(py)(Me)C(CH_2COCH_3)(O)\}_6](ClO_4)_3\\&\qquad + 22NBu^n_4ClO_4 + 22MeOH + 73H_2O \qquad (1)\end{aligned}$$

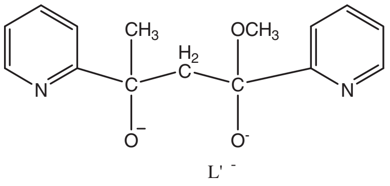
With hindsight we can propose a *simplified* mechanism for the formation of L$^-$ in Scheme 2. The C–H bonds adjacent to the carbonyl group of acetone are polar and important reaction sites [30]. The pK_a of a typical α-hydrogen (hydrogens on a carbon directly attached to a carbonyl are referred to as α-hydrogens) of a ketone is around 20; this makes it much more acidic than alkane C–H bonds (pK_a around 50), but much less acidic than alcohols (pK_a around 17) or carboxylic acids (pK_a around 4). The carbon–oxygen double bond of acetone is a strong electron withdrawing group and polarizes the adjacent C–H bonds, making α-hydrogens weakly acidic. Strong bases, such as MeO$^-$ used here, can abstract an α-hydrogen, forming an equilibrium with the corresponding carbanion [30]. Once formed, the carbanion is resonance-stabilized. Then the ligand L$^-$ forms through a mixed (or crossed)-aldol-reaction-type mechanism [30]. Once the carbanion $CH_3COCH_2^-$ is formed, it attacks the positive carbonyl carbon of (py)(Me)CO by a nucleophilic addition mechanism in an effort to neutralize itself. As the carbanion forms the C–C bond, the π electrons of the carbonyl group of (py)(Me)CO are transferred completely to the oxygen, forming an alkoxide ion. We want to emphasize that the reaction that leads to L$^-$ is *not* an aldol condensation [30]. In organic chemistry the products of the described reactions (aldols) are easily dehydrated, because the resulting double bond is conjugated with the carbonyl group, which creates an extended system of overlapping p orbitals, i.e., a resonance-stabilized structure. Possible reasons for the non-condensation of L$^-$ are the strongly basic medium which does not permit the existence of a neutral alcohol function and/or its stabilization by the Co^{II} ion.

Since both the ligand and the solvent have α-hydrogens, the formation of all four possible anionic ligands namely L$^-$, $Me_2C(CH_2COCH_3)(O)^-$ (from the aldol-type reaction of acetone with itself, Scheme 3), $(py)(Me)C\{CH_2CO(py)\}(O)^-$ (from the aldol-type reaction of 2-acetylpyridine with itself) and $(Me)_2C\{CH_2CO(py)\}(O)^-$ (from attack of the $(py)COCH_2^-$ carbanion on the carbonyl carbon of acetone) is possible, in principle, depending on the reaction conditions. The fact that pale green **1** is precipitated from a brown solution and the moderate yield of its preparation may suggest the existence of other Co species in solution. Note that the ligand $Me_2C(CH_2COCH_3)(O)^-$ (Scheme 3) has formed in situ through a Lewis acid-catalyzed reaction and has crystallographically identified in Ta^V complexes [31]. We are studying this possibility trying to isolate other products from the general Co^{II}/(py)(Me)CO/MeO$^-$ or OH$^-$ reaction system in acetone. A few years ago, Drew, Datta and coworkers [18c] observed another transformation of (py)(Me)CO upon its reaction with Cu sources. They attempted to grow single crystals of $[Cu^I\{(py)(Me)CO\}_2](ClO_4)_2$ by allowing Et_2O diffusion into its reddish solution *in MeOH*. They obtained dark green crystals of $[Cu^{II,II}(L')_2](ClO_4)_2$ instead, where L$'^-$ is the anionic ligand shown in Scheme 4; the $Cu^{II,II}_2$ complex can also be prepared by oxidizing the mononuclear Cu^I precursor with H_2O_2 *in MeOH*. The proposed mechanism involves attack of the generated, coordinated $(py)COCH_2^-$ carbanion on the carbonyl carbon of another coordinated (py)(Me)CO molecule, followed by nucleophilic attack of MeOH on the carbonyl carbon that formerly belonged to the carbanion [18c]. The presence of L$^-$ in **1** and L$'^-$ in $[Cu^{II,II}_2(L')_2](ClO_4)_2$ suggests a rich reactivity potential for (py)(Me)CO.



Scheme 3. The diacetone alcoholate ligand formed in situ through a Lewis acid-catalyzed aldol reaction and crystallographically identified in Ta^V complexes [31].

Another question we tried to answer is whether the formation of L$^-$ is metal-ion promoted (or assisted). With only the structure of **1** available, the answer is difficult. We tried to synthesize LH by the reaction of (py)(Me)CO and acetone in the presence of NBu^n$_4$OMe and in the absence of Co^{II} under several reaction conditions (reaction times, temperatures and reactant ratios), but to date we have obtained oily materials difficult to characterize. We have also failed to isolate the free ligand LH by treatment of **1** with dilute hydrochloric acid. Note that this compound is not known in organic chemistry.



Scheme 4. The ligand identified in the dinuclear complex $[Cu^{II,II}_2(L')_2](ClO_4)_2$; the complex was prepared by oxidation of the mononuclear precursor $[Cu^I\{(py)(Me)CO\}_2](ClO_4)_2$ with H_2O_2 [18c].

The IR spectrum of **1** exhibits a strong band at 3454 cm^{-1} assignable to $\nu(\mathrm{OH})_{\mathrm{OH}^-}$ [32]. The broadness and relatively low wavenumber of this band are both indicative of hydrogen bonding. A strong band at 1678 cm^{-1} is assigned to the ν(C=O) band of lattice acetone that is present in the analytically pure sample **1**·$3Me_2CO$, which was also used for IR spectroscopy; this band completely disappears when the sample is dried under vacuum for 3 h. We thus assign the band at 1636 cm^{-1} to the ν(C=O) mode of the coordinated L^- [33]. The in-plane deformation of the 2-pyridyl ring appears at 626 cm^{-1}; its presence above 620 cm^{-1} indicates the involvement of the ring-N atom in coordination [34]. The spectrum of **1** exhibits a strong band at 1090 cm^{-1} and a medium intensity band at 626 cm^{-1}, due to the $\nu_3(F_2)$ [ν_d(ClO)] and $\nu_4(F_2)$ [δ_d(OClO)] modes, respectively, of the uncoordinated T_d ClO_4^- ions [35]; the broad character and splitting of the band at 1090 cm^{-1} (manifested by the appearance of a band at 1120 cm^{-1} and a shoulder at 1144 cm^{-1}) indicates the involvement of ClO_4^- ions in hydrogen bonding [36], also established by X-ray crystallography (vide infra).

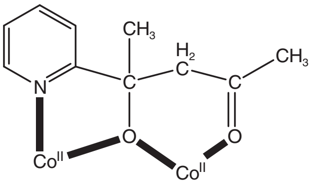
Table 2
Selected interatomic distances (Å) and angles (°) for **1**·$1.6H_2O$.

Distances			
Co(1)···Co(2)	3.116(1)	Co(2)–O(7)	2.146(6)
Co(1)···Co(3)	3.120(1)	Co(2)–O(8′)	2.115(5)
Co(1)···Co(4)	3.130(1)	Co(2)–N(1)	2.118(7)
Co(2)···Co(3)	3.110(2)	Co(3)–O(1)	1.970(5)
Co(3)···Co(4)	3.124(1)	Co(3)–O(2)	2.182(6)
Co(2)···Co(4′)	3.133(2)	Co(3)–O(3)	1.997(5)
Co(2)···Co(2′)	6.232(2)	Co(3)–O(8′)	2.142(5)
Co(3)···Co(3′)	6.240(2)	Co(3)–O(9)	2.115(6)
Co(4)···Co(4′)	6.261(2)	Co(3)–N(2)	2.122(8)
Co(1)–O(7)	1.924(5)	Co(4)–O(3)	1.963(6)
Co(1)–O(8)	1.927(6)	Co(4)–O(4)	2.194(6)
Co(1)–O(9)	1.921(5)	Co(4)–O(5′)	1.987(5)
Co(2)–O(1)	1.989(5)	Co(4)–O(7′)	2.133(5)
Co(2)–O(5)	1.984(5)	Co(4)–O(9)	2.141(5)
Co(2)–O(6)	2.191(6)	Co(4)–N(3′)	2.113(6)
Angles			
O(7)–Co(1)–O(9)	95.8(2)	Co(1)–O(1)–Co(2)	99.8(2)
O(8′)–Co(1)–O(9)	84.2(2)	Co(1)–O(8′)–Co(2)	100.8(2)
O(7)–Co(1)–O(8)	95.4(2)	Co(1)–O(8′)–Co(3)	100.0(2)
O(1)–Co(2)–O(5)	174.4(2)	Co(1)–O(9)–Co(3)	101.1(2)
O(6)–Co(2)–O(7)	158.4(2)	Co(1)–O(7′)–Co(4)	100.9(2)
O(8′)–Co(2)–N(1)	155.0(2)	Co(1)–O(9)–Co(4)	100.7(2)
O(1)–Co(3)–O(3)	175.0(2)	Co(2)–O(1)–Co(3)	103.5(2)
O(2)–Co(3)–O(8′)	157.7(2)	Co(2)–O(8′)–Co(3)	93.8(2)
O(9)–Co(3)–N(2)	154.6(3)	Co(3)–O(3)–Co(4)	104.2(3)
O(3)–Co(4)–O(5′)	175.3(2)	Co(3)–O(9)–Co(4)	94.5(2)
O(4)–Co(4)–O(9)	161.0(2)	Co(2)–O(5)–Co(4′)	104.2(3)
O(7′)–Co(4)–N(3′)	155.3(3)	Co(2)–O(7)–Co(4′)	94.1(2)

Primed atoms are related to the unprimed ones by the symmetry operation 2 − *x*, 2 − *y*, 2 − *z*.

3.2. Description of structure

A partially labeled plot of the $[Co_7(OH)_6(L)_6]^{3+}$ cation that is present in complex **1** is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 2.



Scheme 5. The coordination mode of the anion of 2-(pyridine-2-yl)pentane-2-ol-4-one (L^-) in cluster **1**.

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. The structure consists of heptanuclear $[Co_7(OH)_6(L)_6]^{3+}$ cations, ClO_4^- counterions and solvate H_2O molecules; the latter two will not be further discussed. The cation possesses a wheel-shaped structure comprising a central Co^{III} atom [Co(1)], linked to six peripheral Co^{II} atoms by O atoms provided by the μ_3-OH^- groups. Co(1) is located on an inversion center and there are thus four crystallographically independent Co centers. The six metal ions on the rim are held together by six η^1:η^2:η^1:μ_2·L^- ligands (Scheme 5) and six hydroxo oxygen atoms. The multiple *n* value indicates the hapticity of the alkoxide oxygen donor atom, that is, the number of metal ions to which this donor atom is attached. Each μ_3-OH^- group bridges the central Co^{III} atom with two peripheral Co^{II} atoms and also a pair of Co^{II} atoms on the rim. The metallic skeleton describes a centered, almost perfect hexagon of six edge-sharing triangles with the Co^{III} atom at the center; the $Co^{II}\cdots Co^{II}\cdots Co^{II}$ "angles" involving neighboring metal ions are in the 119.5(1)–120.3(1)° range. The skeleton can be also regarded as six defective cubanes arranged in a circular manner, each sharing two faces. The cation is disk-like with the seven Co centers nearly coplanar [maximum deviation of 0.0162 Å by Co(3)], see Fig 2. The μ_3-OH^- groups serve as the "bottom" for the formation of the disk-like structure. The core is $\{Co^{III}Co^{II}_6(\mu_3\text{-OH})_6(\mu_2\text{-OR}')_6\}^{3+}$, where $R'O^-$ is L^-.

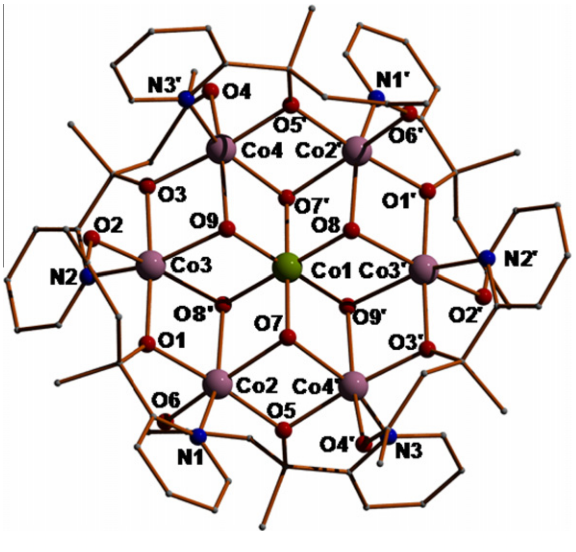


Fig. 1. Partially labeled plot of the cation present in $[Co_7(OH)_6(L)_6](ClO_4)_3$·$1.6H_2O$ (**1**·$1.6H_2O$). Primed and unprimed atoms are related by the crystallographic inversion center. O(7), O(8), O(9) and their symmetry equivalents are the hydroxo oxygen atoms. O(1), O(3), O(5) and their symmetry equivalents are the alkoxide oxygen atoms of the L^- ligands. O(2), O(4), O(6) and their symmetry equivalents are the ketone-type oxygen atoms of the L^- ligands.

The $[Co_7(OH)_6(L)_6]^{3+}$ cation is mixed-valent. Charge considerations, inspection of the metric parameters and BVS calculations [37] identify Co1 as the Co^{III} atom and the others as Co^{II} atoms. The central Co(1) center has all Co–O distances practically the same (∼1.93 Å); such bond lengths are indicative of a low-spin octahedral Co^{III} atom [10,19b,c]. The Co(2,3,4)–O [average 2.083(6) Å] and Co(2,3,4)–N [average 2.118(8) Å] bond distances are characteristic of high-spin octahedral Co^{II} centers [10,17i,19]. The short bonds between Co^{II} and the alkoxide oxygens [Co^{II}–O(1,3,5) = 1.963(5)–1.997(5) Å] and the rather long bonds to the ketonic oxygens [Co^{II}–O(2,4,6) = 2.182(6)–2.194(6) Å] are noteworthy. BVS calculations for the peripheral Co(2), Co(3) and Co(4) ions give the values of 2.09, 2.10 and 2.11, respectively, confirming their +II valence state. Distinguishable C–O single [C–O(1,3,5) = 1.370(8)–1.403(9) Å] and C=O double bonds [C–O(2,4,6) = 1.227(12)–1.243(10) Å] are also evident, confirming the description of L^- as containing one single and one double carbon–oxygen bond (Scheme 2).

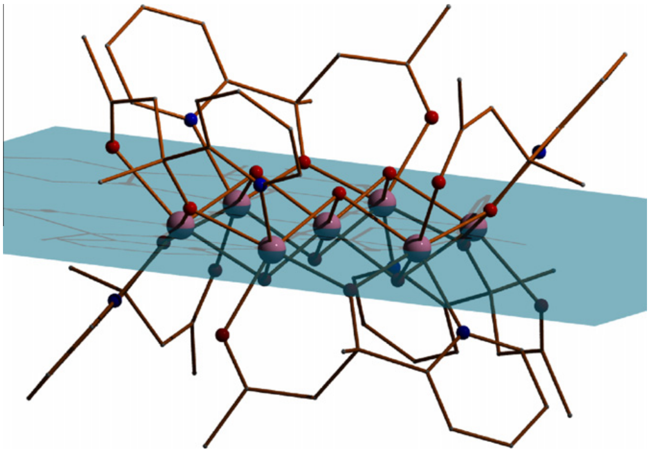
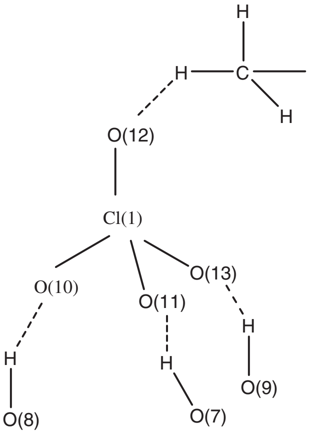


Fig. 2. An unlabeled view of the cation $[Co_7(OH)_6(L)_6]^{3+}$ of complex **1** emphasizing the coplanarity of the seven metal ions.

The six-coordinate Co^{III} atom, which is coordinated by six hydroxo oxygen atoms, possesses a slightly distorted octahedral geometry; the *cis* O–Co(1)–O angles are in the 84.2(2)–95.8(2)° range. The ring Co^{II} ions exhibit identical $Co^{II}O_5N$ chromophores and display a distorted octahedral geometry, the largest and smallest *trans* coordination angles having a difference of 19.4(2), 20.4(3) and 20.0(3)° for Co(2), Co(3) and Co(4) respectively. The bridging $Co^{III}–O_{hydroxo}–Co^{II}$, $Co^{II}–O_{hydroxo}–Co^{II}$ and $Co^{II}–O_{alkoxide}–Co^{II}$ bond angles are in the ranges of 99.8(2)–101.1(2), 93.8(2)–94.5(2) and 103.5(2)–104.2(2)°, respectively.

The crystal structure of $\mathbf{1}\cdot 1.6H_2O$ is stabilized by strong hydrogen bonds involving the hydroxo groups [O(7), O(8), O(9), O(7′), O(8′), O(9′)] as donors and three oxygens of each symmetry-related ClO_4^- anion [O(10), O(11), O(13), O(10′), O(11′), O(13′)] as acceptors. The fourth oxygen atom [O(12), O(12′)] of this perchlorate is involved in a non classical hydrogen bond [38] with a methyl group [C(27)] of a neighboring Co_7 cation. Thus the Cl(1)O(10)O(11)O(12)O(13) anion participates in four hydrogen bonding interactions (Scheme 6). Metric parameters are summarized in Table 3. O(12) also participates in weaker supramolecular interactions with two pyridyl carbon atoms [C(2)···O(12) $(1-x, 1-y, 2-z)$ = 3.513(3) Å, C(24)···O(12) $(1-x, 1-y, 2-z)$ = 3.554(3) Å], not listed in Table 3 and not shown in Scheme 6. All these interactions create a 3D network.

Complex **1** is a new member of a relatively large family of discrete, non organometallic Co_7 clusters [10,12,39,40]. Few of the Co_7 clusters have a wheel-shaped (or disk-like) metal topology similar to that found in **1**. The metal oxidation levels in these complexes are Co^{II}_7 [12a,c,12d,40a,b,d,f], $Co^{II}_6Co^{III}$ [40c], $Co^{II}_3Co^{III}_4$ [10] and $Co^{II}_4Co^{III}_3$ [12b,40e]. Thus complex **1** is becoming the third member of this subfamily with the $Co^{II}_6Co^{III}$ oxidation level; the first two ones are salts of the anions $[Co^{III}Co^{II}_6(thme)_2(O_2CCMe_3)_8Br_2]^-$ and $[Co^{III}Co^{II}_6(thme)_2(O_2CMe)_8(H_2O)_4]^-$, where $thme^{3-}$ is the trianion of 1,1,1-tris(hydroxymethyl)ethane [40c]. Most of the Co_7 clusters with the wheel-shaped topology have been recently reported; we have listed the structurally *and* magnetically characterized complexes of this type in Table 4 for a convenient comparison of their formulae and pertinent magnetic data; an analogous summary has been just reported by Kurmoo and coworkers [12d]. It should be mentioned at this point that the wheel-shaped or disk-like structural motif observed in **1** is not confined to Co chemistry; it has been also observed in other heptanuclear 3d-metal clusters, most of which are mixed-valent [15b,41], but also as a structural subunit in an 1D $\{Co^{II}_5Co^{III}_3\}_n$ coordination polymer [42].



Scheme 6. The participation of the Cl(1)O(10)O(11)O(12)O(13) anion in four hydrogen bonding interactions in the crystal structure of $\mathbf{1}\cdot 1.6H_2O$.

3.3. Magnetic properties

Variable-temperature dc magnetic susceptibility studies were performed on a powdered polycrystalline sample of dried complex **1** in a 0.1 T field and in the 5.0–300 K range. The data are shown as a χ_MT versus T plot in Fig. 3. The χ_MT product gradually decreases from a value of 17.31 $cm^3\,mol^{-1}$ K at 300 K to 13.80 $cm^3\,mol^{-1}$ K at 50 K, before a further rapid fall below 50 K to reach 4.63 $cm^3\,mol^{-1}$ K at 5.0 K. The unpaired electrons of the cation are on the six, high-spin Co^{II} centers, because the central Co^{III} ion is low-spin diamagnetic (t_{2g}^6, $S = 0$).

Explanation of the magnetic behavior of Co^{II} complexes is always difficult, due to the orbitally degenerate ground state of the ion when six-coordinate. For this reason, derivation of the magnitude of the exchange interactions between the Co^{II} centers is very difficult.

The observed value of χ_MT at 300 K corresponds to that for six noninteracting Co^{II} ($S = 3/2$) centers with $g = 2.48$, the latter value indicating a significant orbital contribution. The decrease in χ_MT observed for **1** as T decreases can be attributed to the depopulation of the split $^4T_{1g}$ ground state of the octahedral Co^{II} single ions [11e,40c,42], combined with the large single-ion zero-field splitting of each octahedral Co^{II} and/or intermolecular antiferromagnetic coupling at very low temperatures. Fig. 3 clearly suggests that the ground state is not $S = 0$. A possible explanation for the observed behavior is that the compound is weakly ferromagnetic with each Co^{II} having an effective $S' = 1/2$ spin at low temperatures [10,11h]. Magnetization studies do not help; no saturation is seen up to 5 T (50 kG) at 2 K (Fig. 4). Given the high anisotropy of the ions present and the relatively high nuclearity of the cluster, this is unsurprising [11e].

Alternating current (ac) studies were performed for **1** in the 1.8–16 K range using a 3.5 G ac field oscillating at frequencies (v) in the 5–1000 Hz range. If the magnetization vector can relax fast enough to keep up with the oscillating field, then there is no imaginary (out-of-phase) susceptibility signal (χ_M'') and the real (in-phase) susceptibility (χ_M') is equal to the dc susceptibility at a given temperature. However, if the barrier to magnetization relaxation is significant compared to the thermal energy (kT), then χ_M' decreases and there is a non-zero χ_M''; in addition, χ_M'' will be frequency-dependent. Such frequency-dependent χ_M'' signals are a strong evidence of superparamagnetic-like properties of a SMM, but by themselves do not prove the SMM behavior [17e,43] because intermolecular interactions and phonon bottlenecks can also give such signals. Ac data for complex **1** are shown in Figs. 5 and 6.

$\chi_M'T$ decreases with decreasing temperature below 15 K, reaching a near-plateau value of ~4.8 $cm^3\,mol^{-1}$ K at ~5 K, in agreement

Table 3
Hydrogen bonding interactions in the crystal structure of **1**·1.6H_2O.

Interaction	D···A (Å)	H···A (Å)	D–H···A (°)	Symmetry operator of A
O(7)–H(7)···O(11)	2.973(3)	2.19(1)	156.3(1)	2 − *x*, 1 − *y*, 2 − *z*
O(8)–H(8)···O(10)	3.001(3)	2.18(1)	174.7(1)	2 − *x*, 1 − *y*, 2 − *z*
O(9)–H(9)···O(13)	2.928(3)	2.09(1)	172.8(1)	2 − *x*, 1 − *y*, 2 − *z*
C(27)–H(27)···O(12)	3.377(3)	2.46(1)	160.2(1)	1 − *x*, 1 − *y*, 2 − *z*

A = acceptor atom; D = donor atom.

Table 4
Chemical formulae, selected structural features and magnetic summary for wheel-shaped or disk-like Co_7 clusters comprising a central Co ion (Co_6 + Co).

Complex[a]	μ_3-X bridge[b]	Co-(μ_3-X)-Co (°)	Co-(μ_2-Ψ)-Co[c,d] (°)	Magnetic behavior	Ref.
$[Co^{II}_7(OMe)_3(N_3)_9(bzp)_6]^{2+}$	MeO^-, N_3^-	93.2–95.3	99.1	F/SMM	[12a]
$[Co^{II}_7(N_3)_6(hdeo)_6]^{2+}$	N_3^-	96.2–98.6	107.5	F/SMM	[12c]
$[Co^{II}_7(OMe)_6(immp)_6]^{2+}$	MeO^-	95.4–99.0	102.9	F	[40f]
$[Co^{II}_7(OH)_6(L^1)_6]^{2+}$	OH^-	96.4–98.6	102.6	F	[12d]
$[Co^{II}_7(OMe)_6(L^1)_6]^{2+}$	MeO^-	94.4–98.2	102.7	F	[12d]
$[Co^{II}_7(N_3)_6(L^1)_6]^{2+}$	N_3^-	94.9–98.8	104.2	F/SMM	[12d]
$[Co^{III}Co^{II}_6(thme)_6(O_2CCMe_3)_8Br_2]^-$	RO^-	95.2–101.2	85.1	F	[40c]
$[Co^{III}Co^{II}_6(OH)_6(L)_6]^{3+}$	OH^-	93.8–101.1	104.0	F/SMM	This work
$[Co^{II}_3Co^{III}_4(OMe)_6(L^2)_6]$	RO^-	89.4–101.5	103.9	F	[10]
$[Co^{II}_4Co^{III}_3(HL^3)_6(NO_3)_3(H_2O)_3]^{2+}$	RO^-	95.3–97.7	105.2	F/SMM	[12b]
$[Co^{II}_4Co^{III}_3(dea)_6(dea)_6(O_2CMe)_3]^{2+}$	RO^-	94.4–97.9	106.8	F	[40e]

Abbreviations: AF, antiferromagnetic exchange interactions, bzp, 2-benzoylpyridine, H_2dea, diethanolamine, F, ferromagnetic exchange interactions, Hdeo, 2-hydroxy-[1,2-di(pyridinyl)]ethane-1-one, Himmp, 2-iminomethyl-6-methoxy-phenol, HL, 2-(pyridine-2-yl)pentane-2-ol-4-one, HL^1, 2-methoxy-6-[(methylimino)methyl]phenol, H_2L^2, 1,1,1-trifluoro-7-hydroxy-4-methyl-5-aza-hept-3-en-2-one, H_3L^3, 2-amino-2-(hydroxymethyl)propane-1,3-diol, SMM, single-molecule magnet, H_3thme, 1,1,1-tris(hydroxymethyl)ethane.

[a] Counteranions and solvate molecules have been omitted.

[b] R is part of the polydentate organic ligand.

[c] Mean value.

[d] Ψ is most often a donor atom coming from the polydentate ligand.

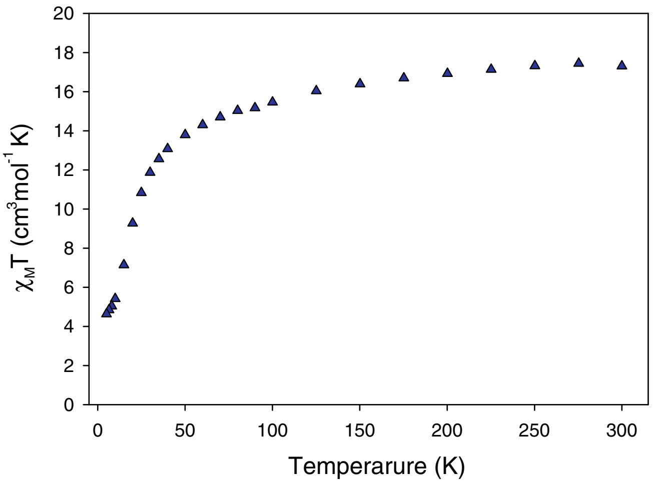


Fig. 3. $\chi_M T$ vs T plot for 1 in a 0.1 T dc field.

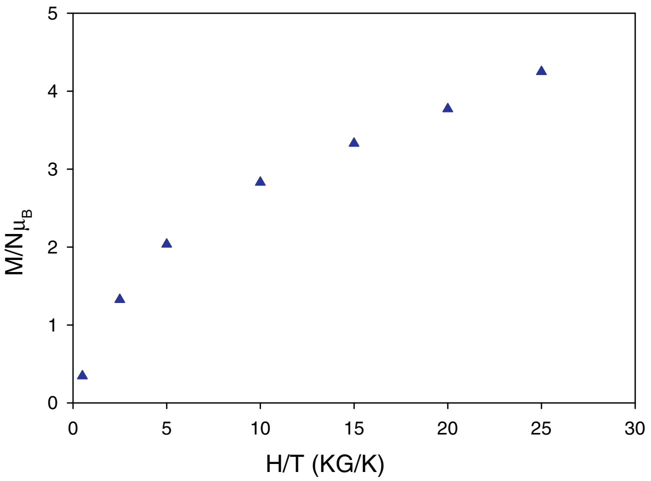


Fig. 4. Plot of reduced magnetization vs. *H*/*T* for complex **1** at 2 K and in the magnetic field range 0.1–5.0 T.

with the dc data of Fig. 3; however, there is a rapid frequency dependent decrease below ~4 K. The frequency-dependent decrease in $\chi_M'T$ is accompanied by the appearance of frequency-dependent χ_M'' signals below ~4 K. Only the tails of peaks are visible above 1.8 K (the operating limit of our SQUID magnetometer); except for the 1000 Hz signal, the peak maxima clearly lie at lower temperatures. This is suggestive of the slow magnetization relaxation of a SMM.

To confirm a possible SMM behavior for **1**, magnetization vs. dc field sweeps were carried out at temperatures below 1.8 K to look for magnetization hysteresis, the diagnostic property of a magnet. Studies were performed on single crystals of **1**·1.6H_2O at temperatures down to 0.04 K using a micro-SQUID apparatus [22]. The obtained magnetization vs. applied dc magnetic field responses are shown in Fig. 7, which include both a temperature dependence at a constant field sweep rate of 0.002 T/s and a field sweep rate dependence at a constant temperature of 0.04 K. The former (Fig. 7, top) shows hysteresis loops becoming evident in the scans at 5 K, but they have a rather small coercivity. The latter (Fig. 7, bottom) shows that at 0.04 K there is both a small scan-rate-independent and scan-rate-dependent coercivity, the latter increasing with increasing field sweep rate, as expected for the superparamagnet-like properties of a SMM below its blocking temperature (T_B). The loops thus confirm that complex **1**·1.6H_2O is a new addition to the family of Co^{II}-based SMMs [11,12] and that are also intermolecular interactions to give an ordered network.

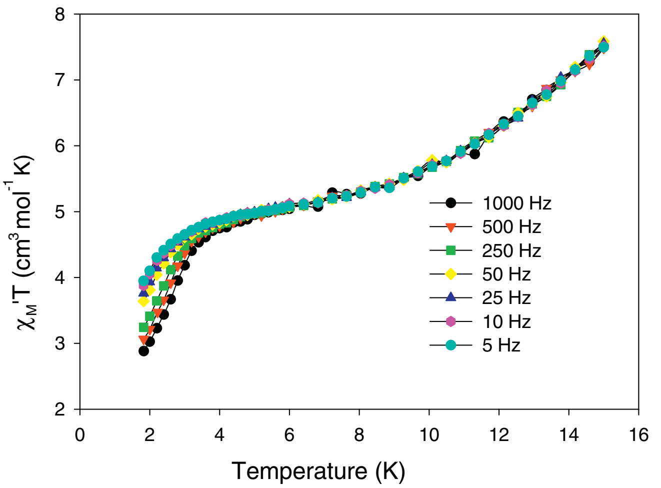


Fig. 5. In phase ac susceptibility (χ'_M) signals, plotted as $\chi'_M T$ vs. T, for complex **1** in a 3.5 G field oscillating at the indicated frequencies.

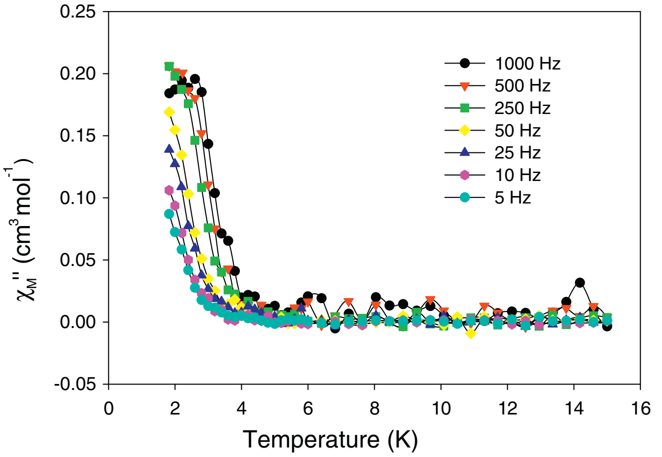


Fig. 6. Out-of-phase ac susceptibility (χ''_M) signals vs. T for complex **1** in a 3.5 G field oscillating at the indicated frequencies.

The most dominating feature of the hysteresis loops in Fig. 7 is the large step at zero-field due to QTM through the anisotropy barrier. The large zero-field step indicates that QTM in zero field is fast. It is also evident that there are intermolecular interactions (also confirmed by the crystal structure of the compound, vide supra) to give a 3D-ordered lattice, which still gives some hysteresis even at 5 K. It is thus likely that the overall behavior of **1** is due to a combination of a small intrinsic barrier to magnetization relaxation for each Co_7 cation and relatively strong exchange interactions between the neighboring Co_7 cations mediated through the ClO_4^- ions [43]. We have noted in the past [44] that the latter half of this statement does not contradict the former: no assembly of SMMs molecules in a crystal can ever be completely free of all possible interactions with neighbors, and the critical question is then exactly how strong are these interactions from a magnetic point of view. If they are weak, as for example they are in $[Mn^{III}_8Ce^{IV}(O_2CMe)_{12}(H_2O)_4]$ [44], then they are merely a perturbation of the single-molecule magnetic properties, and such compounds can be described as exchange-biased SMMs [7]. If antiferromagnetic interactions are relatively strong, as they seem to be for **1**, then the crystal is best described as containing antiferromagnetically ordered 1-, 2- or 3D extended networks.

Perusal of Table 4 shows that only five, out of the eleven structurally and magnetically characterized Co_7 clusters, belonging to the wheel-shaped (or disk-like) group have SMM properties. These complexes are characterized by, at least some, ferromagnetic $Co^{II}\cdots Co^{II}$ exchange interactions. Perhaps more valid is the comparison between **1** and $(NBu^n_4)[Co^{III}Co^{II}_6(thme)_2(O_2CCMe_3)_8Br_2]$ [40c], where H_3thme is 1,1,1-tris(hydroxymethyl)ethane, because both complexes have a central Co^{III} atom and six Co^{II} atoms on the rim. Examination of the core of the latter suggests the existence of two distinct exchange pathways; the first involves two carboxylates (one $\eta^1:\eta^1:\mu$, the other $\eta^1:\eta^2:\mu$) and one alkoxide, and the second involves one alkoxide and one bromide. The $Co^{II}–Z–Co^{II}$ angles (Z = O, Br) fall in the ranges 88.3–88.7° for $Co^{II}–O(O_2CR)–Co^{II}$, 81.7° for $Co^{II}–Br–Co^{II}$ and 89.4–100.0° for $Co^{II}–O_{alkoxide}–Co^{II}$; these values are expected to lead to strong ferromagnetic exchange coupling between the peripheral Co^{II} atoms [40c,45]. The $\chi_M T$ product ($H = 0.05$ T) of this complex decreases from a value of 18.8 $cm^3\ mol^{-1}$ K at 300 K, corresponding to six noninteracting $S = 3/2$ ions with a g value of 2.58, to a minimum at $T = 36$ K and then increases to reach a value of 28.3 $cm^3\ mol^{-1}$ K at $T = 3$ K. The $\chi_M T$ value at 3 K corresponds well to six effective $S' = 1/2$ states, each with a g' value of 4.34, interacting in a ferromagnetic manner [40c]. In our complex, the corresponding $Co^{II}–Z–Co^{II}$ angles (Z=O) fall in the ranges 93.8–94.5° for $Co^{II}–O_{hydroxo}–Co^{II}$ and 103.5–104.2° for $Co^{II}–O_{alkoxide}–Co^{II}$. The largest $Co^{II}–Z–Co^{II}$ angles [12d], combined with the different nature of the monoatomic bridges are most probably responsible for the weaker ferromagnetic exchange interactions in **1**. The absence of a blocking of the magnetization in $(NBu^n_4)[Co^{III}Co^{II}_6(thme)_2(O_2CCMe_3)_8Br_2]$ was attributed [40c] to the presence of a rhombic (transverse)

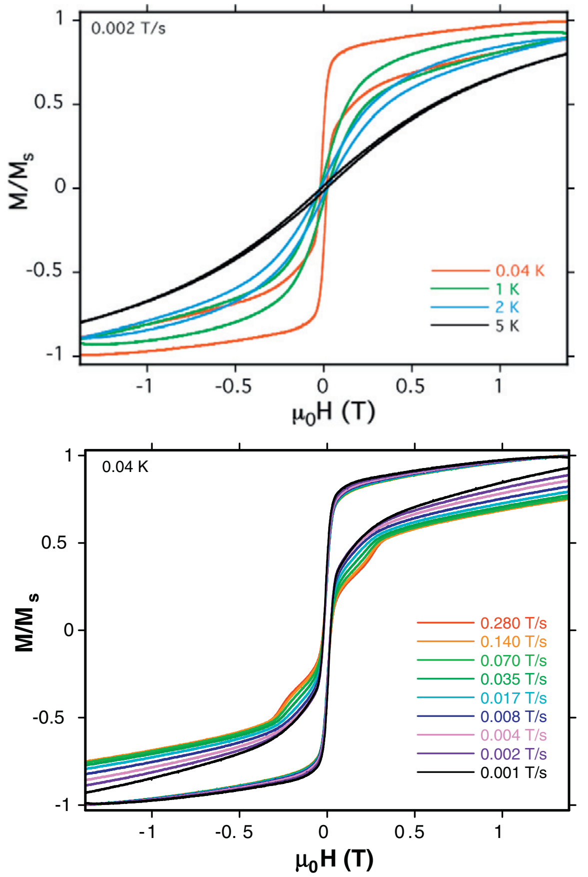


Fig. 7. Magnetization (M) vs. dc field hysteresis loops for a single crystal of **1**.$1.6H_2O$ at the indicated temperatures and a fixed field sweep rate at 0.002 T/s (top), and at the indicated field sweep rates and a fixed temperature of 0.04 K (bottom). The magnetization is normalized to its saturation value, M_S.

component of the anisotropy that induces a mixing of the low-lying sublevels leading to a fast relaxation of the magnetization; indeed, the complex possesses a principal 2-fold axis that lies within the plane of the anion so that the transverse component of the anisotropy tensor will be nonzero. Undoubtedly, Co^{II}-based clusters seem to show a much more complex magnetization dynamics than clusters based on orbital non-degenerate metal ions.

4. Conclusions and perspectives

It is difficult to conclude on a project which is still at its infancy. We began this work asking two questions: (i) whether we could contribute to the chemistry of Co^{II}-based SMMs, and (ii) if the replacement of one 2-pyridyl ring of di-2-pyridyl ketone $[(py)_2CO]$ by a methyl group would lead to reactivity towards nucleophiles in the presence of metal ions and whether this would provide routes to cluster types not available from di-2-pyridyl ketone itself; the answer is clearly “yes” for both questions. The initial use of 2-acetylpyridine [(py)(Me)CO] in Co chemistry under strongly basic conditions has provided access to the new mixed-valence $Co^{III}Co^{II}_6$ cluster **1** with a wheel-shaped Co^{II}_6 topology comprising a seventh Co^{III} atom in the center; this cluster type is not known in $(py)_2CO$-based metal cluster chemistry. It has been shown that (py)(Me)CO is capable of undergoing an impressive reactivity in acetone which is possibly due to the presence of a weakly acidic α-hydrogen in the solvent and to the δ+ character of the carbonyl carbon atom of (py)(Me)CO; the anion of the β-hydroxy ketone formed bridges two Co^{II} atoms facilitating the formation of the cluster. In addition, **1** has proven to be a new Co^{II}-based SMM, as confirmed by single-crystal micro-SQUID studies. It seems that there are two parts in the 0.04 K magnetization vs. dc field plot, the scan-rate-independent coercivity and the scan-rate-dependent one. The former is due to intermolecular interactions, and it is that that we can still see at 5 K, and the latter is the weak SMM behavior. However, in search for new SMMs with higher blocking temperatures, further detailed studies of the low-temperature dynamic behavior of the magnetization of the Co(II) clusters are needed. It is clear that further work is required in an attempt to create a database of experimental results in order to better understand the magnetic properties of Co^{II} SMMs.

The combined results presented here have shown that substitution of a 2-pyridyl group of $(py)_2CO$ by a non-donor R″ group is a good way to obtain new cluster types in 3d-metal chemistry and to control the reactivity of organic molecules bearing a ketone group. Variation of the size and electronic properties of the R″ groups may provide a systematic modification of products, even though their exact structure can not be *a priori* predicted. We are currently working on this idea using distinctly different R″ groups, and results will be reported in due course. In parallel, we have just begun to realize the importance of acetone for cluster synthesis in the presence of strong bases and recent work has unearthed the unique clusters $[Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4](ClO_4)_4$ and $[Ni_5\{(py)_2C(CH_2COCH_3)(O)\}\{(py)_2CO_2\}\{(py)_2C(OH)O\}_4](ClO_4)_3$ [15c,46]; these complexes contain the novel $(py)_2C(CH_2COCH_3)(O)^-$ ligand, formed in situ through a Ni^{II}-assisted crossed-aldol reaction involving the attack of the carbanion of acetone $(CH_3COCH_2^-)$ on the carbonyl carbon atom of $(py)_2CO$.

Acknowledgements

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Appendix A. Supplementary data

CCDC 786388; contains the supplementary crystallographic data for $\mathbf{1}\cdot1.6H_2O$. 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.

References

[1] (a) R.E.P. Winpenny, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 7, Elsevier, Amsterdam, ch. 7.3, 2004, pp. 125–175;
(b) E.K. Brechin, Chem. Commun. (2005) 5141. Feature Article;
(c) Th.C. Stamatatos, G. Christou, Philos. Trans. R. Soc. London, Ser. A 366 (2008) 113.
[2] For example, see A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, Angew. Chem., Int. Ed. 43 (2004) 2117.
[3] (a) E.C. Theil, M. Matzapetakis, Z. Liu, J. Biol. Inorg. Chem. 11 (2006) 803;
(b) J. Barber, J.W. Murray, Coord. Chem. Rev. 252 (2008) 233.
[4] (a) For recent reviews, see R. Bagai, G. Christou, Chem. Soc. Rev. 38 (2009) 1011;
(b) M. Murrie, D.J. Price, Annu. Rep. Prog. Chem. Sect. A: Inorg. Chem. 103 (2007) 20;
(c) G. Aromi, E.K. Brechin, Struct. Bonding (Berlin) 122 (2006) 1.
[5] (a) J.R. Friedman, M.P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 76 (1996) 3830;
(b) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, R. Barbara, Nature 383 (1996) 145.
[6] W. Wernsdorfer, R. Sessoli, Science 284 (1999) 133.
[7] (a) W. Wernsdorfer, N. Aliaga-Alcalde, D.N. Hendrickson, G. Christou, Nature 416 (2002) 406;
(b) S. Hill, R.S. Edwards, N. Aliaga-Alcalde, G. Christou, Science 302 (2003) 1015.
[8] (a) L. Bogani, W. Wernsdorfer, Nature Mater. 7 (2008) 179;
(b) B. Cage, S.R. Russek, R. Shoemaker, A.J. Barker, C. Stoldt, V. Ramachandran, N.S. Dalal, Polyhedron 26 (2007) 2413;
(c) J. Tejada, E.M. Chudnovsky, E. del Barco, J.M. Hernandez, T.P. Spiller, Nanotechnology 12 (2001) 181;
(d) M.N. Leuenberger, D. Loss, Nature 410 (2001) 789.
[9] A. Bencini, D. Gatteschi, EPR of Exchange Coupled Systems, Springer, Berlin, 1990.
[10] L.F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet, D. Luneau, J. Am. Chem. Soc. 130 (2008) 12445.
[11] (a) E.-C. Yang, D.N. Hendrickson, W. Wernsdorfer, M. Nakano, L.N. Zakharov, R.D. Sommer, A.L. Rheingold, M. Ledezma-Gairaud, G. Christou, J. Appl. Phys. 91 (2002) 7382;
(b) M. Murrie, S.J. Teat, H. Stoeckli-Evans, H.U. Güdel, Angew. Chem., Int. Ed. 42 (2003) 4653;
(c) S.J. Langley, M. Helliwell, R. Sessoli, P. Rosa, W. Wernsdorfer, R.E.P. Winpenny, Chem. Commun. (2005) 5029;
(d) M.-H. Zheng, M.-X. Yao, H. Liang, W.-X. Zhang, X.-M. Chen, Angew. Chem., Int. Ed. 46 (2007) 1832;
(e) S.J. Langley, M. Helliwell, R. Sessoli, S.J. Teat, R.E.P. Winpenny, Inorg. Chem. 47 (2008) 497;
(f) B. Moubaraki, K.S. Murray, T.A. Hudson, R. Robson, Eur. J. Inorg. Chem. (2008);
(g) S.J. Langley, M. Helliwell, R. Sessoli, S.J. Teat, R.E.P. Winpenny, Dalton Trans. (2009) 3102;
(h) F. Klöwer, Y. Lan, J. Nehrkorn, O. Waldmann, C.E. Anson, A.K. Powell, Chem. Eur. J. 15 (2003) 7413;
(i) D. Wu, D. Guo, K. Song, W. Huang, C. Duan, Q. Meng, O. Sato, Inorg. Chem. 48 (2009) 854.
[12] (a) Y.-Z. Zhang, W. Wernsdorfer, E. Pan, Z.-M. Wang, S. Gao, Chem. Commun. (2006) 3302;
(b) A. Ferguson, A. Parkin, J. Sanchez-Benitez, K. Kamenev, W. Wernsdorfer, M. Murrie, Chem. Commun. (2007) 3473;
(c) X.-T. Wang, B.-W. Wang, Z.-M. Wang, W. Zhang, S. Gao, Inorg. Chim. Acta 361 (2008) 3895;
(d) Y.-L. Zhou, M.-H. Zeng, L.-Q. Wei, B.-W. Li, M. Kurmoo, Chem. Mater. 22 (2010) 2114.
[13] (a) G. Christou, Polyhedron 24 (2005) 1809;
(b) C.J. Milios, S. Piligkos, E.K. Brechin, Dalton Trans. (2008) 1809 (Perspective).
[14] T. Taguchi, W. Wernsdorfer, K.A. Abboud, G. Christou, Inorg. Chem. 49 (2010) 199.
[15] (a) For reviews concerning the coordination chemistry of $(py)_2CO$, see G.S. Papaefstathiou, S.P. Perlepes, Comments Inorg. Chem. 23 (2002) 249;
(b) A.J. Tasiopoulos, S.P. Perlepes, Dalton Trans. (2008) 5537 (Perspective);
(c) T.C. Stamatatos, C.G. Efthymiou, C.C. Stoumpos, S.P. Perlepes, Eur. J. Inorg. Chem. (2009) 3361 (Microreview).
[16] (a) T.C. Stamatatos, K.A. Abboud, W. Wernsdorfer, G. Christou, Inorg. Chem. 48 (2009) 807;

(b)M.L. Tong, M. Monfort, J.-M. Clemente Juan, X.-M. Chen, X.-H. Bu, M. Ohba, S. Kitagawa, Chem. Commun (2005) 233;
(c) Y. Li, S. Xiang, T. Sheng, J. Zhang, S. Hu, R. Hu, R. Fu, X. Huang, X. Wu, Inorg. Chem. 45 (2006) 6577;
(d) B.F. Abrahams, T.A. Hudson, R. Robson, Chem. Eur. J. 12 (2006) 7095;
(e) C.G. Efthymiou, A. Tezis, A.J. Tasiopoulos, A. Escuer, S.P. Perlepes, unpublished data.

[17] (a) Recent papers from our groups C.C. Stoumpos, O. Roubeau, G. Aromi, A.J. Tasiopoulos, V. Nastopoulos, A. Escuer, S.P. Perlepes, Inorg. Chem. 49 (2010) 359;
(b) C.C. Stoumpos, I.A. Gass, C.J. Milios, N. Lalioti, A. Terzis, G. Aromi, S.J. Teat, E.K. Brechin, S.P. Perlepes, Dalton Trans. (2009) 307;
(c) T.C. Stamatatos, K.A. Abboud, W. Wernsdorfer, G. Christou, Angew. Chem., Int. Ed. 47 (2008) 6694;
(d) T.C. Stamatatos, V. Tangoulis, C.P. Raptopoulou, A. Terzis, G.S. Papaefstathiou, S.P. Perlepes, Inorg. Chem. 47 (2008) 7969;
(e) T.C. Stamatatos, V. Nastopoulos, A.J. Tasiopoulos, E. Moushi, W. Wernsdorfer, G. Christou, S.P. Perlepes, Inorg. Chem. 47 (2008) 10081;
(f) A.K. Boudalis, Y. Sanakis, J.M. Clemente-Juan, B. Donnadieu, V. Nastopoulos, A. Mari, Y. Coppel, J.-P. Tuchagues, S.P. Perlepes, Chem. Eur. J. 14 (2008) 2514;
(g) G.S. Papaefstathiou, A.K. Boudalis, T.C. Stamatatos, C.J. Milios, C.G. Efthymiou, C.P. Raptopoulou, A. Terzis, V. Psycharis, Y. Sanakis, R. Vicente, A. Escuer, J.-P. Tuchagues, S.P. Perlepes, Polyhedron 26 (2007) 2089;
(h) G.S. Papaefstathiou, A. Escuer, F.A. Mautner, C. Raptopoulou, A. Terzis, S.P. Perlepes, R. Vicente, Eur. J. Inorg. Chem. (2005) 879;
(i) G.S. Papaefstathiou, A. Escuer, M. Font-Bardia, S.P. Perlepes, X. Solans, R. Vicente, Polyhedron 21 (2002) 2027.

[18] (a) For example, see R. Vicente, B. Bitschnau, A. Egger, B. Sodin, F.A. Mautner, Dalton Trans. (2009) 5120;
(b) M. Tatucu, A. Kriza, C. Maxim, N. Stanica, J. Coord. Chem. 62 (2009) 1067;
(c) M.G.B. Drew, J.P. Naskar, S. Chowdhury, D. Datta, Eur. J. Inorg. Chem. (2005) 4834;
(d) G.A. Bowmaker, R. Effendy, M. Nitiatmodjo, B.W. Skelton, A.H. White, Inorg. Chim. Acta 358 (2005) 4327;
(e) F. Gross, H. Vahrenkamp, Inorg. Chem. 44 (2005) 3321.

[19] (a) For example, see Th.C. Stamatatos, E. Katsoulakou, A. Terzis, C.P. Raptopoulou, R.E.P. Winpenny, S.P. Perlepes, Polyhedron 28 (2009) 1638;
(b) Th.C. Stamatatos, A.K. Boudalis, K.V. Pringouri, C.P. Raptopoulou, A. Terzis, J. Wolowska, E.J.L. McInnes, S.P. Perlepes, Eur. J. Inorg. Chem. (2007) 5098;
(c) Th.C. Stamatatos, S. Dionyssopoulou, G. Efthymiou, P. Kyritsis, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S.P. Perlepes, Inorg. Chem. 44 (2005) 3374.

[20] (a) C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, A. Escuer, R. Vicente, S.P. Perlepes, Polyhedron 23 (2004) 83;
(b) C.J. Milios, P. Kyritsis, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S.P. Perlepes, Dalton Trans. (2005) 501;
(c) C.C. Stoumpos, R. Inglis, O. Roubeau, H. Sartzi, A.A. Kitos, C.J. Milios, G. Aromi, A.J. Tasiopoulos, V. Nastopoulos, E.K. Brechin, S.P. Perlepes, Inorg. Chem. 49 (2010) 4388.

[21] R.C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Inc., Boca Raton, FL, 1984.

[22] W. Wernsdorfer, Adv. Chem. Phys. 118 (2001) 99.

[23] SIR92 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M.J. Camalli, J. Appl. Crystallogr. 27 (1994) 435.

[24] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.

[25] CrysAlis CCD and CrysAlis RED, Oxford Diffraction Ltd., Abingdon, England, 2009.

[26] WINGX, L. J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[27] MERCURY, I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. MaCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.

[28] K. Bradenburg, DIAMOND, Release 3.1f, Crystal Impact GbR, Bonn, Germany, 2008.

[29] A. Kitos, C.G. Efthymiou, A.J. Tasiopoulos, S.P. Perlepes, unpublished results.

[30] P.S. Bailey Jr., C.A. Bailey, Organic Chemistry, 5th ed., Prentice Hall, Upper Saddle River, New Jersey, USA, 1995. pp. 359–365.

[31] (a) F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. (2007) 4343;
(b) C.K. Sperry, W.D. Cotter, R.A. Lee, R.J. Lachicotte, G.C. Bazan, J. Am. Chem. Soc. 120 (1998) 7791.

[32] C.C. Stoumpos, Th.C. Stamatatos, V. Psycharis, C.P. Raptopoulou, G. Christou, S.P. Perlepes, Polyhedron 27 (2008) 3703.

[33] W. Wang, B. Spingler, R. Alberto, Inorg. Chim. Acta 355 (2003) 386.

[34] (a) C.G. Efthymiou, A.A. Kitos, C.P. Raptopoulou, S.P. Perlepes, A. Escuer, C. Papatriantafyllopoulou, Polyhedron 28 (2009) 3177;
(b) A.B.P. Lever, A. Mantovani, Inorg. Chem. 10 (1971) 817.

[35] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986. pp. 139–251.

[36] C.C. Stoumpos, Th.C. Stamatatos, H. Sartzi, O. Roubeau, A.J. Tasiopoulos, V. Nastopoulos, S.J. Teat, G. Christou, S.P. Perlepes, Dalton Trans. 1 (2009) 1004.

[37] (a) I.D. Brown, D. Altermatt, Acta Crystallogr. B41 (1985) 244;
(b) W. Liu, H.H. Thorp, Inorg. Chem. 32 (1993) 4102.

[38] (a) T. Steiner, Cryst. Rev. 6 (1996) 1;
(b) J.-A. VandenBerg, K.R. Seddon, Cryst. Growth Des. 3 (2003) 643.

[39] (a) E.K. Brechin, A. Graham, A. Parkin, S. Parsons, A.M. Seddon, R.E.P. Winpenny, J. Chem. Soc., Dalton Trans. (2000) 3242;
A.E. Malkov, I.G. Famina, A.A. Sidorov, G.G. Aleksandrov, I.M. Egorov, N.I. Latosh, O.N. Chupakhin, G.L. Rusinov, Yu.V. Rakitin, V.M. Novotortsev, V.N. Ikorskii, I.L. Eremenko, I.I. Moiseev, Mol. Struct. 656 (2003) 207;
(c) G. Aromi, A.S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A.A. Smith, G.A. Timco, R.E.P. Winpenny, Chem. Eur. J. 9 (2003) 5142;
(d) V. Niel, V.A. Milway, L.N. Dawe, H. Grove, S.S. Tandon, T.S.M. Abedin, T.L. Kelly, E.C. Spenser, J.A.K. Howard, J.L. Collins, D.O. Miller, L.K. Thompson, Inorg. Chem. 47 (2008) 176;
(e) M. Kondo, S. Sugahara, Y. Nakamura, M. Miyazawa, S. Yasue, K. Maeda, F. Uchida, G. Sakane, H. Kawaguchi, Cryst. Eng. Commun. 10 (2008) 1516;
(f) W.-Z. Wang, R.H. Ismayilov, G.-H. Lee, I.P.-C. Liu, C.-Y. Yeh, S.-M. Peng, Dalton Trans. (2007) 830;
E.K. Brechin, S.G. Harris, S. Parsons, R.E.P. Winpenny, Chem. Commun. (1996) 1439.

[40] (a) H. Ackermann, R. Leo, W. Massa, K. Dechnicke, Z. Naturforsch 626 (2000) 608;
(b) H. Ackermann, R. Leo, W. Massa, K. Dechnicke, Z. Anorg. Allg. Chem. 626 (2000) 608;
(c) M. Moragues-Canovàs, C.E. Talbot-Eeckelaers, L. Catala, F. Lloret, W. Wernsdorfer, E. Brechin, T. Mallah, Inorg. Chem. 45 (2006) 7038;
(d) A.A. Sidorov, M.E. Nikiforova, E.V. Pakhamutova, G.G. Aleksandrov, V.N. Ikorskii, V.M. Novotortsev, I.L. Eremenko, I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim (Russ. Chem. Bull.) (2006) 1851;
(e) V. Tudor, G. Marin, F. Lloret, V.Ch. Kravtsov, Y.A. Simonov, M. Julve, M. Andruh, Inorg. Chim. Acta 361 (2008) 3446;
(f) S.-H. Zhang, Y. Song, H. Liang, M.-H. Zeng, Cryst. Eng. Commun. 11 (2009) 865.

[41] (a) For example, see H. Oshio, N. Hashino, T. Ito, M. Nakano, F. Renz, P. Gutlich, Angew. Chem., Int. Ed. 42 (2003) 223;
(b) S. Koizumi, M. Nihei, T. Shiga, M. Nakano, H. Nojiri, R. Bircher, O. Waldmann, S.T. Ochsenbein, H.U. Güdel, F. Fernandez-Alonso, H. Oshio, Chem. Eur. J. 13 (2007) 8445;
(c) R.W. Saalfrank, A. Scheurer, R. Prakash, F.W. Heinemann, T. Nakajima, F. Hampel, R. Leppin, B. Pilawa, H. Rupp, P. Müller, Inorg. Chem. 46 (2007) 1586;
R.W. Saalfrank, T. Nakajima, N. Mooren, A. Scheurer, H. Maid, F. Hampel, C. Trieflinger, J. Daub, Eur. J. Inorg. Chem. (2005) 1149;
(e) A.M. Ako, O. Waldman, V. Mereacre, F. Klöwer, I.J. Hewitt, C.E. Anson, H.U. Güdel, A.K. Powell, Inorg. Chem. 46 (2007) 756.

[42] K.G. Alley, R. Bircher, O. Waldmann, S.T. Ochsenbein, H.U. Güdel, B. Moubaraki, K.S. Murray, F. Fernandez-Alonso, B.F. Abrahams, C. Boskovic, Inorg. Chem. 45 (2006) 8950.

[43] E. Moushi, C. Lampropoulos, W. Wernsdorfer, V. Nastopoulos, G. Christou, A.J. Tasiopoulos, Inorg. Chem. 46 (2007) 3795.

[44] A. Mishra, A.J. Tasiopoulos, W. Wernsdorfer, E. Moushi, B. Moulton, M.J. Zaworotko, K.A. Abboud, G. Christou, Inorg. Chem. 47 (2008) 4832.

[45] J.M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, J.R. Galan-Mascaros, C. Gimenez-Saiz, C.J. Gomez-Garcia, Inorg. Chem. 43 (2004) 2869.

[46] C.G. Efthymiou, C. Papatriantafyllopoulou, C.P. Raptopoulou, V. Psycharis, S.P. Perlepes, G. Christou, unpublished results.