The first 1-D cyanide-bridged complex assembled from a covalently tethered \([\text{Co}^{II}(\text{N}_3\text{O}_2)\text{Cl(OH}_2\text{))]^{2+}\) macrocyclic building block

Roland T. Acha a, Emma L. Gavey a, Jian Wang a, Jeremy M. Rawson b, Melanie Pilkington a,

a Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario L2S3A1, Canada
b Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, Ontario N9B3P4, Canada

A R T I C L E   I N F O

Article history:
Received 12 January 2014
Accepted 1 April 2014
Available online 12 April 2014

Keywords:
Schiff-base macrocycle
N,O ligand
Cyanide-bridged Coordination polymer
Dimeric complex

A B S T R A C T

The metal-templated synthesis of the bimetallic macrocyclic complex \([\text{Co}^{II}(\text{N}_3\text{O}_2)\text{Cl(OH}_2\text{)})_2\text{C}_2\text{H}_5\text{O}_2\text{]} (2)\)
containing two \(\text{N}_3\text{O}_2\) macrocyclic binding pockets was achieved from the metal-templated Schiff-base condensation of 2,2'-tetracyanobipyrindine with 3,6-dioxoctane-1,8-diamine. Slow diffusion of (2) with \(K_2[\text{Fe(CN)}_6]_3\) in a (1:1) mixture of methanol and water afforded the 1-D coordination polymer \([\text{Co}(\text{N}_3\text{O}_2)\text{Cl(OH}_2\text{)}]_2[\text{Fe(CN)}_6]_3\text{SH}_2\text{O} (5)\) whose structure was determined by X-ray diffraction. The polymer comprises two covalently tethered pentagonal bipyramidal Co(II) macrocycles both axially coordinated to a single \([\text{Fe(CN)}_6]^{4+}\) unit in a zig-zag arrangement, highlighting the versatility of this family of dimeric building blocks for the self-assembly of higher order structures. Magnetic studies on (2) reveal that the ions exist as isolated \(S = \frac{3}{2}\) spin systems with no first-order spin–orbit coupling, but with significant atom zero field splitting \((D = 23 \text{ cm}^{-1}, g_{\text{iso}} = 2.37)\), indicating that the back-to-back \(\text{N}_3\text{O}_2\) macrocyclic ligand does not offer an efficient magnetic exchange pathway. The magnetic response of (5) in the high temperature region \((T > 50 \text{ K})\) is identical to (2) indicating dominant zero field splitting effects. However, on further cooling an upturn in \(\chi T\) is consistent with weak antiferromagnetic exchange \((J/k = +7.8 \text{ K})\) via the \([\text{Fe(CN)}_6]^{4+}\) bridging unit, affording weakly-coupled Co\textsuperscript{II} dimer units within the polymer chain of (5).

1. Introduction

The synthesis and characterization of coordination polymers has played an interesting and often pioneering role in the development of new materials. At the heart of these studies is an understanding of how to control the structure and properties of metal-containing polymers via the design of appropriate ligands and careful choice of metal ions in order to control the metal ion coordination geometry [1]. Whilst a range of polycarboxylate ligands have been exploited as useful ligands for constructing metal organic frameworks [2], cyanometallate complexes have emerged as one of the most popular building blocks for the construction of supramolecular architectures in the field of molecular magnetism [3]. This is largely due to the fact that the nature of the magnetic exchange interactions in these materials can be anticipated in advance from basic orbital interaction arguments, together with the predictable structure-directing nature of the cyanide bridge that facilitates supramolecular self-assembly and network design [4]. In the past decade, researchers have focused efforts on the synthesis of polynuclear clusters and chains for which the ground state spin and zero field splitting parameters \((S \text{ and } D)\) have been varied in order to shift the energy barrier for the reorientation of the magnetization and subsequent blocking of single molecule magnets (SMMs) and single chain magnets (SCM) to more ambient temperatures [5]. The current research goals are to develop new classes of magnets suitable for storing and processing information at the molecular level [6]. In this respect, access to transition metal polynuclear complexes with large spin ground states is now achievable. In contrast, the realization of polynuclear complexes and chains with large axial magnetic anisotropies \((D)\) remains a significant challenge. A large axial anisotropy arises from the simultaneous effects of residual spin–orbit coupling and the axial symmetry of the metal complex.

To-date, the most common approach to assembling magnetic clusters is to use known building blocks, many of which are either commercially available, or prepared in one or two steps from simple precursors [7]. Whilst the ready availability of such precursors offers its own advantages, in many cases the formation of SMM or SCM materials is entirely fortuitous with little synthetic control...
over nuclearity or coordination geometry at the metal centres. Whilst these have led to some of the most exciting fundamental discoveries in molecular magnetism over the last decade in bulk magnetism, photomagnetic materials, single chain magnets (SCMs) and single molecule magnets (SMMs) [8], there is an important niche for the tailored design of molecular clusters and polymers. In particular, control of the coordination geometry of the metal centers is fundamental to the manipulation of the magnetism of the spin carriers and is therefore an alternative approach that can be exploited in order to control the single ion anisotropy of molecular building blocks [9,10].

Pioneering work by Nelson and co-workers in the 1970’s showed that pentadentate macrocycles could be prepared in which a wide range of first row transition metals are confined in a pentagonal bipyramidal geometry [11]. Such species typically have labile axial ligands permitting them to be used as potential building blocks in coordination polymers. In recent years we have extended their methodology to develop (i) more complex structures exhibiting two covalently-linked binding pockets and; (ii) commenced an examination of ligand substitution reactions in the axial position to construct well-defined topologies. In 2007, we reported our design strategy for the preparation of the first covalently tethered dinuclear macrocyclic building block and characterized its dimeric MnII complex, \([\text{Mn}^\text{II}(\text{N}_3\text{O}_2\text{Cl})\text{(OH}_2\text{)}]^2\) (1) which comprises two pentagonal bipyramidal Mn(II) centers (Fig. 1) [12].

We proposed that substitution of the labile axial ligands in this or related complexes with cyanometallate precursors would provide a useful strategy for the self-assembly of cyanide-bridged structures such as molecular chains and ladders [12]. Furthermore, replacing the isotropic Mn(II) ions with other paramagnetic ions should retain the structural topology of the macrocage, but affect the single ion anisotropy of the corresponding complex. During the past decade the magnetic anisotropy of Co(II) ions has motivated studies on a range of cobalt(II) clusters [13]. Indeed, previous studies on pentagonal bipyramidal Co(II) complexes reveal that the seven coordinate geometry may enforce a marked axial anisotropy in relation to conventional 4- and 6-coordinate metal complexes [14]. Yet a review of the literature reveals just a handful of seven coordinate Co(II) complexes suitable for cluster development, since the majority of systems do not contain labile ligands that can be substituted with hexacyanoferrate ions to allow the self-assembly of a polymeric 1-D complex.

2. Experimental

2.1. General remarks and physical measurements

All experiments were carried out in air, 2.2’-6,6’-tetraacetyl-4,4’-bipyridine was prepared following the previously reported procedure [12]. Elemental analyses (C, H and N) were obtained from Atlantic Microlab, Norcross GA. IR data was recorded as a KBr pellet on a ThermoMattson RS-1 FT-IR spectrometer. FAB mass spectrometry data was collected on a Kratos Concept 15 High Resolution E/B mass spectrometer. Variable temperature magnetic susceptibility data were collected on a Quantum Design SQUID magnetometer in an applied field of 1000 G between 2 and 300 K. Pascal’s constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities (\(\chi_m\)).

2.2. Compound preparation

2.2.1. \([\text{Co(N}_3\text{O}_2\text{Cl)(OH}_2\text{)}]^2\)-(2)

2.2.6,6’-Tetraacetyl-4,4’-bipyridine (162 mg, 0.50 mmol) was added to a solution of CoCl2·6H2O (234 mg, 1.00 mmol) in MeOH (20 mL). The reaction mixture was warmed to 50°C after which time a solution of 3,6-dioxa-octano-1,8 diamine (0.148 g, 1.048 g, 1.00 mmol) in MeOH (5 mL) was added dropwise. The resulting solution was refluxed for 5 h and the solvent was partially removed to afford a precipitate that was isolated by filtration, washed with diethyl ether and dried to afford (2) as a brown solid. Yield (198 mg, 47%). IR (KBr, cm⁻¹): 3423 (br) (OH), 1644 (s) (C≡N); 1120–1093 (s) (C–O–C), MS (FAB): m/z [M·Cl·H2O]+ (3%) 806; [M·Cl·2H2O]+ (5%) 789; 771; [M·2Cl·2H2O]+ (100%) 736. Elemental analysis (%) calced for Co(II)H6N6P4Cl4Co(II)2: C 41.78; H 5.46; N 16.78; F 4.6; Cl 10.1; O (234 mg, 1.00 mmol) in MeOH (20 mL)

2.2.2. \([\text{Co(N}_3\text{O}_2\text{Cl)(OH}_2\text{)}]^2\)-(2)

Small red blocks suitable for X-ray analysis were obtained via the slow diffusion of K3[Fe(CN)6] 3H2O (0.2 mmol) in H2O (6 mL) into a solution of (2) (0.2 mmol) in a (1:1) mixture of MeOH and H2O (6 mL) after a month. Yield 30%. Elemental analysis (%) calced for C9H16Fe3Co6N12O32: C 43.04; H 5.42; N 16.73. Found C 43.12; H 5.59; N 16.92%.

2.3. Crystal structure determination

Suitable single crystals of (5) for X-ray structural analysis were mounted in inert oil on a nylon loop suspended in a copper pin and flash cooled to 100 K. The diffraction data was collected at 100 K on a Bruker Kappa X-ray diffractometer equipped with a SMART APEX II CCD detector. The data were integrated with SAINT [16] and a semi-empirical absorption correction with SADABS [17] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on \(F^2\) (SHELX-97) [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions by using a riding model with their \(U_{iso}\) values constrained to 1.5 \(U_{eq}\) of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms. Unit cell parameters and structure solution and refinement data for (5) are listed in Table 1.
3. Results and discussion

3.1. Synthesis and spectroscopic studies

The covalently tethered dicobalt macrocycle (2) was prepared via the metal-templated Schiff-base condensation of 2,2’-6,6’-tetraacetyl-4,4’-bipyridine together with 3,6-dioxaoctane-1,8-diamine (Scheme 1) in an analogous fashion to (1) [11,12].

The complex was isolated as a brown crystalline solid in 47% yield. A V(C) stretching mode was observed at 1644 cm⁻¹ in the IR spectrum of (2) Supporting Schiff-base bis-imine formation [11]. The FAB mass spectroscopy data for (2) is directly comparable with that reported for the Mn³⁺ derivative (1) [12]. The elemental analysis data for the complex is also in excellent agreement with the proposed molecular formula of [Co(N_3O_2)(OH_2)]_2 Fe(CN)_6 for (2). Subsequent reaction of (2) with K$_4$[Fe(CN)_6] in a 1:1 ratio in a MeOH/H$_2$O mix afforded an amorphous powder [PXRD] (see ESI S-1) whose micro-analytical data were consistent with the formula [Co(N_3O_2)(OH_2)]_2 Fe(CN)$_6$·5H$_2$O (5). Slow diffusion reactions in an H-tube afforded a few tiny red crystals over a period of 4 weeks with the same chemical composition whose structure was determined by X-ray diffraction.

3.2. Description of X-ray structure ([Co(N_3O_2)(OH_2)]_2 Fe(CN)$_6$·5H$_2$O (5))

Complex (5) crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of one half of a [Fe(CN)$_6$]$^{4-}$ anion, one half of the [Co(N$_3$O$_2$)(OH$_2$)]$^{2+}$ macrocycle together with three water molecules, one of which sits on a special position. A crystallographic inversion center runs through the middle of the two 4,4’-bipyridine rings rendering the two macrocycles of the dimer crystallographically equivalent. The Fe$^{II}$ sits on a second crystallographic inversion center and is octahedrally coordinated to six cyanide ligands with Fe–C bond lengths ranging from 1.927(8) to 1.954(9) Å, consistent with low spin Fe(II) and bite angles from 87.0(4)° to 93.0(3)°. The crystallographically unique Co$^2+$ ion adopts a pentagonal bipyramidal coordination environment, consisting of the (N$_3$O$_2$) donor set of the macrocycle forming the basal plane and a bridging cyanide ligand and a water molecule occupying the two apical positions (Fig. 2). The Co–N bond lengths are between 2.050(6) and 2.177(6) Å and the Co–O bond lengths are 2.264(5) and 2.248(5) Å for the ethylene bridged oxygen atoms and 2.140(6) Å for the axial Co(1)–O(1W) bond. The Co–N/O ligand bite angles range from 71.9(2)° to 73.6(9)°. The Co$^{II}$ centers are bound through the end of the axial cyanide ligand with a Co–N(5) separation of 2.085(6) Å. The Co–N/C-O bonds deviate distinctly from linearity with a Co(1)-(N(4)-(C(16)) angle of 161.3(6)°. In contrast to the previously reported dimeric Mn$^{II}$ macrocycle (1), (where the macroyclic rings are twisted by 41°) [12], the two dimeric macrocyclic rings in the 1-D chain are completely planar resulting in a colinear arrangement of the two Co$^{II}$ centers which are 11.251(3) Å apart. Both (N$_3$O$_2$) macrocycles of the dimer are coordinated to a single [Fe(CN)$_6$]$^{4-}$ anion in a trans manner such that the N(4)-Co(1)-(N(1)) angles are close to 90° affording a zig-zag chain (Fig. 2).

Conversely, within the chain, each [Fe(CN)$_6$]$^{4-}$ unit is linked to two [Co(N$_3$O$_2$)(OH$_2$)]$^{2+}$ macrocycles via the axial cyanide groups, leaving the four Co$^{II}$ ligands in the equatorial positions intact affording a Co$^{3+}$...Fe$^{6+}$ separation of 5.091(2) Å. Furthermore, the intramolecular distances between the two Co$^{II}$ ions bridged via the [Fe(CN)$_6$]$^{4-}$ anions are 10.181(3) Å. Examination of the crystal packing reveals that the zig-zag chains are connected via a network of H-bonding interactions involving the water and cyanide ligands, as well as the solvent water molecules in the crystal lattice (Fig. 3). The shortest intramolecular H-bonding interactions are between the axially coordinated H$_2$O ligand of the macrocycle and an equatorial CN ligand from the [Fe(CN)$_6$]$^{4-}$ anion of a neighboring chain (O1(W)–N(4) = 2.72(7) Å). All four equatorial cyanide ligands of the [Fe(CN)$_6$]$^{4-}$ unit are H-bonded to water molecules in the crystal lattice.

3.3. Magnetic susceptibility studies

Variable temperature magnetic susceptibility data for (2) were measured between 5 and 300 K in an applied field of 2000 G, whilst single crystals of (5) were measured between 2 and 300 K in an
applied field of 1000 G. Data were corrected for sample diamagnetism (Pascal’s constants) and sample holder [19].

The pentagonal bipyramidal geometry at CoII affords an orbitally singly-degenerate ground state (Fig. 4, inset). A number of groups have reported room temperature magnetic moments for such 7-coordinate CoII complexes [14]. Whilst there is some considerable variation in $\mu_{eff}$, the most common reported values typically fall in the range 4.1–4.2 B.M. ($\chi T = 2.15 \text{ emu K mol}^{-1}$) consistent with $S = 3/2$ and $g > 2$ but, in most cases, detailed variable temperature magnetic measurements and/or EPR studies were absent. EPR studies were reported by Lewis and coworkers on a pentagonal bipyramidal CoII centre with $g = 2.9$ [14a], whilst Sessler reported $g = 4.1$ for another formally pentagonal bipyramidal CoII centre [14b]. Both values seem anomalously high for systems in which the orbital angular momentum is quenched, though these may reflect one component of the solid state EPR spectrum. Three detailed magnetic studies on pentagonal bipyramidal geometries have been made; In 1979 Gerloch et al. reported single crystal magnetic studies on two pentagonal bipyramidal CoII complexes in the region 20–300 K [14f]. An analysis of their data affords powder $\chi T$ values of 2.24 and 2.22 emu.K.mol$^{-1}$ decreasing to between 1.54 and 1.80 emu.K.mol$^{-1}$ at 20 K. Their studies revealed essentially axial symmetry and a marked difference in parallel and perpendicular susceptibilities with the axial susceptibility essentially perpendicular to the pentagonal plane. These complexes both reveal similar room temperature $\chi T$ values around 2.26–2.30 emu K mol$^{-1}$, consistent with $S = 3/2$ and $g = 2.15 – 2.22$ [14f]. Whilst the $g$-values deviate from the spin-only value (2.00),
they are consistent with significant second-order contributions to the orbital angular momentum. Similar behavior was reported for polycrystalline samples of pentagonal bipyramidal Co⁵⁷ complexes reported by Gerloch, Real and Mallah (2003). In both cases the $\chi T$ values undergo a rapid decline below 75 K which has been attributed to substantial zero field splitting of the $S=3/2$ ground term ($D=25-32$ cm⁻¹). A similar analysis of the single crystal magnetic susceptibility data reported by Gerloch afforded $D \approx 37$ cm⁻¹ and $g \approx 2.15$ and is provided as ESI, S-3) With these previous observations in mind we examined the magnetic response of (2) and (5).

The dinuclear complex (2) exhibits Curie–Weiss behavior down to 50 K ($R^2 = 0.999$) with $C = 5.35$ emu K mol⁻¹ (C = 2.68 emu K mol⁻¹ per Co²⁺ centre), consistent with two $S = 3/2$ spins with $g = 2.38$, and comparable with the 7-coordinate studies of Real and Mallah described above. A similar collapse in temperature is observed for (2), consistent with significant single ion anisotropy. The data were modeled using an axial $S = 3/2$ spin Hamiltonian with three fitting parameters: $g_\|$, $g_\perp$, and the axial zero-field splitting parameter, $D$ (Eq. 1). An excellent fit to the entire data range was achieved using $g_\| = 2.62$, $g_\perp = 2.25$ ($g = 2.37$) and a large axial anisotropy $D = 23$ cm⁻¹ (Fig. 4). These parameters are comparable with those for other pentagonal bipyramidal Co²⁺ complexes reported by Gerloch, Real and Mallah ($g = 2.15-2.22$ and $D = +25$ to +37 cm⁻¹ [14f–h]).

The behavior of (5) in the high temperature region ($T > 50$ K) is identical to that of (2) (Fig. 5), consistent with a similar coordination environment and single ion effects and was modeled with essentially the same parameters ($g_\| = 2.61$, $g_\perp = 2.25$, $D = 23$ cm⁻¹). Below 50 K, the behavior of (5) deviates from that of (2) with an upturn in $\chi T$ consistent with local ferromagnetic interactions. The absence of an out of phase component in additional ac susceptibility studies (see Supplementary Information, S3) precludes the presence of long range order, single-chain magnetism or ferromagnetic impurities. As a consequence, the upturn and eventual downturn below 4 K is likely due to short range local ferromagnetic interactions. Since the back-to-back $N_2O_2$ macrocycle did not propagate magnetic exchange in (2), the difference in the magnetic response in (5) at low temperature can be attributed to either magnetic exchange between Co⁵⁺ centres via the diamagnetic [Fe(CN)₆]⁴⁻ ion leading to discrete Co⁵⁺ dimers within the polymerizing structure, or to through space dipolar exchange. Since the origin of the exchange interaction is uncertain, attempts to model the magnetic exchange should be viewed with caution. Nevertheless, in the simplest case of exchange coupling via the diamagnetic Fe(CN)₆⁴⁻ bridge, a simple dimer model can be employed to gain a qualitative estimate of the strength of the magnetic exchange. Both an isotropic Heisenberg model and an anisotropic Ising spin model implementing effective $S = 1/2$ spins for the Kramer’s doublet ground state were used to model the magnetic interactions between Co⁵⁺ sites, with the Ising model (Eq. 2) [20], providing a substantially improved fit consistent with the large single ion anisotropy.

$$\chi = \frac{Ng^2|\beta|^2}{kT} \left[ 1 + \exp(-2D/kT) \right]$$

$\chi = \frac{Ng^2|\beta|^2}{kT} \left[ 1 + \exp(-2D/kT) \right]$ (2)

The best fit to Eq. (2) afforded $g = 4.6$ and $J/k = +7.8$ K, but required an additional mean field term ($\theta = -1.6$ K) in order to reproduce the downturn in $\chi$ below 4 K, reflecting additional weak antiferromagnetic interactions between dimers (Fig. 5).

4. Conclusion

A new pentagonal bipyramidal coordinated dimeric Co⁴⁺ macrocycle has been prepared and structurally characterized. We have demonstrated for the first time that such back-to-back dimeric complexes are attractive building blocks for the self-assembly of cyanide-bridged polynuclear clusters. Magnetic measurements on both (2) and (5) reveal a large zero field splitting of the $S = 3/2$ state indicating that the anisotropy associated with simple pentagonal bipyramidal Co⁵⁺ complexes can be successfully transplanted into more complex structural topologies. Work is underway to study the photomagnetism of this complex and to prepare new families of $N_2O_2$ macrocycles with labile axial ligands for incorporation into larger magnetic clusters and frameworks, particularly including paramagnetic $[\text{M(CN)}_6]^{2-}$ ions which will more effectively propagate magnetic exchange.

Acknowledgements

We gratefully acknowledge support from NSERC (DG and RTI), Early Researchers Award (M.P), CFI and the Canada Research Chair program (M.P. and J.M.R.).

Appendix A. Supplementary data

CCDC 953704 contains the supplementary crystallographic data for this paper. 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.2014.04.001.

References
