Introduction

Alongside its prominent role in polyoxometalate chemistry, vanadium has had significant impact in the field of molecule-based magnetism. For example, orthogonal magnetic orbitals were exploited to produce ferromagnetic exchange in a \([\text{V}^{IV}\text{O}]^{-}\) dimer,\(^2\) the Prussian blue \(\text{V}[(\text{CN})_6]_{0.86}\) was one of the initial examples of a coordination compound exhibiting room temperature magnetic order,\(^3\) single-molecule magnet behaviour was observed in a \([\text{V}^{III}]\) butterfly,\(^4\) \([\text{V}_30]\) and \([\text{V}_{15}]\) have been widely studied to examine the influence of geometrical spin-frustration and antisymmetric exchange,\(^5\) and most recently monometallic \(\text{V}^{IV}\) compounds such as \((\text{Bu}_4\text{N})_2[\text{V}(\text{C}_8\text{S}_8)]_{4}\) and \([\text{VO}_{PC}]\) have been touted as excellent candidates for electron-spin based qubits.\(^6\)

Heterometallic 3d cages containing vanadium are however rather rare, and indeed those containing nickel or cobalt are relatively scarce. A search of the Cambridge Structural Database reveals only eight (Ni) and sixteen (Co) unique structure types with a nuclearity of four or more. When the nuclearity is increased to seven or more metal ions this number reduces to just four (Ni) and five (Co) examples.\(^7\) Restricting the search to complexes of any nuclearity containing the \(\text{V}^{IV}–\text{O}–\text{M}^{II}\) (M = Ni, Co) moiety, and excluding polyoxometalates, \(^8\) surprisingly affords only two different structure types: \([\text{VO}M]\) dimers,\(^9\) and a single \([\text{VO}_6]\) wheel.\(^10\) The latter complex has the formula \([\text{MV}_5\text{O}_{16}((\text{OCH}_2\text{CH}_2)_2\text{N}[\text{CH}_2\text{CH}_2\text{OH}])_{12}]X\) (X = halide) in which the six vanadyl moieties form a wheel that ‘encapsulates’ a variety of s- and 3d metal ions (M).\(^10\) Given the paucity of such species we have begun a program of research aimed at synthesising a variety of heterometallic \(\text{V}^{IV}\text{O}_{3}\text{d}3\) cluster compounds. The recent success we have had in employing the ligand 2-(hydroxymethyl)pyridine (hmpH) in the construction of heterometallic Anderson wheels of general formula \([\text{M}^{III}\text{M}^{II}(\text{hmp})_{12}]^{2+}\) (where \(\text{M}^{III} = \text{Cr}, \text{Al} \) and \(\text{M}^{II} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}\))\(^11\) hinted that this might be a viable route to isolating similar \(\text{M}^{IV}–\text{M}^{II}\) cages.

Experimental

Experimental procedures

All chemicals were procured from commercial suppliers and used as received (reagent grade). Caution: although no issues were encountered here care should be taken when handling potentially explosive perchlorate salts.

Synthesis of \([\text{VO}_2\text{Ni}_5(\text{hmp})_{10}\text{Cl}_2]\)[\text{ClO}_4]_2\cdot2\text{MeOH} (1)

\(\text{Ni(ClO}_4)_2\cdot6\text{H}_2\text{O} (0.366 \text{ g}, 0.5 \text{ mmol})\) and \(\text{VCl}_3 (0.079 \text{ g}, 0.5 \text{ mmol})\) were dissolved in \(\text{MeOH} (24 \text{ ml})\) with \(\text{NaOMe} (0.162 \text{ g}, 3 \text{ mmol})\) to give a green solution. Upon full dissolution, \text{hmpH} (0.285 \text{ ml}, 3 \text{ mmol}) was added dropwise resulting in a darkening of the solution colour. The reaction was left overnight with continuous stirring, 10 ml samples of the resulting dark green solution...
were heated in Teflon-lined autoclaves at 140 °C for 24 hours. After slowly cooling to room temperature the reaction vessels were allowed to sit undisturbed for 24 hours yielding red, green, triangular prism-shaped crystals suitable for X-ray diffraction. Yield 0.126 g (34.2% by Ni weight). Anal. Calcd (%) for C_{62}H_{68}Cl_{4}N_{10}Ni_{5}O_{22}V_{2}: C 40.24, H 3.42, N 7.34, Ni 16.00, V 5.75.

**Synthesis of \([\text{VO}]_{2}\text{Co}([\text{hmp}]_{10}\text{Cl}_{2}])_{2}\text{ClO}_{4} \cdot 2\text{MeOH} (2)\)**

Co(ClO₄)₂·6H₂O (0.366 g, 1 mmol) and VCl₃ (0.079 g, 0.5 mmol) were dissolved in MeOH (24 ml) with NaOMe (0.162 g, 3 mmol) to give a red/orange solution. Upon full dissolution, hmpH (0.285 ml, 3 mmol) was added dropwise resulting in a darkening of the solution colour. The reaction was left overnight with continuous stirring. 12 ml samples of the resulting solution were heated in Teflon-lined autoclaves at 100 °C for 12 hours. After slowly cooling to room temperature the reaction vessels were allowed to sit undisturbed for 24 hours yielding red, plate-shaped single crystals suitable for X-ray diffraction. Yield 0.130 g (35.3% by Co weight). Anal. Calcd (%) for C_{62}H_{68}Cl_{4}N_{10}Co_{5}O_{22}V_{2}: C 40.39, H 3.72, N 7.58, Co 15.98, V 0.13.

**Table 1 Crystallographic information for compounds 1–2**

| Compound | 1 | 2 |
|----------|---|---|
| Formula  | C_{62}H_{68}Cl_{4}N_{10}Ni_{5}O_{22}V_{2} | C_{62}H_{68}Cl_{4}Co_{5}N_{10}O_{22}V_{2} |
| D_{calc.}/g cm⁻³ | 1.721 | 1.712 |
| μ/μm⁻¹ | 1.779 | 1.613 |
| Formula weight | 1842.49 | 1843.59 |
| Colour | Dark green | Pale brown |
| Shape | Block | Plate |
| Size/mm³ | 0.52 × 0.29 × 0.16 | 0.50 × 0.14 × 0.06 |
| T(K) | 120.0 | 120.0 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2₁/n | P2₁/n |
| a/Å | 15.7800(3) | 15.7439(9) |
| b/Å | 12.4392(2) | 12.4867(5) |
| c/Å | 19.0165(4) | 18.9773(12) |
| α/° | 90 | 90 |
| β/° | 107.745(2) | 106.391(6) |
| γ/° | 90 | 90 |
| V/Å³ | 3555.16(12) | 3575.4(4) |
| Z (Z') | 2 (0.5) | 2 (0.5) |
| Wavelength/Å | 0.71073 | 0.71073 |
| Radiation type | MoKα | MoKα |
| θ_{min}/°–θ_{max}/° | 3.072–32.985 | 3.079–28.897 |
| Measured refl. | 90 810 | 37 370 |
| Independent refl. | 12 777 | 8344 |
| Reflections used | 10 678 | 5599 |
| R_{int} | 0.0447 | 0.0715 |
| Parameters | 516 | 479 |
| Restraints | 155 | 1 |
| Largest peak | 0.678 | 1.013 |
| Deepest hole | −0.475 | −0.678 |
| GoF | 1.042 | 1.041 |
| wR² | 0.0770 (0.0719) | 0.1612 (0.1465) |
| R¹ | 0.0461 (0.0341) | 0.1147 (0.0704) |

Magnetic susceptibility and magnetisation measurements in the temperature range Θ = 2–290 K were performed on a Quantum Design MPMS XL SQUID magnetometer equipped with a 5 T dc magnet in the field range, B = 0.1–5.0 T. Samples were mounted in gelatine capsules and restrained by addition of a small quantity of hexadecane. The observed paramagnetic susceptibilities were corrected for diamagnetic contributions using Pascal’s constants.

**Results and discussion**

The reaction of M(ClO₄)₂·6H₂O with VCl₃ and hmpH in a basic MeOH solution under solvothermal conditions produces crystals of \([\text{VO}]_{2}M_{2}([\text{hmp}]_{10}\text{Cl}_{2}])_{2}\text{ClO}_{4} \cdot 2\text{MeOH} (M = Ni, 1; Co, 2) in approximately 35% yield. Complexes 1–2 crystallise in the monoclinic space group P2₁/n (Table 1) with half the cationic cage, one perchlorate counter ion and one molecule of methanol in the asymmetric unit. The metallic skeleton (Fig. 1)
describes a centred \([(\text{VIVO})_2\text{MII}_4]\) wheel in which the vanadyl moieties (V1 and symmetry equivalent, s.e.) oppose each other on the outer \([\text{VIV}_2\text{MII}_4]\) rim, i.e. they occupy positions 1, 4 (Fig. 4). The central MII ion (M2, position 7, Fig. 4) is bridged to the six outer ring metals by six µ3-OR groups from six deprotonated hmp ligands. The four remaining hmp ligands each provide a µ-OR bridge on the exterior of the ring between one VIV ion and one MII ion. The two opposing Cl ions also µ-bridge in the external wheel, between M1 and M3 (positions 2 and 6, respectively, Fig. 4) and s.e. All seven metal ions display distorted octahedral coordination geometries, with the vanadyl moiety having a V–O bond length of \(\sim 1.6\) Å (Tables S1 and 2†).

The perchlorate anions and MeOH molecules of crystallisation H-bond to each other (O⋯O, \(\sim 2.8\) Å), sitting in-between the planes of the cationic cages (Fig. S2†). The closest intermolecular contacts between cations exist between aromatic rings on neighbouring molecules with C(Ar)⋯H(Ar) separations in the range \(2.3–2.8\) Å, and between the aromatic rings and the Cl ions, (Ar)⋯Cl at \(\sim 2.9\) Å.

In the extended structure the cations pack in columns down the \(b\) axis, with the columns arranged into rows with each neighbouring column composed of molecules which are eclipsed with respect to the adjacent column (Fig. S3†).

Complexes 1–2 are structurally related to the \([\text{M}_{12}^{\text{III}}\text{M}_{12}^{\text{II}}\text{(hmp)}_{12}]^{14+}\) (MIII = Cr, Al and MII = Mn, Fe, Co, Ni, Cu, Zn) family of Anderson wheels,\textsuperscript{11} the species \([\text{MV}_{5}^{\text{IV}}\text{O}_{6}(\text{OCH}_{2}\text{CH}_{2})_{2}\text{N(CH}_{2}\text{CH}_{2}\text{OH})]^{9+}\) (M = Li, Na, Mg, Mn, Fe, Co, Ni) reported by Khan,\textsuperscript{10} and the complex \([\text{M}_{12}^{\text{IV}}\text{Cr}(\text{HL}_{2}\text{o})_{6}\text{(HL)}_{6}]^{3+}\) (M = Ni, Co; HL = 2-hydroxy-4-methyl-6-phenylpyridine-3-amidoxime) published by Murrie and Milios.\textsuperscript{17} This highlights the apparent stability of the Anderson wheel structure, and the modular nature of the molecule whereby different metals in different oxidation states can be combined with the same (or similar) ligand sets to afford analogous species.\textsuperscript{18} Note that in the \([\text{M}_{12}^{\text{III}}\text{M}_{12}^{\text{II}}\text{(hmp)}_{12}]^{14+}\) family, the MIII ion is positionally disordered around the external wheel. In \([\text{M}_{12}^{\text{IV}}\text{M}_{12}^{\text{II}}\text{(hmp)}_{10}]^{2+}\) (1–2) the MIV is not positionally disordered.

**Magnetic properties**

The direct-current molar magnetic susceptibility, \(\chi\), of polycrystalline samples of complexes 1 and 2 were measured in an applied magnetic field, \(B\), of 0.1 T, over the 2–290 K temperature, \(T\), range. The experimental results are shown in Fig. 2 and 3 as the \(\chi T\) product versus \(T\), where \(\chi = M/B\) and \(M\) is the magnetisation.
At room temperature the $\chi T$ product of 1 is $7.5 \, \text{cm}^3 \, \text{K mol}^{-1}$, from where a $g$-value of $g_{\text{Ni}} = 2.32$ can be inferred based on the sum of Curie constants of five uncorrelated Ni$^{II}$ ions ($S_{\text{Ni}} = 1$) and two uncorrelated V$^{IV}$ ions ($S_{\text{V}} = 1/2$), with $g_{\text{V}} = 2.00$. Upon cooling the value of the $\chi T$ product of 1 first slowly drops to reach $7.4 \, \text{cm}^3 \, \text{K mol}^{-1}$ at 100 K, then it slowly increases to reach $7.6 \, \text{cm}^3 \, \text{K mol}^{-1}$ at 30 K and finally rapidly increases below 30 K to reach $13.6 \, \text{cm}^3 \, \text{K mol}^{-1}$ at 2 K. This behaviour is indicative of competing antiferromagnetic and ferromagnetic interactions. To better define the low-temperature magnetic properties of 1, variable-temperature-variable-field (VTVB) magnetisation measurements were performed in the temperature and field ranges 2 to 10 K and 0.5 to 5 T, respectively (inset of Fig. 2). The VTVB magnetisation of 1 at 2 K and 5 T reaches a maximum of $8.7\mu_B$ ($\mu_B$ is the Bohr magneton). Notably, when the VTVB magnetisation data of 1 are plotted against the reduced quantity $\mu_B B/kT$ ($k$ is the Boltzmann constant) no nesting of the VTVB curves is observed (Fig. S4†), indicative of negligible magnetic anisotropy.

For 2, magnetisation measurements were performed on wet polycrystalline samples (of known mass, solvent content) because measurements performed on dry, powdered samples evidenced deterioration over time, consistent with PXRD data (Fig. S1†). This is likely due to lattice solvent loss, exacerbated by the reduced pressure conditions experienced by the sample during the SQUID measurements. The room temperature value of the $\chi T$ product of 2 (Fig. 3) is $9.6 \, \text{cm}^3 \, \text{K mol}^{-1}$, somewhat lower than the value of $10.125 \, \text{cm}^3 \, \text{K mol}^{-1}$ expected for five uncorrelated Co$^{II}$ ions and two uncorrelated V$^{IV}$ ions, assuming (vide infra) both that $g = 2$ for all centres (to avoid over-parameterisation) and that a low symmetry ligand field quenches the orbital angular momentum of the octahedral Co$^{II}$ ions (i.e. spin-only $S_{\text{Co}} = 3/2$). Upon cooling the $\chi T$ product of 2 drops continuously reaching a plateau value of $8.3 \, \text{cm}^3 \, \text{K mol}^{-1}$ at 20 K, whereupon it slightly increases to a local maximum of $8.5 \, \text{cm}^3 \, \text{K mol}^{-1}$ at 9 K, after which it drops to reach $7.1 \, \text{cm}^3 \, \text{K mol}^{-1}$ at 2 K. In contrast to 1, when the VTVB magnetisation data of 2 are plotted against the reduced quantity $\mu_B B/kT$, significant nesting of the VTVB curves is observed (inset of Fig. 3), indicative of significant anisotropy.

The quantitative interpretation of the magnetic properties of 1 and 2 were performed by numerically fitting the experimental data to the full spin-Hamiltonian matrix, of dimension 972 for 1 and 4096 for 2, by use of the simplex algorithm19 and spin-Hamiltonian (1):

$$\hat{H} = \sum_i \mu_i B g_i S_i + D_i \left( S_i^2 - \frac{S_i(S_i + 1)}{3} \right) - \sum_{ij < i} J_{ij} \hat{S}_i \hat{S}_j$$

(1)

where the indices refer to the constituent metal ions, $\hat{S}$ is a spin operator, $D_i$ is the single-ion uniaxial second order magnetic anisotropy parameter and $J_{ij}$ is the pairwise isotropic exchange interaction. For simplicity, we assume all magnetic exchange interactions between M$^{II}$-M$^{II}$ ions ($J_{M-M}$) and V$^{IV}$-M$^{II}$ ($J_{V-O-M}$) ions to be equivalent (Fig. 4, left). For 1, given that the magnetic anisotropy is small, we fitted the temperature dependence of the $\chi T$ product by neglecting the anisotropy terms in spin-Hamiltonian (1). This resulted in the best-fit parameters $J_{\text{Ni-Ni}} = +1.30 \, \text{cm}^{-1}$ and $J_{\text{Ni-VO}} = -3.49 \, \text{cm}^{-1}$. Under these conditions the ground spin-state of 1 is an $S = 4$ state separated by about $6.2 \, \text{cm}^{-1}$ from the first excited state which is an $S = 3$ state (Fig. S5†). The magnetic anisotropy of the Ni$^{II}$ ion was subsequently determined by fitting the VTVB data to spin-Hamiltonian (1) by varying the value of $D_{\text{Ni}}$, whilst keeping the $J$ values fixed. This resulted in $D_{\text{Ni}} = 0.66 \, \text{cm}^{-1}$.

For 2, the temperature dependence of the $\chi T$ product was fitted to the full spin-Hamiltonian (1) resulting in the best fit parameters $J_{\text{Co-Co}} = -0.45 \, \text{cm}^{-1}$, $J_{\text{Co-VO}} = -4.85 \, \text{cm}^{-1}$ and $|D_{\text{Co}}| = 6.65 \, \text{cm}^{-1}$. However, these parameters do not accurately reproduce the VTVB data (Fig. S6†). In order to obtain a better estimate of $D_{\text{Co}}$, the VTVB data of 2 were therefore fitted to spin-Hamiltonian (1) by fixing the values of the isotropic exchange and letting $D_{\text{Co}}$ vary. This resulted in the best-fit parameter $|D_{\text{Co}}| = 21.40 \, \text{cm}^{-1}$, with the resulting VTVB curves shown in the inset of Fig. 3. The persistent deviation of the calculated curves from the experimental data, originating from the simplicity of the model employed and assumptions made, therefore only allows us at this stage to estimate that $|D_{\text{Co}}|$ likely lies in the range 5 to 25 cm$^{-1}$.

The sign and magnitude of the exchange interactions in 1 and 2 are consistent with previous examples reported in the literature for both dialkoxo- and alkoxo/chloro-bridged M$^{II}$ units, and alkoxo-bridged (VO)-M$^{II}$ moieties with similar bridging angles.9,20-22

Theoretical calculations

In order to further probe the magnitude and origin of the exchange interactions, and anisotropy of the Co$^{III}$ ions, we now turn to theoretical methods. For this purpose we no longer assume that all magnetic exchange interactions between M$^{II}$-M$^{II}$ ions ($J_{M-M}$) and V$^{IV}$-M$^{II}$ ($J_{V-O-M}$) ions are equivalent, but assign individual pairwise exchange interactions between the

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Fig. 4 (Left) Representation of the isotropic exchange interactions included in spin–Hamiltonian (1) used in the experimental fit of the susceptibility and magnetisation data for complexes 1 and 2. (Right) The exchange interaction scheme used in the theoretical modelling of the magnetic data. Colour code as Fig. 1.
constitutive centres in 1 and 2 (Fig. 4, right). Pairwise exchange interactions between neighbouring paramagnetic centres have been computed using the broken symmetry approach (Scheme S1,† eqn (S1)).‡ Four different isotropic exchange pathways \( J_{1-2} \) have been considered: \( J_1 = J_{33} = J_{56} \) (MII\(_{(\text{ring})}\) – Cl\((\text{O})\) – MII\(_{\text{(centre)}}\)), \( J_2 = J_{12} = J_{34} = J_{56} \) (MII\(_{(\text{ring})}\) – O\((\text{O})\) – VIV\(_{(\text{ring})}\)), \( J_3 = J_{27} = J_{37} = J_{57} \) (MII\(_{(\text{ring})}\) – O\((\text{O})\) – MII\(_{\text{(centre)}}\)), \( J_4 = J_{17} = J_{47} \) (MII\(_{(\text{centre})}\) – O\((\text{O})\) – VIV\(_{(\text{ring})}\)).

For 1, the computed \( J \) values are shown in Table 2, together with the values obtained from numerical fitting of the experimental data for comparison. Calculation of the temperature dependence of the \( \chi T \) product and of the VTVB data using the DFT computed \( J \) values and neglecting the uniaxial anisotropy parameter for all metal centres results in good agreement with the experimental data (Fig. 2), with deviations mainly arising for the lower temperatures as a consequence of the isotropic model. The DFT computed \( J \) values suggest that the \( J_2 \) (MII\(_{(\text{ring})}\) – O\((\text{O})\) – VIV\(_{(\text{ring})}\)) interaction is relatively strongly antiferromagnetic, with all other interactions being weakly ferromagnetic in nature. This results in an \( S = 4 \) ground state, with the spin of the two V ions being antiparallel to the spins of the five Ni ions (Fig. S5†). The computed spin densities for the high spin state, as well as four broken symmetry (bs) solutions, provide values in the range of 1.66–1.74 for the Ni\(^{II}\) centres, and a spin polarized value of 1.12(1) for the VO centres (Fig. 5, S7, Table S3†). These are in good agreement with previously reported six coordinate Ni\(^{II}\) and V\(^{IV}\) species. The reduced spin density values on the Ni ions indicate strong spin delocalisation onto the coordinating O, N and Cl ligand orbitals. The increased spin density value on the VO moiety reflects strong spin polarisation.

The computed isotropic exchange interactions for complex 1 can be rationalised by analysing the overlap of magnetic orbitals between interacting pairs of metal centres (Table S4 and Fig. S8†), together with their corresponding bridging angles (Table S1†). In the case of \( J_1 \) (MII\(_{(\text{ring})}\) – Cl\((\text{O})\) – MII\(_{\text{(centre)}}\)), the Ni–Cl–Ni and Ni–O–Ni angles (84.2° and 103.2°, respectively) would be expected to result in a weak ferromagnetic interaction. For \( J_2 \) (MII\(_{(\text{ring})}\) – O\((\text{O})\) – VIV\(_{(\text{ring})}\)) the alkoxide bridging angles (Ni–O–V) are 104.27° (102.11°) and 96.81° (95.93°) and lead to significant antiferromagnetic coupling. Computation reveals significant overlap (\( S_{\text{Ni-V}} = 0.07 \)) between the \( d_{xy} \) orbital of VIV and the \( d_{3z^2-r^2}/d_{2z^2} \) orbitals of NiII – the lower symmetry and strong spin polarisation of the bridging oxygen atom maximises the V\( d_{xy} \)–Ni\( d_{3z^2-r^2}/d_{2z^2} \) orbital overlap. \( J_3 \) (MII\(_{(\text{ring})}\) – O\((\text{O})\) – MII\(_{\text{(centre)}}\)) is weakly ferromagnetic in nature, due to the presence of small Ni–O–Ni angles (96°–100°), and \( J_4 \) is also weakly ferromagnetic because of minimal overlap between magnetic orbitals.

For 2 the magnetic anisotropy parameters of the Co\(^{(II)}\) centres were estimated by \textit{ab initio} calculations. In this case the zfs parameters \( D_{\text{Co}} \) were found to be much larger than the exchange parameters as Co\(^{(II)}\) ions in distorted octahedral environments possess sizeable magnetic anisotropy. The local anisotropy parameters, computed from the NEVPT2-QDPT-EHA level of theory, were found to be \( D_{\text{Co(central})} = \pm 87 \text{ cm}^{-1} \), \( E/D = 0.27 \) and \( D_{\text{Co(ring)}} = +82 \text{ cm}^{-1} \), \( E/D = 0.19 \) (Tables S5 and S6†), about a factor of four larger than the best fit \( D_{\text{Co}} \) parameter obtained by numerically fitting the experimental data to spin-Hamiltonian (1). Due to the very strong anisotropy, single determinant DFT calculations are unable to yield reasonable exchange values (\( J_1 = -18.7 \text{ cm}^{-1} \), \( J_2 = 54.42 \text{ cm}^{-1} \), \( J_3 = -0.66 \text{ cm}^{-1} \) and \( J_4 = 84.71 \text{ cm}^{-1} \)). Thus attempts to simulate the experimental susceptibility and magnetisation data of 2 using the DFT computed \( J \) values along with the highly anisotropic \( D \) values were unsuccessful. Therefore, for the quantitative interpretation of the experimental data, we fix the anisotropy parameters of the Co\(^{(II)}\) centres to those calculated as described above and fit the four exchange parameters in spin-Hamiltonian (1). This resulted in the best fit parameters: \( J_1 = -1.48 \text{ cm}^{-1} \), \( J_2 = -8.19 \text{ cm}^{-1} \), \( J_3 = 3.72 \text{ cm}^{-1} \) and \( J_4 = 6.13 \text{ cm}^{-1} \) (solid blue line and dashed lines in Fig. 3). In order to further investigate the origin of the magnetic anisotropy of the Co\(^{(II)}\) ions, we have plotted the ligand-field d-orbital splitting diagram of the central Co ion (M2 in Fig. 1) of complex 2 (Fig. 6). 58% of the ground state electronic con-
Fig. 6 Ab initio ligand field d-orbital splitting diagram of the central CoII ion.

The observation of structurally analogous homo- and heterovalent Anderson theory. The multi-determinant nature of the wavefunction also suggests that a single electronic configuration is sufficient to describe the true electronic structure of the CoII centres. The anisotropy axes (D_{zz} axes) of the five CoII ions are oriented in a ‘random’ fashion (Fig. S9f).

Conclusions

A structurally unique Anderson-type wheel of formula [(VO)_{2}M_{5}(hmp)_{10}Cl_{2}]2MeOH (M = Ni, Co), in which the V^{IV} ions oppose each other in the outer wheel has been synthesised via solvothermal methods using the pro-ligand hmpH. Complexes 1-2 are rare examples of heterometallic V^{IV}-Ni^{II}/Co^{II} cluster compounds. Magnetic susceptibility and magnetisation studies reveal competing ferro- and antiferromagnetic exchange interactions; the strongest interaction in each case being the antiferromagnetic exchange between M_{II}^{n+}/M_{II}^{(n+1)+} oxidation states points toward the exceptional stability of the structure type. It further suggests that an enormous number of similar [M_{2}] complexes containing a combination of different metal ions in different oxidation states and displaying different magnetic behaviours have yet to be isolated. Given the prevalence of “brucite-like” molecular 2D sheets based on shared [M_{3}] triangular building blocks in 3d polynmetallic coordination chemistry,11 we also speculate that similar species to 1 and 2 but with larger nuclearities in sheet-like “2D” frameworks can be formed.

Conflicts of interest

There are no conflicts to declare.

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