A unique single carboxylate-bridged spin-frustrated chiral Mn(II) metallatriangle†

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Received 6th June 2010, Accepted 26th July 2010
DOI: 10.1039/c0dt00613k

The reaction between Hmbpymca ligand (prepared in situ from the hydrolysis of 5-methyl-4-cyano-bispyrimidine with NaOH and further neutralization with 2 M HCl) and Mn(ClO4)2·4H2O in 1 : 1 molar ratio afforded the triunagulo-trimanganese(II) complex [Mn₃(bpymca)₃(H₂O)₆]Cl·6H₂O 1. The chloride anions in this complex come from the HCl used in the neutralization process. The molecular structure of 1 consists of cationic molecular triangles [Mn₃(μ-mbpymca),(H₂O)₃]³⁺ with C₃ symmetry, chloride anions and crystallization water molecules, all of them involved in an extensive network of hydrogen bonds, leading to a chiral network. Within the [Mn₃(μ-mbpymca),(H₂O)₃]³⁺ cations, seven-coordinated Mn(II) ions are bridged by both oxygen atoms of the carboxylate groups and exhibit a MnO₅N₂ compressed pentagonal bipyramidal coordination environment. The temperature dependence of the magnetic susceptibility shows the presence of weak antiferromagnetic interactions between Mn⁴⁺ ions mediated by the carboxylate group of the mbpymca ligand and the existence of a 3D antiferromagnetic ordering below 4 K, which has its origin in the AF inter-trimer exchange interactions mediated by the strong hydrogen bonds present in the crystal of 1. The experimental magnetic susceptibility data above 7 K could be satisfactorily fitted to the theoretical analytical expression derived from the spin Hamiltonian $H = -J_S S_1 S_2 + S_2 S_3 + S_3 S_1$ with $J = -0.782(3)$ cm⁻¹ and $g = 2.092(3)$. The model predicts a degenerate ground state with an $S = 1/2$, which is typical of triangular trimetallic spin frustrated systems containing metal with non-integer spins. DFT calculations were performed on the molecular structure as found in the solid state to support the experimental $J$ value and the Mn-Ocarb-Mn as the primarily exchange pathway.

Introduction

The design, synthesis and study of the properties inherent to metallatriangles, the simplest metal-mediated polygons, currently pose an intriguing task in areas such as supramolecular chemistry and magnetochemistry. In regard to the supramolecular chemistry area, it remains to be established how the formation of molecular triangles can be anticipated by playing with geometrical factors such as the flexibility of the coordination geometry of the ligand, the steric demand of the ancillary ligands, the preferred geometry of the metal ion etc. As for the magnetic point of view, metallatriangles bearing paramagnetic metal ions can behave as geometrically spin-frustrated molecules when the magnetic exchange interaction between neighbouring metal ions is antiferromagnetic in nature. Spin frustration occurs because all the interactions between spin pairs can not simultaneously have their optimal values. In recent years, this phenomenon has attracted much attention from the view point of its anomalous behaviour on magnetism and the relationship with the spin-mediated superconductivity. The study of metallatriangles has experienced a renaissance with the discovery that oxide-based [Mn₃O(O,CR)₃(L)₃]⁺ complexes (L = oximate) exhibited hysteresis loops and therefore a SMM (single molecule magnet) behaviour. It should be noted that non-X centered trinuclear metallaacyles with paramagnetic metal ions are relatively rare and those of Mn⁴⁺ are restricted only to a few examples. In this paper, we report the synthesis and characterization of a new type of Mn₃²⁺ metallatriangle obtained by a reaction employing the 5-methyl-bispyrimidine-4-carboxylic acid (hereafter Hmbpymca). This new multidentate ligand, which exhibits a rich variety of potential coordination modes, has been designed with the aim of obtaining robust building blocks that could be further used to prepare homo- and heteronuclear metal complexes through the non-coordinated bispyrimidine nitrogen atoms.

Experimental

General

Unless stated otherwise, reactions were conducted in oven-dried glassware upon aerobic conditions, and the reagents were purchased at the highest commercial quality being used without previous purification. The ligand was prepared according to the sequence of reactions given in Scheme 1.
One-pot conversion of 2-chloropyrimidine (A) into the N-hydroxy amide derivative (B), condensation of (B) with 3-ethoxymethacrolein leading to the corresponding N-oxide, and the Reissert-modified reaction giving rise to 5-methyl-2,2'-bipyrimidine-4-carbonitrile (C) were carried out according to procedures previously described in the literature.7

(C) IR (KBr) νmax/cm⁻¹, 3069, 3027, 2955, 2925 and 2854 (w, C–Harom), 2236 (w, C≡N) 1563, 1538, 1411 and 1386, 1260, 1200, 1121, 989, 877, 841; ¹H NMR (400 MHz, CDCl3) δ 7.60 (3H, s, C-3), 7.43 (1H, m, C-5′(H)), 7.21 and 7.01 (2H, m, 2 × C-4′(H)), 9.03 (1H, s, C-6(H)); ¹³C NMR (101 MHz, CDCl3) δ 15.9 (C₁), 114.1 (C≡N), 121.9 (CH-5′), 134.9 (C-5), 142.3 (C-4), 158.2 (2 × CH-4′), 160.5 (CH-6), 161.0 (C-2), 161.1 (C-2′); Anal. Calcd (Found) for C₁₀H₇N₅ (C₁₀H₇N₅) (C): 60.91 (60.70); C, 60.91 (60.70); H, 3.58 (3.98); N, 35.51 (35.52).

Mn(mbpmca)₃(H₂O)₃Cl₃·6H₂O (1)

A stirred solution of nitrile (1) (387 mg, 1.96 mmol) and sodium hydroxide (800 mg, 20 mmol) in distilled water (30 mL) was gently refluxed until total completion of the starting material hydrolysis, as judged by TLC analysis (ca. 2 h). Then it was allowed to cool down and neutralised with an aqueous solution of HCl (2 M). The solvent was removed in vacuo and the remaining brown residue was dissolved in methanol and filtered off washing thoroughly the precipitate. The resulting filtrate was left undisturbed to concentrate slowly by evaporation down and neutralised with an aqueous solution of HCl (2 M). The precipitate was washed five times with ethyl acetate and filtered. The yellow product was recrystallized from methanol giving yellow block-like crystals of 1. X-Ray quality single crystals of 1 were obtained after nearly three months. These were collected by filtration and air-dried. IR (KBr) νmax/cm⁻¹, 3324 (br, OH), 1621 and 1557 (s, COO), 1457, 1433, 1403, 1355 and 1327 (s, COO), 1282, 1261, 1227, 1156, 1009, 924, 834; Yield: 37%. Anal. Calcd (Found) for C₉₀H₄₅N₁₂O₁₈Cl₃Mn₃ (C₉₀H₄₅N₁₂O₁₈Cl₃Mn₃) (C): 31.80 (31.67); C, 31.80 (31.67); H, 4.00 (4.09); N, 15.90 (15.89).

Physical measurements

Elemental analyses were carried out at the “Centro de Instrumentación Científica” (University of Granada) on a Fisons-Carlo Erba analyser model EA 1108. The IR spectra on powdered samples were recorded with a ThermoNicolet IR200FTIR by using KBr pellets. Magnetization and variable temperature (1.9–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at different magnetic fields. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal’s tables.

Single-crystal structure determination†

Crystallographic data for 1 were collected at 123(2) K on an Enraf Nonius Kappa CCD area-detector diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Data collection was performed using φ and ω scans and the data were processed using DENZO-SMN v0.3.0.9 and corrected for absorption using SADABS. The structure was solved by direct methods using the SIR-97 program and all-matrix least-squares refinements on F² were performed using the SHELXL-97 program. Figures were drawn with ORTEP-3 for Windows. The heavy atoms were refined anisotropically.

All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times or 1.5 times those of the respective atoms. Final R1(F), wR2(F²), and goodness of fit agreement factors, as well as details on data collection and analyses for 1 can be found in Table 1.

Computational details

All theoretical calculations were carried out with the hybrid B3LYP method, as implemented in the Gaussian03 program. A quadratic convergence method was employed in the SCF process. Triple-ζ quality basis set proposed by Ahlrichs and co-workers has been used for all atoms. The calculations were performed on the complexes built from the experimental geometries. More details about the models can be found in the discussion of the results. The electronic configurations used as starting points were created using Jaguar 6.0 and 7.5 software. The approach that we used herein to determine the exchange coupling constants for polynuclear complexes has been described in detail elsewhere.

Scheme 1 Synthesis of the ligand.
Table 1  Summary of crystallographic data for compound 1 at 123(2) K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Formula</td>
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</tr>
<tr>
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<td>β°</td>
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<td>γ°</td>
<td>120</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>Unique reflections</td>
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<td>Rₑ</td>
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<tr>
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<tr>
<td>wR²</td>
<td>0.106(0.104)</td>
</tr>
<tr>
<td>Flack’s parameter</td>
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</table>

* R₁ = ∑ |Fᵣ| - |Fₒ| / ∑ |Fᵣ|; Rₑ = {∑[w(F² − Fᵣ²)]/∑[w(Fᵣ²)]}¹/₂ and w = 1/[σ(Fᵣ²) + (aP)² + bP²], where P = (2Fᵣ² + Fₒ²)/3.

Results and discussion

The serendipitous synthesis of [Mn₃(mbpymca)(H₂O)₆]Cl₃·6H₂O (I) was accomplished by the reaction of a solution of Hmbpymca ligand (prepared in situ from the hydrolysis of 5-methyl-4-cyano-bispyrimidine with NaOH and further neutralization with 2 M HCl) with Mn(ClO₄)₂·4H₂O (1:1 molar ratio) in a MeOH–water mixture leading to a yellow solution. Yellow block-like crystals of I were slowly grown from the filtered solution. The chloride anions in I come from the HCl used in the neutralization process.

The molecular structure of I was determined by single-crystal X-ray diffraction and consists of cationic molecular triangles [Mn₃(μ-mbpymca)(H₂O)]⁺ (hereafter Mn₃⁺) with C₃ symmetry (Fig. 1), chloride anions and crystallization water molecules, all of them involved in an extensive network of hydrogen bonds.

Within the Mn₃⁺ cations, seven-fold coordinated Mn(II) ions are bridged by both oxygen atoms of the carboxylate groups and exhibit a MnO₅N₂ coordination environment. The degree of distortion of the Mn(II) coordination polyhedron with respect to ideal seven-vertex polyhedra was quantified by the continuous shape measure theory (CShM).²⁸ By using the SHAPE software we compute the shape measure relative to the pentagonal bipyramid (D₁₀h), capped trigonal prism (C₃v) and capped octahedron (Cᵥ) with values of 3.42, 6.37 and 7.88, respectively. The shape measures relative to other reference polyhedra are significantly larger. Therefore, the MnO₅N₂ coordination sphere is closer to pentagonal bipyramid (PBP). We have analyzed a variety of MnOₓNₓ (X = non-metal atom) heptacoordinate complexes with multidentate ligands (bearing three or more donor atoms). The symmetry measures for these compounds are given in Table 1, ESI.† and represented in the cCO/cCTP symmetry map (Fig. 2).

As it can be observed in this figure, the majority of these Mn(II) complexes are closer to the PBP polyhedron regardless of the nature of the ligand and nuclearity of the complex.

Fig. 1  Up view of the Mn₃⁺ cation of I. Mn(1)–O(1) 2.241(3); Mn(1)–O(2) 2.241(3); Mn(1)–O(3) 2.165(4); Mn(1)–O(4) 2.149(4); Mn(1)–O(5) 2.476(3); Mn(1)–N(1) 2.284(3); Mn(1)–N(2) 2.406(4); C(13)–O(1)–Mn(1) 119.9(3); C(13)–O(1)–Mn(1) ii 85.5(2); C(13)–O(2)–Mn(1) 96.7(3); Mn(1)–O(1)–Mn(1) ii 153.69(15). i = 1 + x, −y, −z; ii = 2 − y, + x, − z.

Fig. 2  cCO-cCTP symmetry map of the experimental structures of MnOₓNₓ heptacoordinate complexes.

In the PBP description, the O1 carboxylic oxygen atom and the N1 and N2 nitrogen atoms of the same mbpymca ligand, as well as the O1 and O2 carboxylic oxygen atoms belonging to a mbpymca ligand coordinated to a neighbouring Mn(II) atom, are located in the equatorial plane with Mn–O and Mn–N distances in the ranges 2.241(3)–2.476(3) Å. The axial positions below and above the equatorial plane are occupied by water molecules at shorter distances of 2.149(4) and 2.165(4) Å, respectively, thus indicating a compression of the pentagonal bipyramidal geometry. The cis–O–Mn–O, -O–M–N and the -N–Mn–N angles in the equatorial plane fall into the 55.94(12)–85.73(15)° range whereas the axial O–Mn–O angle is 171.50(16)°. As it is expected, the most important distortion affecting bond angles around Mn(II) ions is promoted by the small O₁,O₂ bite angle of the carboxylate group (55.94°). In addition, the geometric constraints of the mbpymca terdentate ligand cause significant reduction of the N–Mn–N and N–Mn–O bond angles from the ideal bipyramidal pentagonal geometry. The ligand therefore exhibits a x²-N1,N2,O1:x²-O1,O2 µ-pentadentate/bridging coordination mode giving rise to two...
different types of carboxylate bridges between the Mn(II) atoms: (i) O-monoatomic and (ii) asymmetric *syn-anti*, with a Mn···Mn distance of 4.5938(7) Å. The Mn3+ cations are not planar but curved with an umbrella-like shape (Fig. 3). The triangulo Mn3+ unit I resembles the triangulo-tricopper(II) unit in the complex [Cu3(cpse)3(H2O)3]·8.5H2O (H2cpse = N-[2-hydroxy-1(S)-methyl-2(S)-phenylethyl]-N-methylglycine).21

As a consequence of this, the three O3–Mn–O4 axes are tilted in such a way that the three molecules of water coordinated in the convex part of the Mn3+ cation (O4) are tilted away from the C3 molecular axis, whereas those coordinated in the concave part (O3) are tilted toward the three-fold axis. Because the Mn3+ possesses C3 symmetry and therefore lacks any S4 axis, the whole cation is chiral. In fact, only right hand Mn3+ cations (methyl groups in fifth position of the ligand clockwise oriented) are observed in the chiral crystal.

The coordinated water molecules in the concave part of the Mn3+ cation form strong bifurcated hydrogen bonds with the chloride anions (Cl···O3 distances of 3.076(5) Å and 3.140(4) Å) giving rise to an hexagonal ring with chair-like conformation. The coordinated water molecules in the convex part of the Mn3+ cations are also involved in strong bifurcated hydrogen bond with the crystallization water molecules (O4···O5 and O4···O6 distances of 2.673(7) Å and 2.672(5) Å, respectively). In addition, one of the crystallization water molecules forms strong bifurcated hydrogen bonds with the chloride anions; the O5···Cl distance being of 3.059(6) and 3.377(6) Å. All the above hydrogen bond interactions give rise to a chain of Mn3+ cations propagating along the c direction (Fig. 4). Chains are further glued by Cl···O6 and N5···O6 interactions (3.253(4) Å and 2.932(5) Å), leading to a 3D chiral network. The overall ensemble of the crystals in a batch of I can be expected to contain crystals with clockwise and anticlockwise methyl configurations for the Mn3+ unit in equal amounts and therefore to be racemic.

To the best of our knowledge the structure of this compound is unique because: (i) it represents the first example of a metallotriangle containing only single carboxylate-bridging groups between metal ions, (ii) this is the only reported non-X centered or capped Mn3+ molecular triangle containing heptacoordinated Mn(II) ions and (iii) the Mn3+ species displays C3 symmetry and is chiral.

**Magnetic properties**

The temperature dependence of $\chi_M T$ ($\chi_M$ being the magnetic susceptibility per Mn3+ unit) for I is shown in Fig. 5.

At room temperature, the $\chi_M T$ product (13.49 cm3 K mol⁻¹) matches well with the expected value for three isolated Mn3⁺ atoms with $g = 2.0$ (13.12 cm3 K mol⁻¹). Upon cooling down, the $\chi_M T$ product decreases continuously, first slowly to 75 K and
further sharply to reach a value of 1.86 cm$^3$ K mol$^{-1}$ at 2 K, thus supporting the presence of weak antiferromagnetic interactions between Mn$^{II}$ ions mediated by the carboxylate group of the mbpymca ligand. In keeping with the $C_3$ symmetry of the Mn$_3$ unit, an isotropic Heisenberg–Dirac–Van Vleck Hamiltonian for an equilateral triangle, which assumes equal $J$ coupling between the three Mn(II) centers, was considered to analyze the magnetic susceptibility data [eqn (1)]

$$H = -J(S_1S_2 + S_2S_3 + S_3S_1)$$

with $S_i = 5/2$ and $J$ being the isotropic coupling between the Mn(II) ions. The energy levels for the states described for this Hamiltonian were obtained from the Kambe’s vector coupling method and are represented in the Fig. 6.

As it can be observed, the model predicts a degenerate ground state with an $S = 1/2$, which is typical of triangular trimetallic spin frustrated systems containing metals with non-integer spins. Application of the van Vleck equation to this scheme of energy levels by means of the MAGMUM program$^{23}$ and further fit of the experimental magnetic susceptibility data to the theoretical analytical expression leads to the following parameters: $J = -0.73(1)$ cm$^{-1}$ and $g = 2.066(1)$. It should be noted that at very low temperature the experimental data are below the theoretical ones, which might be due to normal field saturation effects and/or intermolecular interactions. Nevertheless, the fact that the $\chi_m$ vs. $T$ plot (inset Fig. 4) displays a maximum at around 4 K (0.95 cm$^3$ K mol$^{-1}$) seems to indicate the existence of a 3D antiferromagnetic ordering below this temperature. This has been confirmed by the temperature dependence of the in phase $a.c.$ magnetic susceptibility ($\chi'_m$) at zero $d.c.$ field, which shows a maximum at 4 K (Fig. 7, inset). The origin of this phase transition to long-range order would be the AF intertrimmer exchange interactions mediated by the strong hydrogen bonds present in the crystal of 1. In view of this, only the experimental susceptibility data down to 7 K were fitted to the equilateral triangular model leading to $J = -0.782(3)$ cm$^{-1}$ and $g = 2.092(3)$. It should be noted that the experimental $J$ value is similar to those found for other Mn(II) complexes containing the type of carboxylate bridges present in 1, with reported values ranging from $-0.63$ to $-2.35$ cm$^{-1}$. It should be noted at this point that the magnetic data can be also fitted with the following parameters:

$$J = -0.17 \text{ cm}^{-1}, \quad g = 2.046, \quad D = 3.17 \text{ cm}^{-1}, \quad E = 0.76 \text{ cm}^{-1}$$

with $R = 1.0 \times 10^5$, where $D$ and $E$ are single-ion anisotropy parameters of Mn(II) ions. Although, these values reproduce well the $M$ vs. $H$ experimental data below 2 T (see Fig. S1, ESIF), they are exceedingly high for the $S, d$1 configuration of Mn(II) and more specifically hepta-coordinated Mn(II) complexes, which typically exhibit $D$ values lower than 0.2 cm$^{-1}$. In other words, this model, although it reproduces the magnetic data, can not be considered physically sound.

In order to assure the right interpretation of magnetic data, we also performed HFEP experiments at frequencies in the 100–300 GHz range, and temperatures in the 4.2–290 K. An exemplary HFEP spectrum of 1 at 224 GHz (Fig. S2, ESIF) shows a single unstructured resonance at $g = 2$ from room temperature down to ca. 70 K. This is characteristic of a spin system with sufficiently strong spin inter-cluster exchange to average out possible anisotropic interactions. As mentioned before, the crystal structure of 1 shows multiple hydrogen bonds that might enable this effect. As temperatures fall below 70 K, the resonance starts to show a structure, which spreads on the field scale at lower temperatures, but cannot be quantitatively interpreted. However, it clearly scales with field, as observed in multifrequency experiments, which means that it originates from a field-dependent term in the spin Hamiltonian such as the Zeeman effect, and not from field-independent zero-field splitting. In other words, it most probably reflects $g$ anisotropy of the cluster, and not zfs. Since one would expect the tentatively large single-ion anisotropy to be reflected in the zfs characteristic for the excited spin states ($S > 1/2$) of the cluster, which are increasingly populated at high temperatures, the EPR experiment provides an indirect proof that the model based on large single-ion anisotropy of Mn(II) can be ruled out.

The magnetization vs. applied magnetic field plot for 1 at 2 K (Fig. 7) is typical of an antiferromagnetic material and shows a relative slow linear increase of the magnetization at low fields (below 1.5 T) and then a faster linear increase without saturation at the maximum applied field of 5 T with a value of 11 $\mu_B$. The field at which the change in slope of the magnetization takes place, should correspond to the magnetic field needed to overcome the intermolecular interactions and hence to destroy the 3D magnetic ordering. In fact, the in phase $a.c.$ magnetic susceptibility at a $d.c.$ field of 1.6 T does not show any maximum (Fig. 7, inset). The high field linear variation of the magnetization suggests the presence of low lying excited states that are partially thermally...
and field induced populated. These low lying excited states are in agreement with weak magnetic interactions inside the Mn$_{3}^{2+}$ metallacycle.

As indicated elsewhere, there exist two different types of carboxylate bridging groups between the Mn(II) atoms in 1: (i) O-monoatomic and (ii) asymmetric triatomic syn-anti with a Mn···Mn distance of 4.5938(7) Å. Experimental data on Mn$^{II}$ carboxylate-bridged polynuclear complexes have shown that, in general, the O-monoatomic carboxylate bridge seems to be more efficient in transmitting the magnetic exchange interaction than the triatomic syn-anti one.$^{25}$ Therefore, the observed magnetic exchange interaction for 1 must be primarily mediated by the Mn–Ocarb–Mn pathway. In order to support this hypothesis and the experimental $J$ value, DFT calculations were performed on the molecular structure as found in the solid state. We have used the approximation that polynuclear magnetic couplings can be expressed as a sum of pairwise interactions. The $J$ value for each pairwise interactions between Mn(II) atoms have been determined by calculating the energy difference between the high spin state ($E_{HS}$) and broken symmetry state ($E_{BS}$), according to the following equation

$$E_{HS} - E_{BS} = -S_{HS}(S_{HS} + 1)J/2$$

using the Heisenberg Hamiltonian $\hat{H} = -JS_{1}S_{2}$. Here $S_1$ and $S_2$ are the spin of the paramagnetic centers. Applying this equation to each pairwise interaction between Mn(II) atoms of the spin configurations indicated in Scheme 2, gives rise in all cases to the relationship $-J = (E_{HS} - E_{BS})/30$ ($i = 1, 2, 3$). The final value of $J$ is the average of the three values obtained from this relationship. The DFT calculation predicts for the Mn$_{3}^{2+}$ a weak antiferromagnetic interaction with $J = -2.9$ cm$^{-1}$, which is not far from the experimental value of $-0.76$ cm$^{-1}$.

The calculated spin density for the ground singlet state of 1 is given in Fig. 8 and offers information on the mechanism of the magnetic exchange interaction. The spin density distribution suggests that the main mechanism for the exchange is spin delocalization. The shape of the Mn(II) atoms is quasi spherical as expected for a set of five d orbitals with one unpaired electron each. The sphere is somewhat flattened in the directions of the metal–ligand bonds and small spin densities of the same sign appear on the atoms of the ligands directly attached to the metallic centre.

It should be noted that the whole spin density is mainly located on the metallic centers (average value 4.835 e$^{-}$). The oxygen atoms of the carboxylate bridging group region show average values of 0.011 e$^{-}$ and 0.010 e$^{-}$ for O1 and O2, respectively, thus indicating that the delocalization process does not significantly operate in this case, which is in agreement with the weak magnetic coupling observed.

\[\text{Scheme 2} \quad \text{Different spin distributions to obtain the exchange coupling constants.}\]
Conclusions

The 5-methyl-bispyrimidine-4-carboxylic acid ligand has been successfully used to generate the metallotriangle [Mn₃(bpymca)(H₂O)₆]Cl₆·H₂O 1. This complex arises from a self-assembly process, which is controlled by the disposition of the donor atoms on the ligand backbone. The structure of 1 is unique because: (i) it represents the first example of a metallotriangle containing single carboxylate-bridging groups, (ii) it is the only reported non-X centered or capped Mn³⁺ molecular triangle containing heptacoordinated Mn(II) ions and (iii) the [Mn₃(bpymca)(H₂O)₆]⁺ species displays C₃ symmetry and is chiral. The ligand exhibits a 2-O1,O2 µ-pentadentate/bridging coordination mode, which mediates a weak antiferromagnetic interaction between the Mn(II) ions, leading to a spin-frustrated systems with an S = 1/2 degenerate ground state. Nevertheless, the AF intertrimer exchange interactions mediated by the strong hydrogen bonds present in the crystal of 1 lead to a 3D antiferromagnetic order below 4 K.

Acknowledgements

This work was supported by the MEC (Spain) (Projects CTQ2005/0935, CTQ2008-02269/BQU, the Junta de Andalucía (FQM-195 and proyectos de excelencia P08-FQM-03705 and P07-FQM-03092), the University of Granada (post-doctoral contract to Antonio J. Mota) and the Academy of Finland (financial agreement DMR0654118, the State of Florida, and the HFEPR studies were supported by the National High Magnetic Field Laboratory (University of Florida) and the Centro de Supercomputación de la Universidad de Granada. HFEPR studies were supported by the National High Magnetic Field Laboratory, which is funded by the NSF through Cooperative Agreement DMR0654118, the State of Florida, and the DOE.

References

5 Jaguar 6.0; Schrödinger, Inc. Portland, 2005.
10 MAGMUN4.0/OW0L is available as a combined package free of charge from the authors at http://www.ucs.mun.ca/_lthomp/. MAGMUN has been developed by Dr Zhijiang Xu and Laurence K. Thompson (Memorial University), and OW01.exe, by Dr O Waldmann (University of Bern). The software calculates the total spin state values into the van Vleck equation and then substitutes the Sₜ and their associated energies (Eₜ) using the Kambe approach₂ and then substitutes the Sₜ and Eₜ values into the van Vleck equation to generate the variable-temperature susceptibility profile (degenerate states are accounted for).