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Graphical Abstract

The first Ni(II) complex with 2-di1*H*-2-imidazolylmethylmalonate (DIMMAL) presents an original quadruple imidazolyl embrace (QIE) and weak antiferromagnetic interactions.

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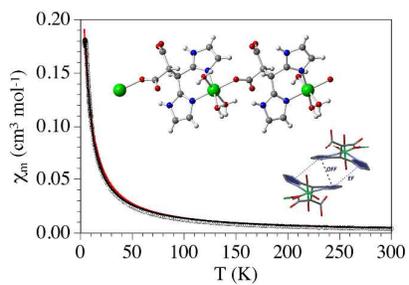
ARTICLE

A rare example of nickel(II) chain based on an heteroscorpionate-like ligand with quadruple imidazolyl interactions

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In memoriam of Purificación Escribano and Juan José Server Carrió

The first nickel(II) complex with the heteroscorpionate-like bridging ligand DIMMAL (2-di1H-2-imidazolylmethylmalonate), [Ni(DIMMAL)(H$_2$O)$_3$]$_n$·3nH$_2$O (**1**), is a one-dimensional coordination polymer whose structure presents regular Ni(II) chains with H-bonding interchain interactions and a rare example of Quadruple Imidazolyl Embrace (QIE). The Ni(II) chain presents a weak antiferromagnetic interaction that can be modelled with a regular S = 1 chain model including a zero field splitting with g = 2.270, J = -1.5 cm^{-1} and D = -2.26 cm^{-1}.

Introduction

One of the major challenges in the area of molecular magnetism is the construction of magnetic frameworks that show spontaneous magnetization and hysteretic behaviour.[1-6] The search for new poly-nuclear transition metal complexes presenting these interesting magnetic properties demands the synthesis of new poly-nucleating ligands whose bridging abilities may give rise to discrete poly-nuclear complexes or isolated chains.[7-10]

As part of our continuing studies on metal complexes of imidazole/carboxylate-based ligands[11-14] we are exploring the ability of the ligand DIMMAL (2-di1H-2-imidazolylmethyl-malonate) to build-up metal-organic frameworks and poly-nuclear complexes with interesting magnetic properties. DIMMAL is a versatile poly-functional ligand with a potential [N,N',N'',N''',O,O'] coordination set which combines the donor function of the imidazole groups with that of two carboxylic groups.[15,16] This recently synthesized ligand has shown a unusual ability to form complexes with Cu(II), either alone or in combination with other co-ligands, presenting different coordination modes. Thus, up to four discrete Cu(II) complexes have been reported with this ligand: a dianionic monomer, (NH$_4$)$_2$[Cu(DIMMAL)$_2$]·4H$_2$O,[15] two neutral monomers, [Cu(HDIMMAL)$_2$][16] and [Cu(DIMMAL)$_2$(en)(H$_2$O)]·5H$_2$O,[15] and a dimer, [Cu$_2$(DIMMAL)$_2$(H$_2$O)$_2$]·2H$_2$O,[16] whereas the only extended system is the sodium salt of the ligand, which forms the chain Na$_2$(HDIMMAL)·5H$_2$O.[16] These five structures exemplify the variety in the coordination modes of the DIMMAL ligand, which is κ-N,N',O in the three monomeric Cu(II) complexes, κ-O,O' in the Na$^+$ chain and κ-N,N',O,O' in the Cu(II) dimer. Note that the dimethyl ester of DIMMAL (bis(methoxycarbonyl)methylmethane or BIBM) also shows different coordination modes as κ-N,N' or κ-N,N',O in the four reported complexes of this ligand.[17-19]

Interestingly, Cu(II) is the only transition metal that has formed DIMMAL complexes to date and, thus, in order to determine the ability of this ligand to complex other transition metal ions and its many different coordination modes, we have undertaken a systematic study of the reaction of DIMMAL with different transition metals and synthetic conditions (pH, ligand to metal ratio, presence of other co-ligands,...). Herein we report the synthesis, X-ray crystal structure, and magnetic properties of the first Ni(II) complex with DIMMAL: the one-dimensional polynuclear complex [Ni(DIMMAL)(H$_2$O)$_3$]$_n$·3nH$_2$O.

Results and discussion

Crystal structure of [Ni(DIMMAL)(H$_2$O)$_3$]$_n$·3nH$_2$O (1)

[Ni(DIMMAL)(H$_2$O)$_3$]$_n$·3nH$_2$O (**1**) crystallizes in the monoclinic space group $P2_1/n$. The crystal structure is built up of regular Ni(II) chains formed by Ni(II) ions connected through the DIMMAL ligand (figure 1).
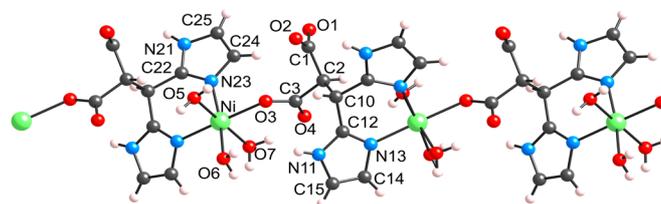
Figure 1. View of the chain structure in compound **1** with the labelling scheme

The asymmetric unit of **1** consists of a nickel(II) ion with a distorted octahedral [NiN$_2$O$_4$] coordination sphere, one DIMMAL ligand, three aquo ligands and three water molecules of crystallization. The [Ni(DIMMAL)(H$_2$O)$_3$] entities are connected through a carboxylate group from the DIMMAL

molecule -which acts as bidentate-monodentante $1\kappa^2 N,N':2\kappa O$ bridging ligand- thus affording chains running along the [1,0,1] direction (see Figure 1). The shortest Ni-Ni distance along these chains is 7.731(1) Å.

The coordination polyhedron around the nickel(II) ion is a *cis*-NiN_2O_4 distorted octahedron. The basal plane is formed by two nitrogen atoms from two imidazole rings, an oxygen atom from the coordinated carboxylate group and a water molecule, with Ni-N and Ni-O mean bond lengths of 2.08 and 2.05 Å respectively. The axial sites are occupied by two water molecules with Ni-O average distances of 2.15(2) Å, with a tetragonality parameter, T -defined as the ratio between the in-plane and out-of-plane mean Cu-X bond lengths- of 0.96.[20] Besides the different bond lengths, the distortions from the regular octahedral geometry in the NiN_2O_4 chromophore are revealed by the range of the *cis* angles, (from 82.61(4)º to 96.89(4)º), and of the *trans* ones (from 170.57(4)º to 178.40(4)º).

The H-bonding interaction is the determinant force involved in the self-assembly process. The $[Ni(DIMMAL)(H_2O)_3]_n$ chains are linked together into sheets parallel to the *ac* planes by hydrogen bonds formed between the coordinated water molecules (table S2). Thus, O6 and O7 act as H-donor towards two carboxylate oxygen atoms, O1[$5] and O2[$5] ($5 = x+1,y,z) belonging to a neighbouring chain. In addition, N-H···O and O-H···O hydrogen bonds involving crystallization water molecules as well as aromatic-aromatic interactions serve as connection between the layers (see Figure 2).
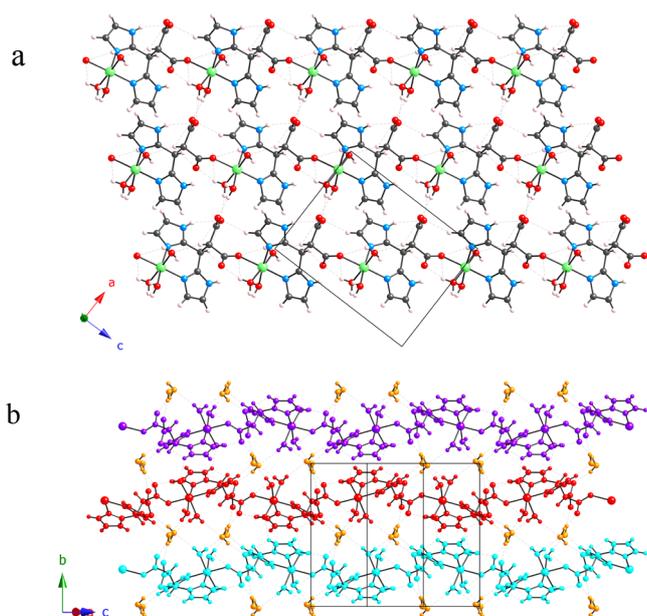
Figure 2. (a) Inter- and intra-chain hydrogen bonding interactions in the *ac* plane (b) Hydrogen bonding interactions connecting the *ac* planes along the b direction.

It must be stressed the existence of concerted sets of intermolecular imidazolyl-imidazolyl π–π interactions (both, offset face-to-face –OFF– and edge-to-face, EF) that associate the four imidazolyl rings from two neighbouring $[Ni(DIMMAL)(H_2O)_3]$ entities (belonging to two adjacent chains) along the *b* axis (see figure 3). The geometrical parameters of these interactions are: d_c = 3.50 Å (d_c = centroid-to-centroid distance), d_p = 3.34 Å (d_p = centroid-to-plane distance) and γ = 17.4º (γ = angle between the centroid-centroid

vector and the vector perpendicular to the imidazole ring plane) for the OFF interaction and d_c = 4.20 Å for the EF ones.[21,22] These parameters are similar to those previously found in other related compounds as $[Na_2(HDIMMAL)_2 \cdot 5H_2O]$, $[Cu(HDIMMAL)_2]$ and $[Cu_2(DIMMAL)_2(H_2O)_2] \cdot 2H_2O$[16] and $[Mn_2Cl(BIP)(HBIMAM)(H_2O)_5]Cl_3 \cdot 4H_2O$[23] and may be considered as a quadruple imidazolyl embrace (QIE), by analogy to the related quadruple pyrazolyl embrace observed in several containing poly(pyrazolyl)-methane and -borate compounds and to the quadruple phenyl Embrace (QPE).[24-36]
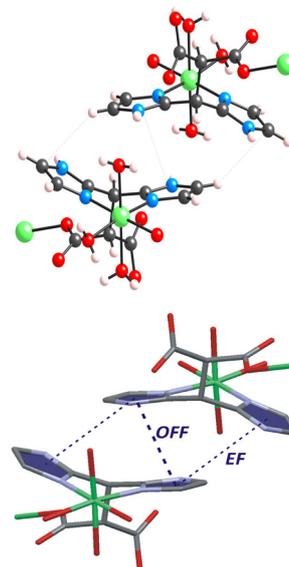
Figure 3. Detail of the concerted π-π interactions (edge-to-face and offset face-to-face) in the supramolecular motif QIE (see text)

Magnetic properties of $[Ni(DIMMAL)(H_2O)_3]_n \cdot 3nH_2O$ (1)

The product of the molar magnetic susceptibility per Ni(II) ion times the temperature ($\chi_m T$) of **1** shows a room temperature value of ca. 1.25 cm^3 K mol^{-1}, which is the expected value for an isolated S = 1 Ni(II) ion with g = 2.2 (figure 4). When the temperature is decreased the $\chi_m T$ product remains constant down to ca. 50 K and below this temperature it shows a progressive decrease to reach a value of ca. 0.40 cm^3 K mol^{-1} at 2 K (inset in figure 4).
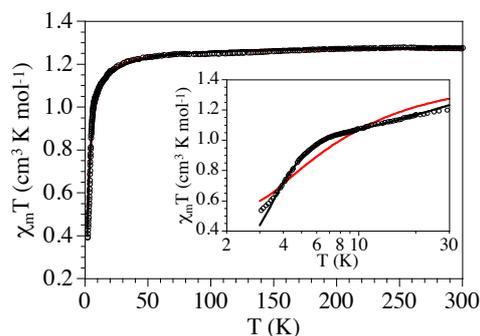
Figure 4. Thermal variation of the $\chi_m T$ product per Ni(II) ion for compound **1**. Inset shows the low temperature region in a logarithmic scale. Solid lines are the best fit to a regular S = 1 chain model with positive (red) and negative (black) D values.

Since the structure of compound **1** shows the presence of Ni(II) centres connected through the long DIMMAL ligands, we can, in principle, assume that the Ni(II) ions are magnetically coupled and, therefore, that the decrease observed in the $\chi_m T$ product at low temperatures is due to the presence of a weak antiferromagnetic coupling together with a zero field splitting (ZFS) in the S = 1 ground spin state. This assumption is confirmed by the presence of a maximum at ca. 4.5 K in the χ_m vs. T plot in the low temperature region (Figure 5). Accordingly, we have fit the magnetic properties to a regular S = 1 chain (α = 1) model including a ZFS.[37] Since a priori we cannot determine the sign of the D parameter with powdered samples, we have used the two available models (for positive and negative D values). Both models give very satisfactory fits of the magnetic properties with the following parameters: g = 2.264, J = -1.0 cm^{-1} and D = 0.49 cm^{-1} for the D > 0 model (red line in figures 4 and 5) and g = 2.270, J = -1.1 cm^{-1} and D = -0.98 cm^{-1} for the D < 0 model (black lines in figures 4 and 5). Note that from the fit of the $\chi_m T$ product (figure 4), it seems that the model with D < 0 seems to better reproduce the magnetic properties in the low temperature region with a weak antiferromagnetic coupling of ca. -1 cm^{-1} and a small D value, within the normal range found in other octahedral Ni(II) complexes.[38] This better agreement is even better observed in the thermal variation of χ_m that shows the presence of a rounded maximum at ca. 4.5 K allowing a better evaluation of the quality of the fits (figure 5). Accordingly, we have also fit the thermal variation of the molar magnetic susceptibility in the low temperature region. These fits give similar parameters (g = 2.264, J = -1.3 cm^{-1} and D = 0.24 cm^{-1} for the D > 0 model and g = 2.270, J = -1.5 cm^{-1} and D = -2.26 cm^{-1} for the D < 0 model) to those obtained fitting the $\chi_m T$ product and again the fit is significantly better for the D < 0 model (black line in figure 5) than for the D > 0 model (red line in figure 5). We can, therefore, conclude that the best fit is obtained with a negative D value and a weak antiferromagnetic coupling.
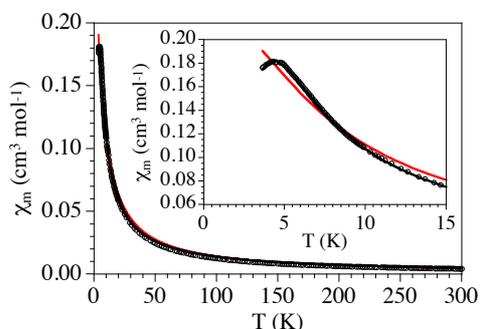
Figure 5. Thermal variation of χ_m per Ni(II) ion for compound **1**. Inset shows the low temperature region. Solid lines are the best fit to a regular S = 1 chain model with positive (red) and negative (black) D values

The isothermal magnetization at 2 K (figure S1, supporting information) shows a saturation value slightly below 2.0 μ_B and the experimental points are below the corresponding Brillouin function for isolated S = 1 ions with g = 2.27, confirming the presence of a non negligible antiferromagnetic coupling.

Note that the weak antiferromagnetic coupling found in compound **1** is not surprising given the long exchange pathway connecting the Ni(II) ions. In fact, it is very similar to the one observed (-1.6 cm^{-1}) in a Cu(II) dimer with the same bridging ligand and the same exchange pathway.[16]

Experimental

Synthetic procedures

The compound Na$_2$(DIMMAL)·5H$_2$O was prepared as previously described[16] and characterized by elemental analysis and powder X-ray diffraction. All other reagents were used as supplied. Elemental analyses (C, H, N) were performed by Servei de Microanalisi, CSIC, Barcelona, Spain.

Compound **1** was obtained by mixing aqueous solutions of Na$_2$(DIMMAL)·5H$_2$O (192 mg, 0.5 mmol in 20 mL) and Ni(NO$_3$)$_2$.6H$_2$O (145 mg, 0.5 mmol in 10 mL) with stirring. The final pH value was 6.05. After standing at 20.1±0.1 ºC for one week, the resulting blue-greenish solution afforded X-ray quality blue crystals of the title compound. Anal. Calc. for C$_{10}$H$_{18}$N$_4$NiO$_9$: C, 30.26; H, 4.57; N, 14.11; Ni, 14.78. Found: C, 30.18; H, 4.64; N, 14.23; Ni, 14.83 %.

Phase purity was established by X-ray powder diffraction (*vide infra*).

Magnetic measurements

DC Variable temperature susceptibility measurements were carried out in the temperature range 2-300 K with an applied magnetic field of 0.1 T on a ground polycrystalline sample of compound **1** (38.50 mg) with a SQUID magnetometer (Quantum Design MPMS-XL-7). The isothermal magnetization measurements were performed at 2 K with magnetic fields up to 7 T. The susceptibility data were corrected for the diamagnetic contributions of the sample as deduced by using Pascal´s constant tables (χ_{dia} = -194.28x10^{-6} cm^3 mol^{-1}).[39] The purity of the measured sample was confirmed by its powder X-ray diffraction pattern that perfectly matches with the simulated one from the structure (figure S2, supporting information).

Crystallography

Single crystal X-ray diffraction. A single crystal of **1** was mounted on a glass fibre using a viscous hydrocarbon oil to coat the crystal. X-ray data were collected at 120 K on a Supernova diffractometer equipped with a graphite-monochromated enhance (Mo) X-ray source (λ = 0.71073 Å). Crystal data: C$_{10}$H$_{18}$N$_4$NiO$_9$, M = 396.99, Monoclinic, a = 9.4748(3), b = 13.1587(3), c = 12.2363(4), β = 90.169(3) Å, V = 1525.57(8) Å^3, T = 120(2) K, P2$_1$/n, Z = 4. 30625 reflections were collected of which 5060 were independent (R$_{int}$ = 0.0329). The program CrysAlisPro, Oxford Diffraction Ltd., was used for unit cell determinations and data reduction. Empirical absorption correction was performed using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Crystal structures were solved and refined against all F^2 values using the SHELXL-2014 program.[40] Non-hydrogen atoms of the frameworks were refined anisotropically. Hydrogen atoms were placed in calculated positions that were refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Water hydrogen atoms were refined as free with O-H distances restrained to be equal. A summary of the data collection and structure refinements is provided in Table S1. CCDC 996415 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray powder diffraction measurements. The polycrystalline sample **1** was lightly ground in an agate mortar and pestle and filled into 0.5 mm borosilicate capillary prior to being mounted and aligned on a Empyrean PANalytical powder diffractometer, using Cu K_α radiation (λ = 1.54056 Å). Two repeated measurements were collected at room temperature (2θ = 2-50º) and merged in a single diffractogram. Pawley refinement[41] was performed using the TOPAS computer program[42] and revealed an excellent fit to a one-phase model (R_{wp} = 0.0278; GOF = 1.488, Figure S2),

Conclusions

We have prepared the first Ni(II) complex with the scorpionate ligand DIMMAL (2-di1*H*-2-imidazolylmethylmalonate) and the first transition-metal complex of this ligand with a chain structure demonstrating the ability of this ligand to form chain compounds by using its carboxylate oxygen atoms and the imidazol nitrogen ones. Furthermore, the chains present a very original concerted sets of intermolecular imidazolyl-imidazolyl $\pi-\pi$ interactions that can be classified as a quadruple imidazolyl embrace (QIE). This chain compound presents weak antiferromagnetic interactions that can be very well reproduced with a S = 1 regular chain model with a negative zero field splitting. This result opens the possible use of this ligand to prepare other coordination polymers with different transition metal and lanthanide ions (given the large number of available coordination sites and the flexibility offered by this ligand). These compounds (prepared either as discrete complexes or as coordination polymers) might result in single molecule or single chain magnets. Attempts to prepare complexes of this ligand with other magnetic metal atoms and also with other terminal and bridging co-ligands providing strong magnetic couplings are in progress.

Acknowledgements

Notes and references
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Electronic Supplementary Information (ESI) available: Plot of the isothermal magnetization at 2 K. Experimental, simulated and difference powder X-ray diffractograms of **1**. Table of crystal data See DOI: 10.1039/b000000x/

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