Polyhedron 70 (2014) 155-163

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Homo and heterometallic rhomb-like Ni₄ and Mn₂Ni₂ complexes



POLYHEDRON

Ritwik Modak^a, Yeasin Sikdar^a, Senjuti Mandal^a, Carlos J. Gómez-García^c, Samia Benmansour^c, Sudipta Chatterjee^b, Sanchita Goswami^{a,*}

^a Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

^b Department of Chemistry, Serampore College, West Bengal, India

^c Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, C/Catedrático José Beltrán, 2, 46980 Paterna, Spain

ARTICLE INFO

Article history: Received 23 October 2013 Accepted 28 December 2013 Available online 8 January 2014

Keywords: Hydroxyl rich ligand Defective dicubane core XRD analysis Homometallic Ni^{II}₄ Heterometallic Mi^{III}₂Ni^{II}₂ Antiferromagnetic coupling

ABSTRACT

Two new polynuclear complexes with hydroxyl-rich Schiff base ligand 3-[(2-Hydroxy-benzylidene)amino]-propane-1,2-diol (H₃L), namely [Ni^{II}₂(HL)(H₂L)(SCN)]₂·DMF (**1**) and [Mn^{III}₂Ni^{II}₂(HL)₂(L)₂] (**2**) have been synthesized and characterized by single crystal X-ray diffraction, elemental analyses, FTIR, UV–Vis spectroscopy and variable temperature magnetic susceptibility measurements. The X-ray refinements reveal that both compounds present defective rhomb-like dicubane central cores (Ni₄ in **1** and Mn₂Ni₂ in **2**). Magnetic susceptibility measurements indicate the presence of overall antiferromagnetic exchange interactions in **1** along the side connected by a N and O atoms ($J_1 = -43.6 \text{ cm}^{-1}$) and along the short diagonal of the rhomb ($J_3 = -3.9 \text{ cm}^{-1}$) and a weak ferromagnetic coupling ($J_2 = +5.8 \text{ cm}^{-1}$) along the side of the rhomb connected by a double O-bridge. In **2** the three exchange interactions are negative ($J_1 = J_2 =$ -0.3 cm^{-1} and $J_3 = -0.7 \text{ cm}^{-1}$). A magneto-structural correlation with the ratio between the Ni–O–Mn bond angle and the Mn–O bond length is also discussed for double O-bridged Mn–Ni pairs.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The design and synthesis of polynuclear transition-metal clusters has been an active area of study for the last couple of decades [1,2]. The presence of polynuclear transition-metal clusters in the active sites of many enzymes has stimulated scientists to explore this fascinating area of research [3]. Manganese and nickel are both very important metal ions present in biological systems [4,5]. Apart from the biological importance, a growing interest in polynuclear transition-metal clusters originates from the prospects of application in many other directions [6,7]. One of the most appealing ones is related to the presence of interesting magnetic properties in polynuclear transition-metal clusters as in molecule-based magnets, whose possible applications in different areas as data storage and magnetic refrigeration have encouraged an extensive research interest in new transition-metal clusters [1,8–13]. Thus, numerous research groups around the world are actively engaged in the development of new synthetic procedures for the preparation of high nuclearity transition metals clusters. Among the different strategies employed to reach this aim, the use of polyalkoxide ligands [14–17] has become one of the most efficient strategy to design and synthesize polynuclear transition-metal clusters. Although there is a large number of homometallic cubane-like Mn and Ni clusters [18–20] and there are also many coordination

compounds containing heterometallic Mn-Ni cores [21-26], the number of mixed metal Mn-Ni rhomb-like cubane clusters is very limited [27]. Such clusters show interesting magnetic properties, including single-molecule magnets [24]. Inspired by these studies, research efforts have been made to synthesize homo- and heterometallic mixed-metal clusters, using Mn and Ni as paramagnetic units. In this context, we have chosen the hydroxyl-rich Schiff base ligand 3-[(2-Hydroxy-benzylidene)-amino]-propane-1,2-diol (H₃L) [28-30] that presents four potential donor sites (one imine nitrogen, one phenoxido oxygen and two alkoxido oxygen atoms) (Scheme 1). Gorden and co-workers utilized this ligand for the first time and reported the syntheses and structural characterization of four dinuclear uranyl complexes [28]. Recently the ligand has been explored to construct polynuclear complexes with various core structures, such as Cu₄, Ni₄, Mn^{III}₃Mn^{II}Na, Gd₁₂Mo₄ etc., [29–38]. Herein we describe the syntheses and characterization of two novel defective rhomb-like dicubane clusters of the type Ni₄ and Mn₂₋ $Ni_{2}:[Ni_{2}^{II}(HL)(H_{2}L)(SCN)]_{2}.DMF$ (1) and $[Mn_{2}^{III}Ni_{2}^{II}(HL)_{2}(L)_{2}]$ (2), prepared with the ligand H₃L.

2. Experimental

2.1. Physical measurements

Elemental (C, H and N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded in the region 400– 4000 cm⁻¹ with a Bruker Optics Alpha-T spectrophotometer as KBr



^{*} Corresponding author. Tel.: +91 33 2350 9937; fax: +91 33 2351 9755. *E-mail address:* sgchem@caluniv.ac.in (S. Goswami).

^{0277-5387/\$ -} see front matter @ 2014 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2013.12.031



Scheme 1. Synthetic route of formation 1 and 2.

pellets. NMR spectra were recorded with a Bruker AV 300 MHz Supercon NMR system Dual Probe. Magnetic susceptibility measurements were carried out in the temperature range 2-300 K with an applied magnetic field of 0.1 T on polycrystalline samples of compounds **1** and **2** (with masses of 29.97 and 42.30 mg, respectively) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascals constant tables ($\chi_{dia} = 662 \times 10^{-6}$ and 500×10^{-6} emu mol⁻¹ for **1** and **2**, respectively) [39].

Phase purity of polycrystalline samples **1** and **2** was established by XRPD. Polycrystalline samples were lightly ground in an agate mortar and pestle and filled into 0.7 mm borosilicate capillaries. Data were collected at room temperature in the 2θ range 5–40° on a Empyrean PANalytical powder diffractometer, using Cu K α radiation (λ = 1.54177 Å). In both cases, the powder diffraction pattern of the bulk sample was consistent with the pattern calculated from single-crystal data (see Figs. S1 and S2).

2.2. X-ray crystallographic data collection and refinement of the structures

The crystallographic data of the compounds are summarized in Table 1. Diffraction data were collected on a Nonius APEX-II diffractometer with CCD-area detector at 150 K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystal structure was determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F² using SHELXL-97 [40]. Absorption correction was done by SADABS method. Hydrogen atoms were located and refined freely. The hydrogen atoms were refined anisotropically, while the non hydrogen atoms were refined anisotropically. The contribution of the electron density associated with disordered solvent molecules was removed by the SQUEEZE subroutine in PLATON [41].

2.3. Synthesis

All the chemicals were purchased from Sigma–Aldrich. All chemicals were of reagent grade and were used as received.

2.3.1. Synthesis of the ligand3-[(2-Hydroxy-benzylidene)-amino]propane-1,2-diol (H₃L)

The mono-condensed Schiff base (H_3L) was prepared by a standard method [28]: 10 mmol of salicylaldehyde(1.05 mL) were mixed with 10 mmol of 3-amino-1,2-propanediol (0.911 g) in 10 mLof absolute ethanol. The resulting mixture was refluxed for one hour, after removal of the solvent under reduced pressure; the crude product was washed with diethyl ether and dried under vacuum (Yield: 74%).

2.3.2. Synthesis of $[Ni^{II}_{2}(HL)(H_{2}L)(SCN)]_{2}$.DMF (1)

A methanolic solution (5 mL) of NaSCN (0.160 g, 2 mmol) was added drop-wise to a methanolic solution (10 mL) of NiCl₂·6H₂O (0.951 g, 4 mmol). The resulting solution was stirred for one hour and then a methanolic solution (5 mL) of H₃L (0.780 g, 4 mmol) was added to the mixture followed by 0.606 g (6 mmol) of Et₃N. The resulting green solution was stirred for 2.5 h and was evaporated to dryness under reduced pressure. The resulting solid was dissolved in DMF. Crystals suitable for X-ray studies were obtained by slow diffusion of diethyl ether into this DMF solution.

Complex **1**: Yield: (~72%). *Anal.* Calc. for $C_{42}H_{46}N_6Ni_4O_{12}S_2$: C, 44.81; H, 4.12; N, 7.47. Found: C, 44.71; H, 4.09; N, 7.28%. Selected IR data (KBr, cm⁻¹) (Fig. S3): $v_{(OH)}$ = 3424, $v_{(SCN)}$ = 2031, $v_{(C=N)}$ = 1632, $v_{(C-O,Phen)}$ =1193, $v_{(C-O,Alco)}$ = 1093 cm⁻¹.

2.3.3. Synthesis of $[Ni^{II}_{2}Mn^{III}_{2}(HL)_{2}(L)_{2}]$ (2)

A solution of NiCl₂.6H₂O (0.951 g, 2 mmol) in methanol (5 mL) was added to a solution of H₃L (0.901 g, 4 mmol) in methanol (10 mL) followed by the addition of a methanolic solution (5 mL) of MnCl₂·4H₂O (0.394 g, 2 mmol). To the resulting solution, Et₃N (0.404 g, 4 mmol) was added dropwise. The resulting mixture was stirred for 2 h and filtered to remove any insoluble material. The filtrate was left at room temperature overnight resulting in the precipitation of brown block shaped crystals of compound **2**.

Complex **2**: Yield: (~ 62%). *Anal.* Calc. for $C_{40}H_{42}Mn_2N_4Ni_2O_{12}$: C, 48.14; H, 4.24; N, 5.61. Found: C, 48.04; H, 4.10; N, 5.40%. Selected IR data (KBr, cm⁻¹) (Fig. S4): $v_{(O-H)} = 3407$, $v_{(C-N)} = 1612$, $v_{(C-O,Phen)} = 1208$, $v_{(C-O,Alco)} = 1095$ cm⁻¹.

3. Results and discussion

3.1. Syntheses and IR spectra of the complexes

The reaction of methanolic solution of NaSCN and NiCl₂.6H₂O with H₃L in presence of Et₃N afforded the tetranuclear complex $[Ni^{II}_{2}(HL)(H_{2}L)(SCN)]_{2}$.DMF (1) by slow diffusion of diethyl ether into DMF solution. When methanolic solutions of NiCl₂·6H₂O and MnCl₂·4H₂O are used with H₃L in presence of Et₃N, a Ni^{II}₂Mn^{III}₂ based tetranuclear complex, $[Ni^{II}_{2}Mn^{III}_{2}(HL)_{2}(L)_{2}]$ (2) is formed. The two complexes, 1 and 2 are characterized elemental microanalysis, infrared (IR) spectroscopy and single crystal X-ray crystal-lography (Scheme 1).

IR spectra provided valuable information about the coordination environment of the complexes. In the IR spectra of **1** and **2**, the strong peaks at 1632 and 1612 cm⁻¹ may be ascribed to the presence of coordinated imine group. The spectrum of **1** reveals

 Table 1

 Crystallographic data and determination summery of the complexes 1 and 2.

	1	2
Formula	$C_{42}H_{46}N_6Ni_4O_{12}S_2$	$C_{40}H_{42}Mn_2Ni_2N_4O_{12}$
Molecular weight	635.97	998.04
Crystal system	trigonal	triclinic
Space group	R-3	PĪ
a (Å)	36.978(6)	10.947(4)
b (Å)	36.978(6)	12.003(8)
<i>c</i> (Å)	11.540(2)	12.012(5)
α (°)	90.00	107.808(19)
β (°)	90.00	116.010(13)
γ (°)	120.00	99.616(18)
V (Å ³)	13665(4)	1264.1(11)
Ζ	18	1
$ ho_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.391	1.311
$\mu (\mathrm{mm}^{-1})$	1.353	1.276
F(000)	5940	512.0
Crystal size (mm ³)	$0.15\times0.13\times0.12$	$0.14 \times 0.13 \times 0.11$
θ (°)	1.10-25.13	1.90-24.51
Limiting indices	$-43 \leqslant h \leqslant 44$, $-43 \leqslant k \leqslant 44$, $-13 \leqslant l \leqslant 13$	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 14$, $-13 \leqslant l \leqslant 14$
No. of reflections collected	31286	13027
No. of independent reflections (R_{int})	5358 (0.0402)	4093 (0.0501)
Completeness to θ /%	98.7	97.4
No. of data/restraints/params	5430/0/357	4202/0/268
Goodness of fit (GOF) on F^2	1.083	1.070
Final R indices $(I > 2\theta(I))$		
R_1	0.0504	0.0693
wR ₂	0.1269	0.2013
R indices (all data)		
R_1	0.0611	0.0892
wR ₂	0.1332	0.2194
Largest difference in peak, hole ($e Å^{-3}$)	1.359, -1.048	1.047, -0.461

strong band at 2031 cm^{-1} suggesting the presence of isothiocyanate moiety.

3.2. Description of the crystal structures

3.2.1. [Ni^{II}₂(HL)(H₂L)(SCN)]₂.DMF (**1**)

Single crystal X ray diffraction analysis reveals that complex **1** crystallizes in the trigonal R-3 space group and that the asymmetric unit is built up by a dinuclear Ni(II) fragment and one DMF solvent molecule (Fig. 1). Selected bond distances and angles are shown in Table S1. Fig. 2 shows that the dinuclear unit further

dimerizes via a triply bridging alkoxido oxygen atom (O3) and doubly bridging phenoxido oxygen atom (O4) of the Schiff base ligand as well as the nitrogen (N3) of the thiocyanate ligand to generate a tetranuclear moiety that can be formulated as $[Ni_4(\mu_3-O_{alkoxido})_2(\mu_2-O_{phenoxido})_2(\mu_2-NCS)_2]^{2+}$. The topology of the core can be described as face sharing distorted double cubane with two missing vertices. A search in the CCDC database (updated August 2013) shows that this is the first Ni₄ tetramer of this type with thiocyanate bridges. The Ni(II) atoms in **1** present a distorted octahedral environment. The octahedral coordination around Ni1 center is formed by two phenoxo oxygen atoms (O1, O4), two alkoxo oxygen



Fig. 1. (a) Structure of the $[Ni^{II}/2(HL)(H_2L)(SCN)]_2$ cluster in compound **1** (b) View of the vacant rhomb-like dicubaneNi₄N₂O₄ central core in **1**showing the coordination environment of the four Ni(II) centers. Hydrogen atoms and the solvent molecule have been omitted for clarity. Color code: Ni = green, N = blue, O = red, S = yellow and C = gray. (Colour online.)



Fig. 2. Coordination environments in compound 1.

atoms (O3, O3#), one imine nitrogen (N2) and a thiocyanate nitrogen (N3). The Ni2 center is surrounded by one phenoxo oxygen (O4), three alkoxo oxygen atoms (O2, O3, O5), an imine nitrogen (N2) and a thiocyanate ligand (N3). The average Ni-N_{imine} and Ni-N_{SCN} distances are 1.9875 and 2.162 Å, respectively. The Ni-O distances range from 1.990 to 2.139 Å. Each μ_3 -O_{alkoxido}group presents one short and two longer bonds to the nickel centers (Ni2-O3 = 1.993 Å, Ni1–O3 = 2.052 Å and Ni1#–O3 = 2.055 Å). These Ni-N and Ni-O bond lengths are in the normal range of those reported for other six coordinate Ni(II) complexes.[30,42,43] The thiocyanate ligand shows an almost linear geometry, with a N-C-S bondangle of 178.95°. The bridging angles between Ni ions range from 88.93° to 101.81° (Ni1–N_{SCN}–Ni2 = 88.93°, Ni1–O_{phenox-} $_{ido}$ -Ni2 = 94.60°, Ni1-O_{alkoxido}-Ni2 = 101.81°). The alkoxo oxygen atom (O2) and the DMF solvent molecule participate actively in hydrogen bonding interactions (O2-H20...O7 = 2.608 Å) resulting in a 3D H-bonded structure (Fig. 3).

3.2.2. $[Ni^{II}_{2}Mn^{III}_{2}(HL)_{2}(L)_{2}]$ (2)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ and the selected bond distances and angles are listed in Table S2. The molecular structure of **2** contains the discrete cluster moiety $[Mn^{III}_{2}Ni^{II}_{2}(L^{3-})_{2}(HL^{2-})_{2}]$ as depicted in Fig. 4. As in **1**, here the asymmetric unit also contains a crystallographically independent



Fig. 3. Crystal packing diagram of 1.

[MnNi] unit which undergoes a dimerization by means of a triply bridging alkoxo oxygen group (O6). The valence states of the metal ions are confirmed by charge balance considerations, bond valence sum (BVS) calculations [43] and by a close examination of structural parameters [23,37,44] that show that the heteronuclear moiety contains two Ni(II) and two Mn(III) centers (see Table S3). In this moiety, the four metal ions are held together by means of two triply deprotonated (L^{3-}) and two doubly deprotonated Schiff base ligands(HL²⁻). The deprotonated alkoxo oxygen atom O6 bridges the two Ni(II) centers with a Ni-O-Ni bond angle of 98.15°. The Mn(III) and Ni(II) centers are connected by the alkoxo oxygen atoms O3 and O6 with Ni-O-Mn bond angles of 102.71° and 97.74°, respectively. In the adjacent face, the phenoxo oxygen atom O1 and the alkoxo oxygen atom O6 bridge the metals with Ni-O-Mn bond angles of 97.05° and 100.12°, respectively. Thus, as in 1, the overall arrangement takes the form of a face sharing di-vacant, slightly distorted, rhomb-like double cubane where the alkoxo oxygen atom O6 connects the three adjacent faces. All the metal centers adopt a distorted octahedral environment (Fig. 5), where three coordinating atoms O1, N1 and O3 of a Schiff base ligand coordinate each Ni(II) ion. The remaining sites are occupied by two bridging alkoxo groups (O6 and O6a) and a terminal alkoxo atom (O5) of another Schiff base ligand. The coordination geometry of the Mn(III) ions is an elongated octahedral environment, as expected for high spin d⁴ ions with Jahn–Teller distortion. The equatorial plane if formed by a phenoxo oxygen atom (O4), imine nitrogen (N2) and two alkoxo oxygen atoms (O3 and O6). The axial positions are occupied by an alkoxo (O2a) and a phenoxo oxygen atom (O1) with much longer Mn-O bond lengths (2.394(9) and 2.188(4) Å, respectively) compared to the equatorial ones (in the range 1.856–2.001 Å, Table S3). The adjacent Mn₂Ni₂ entities are held together by weak van der Waals interaction and propagate along *a* axis to generate a one dimensional chain like form (Fig. S5).

3.3. Magnetic properties

The thermal variation of the molar magnetic susceptibility per Ni(II) tetramer times the temperature ($\chi_m T$) for compound **1** shows a value of ca. 4.8 emu K mol⁻¹ at room temperature. This value is the expected one for four non interacting Ni(II) *S* = 1 ions with $g \approx 2.2$ (Fig. 6). When the sample is cooled, $\chi_m T$ shows a progressive decrease and reaches a smooth plateau of ca. 2.4 emu K mol⁻¹ between ca. 10 and 5 K. Below 5 K $\chi_m T$ shows a more abrupt decrease to reach a value of ca. 1.4 emu K mol⁻¹ at 2 K. This behavior indicates that complex **1** presents predominant antiferromagnetic interactions between the Ni(II) ions. The structure of **1** shows the presence of a rhomb-like Ni(II) tetramer with Ni–Ni exchange interactions along the sides of the rhomb and along the short diagonal. From the symmetry of the cluster (Scheme 2), the exchange



Fig. 4. (a) Structure of the $[Ni^{II}_2Mn^{III}_2(HL)_2(L)_2]$ cluster in compound **2** (b) View of the vacant rhomb-like dicubane Ni₂Mn₂O₆ central core in **2** showing the coordination environment of the two Ni(II) and two Mn(III) centers. Hydrogen atoms and the solvent molecule have been omitted for clarity. Color code: Ni = green, Mn = Orange, N = blue, O = red and C = gray. (Colour online.)



Fig. 5. Coordination environments in compound 2.





Scheme 2. Magnetic exchange scheme in compound 1.

i and *j* is written as $-JS_iS_j$. The fit obtained reproduces very satisfactorily the magnetic properties of compound **1** in the whole temperature range with the following parameters: g = 2.292, $J_1 = -43.6 \text{ cm}^{-1}$, $J_2 = +5.8 \text{ cm}^{-1}$, $J_3 = -3.9 \text{ cm}^{-1}$ and a paramagnetic monomeric S = 1 impurity of 0.7% (solid line in Fig. 6).

The thermal variation of $\chi_m T$ per $Mn^{III}_2Ni^{II}_2$ tetramer for complex **2** shows at room temperature a value of ca. 8.3 emu K mol⁻¹, slightly above the expected value for two isolated Mn(III) *S* = 2 ions (6 emu K mol⁻¹) plus two isolated Ni(II) *S* = 1 ions (2 emu K mol⁻¹) with *g* = 2 (Fig. 7). When the temperature is lowered $\chi_m T$ remains constant down to ca. 25 K and below this temperature $\chi_m T$ shows a progressive decrease to reach a value of ca. 6.0 emu K mol⁻¹ at 2 K. This behavior indicates that in complex **2** the magnetic coupling is also antiferromagnetic but significantly weaker than in **1**. Since the structure of **2** from the magnetic point of view is similar to **1**

Fig. 6. Thermal variation of the $\chi_m T$ product per Ni(II) tetramer for compound **1**. Solid line represents the best fit to the model (see text).

between Ni atoms 1–2 and 3–4 is the same (J_1 , through the O3 and N3 bridge) and the exchange between Ni atoms 2–3 and 1–4 is also identical (J_2 , through the O3 and O4 bridge). Finally, we have included a third exchange constant along the short diagonal of the rhomb (J_3 , through the double O3 bridge).

Accordingly, we have fitted the magnetic properties of **1** to a spin model that takes into account the structural features of this Ni₄ cluster using the package MAGPACK [45,46]. In this model, the Hamiltonian describing the exchange interaction between sites



Fig. 7. Thermal variation of the $\chi_m T$ product per $Mn^{III}_2 Ni^{II}_2$ tetramer for compound **2.** Solid line represents the best fit to the model (see text).



Scheme 3. Magnetic exchange scheme in compound 2.

(except for the change of two Ni(II) ions by two Mn(III) ions), we have used a similar magnetic scheme (Scheme 3) to fit the magnetic properties of **2** using the package MAGPACK [45,46]. The fit so obtained reproduces very satisfactorily the magnetic properties of compound **2** in the whole temperature range with the following parameters: g = 2.032, $J_1 = J_2 = -0.3$ cm⁻¹ and $J_3 = -0.7$ cm⁻¹ (solid line in Fig. 7). Note that J_2 was allowed to vary free but the resulting value was equal to J_1 .

The fitting of the magnetic properties of **1** shows that one of the exchange coupling constants along the sides of the rhomb and the one along the short diagonal are antiferromagnetic $(J_1 = -43.6 \text{ cm}^{-1} \text{ and } J_3 = -3.9 \text{ cm}^{-1})$ whereas the coupling along the other side of the rhomb is ferromagnetic ($J_2 = +5.8 \text{ cm}^{-1}$). In order to rationalize these values, we have searched in the CCDC database all the reported magnetically characterized Ni₄ tetramers with a similar Ni₄O₄N₂core (Scheme 2, Table 2) [18-20,47-49]. In the seven cases found, the coupling along the sides $(J_1 \text{ and } J_2)$ and along the short diagonal (J_3) of the rhomb are all ferromagnetic, in contrast to the antiferromagnetic J_1 and J_3 coupling constants found in 1. The reasons for this discrepancy can be explained from the differences in the structures of complex 1 and of all the other Ni₄ tetramers. Thus, in the seven reported Ni₄ tetramers the N atoms belong to $\mu_{1,1}$ -N₃⁻ bridges, which are well known to give rise to ferromagnetic interactions [50]. In contrast, in compound **1** the N atom belongs to a μ -(κ N)-SCN⁻ bridge and, therefore, compound **1** is the first example of a $Ni_4O_4N_2$ core with SCN⁻ bridging ligands.

Since there are no precedents in this kind of Ni₄ complexes, in order to estimate the sign and magnitude of such a Ni–Ni interaction through an O-bridge and a μ -(κ N)-SCN⁻ bridge, we have searched in the CCDC database this kind of bridge in Ni clusters with any nuclearity. There is a total of five magnetically characterized Ni complexes containing this kind of bridge (Table 3) [51–53].

These five examples show coupling constants ranging from moderate antiferromagnetic (-19 cm^{-1}) to moderate ferromagnetic (20 cm⁻¹) (Table 3). Unfortunately, in two of these five complexes there is an additional bridge (a water molecule in one case [61] and a carboxylate bridge in the other [52]) and in two of the three remaining examples, one of the Ni(II) ions presents a square pyramidal structure. Therefore, only in one case the two nickel atoms are octahedrally coordinated as in 1. This lack of examples similar or close to complex 1 precludes any attempt to establish a magneto-structural correlation in this kind of double bridge formed by an O-bridge plus a μ -(κN)-SCN⁻ bridge (J_1). Fortunately, the two other coupling constants found in 1 are more easy to explain since previous magneto-structural correlations have established that double O-bridges give rise to ferromagnetic coupling between Ni(II) ions when the Ni-O-Ni bond angle is below ca. 98-99° [20,47,48,54–60]. In compound **1** the *J*₂ interaction $(+5.8 \text{ cm}^{-1})$ corresponds to a double O-bridge along the side of the rhomb with an average Ni-O-Ni bond angle of 96.9°, close, but inside the range for ferromagnetic interaction. In contrast, the J_3 interaction (-3.9 cm⁻¹) corresponds to a double O-bridge along the short diagonal of the rhomb with an average Ni-O-Ni bond angle of 101.8°, out of the ferromagnetic region. Note that although the bond lengths also play an important role in determining the strength of the interaction, in compound 1 these are similar to those found in many other Ni clusters (Table 3).

The coupling constants found in compound 2 are weak and antiferromagnetic, in the normal range found in the eight magnetically and structurally reported Mn₂Ni₂O₆ clusters similar to 2, where the coupling constant values expand from ca. -20 to 20 cm⁻¹ (Table 4) [21,23–26,27,61]. As in **1**, here again there is no magneto-structural correlation because only in three of the eight cases the authors have considered a model with two different coupling constants along the sides. If we look at these three examples (MAJZON, SUDWOD and WEFZAK, Table 4) we can see that the first one presents ferromagnetic Ni...Mn interactions whereas in the other two, these are antiferromagnetic. The average Ni-O-Mn bond angles in the ferromagnetic cluster MAIZON (97.9° and 99.3°) are very similar to those of the antiferromagnetic cluster DUSWOD (97.3° and 99.4°) but very different to those of the other antiferromagnetic cluster WEFZAK (93.2° and 102.6°). These values, together with the large dispersion observed in other structural parameters, as the Ni-O and Mn-O bond lengths, preclude the establishment of any simple magneto-structural correlation between the J values and the Ni-O-Mn bond angles nor the Ni-O or Mn-O bond lengths in this kind of tetranuclear clusters. The main reason for this lack of clear simple correlation may be the existence of the additional coupling through the short diagonal of the rhomb (J_3) and the presence of a zero field splitting and interclusters interactions (which are included in some of them). Both parameters may be strongly correlated to the J values, especially when these are weak, precluding any accurate determination of their values.

If we do not limit to tetranuclear $Mn_2Ni_2O_6$ clusters, we can find up to seven magnetically and structurally characterized additional examples presenting a Ni-Mn interaction through a double Obridge (Table 5) [62–64]. Surprisingly, the magnetic coupling in these seven complexes ranges from weak antiferromagnetic (-10.8 cm^{-1}) to moderate ferromagnetic (32 cm^{-1}). If we analyze the structural parameters of these bridges we can observe that the main parameter governing the magnetic coupling seems to be the Mn–O bond lengths and the Mn–O–Ni bond angles. Thus, the three compounds presenting ferromagnetic Ni–Mn interactions are those presenting the largest Ni–O-Mn bond angles (above 101°) whereas in the four compounds with antiferromagnetic Ni–Mn couplings these angles are smaller (below 100°). On the other hand, the three ferromagnetic compounds present short Mn–O

Table 2

Magnetic and structural parameters (average values) of all the reported Ni_4 tetramers with $Ni_4O_4N_2$ core similar to compound **1**.

CCDC code	$J(cm^{-1})$	Ni-X (Å)	Ni-X-Ni (°)	Refs.
AQUFUO	$J_1 = 15.32$	2.042 (0)	102.2 (0)	[20]
	-	2.122 (N)	97.0 (N)	
	$J_2 = 4.51$	2.030(0)	93.5 (0)	
	$J_3 = 4.51$	2.101 (0)	98.4 (0)	
AQUGAV	$J_1 = 15.53$	2.030(0)	101.9 (0)	[20]
	-	2.104 (N)	97.1 (N)	
	$J_2 = 4.32$	2.029(0)	93.2 (0)	
	$J_3 = 4.32$	2.071 (0)	99.4 (0)	
AQUGEZ	$J_1 = 17.86$	2.040 (0)	102.0 (O)	[20]
		2.114 (N)	97.2 (N)	
	$J_2 = 4.68$	2.041 (0)	93.7 (0)	
	$J_3 = 4.68$	2.092 (O)	97.4 (0)	
CUFTUS01	$J_1 = 5.6$	2.112 (0)	100.6 (O)	[40]
		2.093 (N)	101.8 (N)	
	$J_2 = 5.6$	2.072 (O)	94.9 (0)	
	$J_3 = 11.8$	2.056 (O)	99.2 (0)	
HOWQUF	$J_1 = 18.8$	2.120(O)	99.6(0)	[41]
		2.066(N)	103.2(N)	
	$J_2 = 6.9$	2.081 (0)	94.8 (0)	
	$J_3 = 1.3$	2.069 (O)	99.0 (0)	
IGIGAH ^a	$J_1 = 29.5$	2.037 (O)	102.3 (0)	[18]
		2.103 (N)	97.9 (N)	
		2.040 (O)	102.3 (0)	
		2.098 (N)	98.5 (N)	
	$J_2 = 11.6$	2.037 (O)	93.1 (0)	
		2.041 (0)	92.7 (0)	
	$J_3 = 11.6$	2.081 (0)	99.2 (0)	
		2.073 (0)	99.6 (0)	
RICQAW	$J_1 = 7.07$	2.118 (0)	100.4 (0)	[42]
		2.088 (N)	102.4 (N)	
	$J_2 = 7.08$	2.078 (0)	95.5 (0)	
	$J_3 = 11.4$	2.060 (O)	99.9 (0)	
1	$J_1 = -43.6$	2.025 (O)	96.9 (0)	This work
		2.157 (N)	88.9 (N)	
	$J_2 = +5.8$	2.044 (0)	96.0 (O)	
	$J_3 = -3.9$	2.054 (0)	101.8 (0)	

Table 4

Magnetic and structural parameters (average values) of all the reported Mn_2Ni_2 tetramers with the same $Mn_2Ni_2O_6$ core than compound **2**.



CCDC code	$J(cm^{-1})$	Ni–O (Å)	Mn–O (Å)	Ni-O-M (°)	Refs.
JAZRUY	$J_1 = 1.5$	2.039	2.121 ^a	96.2 (Mn)	[25]
	$J_2 = 1.5$	2.084	1.936	100.3 (Mn)	
	$J_3 = 20$	2.105		96.1 (Ni)	
LICVID	$J_1 = -3.6$	2.050	2.153 ^a	98.9 (Mn)	[21]
	$J_2 = -3.6$	2.052	1.920	96.5 (Mn)	
	$J_3 = -6.8$	2.086		98.2 (Ni)	
LICVOJ	$J_1 = 7.2$	2.053	2.111 ^a	97.3 (Mn)	[21]
	$J_2 = 7.2$	2.059	1.928	101.0 (Mn)	
	$J_3 = -15.6$	2.098		97.9 (Ni)	
MAJZON	$J_1 = 9.0$	2.106	2.004	97.9 (Mn)	[24]
	$J_2 = 8.6$	2.099	1.924	99.3 (Mn)	
	$J_3 = -15.8$	2.180		101.7 (Ni)	
RABJIP ^b	$J_1 = -5.8$	2.004	2.070 ^a	98.3 (Mn)	[23]
		2.018	2.081 ^a	99.5 (Mn)	
	$J_2 = -5.8$	2.087	1.930	97.3 (Mn)	
		2.098	1.933	97.3 (Mn)	
	$J_3 = -5.6$	2.077		97.8 (Ni)	
		2.078		97.4 (Ni)	
SUDWOD	$J_1 = -3.0$	2.080	2.122ª	99.4 (Mn)	[54]
	$J_2 = -3.9$	2.122	2.139 ^a	97.3 (Mn)	
	$J_3 = -5.2$	2.051		98.7 (Ni)	
TEBMOE	$J_1 = -10.5$	2.048	2.106	102.4 (Mn)	[26]
	$J_2 = -10.5$	2.072	1.927	94.2 (Mn)	
	$J_3 = 16.2$	2.097		98.1 (Ni)	
WEFZAK	$J_1 = -23.7$	2.090	2.097ª	102.6 (Mn)	[28]
	$J_2 = -12.9$	2.082	1.923	93.2 (Mn)	
	$J_3 = 0.7$	2.131	0.0003	100.3 (Ni)	
2	$J_1 = -0.3$	2.062	2.069*	98.6 (Mn)	I IIIS WORK
	$J_2 = -0.3$	2.089	1.933	100.2 (Mn)	
	$J_3 = -0.7$	2.139		98.1 (NI)	

^a This length includes the Jahn-Teller ellongation in Mn(III).

^b This compound contains two independent Mn₂Ni₂ tetramers.

^a There is an additional carboxylate bridge.

bond lengths (below 2.0 Å) whereas the four antiferromagnetic compounds show much longer Mn-O bond lengths (above 2.1 Å, except compound **2** that presents an intermediate value, in agree-

ment with the very weak antiferromagnetic coupling observed in this compound). Note that the Ni-O bond lengths do not show any clear tendency. From this observations we can deduce that if we represent the J value as a function of the ratio between the Ni-O-Mn bond angle (α) and the Mn-O bond length (R) we expect to observe a linear trend (Fig. 8). Note also that the so obtained linear relation, $J(\text{cm}^{-1}) = -270 + 5.556^*(\alpha/\text{R})$ (solid line in Fig. 8), fits

Table 3 Magnetic and structural parameters of all the reported Ni complexes with an O-bridge and a κ -N-SCN⁻ bridge connecting two Ni ions.

CCDC code	$J(cm^{-1})$	Ni–O (Å)	Ni–N (Å)	Ni-O-Ni (°)	Ni-N-Ni (°)	Refs.
IXUDUA	-3.7	2.049	2.207	110.5	96.6	[44]
		2.003	2.250			
NIWZAU ^a	-19.0	2.097	2.277	85.6	80.1	[45]
		2.090	2.142			
NOBNUN ^b	-3.4	2.027	2.131	94.7	88.1	[46]
		2.042	2.172			
NOBPEZ	+20	2.014	2.039	101.4	96.5	[46]
		2.044	2.170			
NOBPID	+20	1.992	2.077	102.4	95.1	[46]
		2.058	2.197			
1	-43.6	1.993	2.129	96.9	88.9	This work
		2.056	2.195			

^a This complex presents and additional carboxylate bridge.

^b This complex presents an additional H₂O bridge.

Table 5

CCDC code	$J(cm^{-1})$	Ni–O (Å)	Mn–O (Å)	Ni-O-Mn (°)	α/R^a	Refs.
GIQFOC	-10.4	2.057	2.171	99.1	45.65	[55]
IBOTUQ	17.0	2.087	1.936	101.1	52.22	[56]
MIYXOI	-10.8	2.052	2.127	99.6	46.83	[55]
MIYXUO	-10.4	2.067	2.111	99.3	47.04	[55]
MIYYAV	-10.2	2.048	2.135	99.7	46.70	[55]
		2.059	2.139	99.9	46.70	
OVISES	32.0	2.053	1.889	101.1	53.52	[57]
OVISIW	29.2	2.056	1.889	101.0	53.47	[57]
2	-0.3	2.076	2.001	99.4	49.68	This work

Magnetic and structural parameters (average values) of all the reported complexes with Mn and Ni connected through a double O-bridge as in compound 2.

 a α is the Ni–O–Mn angle (°) and R is the Mn–O bond length (in Å).



Fig. 8. Correlation between the *J* values and the α/R ratio found in Ni–Mn complexes connected through double O-bridges (α = average Ni–O–Mn bond angle, in degrees and R = average Ni–O bond length, in Å).

well the very weak antiferromagnetic Ni-Mn coupling found in compound **2**.

4. Conclusions

In summary, we have prepared two novel homo and heterometallic defective rhomb-like dicubane Ni₄ and Ni₂Mn₂ complexes, [Ni^{II}₂(HL)(H₂L)(SCN)]₂.DMF (**1**) and [Mn^{III}₂Ni^{II}₂(HL)₂(L)₂] (**2**), utilizing the hydroxyl-rich Schiff base ligand, 3-[(2-Hydroxy-benzylidene)-amino]-propane-1,2-diol (H₃L). Compound **1** is the first rhomb-like Ni tetramer with SCN⁻ ligands. Both compounds show predominant moderate antiferromagnetic exchange interactions that have been analyzed using the appropriate tetranuclear models with interactions along the sides (J₁ and J₂) and the short diagonal (J₃) of the rhomb. These results show the potential of hydroxyl-rich ligands in designing polynuclear transition metal clusters with different structural topologies.

Acknowledgements

Financial support from the University Grants Commission for RFSMS fellowship (Sanction No. UGC/740/RFSMS) to R. Modak and junior research fellowship to S. Mandal [Sanction No. UGC/749/Jr. Fellow(Sc.)] is gratefully acknowledged. We thank DST for a junior research fellowship to Y. Sikdar (Sanction No. SR/FT/CS-107/2011). DST-FIST is acknowledged for providing the X-ray diffraction facility at the Department of Chemistry, University of Calcutta. We also acknowledge the Spanish MINECO (project CTQ2011-26507) and the GeneralidadValenciana (Prometeo2009/095 and ISIC programs) for financial support. Thanks are given to the Consejo Superior de Investigaciones Cientificas (CSIC) of Spain for the award of a license for the use of the Cambridge Crystallographic Data Base (CSD).

Appendix A. Supplementary data

CCDC 917971 and 929633 contains the supplementary crystallographic data for **1** and **2**. 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.2013.12.031.

References

- [1] R. Sessoli, H.L. Tsai, A.R. Schake, S.Y. Wang, J.B. Vincent, K. Folting, D. Gatteschi,
- G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 115 (1993) 1804.
 [2] A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, Angew.
- Chem., Int. Ed. 43 (2004) 2117.
- [3] D.C. Rees, J.B. Howard, Science 929 (2003) 3009.
- [4] S. Mukhopadhyay, S.K. Mandal, S. Bhaduri, W.H. Armstrong, Chem. Rev. 104 (2004) 3981.
- [5] M.A. Halcrow, G. Christou, Chem. Rev. 94 (1994) 2421.
- [6] G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli, MRS Bull. 25 (2000) 66.
- [7] R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141.
- [8] D. Gatteschi, Adv. Mater. 6 (1994) 635.
- [9] W. Wernsdorfer, N. Aliaga-Alcalde, D.N. Hendrickson, G. Christou, Nature 416 (2002) 406.
- [10] O. Kahn, Molecular Magnetism, VCH, New York, 1993. p. 131.
- [11] J.S. Miller, A.J. Epstein, Angew. Chem., Int. Ed. Engl. 33 (1994) 385.
- [12] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, Coord. Chem. Rev. 193–195 (1999) 1027.
- [13] M. M. Turnbull, T. Sugimoto, L. K. Thompson, Molecule-Based Magnetic Materials—Theory, Techniques and Applications, vol. 644, ACS, Washington, 1996.
- [14] A.M. Ako, I.J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C.E. Anson, A.K. Powell, Angew. Chem., Int. Ed. 45 (2006) 4926.
- [15] S. Nayak, L.M.C. Beltran, Y.H. Lan, R. Clerac, N.G.R. Hearns, W. Wernsdorfer, C.E. Ansona, A.K. Powell, Dalton Trans. (2009) 1901.
- [16] S. Nayak, Y.H. Lan, R. Clerac, C.E. Anson, A.K. Powell, Chem. Commun. (2008) 5698.
- [17] T.C. Stamatatos, K.A. Abboud, W. Wernsdorfer, G. Christou, Angew. Chem., Int. Ed. 45 (2006) 4134.
- [18] S.S. Tandon, S.D. Bunge, R. Rakosi, Z. Xu, L.K. Thompson, Dalton Trans. (2009) 6536.
- [19] Z.E. Serna, L. Lezama, M.K. Urtiaga, M.I. Arriortua, M.G. Barandika, R. Cortes, T. Rojo, Angew. Chem., Int. Ed. 39 (2000) 344.
- [20] S-Y. Lin, Gong-FengXu, Lang Zhao, Yun-Nan Guo, Jinkui Tang, Qing-Lun Wang, Gui-Xia Liu, Inorg. Chim. Acta 373 (2011) 173.
- [21] M. Nihei, A. Yoshida, S. Koizumi, H. Oshio, Polyhedron 26 (2007) 1997.
- [22] G. Wu, R. Clerac, W. Wernsdorfer, S.L. Qiu, C.E. Anson, I.J. Hewitt, A.K. Powell, Eur. J. Inorg. Chem. (2006) 1927.
- [23] S. Nayak, G. Aromí, S.J. Teat, J. R-A, P. Gamez, J. Reedijk, Dalton Trans. 39 (2010) 4986.
- [24] H. Oshio, M. Nihei, S. Koizumi, T. Shiga, H. Nojiri, M. Nakano, N. Shirakawa, M. Akatsu, J. Am. Chem. Soc. 127 (2005) 4568.
- [25] M. Koikawa, M. Ohba, T. Tokii, Polyhedron 24 (2005) 2257.
- [26] S. Nayak, G. Novitchi, S. Muche, D. Luneau, S. Dehne, Z. Anorg. Allg. Chem. 638 (2012) 1127.
- [27] Y. Ding, J. Xu, Z. Pan, H. Zhou, X. Lou, Inorg. Chem. Commun. 22 (2012) 40.
- [28] M.S. Bharara, K. Strawbridge, J.Z. Vilsek, T.H. Bray, A.E.V. Gorden, Inorg. Chem. 46 (2007) 8309.
- [29] S. Nayak, H.P. Nayek, S. Dehnen, A.K. Powell, J. Reedijk, Dalton Trans. 40 (2011) 2699.
- [30] P.-P. Yang, C.-Y. Shao, Y. Xu, L.-L. Zhu, Z. Anorg. Allg. Chem. 639 (2013) 548.
- [31] C.-M. Liu, R.-G. Xiong, D.-Q. Zhang, D.-B. Zhu, J. Am. Chem. Soc. 132 (2010) 4044.
- [32] Y. Li, Acta Crystallogr., Sect. E 64 (2011) 1539.
- [33] S.-Y. Zhang, W.-Q. Chen, B. Hu, Y.-M. Chen, W. Li, Y. Li, Inorg. Chem. Commun. 16 (2012) 74.

- [34] S. Zhang, W. Chen, B. Hu, Y. Chen, L. Zheng, Y. Li, W. Li, J. Coord. Chem. 65 (2012) 4147.
- [35] C. Ding, F. Zeng, J. Ni, B. Wang, Y. Xie, Cryst. Growth Des. 12 (2012) 2089.
- [36] Y. Zheng, Chem. Commun. 49 (2013) 36.
- [37] C. Ding, C. Gao, S. Ng, B. Wang, Y. Xie, Chem. Eur. J. 19 (2013) 9961.
- [38] R. Modak, Y. Sikdar, S. Mandal, S. Goswami, Inorg. Chem. Commun. 37 (2013) 193.
- [39] G.A. Bain, J.F. Berry, J. Chem. Educ. 85 (2008) 532.
- [40] G.M. Sheldrick, SHELKI-97, Crystal Structure Refinement Program, University of Göttingen, 1997.
- [41] P. Van der Sluis, A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) 194.
- [42] G. Aromi, A.J. Tasiopoulos, V. Nastopoulos, C.P. Raptopoulou, S.J. Teat, A. Escuer, S.P. Perlepes, Eur. J. Inorg. Chem. 18 (2007) 2761.
- [43] T.C. Stamatatos, E. Diamantopoulou, A. Tasiopoulos, V. Psycharis, R. Vicente, C.P. Raptopoulou, V. Nastopoulos, A. Escuer, S.P. Perlepes, Inorg. Chim. Acta 359 (2006) 4149.
- [44] W. Liu, H.H. Thorp, Inorg. Chem. 32 (1993) 4102.
- [45] J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, B.S. Tsukerblat, Inorg. Chem. 38 (1999) 6081.
- [46] J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, B.S. Tsukerblat, J. Comput. Chem. 22 (2001) 985.
- [47] Z.E. Serna, N. De la Pinta, M.K. Urtiaga, L. Lezama, G. Madariaga, J.M. Clemente-Juan, E. Coronado, R. Cortés, Inorg. Chem. 49 (2010) 11541.
- [48] Z.E. Serna, M.G. Barandika, R. Cortes, M.K. Urtiaga, G.E. Barberis, T. Rojo, J. Chem. Soc., Dalton Trans. (2000) 29.
- [49] D. Wu, Huang, W. Hua, W. Song, Y. Duan, C. Li, S. Meng, Q. Dalton Trans. (2007) 1838.
- [50] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.

- [51] S.K. Dey, N. Mondal, M.S. El Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich, S. Mitra, Inorg. Chem. (2004) 2427.
- [52] S. Mohanta, K.K. Nanda, R. Werner, W. Haase, A.K. Mukherjee, S.K. Dutta, K. Nag, Inorg. Chem. 36 (1997) 4656.
- [53] T. Koga, H. Furutachi, T. Nakamura, N. Fukita, M. Ohba, K. Takahashi, H. Okawa, Inorg. Chem. 37 (1998) 989.
- [54] W.L. Gladfelter, M.W. Lynch, W.P. Schaefer, D.N. Hendrickson, H.B. Gray, Inorg. Chem. 20 (1981) 2390.
- [55] J.M. Clemente-Juan, E. Coronado, J.R. Galan-Mascaros, C.J. Gómez-García, Inorg. Chem. 38 (1999) 55.
- [56] C.J. Gómez-García, E. Coronado, L. Ouahab, Angew. Chem., Int. Ed. 31 (1992) 649.
- [57] C.J. Gómez-García, J.J. Borras-Almenar, E. Coronado, L. Ouahab, Inorg. Chem. 33 (1994) 4016.
- [58] M.A. Halcrow, J. Sun, J.C. Huffman, G. Christou, Inorg. Chem. 34 (1995) 4167.
 [59] J.M. Clemente-Juan, B. Chansou, B. Donnadieu, J. Tuchagues, Inorg. Chem. 39
- (2000) 5515.
- [60] S. Shit, M. Nandy, G. Rosair, C.J. Gómez-García, J.J. BorrasAlmenar, S. Mitra, Polyhedron 61 (2013) 73.
- [61] Y. Sunatsuki, H. Shimada, T. Matsuo, M. Nakamura, F. Kai, N. Matsumoto, N. Re, Inorg. Chem. 37 (1998) 5566.
- [62] P.L. Feng, C.C. Beedle, C. Koo, W. Wernsdorfer, M. Nakano, S. Hill, D.N. Hendrickson, Inorg. Chem. 47 (2008) 3188.
- [63] H. Chen, C. Ma, D. Yuan, M. Hu, H. Wen, Q. Liu, C. Chen, Inorg. Chem. 50 (2011) 10342.
- [64] A. Das, K. Gieb, Y. Krupskaya, S. Demeshko, S. Dechert, R. Klingeler, V. Kataev, B. Büchner, P. Müller, F. Meyer, J. Am. Chem. Soc. 133 (2011) 3433.