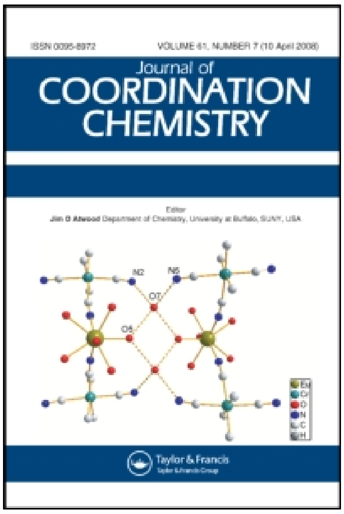

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Structural determinations and magnetic studies of two new binuclear complexes: azido-bridged Ni(II) dimer and di-(μ-hydroxo)-bridged Cr(III) dimer

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Structural determinations and magnetic studies of two new binuclear complexes: azido-bridged Ni(II) dimer and di-(μ-hydroxo)-bridged Cr(III) dimer

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Polydentate ligands 2-[(2-hydroxypropylimino)methyl] phenol (L) and pyridine-2,6-dicarboxylic acid (H_2pda) have been used in the synthesis of binuclear transition metal complexes. A new doubly end-on azido-bridged binuclear nickel(II) complex with formula $[Ni^{II}_2(\mu_{1,1}\text{-}N_3)_2(L)_2(N_3)_2]\cdot H_2O$ (**1**) and a *bis*-μ-hydroxo-bridged dinuclear chromium(III) complex with the formula $[Cr^{III}_2(OH)_2(pda)_2(H_2O)_2]$ (**2**) have been synthesized and characterized by single crystal X-ray diffraction and magnetic studies. Compound **1** displays intramolecular intermetallic ferromagnetic coupling with $J = 28.32\,cm^{-1}$ and $D = -19.30\,cm^{-1}$ based on the Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2 - D(\hat{S}^2_{1z} + \hat{S}^2_{2z}) - g\beta H(\hat{S}_1 + \hat{S}_2)$. Compound **2** displays intramolecular intermetallic antiferromagnetic coupling with $J = -6.56\,cm^{-1}$ based on the Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2 - j(\hat{S}_1\hat{S}_2)^2$.

Keywords: Binuclear complex; Crystal structure; Magnetic properties

1. Introduction

Intra- and intermolecular coupling of transition metal complexes is an important aspect of molecule-based magnets [1]. Structural features, which correlate with strength and sign of such interactions constitute a necessary step. In the case of binuclear transition metal complexes, the nature of the two metal ions, bridging ligands, and the distance between them are the key elements in assembling exchange interaction species [2].

Many bridged transition metal binuclear complexes with a wide variety of bridging ligands, such as mono-cyanide [3] (CN^-, S–CN^-, and O–CN^-), chloro [4], azido [5], oxo [6, 7], hydroxo [8], oxalate [9], or even more complex bridges have been described.

Azido has two typical bridging coordination modes: end-to-end (EE or μ-1,3) and end-on (EO or μ-1,1); the EE linking mode usually gives antiferromagnetic interaction

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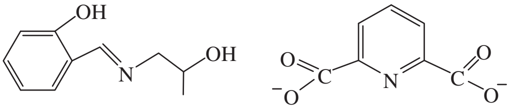

Scheme 1. Structure of polydentate ligands L (left) and pda^{2-} (right).

while the EO mode leads to ferromagnetic interaction, although there are some exceptions [10]. Density functional theory (DFT) calculations on EO or EE azido-bridged transition metal dimeric complexes provide good predictions for magnetic properties [11]. A few binuclear EO-azide Ni(II) systems have been prepared and magnetically studied, helping to elucidate magneto-structural relationships [12–21].

A number of studies [22] have been devoted to chromium(III) dimers $[Cr_2(\mu\text{-}OH)_2L_x]^y$ with a *bis*(μ-hydroxo) bridge, where L is a bidentate or polydentate ligand. For these dimers, Hoffmann and coworkers [22a] have characterized the exchange coupling constant J as the sum of ferromagnetic (J_f) and antiferromagnetic (J_{af}) terms, where $J = J_{af} + J_f$. The contributions J_f and J_{af} can be correlated with structural parameters.

In this study, we have synthesized a new EO azido-bridged binuclear Ni(II) complex and a new μ-hydroxo-bridged Cr(III) complex. Our strategy is the introduction of polydentate ligands to control coordination of the complexes. For example, 2-[(2-hydroxypropylimino)methyl] phenol (L) and pyridine-2,6-dicarboxylic acid (H_2pda) were used as terminal ligands (scheme 1). Herein, we report the synthesis, crystal structures, and magnetic properties of an azido-bridged dinuclear nickel(II) complex, $[Ni^{II}_2(\mu_{1,1}\text{-}N_3)_2(L)_2(N_3)_2]$ (**1**), and a *bis*-μ-hydroxo bridged dinuclear chromium(III) complex, $[Cr^{III}_2(OH)_2(pda)_2(H_2O)_2]$ (**2**).

2. Experimental

Carbon, hydrogen, and nitrogen analyses were carried out with an Elementary Vario El. Infrared (IR) spectra were taken on a Perkin-Elmer SYSTEM 2000 FT-IR spectrometer using KBr pellets. X-ray measurements for **1** and **2** were taken at room temperature on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), operating in ω–2θ scanning mode using suitable crystals for data collection. Variable temperature magnetic susceptibility measurements were performed on a Quantum Design MPMS SQUID magnetometer in a field of 0.3 T. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

2.1. *Syntheses*

The chemicals were purchased from TCI and used as received. *Caution!* Azide salts of metal complexes are potentially explosive and should be handled in small quantities with care. The Schiff-base 2-[(2-hydroxypropylimino)methyl] phenol (L) was prepared according to the literature procedures [23].

2.1.1. $[Ni_2^{II}(\mu_{1,1}\text{-}N_3)_2(L)_2(N_3)_2]\cdot H_2O$ (1).

An aqueous/acetonitrile solution (1 : 1, 30 mL) containing NaN_3 (0.65 g, 10.0 mmol) and 2-[(2-hydroxypropylimino)methyl] phenol (L) (0.89 g, 5.0 mmol) was added to $NiCl_2\cdot 4H_2O$ (1.0 g, 5.0 mmol), dissolved in 10 mL of distilled water with stirring. The mixture was further stirred for 3 h and then filtered. Several days later, well-shaped dark green crystals were separated by filtration and washed with cold water and ethanol. Yield: 0.81 g, 49%. IR (cm^{-1}): 3350, 2971, 2839, 2062, 2020, 1648, 1599, 1470, 1446, 1300, 1031, 899, 762, 610. Anal. Calcd for $C_{20}H_{28}N_{14}Ni_2O_5$ (%): C, 36.26; H, 4.23; N, 29.61. Found: C, 36.67; H, 4.55; N, 29.37.

2.1.2. $[Cr_2^{III}(OH)_2(pda)_2(H_2O)_2]$ (2).

This complex was prepared using mild hydrothermal conditions under autogenous pressure. The compound was prepared from H_2pda (1.0 mmol, 0.167 g,) and $CrCl_3\cdot 6H_2O$ (ratio of $H_2pda : Cr^{3+} = 1 : 1$) in water (15 mL). The pH of the reaction mixture was adjusted to ~9.0 by using NaOH (6 M) and the mixture was stirred for 1 h. After that, the reagents were sealed in a Teflon-lined stainless steel pressure vessel (25 mL, fill factor 65%) and heated at 140°C for 72 h, followed by slow cooling to room temperature. Well-shaped blue–violet crystals suitable for X-ray diffraction were isolated by filtration, washed with water, and dried under vacuum. Yield: 0.13 g (52%). IR (cm^{-1}): 3467, 3074, 1663, 1633, 1435, 1374, 1273, 1128, 1086, 923, 777, 687, 561, 538. Anal. Calcd for $C_{14}H_{12}Cr_2N_2O_{12}$ (%): C, 33.32; H, 2.38; N, 5.55%. Found: C, 33.54; H, 2.23; N, 5.18.

2.2. *X-ray structure determination*

The crystal data are summarized in table 1. The structures were solved by direct methods (SHELXS-97) [24] and refined by full-matrix least-squares (SHELXL-97) [25] on $|F|^2$. Anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic parameters for the hydrogens. Hydrogens were added geometrically and refined using a riding model.

3. Results and discussion

3.1. *IR spectra*

A summary of the most important IR bands corresponding to **1** with tentative assignments are given in table 2. Compound **1** shows two intense IR absorptions at 2062 and 2020 cm^{-1} which can be assigned to ν_{asym} of the terminal and EO azide ligands, respectively. Similarly, a weak signal at 1300 cm^{-1}, expected for the azide symmetric stretching mode, ν_{sym}, is observed. Additionally, a split signal corresponding to the azide bending vibration, δ, can also be observed at 610 cm^{-1} [26]. The IR spectrum of **1** also exhibits a broad signal at 3350 cm^{-1} associated with crystallization of water.

Two strong absorptions at 1300–1700 cm^{-1} were observed in IR spectra of **2**, attributed to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ of pyridyldicarboxylate dianions. If $\Delta\nu(\nu_{as}-\nu_s) > 200\,cm^{-1}$, carboxylate is monodentate and if $\Delta\nu\ (\nu_{as}-\nu_s) < 200\,cm^{-1}$, carboxylate is bidentate [27]. IR spectra of $[Cr_2^{III}(OH)_2(pda)_2(H_2O)_2]$ indicate that $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are separated by 289 cm^{-1}, suggesting monodentate coordination.

Table 1. Crystallographic data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{20}H_{28}N_{14}Ni_2O_5$	$C_{14}H_{12}Cr_2N_2O_{12}$
Formula weight	661.93	504.22
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$C2/m$
Unit cell dimensions (Å, °)		
a	12.925(3)	12.371(4)
b	11.367(2)	10.866(2)
c	20.340(4)	7.1666(14)
α	90	90
β	97.85(3)	117.32(2)
γ	90	90
Volume (Å^3), Z	2960.3(10), 4	855.9(4), 2
Calculated density (mg mm^{-3})	1.474	1.941
Absorption coefficient μ (mm^{-1})	1.327	0.336
Scan range (°)	$1.59 < \theta < 27.48$	$2.64 < \theta < 26.04$
$F(000)$	1348	500
Measured reflections	$-16 \le h \le 16$; $-14 \le k \le 14$; $-26 \le l \le 26$	$-8 \le h \le 7$; $-13 \le k \le 13$; $-13 \le l \le 12$
Number of reflections collected	13,008	2408
Number of independent reflections	6796 [R(int) = 0.0389]	891 [R(int) = 0.0180]
Goodness-of-fit on F^2	1.011	1.026
Final R indices [$I > 2\sigma(I)$]	$R_a = 0.0675$, $wR_a = 0.0931$	$R_a = 0.0381$, $wR_a = 0.0410$
R indices (all data)	$R_b = 0.1891$, $wR_b = 0.2102$	$R_b = 0.1155$, $wR_b = 0.1188$
Largest difference peak and hole (e Å^{-3})	1.013 and −1.259	0.383 and −0.467

Table 2. Characteristic bands (cm^{-1}) in the IR spectra of **1** together with the tentative assignments.

$\nu_{asym}(N_3)$	$\nu_{sym}(N_3)$	$\delta(N_3)$	ν_3 H_2O_{crys}
2062 (i)	1300 (m)	610w (s)	3350 (br)

i, intense; m, medium; w, weak; br, broad; s, split.

Large absorptions in the 3600–2800 cm^{-1} region are attributed to ν(OH) of double hydroxyl bridges and water involved in hydrogen bonds.

3.2. *Crystal structures*

3.2.1. $[Ni^{II}_2(\mu_{1,1}\text{-}N_3)_2(L)_2(N_3)_2]\cdot H_2O$ (1). The labeling scheme for the crystal structure of **1** is depicted in figure 1 and some selected bond lengths and angles are presented in table 3. The structure of **1** consists of neutral, well-isolated dinuclear units in which nickel(II) ions are bridged by two EO azide groups. The coordination polyhedra around each metal ion is a NiN_4O_2 distorted octahedron. Four nitrogens occupy equatorial positions with three from three azides (two EO and one terminal) and the other nitrogen from 2-[(2-hydroxypropylimino)methyl] phenol. The axial coordination sites are occupied by oxygens of 2-[(2-hydroxypropylimino)methyl] phenol (L). The EO azides

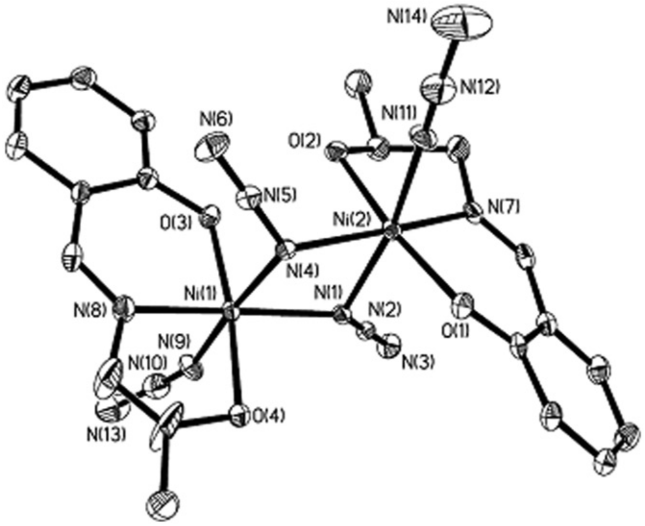

Figure 1. The ORTEP drawing of $[Ni_2^{II}(\mu_{1,1}\text{-}N_3)_2(L)_2(N_3)_2]\cdot H_2O$; thermal ellipsoids are drawn at the 30% probability level. Hydrogens and solvated water have been omitted for clarity.

Table 3. Selected bond distances (Å) and angles (°) for **1**.

Ni(1)–N(8)	1.998(4)	Ni(1)–O(3)	2.003(4)
Ni(1)–N(9)	2.073(4)	Ni(1)–N(1)	2.075(4)
Ni(1)–O(4)	2.121(4)	Ni(1)–N(4)	2.132(4)
Ni(2)–N(7)	1.986(4)	Ni(2)–O(1)	2.020(4)
Ni(2)–N(11)	2.058(4)	Ni(2)–N(4)	2.080(4)
Ni(2)–N(1)	2.131(4)	Ni(2)–O(2)	2.150(4)
N(8)–Ni(1)–O(3)	91.02(16)	N(8)–Ni(1)–N(9)	90.77(18)
O(3)–Ni(1)–N(9)	88.88(17)	N(8)–Ni(1)–N(1)	171.73(17)
O(3)–Ni(1)–N(1)	94.01(15)	N(9)–Ni(1)–N(1)	95.88(17)
N(8)–Ni(1)–O(4)	81.10(16)	O(3)–Ni(1)–O(4)	172.07(14)
N(9)–Ni(1)–O(4)	92.11(17)	N(1)–Ni(1)–O(4)	93.12(15)
N(8)–Ni(1)–N(4)	93.75(17)	O(3)–Ni(1)–N(4)	91.75(15)
N(9)–Ni(1)–N(4)	175.43(17)	N(1)–Ni(1)–N(4)	79.55(15)
O(4)–Ni(1)–N(4)	87.90(15)	N(7)–Ni(2)–O(1)	90.62(16)
N(7)–Ni(2)–N(11)	95.74(18)	O(1)–Ni(2)–N(11)	90.76(17)
N(7)–Ni(2)–N(4)	169.01(16)	O(1)–Ni(2)–N(4)	97.76(15)
N(11)–Ni(2)–N(4)	91.25(17)	N(7)–Ni(2)–N(1)	92.83(16)
O(1)–Ni(2)–N(1)	94.53(15)	N(11)–Ni(2)–N(1)	169.88(17)
N(4)–Ni(2)–N(1)	79.50(15)	N(7)–Ni(2)–O(2)	80.80(16)
O(1)–Ni(2)–O(2)	171.36(13)	N(11)–Ni(2)–O(2)	89.12(17)
N(4)–Ni(2)–O(2)	90.88(15)	N(1)–Ni(2)–O(2)	86.93(14)
Ni(1)–N(1)–Ni(2)	98.66(16)	Ni(1)–N(4)–Ni(2)	98.47(16)

are located upwards and downwards from the bridge plane. The terminal azides are in relative *trans*-positions, each being practically perpendicular to the EO azides. The distance between metallic cations through the EO-azido bridges is 3.190 Å.

The two nickel centers of the dinuclear unit have different bond parameters as shown in table 3. All the O–Ni–O, O–Ni–N, or N–Ni–N angles deviate a few degrees from 90° or 180°. Ni(II) and the four equatorially atoms are nearly coplanar. The equatorially

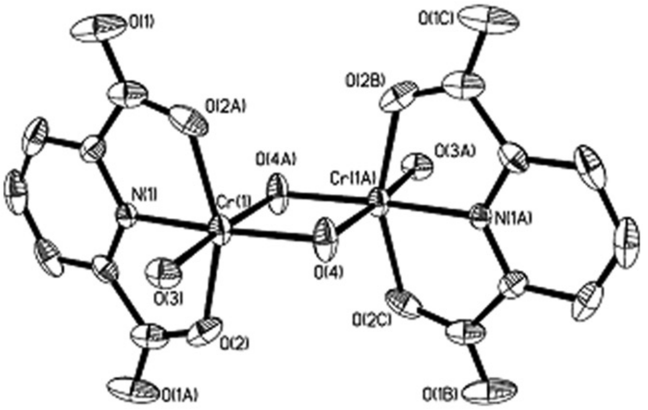

Figure 2. ORTEP drawing of $[Cr_2^{III}(OH)_2(pda)_2(H_2O)_2]$; thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected bond distances (Å) and angles (°) for **2**.

Cr(1)–O(2)	2.015(3)	Cr(1)–O(4)#1	1.955(3)
Cr(1)–O(3)	1.994(3)	Cr(1)–N(1)	1.969(3)
Cr(1)–O(4)	1.952(3)	Cr(1)–O(4)#1	1.955(3)
O(4)#1–Cr(1)–O(2)	102.13(8)	O(4)–Cr(1)–O(4)#1	79.41(14)
N(1)–Cr(1)–O(2)	78.19(8)	O(4)–Cr(1)–N(1)	92.42(13)
O(3)–Cr(1)–O(2)	87.63(7)	O(4)#1–Cr(1)–N(1)	171.83(12)
O(4)–Cr(1)–O(2)	93.55(7)	O(4)–Cr(1)–O(3)	174.23(13)
O(4)#1–Cr(1)–O(2)#2	102.13(8)	O(4)#1–Cr(1)–O(3)	94.83(13)
N(1)–Cr(1)–O(2)#2	78.20(8)	N(1)–Cr(1)–O(3)	93.35(14)
O(3)–Cr(1)–O(2)#2	87.63(7)	O(2)–Cr(1)–O(2)#2	155.59(16)

Symmetry transformations used to generate equivalent atoms: #1: $-x+2$, $-y+1$, $-z+1$; #2: x, $-y+1$, z.

coordination plane suffers a very small distortion as indicated by deviations of the relevant atoms (the deviations from the average planes are 0.0361 Å for Ni(1) and 0.0294 Å for Ni(2)) and the deviation of Ni(II) from the least-square plane is 0.0495 Å for Ni(1) and 0.1158 Å for Ni(2), respectively.

The central $Ni(N_3)_2Ni$ ring is quite distorted from planarity (torsion Ni(1)–N(1)–Ni(2)–N(4) of 14.99°) and slightly asymmetric, showing Ni(1)–N(1) = 2.075(4), Ni(1)–N(4) = 2.121(3), Ni(2)–N(1) = 2.131(4), and Ni(2)–N(4) = 2.080(4) Å bond distances and Ni(1)–N(1)–Ni(2) = 98.66(16) and Ni(1)–N(4)–Ni(2) = 98.47(16)° bond angles.

An analysis performed using the CSD revealed that the Ni···Ni, Ni···O, and Ni···N distances for **1** are comparable to those similar Ni(II) complexes previously reported [28].

3.2.2. $[Cr_2^{III}(OH)_2(pda)_2(H_2O)_2]$ (2).

A perspective view of the centrosymmetric dinuclear **2** is shown in figure 2 and some selected bond lengths and angles are presented in table 4. The structure of **2** consists of neutral, well-isolated dinuclear units in which the chromium(III) ions are bridged by two OH^- groups. The coordination

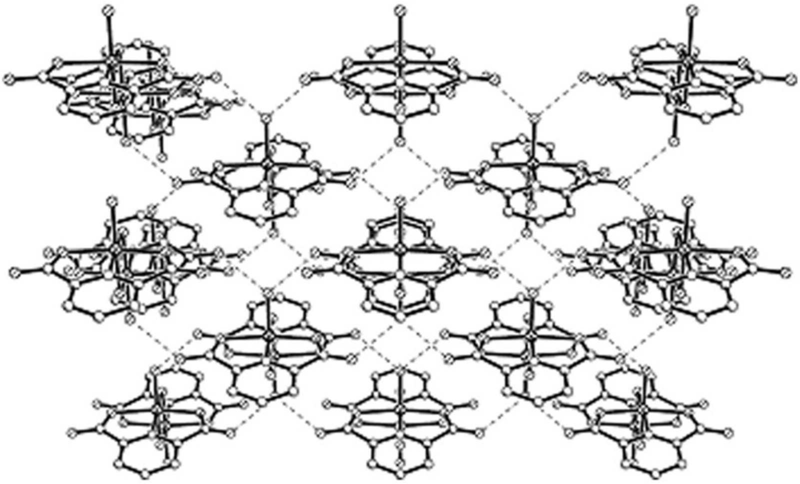

Figure 3. View of the 2-D polymeric layer in **2**. Hydrogens have been omitted for clarity.

Table 5. Hydrogen bond lengths and angles of **2**.

D–H	*d*(D–H)	*d*(H $\cdots$ A)	∠DHA	*d*(D $\cdots$ A)	A
O3–H3	0.820	1.86	150.6	2.603(3)	O1#

Symmetry transformations used to generate equivalent atoms: $-x+3/2$, $-y+1/2$, $-z$.

polyhedron around Cr(III) can be described as $CrNO_5$ distorted octahedron. The chromium is linked to N, O, O of pda^{2-}, one coordinated water molecule and two bridging OH^- groups. The Cr–N bond in **2** is 1.969(3), while Cr–O are 1.952(3) to 2.015(3) Å. The Cr–(μ-OH) bond length is 1.955(3) Å. The Cr $\cdots$ Cr separation is 3.0058(16) Å. The central Cr_2(μ-OH)$_2$ ring is quite distorted from rectangular, showing Cr–O–Cr = 100.568(14) and O–Cr–O = 79.41(14)° bond angles, as in previously published Cr_2(μ-OH)$_2$ fragments [29].

Oxygens of coordinated water and carboxylate form hydrogen bonds, with D $\cdots$ A = 2.603 Å, connecting the dimers to yield a 2-D supramolecular structure (figure 3). Table 5 shows the hydrogen bond lengths and angles of **2**.

3.3. *Magnetic properties*

The magnetic properties of **1** as χ_M and $\chi_M T$ against T plots (χ_M is the magnetic susceptibility per Ni(II) dimer) are shown in figure 4. The Curie–Weiss law is followed in the high-temperature range for which $C_m = 1.24\,cm^3\,K\,mol^{-1}$ and $\theta = 21.30$ K have been calculated along with g values of 2.20. The $\chi_M T$ product increases with decreasing temperature, reaching a maximum after which it rapidly decreases. The maximum is located at 22 K. This behavior indicates ferromagnetic coupling between metal centers which has been associated with EO azide bridges and a large nickel(II) single-ion zero-field splitting.

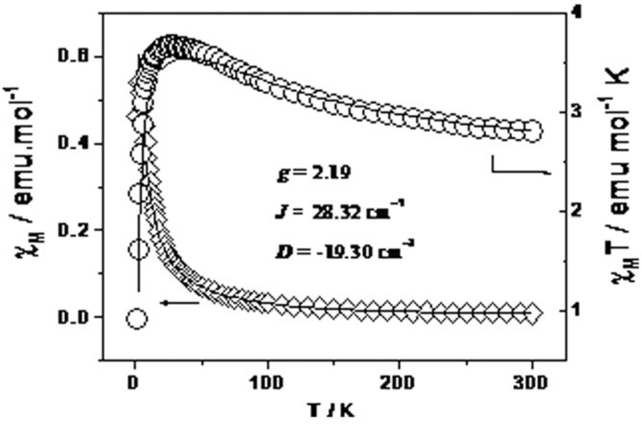

Figure 4. Plots of χ_M and $\chi_M T$ *vs.* T for **1**; the solid line represents the best fitting with $J = 28.32\,\mathrm{cm}^{-1}$, $D = -19.30\,\mathrm{cm}^{-1}$, and $g = 2.19$.

For the theoretical analysis of the magnetic behavior of **1**, the analytical expression based upon the Hamiltonian (1) was used [30]. Accordingly, the temperature dependence of the magnetic susceptibility of **1** was fitted to equation (2),

$$\widehat{H} = -2J\widehat{S}_1\widehat{S}_2 - D\left(\widehat{S}_{1z}^2 + \widehat{S}_{2z}^2\right) - g\beta H\left(\widehat{S}_1 + \widehat{S}_2\right), \tag{1}$$

$$\chi_{\mathrm{dimer}} = \frac{2Ng^2\beta^2}{3\alpha}\left[\frac{F_1}{kT} + \frac{2F_2}{D} + \frac{6c_1^2F_3}{3J-\delta} + \frac{6c_2^2F_4}{3J+\delta}\right] \tag{2}$$

with

$$\begin{aligned}
\alpha &= 2 + e^{D/kT} + e^{J/kT}e^{-\delta/kT} + e^{J/kT}e^{\delta/kT} + 2e^{4J/kT} + 2e^{4J/kT}e^{D/kT},\\
\delta &= [(3J+D)^2 - 8JD]^{1/2},\\
c_1 &= 2\sqrt{2}D/[(9J - D + 3\delta)^2 + 8D^2]^{1/2},\\
c_2 &= (9J - D + 3\delta)/[(9J - D + 3\delta)^2 + 8D^2]^{1/2},\\
F_1 &= 1 + e^{4J/kT} + 4e^{4J/kT}e^{D/kT},\\
F_2 &= 2e^{4J/kT}e^{D/kT} + e^{D/kT} - 1 - 2e^{4J/kT},\\
F_3 &= e^{4J/kT} - e^{J/kT}e^{\delta/kT},\\
F_4 &= e^{4J/kT} - e^{J/kT}e^{-\delta/kT},
\end{aligned}$$

where nickel(II) is assumed to be magnetically isotropic and the interdimer interaction is neglected; J is the usual intradimer exchange parameter; and D the zero-field-splitting term of the ${}^3A_2$ ground state. Using the above equation, the best fit was obtained with the values of $J = 28.32\,\mathrm{cm}^{-1}$, $D = -19.30\,\mathrm{cm}^{-1}$, $g = 2.19$, and the agreement factor $R = \sum[(\chi_M)_{\mathrm{obs}} - (\chi_M)_{\mathrm{calc}}]^2/\sum[(\chi_M)_{\mathrm{obs}}]^2 = 6.22 \times 10^{-4}$. Both theoretical curves can be seen in figure 4. The ferromagnetic interactions in the doubly EO azido-bridged complexes can be interpreted by the concept of accidental orthogonality based on the DFT calculation [31]. Considering the occurrence of spin delocalization [31], the

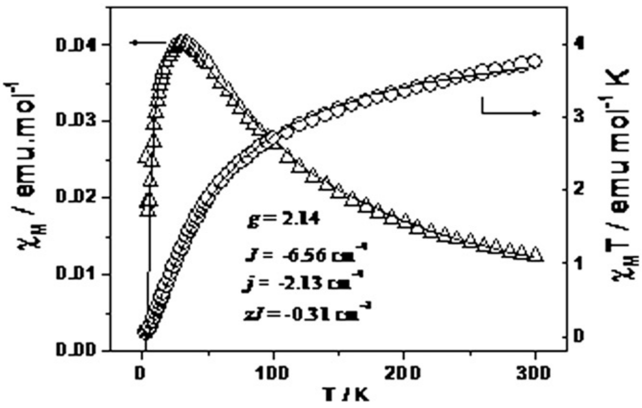

Figure 5. Plots of χ_M and $\chi_M T$ *vs.* T for **2**; the solid line represents the best fitting with $J = -6.56\,\mathrm{cm}^{-1}$, $j = 2.13\,\mathrm{cm}^{-1}$, $zJ = -0.31\,\mathrm{cm}^{-1}$, and $g = 2.14$.

strength of the ferromagnetic exchange is, therefore, dependent on the M–N$_{\mathrm{azido}}$ bond distance and the M–N$_{\mathrm{azido}}$–M bond angles. The Ginsberg equation [30] provides accurate values of J and g, while the value of D is less accurate. However, the effects of the latter parameters are most important in the low-temperature region where the experimental uncertainties are the greatest. Excellent agreement between the experimental and calculated data for **1** should be interpreted in terms of an increasing population of the $S = 2$ ground state with decreasing temperature and the subsequent increasing values of $\chi_M T$. At lower temperature, the single-ion zero-field splitting causes depopulation into a diamagnetic ground state which accounts for decreasing $\chi_M T$.

The magnetic behavior of **2** has been studied from 2–300 K. At 300 K, $\chi_M T$ is equal to $3.74\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ which corresponds to the expected value for two uncoupled metal ($S = 3/2$) ions both in the $^4A_{2g}$ ground state. As usual, the appropriate model for obtaining a fairly good agreement between the theoretical and experimental data may include a biquadratic exchange term (equation (3)). The resultant Hamiltonian is [32]

$$\hat{H} = -2J\widehat{S}_1 \cdot \widehat{S}_2 - j(\widehat{S}_1 \cdot \widehat{S}_2)^2, \tag{3}$$

and this leads to the following expression (equation (2)).

$$\chi_{\mathrm{dimer}} = \frac{2Ng^2\beta^2}{kT}\frac{\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j)/kT] + 14\exp[(12J - 9j)/kT]}{1 + 3\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j]/kT] + 7\exp[(12J - 9j)/kT]}, \tag{4}$$

where the variable magnetic parameters J and j determine triplet, quintet, and septet electronic ground states $E(^3A_2'') = -2J + 6.5j$, $E(^5A_1') = -6J + 13.5j$, and $E(^7A_2'') = -12J + 9j$, respectively [33].

Considering the interaction between binuclear entities, the susceptibility can be corrected by the molecular field approximation [34] (equation (5)), where zJ denotes the intramolecular exchange parameter.

$$\chi_M = \frac{\chi_{\mathrm{dimer}}}{1 - (2zJ/Ng^2\beta^2)\chi_{\mathrm{dimer}}}. \tag{5}$$

The best-fit curves are plotted in figure 5 along with the experimental data. The best-fit parameters obtained for **2** are $-6.56\,\mathrm{cm}^{-1}$ for J, $2.13\,\mathrm{cm}^{-1}$ for j, and $-0.31\,\mathrm{cm}^{-1}$

for zJ, and the agreement factor $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \sum[(\chi_M)_{obs}]^2 = 2.38 \times 10^{-4}$. The negative J value indicates that the main exchange interaction in the dimer is antiferromagnetic. On the contrary, the biquadratic exchange j is positive but of lower amplitude with a $|J|/j$ ratio of 3.08, similar to values found in previously studied di-μ-OH chromium dimers [22d, 33].

4. Conclusions

We have presented the preparation, and structural and magnetic characterizations of a new doubly EO azido-bridged binuclear nickel(II) complex (**1**) and a new *bis*-μ-hydroxo-bridged dinuclear chromium(III) complex (**2**). Analysis of their magnetic data revealed the occurrence of relatively strong ferromagnetic coupling in **1** and of weak but significant antiferromagnetic coupling in **2** through doubly EO azido (**1**)/*bis*-μ-hydroxo (**2**) bridges.

Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 709101 and 709102. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK or Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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