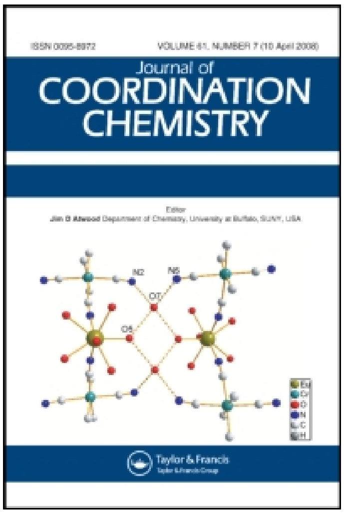

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Trinuclear and dinuclear Ni(II) complexes constructed by bridging oxygen: crystal structures, magnetic, and thermal properties

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Trinuclear and dinuclear Ni(II) complexes constructed by bridging oxygen: crystal structures, magnetic, and thermal properties

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The reaction of H_2L (*N*,*N*′-bis(5-ethyl-1,3,4-thiadiazol-2-yl)-2,6-pyridinedicarboxamide) with Ni(II) salts gave crystals of two new complexes, $[Ni_3(\mu_3\text{-}O)(H_2L)(L)_2]\cdot 2DMF$ (**1**) and $[Ni_2(\mu\text{-}H_2O)(CH_3OH)(DMF)(L)_2]\cdot H_2O\cdot CH_3OH$ (**2**). The complexes were characterized by elemental analysis, IR, thermal analysis, and X-ray single crystal diffraction. Complex **1** is a trinuclear complex containing a triangle frame in the center formed by three Ni(II) atoms with a bridging μ_3-O. Complex **2** is dinuclear formed by two Ni(II) atoms with a bridging H_2O. H_2L coordinates to metal centers as a pentadentate ligand in **1** and tetradentate in **2**. Thermal analysis shows that the thermal stability of **1** is higher than that of **2**. In addition, the magnetic properties of **2** are also reported.

Keywords: Ni complex; Crystal structure; Thermal decomposition; Magnetic properties

1. Introduction

Supramolecular and coordination chemistry have provided important advances in developing strategies for the synthesis of complex molecular architectures. To obtain novel assemblies, coordination of specially designed ligands for metal centers has proven to be very successful [1–3]. This is partly due to the wide range of structural motifs offered by metal centers and also to the relative lability of the coordination bond in comparison to covalent bonds, which provides the possibility of "correcting" errors in the self-assembly process. Furthermore, metal centers can provide unique optical, magnetic, or catalytic properties to the assembly, and hence materials with useful properties can be synthesized [4–6].

We have recently synthesized several transition metal complexes using a new ligand, *N*,*N*′-bis(5-ethyl-1,3,4-thiadiazol-2-yl)-2,6-pyridinedicarboxamide (H_2L), which is a multidentate ligand, to construct various polynuclear complexes [7, 8]. As continuation of our investigation on polynuclear complexes with H_2L, in this article, we report two

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new Ni polynuclear complexes constructed by H_2L together with bridging oxygen, the structures of which are much different from those of mono and dinuclear complexes reported recently [9–11]. The single crystal structures of the complexes were determined by X-ray diffraction, thermal behaviors were investigated by thermogravimetry (TG), and the magnetic properties of **2** were also studied.

2. Experimental

All chemicals used were of analytic reagent grade without purification. Ligand H_2L used in this research was prepared according to the method described in the literature [7].

2.1. *Synthesis of* $[Ni_3(\mu_3\text{-}O)(H_2L)(L)_2]\cdot 2DMF$ *(1)*

$NiC_2O_4 \cdot 2H_2O$ (0.0292 g, 0.16 mmol) was added to a methanol solution (8 mL) with stirring, and then a dimethylformamide (DMF) solution (10 mL) of H_2L (0.0778 g, 0.2 mmol) was added. The resulting mixture was further stirred for 30 min and then sealed in a Teflon-lined stainless steel reactor (size 20 mL) and kept under autogenous pressure at 120°C for 72 h. After cooling naturally to room temperature, green block-like crystals of **1** were filtered, washed with methanol and dried under vacuum (Yield: 45%). Found: C, 40.79%; H, 3.41%; and N, 21.47%. Anal. Calcd for **1** ($C_{51}H_{51}N_{23}Ni_3O_9S_6$): C, 40.84%; H, 3.40%; and N, 21.49%. IR(cm^{-1}): 3440 m, 3079 w, 2970 m, 1601 s, 1582 s, 1452 s, 1423 s, 1374 s, 1303 m, 1076 m, and 900 m.

2.2. *Synthesis of* $[Ni_2(\mu\text{-}H_2O)(CH_3OH)(DMF)(L)_2]\cdot H_2O\cdot CH_3OH$ *(2)*

A DMF solution (10 mL) of H_2L (0.0389 g, 0.1 mmol) and a methanol solution (5 mL) of KSCN (0.0194 g, 0.2 mmol) were mixed well and then added slowly to a solution of $NiSO_4 \cdot 6H_2O$ (0.0525 g, 0.2 mmol) in methanol (10 mL). After continuous stirring for 1 h at room temperature, the mixture was filtered and the filtrate was stored without shaking. Two weeks later, green crystals were formed from the filtrate. The crystals were collected, washed with CH_3OH, and dried under vacuum (Yield: 43.5%). Found: C, 40.01%; H, 4.21%; and N, 19.87%. Anal. Calcd for **2** ($C_{35}H_{45}N_{15}Ni_2O_9S_4$): C, 39.42%; H, 4.22%; and N, 19.35%. IR(cm^{-1}): 3415 m, 2971 m, 2933 m, 1670 m, 1650 s, 1615 s, 1592 m, 1456 s, 1371 s, 1307 m, 1104 m, and 903 m.

2.3. *Physical measurements*

Elemental analyses were performed on a Perkin Elmer 240C analyzer and IR spectra were recorded on a Nicolet IR-470 spectrometer using KBr pellets from 4000 to 400 cm^{-1}. Thermal decomposition experiments were carried out using a Netzsch TG 209 instrument under nitrogen. Variable-temperature magnetic susceptibility data of **2** were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range 5.0–300 K with an applied field of 500 G. All data have been

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

	1	**2**
Chemical formula	$C_{51}H_{51}N_{23}Ni_3O_9S_6$	$C_{35}H_{45}N_{15}Ni_2O_9S_4$
Formula weight	1498.64	1065.52
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P2(1)/n*
Unit cell dimensions (Å, °)		
a	25.264(2)	11.754(2)
b	16.3600(14)	21.612(4)
c	17.248(3)	19.573(4)
α	90	90
β	121.84(10)	106.20(3)
γ	90	90
Volume (Å^3), *Z*	6056.4(13), 4	4774.9(17), 4
Calculated density (g cm^{-3})	1.644	1.482
Absorption coefficient, μ (mm^{-1})	1.026	1.029
Reflections collected	18208	12082
Independent reflection	6951 [R(int) = 0.0379]	7298 [R(int) = 0.0663]
Goodness-of-fit on F^2	1.020	1.072
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$, $wR_2 = 0.1116$	$R_1 = 0.0790$, $wR_2 = 0.1531$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

corrected for diamagnetism using Pascal's constants [12]. In these experiments, the crystals were pre-triturated.

2.4. *X-ray crystallography*

X-ray intensities of the title complexes were recorded by a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The details of crystal structure data of **1** and **2** are listed in table 1. Full atomic data are available as files in the crystallographic information file (CIF) format.

3. Results and discussion

3.1. *Crystal structure of 1*

The selected bond distances and angles are listed in table 2. Single-crystal structural analysis reveals that **1** crystallizes in the monoclinic space group *C2/c*. As shown in figure 1, the structure unit of **1** contains a triangle frame of Ni_3 with a bridged μ_3-O in the center. Three ligands around the [$Ni_3(\mu_3$-O)] core are pentadentate and one is not deprotonated, which can be deduced from the charge balance and the bond lengths. In a unit, each Ni has distorted octahedral geometry $NiON_5$ with a μ_3-O and five nitrogens. The Ni–N bond distances are in the range 1.969(4)–2.196(3) Å and the Ni–O bond lengths are 1.966, 1.966, and 1.936 Å, which are slightly longer than those in the Mn_3 complex previously reported [8]. The Ni $\cdots$ Ni distances 3.388, 3.387, and 3.387 Å lead the frame of Ni_3 core to an equilateral triangle, which is also different from the Mn_3 complex in which the Mn_3 core takes the shape of an isosceles triangle.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Ni(1)–O(2)	1.9679(6)	Ni(1)–N(4)$^{\#1}$	1.969(4)
Ni(1)–N(3)$^{\#2}$	2.123(3)	Ni(1)–N(3)$^{\#1}$	2.123(3)
Ni(1)–N(2)$^{\#3}$	2.196(3)	Ni(1)–N(2)	2.196(3)
O(2)–Ni(1)–N(4)$^{\#1}$	180.0	O(2)–Ni(1)–N(3)$^{\#2}$	101.30(8)
N(4)$^{\#1}$–Ni(1)–N(3)$^{\#2}$	78.70(8)	O(2)–Ni(1)–N(3)$^{\#1}$	101.30(8)
N(4)$^{\#1}$–Ni(1)–N(3)$^{\#1}$	78.71(8)	N(3)$^{\#2}$–Ni(1)–N(3)$^{\#1}$	157.40(17)
O(2)–Ni(1)–N(2)$^{\#3}$	90.12(8)	N(4)$^{\#1}$–Ni(1)–N(2)$^{\#3}$	89.88(8)
N(3)$^{\#2}$–Ni(1)–N(2)$^{\#3}$	90.04(12)	N(3)$^{\#1}$–Ni(1)–N(2)$^{\#3}$	89.92(12)
O(2)–Ni(1)–N(2)	90.12(8)	N(4)$^{\#1}$–Ni(1)–N(2)	89.88(8)
N(3)$^{\#2}$–Ni(1)–N(2)	89.93(12)	N(3)$^{\#1}$–Ni(1)–N(2)	90.02(12)

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x+y+1, -x+1, z$; $^{\#2}y+1/3, x-1/3, -z+1/6$; and $^{\#3}x-y+1/3, -y+2/3, -z+1/6$.

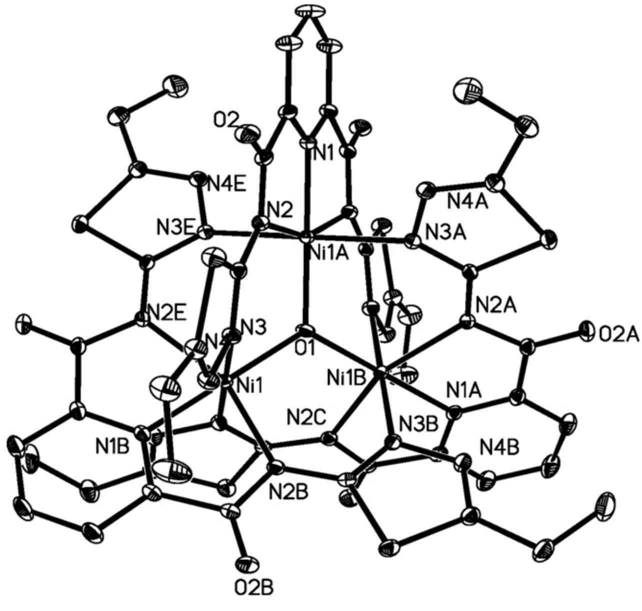

Figure 1. Structure drawing of **1**.

The packing diagram of **1** in the (1 0 1) plane is the same as that of Mn_3 complex [8]. The stacking fault mode in the (0 0 1) plane (figure 2) shows the characteristics of a monoclinic space group, and the structure units are stacked along the *c*-axis to form longitudinal rows, between which packing blocks are arranged like bricklaying. There are no significant molecule interactions between the layers, and DMF molecules are just contained in the crystal.

3.2. *Crystal structure of 2*

Complex **2** is dinuclear, bridged by μ-H_2O, crystallizing in the monoclinic system with space group *P21n*. The selected bond distances and angles are listed in table 3 and the

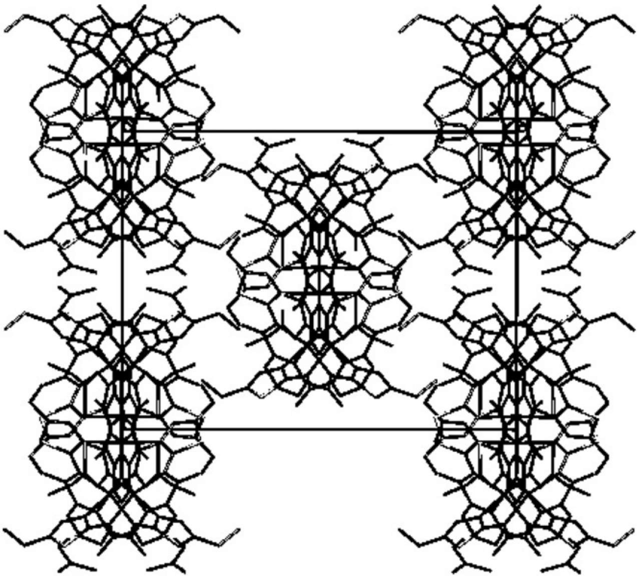

Figure 2. Packing diagram of **1** in the (0 0 1) crystal plane.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Ni(1)–N(4)	1.976(5)	Ni(1)–O(6)	2.051(5)
Ni(1)–N(5)	2.096(5)	Ni(1)–N(3)	2.096(5)
Ni(1)–O(5)	2.123(5)	Ni(1)–N(9)	2.151(6)
Ni(2)–N(11)	1.995(5)	Ni(2)–O(6)	2.061(5)
Ni(2)–N(10)	2.080(6)	Ni(2)–N(12)	2.109(5)
Ni(2)–N(6)	2.126(5)	Ni(2)–O(7)	2.151(5)
Ni(1)–O(6)–Ni(2)	110.6(3)	N(4)–Ni(1)–N(5)	79.0(2)
O(6)–Ni(1)–N(5)	104.3(2)	N(4)–Ni(1)–N(3)	79.0(2)
O(6)–Ni(1)–N(3)	97.6(2)	N(5)–Ni(1)–N(3)	158.0(2)
N(4)–Ni(1)–O(5)	94.1(2)	O(6)–Ni(1)–O(5)	81.2(2)
N(4)–Ni(1)–N(9)	92.7(2)	O(6)–Ni(1)–N(9)	91.9(2)
N(11)–Ni(2)–N(10)	79.2(2)	O(6)–Ni(2)–N(10)	103.5(2)
N(11)–Ni(2)–N(12)	77.8(2)	O(6)–Ni(2)–N(12)	99.1(2)
N(10)–Ni(2)–N(12)	157.0(2)	N(11)–Ni(2)–N(6)	94.3(2)

structure unit is shown in figure 3. In a [$Ni_2(\mu\text{-}H_2O)(CH_3OH)(DMF)(L)_2$] unit, each Ni is coordinated by two oxygens and four nitrogens in a distorted octahedron. In $Ni1O_2N_4$, a carbonyl oxygen (O5) of DMF and a thiadiazole nitrogen (N9) from one ligand occupy axial positions with the angle O5–Ni–N9 of 172.7(2)°, while the μ-H_2O (O6) and the three nitrogens of –NH–CO–pyridine–CO–NH– (N3, N4, and N5) from another ligand comprise the basal plane. The coordination environment of Ni2 is the same as that of Ni1, except that O7 comes from methanol instead of DMF, thereby decreasing the symmetry of the $Ni2O_2N_4$. The Ni1 ··· Ni2 distance is 3.390 Å and the Ni1–O6–Ni2 bond angle is 110.06°. Different from that in **1**, both H_2L in this crystal are

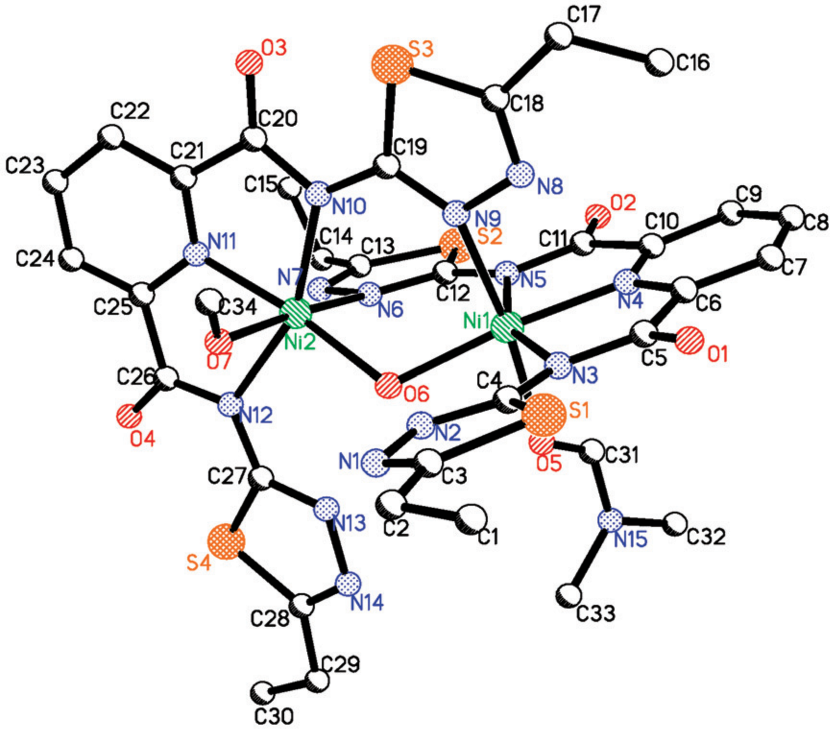

Figure 3. Structure drawing of **2**.

tetradentate with only one thiadiazole nitrogen in the two thiadiazole rings of a H_2L involved in coordination.

Hydrogen bonds exist between hydroxyl oxygen O7 of methanol and the carbonyl O4, connecting two adjacent units into a dimer (figure 4) with bond distances of 3.204 and 3.235 Å. Two H_2L ligands in adjacent dimers (C16A–C30A) and (C16B–C30B), are parallel with a dihedral angle of 9.2°; the centroid distance of 3.4593 Å indicates that π–π stacking interactions exist between dimers to construct a 1-D chain along the *c*-axis (figure 5). The cross-section of this chain looks like a tilt of the "#" character in the (0 0 1) crystal plane.

3.3. *Thermal properties*

Thermal analyses of **1** and **2** are presented in Supplementary material. The TG–derivative thermogravimetry (DTG) curve of **1** shows two transitions in the decomposition process. The first transition from 101°C to 180°C with a DTG peak at 151°C and mass loss of 6.66% is due to the loss of DMF from the crystal. The second transition from 368°C to 615°C is a complicated process in the range 368–480°C (DTG peak at 439.9°C) due to the decomposition of ligands; beyond 480°C it is related to gradual elimination of carbon deposition from complex decomposition in N_2 atmosphere [13]. The total mass loss up to 630°C is 83.74%, which agrees well with the theoretical value (84.16%) calculated by taking NiO as the final product.

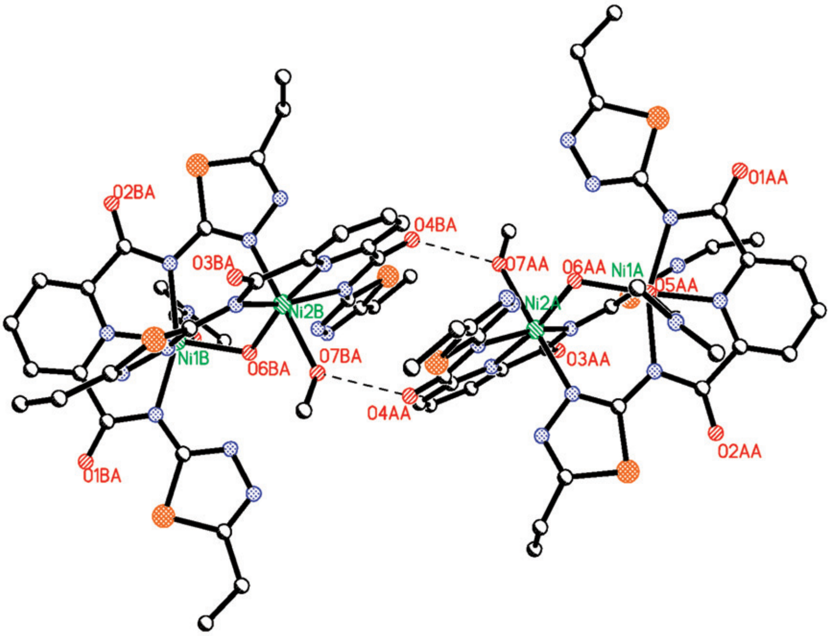

Figure 4. Dimer of **2**.

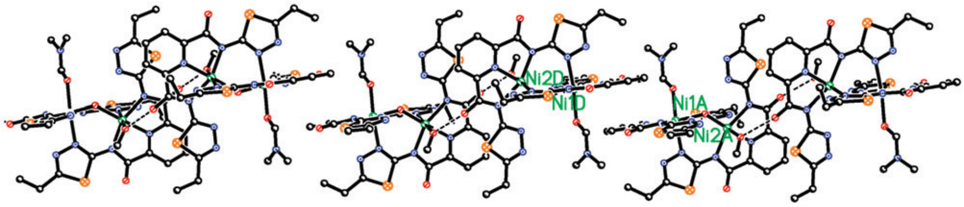

Figure 5. 1-D chain constructed by π–π stacking.

The TG–DTG curve of **2** also shows two transitions. The first one from 98°C to 228°C with a DTG peak at 160.4°C and mass loss of 10.08% is due to the loss of H_2O and CH_3OH in the crystal. The second transition from 244°C to 650°C is a consecutive process containing a DTG peak at 317.8. The total mass loss to 650°C is 84.36%, and the remaining residue of 15.64% agrees well with the theoretical value (15.00%) calculated by taking NiO as the final product.

3.4. *Magnetic properties of 2*

Variable-temperature magnetic study on **2** was carried out from 5.0 to 300 K. The variation of the inverse of magnetic susceptibility, χ_M^{-1} and χ_M^T of **2** are shown in figure 6. The thermal evolution of χ_M^{-1} obeys Curie–Weiss law, $\chi_M = C/(T-\theta)$ in the range 30–300 K with Weiss constant, θ, of -0.103 K, the Curie constant, C_M, of 1.612 $cm^3\,K\,mol^{-1}$. At 300 K, χ_M^T is equal to 1.615 $cm^3\,K\,mol^{-1}$, which is slightly

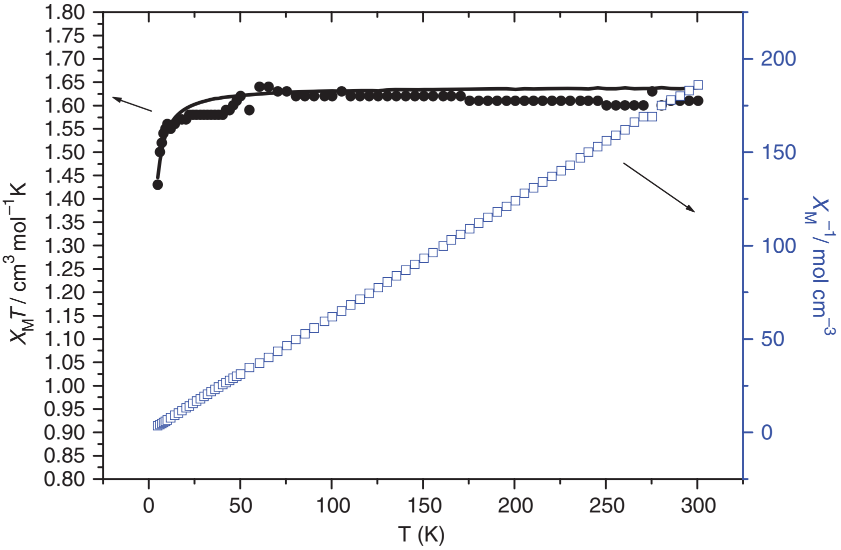

Figure 6. Plots of χ_M^{-1} and χ_M^T *vs.* T for **2**. The solid line is the theoretical curve obtained with $g = 1.811$ and $J = -0.3\,\mathrm{cm}^{-1}$.

lower than the reported value for $[Ni_2(LH)_2][ClO_4]_2(H_2O)$ (L = 2-((bis(2-aminoethyl) amino)-methyl)phenol) [14].

As the temperature is lowered, $\chi_M T$ remains approximately unchanged including a slight increase to reach a maximum at 54 K, and then slowly decreases to $1.43\,\mathrm{cm^3\,K\,mol^{-1}}$ at 5.0 K. Such behavior indicates the presence of weak antiferromagnetic exchange behavior.

A preliminary analysis of the experimental susceptibility was performed using equation (1) [15], derived from the isotropic (Heisenberg) exchange Hamiltonian, $H = -2JS_1S_2$, with the quantum numbers $S_1 = S_2 = 1$, where each symbol has its usual meaning.

$$\chi_M = \frac{2Ng^2\beta^2}{KT}\left[\frac{\exp(2J/KT) + 5\exp(6J/KT)}{1 + 3\exp(2J/KT) + 5\exp(6J/KT)}\right] \tag{1}$$

Magnetic parameters thus determined are $g = 1.811$ and $J = -0.3\,\mathrm{cm}^{-1}$. The discrepancy factor $\sigma = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}]^{1/2}$ is 4.1×10^{-4}.

When the Ni–O–Ni bond angle is large, the interaction between nickels is generally antiferromagnetic with $J < 0$, such as $[Ni_2(L^1)(py)_2](ClO_4)_2$ (L^1 = tetraaminediphenol macrocyclic ligand; 105.7°) and $[Ni_2(L^2)im]_2](ClO_4)_2$ (L^2 = tetraaminodiphenol macrocyclic ligand; 105.7°) [16], while if the Ni–O–Ni bond angle is smaller these magnetic interactions mainly tend to be ferromagnetic with $J > 0$, such as $[Ni_2(L^3)(OAc)_2] \cdot 10H_2O$ (L^3 = 2,6-di(aminomethyl)-4-methylphenol macrocyclic ligand; 95.6°) and $[Ni_2(L^4)(l\text{-}O_2CCH_2NH_3)(H_2O)_2] \cdot (ClO_4)_2 \cdot 2H_2O$ (L^4 = tetraaminediphenol macrocyclic ligand; 93.8°) [17, 18].

In **2**, the theoretical fitting shows that there is antiferromagnetic coupling in the structure, and the Ni1–O6–Ni2 bond angle size is relatively larger with the value of 111.1°, which is consistent with previous work.

4. Conclusion

Two new Ni complexes, $[Ni_3(\mu_3\text{-}O)(H_2L)(L)_2] \cdot 2DMF$ (**1**) and $[Ni_2(\mu\text{-}H_2O)(CH_3OH)(DMF)(L)_2] \cdot H_2O \cdot CH_3OH$ (**2**), have been synthesized and characterized. Complex **1** contains triangle frames constituted by three metal ions bridged by μ_3-O. Complex **2** is dinuclear with two metal atoms bridged by a μ-H_2O. The ligand **L** is pentadentate in **1** and tetradentate in **2**. Complex **1** exhibits higher thermal stability than **2**. Magnetic study shows that there is antiferromagnetic coupling in the structure of **2**.

Supplementary material

The supplementary crystallographic data for this article can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). CCDC reference nos. 299900 (**1**) and 294103 (**2**).

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