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# A novel polymeric Cu(II) assemblage and a monomeric Ni(II) complex from a new easy-to-prepare flexible polytopic ligand: Synthesis, structural and magnetic studies

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## Abstract

The difference in coordination behavior of one new flexible polytopic ligand **H<sub>2</sub>L** (**L** = C<sub>16</sub>H<sub>14</sub>N<sub>6</sub>O<sub>2</sub>) has been examined with Cu(II) and Ni(II) acetate. It leads to the formation of a polynuclear pentacoordinated Cu(II) assemblage and a mononuclear four coordinated Ni(II) complex. Both the compounds are characterized spectroscopically and electrochemically. In the complexes **1** and **2** the ligand binds the metal centers in *trans*- and *cis*-orientation (*exo* and *endo*-fashion), respectively. The polynuclear copper complex exhibits strong anti-ferromagnetic behavior at low temperature with  $J = -327 \text{ cm}^{-1}$  and DFT calculation is also carried out for this complex.

**Keywords:** Copper(II), nickel(II) complexes; Bis-tridentate ligand; Crystal structures; Magnetic study

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## 1. Introduction

Polynucleating ligands with contiguous coordination pockets arranged in a linear fashion can align metal centers in chains [1,2] or grids [3–6], depending on chelate ring sizes involved and coordination requirement of the concerned metal ion. However, the ability of the metal ion to participate in bonding to all possible coordination sites depends in part on its preferences for the donor atoms of the coordinated ligand, the flexibility and conformational adaptability of the ligand used, as well as on the competition from other Lewis acids and different entities capable of occupying a coordination pocket. Specifically, diazine

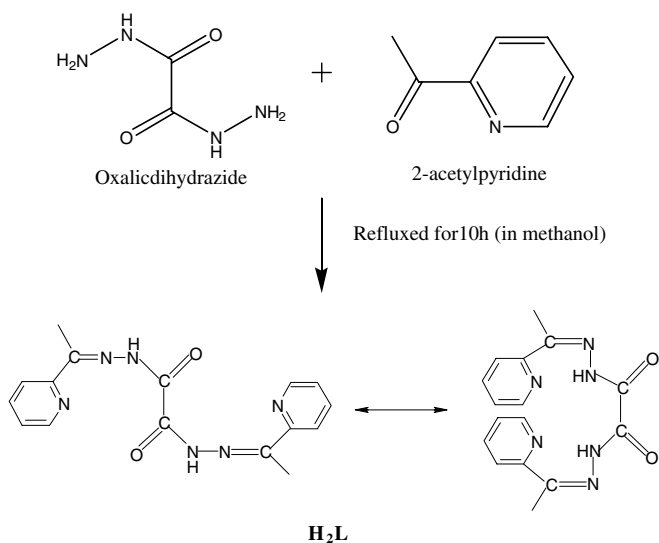
and oxamido type ligands are very flexible and can bind two or more metal centers through diazine (N–N single bond) bridges [7] and/or oxamido bridges [8], etc. Moreover, both diazine and oxamido based ligands are very efficient in propagating the magnetic interaction when they bind two metal centers [9–11].

A diazine based ligand synthesized from dipyriddyketone and oxalicedihydrazide was reported by Thompson and co-workers [12], which forms flexible N–N single bond bridged octanuclear Ni(II) cyclic ring complex.

Encouraged by the interesting properties of the diazine and oxamido type ligands, we introduce a new bistridentate ligand (**H<sub>2</sub>L**) obtained by the condensation of 2-acetylpyridine and oxalicedihydrazide in methanol (**Scheme 1**) solution. The ligand contains two tridentate chelating sites with pyridine, imine nitrogen and carbonyl oxygen atoms. Though the ligand is very similar to that reported by

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Scheme 1.

Thompson and co-workers [12] but behaves in a complete different fashion (*vide infra*).

In the present case, we employed copper(II) acetate and nickel(II) acetate, so that carboxylate might be able to connect the neighbouring dimeric subunits bridged by this flexible ligand and anticipated to get a polymeric or other architectures excluding molecular squares. From the molecular point of view, the nature of acetate bridging is magnetically very significant. For one atom acetate bridges between two paramagnetic transition metal centers, the magnetic interactions have been related to the magnitude of bridging angle ( $\theta$ ) and other structural features [13]. This has been especially studied for oxygen bridged metal atoms such as Cu–O–Cu. Small  $\theta$  angles near  $96^\circ$  should lead to ferromagnetic interaction while larger value should make the interaction increasingly strongly antiferromagnetic [14,15].

Here, we use Cu(II) and Ni(II) as metal ions to observe the difference in coordination behavior of the ligand according to the geometrical preferences of the two metal centers. In case of Cu(II), we get a polymeric complex, where the ligand (**L**) in *trans* form binds two metal centers in *exo* fashion through the oxamido-type bridge in a bis-tridentate mode instead of the anticipated diazine bridging as observed for the ligand reported by Thompson and co-workers [12] and the dimeric subunits are connected by  $\mu_{1,1}$ -acetate bridges that lead to the formation of 1-D polymer. In the case of nickel(II) the ligand adopts a *cis*-conformation and binds in *endo* fashion as a tetradentate unit to lead to a four coordinated complex. The flexible ligand reorients itself in *trans*- and *cis*-forms by the unhindered rotation around C–C bond.

In this paper, we describe the synthesis, spectral characterization and crystal structures of two novel Cu(II) and Ni(II) complexes derived from the new flexible bistridentate ligand. The magnetic behavior for complex **1** was found to be driven by strong antiferromagnetic interactions.

## 2. Experimental

### 2.1. Materials

Oxalaldehyde, 2-acetylpyridine, copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate were purchased from commercial sources and used as received.

### 2.2. Physical measurements

The infrared spectra were recorded on a Perkin–Elmer FT-IR spectrophotometer in KBr matrices. The electronic spectra were obtained as Nujol mulls as well as in acetonitrile solution on a Perkin–Elmer Lambda 40 (UV–Vis) spectrophotometer. Elemental analyses were carried out using a Perkin–Elmer 2400 II elemental analyser. Electrochemical studies were carried out with a CH600A cyclic voltammeter using tetrabutyl ammonium perchlorate as the supporting electrolyte.

Magnetic susceptibility measurement was carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe. Diamagnetic correction was estimated from Pascal table and magnetic data were corrected for diamagnetic contribution of the sample holder. The temperature dependence of the molar magnetic susceptibility,  $\chi_M$ , for the complex **1** was measured on polycrystalline sample in the temperature range 5–300 K.

### 2.3. Computational methodology

The computational methodology adopted in previous studies [16] on exchange-coupled dinuclear complexes has been used. For the evaluation of each coupling constant, two separate DFT calculations have been carried out, one for the highest spin state (triplet state in that case) and one for the broken symmetry state. The hybrid B3LYP functional [17] has been used as implemented in GAUSSIAN-98 [18]. For the Cu atoms a basis set of triple- $\zeta$  quality [19] was used for the valence orbitals supplemented with two p orbitals (“polarization functions”), whereas a double- $\zeta$  basis set [20] was used for C, H, N and O atoms. The  $J$  values are obtained by simply subtracting  $E_{HS}$  to  $E_{BS}$  ( $J = E_{BS} - E_{HS}$ ) where  $E_{HS}$  and  $E_{BS}$  are the energies of high spin and broken symmetry states, respectively. Using this equation, we assume that the energy of the broken symmetry state is a good approximation of low spin state energy, following Ruiz et al. [21].

### 2.4. Synthesis of ligand and complexes

#### 2.4.1. Ligand (**H<sub>2</sub>L**)

Oxalic dihydrazide (1.18 g, 10 mmol) was added to a solution of 2-acetylpyridine (2.24 ml, 20 mmol) in methanol (100 mL) and the mixture was refluxed for 10 h. A white solid formed which was filtered off, washed with methanol and vacuum dried (Yield: 70%). M.p.  $>270^\circ\text{C}$ . IR  $\nu_{\text{max}}$

cm<sup>-1</sup> (KBr) 1685 (CO), 1579, 1568 (CN), 979 (pyr). *Anal. Calc.* for C<sub>16</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub>: C, 59.3; H, 4.9; N, 24.9. Found: C, 59.2; H, 4.9; N, 24.8%.

#### 2.4.2. [*{Cu<sub>2</sub>(L)(CH<sub>3</sub>COO)<sub>2</sub>} · 8H<sub>2</sub>O]<sub>n</sub> (1)*

Ligand **H<sub>2</sub>L** (0.324 g, 1 mmol) was added to a solution of Cu(OAc)<sub>2</sub> · H<sub>2</sub>O (0.398 g, 2 mmol) in 2-propanol/water (5:1) and the mixture was heated with stirring for 40 min. forming a green solution. The solution was filtered and kept in refrigerator. After five days dark green hexagonal shaped crystals suitable for X-ray diffraction were formed (Yield: 60%). IR  $\nu_{\max}$  cm<sup>-1</sup> (KBr) 1563(CN), 455 (Cu–N), 379 (Cu–O). *Anal. Calc.* for C<sub>10</sub>H<sub>18</sub>N<sub>3</sub>O<sub>7</sub>Cu: C, 33.7; H, 5.09; N, 11.8; Cu, 17.9. Found: C, 33.6; H, 4.9; N, 11.7; Cu, 17.7%.

#### 2.4.3. [Ni(L)]H<sub>2</sub>O (2)

Compound **2** was prepared in a similar manner like complex **1** taking Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O instead of Cu(OAc)<sub>2</sub> · H<sub>2</sub>O. After seven days red rectangular crystals suitable for X-ray diffraction were formed (Yield: 65%). IR  $\nu_{\max}$  cm<sup>-1</sup> (KBr) 1673(CO), 1562(CN), 453 (Ni–N), 375 (Ni–O). *Anal. Calc.* for C<sub>16</sub>H<sub>16</sub>N<sub>6</sub>O<sub>3</sub>Ni: C, 48.1; H, 4.0; N, 21.0; Ni, 14.7. Found: C, 48.0; H, 3.9; N, 20.8; Ni, 14.3%.

### 2.5. X-ray crystallographic studies

Crystallographic data were collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using oil-coated rapidly cooled single crystals

[22]. Crystallographic parameters [23], details of data collection and refinement procedures are summarized in Table 1. The structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97 [24,25]. Neutral scattering factors were taken from Cromer and Mann [26] and for the hydrogen atoms from Stewart et al. [27]. The non-hydrogen atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms.

## 3. Results and discussion

### 3.1. Description of the structures

#### 3.1.1. [*{Cu<sub>2</sub>(L)(CH<sub>3</sub>COO)<sub>2</sub>} · 8H<sub>2</sub>O]<sub>n</sub> (1)*

The molecular structure as well as the atom numbering scheme of [*{Cu<sub>2</sub>(L)(CH<sub>3</sub>COO)<sub>2</sub>} · 8H<sub>2</sub>O]<sub>n</sub> (**1**) illustrated in Fig. 1. Relevant bond lengths and angles are listed in Table 2. In the titled copper(II) complex **1**, one molecule of the deprotonated hexadentate ligand **L** binds two metal centers in *trans* orientation. The polynuclear complex involves distorted five coordinated copper(II) centers, each surrounded by NNO donor sets from hexadentate **L** and by two additional O-atoms from two acetate anions. For a pentacoordinated metal center, the distortion of structure from trigonal bipyramidal (TBP) to square pyramidal (SP) can be evaluated by the Addison distortion index  $\tau$  [28]:  $\tau = (\beta - \alpha)/60^\circ$ ,  $\alpha$  and  $\beta$  being the two largest angles around the central atom; values for  $\tau$  are 1.0 for perfect TBP and 0.0 for perfect SP. In this complex the geometry of the Cu(II) centers are close to square pyramidal ( $\tau = 0.016$ ) with short*

Table 1  
Crystallographic data for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>10</sub> H <sub>18</sub> N <sub>3</sub> CuO <sub>7</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>6</sub> NiO <sub>3</sub>
Formula weight	355.81	398.82
<i>T</i> (K)	193	193
Radiation	Mo K $\alpha$	Mo K $\alpha$
$\lambda$ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	16.933(1)	7.638(4)
<i>b</i> (Å)	12.938(1)	18.626(1)
<i>c</i> (Å)	13.463(1)	11.892(1)
$\alpha$ (°)	90	90
$\beta$ (°)	102.199(1)	105.910(1)
$\gamma$ (°)	90	90
<i>Z</i>	8	4
Crystal size (mm)	0.10 × 0.20 × 0.55	0.4 × 0.3 × 0.1
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.639	1.629
Adsorption coefficient (mm <sup>-1</sup> )	1.552	1.224
<i>F</i> (000)	1472	824
$\theta$ Range for data collection (°)	2.0, 23.3	2, 23.3
Reflections collected	6415	7231
Independent reflections ( <i>R</i> <sub>int</sub> )	1904 (0.0212)	2086 (0.0252)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.109	1.045
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0336, <i>wR</i> <sub>2</sub> = 0.0913	<i>R</i> <sub>1</sub> = 0.0303, <i>wR</i> <sub>2</sub> = 0.0771
Final <i>R</i> indices [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.0303, <i>wR</i> <sub>2</sub> = 0.0902	<i>R</i> <sub>1</sub> = 0.0270, <i>wR</i> <sub>2</sub> = 0.0740
Largest difference peak and hole (e Å <sup>-3</sup> )	0.421 and -0.312	0.278 and -0.432

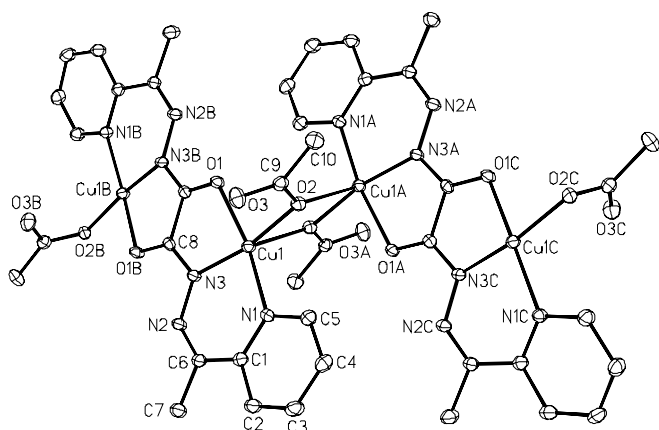


Fig. 1. ORTEP diagram of complex **1** with atom numbering scheme (thermal ellipsoids are drawn at 30% probability level). The H atoms are omitted for clarity reasons. Symmetry related atoms are marked with the letters A ( $-x + 1, -y + 1, -z$ ), B ( $-x + 1, y, -z + 1/2$ ) and C ( $x, -y + 1, z + 1/2$ ).

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

Cu1–N1	1.992(3)	Cu1–O2	1.950(2)
Cu1–N3	1.923(3)	Cu1–O2A	2.401(2)
Cu1–O1	2.017(2)		
O1–Cu1–O2	86.61(9)	O2–Cu1–O2A	75.59(7)
O1–Cu1–N3	83.17(9)	N1–Cu1–N3	90.25(10)
O1–Cu1–O2A	84.09(7)	O1–Cu1–N1	169.44(9)
O2–Cu1–N1	99.42(10)	O2–Cu1–N3	169.36(9)
O2A–Cu1–N1	105.75(8)	O2A–Cu1–N3	106.17(8)

Symmetry operations used for equivalent atoms A:  $-x + 1, -y + 1, -z$ .

Table 3  
Deviation (in Å) of the atoms for the complex **1** from the best plane calculated from O1, N3, O2, N1 and Cu1

Atoms	Deviation (Å)
Cu1	+0.246
O1	–0.033
N3	+0.034
O2	–0.033
N1	+0.034

equatorial contacts [1.993(3)–2.017(2) Å] by N<sub>2</sub>O donor (N1, N3, O1 for Cu1) from the **L** and one acetato oxygen atom (O2 for Cu1) from the **L** and a longer axial coordination [2.401(2) Å] by the oxygen atom (O2A for Cu1) of another acetate ligand. These bond lengths are comparable to the values obtained for the similar square pyramidal copper(II) systems [29]. Distortion from the square pyramidal geometry is evident from the deviation of the atoms forming the least square plane (Table 3). The two five-membered chelate rings formed by each **L** connecting two copper(II) centers are almost coplanar and make 5.229 Å separation between these two centers. The diazine subunit present in the complex is tilted with respect to the mean square plane at an

angle of 1.3° and the N–N diazine bond length [1.386(4) Å] is consistent with a N–N single bond [30]. The carbon–carbon bond distance (1.489(7) Å) in the coordinating ligand **L** is consistent with the C–C single bond [31]. Each of the two copper centers in one asymmetric unit is connected to neighbouring copper centers through double  $\mu_{1,1}$ -acetato bridges and forms an infinite polymeric network parallel to *a*-axis shown in Fig. 2. The non-bonding Cu–Cu separation in the double acetato bridging amounts to 3.449 Å. There are eight water molecules in the lattice for each dimeric subunit.

### 3.1.2. $\{[Ni(L)]H_2O\} (2)$

The ORTEP diagram of complex **2** with atom numbering scheme is illustrated in Fig. 3 and the relevant bond lengths and angles are listed in Table 4. Unlike **1** here, the deprotonated ligand **L** in *cis* form binds only one nickel center and forms a monomeric Ni(II) complex. The Ni(II) ion displays a distorted square planar coordination with a N<sub>4</sub> donor set from **L**. The square plane suffers a tetrahedral distortion as indicated by the deviation of the coordination sites from the mean plane calculated for the four N atoms

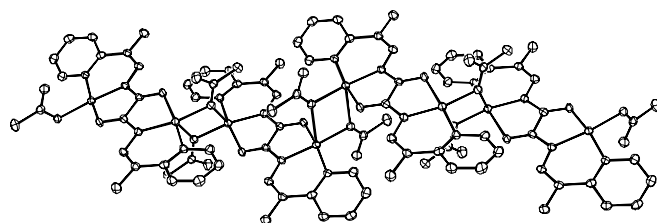


Fig. 2. Part of 1-D polymeric layer of complex **1** to show the arrangement of molecules.

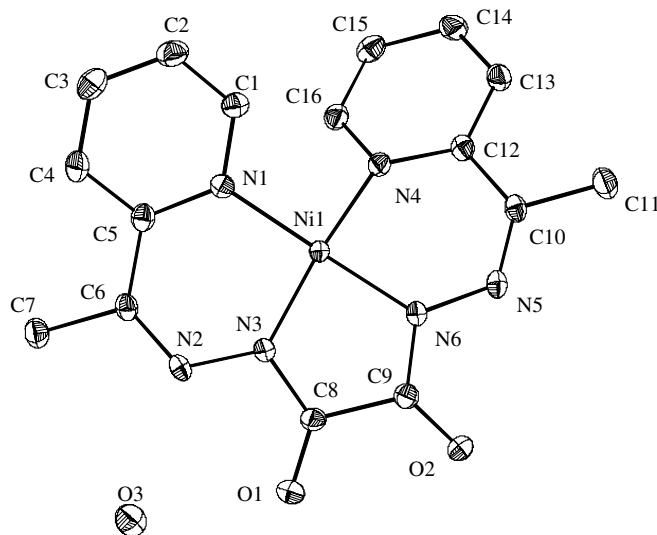


Fig. 3. ORTEP diagram of complex **2** (with water) with atom numbering scheme (thermal ellipsoids are drawn at 30% probability level). The H atoms are neglected for clarity reasons.

(N1, N3, N4 and N6) coordinated with the nickel(II) center (Table 5). This deviation from the planar arrangement of **L** is clearly seen from the torsion angle [N1–N3–N6–N4] of the coordinating Lewis bases with a value of  $-23.3^\circ$ . The bite angles associated with six-membered rings [N1–Ni1–N3 =  $91.79(8)^\circ$ , N6–Ni1–N4 =  $91.45(8)^\circ$ ] are within normal range [32]. In the title complex, the angle between the planes containing the two pyridine rings is  $119.8^\circ$ . The torsion angles for N1–C5–C6–N2 and N4–C12–C10–N5 with values of  $20.9^\circ$  and  $12.4^\circ$ , respectively, also show the twisting of the pyridine rings. The cause of all of these distortions (including the deviation from the planar environment of Ni1) is the steric strain induced by the hindrance of the hydrogen atoms at C1 and C16. Therefore, the pyridyl substituents are twisted away from each other thus destroying the planarity of the molecule. This fact leads to the formation of a chiral molecule, however, due to the crystallization of complex **2** in the centrosymmetric space group  $P2_1/c$  the  $\Delta$  and  $\Lambda$  isomers form a racemate in the solid state. One water molecule is present in the lattice.

The structural parameters of ligand **L** are comparable to those discussed for complex **1**. The electrical charge distribution of the ligand is symbolized by the mesomeric forms according to Fig. 4. The C8–C9 distance of  $1.527(3)$  Å is a characteristic value for a C–C single bond [31]. This fact as well as the C5–C6 ( $1.480(3)$  Å) and C10–C12 ( $1.479(3)$  Å) bonds show that the  $\pi$ -systems of this ligand are well separated and a more extended delocalization of the anionic charge can clearly be excluded. The Ni1–N distances to the pyridyl groups are larger than those to the anionic nitrogen atoms N3 and N6 due to the additional electrostatic attraction of Ni1 to the latter ones. The C8–C9 single bond allows an unhindered rotation around this bond which offers the reorientation and adjustment to the copper and nickel cations.

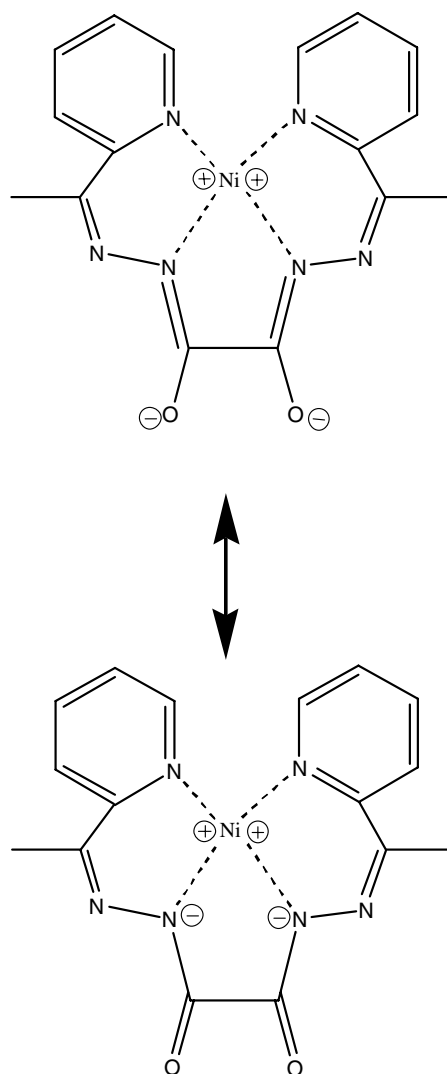


Fig. 4. Mesomeric forms of complex **2** to show the electrical charge distribution.

Table 4  
Selected bond distances (Å) and bond angles ( $^\circ$ ) for complex **2**

Ni1–N6	1.850(2)	Ni1–N3	1.850(2)
Ni1–N4	1.895(2)	Ni1–N1	1.907(2)
N6–Ni1–N3	85.04(8)	N6–Ni1–N4	91.45(8)
N3–Ni1–N4	164.72(9)	N6–Ni1–N1	161.48(9)
N3–Ni1–N1	91.79(8)	N4–Ni1–N1	96.07(8)

Table 5  
Deviation (in Å) of the atoms for the complex **2** from the best plane calculated from N1, N3, N4, N6, and Ni1

Atoms	Deviation (Å)
Ni1	0.029
N1	-0.275
N3	-0.275
N6	0.276
N4	0.276

### 3.2. Electronic spectra

Although the electronic spectra of the copper complexes with multidentate Schiff base ligands are not in general good indicators of geometry [33] but act as supporter of it. The solid-state Nujol mull absorption electronic spectrum for **1** appeared at 650, 340 and 244 nm. The broad absorption band at 650 nm is attributable to a copper ion in square pyramidal chromophore  $\text{CuN}_2\text{O}_3$  [34]. This broad visible absorption band at 650 nm is shifted slightly to a lower energy (678 nm) in acetonitrile solution, consistent with square pyramidal geometry in solution phase. The complex displays two strong absorption bands at 340 and 244 nm in solid which are clearly charge transfer in origin and these two bands are shifted to 348 and 248 nm, respectively, in solution. The similarity in the spectrum of this complex in both solution phase and solid state indicates that the 1-D chain structure retains in the solution.

The absorption band in the solid-state Nujol mull electronic spectrum for **2** shows one band at 423 nm, which



is shifted to 432 nm in acetonitrile solution. This band corresponds to the d–d transition in square planar Ni(II) complex [35]. The solid state spectrum of this complex contains another more intense band at 310 nm, which is shifted to 316 nm in solution, is charge transfer in origin.

### 3.3. Electrochemical studies

The electrochemical study of the complexes **1** and **2** was performed using acetonitrile as solvent and tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of  $100 \text{ mV s}^{-1}$ . Cyclic voltammetry of the complex **1** shows two reductive responses on the negative side of SCE (at  $-0.55$ ,  $-1.00 \text{ V}$ ), both of which are irreversible in nature. The observed potential gap (450 mV) between the two reductions is considerably large and is believed to be due to the effective communication between the two copper centers through the bridging ligands. One irreversible oxidation response is also observed on the positive side of SCE and which can be tentatively assigned to oxidation of the coordinated ligand.

The complex **2** exhibits an irreversible Ni(II)–Ni(III) oxidation at 1.26 V. This result suggests that Ni(III) species is unstable and undergoes rapid decomposition. One additional irreversible oxidation response is also observed on the positive side of SCE and can be tentatively assigned to oxidation of the coordinated ligand.

### 3.4. Magnetic studies

The magnetic behavior for complex **1** is given in Fig. 5 as  $\chi_M$  versus  $T$  and  $\chi_M T$  versus  $T$ , where  $\chi_M$  is the magnetic susceptibility of a dinuclear unit. The rapid decrease of the  $\chi_M T$  reaching very small values below 50 K and the rounded maximum exhibited by the  $\chi_M$  curve around 250 K indicate that substantial antiferromagnetic interactions are operative between the Cu(II) ions. For this

compound, the adjacent Cu(II) ions are linked alternatively by an oxamido-type ligand and two bridging O-atoms developing a 1-D supramolecular organization. However, considering the coordination sphere of these ions it appears that a bridging O-atom occupies an equatorial position on one Cu(II) whereas it is linked to the second center in apical position. The latter is characterized by a larger bond-length (2.399 versus  $1.954 \text{ \AA}$ ) due to the Jahn–Teller distortion along the  $z$ -direction. Taking into account that the unpaired electron of the Cu(II) is located in the  $d_{x^2-y^2}$  orbital, no direct overlap exists between the magnetic orbitals of O-bridged Cu centers. Consequently, the exchange interaction mediated by this pathway should be weak. Conversely, it is well documented that the exchange interaction between two Cu(II) ions through the oxamido-bridge is strong [11]. A first attempt was made to analyze the experimental behavior with an alternating chain model derived from the spin Hamiltonian  $\mathbf{H} = -J \sum_{i=1}^{n/2} [\mathbf{S}_{A2i} \cdot \mathbf{S}_{A2i-1} + \alpha \mathbf{S}_{A2i} \cdot \mathbf{S}_{A2i+1}]$  [11]. Best fit to the temperature dependence of  $\chi_M T$  yielded  $J = -330 \pm 2 \text{ cm}^{-1}$  and  $\alpha J = -79 \text{ cm}^{-1}$  ( $\alpha = 0.24 \pm 0.02$ ),  $g = 2.14 \pm 0.01$ , and a contribution of 0.01 mol of a  $S = 1/2$  paramagnetic impurity with same molecular mass. However, the value obtained for the smallest exchange interaction,  $-79 \text{ cm}^{-1}$ , is not realistic if we consider it to correspond to the exchange occurring through the O-bridge. Therefore, we considered the observed magnetic behavior to result only from the strongest exchange interaction and the magnetic data have been analyzed with the Bleaney-Bowers equation [36] ( $\mathbf{H} = -J \mathbf{S}_1 \cdot \mathbf{S}_2$ ). The contribution of a paramagnetic  $S = 1/2$  impurity was also taken into account. Best fit to the temperature dependence of  $\chi_M T$  (Fig. 5) in the 5–310 K domain led to  $J = -327 \pm 1 \text{ cm}^{-1}$ ,  $g = 2.02$ , and 0.02 mole of a paramagnetic impurity. Fitting to the variation of  $\chi_M$  yielded  $J = -307 \pm 2 \text{ cm}^{-1}$ ,  $g = 1.95$ . The exchange parameter found is well in the range of those reported for related oxamato- or oxalate-bridged Cu(II) ions [37,38].

The magnetic behavior in the high-temperature domain deserves a short comment. Around 320 K both the  $\chi_M T$  and  $\chi_M$  curves exhibit a sudden slope break suggesting a modification of the magnetic behavior for the compound at this temperature. Such a disruption can be related to a structural modification occurring for a given temperature which does alter the magnetic behavior [39,40]. In the present case, the structural modification could be ascribed the water release.

### 3.5. DFT calculations of the exchange constants

In an effort to gain complementary information on compound **1** and in order to confirm our assumption, DFT calculations on the exchange interactions as function of the pathway were carried out. All calculations for high spin and broken symmetry states were done on dinuclear fragments with the X-ray coordinates, without any geometric optimization by theoretical methods. In order to evaluate the exchange coupling mediated by the oxamido bridge,

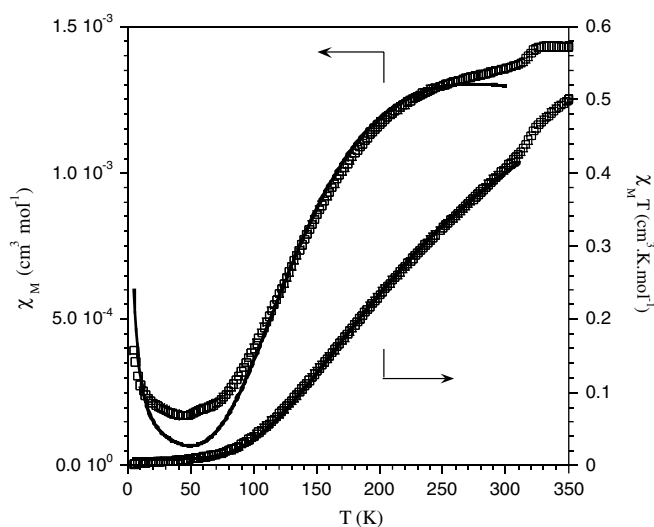


Fig. 5. Experimental ( $\square$ ) and calculated (—) temperature dependence of  $\chi_M$  and  $\chi_M T$  for complex **1**.

the calculation was done with the complete ligand set, i.e., the oxamido-ligand and the four acetates linked to the two Cu(II) centers. For the interaction through the acetate oxygen, another dinuclear cluster was extracted which contained two Cu(II) ions, two acetate ligands bridging the two copper atoms, and two shortened oxamido-ligands. These latter ligands have been shortened in the sense that the aromatic pyridine ring which is not involved in the coordination of the considered copper has been replaced by a methyl group. Both considered systems have a global charge of  $-2$ . The exchange coupling constants calculated are  $J = -181$  and  $+1.3 \text{ cm}^{-1}$  for oxamido- and oxygen-bridges, respectively. The main exchange interaction parameter calculated points to a somewhat smaller value than the one deduced from the experimental behavior ( $J = -327 \text{ cm}^{-1}$ ) but the sign and the order of magnitude are correctly reproduced. More important, these calculations validate the analysis of the experimental data by a dimer model. Indeed, the computed interaction through the oxygen bridges is found to be ferromagnetic and very small compared to the antiferromagnetic interaction through the oxamido unit. In no way this weak ferromagnetic interaction can be revealed by the experimental behavior.

#### 4. Conclusion

The design of polytopic ligand to prepare polymeric complexes is dependent on a number of factors, including the topological complexity of the ligand itself. The individual coordinating components in the ligand do not behave in a similar way for all metal ions. Here, in summary one 1-D polymeric copper(II) and one four coordinated monomeric nickel(II) complexes were assembled from copper(II) acetate and nickel(II) acetate with an easy to prepare flexible bistridentate ligand, in a rational fashion. The choice of different metal centers, in this case copper(II) or nickel(II), give rise to different products and is accomplished by the unhindered rotation of the C–C single bond, which offers the reorientation of the same ligand in *trans* and *cis*-form, respectively. This variation in the coordination behavior of the same ligand for copper(II) and nickel(II) occurred because Ni(II) has a better affinity for N-donor sites than for O ones.

#### 5. Supplementary data

CCDC-265377 (1) and 265378 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk) [or from Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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#### References

- [1] C.C. Wang, W.C. Lo, C.C. Chou, G.H. Lee, J.M. Chen, S.M. Peng, *Inorg. Chem.* 37 (1998) 4059.
- [2] G.A. Van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Eur. J. Inorg. Chem.* (1998) 547.
- [3] P.N.W. Baxter, J.-M. Lehn, J. Fischer, M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 2284.
- [4] C.J. Matthews, K. Avery, Z. Xu, L.K. Thompson, L. Zhao, D.O. Miller, K. Biradha, K. Poirier, M.J. Zaworotko, C. Wilson, A.E. Goeta, J.A.K. Howard, *Inorg. Chem.* 38 (1999) 5226.
- [5] G.S. Hanan, D. Volkmer, U.S. Schubert, J.-M. Lehn, G. Baum, D. Fenske, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 1842.
- [6] P.N.W. Baxter, J.-M. Lehn, B.O. Kneisel, D. Fenske, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 1978.
- [7] Z. Xu, L.K. Thompson, C.J. Matthews, D.O. Miller, A.E. Goeta, C. Wilson, J.A.K. Howard, M. Ohba, H. Okawa, *J. Chem. Soc., Dalton Trans.* (2000) 69.
- [8] R. Costa, A. Garcia, J. Ribas, T. Mallah, Y. Journaux, J. Sletten, X. Solans, V. Rodriguez, *Inorg. Chem.* 32 (1993) 3733.
- [9] C. Mathonière, J.-P. Sutter, J.V. Yakhmi, in: J.S. Miller, M. Drillon (Eds.), *Magnetism: Molecules to Materials*, vol. 4, Wiley-VCH, Weinheim, 2002, p. 1.
- [10] L.K. Thompson, O. Waldmann, Z. Xu, in: J.S. Miller, M. Drillon (Eds.), *Magnetism: Molecules to Materials*, vol. 4, Wiley-VCH, Weinheim, 2002, p. 173.
- [11] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.
- [12] Z. Xu, L.K. Thompson, V.A. Milway, L. Zhao, T. Kelly, D.O. Miller, *Inorg. Chem.* 42 (2003) 2950.
- [13] A.M. Greenaway, C.J. O'Connor, J.W. Overman, E. Sinn, *Inorg. Chem.* 20 (1981) 1508, and references cited there in.
- [14] P.J. Hay, J.C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* 97 (1975) 4884.
- [15] S. Mukhopadhyay, D. Mandal, P.B. Chatterjee, C. Desplanches, J.-P. Sutter, R.J. Butcher, M. Chaudhury, *Inorg. Chem.* 43 (2004) 8501.
- [16] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* 119 (1997) 1297.
- [17] A.D.J. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [18] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, *GAUSSIAN-98: Revision A.11*, Gaussian, Inc., Pittsburgh, PA, 1998.
- [19] A. Schaefer, C. Huber, R. Alrichs, *J. Chem. Phys.* 100 (1994) 5829.
- [20] A. Schaefer, H. Horn, R. Alrichs, *J. Chem. Phys.* 97 (1992) 2571.
- [21] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* 20 (1999) 1391.
- [22] (a) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* 26 (1993) 615; (b) D. Stalke, *Chem. Soc. Rev.* 27 (1998) 171.
- [23] T. Hahn (Ed.), *International Tables for Crystallography*, 2nd ed., Space Group Symmetry, vol. A, D. Reidel, Dordrecht, 1984.
- [24] G.M. Sheldrick, *SHELXL-93*, Universität Göttingen, Göttingen, Germany, 1993.
- [25] G.M. Sheldrick, *SHELXL-97*, Universität Göttingen, Göttingen, Germany, 1997.



- [26] D.T. Cromer, J.B. Mann, *Acta Crystallogr.* 24 (1968) 321.
- [27] R.F. Stewart, E.R. Davidson, W.T. Simpson, *J. Chem. Phys.* 42 (1965) 3175.
- [28] (a) A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, C.G. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349;  
(b) H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, E. Floriani, *Inorg. Chem.* 36 (1997) 670.
- [29] L.K. Thompson, Z. Xu, A.E. Goeta, J.A.K. Howard, H.J. Cluse, D.O. Miller, *Inorg. Chem.* 37 (1998) 3217.
- [30] Z. Xu, S. White, L.K. Thompson, O.D. Miller, M. Ohba, H. Okawa, C. Wilson, J.A.K. Howard, *J. Chem. Soc., Dalton Trans.* (2000) 1751.
- [31] I.L. Finar, *Organic Chemistry*, 6th ed., vol.1, ELBS, p. 197.
- [32] N. Mondal, S. Mitra, V. Gramlich, O.S. Ghodsi, K.M.A. Malik, *Polyhedron* 37 (2001) 135.
- [33] M. Suzuki, A. Uehara, *Bull. Chem. Soc. Jpn.* 57 (1984) 3134.
- [34] J.P. Costes, J.P. Laurent, J.M.M. Sanchez, J.S. Varela, M. Ahlgren, M. Sundberg, *Inorg. Chem.* 36 (1997) 4641.
- [35] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, New York, 1984, p. 534.
- [36] B. Bleaney, K.D. Bowers, *Proc. R. Soc. London, Ser. A* 214 (1952) 451.
- [37] M. Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalles, O. Kahn, *Inorg. Chem.* 23 (1984) 3808.
- [38] A. Aukauloo, X. Ottenwaelder, R. Ruiz, Y. Journaux, Y. Pei, E. Rivière, M. Carmen Munõz, *Eur. J. Inorg. Chem.* (2000) 951.
- [39] M. Fettouhi, B. El Ali, A.M. El-Ghanam, S. Golhen, L. Ouahab, N. Daro, J.-P. Sutter, *Inorg. Chem.* 41 (2002) 3705.
- [40] M. Fettouhi, B. El Ali, M. Morsy, S. Golhen, L. Ouahab, B. Le Guennic, J.-Y. Saillard, N. Daro, J.-P. Sutter, E. Amouyal, *Inorg. Chem.* 42 (2003) 1316.