

# Antiferro- and Ferromagnetic Behaviors of Two New $\mu_{1,3}$ -N<sub>3</sub> and $\mu_{1,1}$ -N<sub>3</sub> Bridged Dinuclear Nickel(II) Complexes with 2,6-Bis(2-pyridyl)-4(1H)-pyridone and 2,6-Dimethyl-2,3-bis(2-pyridyl)quinoxaline Ligands

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## Abstract

Two new N<sub>3</sub>-bridged dinuclear nickel(II) complexes, [Ni(ddqx)<sub>2</sub>( $\mu_{1,3}$ -N<sub>3</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·8CH<sub>3</sub>OH **1** and [Ni(tpd)( $\mu_{1,1}$ -N<sub>3</sub>)(H<sub>2</sub>O)]<sub>2</sub> **2**, (ddqx = 2,6-dimethyl-2,3-bis(2-pyridyl)quinoxaline and Htpd = 4-terpyridone = 2,6-bis(2-pyridyl)-4(1H)-pyridone), have been synthesized. Complex **1** crystallizes in the orthorhombic system with Ccca space group; the structure consists of isolated dimer and each Ni(II) atom is coordinated by two bidentate ddqx ligands and two end-to-end  $\mu_{1,3}$ -N<sub>3</sub> groups. Complex **2** crystallizes in monoclinic P2<sub>1</sub>/n space group; the structure consists of hydrogen-bonding linked 2-D chain of dinuclear Ni(II) complex, and each Ni(II) atom is coordinated by tridentate tpd ligand, water molecule and bridging  $\mu_{1,1}$ -N<sub>3</sub> ligand; the hydrogen bonding formed between the hydrogen atom of H<sub>2</sub>O and oxygen atom of tpd ligand. Magnetic susceptibility data, measured from 2-300 K, reveal that complex **1** exhibits antiferromagnetic interaction with  $J = -29 \text{ cm}^{-1}$ ,  $D = 10 \text{ cm}^{-1}$ ,  $g = 2.0$ , whereas complex **2** exhibits ferromagnetic interaction with  $J = 17 \text{ cm}^{-1}$ ,  $D = -8.5 \text{ cm}^{-1}$ ,  $g = 2.18$ . The magneto-structural correlation has been discussed.

**Key Words:** Azide bridged, Dinickel(II), Crystallographic Equivalence, Distortion of Azide Bridge.

## 1. Introduction

The azide bridged coordination compounds of paramagnetic metal ions have been one of the most widely studied systems in molecular magnetism [1-23]. Several magnetostructural correlations, both experimentally [1,2-6] and theoretically [5,6,11-14], have been developed and the derived ideas have been successfully used for the construction of multidimensional systems to exhibit long-range magnetic ordering [1,15-21]. Two prime bridging modes of azide are end-on (EO) and end-to-end (EE). When azide bridges crystallographically equivalent metal ions in

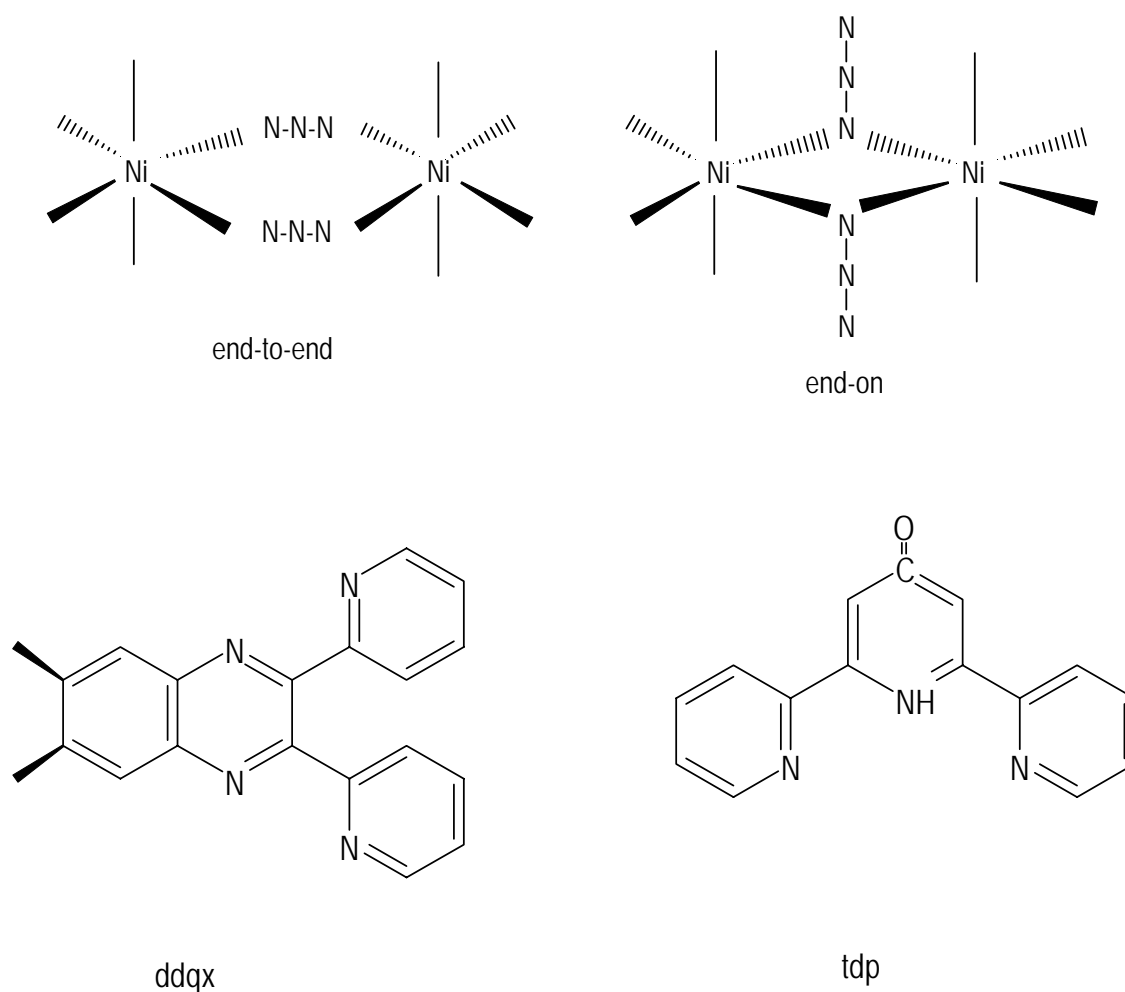
single or double EO or EE fashion, there arises several situations regarding the equivalence of bridging nitrogens and bond parameters [1-10,15-23]. For double EO bridged compounds, one azide is symmetry related to another resulting two types of M-N separations. When metal centers are bridged by single EE azide, all the three nitrogens may be independent or the two terminal nitrogens may be symmetry related resulting, respectively, similar or two types bond parameters. For double EE bridged compounds, the number of independent nitrogens may be three or four which, in both cases, results two sets of bond parameters. There is no example of only two

crystallographically different nitrogens in double azide bridged systems, which would result all the respective bond parameters identical. This type of systems is more important for magnetostructural correlations. To be mentioned that average and identical values of bond distances, bond angles, dihedral angles or torsion angles have been considered in most cases of quantum chemical understanding of exchange couplings in azide bridged systems [5,6,11-14].

Regarding double end-to-end azide bridged compounds, generally, the two azides remain parallel to each other where the metal ions are either placed almost in the same plane to form a eight membered pseudo-planar structure or deviated symmetrically from the azide-N<sub>6</sub> plane to afford the chair arrangement (the distortion type  $\delta$ ) [1]. To the best of our knowledge, only in one dinuclear and one alternatively single and

double bridged one-dimensional chain compounds, another type of distortion has been observed. In this second type of distortion, the metal ions and the central nitrogens remains in the same plane keeping the other four nitrogens up and down (“crossed azides”, distortion type  $\tau$ ) [1,6,22,23].

Herein we report two novel double azide-bridged dinuclear nickel(II) complexes, [Ni(ddqx)<sub>2</sub>( $\mu_{1,3}$ -N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·8CH<sub>3</sub>OH **1** and [Ni(tpd)( $\mu_{1,1}$ -N<sub>3</sub>)(H<sub>2</sub>O)]<sub>2</sub> **2**, (ddqx = 2,6-dimethyl-2,3-bis(2-pyridyl)quinoxaline and Htpd = 4-terpyridone = 2,6-bis(2-pyridyl)-4(1H)-pyridone) in which **1** is the first example of the presence of only two crystallographically different azide nitrogens in a double azide bridged system resulting equivalent set of bond parameters.



Scheme 1

## 2. Experimental

**Caution!** Perchlorate and azide compounds of metal ions are potentially explosive. Only a small amount of samples should be prepared, and it should be handled with caution.

### 2.1 Synthesis of the New Complexes

#### 2.1.1 [Ni(ddqx)<sub>2</sub>( $\mu_{1,3}$ -N<sub>3</sub>)<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·8CH<sub>3</sub>OH (1)

Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.183 g, 0.5 mmol) in 10 cm<sup>3</sup> of MeOH was mixed with an aqueous solution (5 cm<sup>3</sup>) of NaN<sub>3</sub> (0.13 g, 2 mmol) and to the resulting solution was added a methanol solution (15 cm<sup>3</sup>) of 2,6-dimethyl-2,3-bis(2-pyridyl)quinoxaline (0.312 g, 1 mmol) with stirring. After few minutes a yellow precipitate was appeared. The stirring was continued for two hours. The mixture was filtered and the yellow colored filtrate was kept in room temperature for slow evaporation. After a few days, yellow crystals suitable for x-ray diffraction was obtained. Anal. Calcd. for C<sub>88</sub>H<sub>96</sub>N<sub>22</sub>Cl<sub>2</sub>O<sub>16</sub>Ni<sub>2</sub>: C, 55.45; H, 5.07; N, 16.17 %. Found: C, 54.98; H, 4.95; N, 15.87 %. IR(cm<sup>-1</sup>) (KBr pellets)  $\nu$ (N<sub>3</sub>): 1302, 2044, 2098.

#### 2.1.2 [Ni(tpd)( $\mu_{1,1}$ -N<sub>3</sub>)(H<sub>2</sub>O)]<sub>2</sub> (2)

NiSO<sub>4</sub>·6H<sub>2</sub>O (0.282 g, 1 mmol) in 10 cm<sup>3</sup> of H<sub>2</sub>O was mixed with an aqueous solution (5 cm<sup>3</sup>) of NaN<sub>3</sub> (0.26 g, 4 mmol) and to the resulting solution was added a methanol solution (10 cm<sup>3</sup>) of 2,6-bis(2-pyridyl)-4(1H)-pyridone (0.319 g, 1 mmol) with stirring. After few minutes a yellow precipitate was appeared. The stirring was continued for two hours. The mixture was filtered and the yellow colored filtrate was kept in room temperature for slow evaporation. After a few days, yellow brown crystals suitable for x-ray diffraction was obtained. Anal. Calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>12</sub>O<sub>4</sub>Ni<sub>2</sub>: C, 40.09; H, 3.30; N, 22.90 %. Found: C, 48.75; H, 3.15; N, 22.95 %. IR (cm<sup>-1</sup>) (KBr pellets)  $\nu$ (N<sub>3</sub>): 1296, 2036, 2092.

### 2.2 Physical Measurements

IR spectra were recorded on a BIO-RAD FT-40 spectrometer. Magnetic susceptibility measurements were carried out on polycrystalline samples with a Quantum Design MPMS SQUID Magnetometer at 1 T in the temperature range 4-300K. Diamagnetic corrections were estimated from Pascal constants.

### 2.3 Crystal Structure Determination and Refinement

Diffraction data for complex **1** were collected at 150 K with an Enraf-Nonius CAD4 four-circle diffractometer, and for complex **2** were collected at 293 K with a Siemens P4 diffractometer. Crystal parameters and pertinent refinement results are summarized in Table 1. Unit cell parameters were determined from automatic centering of 25 reflections. For **1**, 33976 reflections were measured in the range  $1.66 < \theta < 26.45$ ; 4644 were nonsymmetry equivalent (Rint (on *I*) was 0.116). For **2**, 2277 reflections were measured in the range  $2.34 < \theta < 29.98$ ; 2110 were nonsymmetry equivalent (Rint (on *I*) was 0.0493). The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least-squares (on *F*<sup>2</sup>) using SHELX93 computer programs [24].

## 3. Results and Discussion

### 3.1 Description of the Structures

#### 3.1.1 [Ni(ddqx)<sub>2</sub>( $\mu_{1,3}$ -N<sub>3</sub>)<sub>2</sub>·(ClO<sub>4</sub>)<sub>2</sub>·8CH<sub>3</sub>OH (1)

The molecular structure of complex **1** (Figure 1) reveals that this is a double end-to-end azide bridged dinuclear nickel(II) compound. Each metal center is coordinated by two ddqx ligands, each of which chelates by two imine nitrogens. The remaining two positions are occupied by two azide nitrogens. The metal centers are in distorted octahedral geometry. The best square plane is defined by N(1)N(1A)N(5)N(5A) with an average deviation of 0.091 Å of the ligand atoms, while the Ni(1) occupies the matching position of this plane. The *transoid* and *cisoid* angles lie in the range  $170.07(16)^\circ$  -  $174.73(13)^\circ$  and  $80.13(12)^\circ$  -  $107.14(12)^\circ$ , respectively. The equatorial bond distances with imine and azide nitrogens are significantly different; Ni-N(imine) and Ni-N(azide) being 2.057(3) and 2.120(3) Å, respectively, implying high distortion even in the equatorial plane. The axial bond distances (Ni(1)-N(2) = 2.142(3)) are not very far from the longer in-plane bond lengths.

Table 1. Crystallographic Data for  $[\text{Ni}(\text{ddqx})_2(\mu_{1,3}\text{-N}_3)]_2 \cdot (\text{ClO}_4)_2 \cdot 8\text{CH}_3\text{OH}$  **1** and  $[\text{Ni}(\text{tpd})(1,1\text{-N}_3)]_2$  **2**

	<b>1</b>	<b>2</b>
Formula	$\text{C}_{88}\text{H}_{96}\text{Cl}_2\text{Ni}_2\text{N}_{22}\text{O}_{16}$	$\text{C}_{30}\text{H}_{24}\text{Ni}_2\text{N}_{12}\text{O}_4$
<i>M</i>	1906.19	734.03
Crystal system	orthorhombic	Monoclinic
Space group	<i>Ccca</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	18.5568(8)	9.8544(10)
<i>b</i> (Å)	24.4629(9)	10.764(2)
<i>c</i> (Å)	19.8205(8)	13.925(2)
$\alpha$ (°)	90	90
$\beta$ (°)	90	100.89(3)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	8997.6(6)	1450.5(3)
<i>Z</i>	4	4
<i>T</i> (K)	150(1)	293(2)
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	1.407	1.681
<i>N</i>	33976	2277
<i>N</i> <sub>o</sub>	4644	2110
<i>R</i> <sub>1</sub>	0.0554	0.0535
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )	0.1387	0.1196

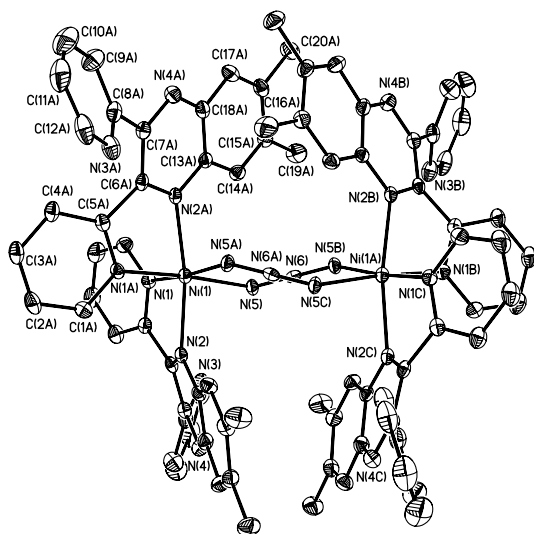


Figure 1. Perspective view of complex **1** with the atom numbering scheme, the anion  $\text{ClO}_4^-$  and solvent  $\text{CH}_3\text{OH}$  are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level.

One interesting feature of this compound is the presence of only two crystallographically different azide nitrogens. The central nitrogens, N(6) and N(6A), are symmetry related as observed in most cases of double-azido bridged systems. But, instead of the two different terminal nitrogens, all the four terminal nitrogens are symmetry related

resulting one kind of Ni-N (2.120(3) Å) bond distance, Ni-N-N bond angles (130.0(3)°), and other kinds of bond parameters.

Another important characteristic of this molecule is the geometry of the bridging moiety. The metal ions and the two central nitrogens (N(6) and N(6A)) form a perfect plane. The deviation of N(5B) and N(5A) from this plane is 0.2856 Å and that for N(5) and N(5C) is -0.2856 Å. The azido group is almost linear (N-N-N=177.3(5)°) and the dihedral angle between the two azides is 28.1°. All these values of bond parameters indicate that the bridging moiety undergoes  $\tau$  type distortion i.e. the two azide groups are 'crossed'.

### 3.1.2 $[\text{Ni}(\text{tpd})(\mu_{1,1}\text{-N}_3)(\text{H}_2\text{O})]_2$ (**2**)

The structure of **2** consists of self-assembled 2-D chain of dinuclear Ni(II) complex. The structures of the dinuclear unit and the packing diagram are shown in Figure 2 and 3, respectively. The selected bond lengths and angles are listed in Table 2. In the structure each Ni(II) atom is in a distorted octahedral environment, which is coordinated by two azido ligands in *cis* configuration, three nitrogens from tridentate tpd imine ligand, and one oxygen atom of  $\text{H}_2\text{O}$ . In addition, the hydrogen atom of ligand  $\text{H}_2\text{O}$  interacts with the oxygen atom of tpd (carbonyl) to form a hydrogen-bonding (as shown in Figure 3), and to make formation of 2-D chain structure (Figure 3). The mean bond length, 2.096 Å of Ni-N

(azido) is longer than that of 1.977 Å of Ni-N (tpd). The bond angles of Ni(1)-N(4)-Ni(a), Ni-N(4)-N(5), and Ni(a)-N(4)-N(5) are 102.1(3), 119.8 (5), and 120.1(3)°, respectively. The intermolecular hydrogen bonding distance of 1.911 Å for O(1)⋯O(2)\* estimated.

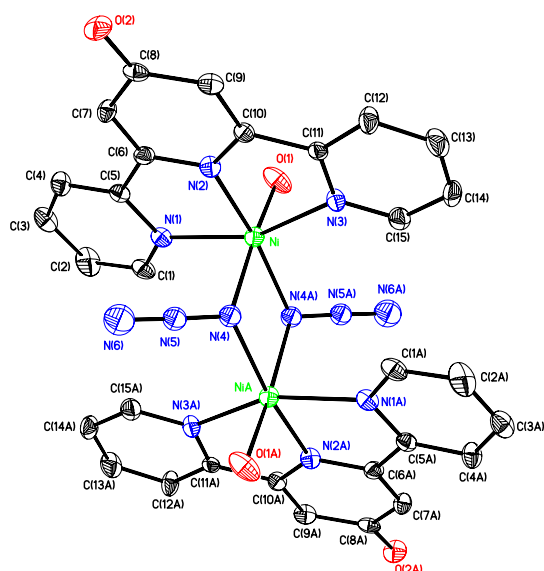


Figure 2. Perspective view of complex **2** with the atom numbering scheme, thermal ellipsoids are drawn at 50 % probability level.

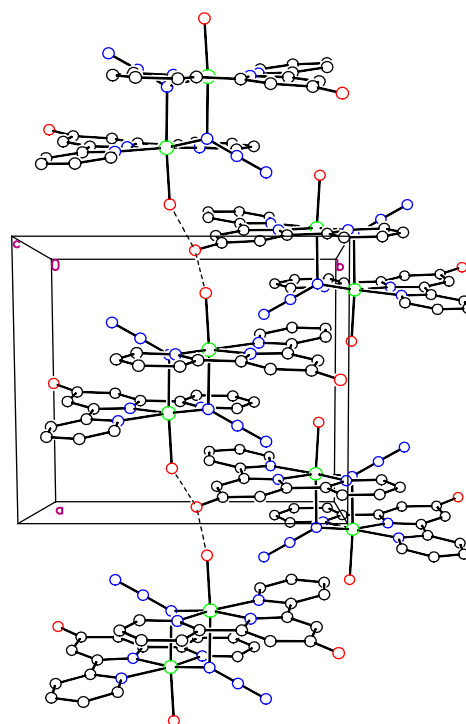


Figure 3. View of the formation of two-dimensional molecular chain in complex **2**, the intermolecular hydrogen bonds are shown by dotted lines.

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

<b>Compound 1</b>			
Ni(1)-N(1)	2.057(3)	Ni(1)-N(2)	2.142
Ni(1)-N(5)	2.120(3)		
N(1a)-Ni(1)-N(5)	174.73(13)	N(1)-Ni(1)-N(5a)	174.73(13)
N(1)-Ni(1)-N(5)	89.56(12)	N(2)-Ni(1)-N(2a)	170.07(16)
Ni(1)-N(5)-N(6)	130.0(3)	N(1)-Ni(1)-N(2)	77.61(13)
N(1)-Ni(1)-N(1a)	92.27	N(1a)-Ni(1)-N(2a)	95.43(13)
<b>Compound 2</b>			
Ni-N(1)	2.112(5)	Ni-N(2)	1.977(5)
Ni-N(3)	2.136(5)	Ni-N(4)	2.201(7)
Ni-O(1)	2.079(5)		
O(1)-Ni-N(4)	170.2(2)	N(2)-Ni-N(4a)	170.4(3)
N(1)-Ni-N(3)	156.0(2)	N(4a)-Ni-N(3)	103.5(2)
N(4a)-Ni-N(1)	100.5(2)	N(5)-N(4)-Ni	119.8(5)
Ni(1)-N(4)-Ni(1a)	102.1(3)	N(5)-N(4)-Ni(1a)	120.7(5)
N(2)-Ni-O(1)	96.7(2)	N(3)-Ni-O(1)	92.5(2)
O(1)-Ni-N(1)	86.2(2)	N(2)-Ni-N(1)	78.4(2)

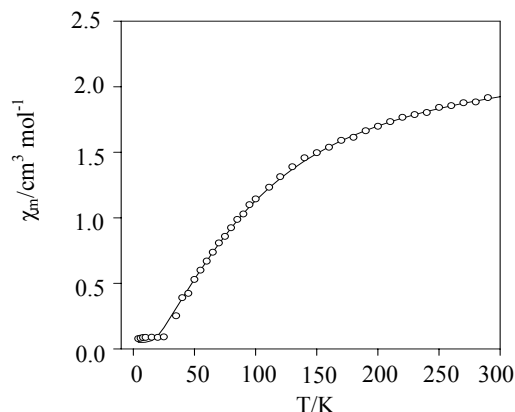


Figure 4.  $\chi_m$  (- o -), and  $\chi_m T$  (-  $\Delta$  -) for complexes **1**. The solid line is calculated with the fitted parameters reported in the text.

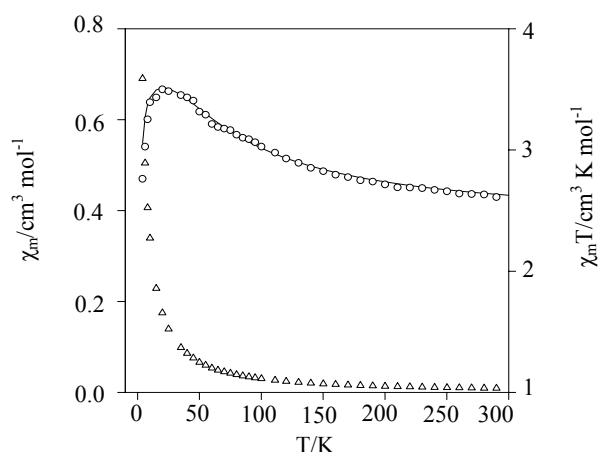


Figure 5.  $\chi_m$  (- o -), and  $\chi_m T$  (-  $\Delta$  -) for complexes **2**. The solid line is calculated with the fitted parameters reported in the text.

### 3.2 Magnetic Properties

The molar magnetic susceptibility,  $\chi_m$  and  $\chi_m T$  vs.  $T$  of **1** and **2** are plotted in Figure 4 and 5 respectively. For **1**, as shown in Figure 4, the  $\chi_m T$  value decreases from  $1.93 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K with decreasing temperature down to  $0.08 \text{ cm}^3 \text{ K mol}^{-1}$  at 4 K, indicating the presence of antiferromagnetic exchange interaction. For **2**, the  $\chi_m T$  per dinuclear Ni(II) unit increases from  $2.61 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K with decreasing temperature to  $3.50 \text{ cm}^3 \text{ K mol}^{-1}$  at 20 K, and then decreases to  $2.76 \text{ cm}^3 \text{ K mol}^{-1}$  at 4 K. The increase of  $\chi_m T$  with temperature is characteristic of a ferromagnetic coupling between the two Ni(II) ions in **2**.

The ground state of a nickel(II) in an octahedral environment is orbitally non-

degenerate and as such it possible to represent the intradimer magnetic interaction ( $J$ ) with the isotropic spin Hamiltonian  $H = -JS_1 \cdot S_2$ . The magnetic behavior of nickel(II) dimers closely follows this formula when a relatively strong antiferromagnetic interaction is operative. However, nickel(II) in axial symmetry can have a zero-field splitting,  $D$ , if the antiferromagnetic coupling is weak or the coupling is ferromagnetic, the effect of  $D$  can relevant to describe the magnetic behavior at low temperature. Ginsberg-Journaux [25] have consider the effect of  $D$  on the magnetic susceptibility of nickel (II) dimmers [ $H = -JS_1 \cdot S_2 - D(S_{z12} + S_{z22})$ ], and the molar magnetic susceptibility for a dinuclear Ni(II) complex is given by expression (1):

$$\chi_m = (2N\mu_B^2 g^2 / 3\alpha) [(F_1/kT) + (2F_2/D + 6a^2 F_3 / (3J - D) + 6b^2 F_4 / (3J + \Delta))(1-\rho) + (N\mu_B^2 g^2 / 3kT)S(S+1)\rho + N_\alpha] \quad (1)$$

where  $F_1 = 1 + \exp(2x) + 4\exp(2x + y)$

$x = 2J/kT$

$F_2 = -1 + 2\exp(2x + y) \exp(y) - 2\exp(2x)$

$y = D/kT$

$F_3 = \exp(2x) - \exp(x/2 + z)$

$z = \Delta/kT$

$F_4 = \exp(2x) - \exp(x/2 - z)$

$\Delta = [(3J + D)^2 - 8JD]^{1/2}$

$\alpha = 2 + \exp(y) + \exp(x/2 - z) + \exp(x/2 + z) + 2\exp(2x) + 2\exp(2x + y)$

$a = (9J - D + 3\Delta) / [(9J - D + 3\Delta)^2 + 8D^2]^{1/2}$

$b = 2(2D)^{1/2} / [(9J - D + 3\Delta)^2 + 8D^2]^{1/2}$

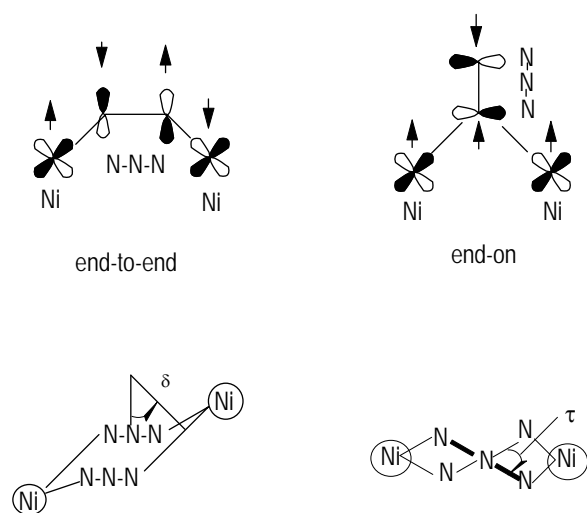
Least-squares analysis of all data for complexes **1** and **2** using equation (1) led to  $J = -29 \text{ cm}^{-1}$ ,  $D = -10 \text{ cm}^{-1}$ ,  $g = 2.1$  for **1**, whereas complex **2** exhibits ferromagnetic interaction with  $J = 17 \text{ cm}^{-1}$ ,  $D = -8.5 \text{ cm}^{-1}$ ,  $g = 2.1$  for **2**. The agreement factor  $R$  defined as  $\sum [(\chi_m)_{\text{obs}}(i) - (\chi_m)_{\text{calc}}(i)]^2 / \sum [(\chi_m)_{\text{obs}}(i)]^2$  is equal to  $5.0 \times 10^{-4}$  for **1** and  $1.8 \times 10^{-4}$  for **2**.

It is relevant to mention the calculated result for **2** that the key structural parameters governing the exchange interactions and to compare them with the average values of two previously reported crossed compounds  $[\text{Ni}^{\text{II}}_2 \text{L}_2(\mu_{1,3}\text{-N}_3)_{22}(\text{N}_3)_2]$  **3**,  $\text{L} = 1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}$  [1,22] and  $[\{\text{Ni}^{\text{II}}_2(\text{dpt})_2(\mu_{1,3}\text{-N}_3)(\mu_{1,3}\text{-N}_3)\}_n]$

(ClO<sub>4</sub>)<sub>n</sub> **4**, (dpt = bis(3-aminopropyl)amine) [1,6, 23]. For **1**, the Ni-N-N angle ( $\alpha$ ), the dihedral angle ( $\tau$ ) between Ni(1)N(6)N(6A)Ni(1A) and N(5)N(6)N(5B) planes, the Ni-N<sub>3</sub>-Ni torsion angle ( $\theta$ ), and the dihedral angle ( $\delta$ ) between N-Ni-N and one azido planes are, respectively, 130.0°, 14°, 46.7°, 17.8° and  $J = -29 \text{ cm}^{-1}$ . The values of  $\alpha$ ,  $\delta$ , and  $\tau$  and  $J$  for compound **3** have been observed as, respectively, 126.4°, 15.6°, 21.4°, and  $-36.6 \text{ cm}^{-1}$ , while the reported values of  $\alpha$ ,  $\theta$ ,  $\tau$ , and  $J$  for **4** are 126.3°, 57.4°, 20° and  $-21.7 \text{ cm}^{-1}$ . Thus, show a good magneto-structural correlation.

### 3.3 Superexchange Pathway and Structural Correlation

The properties of antiferromagnetic and ferromagnetic interactions of dinuclear nickel complexes can be described as a superexchange between nickel centers through double spin exchange interaction between the magnetically active atomic orbitals of the nickel ion and the non-bonding  $\pi$  MO of the azido bridges (see the following scheme 2). Here two dihedral angles are used for magnetostructural correlations:  $\tau =$  the crossing angle between the mean plane N-N-N and N-N-N and  $\delta =$  the dihedral angle between the plane defined for the six N azido atoms and the N-Ni-N plane. Complex **1** show large zero-field axial anisotropic energy,  $D = -10 \text{ cm}^{-1}$ , due to its distortion of ligand field which is raised from two Ni-N<sub>3</sub> crossing bonding with  $\tau = 14.0^\circ$ .



scheme 2

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