Polyhedron 191 (2020) 114813



Contents lists available at ScienceDirect

Polyhedron



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

Dinickel(II) complexes with pyridine-substituted bis(triazolylmethyl) amine ligands: Structures and magnetic properties



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ARTICLE INFO

Article history: Received 22 July 2020 Accepted 16 September 2020 Available online 24 September 2020

Keywords: Amine-triazole ligands Bridging triazole Dinickel complex Antiferromagnetism

ABSTRACT

The coordination behavior of the newly prepared bis(triazolylmethyl)amine-type ligands bis[(1-*R*-1*H*-1,2,3-triazol-4-yl)methyl]amine [R = CH₂Ph (**L1**), CH₂-2-pyridyl (**L2**)] and 1-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-*N*-((1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazol-4-yl)methyl)methanamine (**L3**) toward Ni^{II} ions was investigated. The reaction of NiCl₂-6H₂O with the benzyl-substituted bis(triazolylmethyl)amine ligand **L1** afforded the mononuclear Ni^{II} complex Ni(**L1**)₂Cl₂ (1). On the other hand, dinuclear Ni^{II} complexes, [Ni₂(**L2**)₂Cl₂]Cl₂ (2) and [Ni₂(**L3**)₂Cl₂]Cl₂ (3), were obtained when NiCl₂-6H₂O was reacted with the pyridine-substituted ligands **L2** and **L3**, respectively. Single-crystal X-ray analysis revealed that the two octahedral Ni^{II} centers in **2** and **3** are bridged by two triazole rings through nitrogen donors to generate the dinuclear complexes with a *syn* arrangement. Meanwhile, treatment of Ni(NO₃)₂ with **L2** afforded the related dinickel(II) complex [Ni₂(**L2**)₂(NO₃)₂](NO₃)₂ (**2'**), in which two non-bridging triazole rings and two nitrate ions are positioned in an *anti* arrangement. Complexes **2** and **3** showed antiferromagnetic coupling between the two Ni^{II} centers (*S* = 1), with *J* values following the trend: **2'** > **2** > **3**.

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1. Introduction

The use of bridging ligands to construct dinuclear transition metal complexes containing unpaired *d* electrons allows some controls over the intramolecular metal–metal distances and spin–spin interactions, which directly influence the properties of the resulting complexes, including magnetism and catalytic activities [1-3]. Among this class of compounds, dinuclear nickel(II) complexes are of particular interest due to their interesting ferro- and antiferromagnetic properties [4-6], as well as their unique catalytic activities [7].

Amine–1,2,3-triazole-based chelate ligands have gained considerable interest in a wide range of research fields, including coordination chemistry, material science and catalysis [8–13]. For example, tris(benzyltriazolylmethyl)amine (TBTA), which is a well-known amine–triazole featuring a tertiary amine and three 1,2,3-triazole functional groups, has been shown to bind various transition metal centers, typically in a tetradentate tripodal fashion. Based on its unique coordination behavior, TBTA has been used

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as a multidentate ligand to enhance the rates of Cu-catalyzed azide-alkyne cycloaddition (CuAAC or "click" reaction) [14]. On the contrary, the related, but more flexible tridentate ligand bis (benzyltriazolylmethyl)amine (BBTA), which contains two triazole rings connected by a secondary amine group, has been much less explored. Although the metal binding affinity of BBTA is expected to be lower than that of TBTA, thermodynamic studies have shown that the binding constants of TBTA and BBTA to Cu^{II} and Ni^{II} centers are not significantly different. Specifically, the binding constant ratios of TBTA to BBTA are 2.2 for Cu^{II} and 4.7 for Ni^{II} ions [15]. Despite its structural similarity to TBTA, BBTA has been much less explored in coordination chemistry as well as in catalytic applications, with only two reports involving Cu-catalyzed azide-alkyne cvcloaddition (CuAAC) [16] and Ru-catalyzed hydrogenation of ketones to secondary alcohols *via* outer-sphere hydrogenation (i.e. the N-H and Ru-H moieties participate in ketone coordination) [17]. Also surprisingly, no crystal structures of metal complexes supported by bis(triazolyl)amine-type ligands have previously been reported, although a nickel complex with a related triazole-2° amine-pyridyl ligand has been crystallographically characterized [18]. Given the good binding constants with more structural flexibility, bis(triazolylmethyl)amine is an attractive

ligand, in addition to tris(triazolylmethyl)amine, based on their potential applications in molecular magnetism and catalysis.

In this work, we prepared a series of bis(triazolylmethyl)amine ligands bearing benzyl and 2-pyridylmethyl substituents on the triazole rings (L1-L3; Scheme 1) and investigated their coordination behavior to Ni^{II} ions. For the symmetric L2 and the unsymmetric L3 ligands, the pyridyl substituent(s) was incorporated into the ligand framework to promote the binding to a Ni^{II} center and to generate a dinuclear Ni^{II} structure. The dinickel(II) complexes obtained in this study were all characterized by X-ray crystallography, representing the first structurally characterized multinuclear Ni^{II} complexes bridged by bis(triazolyl)amine-based ligands (L2 and L3). Furthermore, it was found that different Ni^{II} substrates, NiCl₂·6H₂O and Ni(NO₃)₂, afforded dinickel(II) structures with different geometrical configurations (syn vs. anti). The magnetic properties of these dinickel(II) complexes were also investigated in order to evaluate the magnetic interactions between the two Ni^{II} centers in the solid state.

2. Experimental section

2.1. General.

Air-sensitive experiments were carried out under dry N_2 using standard Schlenk techniques. Unless otherwise noted, all chemicals were obtained from commercial sources and used as received and all reactions were carried out under standard air atmosphere. Benzyl azide [19], 2-(azidomethyl)pyridine [20] and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) [21] were prepared according to the literature methods. All solvents were of analytical grade and used without further purification.

2.2. Characterization.

Nuclear magnetic resonance (NMR) spectra were recorded using a 400 MHz Bruker Avance spectrometer for ¹H (400 MHz) and ¹³C{¹H} (100 MHz) nuclei. Chemical shifts are reported in ppm (part per million) using residual solvent peaks as references. Fourier transform infrared spectroscopy (FT-IR) (400–4000 cm⁻¹) were collected on a Bruker Alpha instrument (Bruker Optics GmbH, Ettlingen, Germany). Elemental analyses for carbon, hydrogen and nitrogen were performed on a Yanaco MT-6 CHN Corder, whereas high-resolution mass spectra were acquired from a Bruker micrO-TOF II-OS mass spectrometer (ESI mode). Magnetic properties were measured on a Quantum Design MPMS2 superconducting quantum interference device magnetometer (SQUID). Electron spin resonance (ESR) spectra were obtained from a JEOL JES-FA200 spectrometer at 103 K using a JEOL ES-13060DVT5 temperature control device. Powder X-ray diffraction patterns were recorded at room temperature in the reflection mode $[2\theta \text{ range of } 5-40^\circ$ with a step size of 0.02°] by Malvern Panalytical Aeris XRD, equipped with a PIXcel1D-Medipix3 detector and Cu K α radiation $(\lambda = 1.5419 \text{ Å})$, operating at a tube voltage of 40.0 kV and tube current of 15 mA.

2.3. Magnetic measurements.

The crystalline sample was packed into a hand-made aluminum sample holder and loaded into a plastic straw. The plastic straw was injected into the SQUID instrument under a helium atmosphere. The temperature dependency of the magnetic susceptibility was recorded at temperatures ranging from 2 to 300 K with 0.5 T. The field dependency of the magnetization was recorded at 2 K from 0.01 T to 7 T. After applying diamagnetic corrections using Pascal's constant, the data were analyzed using the PHI program [22].

2.4. X-ray crystallography.

Single-crystal X-ray crystallography was performed on a Bruker D8 venture. Diffraction measurements were made on a Photon II detector using IµS 3.0 Microfocus source Mo K_{α} radiation (λ = 0.71073 Å) at 100 K. The structures of the complexes were solved by direct methods using intrinsic phasing (XT program) and refined by full-matrix least squares against F^2 using the *XL* program. The intensity data were corrected using SADABS and data integration was acquired using *SAINT*.

3. Synthesis of the ligands

3.1. $Bis[(1-R-1H-1,2,3-triazol-4-yl)methyl]amine [R = CH_2Ph (L1), CH_2-2-pyridyl (L2)]$

Both ligands were prepared according to the synthetic procedures of the previously reported methods, although the procedure for **L1** was slightly modified [16]. To a 40 mL 1:1 CH₂Cl₂:H₂O solution of dipropargylamine (0.47 g, 5.0 mmol) were added RN₃, sodium ascorbate (0.030 g, 0.15 mmol, 3.0 mol%), tris(benzyltriazolylmethyl)amine (TBTA; 0.027 g, 0.050 mmol, 1.0 mol%) and CuSO₄·5H₂O (0.012 g, 0.050 mmol, 1.0 mol%). The reaction mixture was left to stir at room temperature for 24 h, after which an aqueous solution of EDTA/NH₄OH (50 mL) was added and the resulting mixture was allowed to stir for 3 h. The reaction mixture was then extracted with CH₂Cl₂ (3×70 mL) and the organic layer was dried over anhydrous Na₂SO₄, filtered and dried *in vacuo* to afford the product, which was used in the next step without further purification.

L1. RN₃ = PhCH₂N₃ (1.5 g, 11.0 mmol) was used. The product was obtained as a pale yellow solid in 80% yield (1.4 g, 4.0 mmol). ¹H NMR (400 MHz, CDCl₃) δ , ppm: 7.39 (s, 2H, trzH), 7.34–7.27 (m, 6H, ArH), 7.21 (dd *J* = 7.3, 2.3 Hz, 4H, ArH), 5.44 (s, 4H, CH₂), 3.85 (s, 4H, CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ , ppm: 128.1, 127.7, 127.1, 120.8 (aromatic Cs), 53.1, 42.9 (CH₂). HRMS: calcd for C₂₀H₂₂N₇ [M + H]⁺: 360.1937; found: 360.1946.

L2. RN₃ = 2-pyCH₂N₃ (1.4 g, 10.3 mmol) was used. The product was obtained as a yellow brown oil in 82% yield (1.5 g, 4.1 mmol). ¹H NMR (400 MHz, DMSO d_6) δ , ppm: 8.54 (d *J* = 4.8 Hz, 2H, py*H*), 8.35 (s, 2H, trz*H*), 7.83 (td *J* = 7.7, 1.8 Hz, 2H, py*H*), 7.40–7.26 (m, 4H, py*H*), 5.77 (s, 4H, CH₂), 4.28 (s, 4H, CH₂). ¹³C{¹H} NMR



Scheme 1. Structures of the ligands L1-L3.

(100 MHz, DMSO d_6) δ , ppm: 154.8, 149.5, 139.0, 137.5, 126.4, 123.4, 122.4 (aromatic Cs), 54.5, 41.0 (CH₂). HRMS: calcd for C₁₈H₂₀N₉ [M + H]⁺: 362.1842; found: 362.1817.

(1-Benzyl-1H-1,2,3-triazol-4-yl)methanamine (I). Compound **I** was prepared following the synthetic procedure of **L1**. Propargylamine (0.55 g, 10 mmol), PhCH₂N₃ (1.5 g, 11 mmol), TBTA (0.050 g, 0.10 mmol, 1.0 mol%), sodium ascorbate (0.060 g, 0.30 mmol, 3.0 mol%) and CuSO₄·5H₂O (0.030 g, 0.10 mmol, 1.0 mol%) were mixed in a 40 mL 1:1 CH₂Cl₂:H₂O solution. The product was obtained as a pale yellow solid in 79% yield (1.5 g, 7.9 mmol). ¹H NMR (400 MHz, DMSO *d*₆) δ, ppm: 7.94 (s, 1H, trz*H*), 7.33 (dd *J* = 11.2, 7.3 Hz, 5H, Ar*H*), 5.56 (s, 2H, *CH*₂), 3.76 (s, 2H, *CH*₂). ¹³C {¹H} NMR (100 MHz, DMSO *d*₆) δ, ppm: 149.8, 136.2, 128.7, 128.1, 128.0, 122.0 (aromatic Cs), 52.8, 37.1 (*CH*₂). HRMS: calcd for C₁₀H₁₃N₄ [M + H]⁺: 189.1140; found: 189.1134.

Tert-butyl-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)carbamate (II). To a 40 mL THF solution of I (0.94 g, 5.0 mmol) was added di-*tert*-butyl bicarbonate (1.3 g, 6.0 mmol) and the reaction mixture was left stirring at room temperature. After 24 h, the mixture was extracted with CH₂Cl₂ (3 × 70 mL), after which the organic layer was dried over anhydrous Na₂SO₄ and filtered. Finally, all volatiles were removed under reduced pressure to afford a yellow powder in 78% yield (1.1 g, 3.9 mmol). ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.42 (s, 1H, trzH), 7.36–7.13 (m, 5H, ArH), 5.45 (s, 2H, CH₂), 5.25 (s, 1H, NH), 4.32 (d *J* = 6.0 Hz, 2H, CH₂), 1.37 (s, 9H, (CH₃)₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ, ppm: 155.9, 145.9, 134.6, 129.0, 128.7, 128.0, 121.9 (aromatic Cs), 79.5, 54.1, 36.1, 28.3 (aliphatic Cs). HRMS: calcd for C₁₅H₂₁N₄O₂ [M + H]⁺: 289.1665; found: 289.1614.

Tert-butyl((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)(prop-2yn-1-yl)carbamate (III). Under N₂, compound II (0.87 g, 3.0 mmol) and 60% of NaH in mineral oil (0.13 g, 3.3 mmol) were stirred in DMF at 0 °C for 30 min. At this temperature, propargyl bromide 80% in toluene (0.30 mL, 6.0 mmol) was added slowly to the reaction flask, after which the reaction mixture was allowed to stir at room temperature overnight. Solvent evaporation under vacuum afforded a red brown oil in 81% yield (0.70 g, 2.4 mmol). ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.45 (s, 1H, trzH), 7.36–7.20 (m, 5H, ArH), 5.49 (s, 2H, CH₂), 4.56 (s, 2H, CH₂), 4.04 (s, 2H, CH₂), 2.12 (s, 1H, \equiv CH), 1.42 (s, 9H, (CH₃)₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ, ppm: 154.8, 134.8, 131.0, 129.2, 128.9, 128.2 (aromatic Cs), 80.9, 79.5, 72.5, 54.3, 41.6, 36.5, 30.7, 28.4 (aliphatic Cs). HRMS: calcd for C₁₈H₂₃N₄O₂ [M + H]⁺: 327.1821; found: 327.1813.

Tert-butyl((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)((1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamate (IV). Compound IV was synthesized following the procedure of L1, except with the use of compound III (1.3 g, 4.0 mmol) and 2-(azidomethyl)pyridine (0.59 g, 4.4 mmol) as alkyne and azide substrates. The reaction gave a dark brown solid in 53% yield (0.98 g, 2.1 mmol). ¹H NMR (400 MHz, CDCl₃) δ, ppm: 8.50–8.45 (m, 1H, pyH), 7.63–7.56 (m, 2H, trzH), 7.25 (t *J* = 6.1 Hz, 4H, ArH), 7.19–7.12 (m, 4H, pyH), 5.52 (s, 2H, CH₂), 5.40 (s, 2H, CH₂), 4.44 (d *J* = 7.4 Hz, 4H, CH₂), 1.28 (s, 9H, (CH₃)₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ, ppm: 155.2, 154.4, 149.6, 148.6, 137.7, 137.3, 134.7 129.0, 128.6, 128.0, 123.3, 122.3 (aromatic Cs), 80.4 (C(CH₃)₃), 55.5, 54.0, 31.2 (CH₂), 28.29 (CH₃). HRMS: calcd for C₂₄H₂₈N₈O₂Na [M + Na]⁺: 483.2233; found: 483.2232.

1-(1-Benzyl-1H-1,2,3-triazol-4-yl)-N-((1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-4-yl)methyl)methanamine (L3). A mixture of **IV** (2.3 g, 5.0 mmol) and trifluoroacetic acid (3.8 mL,

solution of NaHCO₃. Solvent evaporation afforded a brown solid in 67% yield (1.2 g, 3.4 mmol). ¹H NMR (400 MHz, DMSO d_6) δ , ppm: 8.52 (dd *J* = 4.9, 1.6 Hz, 1H, pyH), 8.25 (s, 1H, trzH)), 8.22 (s, 1H, trzH), 7.81 (td *J* = 7.7, 1.8 Hz, 1H, ArH), 7.33 (ddd *J* = 15.2, 8.2,

5.1 Hz, 7H, Ar*H*), 5.73 (s, 2H, CH_2), 5.62 (s, 2H, CH_2), 4.13 (d J = 4.8 Hz, 4H, CH_2). ¹³C{¹H} NMR (101 MHz, DMSO d_6) δ , ppm: 154.9, 150.0, 141.1, 141.0, 137.5, 136.0, 128.9, 128.3, 128.1, 125.7, 125.01, 123.5, 122.5 (aromatic Cs), 54.6, 53.0, 41.8 (CH₂). HRMS: calcd for C₁₉H₂₁N₈ [M + H]⁺: 361.1889; found: 361.1881.

4. Synthesis of the nickel(II) complexes

[Ni(L1)₂Cl₂] (1). To a solid mixture of NiCl₂·6H₂O (0.24 g, 1.00 mmol) and **L1** (0.72 g, 2.0 mmol) was added 6 mL of CH₃OH. After 24 h of stirring at room temperature, all volatiles were removed under reduced pressure. Layer diffusion of dimethylacetamide (DMAc) onto the diethyl ether solution of **1** at –18 °C provided a pink solid in 53% yield (0.45 g, 0.53 mmol). Anal. Calcd For Ni(**L1**)₂Cl₂·2H₂O0.5CH₃OH (MW = 900.52 g/mol), C_{40.5}H₄₈Cl₂N₁₄-NiO_{2.5}: C, 54.02; H, 5.37; N, 21.78; found: C, 54.11; H, 5.28; N, 21.89. ESI-MS: calcd for [Ni(**L1**)₂Cl]⁺, C₄₀H₄₂ClN₁₄Ni: 811.2759; found: 811.2828. FT-IR (cm⁻¹): 3363 (O–H), 3216 (N–H).

syn-[Ni₂(L2)₂Cl₂][Cl]₂ (2). The synthesis of **2** followed that of **1** but one equiv. of **L2** (0.36 g, 1.0 mmol) was used instead of **L1**. Crystallization by layer diffusion of ^tBuOH onto the CH₃OH solution of **2** at room temperature afforded a violet crystalline solid, suitable for X-ray crystallographic analysis, in 39% yield (0.19 g, 0.20 mmol). Anal. Calcd For Ni₂(**L2**)₂Cl₄·9H₂O (MW = 1144.17 g/mol), C₃₆H₅₆Cl₄N₁₈O₉Ni₂: C, 37.79; H, 4.93; N, 22.04; found: C, 37.75; H, 4.89; N, 21.83. ESI-MS: calcd for [Ni₂(**L2**)₂Cl₃]⁺, C₃₆H₃₈Cl₃N₁₈Ni₂: 945.1254; found: 945.1370. FT-IR (cm⁻¹): 3365 (O–H), *ca*. 3200 (N–H).

anti-[Ni₂(L2)₂(NO₃)₂][NO₃]₂ (2'). To a solid mixture of Ni $(NO_3)_2$ ·6H₂O (0.29 g, 1.00 mmol) and L2 (0.36 g, 1.0 mmol) was added 6 mL of CH₃OH. After 24 h of stirring at room temperature, purple precipitates were generated and collected by filtration. Layer diffusion of ^tBuOH onto an aqueous solution of these precipitates at room temperature afforded a purple crystalline solid, suitable for X-ray crystallographic analysis, in 58% yield (0.34 g, 0.29 mmol). Calcd For Ni₂(L2)₂(NO₃)₄·3H₂O (MW = 1142.31 g/mol), C₃₆H₄₄N₂₂O₁₅Ni₂: C, 37.85; H, 3.92; N, 26.98; found: C, 37.68; H, 3.83; N, 26.79. ESI-MS: calcd for [Ni₂(L2)₂(NO₃)₃]⁺, C₃₆H₃₈N₁₉O₃Ni: 842.276; found: 842.269. FT-IR (cm⁻¹): *ca*. 3300 (O–H), 3210 (N–H).

syn-[Ni₂(L3)₂Cl₂][Cl]₂ (3). The synthesis of **3** followed that of **2** but one equiv. of **L3** (0.36 g, 1.0 mmol) was used instead of **L2**. Crystallization by layer diffusion of ^{*t*}BuOH onto a CH₃OH solution of **3** at room temperature afforded a violet crystalline solid, suitable for X-ray crystallographic analysis, in 41% yield (0.20 g, 0.20 mmol). Anal. Calcd. For Ni₂(**L3**)₂Cl₄·4.5H₂O (MW = 1061.11 g/mol), C₃₈H₄₉Cl₄N₁₆O_{4.5}Ni₂: C, 43.01; H, 4.65; N, 21.12; found: C, 43.10; H, 4.72; N, 21.02. ESI-MS: calcd for [Ni₂(**L3**)₂Cl₃]⁺, C₃₈H₄₀Cl₃N₁₆Ni₂: 943.1349; found: 943.1620. FT-IR (cm⁻¹): 3365 (O–H), 3245 (N–H).

5. Results and discussion

5.1. Synthesis of the ligands (L1, L2 and L3)

Symmetric, multidentate bis(triazolylmethyl)amine ligands containing benzyl (for **L1**) and 2-pyridylmethyl substituents (for **L2**) on the triazole rings were prepared in high yields (*ca.* 80%) from CuAAC of dipropargylamine and the corresponding azides, catalyzed by CuSO₄·5H₂O/TBTA (TBTA = tris(triazolylmethyl) amine). Meanwhile, the unsymmetric amine–triazole-based ligand **L3**, featuring both benzyl and 2-pyridylmethyl substituents, was synthesized *via* a multi-step synthesis (Scheme 2). First, the 1° amine group of (1-benzyl-1*H*-1,2,3-triazol-4-yl)methanamine (**I**)

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Scheme 2. Synthetic pathway for L3.

was protected by the *tert*-butyloxycarbonyl (Boc) group to give the product **II**. Subsequent nucleophilic addition of propargyl bromide followed by CuAAC with 2-pyridylmethylazide yielded the compounds **III** and **IV**, respectively. Finally, selective cleavage of *N*-Boc using trifluoroacetic acid afforded the unsymmetric ligand **L3** in approximately 22% total yield.

5.2. Synthesis and characterization of the nickel(II) complexes (1, 2, 2' and 3)

Complexation of bis(triazolylmethyl)amine ligands (L1, L2, L3) to Ni^{II} centers was carried out in CH₃OH at room temperature. The reaction of NiCl₂· Θ H₂O with two equiv. of the symmetric bis



Fig. 1. ORTEP structure of $syn-[(\mu-L3)_2Ni_2Cl_2][Cl]_2$ (3). Thermal ellipsoids are shown at 30% probability. Solvent molecules and H atoms, with the exception of N–H, are omitted for clarity. Selected bond distances (Å): Ni(1)–Cl(1) 2.409(1); Ni(1)–N(1) 2.097(4); Ni(1)–N(4) 2.145(4); Ni(1)–N(5) 2.092(3); Ni(1)–N(14) 2.075(4); Ni(1)–N(16) 2.119(3). Selected bond angles (°): N(1)–Ni(1)–N(5) 90.8(1); N(1)–Ni(1)–N(4) 80.2(1); N(1)–Ni(1)–N(16) 85.4(1); N(5)–Ni(1)–N(4) 77.3(1); N(14)–Ni(1)–N(16) 87.9(1); Cl(1)–Ni(1)–N(1) 167.8(1); N(4)–Ni(1)–N(14) 168.0(1); N(5)–Ni(1)–N(16) 175.6(1).

(benzyltriazolylmethyl)amine **L1** gave a pink solution. Crystallization by layer diffusion of dimethylacetamide (DMAc) onto the diethyl ether solution of the product at -18 °C resulted in pink precipitates (**1**). Although X-ray quality crystals could not be obtained for complex **1**, elemental analysis data are consistent with the empirical formula of Ni(**L1**)₂Cl₂·2H₂O·0.5CH₃OH. The ESI-MS spectrum of **1** exhibits only a cluster of signals at m/z = 811.28, of which the isotope pattern matches well with the simulation pattern for [Ni(**L1**)₂Cl]⁺ (Fig. S17). Thus, it is most likely that **1** has a mononuclear structure of the type Ni(**L1**)₂Cl₂, in which two **L1** ligands possibly coordinate to an octahedral Ni^{II} center in a tridentate mode using an amine N and two triazole N donors.

Similar reactions between NiCl₂·6H₂O with one equiv. of the symmetric **L2** and the unsymmetric **L3** ligands, containing 2-pyridylmethyl substituent(s) on the triazole ring, also produced pink solutions. Recrystallization of the solids by layer diffusion of 'BuOH into the CH₃OH solution afforded crystalline solids of **2** and **3**.

Single crystal X-ray crystallographic analysis of 2 gave large R values (e.g., $R_1 = 15.0\%$) due to major disorders of the outer sphere Cl⁻ ions as well as the poor crystal quality. Thus, only the atom connectivity of its overall structure was determined (Fig. S21). Fortunately, we were able to obtain crystal data for 3, which possesses in a structure closely related to that of 2. As shown in Fig. 1, the two Ni^{II} centers in **3** are linked by two 1,2,3-triazole rings through the medial and proximal N donors to form a dinickel(II) structure in $[Ni_2(\mu-L3)_2Cl_2]^{2+}$. Both Ni^{II} centers are almost co-planar with the linking triazole rings, with small deviations of 0.002-0.246 Å. In addition, each L3 ligand with a pyridine substituent connects two Ni^{II} centers in a μ - κ ⁵ coordination mode. In particular, the L3 ligand facially chelates to one Ni^{II} center through the $N3_{trz}$, N_{amine} and $N3'_{trz}$ donors and to the other Ni^{II} center via the $N2_{trz}$ and N_{py} donors. As a result, a six-membered, boat-shaped metallacyclic with a Ni...Ni separation of 4.1262(8) Å is formed in 3. Notably, two Cl⁻ ions, each of which completes the octahedral Ni^{II} environment featuring an N₅Cl donor set, coordinate to the two Ni^{II} centers in a *svn* arrangement. There exist two crystallographically independent Cl⁻ counter ions that weakly interact with coordinated amine groups with Cl-Namine distances of 3.217(4) and 3.428(4) Å [23]. In addition, inner-sphere and outer-sphere Cl⁻ ions weakly interact with lattice H_2O molecules ($Cl \cdot \cdot O_w = 3.058$ (7)-3.280(6) Å) and triazolyl protons $(Cl + C_{trz} = 3.420(4)$ Å) (Fig. S22).

To obtain good quality crystals with the ligand L2, $Ni(NO_3)_2$ was employed as a substrate, instead of NiCl₂·6H₂O. Fortunately, this reaction afforded X-ray quality purple crystals (2'). As shown in Fig. 2, the entire complex cation features a dinickel(II) structure of the type $[Ni_2(\mu-L2)_2(NO_3)_2]^{2+}$, in which two Ni^{II} centers are linked by two triazole rings from two L2 ligands, each adopting a μ - κ ⁵ coordination mode. While this dinickel(II) structure in **2**' is very similar to that observed in 2, two NO₃ ions coordinate to both Ni^{II} centers in an *anti* arrangement to form a centrosymmetric structure with an inversion center at the center of the six-membered $Ni_2(\mu-L2)_2$ ring. In addition, the $Ni_2(\mu-L2)_2$ ring adopts a chair configuration in 2', rather than the boat configuration as observed in **2**. Compared to **3**, the Ni^{II} centers in **2**' are much more deviated from the mean plane of the triazole rings (0.177 Å, 0.677 Å), with a slightly shorter Ni…Ni separation of 4.0698(5) Å. The packing structure of **3**, shown in Fig. **3**, reveals short contacts between the coordinated NO_3^- ions and the triazolyl proton (H7; $O3 \cdots C7 = 3.221(2)$ Å) as well as the methylene hydrogen atom of trzCH₂Ph (H6A; $O1 \cdots C6 = 3.328(2)$ Å), compared to the typical C···O van der Waals distance of 3.7 Å [24]. Meanwhile, the amine group forms a relatively strong hydrogen bond with the outersphere NO_3^- ion, with an N···O distance of 2.82(2) Å [25]. For all four Ni^{II} complexes, the infrared spectra contain moderate-to-weak



Fig. 2. ORTEP structure of *anti*-[(μ -L2)₂Ni₂(NO₃)₂][NO₃]₂ (2'). Thermal ellipsoids are shown at 30% probability. A water molecule, two nitrate ions and H atoms, with the exception of N—H, are omitted for clarity. Selected bond distances (Å): Ni(1)–O(1) 2.0818(9); Ni(1)–N(1) 2.095(1); Ni(1)–N(3) 2.052(1); Ni(1)–N(4) 2.060(1); Ni(1)–N(5) 2.137(1); Ni(1)–N(6) 2.087(1). Selected bond angles (°): N(1)–Ni(1)–Ni(3) 89.08 (5); N(4)–Ni(1)–N(5) 80.75(5); N(5)–Ni(1)–N(6) 78.84(5); N(1)–Ni(1)–N(4) 170.10 (5); N(3)–Ni(1)–N(5) 171.60(5); O(1)–Ni(1)–N(6) 164.68(5).

broad absorption bands at *ca.* 3200 cm^{-1} , assignable to 2° N–H stretching vibrations (Fig. S13–S16). In addition, the elemental analyses of **2**, **2**' and **3** are consistent with the formulas obtained from the X-ray data. With some water molecules present (*vide supra*).

It should be noted that only a few dinuclear metal complexes, whose metal centers are bridged by an amine-1,2,3-triazole chelate through two N donors, have been reported and structurally characterized, likely due to the relatively weak electron-donating ability of triazolyl N donors. Pioneering work by P. S. Donnelly and co-workers demonstrated dinuclear Cu^I and Ag^I structures with bridging TBTA ligands by single-crystal X-ray analysis [12,26], whereas no crystal structure of nickel complexes bridged by an amine-triazole chelate via both triazole N^2 , N^3 donors has been reported. The successful synthesis and structurally characterization of 2, 2' and 3 are most likely due to the presence of the 2-pyridylmethyl substituent in L2 and L3, which enhances the ability of the ligand to bridge two metal centers. This hypothesis is also consistent with the formation of the mononuclear Ni^{II} complex Ni $(L1)_2Cl_2$ (1) generated in the presence of the benzyl-substituted ligand L1. In addition, based on the crystal structures of 2 and 3, only one pyridyl substituent in the bis(triazolyl)amine ligands



Fig. 3. A view from the *b*-axis showing intermolecular hydrogen bonding in 2'. All solvent molecules, one nitrate ion, and some H atoms are omitted for clarity. H-bonding interactions are shown as blue dotted lines.

participates in the metal coordination. In fact, coordination of the other pendent pyridylmethyl group in **2** to an adjacent dinickel (II) moiety appears to be prevented due to steric reasons.

To investigate the effect of NO_3^- ions on the dinickel(II) structure, the chloride-containing complex 2 was treated with 4 equiv. of AgNO₃ in CH₃OH at room temperature, immediately resulting in grey precipitates. After 24 h of stirring, the mixture was filtered to remove insoluble materials. Layer diffusion of CH₃OH onto the filtrate afforded purple crystals (24% yield). The powder X-ray diffraction pattern of this product was identical with that of 2'(Fig. S23). This result demonstrates not only that Cl⁻ ions are replaced by NO₃, but the structural conversion from the syn to anti configuration also occurs. In other words, the dinickel(II) structure is fluxional in solution and the syn vs. anti configuration of the complex is dependent of the auxiliary Cl⁻ vs. NO₃⁻ ligand. The ESI mass spectra of 2, 2' and 3 commonly feature a fragmented signal corresponding to $[Ni(L2 \text{ or } L3)_2(Cl \text{ or } NO_3)]^+$, in addition to a parental signal corresponding to [Ni₂(L2 or L3)₂(Cl or NO₃)₃]⁺ (Fig. S18-20). This suggests that the dinickel(II) structures in 2, 2' and 3 are in equilibrium with their respective mononuclear structures in solution, which allow for the syn-to-anti conversion, accompanied by the replacement of coordinated Cl^- ions in **2** by NO_3^- ions.

5.3. Magnetic studies of the dinickel(II) complexes (2, 2' and 3)

Since **2**, **2**' and **3** are the first examples of amine-triazolylbridged dinickel(II) complexes, an investigation of their magnetic behaviors should provide insight into the effect of the bridging triazolyl group and the coordinated inorganic anions (NO₃ *vs.* Cl) on the magnetic interactions between the two Ni^{II} centers. The temperature-dependent magnetic features of all three complexes in the form of $\chi_M T vs. T$ plots are shown in Fig. 4 (red plots). The observed $\chi_M T$ values at 300 K of **2**, **2'** and **3** are 2.56, 2.38 and 2.44 cm³ mol⁻¹ K, respectively, indicative of S = 1 for this dinickel(II) system (the theoretical value is 2.00 cm³ mol⁻¹ K for $g_{iso} = 2$). Upon cooling, the $\chi_M T$ values decrease steadily, suggesting antiferromagnetically coupled spins. Below ca. 40 K, the observed $\chi_M T$ values lower sharply and vanish when the temperatures are close to zero. Based on the χ_M curves, the antiferromagnetic couplings of **2**, **2'** and **3** are confirmed to be maximum at ca. 20 K (Fig. 4).

The temperature dependency of the $\chi_M T$ values (2–300 K, 0.5 T) and the field dependency of the magnetization (M) curves (0.01 -7 T, 2 K) were fitted to a theoretical curve based on the Hamiltonian, $\hat{H} = -2JS_1 \cdot S_2 + g\beta H(S_1 + S_2) + 2D[\hat{S}_z^2 - \frac{1}{3}S(S+1)]$, where g is the Landé's factor, J is the isotropic exchange constant between the two Ni^{II} centers, D is the axial single-ion zero-field splitting parameter. The temperature independent paramagnetism (T.I.P.) values and the fraction of monomeric magnetic impurity (ρ) were also considered. We could not reproduce the M vs. H plot without considering ρ or D. The best fitted parameters are summarized in Table 1. The negative *I* values of all the three complexes further confirm the intramolecular antiferromagnetic coupling between the two Ni^{II} centers, whereas their magnitudes decrease in the order $\mathbf{2}'$ (-7.8 cm⁻¹) > $\mathbf{2}$ (-5.8 cm⁻¹) > $\mathbf{3}$ (-4.8 cm⁻¹). The highest *I* value of **2**′ is attributed to better overlap between the magnetic orbitals of $d_x 2_{-y} 2$ (Ni) and those of the bridging triazolyl ligands [27]. This is explained by the dihedral angle (20.39°) between the plane generated from N3-Ni1-N4 (Fig. 2) and the mean plane of the bridging triazolyl rings, which is slightly smaller than the



Fig. 4. Plots of $\chi_M T$ vs. T (red, left), χ_M vs. T (blue, left) and M vs. H (green, right) of the dinickel(II) complexes 2 (a), 3 (b) and 2' (c). Black lines indicate the fitted curves.

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Table 1

The best fitted parameters for the magnetic data of 2, 3 and 2'.

Compound	G	J/cm ⁻¹	D/cm^{-1}	T.I.P./cm ³ mol ⁻¹	ρ
2	2.2687(5)	-5.774(2)	+4.31(2)	$\begin{array}{l} 4.10(6)\times10^{-4}\\ 5.71(5)\times10^{-4}\\ 5.87(6)\times10^{-4} \end{array}$	0.019
3	2.1714(4)	-4.8406(10)	+4.250(16)		0.021
2'	2.2049(6)	-7.857(7)	+9.97(5)		0.077

dihedral angles observed in **3** (22.70°–23.69°). It should be noted that the magnetic properties of the present dinickel(II) complexes are comparable to those of the related pyrazolate-bridged dinickel (II) complexes reported by Mukherjee and co-workers [27]. However, the more planar Ni₂(μ -L')₂ core (L' = 3-(2-pyridyl)pyrazole) features a much smaller dihedral angle (5.53(17)°) between the planes of the pyrazolate ring of the {Ni1(μ -L')} unit and {Ni2(μ -L')}, which leads to the higher *J* value of –10.3 cm⁻¹. Thus, the lower dihedral angle, together with the Ni…Ni separation that is shorter than that in **3** by *ca*. 0.06 Å, most likely accounts for the improved intramolecular antiferromagnetic coupling for **2**′. The non-zero *D* values for **2**, **3** and **2**′ indicate the presence of a magnetic anisotropy for each Ni^{II} center, which is in line with the silent X-band EPR spectra of these complexes at 103 K (Fig. S24).

6. Conclusion

In this work, two new bridging amine-triazole ligands, bis[(1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-4-yl)methyl]amine (L2) and 1-(1-benzyl-1H-1,2,3-triazol-4-yl)-N-((1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-4-yl)methyl)methanamine (L3), were prepared by incorporating 2-pyridylmethyl substituents into the 1,2,3-triazole ring. The reactions of L2 and L3 with Ni^{II} ions afforded the dinickel(II) complexes $[Ni_2(\mu-L2)_2Cl_2]Cl_2$ (2), $[Ni_2(\mu-L2)_2(NO_3)_2]$ $(NO_3)_2$ (2'), and $[Ni_2(\mu-L3)_2Cl_2]Cl_2$ (3). On the other hand, the mononuclear Ni^{II} complex $[Ni(L1)_2]Cl_2$ (1) was produced when bis[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (L1), which does not have pyridyl substituents, was employed for the reaction. This is indicative of the importance of triazolvl substituents in the formation of multinuclear metal complexes. Notably, the replacement of coordinated Cl^{-} ions in **2** by NO_{3}^{-} ions was found to result in a syn-to-anti structural transformation to give 2', accompanied by the boat-to-chair conformational change of the six-membered $[Ni_2(\mu-Ln)_2]$ ring. Magnetic susceptibility measurements reveal that all three dinickel(II) complexes, 2, 2' and 3, possess antiferromagnetically coupled spins of S = 1. When the magnetic profiles of **2** and **3** are compared, it appears that the triazolyl substituents (*i.e.* benzyl vs. 2-pyridylmethyl) have a minor effect on the magnetic interactions between the two Ni^{II} centers. However, **2**' showed a stronger magnetic coupling than that of 2 via bridging triazolyl ligands. We propose that compared with the structure of 2, the presence of NO₃⁻ ions lead to structural changes, including a more planar chair-type $[Ni_2(\mu-L2)_2]$ ring and a shorter Ni...Ni separation, both of which increase the magnetic interactions between the Ni^{II} ions. These findings should contribute to the future design of triazole-based ligands that are readily available for the construction of new multinuclear metal complexes with potential applications in molecular magnets and catalysis.

CRediT authorship contribution statement

Jeeranun Inthong: Methodology, Investigation, Visualization, Writing - original draft. Vasut Nakarajouyphon: Investigation, Validation, Data curation. Kwanchanok Udomsasporn: Formal analysis. Khamphee Phomphrai: Resources. Nobuto Yoshinari: Formal analysis, Writing - review & editing. Takumi Konno: Resources, Writing - review & editing. Preeyanuch Sangtrirut**nugul:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research is funded by the Thailand Research Fund (Grant No. RSA6080082) and through the Royal Golden Jubilee Ph.D. Program, Thailand Grant No. PHD/0220/2557 (for V. N.). We also gratefully acknowledge financial support from the Center for Excellence for Innovation in Chemistry (PERCH-CIC), Ministry of Higher Education, Science, Research and Innovation, CIF Grant, Faculty of Science, Mahidol University and Mahidol University under the National Research Universities Initiative.

Appendix A. Supplementary data

Characterization data of ligands **L1–L3**, their intermediates and the nickel(II) complexes **1**, **2**, **2'** and **3**, including multinuclear NMR spectra, FT-IR and ESI-MS. CCDC-2008186 (**2'**) and CCDC-2008185 (**3**) contain the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114813.

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