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Phenoxido mediated antiferromagnetic and azide mediated ferromagnetic coupling in two dinuclear ferromagnetic nickel(II) complexes with isomeric Schiff bases: a theoretical insight on the pathway of magnetic interaction[†]

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Two new dinuclear nickel(ii) complexes, $[(H_2O)Ni(N_3)(L^1)(\mu_{1,1}-N_3)Ni(L^1)]$ and $[(H_2O)Ni(N_3)(L^2)(\mu_{1,1}-N_3)Ni(L^1)]$ Ni(L²)]-MeOH, derived from two isomeric Schiff base ligands, HL¹ [2-{(2-(ethylamino)ethylimino)methyl}-6ethoxyphenol] and HL² [2-{(2-(dimethylamino)ethylimino)methyl}-6-ethoxy-phenol], have been synthesized and characterized. Variable temperature (2-300 K) magnetic susceptibility measurements indicate the presence of moderate ferromagnetic exchange coupling between nickel(II) centers. In each complex, antiferromagnetic exchange takes place through the phenoxido bridge and ferromagnetic through the $\mu_{1,1}$ -azido bridge. The competitive interactions therefore reduce the overall magnetic coupling. In a theoretical complex, where the bridging azido ligand has been eliminated and the rest of the geometry is kept frozen, the magnetic coupling becomes antiferromagnetic which suggests that the ferromagnetic exchange occurs via the µ11-azido bridge. Mulliken population analysis and spin density plots clearly show that the spin distributed spherically in the Ni centers is due to the presence of one unpaired electron in both the $d_{x^2-y^2}$ and d_{z^2} orbitals. The shape of the spin density at the bridging O-atom and azide evidences the participation of their p orbitals in the magnetic coupling. The SOMO is basically constituted by the d_{y2} orbital of one nickel(u) center with the participation of the azide π -system. The SOMO-1 is constituted by the $d_{x^2-v^2}$ orbital of the other nickel(II), an oxygen atom and the azide π -system.

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Introduction

The study of dinuclear coordination complexes of 3d metal ions has attained special interest for the last two decades due to their importance to bioinorganic chemistry and magnetochemistry.1 The key aspect of molecular magnetism is understanding the mechanism of spin coupling and determination of magneto-structural correlations.² This can be done by studying discrete molecules, and large clusters or extended systems to obtain molecule-based magnetic materials.³ The magnetic interactions in such complexes mainly occur due to super exchange coupling between the metal centers via bridging ligands, and the strength and nature of this interaction, whether ferromagnetic or antiferromagnetic, depend on the bridging moiety and its subtended angle.4 Coordination complexes based on the nickel(II) ion could have potential applications in molecularbased ferromagnets, such as single molecule magnets (SMMs) and single chain magnets (SCMs), and these are used as data storage devices, nanoscale tools, and quantum computing systems.⁵ Nickel(II) is a preferred spin carrier to prepare molecular ferromagnets due to its large single-ion zero-field splitting.⁶ In this regard, tridentate N₂O donor Schiff base ligands obtained from diamines and salicylaldehyde

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derivatives are widely used for synthesizing oxido or phenoxido bridged nickel(II) complexes along with various bridging anionic coligands such as azide, thiocyanate, cvanate, etc.⁷ However, dinuclear nickel(II) complexes with two dissimilar bridges of azide and phenoxido ligands are still relatively less explored.8 In our previous work, we synthesized a similar $copper(\pi)$ complex with antiferromagnetically coupled copper(II) centers with $I = -46.18 \text{ cm}^{-1.9}$ Herein, we report that replacement of the Cu sites in $[(H_2O)Cu(L^1)(\mu_{1,1}-$ N₃)Cu(L¹)]ClO₄ with Ni results in an isostructural complex $[(H_2O)Ni(N_3)(L^1)(\mu_{1,1}-N_3)Ni(L^1)]$ (1) that exhibits ferromagnetic coupling. We have also replaced the HL¹ by a blocking ligand HL^{2} to prepare $[(H_{2}O)Ni(N_{3})(L^{2})(\mu_{1,1}-N_{3})Ni(L^{2})]$ ·MeOH (2) to check its effect on the overall magnetic behaviour. Density functional theory (DFT) combined with the broken symmetry approach has also been reported to provide a qualitative theoretical interpretation on the overall magnetic behaviour of complexes 1 and 2.

Experimental section

All other chemicals were of reagent grade and used as purchased from Sigma-Aldrich without further purification.

Caution!!

Although no problems were encountered in this work, organic ligands in the presence of azides are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

Preparation of complex $[(H_2O)Ni(N_3)(L^1)(\mu_{1,1}\cdot N_3)Ni(L^1)]$ (1). A methanol solution (10 mL) of 3-ethoxysalicylaldehyde (1 mmol, 0.166 g) and *N*-ethyl-1,2-diaminoethane (1 mmol, 0.105 mL) was refluxed for 1 h to prepare a tetradentate N₂O₂ donor Schiff base, HL¹. The Schiff base was not isolated and was used directly for preparation of the complex. A methanol solution (10 mL) of nickel(II) acetate tetrahydrate (1 mmol, 0.250 g) was added to the methanol solution of the Schiff base followed by the addition of a methanol solution (5 mL) of sodium azide (1 mmol, 0.65 g) with constant stirring. The stirring was continued for 2 h. Diffraction quality single crystals were obtained after a few days upon slow evaporation of a dark green solution of the compound in an open atmosphere.

Yield: 248 mg (72%). Anal. Calc. for $C_{26}H_{40}N_{10}Ni_2O_5$ (FW = 690.06): C, 45.25; H, 5.84; N, 20.30%. Found: C, 45.4; H, 5.6; N, 20.5%. FT-IR (KBr, cm⁻¹): 1638 ($\nu_{C=N}$); 2064 (ν_{N_3}); 3258 (ν_{NH_2}). UV-VIS [λ_{max} (nm)] [ε_{max} (L mol⁻¹ cm⁻¹)] (acetonitrile): 244 (1.73 × 10⁴); 304 (4.76 × 10³); 405 (1.14 × 10³).

Preparation of complex $[(H_2O)Ni(N_3)(L^2)(\mu_{1,1}-N_3)$ Ni(L²)]·MeOH (2). Complex 2 was prepared in a similar method to that of complex 1, except that *N*,*N*'-dimethyl-1,2-diaminoethane (1 mmol, 0.10 mL) was used instead of *N*-ethyl-1,2-diaminoethane. Single crystals, suitable for X-ray diffraction, were obtained upon slow evaporation of the solution after 5 days. Yield: 245 mg (68%). Anal. Calc. for $C_{27}H_{44}N_{10}Ni_2O_6$ (FW = 722.10): C, 44.91; H, 6.14; N, 19.40%. Found: C, 44.7; H, 6.4; N, 19.2%. FT-IR (KBr, cm⁻¹): 1627 ($\nu_{C=N}$); 2061 (ν_{N_3}); 3051, 3267 (ν_{NH_2}); 3446 (ν_{OH}). UV-VIS [λ_{max} (nm)] [ε_{max} (L mol⁻¹ cm⁻¹)] (acetonitrile): 246 (1.73 × 10⁴); 303 (5.4 × 10³); 405 (1.4 × 10²).

Physical measurements. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectra in KBr (4500-500 cm⁻¹) were recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectra in acetonitrile were recorded on a Perkin Elmer Lambda 35 UV-visible spectrophotometer. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu K_{α} radiation. In this process, both complexes were ground with a pestle and mortar to prepare fine powder. The powder was then dispersed with ethanol onto a zero background holder (ZBH). The ethanol was allowed to evaporate to provide a nice, even coating of powder adhered to the sample holder. The variable temperature magnetization measurements of the complexes were carried out at 1 T in the 2-300 K range using a Quantum Design MPMSXL SQUID magnetometer and 51.11 mg of 1 and 54.42 mg of 2. The data were corrected for the diamagnetic contribution of the sample holder and the intrinsic contributions on the basis of Pascal's constants.

X-ray crystallography. Single crystals suitable for diffraction were used for data collection using an Oxford Diffraction X-Calibur System diffractometer for 1 at 150 K and a Bruker SMART APEX II diffractometer for 2 at 296 K equipped with a graphite-monochromated Mo-K_{α} radiation source ($\lambda = 0.71073$ Å). The structures were solved by direct methods using Shelxs and refined by full-matrix least squares on F^2 using the Shelx2016/6 package.¹⁰ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. In 2, the solvent methanol molecule was disordered over three overlapping sites and refined accordingly. However, as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various disordered methanol H atoms, the refinement was completed with no allowance for these methanol H atoms in the model. Empirical absorption corrections were applied for 1 using the ABSPACK program¹¹ and for 2 using SADABS.12 Other programs used included PLATON¹³ and ORTEP.¹⁴ Crystallographic data and refinement details of both complexes are given in Table S1, ESI.†

Hirshfeld surfaces. Hirshfeld surface analysis was explored to evaluate the structural flexibility and magnitude of interchain interactions in both complexes. Hirshfeld surfaces¹⁵ and associated 2D-fingerprint^{16–18} plots were calculated using Crystal Explorer.¹⁹ This analysis is useful for the evaluation of closest intermolecular atomic contacts, even in complex crystal structures.²⁰

Theoretical methods. The study of the magnetic behaviour of the complexes was performed at the B3LYP/6-31+G* level of theory²¹ and using the crystallographic coordinates by means of the Gaussian-16 program.²² To calculate the

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coupling constant (*J*) of the dinuclear nickel complexes, two energy levels are evaluated, corresponding to the high-spin ($E_{\rm hs}$) and broken-symmetry ($E_{\rm bs}$) states. Subsequently, the *J* values used in this work were obtained from the equation and methodology proposed by Ruiz *et al.*²³ The plots of the spin density and SOMOs were generated using Gauss View software v. 6.0.16 (ref. 24) for the HS configuration.

Results and discussion

Synthesis

The potential tetradentate Schiff base ligands HL^1 and HL^2 were prepared by the condensations of *N*-ethyl-1,2diaminoethane and *N*,*N'*-dimethyl-1,2-diaminoethane with 3-ethoxysalicylaldehyde following a literature method.^{25*a*} Methanol solutions of the Schiff base ligands, thus prepared, were added to methanol solutions of nickel(II) acetate tetrahydrate, and stirred for 2 h followed by the addition of sodium azide under constant stirring conditions for 2 h to produce complexes **1** and **2**. Formation of both complexes is shown in Scheme **1**.

The phenoxido group has been known to have a tendency to bridge two or more metal centres for a long time.^{25b} We have therefore used 'salen' or 'half salen' type ligands to prepare many di- and polynuclear complexes of different transition metals for the last decades.^{25d-g} Pseudo-halides, *e.g.* azide, thiocyanate, cyanate, *etc.*, also have the ability to bridge metal centres thereby producing multimetallic complexes.^{25c,h,i} In the present study, we have used two potential tetradentate (isomeric) half-salen type Schiff base ligands and the azide co-ligand to prepare two dinuclear nickel(n) complexes. In each complex, one Schiff base molecule shows a tetradentate coordination mode (where the amine, imine, phenoxido and alkoxy groups participate in coordination) and another molecule of the Schiff base shows a tridentate coordination mode (keeping the alkoxy part pendant). Similarly, one azide is used to bridge two nickel(π) centers and another azide acts as a terminal ligand [*vide infra*]. This synthetic procedure may be extended in the future to prepare a series of mixed bridged dinuclear nickel(π) complexes.

Structural description

 $[(\mathbf{H}_2\mathbf{O})\mathbf{Ni}(\mathbf{N}_3)(\mathbf{L}^1)(\boldsymbol{\mu}_{1,1}\cdot\mathbf{N}_3)\mathbf{Ni}(\mathbf{L}^1)]$ (1). Single crystal X-ray diffraction analysis reveals that complex 1 crystallizes in the orthorhombic space group $P2_12_12_1$ with Z = 4. The molecular structure is built from isolated dinuclear molecules of $[(\mathbf{H}_2\mathbf{O}) \mathbf{Ni}(\mathbf{N}_3)(\mathbf{L}^1)(\boldsymbol{\mu}_{1,1}\cdot\mathbf{N}_3)\mathbf{Ni}(\mathbf{L}^1)]$, in which both nickel(\mathbf{u}) centers are hexacoordinated. A perspective view of the complex is shown in Fig. 1a. The dinuclear complex contains two deprotonated Schiff bases, one acting as a tetradentate ligand and the other as a tridentate one.

Ni(1) has a distorted octahedral geometry, in which an amine nitrogen atom, N(22), one imine nitrogen atom, N(19), one phenoxido oxygen atom, O(11), of a Schiff base ligand and one nitrogen atom, N(1), of a bridged azide constitute the equatorial plane. One oxygen atom, O(1), of a water molecule and a nitrogen atom, N(4), of a terminal azide coordinate in the axial positions to complete the distorted octahedral geometry. The deviations of the coordinating atoms, N(1), O(11), N(19) and N(22), in the basal plane from their least-squares mean plane are -0.041(1), 0.051(1), -0.050(2), and 0.040(1) Å, respectively. The deviation of Ni(1) from the same plane is 0.068(2) Å.

Similarly, Ni(2) also has a distorted octahedral geometry, where an imine nitrogen atom, N(39), of one Schiff base ligand, one phenoxido oxygen atom, O(11), one ethoxy oxygen



Scheme 1 Synthetic route to complexes 1 and 2.

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Fig. 1 ORTEP views of complexes (a) 1 and (b) 2 with 30% thermal ellipsoid probability. Hydrogen atoms have been omitted for clarity. The lattice methanol molecule in 2 has also not been shown.

atom, O(131), of the other Schiff base ligand and a nitrogen atom, N(1), from a bridging azide constitute the equatorial plane. One phenoxido oxygen atom, O(31), and an amine nitrogen atom, N(42), of one Schiff base ligand coordinate in the axial positions to complete the coordination. The deviations of the coordinating atoms, O(11), O(131), N(1) and N(39), in the basal plane from the mean plane passing through them are -0.011(2), 0.009(1), 0.009(1), and -0.007(1)Å, respectively. The deviation of Ni(2) from the same plane is 0.011(2) Å. The equatorial planes from the two metal centers intersect at an angle of $18.2(1)^{\circ}$. Selected bond lengths and bond angles are listed in Tables S2 and S3 (ESI†), respectively.

A nitrogen atom, N(1), of an azide ligand and a phenoxido oxygen atom, O(11), of a Schiff base ligand bridge two nickel(II) centers. The bridging angles Ni(1)–O(11)–Ni(2) and Ni(1)–N(1)–Ni(2) are $103.06(10)^{\circ}$ and $94.82(11)^{\circ}$ respectively. The distance between nickel(II) centers is 3.165(4) Å.

Saturated five membered chelate rings [Ni(1)–N(19)–C(20)–C(21)–N(22)] and [Ni(2)–N(39)–C(40)–C(41)–N(42)] have envelope and half-chair conformations with puckering parameters q = 0.454(3) Å; $\phi = 106.5(3)^{\circ}$ and q = 0.427(3) Å; $\phi = 90.7(3)^{\circ}$ respectively.²⁶

The hydrogen atom, H(22), attached to the nitrogen atom, N(22), participates in hydrogen bonding interaction with the symmetry-related oxygen atom, $O(331)^{c}$ {symmetry transformation c = 1/2 + x, 3/2 - y, -z (Table S4, ESI[†]). The hydrogen atom, H(42), attached to the nitrogen atom, N(42), also participates in an intramolecular hydrogen bonding interaction with nitrogen atom N(6). Similarly, hydrogen atoms, H(1) and H(2), attached to the oxygen atom, O(1), participate in strong hydrogen bonding interaction with the oxygen atom, O(31), and symmetry-related nitrogen atom, $N(4)^a$ {symmetry transformation a = -1/2 + x, 3/2 - y, -z} (Table S4, ESI[†]). All these hydrogen bonding interactions lead to the formation of a supramolecular chain (Fig. 2).



Fig. 2 One-dimensional hydrogen bonded chain structure of complex 1. Selected hydrogen atoms and ethyl group have been omitted for clarity.



Fig. 3 3D supramolecular assembly *via* hydrogen bonding interactions in complex 2. Selected hydrogen atoms have been omitted for clarity.

 $[(H_2O)Ni(N_3)(L^2)(\mu_{1,1}-N_3)Ni(L^2)]$ ·MeOH (2). Complex 2 shows a similar dinuclear molecular structure to complex 1 but crystallizes in the monoclinic space group $P2_1/n$ with Z =4. The structure of $[(H_2O)Ni(N_3)(L^2)(\mu_{1,1}-N_3)Ni(L^2)]$ also contains two hexacoordinated nickel(II) centers. A perspective view of complex 2 is shown in Fig. 1b. It also contains two deprotonated Schiff bases, one acting as a tetradentate ligand and the other as a tridentate one. Ni(1) adopts a distorted octahedral geometry, where an imine nitrogen atom N(19), an amine nitrogen atom, N(22), of one Schiff base ligand, one phenoxido oxygen atom, O(11), and a nitrogen atom, N(1), from a bridging azide constitute the equatorial plane. An oxygen atom of a water molecule, O(1), and a terminal azide nitrogen atom, N(4), coordinate in the axial positions to complete the distorted octahedron. The deviations of the coordinating atoms, N(1), O(11), N(19) and N(22), in the basal plane from the mean plane passing through them are -0.041(1), 0.049(1), -0.047(1), and 0.039(1) Å, respectively. The deviation of Ni(1) from the same plane is 0.037(1) Å. Selected bond lengths and bond angles are listed in Tables S2 and S3 (ESI[†]), respectively.

Ni(2) has a distorted octahedral geometry, where an imine nitrogen atom, N(39), one phenoxido oxygen atom, O(11), an ethanoate oxygen O(131) of a Schiff base ligand and one nitrogen atom, N(1), of a bridged azide constitute the equatorial plane. One phenoxy oxygen atom, O(31), and an amine nitrogen atom, N(42), of a terminal azide coordinate in the axial positions to complete its distorted octahedral geometry. The deviations of the coordinating atoms, N(1), O(11), N(39) and O(131), in the basal plane from their leastsquares mean plane are -0.018(1), 0.022(1), 0.012(1), and -0.018(1) Å, respectively. The deviation of Ni(2) from the plane is 0.028(1) Å. A nitrogen atom, N(1), of an azide ligand and a phenoxido oxygen atom, O(11), of a Schiff base ligand bridge two nickel(II) centers. The bridging angles Ni(1)-O(11)-Ni(2) and Ni(1)-N(1)-Ni(2) are 103.44(8)° and $95.90(10)^{\circ}$ respectively. The distance between nickel(II) centers is 3.129(1) Å. Saturated five membered chelate rings [Ni(1)-N(19)-C(20)-C(21)-N(22)]and [Ni(2)-N(39)-C(40)-C(41)-N(42)] have envelope and half-chair conformations with puckering parameters q = 0.301(4) Å; $\phi = 300.9(6)^{\circ}$ and q= 0.442(3) Å; ϕ = 300.9(6)° respectively.²⁶

Thus, the structure of 2 is basically the same as that found in complex 1, although as is apparent from Table S2,[†] there are significant differences in the dimensions between the two structures. For example, the Ni(2)–O(131) bond length is much longer in 2 at 2.472(2) Å, than in 1 at 2.238(2) Å, but there is no obvious explanation for the differences.

The water hydrogen atoms, H(1) and H(2), attached to O(1) participate in an intermolecular hydrogen bond with the terminal azide N(3)^{*c*} (^{*c*} =1/2 - x, -1/2 + y, 1/2 - z) and a strong intramolecular hydrogen bond with O(31). In addition,



Fig. 4 Hirshfeld surfaces mapped with d_{norm} (left), shape index (middle), and curvedness (right bottom) for complexes 1 (above) and 2 (below).

although their hydrogen atoms were not located, it seems clear that all three alternative oxygen positions for the disordered methanol solvent molecule form intermolecular hydrogen bonds with the terminal azide. All these hydrogen bonding interactions lead to the formation of a 3D supramolecular architecture (Fig. 3).

IR and electronic spectra. In the IR spectra of both complexes, distinct bands corresponding to the azomethine (C=N) stretching vibration appear at around 1640 cm⁻¹.²⁷ Distinct bands at around 2065 cm⁻¹ are indicative of the presence of the EO azido group in both the complexes.²⁸ The bands in the range of 2974–2878 cm⁻¹ may be assigned to alkyl C-H bond stretching vibrations.²⁹ A moderately strong, sharp peak at around 3251 cm⁻¹, may be attributed to the N-H stretching vibration.³⁰ Broad bands at around 3450 cm⁻¹ clearly indicate the presence of water molecules in the complex.³¹

Electronic spectra of both complexes in acetonitrile display absorption bands at around 405 nm.³² Absorption bands at around 305 nm are also observed and may be attributed to ligand to metal charge transfer transitions.³³ The intense absorption bands at a wavelength of 245 nm may be assigned as $\pi \rightarrow \pi^*$ transitions.³⁴ The electronic spectra of complexes **1** and **2** are shown in Fig. S1 and S2 (ESI†) respectively.

Hirshfeld surface analysis. Hirshfeld surfaces of both complexes, mapped over d_{norm} (range of -0.1 to 2.5 Å), shape index and curvedness, are illustrated in Fig. 4. The fingerprint plots can be decomposed to highlight particular atom pair close contacts. This decomposition enables the separation of contributions from different interaction types, which overlap in the full fingerprint. The proportions of

O···H and H···O interactions comprise 3.5% and 5.3% of the Hirshfeld surfaces for each molecule of complexes 1 and 2, respectively. The C···H/H···C {12.9% (1) and 13.6% (2)} and N···H and H···N {21.4% (1) and 13.6% (2)} interactions also contribute to the overall Hirshfeld surfaces of both complexes (Fig. 5).

X-ray powder diffraction pattern. The experimental powder X-ray diffraction pattern of the bulk product agrees well with the simulated XRD pattern generated from cif. This indicates the purity of the bulk samples. Fig. S3, ESI† shows the experimental and simulated XRD patterns of complex **1**.

Magnetic properties of complex 1. The temperature dependence of both the molar magnetic susceptibility (χ_M) and the product of the molar magnetic susceptibility and the temperature $(\chi_M T)$ of **1** is shown in Fig. 6. The χ_M value increases continuously upon cooling, as what usually occurs for a paramagnetic compound. The value of the $\chi_{M}T$ product at room temperature is 2.68 cm³ K mol⁻¹, which is slightly larger than the spin-only value (2.35 cm³ K mol⁻¹) expected for a system with two isolated S = 1 ions assuming g = 2.17(see below). An increase of the $\chi_M T$ product, which suggests the existence of predominant ferromagnetic interactions, is observed upon cooling. As a result, the $\chi_M T$ product reaches a maximum value of 4.26 cm³ K mol⁻¹ at 5.7 K. Further cooling of the sample leads to a decrease of the $\chi_M T$ value, which is 3.44 cm³ K mol⁻¹ at 2.0 K. This decrease is probably due to the existence of a zero-field splitting (D) which is typical of these types of Ni(II) complexes, and/or antiferromagnetic interactions. This behavior is similar to that found in other μ -phenoxido- $\mu_{1,1}$ -azide dinickel(π) complexes.⁸

Experimental magnetic susceptibility data have been fitted using a modification of the model described by Prushan



Fig. 5 2D fingerprint plots: full; O···H/H···O, C···H/H···C and N···H/H···N interactions contributed to the total Hirshfeld surface area of complexes 1 (above) and 2 (below).



Fig. 6 Temperature dependence of the molar susceptibility χ_{M} (circles) and $\chi_{M}T$ (squares) for complex 1. Solid lines show the best fit to the data as described in the text.

*et al.*³⁵ This model considers the existence of intramolecular interactions (*J*), and zero-field splitting (*D*) of the Ni(π) ions by applying the following Hamiltonian:

$$H = \left[-2J\hat{S}_{1}\hat{S}_{2}\right] + D\left[M_{S}^{2} - \frac{1}{3}S(S+1)\right]$$
(1)

Because the sign of *D* cannot be unequivocally determined from magnetization measurements of powder samples, the absolute value of this zero-field splitting parameter has been considered in the equation. A temperature-independent paramagnetism (TIP) term is also included in this model. In addition, intermolecular interactions (zJ) have been also considered using the molecular field approximation.³⁶ Thus, the parameters obtained from the best fit of the magnetic data are g = 2.17, |D| = 0.96 cm⁻¹, J = 11.35 cm⁻¹, zJ = 0.61 cm⁻¹, TIP = 5.42×10^{-4} cm³ mol⁻¹ with $\sigma^2 = 1.48 \times 10^{-3}$. Fig. 6 shows the fit of the experimental data using this model. Comparable $g^{8,35}$ and $D^{8b,g,37,38}$ values have been obtained for similar dinickel(II) complexes.

The small zJ value obtained from the fit of the data (0.61 cm^{-1}) indicates weak ferromagnetic intermolecular interactions. In spite of this small value, it has been necessary to include this parameter in the model in order to obtain good quality fit results. These interactions may take place through the hydrogen bonds that form the 1D supramolecular assembly, as shown in Fig. 2. This kind of magnetic interaction through hydrogen bonds has been previously reported.³⁹

Magnetic properties of complex 2. Fig. 7 shows the variation with the temperature of the molar magnetic susceptibility ($\chi_{\rm M}$) and the product of the molar magnetic susceptibility and the temperature ($\chi_{\rm M}T$) of **2**. There is a continuous increase of the $\chi_{\rm M}$ value with decreasing temperature, showing the usual paramagnetic behaviour. The room temperature value of $\chi_{\rm M}T$ (2.90 cm³ K mol⁻¹) is slightly higher than the spin-only value (2.67 cm³ K mol⁻¹) expected for a g = 2.31 system with two isolated S = 1 Ni(π) ions (see below).





Fig. 7 Temperature dependence of the molar susceptibility χ_M (circles) and $\chi_M T$ (squares) for complex **2**. Solid lines show the best fit to the data as described in the text.

The magnetic behaviour of this compound is analogous to that observed in complex 1. Predominant ferromagnetic interactions are deduced due to the increase upon cooling observed in the $\chi_{M}T$ value, which reaches a maximum value of 5.04 cm³ K mol⁻¹ at 7.5 K and then falls to a value of 3.45 cm³ K mol⁻¹ at 2.0 K caused by antiferromagnetic interactions and/or the presence of a zero-field splitting (D). Therefore, the magnetic data were fitted using the same model used for complex 1. Applying this model, the best fit of the experimental data yielded the following results (Fig. 7): g = 2.31, |D| = 1.26 cm⁻¹, J = 13.24 cm⁻¹, zJ = 0.84 cm⁻¹, TIP = 1.54×10^{-13} cm³ mol⁻¹ and $\sigma^2 = 2.03 \times 10^{-3}$. The TIP value is negligible for this compound. Indeed, the fitting of the data without considering this parameter yields almost the same results (g = 2.30, |D| = 1.28 cm⁻¹, J = 13.60 cm⁻¹, zJ = 0.85 cm⁻¹, $\sigma^2 = 2.00 \times 10^{-3}$). The values of $D^{8b,g,38}$ and $g^{8,35}$ are comparable to those observed in similar Ni(II) complexes.. The differences found in the coordination environments of the Ni(π) centres between complexes 1 and 2, like the Ni(2)-O(131) bond length (mentioned above in the "Structural description" section), can explain the small variations in their values of g and D.

Slight ferromagnetic intermolecular interactions are present in complex 2 as indicated by the low zJ value (0.84 cm⁻¹) obtained from the fit of the experimental data. Similar to compound 1, they may occur through the hydrogen bonds that form the 3D supramolecular structure shown in Fig. 3.

Magneto-structural correlation. The *J* value of complex **1** is 11.35 cm⁻¹. Similar positive *J* values (2.8–25.6 cm⁻¹), indicating the existence of intramolecular ferromagnetic interactions between the two Ni(π) ions, have been obtained from the fit of the magnetic data of analogous heterobridged μ -phenoxido- $\mu_{1,1}$ -azide dinickel(π) complexes.^{8f} It has been described in the literature that the magnitude of the *J* value in these compounds depends on different structural parameters such as the Ni–O–Ni and Ni–N–Ni angles, the Ni–O and Ni–N distances and the asymmetry of the two Ni–N bond lengths.^{8d,f} The high number of parameters that affect

Table 1 Experimental magnetic coupling constant (J_{exp}) and structural parameters of 1, 2 and selected analogous μ -phenoxido- $\mu_{1,1}$ -azide dinickel(\mathfrak{n}) complexes

Complex	$J_{ m exp} \left[m cm^{-1} ight]$	Ni-O-Ni [°]	Ni–N–Ni [°]	Ni–O [Å]	Ni–N [Å]	Asymmetry Ni–N [Å]	Ref.
1	11.35	103.1(1)	94.8(1)	2.037(2), 2.005(2)	2.185(3), 2.113(3)	0.072	This work
$[Ni(L^{1})_{2}(N_{3})(N_{3})]$	15.60	102.67(6)	93.94(7)	2.013(1), 2.008(1)	2.161(2), 2.133(2)	0.028	37
$[Ni(L^2)_2(N_3)(N_3)(H_2O)]$	5.84	102.30(7)	95.43(9)	2.037(2), 2.052(1)	2.095(2), 2.208(2)	0.113	38
2	13.24	103.44 (8)	95.9(1)	2.003(2), 1.984(2)	2.105(2), 2.110(2)	0.003	This work
$[Ni_2(L^3)_2(N_3)(CH_3CN)(H_2O)]$ (ClO ₄) H ₂ O·CH ₃ CN	16.9	104.68(9)	97.02(11)	1.994(2), 2.017(2)	2.125(3), 2.115(3)	0.010	8 <i>d</i>
$\begin{bmatrix} Ni_2(L^4)_2(N_3)(CH_3CN)(CH_3OH) \end{bmatrix}$ (ClO ₄)·CH ₃ CN	18.0	104.55(12)	97.58(15)	2.004(3), 2.000(3)	2.119(3), 2.091(4)	0.028	8 <i>f</i>
-1 -2 -2 -4 -4							

 L^1 , L^2 , L^3 and L^4 are the Schiff base ligands indicated in the corresponding references.

the exchange coupling constant makes it very difficult to predict the value of J only according to these structural parameters. However, a comparison with analogous complexes with similar parameters is possible. For example, compounds $[Ni(L^1)_2(\mu_{1,1}-N_3)(N_3)]^{37}$ and $[Ni(L^2)_2(\mu_{1,1}-N_3)(N_3)(H_2O)]^{38}$ where L^1 and L^2 are Schiff base ligands, show very similar structural parameters to those of the title compounds, apart from the asymmetry in the Ni–N bond lengths (Table 1). There is a difference of 0.028 Å between the two Ni–N bond lengths and a coupling constant of 15.6 cm⁻¹ in the former compound, while the J in the latter is 5.84 cm⁻¹, for a difference of 0.113 Å.

This is in accordance with the observed trend of stronger ferromagnetic interactions in compounds with two almost equal Ni–N distances.^{8d,e} This difference in compound **1** is intermediate between these two extremes at 0.072 Å, which is consistent with a ferromagnetic interaction of intermediate strength (J = 11.35 cm⁻¹).

The *J* value of 13.24 cm⁻¹ obtained for complex 2 is comparable with values observed in complexes with analogous structural parameters: $[Ni(L^1)_2(\mu_{1,1}-N_3)(N_3)]$ (*J* = 15.6 cm⁻¹);³⁷ $[Ni^{II}_2(L^3)_2(\mu_{1,1}-N_3)(CH_3CN)(H_2O)](ClO_4)$ H₂-O·CH₃CN (*J* = 16.9 cm⁻¹);^{8d} and $[Ni^{II}_2(L^4)_2(\mu_{1,1}-N_3)(CH_3CN)$ (CH₃OH)](ClO₄)·CH₃CN (*J* = 18.0 cm⁻¹),^{8f} where L¹, L³, and L⁴ are Schiff base ligands (Table 1). The difference between Ni–N bond lengths shown by these compounds is in the range 0.010–0.028 Å, but complex 2 exhibits two almost identical Ni–N distances. Their *J* values however do not exhibit the usual tendency for higher ferromagnetic coupling constants to be found in complexes with no Ni–N difference.^{8d,e} However, it is obvious that other structural parameters also influence the magnitude of the ferromagnetic interaction, although the differences between these parameters in complex 2 and in the previously cited complexes do not seem very significant.^{8,37}

DFT study. To better understand the magnetic behavior of the complexes, we have obtained the *J* values of complexes **1** and **2** theoretically, which are in good agreement with the experimental results and confirm the ferromagnetic nature of the intramolecular couplings. They are 11.70 cm⁻¹ for **1** and 20.57 cm⁻¹ for **2**, and are in acceptable agreement with the experimental findings (11.35 and 13.24 cm⁻¹ for **1** and **2**, respectively). Since the theoretical *J* value for compound **2** seems overestimated, we have also computed it using a higher level of theory (B3LYP/def2-TZVP instead of B3LYP/6-31+G*) but the resulting *J* value (20.36 cm⁻¹) remains a poor fit to the experimental value of 13.24 cm⁻¹.

It has been previously demonstrated⁸ that, in mixed bridged (μ -oxo, $\mu_{1,1}$ -azido) dinuclear Ni(π) complexes, antiferromagnetic exchange takes place through the



Fig. 8 (a) Graphical representation of spin density (contour 0.004 a.u.) at the ground state (high spin) configuration. (b and c) Pictorial representation of the SOMO involving the d_{z^2} and $d_{x^2-y^2}$ orbitals of nickel(11) for the high spin state of complex **1**.

Table 2 The spin densities on selected atoms for compound 1 at the UB3LYP/6-31G* level of theory. See Fig. 8 for labelling

Atom	Spin density (HS)	Spin density (LS) -1.68		
Ni(1)	1.66			
Ni(2)	1.67	1.67		
O(11)	0.08	0.005		
N(1)	0.06	0.011		
N(4)	0.04	-0.03		
N(19)	0.08	-0.07		
N(22)	0.07	-0.07		
O(1)	0.01	-0.01		
O(31)	0.05	0.05		
O(131)	0.01	0.02		
N(39)	0.07	0.08		
N(42)	0.07	0.07		

phenoxido bridge and ferromagnetic through the $\mu_{1,1}$ -azido bridge. The competitive interaction in this type of complex reduces the overall magnetic coupling. The low experimental values of *J* in compounds **1** and **2** suggest the existence of this compensating effect. To further corroborate this explanation, we have determined the *J* in compound **1** using a theoretical complex where the bridging azido ligand has been eliminated and the rest of the geometry is kept frozen. As a result, the magnetic coupling changes to antiferromagnetic $J = -5.70 \text{ cm}^{-1}$, thus evidencing that the ferromagnetic exchange occurs *via* the $\mu_{1,1}$ -azido bridge.

To examine the magnetic coupling mechanism, the spin density distribution has been analyzed in both complexes 1 and 2 (see Fig. S4, ESI[†] for compound 2). The spin density of compound 1 in the high spin (HS) state is represented in Fig. 8a and the spin density values are summarized in Table 2 for both high spin (HS) and low spin (LS) states, where positive and negative signs denote α and β spin states, respectively. The Mulliken spin population analysis (HS) indicates that a significant spin (ca. 1.33 e) is delocalized through the ligands, and the rest (2.77 e) is carried by the central nickel atoms. The spin carried by the phenoxido oxygen atom is ca. 0.08 e in the high-spin state and only 0.005 e in the broken-symmetry state of complex 1 indicating a polarization competition between the two nickel atoms with α and β spin density, respectively. The spin carried by the bridging N-atom of azide is 0.059 e for the high spin and 0.011 e for the low spin, thus showing a similar behaviour.

In octahedral Ni(π) complexes, the $d_{x^2-y^2}$ and d_{z^2} orbitals contain the unpaired electrons. These orbitals along with the local orbitals of the bridging ligands are involved in the super-exchange pathway. This behavior is also observed in complex **2**. This is clearly evidenced by the Mulliken population analysis and the spin density plot that show the spin distributed spherically in the Ni centers due to the presence of one unpaired electron in both the $d_{x^2-y^2}$ and d_{z^2} orbitals. Moreover, the shape of the spin density at the bridging O-atom and azide evidences the participation of their p orbitals in the magnetic coupling. The SOMO and SOMO-1 are shown in Fig. 8 as examples. The SOMO is basically constituted by the d_{z^2} orbital of one nickel(π) metal center with the participation of the π -system of azide. The SOMO-1 is constituted by the $d_{x^2-y^2}$ orbital of the other nickel(π) and the π -system of azide.

Conclusions

Herein, we report two relatively rare mixed phenoxido and azide bridged dinuclear nickel(II) complexes. Both complexes show strong intermolecular hydrogen bonding interactions to form a supramolecular chain structure in 1 and a 3D network in 2. Variable temperature (2-300 K) magnetic susceptibility measurements indicate the presence of ferromagnetic exchange coupling between nickel(π) centers (J = 11.35 and 13.24 cm^{-1} for complexes 1 and 2). The experimental findings were further checked and rationalized using brokensymmetry DFT calculations, and spin density and SOMO plots, which clearly support the presence of ferromagnetic coupling which is transmitted through the azide bridging ligand and compensates for the antiferromagnetic communication via the phenoxido bridge.

Conflicts of interest

There are no conflicts to declare.

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