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One Ferromagnetic and Two Antiferromagnetic Dinuclear Nickel(II) Complexes Derived from a Tridentate N,N,O-Donor Schiff Base Ligand: A Density Functional Study of Magnetic Coupling

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Three new dinuclear Ni^{II} complexes, $[Ni_2L_2(NO_3)_2]$ (1), $[Ni_2L_2(NO_2)_2]$ (2), and $[Ni_2L_2(CH_3COO)_2(H_2O)]$ (3), have been synthesized by using a tridentate Schiff base ligand, 2-({[3-(dimethylamino)propyl]imino}methyl)phenol (HL), along with a nitrate, nitrite, or acetate ion, respectively, as co-ligand. These three complexes were characterized by spectral analysis, X-ray crystallography, and variable-temperature magnetic susceptibility measurements. The structural analyses revealed that the Ni^{II} ions are coordinated by the deprotonated chelating tridentate Schiff base and possess a distorted octahedral geometry in all three complexes. Complexes 1 and 2 are two di- μ_2 -phenoxido-bridged species in which the nitrate and nitrite act as chelating co-ligands. However, in complex 3_1 , in which the acetate anion is monodentate, an additional water bridge is present along with two µ2-phenoxido bridges making the complex a face-sharing bioctahedron. Magnetic susceptibility measurements indicate

Introduction

The structural and magnetic properties of dinuclear nickel(II) complexes with a variety of bridging ligands have received considerable attention over the past two decades mainly because of their relevance in biological systems (as evidenced by the many existing biochemical polynuclear active complexes)^[1] and because of increasing interest in molecule-based and single-molecule magnets.^[2] Dinuclear µ-O-nickel(II) complexes with mixed N,O donor sets have been extensively investigated due to their potential to act as structural, electronic, and catalytic models for urease.^[3–5] The salicylaldehyde-derived tridentate N,N,O donor Schiff bases, which can bridge two metal ions through the phenoxido oxygen atom, have been used in the synthesis of polynuclear Ni^{II} complexes along with various bridging an-

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an antiferromagnetic intradimer interaction in complexes 1 and **2** with J values of -20.34(5) and -25.25(4) cm⁻¹, respectively, whereas complex **3** shows a dominant ferromagnetic exchange coupling with $J = 19.11(9) \text{ cm}^{-1}$. DFT calculations were performed, and the theoretically obtained J values of -19.99 (for 1), -24.19 (for 2) and 18.81 cm⁻¹ (for 3) corroborate very well the experimental results. An attempt has also been made to correlate the effect of Ni…Ni distances and bridging Ni-O-Ni angles on the coupling constants of the Ni^{II} complexes through DFT calculations. The relative energy calculations show that the diphenoxido-bridged complexes are stable at larger bridging angles, and consequently the coupling is antiferromagnetic, whereas with an additional water bridge, the formation of complexes with the Ni-O-Ni bridging angle in the ferromagnetic region is energetically profitable.

ionic co-ligands.^[6-10] Magneto-structural correlations of such species have been made, and interesting trends have emerged. Ferromagnetic interactions have been found to prevail in octahedrally coordinated dimeric nickel(II) complexes with end-on azide^[11] and cyanate bridges as well as end-to-end thiocyanate^[12,13] and selenocyanate bridges. In the case of the phenoxido-bridged dinuclear nickel(II) complexes, the major factor controlling the exchange coupling is the bridging Ni-O-Ni angle.^[14] On the basis of experimental results, it has been proposed that in the case of phenoxido-bridged nickel(II) complexes, the spins on the Ni^{II} ions interact ferromagnetically if the average Ni-O-Ni angles are less than ca. 93.5 and 99.0°,^[15] depending upon the μ_2 and μ_3 bridging modes of the phenoxido oxygen atoms, and for larger angles, the spin delocalization of the magnetic orbitals will be enhanced thereby giving rise to antiferromagnetic interactions.^[16] To design ferromagnetic phenoxido-bridged Ni^{II} complexes, it is thus necessary to make the bridging angle less than these critical values. Most of the dinickel(II) complexes involving an Ni₂O₂-bridging moiety that are reported in the literature are antiferromagnetically coupled.^[7,17,18] To the best of our knowledge, of the structurally characterized diphenoxido-bridged dinuclear nickel(II) complexes, only two are known to show fer-

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romagnetic coupling.^[19] Very recently we reported two more Ni^{II} compounds containing two μ_2 -phenoxido and one water bridge, which predominantly exhibited ferromagnetic interactions.^[20] In that report we proposed that the presence of the additional water bridge was very important to lowering the bridging angles to below the critical value and consequently to making the exchange coupling ferromagnetic.

In this paper we report on the synthesis, crystal structures, and magnetic properties of three new diphenoxidobridged dinickel(II) complexes, $[Ni_2L_2(NO_3)_2]$ (1), $[Ni_2L_2(NO_2)_2]$ (2), and $[Ni_2L_2(CH_3COO)_2(H_2O)]$ (3), by using a tridentate Schiff base ligand, 2-({[3-(dimethylamino)propyl]imino}methyl]phenol (HL), along with nitrate, nitrite, or acetate, respectively, as co-ligand. We have previously found that the carboxylate ion can stabilize an additional water bridge between the two nickel atoms with the help of strong hydrogen bonds.^[20] As other oxo anions, for example, nitrate or nitrite, also have the potential to form hydrogen bonds, these anions were chosen for this investigation. It was found that compounds 1 and 2 are antiferromagnetically coupled, whereas compound 3, which contains an additional water bridge, is ferromagnetically coupled. Several groups have rationalized the magnetic behavior of Cu^{II} and Ni^{II} complexes through DFT calculations.^[21] For complexes 1-3, a DFT study (using a combination of the hybrid B3LYP functional and the TZVP basis set) resulted in the successful determination of the nature of the magnetic exchange interactions. The variation in the coupling constants with bridging angle Ni-O-Ni was also computed taking complexes 1-3 as models. The relative energy calculations substantiated the importance of the additional water bridge in obtaining such species with bridging angles in the ferromagnetic region. To the best of our knowledge, although theoretical studies showing the dependence of the coupling constant J on the Cu–O–Cu angle in hydroxido/phenoxido-bridged Cu^{II} complexes have been performed in detail,^[22] such investigations with nickel complexes have not yet been reported.

Results and Discussion

Synthesis of Complexes 1–3

The monocondensed tridentate Schiff base ligand HL [2-($\{[3-(dimethylamino)propyl]imino\}methyl)phenol]$ reacted smoothly with nickel(II) nitrate and nickel(II) acetate in methanolic solution in a 1:1 molar ratio to yield complexes 1 and 3, respectively (Scheme 1). Complex 2 was synthesized by adding a methanolic solution of Ni(ClO₄)₂·6H₂O to a methanolic solution of the Schiff base ligand (HL) followed by the addition of an aqueous methanolic solution of NaNO₂ in a 1:1:1 molar ratio. An equimolar amount of triethylamine was then added in each case to deprotonate the Schiff base.



Scheme 1. Synthesis of complexes 1–3.

IR and UV/Vis Spectra of Complexes 1-3

The IR spectra of complexes 1-3 show a strong and sharp band due to azomethine v(C=N) at 1644, 1644, and 1635 cm⁻¹, respectively. For complex 1, the characteristic strong peak of the coordinated nitrate anion is observed at 1289 cm⁻¹ for the asymmetric stretching vibration. For complex 2, absorption bands at 1290, 1200, and 1050 cm^{-1} are tentatively assigned to $v_s(NO_2)$, $v_{as}(NO_2)$, and $\delta(NO_2)$, respectively.^[23] The presence of a band near 3400 cm⁻¹ in the spectrum of 3 indicates the presence of a water molecule. The broad nature of the band is probably due to the participation of these water molecules in hydrogen bonding. The IR spectral bands in the 1300–1650 cm⁻¹ region are difficult to assign due to the presence of several absorption bands from both the Schiff base and the carboxylato ligands. Nevertheless, by comparing the IR spectra of this Ni^{II} complex with those of 1 and 2 with other anions, the strong bands at 1548 and 1580 cm⁻¹ may be assigned to the antisymmetric stretching mode of the carboxylate group, whereas the bands at 1450 and 1412 cm⁻¹ can be assigned to the symmetric stretching modes of the carboxylato ligands in complex 3.

The electronic spectra of compounds 1–3 were recorded in methanol solution. The electronic spectra show absorption bands at 637 and 1012 nm (for 1), 640 and 1025 nm (for 2), and 644 and 1022 nm (for 3). These bands have been assigned to the spin-allowed transitions ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ and ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g(P)$, respectively. The higher-energy d–d bands are obscured by strong ligand-to-metal charge-transfer transitions. Moreover, the intense UV absorption bands observed at 365, 366, and 367 nm for complexes 1–3, respectively, have been assigned to L \rightarrow M charge-transfer transitions, which are characteristic of transition-metal complexes with Schiff base ligands.^[24]

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Description of the Crystal Structures of Complexes 1–3

Compounds $[Ni_2L_2(NO_3)_2]$ (1) and $[Ni_2L_2(NO_2)_2]$ (2)

The crystal structures of both 1 and 2 consist of $di-\mu_2$ phenoxido-bridged discrete centrosymmetric dimeric units of formula $[Ni_2L_2(NO_3)_2]$ and $[Ni_2L_2(NO_2)_2]$, respectively (Figure 1). Selected bond lengths and angles are presented in Tables 1 and 2. In both complexes the nickel atoms are hexacoordinated with an octahedral environment that is significantly distorted primarily by the small bite angles of 59.41(9) and 57.90(9)° at the bidentate chelating nitrate $(\kappa^2 O, O')$ and nitrite $(\kappa^2 O, O')$ ions in 1 and 2, respectively. In addition, each metal center is bonded to the three donor atoms of the deprotonated chelated Schiff base ligand L $(1\kappa^3 N, N', O: 2\kappa O)$ through the secondary amine nitrogen atom N(23), the imine nitrogen atom N(19), and the phenoxido oxygen atom O(11) as well as to a bridging phenoxido oxygen atom O(11)' [': 2 - x, 1 - y, 1 - z (1) and 1/2 - x, 1/2 - y, 1 - z (2)] from the symmetry-related Schiff base ligand $(1\kappa O: 2\kappa^3 N, N', O)$ with bond lengths similar to those observed in related compounds.^[25] As is usually found in this type of double oxido-bridged Ni^{II} dimers, the Ni₂O₂ core is slightly asymmetric, because each Ni^{II} ion is closer to the phenoxido oxygen atom of L [Ni(1)-O(11) 2.008(2) (for 1) and 2.014(2) Å (for 2); Table 1] that is chelated to it than to the phenoxido oxygen atom of the symmetry-related Schiff base ligand [Ni(1)–O(11)' 2.091(2) (for 1) and 2.104(2) Å (for 2)]. The two Ni atoms are separated by 3.124(2) and 3.156(2) Å, and the Ni(1)–O(11)–Ni(1)' bridge angles are 99.31(8) and 100.01(7)° for 1 and 2, respectively. The tridentate ligand coordinates to the metal ion in a facial configuration in both 1 and 2. Note that Ni(1)-O(11)and Ni(1)–N(19) are the two shortest bonds, and bonds *trans* to N(19) [Ni(1)-O(11)'] are significantly lengthened in both structures (Tables 1 and 2). The shortening of the Ni(1)-N(19) bond as well as the lengthening of the bond trans to it seems to stem from the better p-electron-accepting ability of the imine (C=N) functions, which in turn weakens the bond mutually *trans* to it as both of them compete for the same metal d orbital for back-bonding stabilization. The four donor atoms O(11), N(23), O(41), and O(42) describe the basal planes of the Ni(1) atom of complexes **1** and **2**. The deviations of these coordinating atoms from the least-square mean plane through them are 0.019(2), -0.018(3), -0.029(3), and 0.028(2) Å (for **1**) and 0.033(2), -0.032(2), -0.050(2), and 0.049(2) Å (for **2**), respectively. The displacement of the Ni(1) atom from the same plane towards the axially coordinated O(11)' atom is 0.012(3) and 0.029(1) Å for complexes **1** and **2**, respectively. No classic hydrogen bonds are found in either complex **1** or **2**.

Table 1. Bond lengths and angles in the metal coordination spheres of complex $1.^{\left[a \right]}$

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Bond length [Å]		Bond angle [°]		
Bond length [4 Ni(1)-O(11) Ni(1)-N(19) Ni(1)-N(23) Ni(1)-O(11)' Ni(1)-O(41) Ni(1)-O(42)	Å] 2.008(2) 2.009(3) 2.121(3) 2.091(2) 2.218(3) 2.135(2)	Bond angle [°] O(11)-Ni(1)-N(19) O(11)-Ni(1)-N(23) O(11)-Ni(1)-O(11)' N(19)-Ni(1)-N(23) O(11)'-Ni(1)-N(23) O(11)'-Ni(1)-N(23) Ni(1)-O(11)-Ni(1)' O(41)-Ni(1)-O(42) O(41)-Ni(1)-O(11)' O(41)-Ni(1)-O(11)' O(41)-Ni(1)-O(11)' O(42)-Ni(1)-N(19) O(42)-Ni(1)-N(23)	92.64(10) 103.91(11) 80.69(7) 87.00(11) 172.17(10) 98.54(11) 99.31(8) 59.41(9) 161.05(9) 94.95(9) 86.15(10) 90.38(11) 88.92(9) 101.76(10)	
		O(42)–Ni(1)–O(11) O(42)–Ni(1)–O(11)'	154.34(11) 95.32(8)	

[a] Symmetry operator ': 2 - x, 1 - y, 1 - z.

A CSD search revealed that there are many phenoxidobridged dinuclear complexes of Ni^{II} containing a similar type of N,N,O donor tridentate Schiff base along with various anions, but only four have nitrate or nitrite as co-ligand.



Figure 1. ORTEP views of the asymmetric unit of 1 (left) and 2 (right) with ellipsoids at the 30% probability level.

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Table 2. Bond lengths and angles in the metal coordination spheres of complex $2^{[a]}$

Bond length [Å]		Bond angle [°]		
Bond length [Å Ni(1)-O(11) Ni(1)-N(19) Ni(1)-N(23) Ni(1)-O(11)' Ni(1)-O(41) Ni(1)-O(42)	2.014(2) 2.017(2) 2.138(3) 2.104(2) 2.201(3) 2.116(3)	Bond angle [°] O(11)-Ni(1)-N(19) O(11)-Ni(1)-N(23) O(11)-Ni(1)-O(11)' N(19)-Ni(1)-N(23) O(11)'-Ni(1)-N(19) O(11)'-Ni(1)-N(23) Ni(1)-O(11)-Ni(1)' O(41)-Ni(1)-N(23) O(41)-Ni(1)-N(23)	92.29(8) 103.33(8) 79.99(7) 85.18(9) 172.14(9) 97.97(7) 100.01(7) 57.90(9) 159.37(9)	
		$\begin{array}{l} O(41)-Ni(1)-O(11) \\ O(41)-Ni(1)-O(11)' \\ O(41)-Ni(1)-N(19) \\ O(42)-Ni(1)-N(19) \\ O(42)-Ni(1)-N(23) \\ O(42)-Ni(1)-O(11) \\ O(42)-Ni(1)-O(11)' \end{array}$	96.98(8) 89.04(7) 90.44(8) 89.78(9) 101.85(9) 154.82(7) 96.58(7)	

[a] Symmetry operator ': 1/2 - x, 1/2 - y, 1 - z.

Of these, three are dinuclear^[7,10] and the remaining one is polynuclear.^[7] The structures of the three dinuclear complexes are very similar to those of **1** and **2**, whereas in the polynuclear species the dimeric units are further joined together by a nitrite bridge to form a one-dimensional chain.^[7] Although in the majority of such complexes the tridentate Schiff base coordinates meridionally, in the complexes with nitrate or nitrite as co-ligand it is in a facial configuration. The chelating coordination of the nitrate or nitrite, which must span the *cis* position, seems to be responsible for the rather unusual facial coordination of the Schiff base ligand, with a folded conformation in these complexes.

Compound $[Ni_2L_2(H_2O)(CH_3COO)_2] \cdot H_2O(3)$

The structure of **3** is shown in Figure 2 together with the atomic numbering scheme Selected bond lengths and angles are presented in Table 3. The crystal structure of **3** consists of a discrete dinuclear unit of formula $[Ni_2L_2(H_2O)(CH_3-COO)_2]$ ·H₂O. The dinuclear unit is formed of two independent nickel atoms, labeled Ni(1) and Ni(2), bridged by one

water molecule O(3) and two μ_2 -phenoxido oxygen atoms O(11) and O(26). Each of the two metal centers, Ni(1) and Ni(2), present a distorted octahedral environment, being coordinated to the deprotonated chelating Schiff base ligand through the secondary amine nitrogen atoms N(23)and N(38), the imine nitrogen atoms N(19) and N(34), and the phenoxido oxygen atoms O(11) and O(26), respectively, in a facial configuration with typical bond lengths (Table 3).^[7,26] The carboxylate oxygen atoms O(41) and O(51) of the terminally coordinated monodentate acetate ions, the oxygen atom O(3) of the water molecule, and the bridging phenoxido atoms O(26) and O(11) complete the hexacoordination of Ni(1) and Ni(2), respectively. Thus, the two nickel atoms are linked through three oxygen bridges to form a face-shared bi-octahedron with an Ni…Ni distance of 2.872(1) Å, which is significantly shorter than those in complexes 1 and 2 (3.124 and 3.156 Å) and other similar dinuclear nickel(II) complexes with only the two phenoxido bridges.^[14,17,27,28] The two phenoxido bridging angles, Ni(1)-O(11)-Ni(2) and Ni(1)-O(26)-Ni(2), are 86.30(11) and 87.18(10)°, respectively, and the water bridging angle, Ni(1)–O(3)–Ni(2), is $86.71(12)^\circ$. Each bridging phenoxido oxygen atom is asymmetrically bound with one Ni–O bond slightly longer [Ni(1)–O(26) 2.145(3) A, Ni(2)– O(11) 2.172(3) Å than the other [Ni(1)–O(11) 2.025(3) Å, Ni(2)–O(26) 2.019(3) Å]. The Ni–O(water) bonds are identical within experimental error [Ni(1)–O(3) 2.092(3) Å, Ni(2)-O(3) 2.091(3) Å], and these distances are comparable to those found in other reported aqua-bridged dinuclear Ni^{II} complexes, which are in the range 2.09–2.25 Å.^[19,29,30] The four donor atoms O(11), N(19), O(41), and O(3) describe the basal plane of Ni(1) and the deviations of these coordinating atoms from the least-square mean plane through them are -0.083(3), 0.072(4), -0.067(3), and 0.078(3) Å, respectively. The Ni(1) atom is displaced 0.123(1) Å from the same plane. The basal bond lengths around the Ni(1) atom are in the range of 2.017(4)-2.092(3) Å. The apical bond lengths Ni(1)–O(26) and Ni(1)–N(23) are 2.145(3) and 2.155(4) Å, respectively, the O(26)–Ni(1)–N(23) bond angle being 172.54(14)°. Similarly,



Figure 2. (a) ORTEP view of the asymmetric unit of 3 with ellipsoids at the 30% probability level. (b) Face-sharing bi-octahedron representation of complex 3.

in the coordination sphere of Ni(2), the basal plane consists of O(3), O(26), O(51), and N(34) with the bond lengths in the range of 2.000(4)–2.091(3) Å. The apical bond lengths Ni(2)–O(11) and Ni(2)–N(38) are 2.172(3) and 2.159(4) Å, respectively, the O(11)–Ni(2)–N(38) bond angle being 172.96(14)°. Deviation of the coordinating atoms O(3), O(26), O(51), and N(34) from the least-square mean plane through them are 0.082(3), –0.085(3), –0.070(4), and 0.073(4) Å, respectively, and that of the Ni(2) atom from the same plane is –0.149(1) Å. The two hydrogen atoms H(3A) and H(3B) of the bridging water molecule participate in strong intramolecular hydrogen bonding with the

Table 3. Bond lengths and angles in the metal coordination spheres of complex 3.

Bond length [Å]		Bond length [Å]	
Ni(1)-O(11)	2.025(3)	Ni(2)–O(11)	2.172(3)
Ni(1)–O(26)	2.145(3)	Ni(2)–O(26)	2.019(3)
Ni(1)-O(3)	2.092(3)	Ni(2)–O(3)	2.091(3)
Ni(1)-O(41)	2.055(3)	Ni(2)–O(51)	2.033(3)
Ni(1)-N(19)	2.017(4)	Ni(2)–N(34)	2.000(4)
Ni(1)–N(23)	2.155(4)	Ni(2)–N(38)	2.159(4)
Bond angle [°]		Bond angle [°]	
O(11)-Ni(1)-N(19)	89.43(14)	O(26)–Ni(2)–N(34)	90.51(14)
O(11)–Ni(1)–N(23)	102.83(13)	O(26)–Ni(2)–N(38)	104.42(13)
O(11)–Ni(1)–O(41)	166.92(12)	O(26)–Ni(2)–O(51)	164.53(14)
O(41)-Ni(1)-N(23)	88.89(13)	O(51)–Ni(2)–N(38)	89.19(15)
O(26)-Ni(1)-N(19)	100.51(13)	O(11)–Ni(2)–N(34)	99.08(15)
O(26)–Ni(1)–O(41)	88.50(11)	O(11)–Ni(2)–O(51)	87.04(13)
O(26)–Ni(1)–N(23)	172.54(14)	O(11)–Ni(2)–N(38)	172.96(14)
O(3)–Ni(1)–O(11)	79.45(12)	O(3)–Ni(2)–O(11)	76.22(12)
O(3)–Ni(1)–O(41)	93.49(11)	O(3)–Ni(2)–O(51)	92.19(13)
Ni(1)-(O3)-Ni(2)	86.71(12)	O(3)–Ni(2)–O(26)	78.82(11)
O(3)–Ni(1)–O(26)	76.03(12)	O(51)–Ni(2)–N(34)	97.58(16)
O(41)-Ni(1)-N(19)	97.13(14)	N(34)–Ni(2)–N(38)	87.30(16)
N(19)–Ni(1)–N(23)	86.75(15)	O(11)–Ni(2)–O(26)	78.64(10)
O(11)–Ni(1)–O(26)	79.15(11)	Ni(2)–O(11)–C(15)	119.80(3)
Ni(1)-O(11)-C(15)	128.2(3)	O(3)–Ni(2)–N(34)	168.96(14)
Ni(1)–O(11)–Ni(2)	86.30(11)	O(3)-Ni(2)-N(38)	98.01(14)
Ni(1)-O(26)-Ni(2)	87.18(10)		
O(3)-Ni(1)-N(19)	168.77(14)		
O(3)–Ni(1)–N(23)	97.16(14)		



oxygen atoms O(43) and O(53), respectively, of the terminally coordinated acetate anions with D···A distances of 2.566(5) and 2.493(5) Å^[20,31] (see Table S2 in the Supporting Information).

Comparison of the structural parameters of complex **3** with those of the four previously reported similar dinuclear Ni^{II} complexes,^[19,20] with both di- μ_2 -O(phenoxido) and water bridges, revealed that the double bridging Ni– μ_2 -O(phenoxido)–Ni (ca. 85–92°, ca. 1.9–2.1 Å) and Ni– μ H₂O–Ni (ca. 81–87°, ca. 2.0–2.3 Å) angles and distances are comparable. The Ni…Ni distances are also very similar (ca. 2.8–2.9 Å).

Magnetic Properties

The thermal variations of the product of the molar magnetic susceptibility and the temperature $(\chi_M T)$ per two Ni^{II} ions for compounds 1-3 are displayed in Figures 3 and 4 $[\chi_{\rm M}$ vs. T plots are given in Figures S1 (for 1 and 2) and S2 (for 3) in the Supporting Information]. As can be seen, the three compounds show $\chi_{M}T$ values at room temperature of ca. 2.3–2.4 cm³ K mol⁻¹, in agreement with the expected value for two noninteracting Ni^{II} S = 1 ions (the expected spin-only value is $2.0 \text{ cm}^3 \text{ K mol}^{-1}$, g = 2). Compounds 1 and 2 present very similar behavior on lowering the temperature: $\chi_{\rm M}T$ shows a smooth decrease at higher temperatures and a more pronounced decrease as the temperature is further lowered to reach values very close to zero at 2 K (Figure 3). Compound 3 shows different behavior: $\chi_M T$ gradually increases to reach a maximum value of 3.45 cm³ K mol⁻¹ at 15 K followed by a pronounced drop to reach values of 2.94 cm³ K mol⁻¹ at 2 K (Figure 4). These results indicate that compounds 1 and 2 present an antiferromagnetic Ni-Ni exchange coupling inside its dimeric structure, whereas complex 3 is typical of a system that exhibits dominant intramolecular ferromagnetic exchange coupling with the drop in $\chi_M T$ at lower temperatures due to zero-field splitting (ZFS) of the ground state (S = 2) and/ or possible interactions between the dimers.



Figure 3. Plots of $\chi_M T$ vs. T for complex 1 (left) and 2 (right). The points are the experimental data with the solid line generated from the fitted curve.

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The magnetic properties of **1** and **2** were analyzed by a theoretical model considering the interaction between two S = 1 spin centers. We fitted the magnetic properties of compounds **1** and **2** to a simple S = 1 dimer model derived from the isotropic Hamiltonian with $H = -JS_1S_2$ [Equation (1)].^[32]

$$\chi_{M}T = \frac{Ng^{2}\beta^{2}}{k} \times \left(\frac{2e^{x} + 10e^{3x}}{1 + 3e^{x} + 5e^{3x}}\right) \times (1 - \rho) + \frac{2Ng^{2}\beta^{2}\rho}{3k}; x = J/kT$$
(1)

The parameters *N*, β , and *k* in Equation (1) have their usual meanings, *J* is the singlet–triplet splitting, and ρ is the relative content for the paramagnetic impurity in which the spin state *S* = 1 is assumed. The $\chi_{\rm M}T$ versus *T* curves were least-squares fitted by minimizing the function *R* = $\Sigma[(\chi_{\rm M}T)_{\rm exp.} - (\chi_{\rm M}T)_{\rm calcd.}]^2/\Sigma(\chi_{\rm M}T)_{\rm exp.}^2$. The best-fitting parameters are $J = -20.34(5) \text{ cm}^{-1}$, g = 2.24(9), and $\rho =$ 1.2(2)% with $R = 3.6 \times 10^{-6}$ (for 1) and $J = -25.25(4) \text{ cm}^{-1}$, g = 2.27(8), and $\rho = 1.3(1)\%$ with $R = 1.7 \times 10^{-6}$ (for 2) (Table 4).

To achieve a good data fitting for compound 3, we fitted the magnetic data to Equation (2) taking the Weiss constant (θ) as an additional parameter to include the interdimer interaction (zJ') term as well as the anisotropy term (D).

$$\chi_M T = \frac{Ng^2 \beta^2 T}{k(T-\theta)} \times \frac{2e^x + 10e^{3x}}{1+3e^x + 5e^{3x}}; x = J/kT$$
(2)

The best-fitting parameters are $J = 19.11(9) \text{ cm}^{-1}$, g = 2.217(5), and $\theta = -0.074 \text{ K}$ with $R = 1.29 \times 10^{-5}$ (Table 4). Note that the addition of only the anisotropy term (*D*) in the spin Hamiltonian provided poor data fitting at low temperature. Thus, it can be concluded that, besides intradimer

Table 4. Magnetic and structural parameters of compounds 1–3.



Figure 4. Plot of $\chi_M T$ vs. T for complex 3. The points are the experimental data with the solid line generated from the fitted curve.

coupling, ZFS and interdimer coupling are present, but their correct evaluation is not possible due to their close relationship.^[7,33]

The antiferromagnetic exchange observed in compounds 1 and 2 leads to a diamagnetic ground spin state in these compounds, as confirmed by the isothermal magnetization measurements at 2 K, which show values of $<0.1 \mu_B$ at high fields (Figure 5). In contrast, the ferromagnetic coupling of compound 3 leads to S = 2 ground spin states, which is confirmed by the isothermal magnetization measurements at 2 K (Figure 5). Because there are interdimer antiferromagnetic interactions (in compound 3) and zero-field splitting, the magnetization values at 5 T are slightly smaller than the expected values of ca. 4 μ_B .

e	1	1			
Complex	Nature of mag- netic coupling	Experimental J values [cm ⁻¹]	Phenoxido-bridged Ni–O–Ni angles [°]; distances [Å]	Water-bridged Ni–O–Ni angles [°]; distances [Å]	Ni•••Ni distances [Å]
$[Ni_2L_2(NO_3)_2]$ (1)	antiferromagnetic	-20.34(5)	99.31(8); 2.008(2), 2.091(2)	_	3.124
$[Ni_2L_2(NO_2)_2]$ (2)	antiferromagnetic	-25.25(4)	100.01(7); 2.014(2), 2.104(2)	_	3.156
$[Ni_2L_2(CH_3COO)_2(H_2O)]$ (3)	ferromagnetic	19.11(9)	86.30(11), 87.18(10); 2.025(3),	86.71(12); 2.092(3), 2.091(3)	2.872
			2.144(3), 2.172(3), 2.019(3)		



Figure 5. Field dependence of molar magnetizations for compounds 1–3 at 2 K.

Magneto-Structural Correlation and Theoretical Interpretation by DFT Methods

In octahedral Ni^{II}, the $d_{x^2-y^2}$ and d_{z^2} orbitals each contain an unpaired electron. Therefore, for the diphenoxido-bridged compounds 1 and 2, only the $d_{x^2-y^2}$ orbitals of the metal atom along with the local orbitals of the bridging ligands are involved in the super-exchange pathways, whereas for 3, the magnetic orbitals, composed of both the $d_{r^2-\nu^2}$ and d_{r^2} orbitals of nickel(II) and ligand local orbitals, participate in super-exchange phenomena. The magnetostructural correlations for the μ_2 -oxido/phenoxido-bridged Ni^{II} complexes based on the magnetic measurements of structurally characterized species indicate ferromagnetic coupling below the critical Ni-O-Ni angle of 93.5° and above which the exchange coupling is expected to be antiferromagnetic. The majority of the reported diphenoxidobridged dinuclear nickel(II) complexes show strong antiferromagnetic interactions $(-20 > J > -100 \text{ cm}^{-1})$ as the bridging angle is larger than the critical value.^[14,15,18,34,35] To the best of our knowledge, ferromagnetic behavior has been found in only seven u2-phenoxido-bridged complexes^[15,19,20,30,36] that have also been structurally characterized. The Ni-O-Ni bond angles in compounds 1 and 2 [99.31(8) and 100.01(7)°, respectively] indicate that they

should show moderate antiferromagnetic coupling, in agreement with experimental results. In compound **3**, the Ni–O–Ni bond angles are considerably smaller [Ni(1)–(O3)–Ni(2) 86.71(12)°, Ni(1)–O(11)–Ni(2) 86.30(11)°, and Ni(1)–O(26)–Ni(2) 87.18(10)°; Figure 6], and this explains

the observed ferromagnetic coupling in the complex.

To achieve a better understanding of the magneto-structural interrelation, we used DFT calculations with the broken-symmetry approach to calculate J values theoretically. The J values calculated for complexes 1-3 are in good agreement with the experimental results (Table 4). The theoretically obtained J values are -19.99 (for 1), -24.19(for 2), and 18.81 cm^{-1} (for 3), which reveals antiferromagnetic coupling in complexes 1 and 2 and ferromagnetic coupling in complex 3. Thus, the calculated values reproduce the experimental trends correctly. Moreover, we have also performed DFT calculations to gain a better insight into the angular dependence of the exchange coupling interactions of complexes 1-3. The two diphenoxido-bridged dinuclear complexes 1 and 2 allowed us to simplify the study of the magneto-structural correlations, because they have only one exchange pathway through the μ_2 -phenoxido oxygen atom. The DFT calculations for complex 1 were performed by changing the Ni…Ni distance and keeping the rest of the structure unaltered. The change in the Ni…Ni separation is



Figure 6. Structures of the Ni^{II} environments in (a) 1, (b) 2, and (c) 3 with the bridging bond lengths [Å] and angles $[\circ]$.



Figure 7. Dependence of (a) the calculated exchange coupling constant and (b) the relative energy on the phenoxido-bridged Ni–O–Ni angle.

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clearly proportionate to the change in Ni–O–Ni bond angle. A clear dependence of the exchange coupling constant on the Ni–O–Ni angle has been found and is represented in Figure 7a.

From the curve it is clear that on increasing the Ni-O-Ni bridging angle (starting from 78°) first the magnitude of J increases and then decreases passing through a maximum value at about 90°. The parabolic dependence of the exchange coupling on the Ni-O-Ni angle clearly shows that ferromagnetic interactions are expected only when the bridging angles are in the range 84–96°. This type of parabolic relationship of J with the bond angle has also been found by Ruiz et al.^[22b] in azido-bridged Cu^{II}, Ni^{II}, and Mn^{II} complexes. The relative energy calculations (Figure 7b) indicate that the possibility of obtaining the complex on the left side of the parabola with a relatively small Ni–O–Ni angle (<89°) is extremely remote because of the high instability, and therefore it is unlikely to be synthesized. Figure 7b also indicates a flat minimum for the relative energies at larger bond angles, and as a result complexes with a range of large bond angles should be stable.

The magnetic behavior of complex **3** is governed by two dominant factors: (1) The super-exchange pathway through the μ_2 -phenoxido oxygen atom and (2) another super-ex-

change interaction coming from the μ_2 -OH₂ bridge. First, we performed calculations based on density functional theory (see Computational Methodology in the Exp. Sect.) by changing the Ni…Ni distance of complex 3 (Figure 8a). As a result, all three bridging angles $[\angle Ni-OH_2-Ni, \angle Ni O(Ph^1)$ -Ni, and $\angle Ni$ - $O(Ph^2)$ -Ni] changed simultaneously, and this resulted in considerable changes in the coupling constant (J), as shown in Figure 8b for the $\angle Ni-OH_2-Ni$ angle. The plots indicate a nearly linear relationship of Jwith the bond angle/bond length with a slight bending at both ends. Earlier we discussed the parabolic nature of the value of J with the bond angle. In Figure 8, we used a relatively narrow bond angle range. So here the bending feature may arise from the parabolic nature of the overall curve. From Figure 8 it is apparent that the ferromagnetic coupling significantly decreases with increasing Ni…Ni distance, which causes larger phenoxide and water bridging angles. The critical Ni…Ni distance was found to be ca. 3.11 Å and that of the $\angle Ni-OH_2-Ni$ and $\angle Ni-O(phenox$ ido)-Ni bridging angles are ca. 91° (see Table S1 in the Supporting Information). The relative energy calculations (Figure 8c) show that complexes with smaller bond angles for this kind of triple-bridged Ni^{II} system can be synthesized because of their higher stability in this lower range of Ni-O-Ni angles.



Figure 8. (a) Magnetic coupling constant for complex 3 as a function of the Ni $\cdot\cdot\cdot$ Ni distance and (b) Ni $-OH_2$ -Ni bridging angle, and (c) relative energy as a function of the Ni $-OH_2$ -Ni bridging angle.

To have an idea of the contribution of the water bridge to the overall coupling, calculations were also performed on a model complex of 3, removing the water bridge from the structure without making any changes to the bond angle or the distances of phenoxido bridges. The calculated value of J then becomes -12.98 cm^{-1} , which indicates an antiferromagnetic interaction in the model, although our previous calculations with compound 1 as a model complex show that the coupling should be ferromagnetic for the diphenoxido bridging angle of ca. 86-87°. The change in geometry from distorted octahedron to square-pyramidal on removal of the water bridge seems responsible for the apparent disagreement in exchange coupling. It has been documented that, in the cases of mixed bridged polynuclear species, the overall exchange coupling constant cannot be ascribed to the algebraic sum of contributions from different bridges.^[37]

Finally, to check the influence of the bridging water molecule on the values of *J*, we changed only the Ni–OH₂ bond length keeping the other structural parameters [Ni···Ni distance and Ni–O(phenoxido)–Ni bond angles] constant. As a result, the Ni–OH₂–Ni bridging angle changed, and calculations were performed within the range 80–105°. The result is shown in Figure 9.

The plot suggests that starting from 80° the ferromagnetic coupling increases upon increasing the water bridging angle and after passing through a maximum at $\theta \approx 93^\circ$ the value of J decreases. This shows that ferromagnetic coupling preferably occurs in the lower range of Ni-OH₂-Ni angles, and a maximum was found at ca. 93°. The relative energy plot (Figure 9b) shows an inverted unsymmetrical parabolic feature with a minimum at ca. 84.5°. Thus, in this case, complexes with a water bridging angle between 80 and 89° are relatively stable, but in this range the value of Jdecreases with decreasing bond angle. This type of magneto-structural correlation, in which the J value increases with increasing bond angle, is expected to occur for complexes in which the bond angles are on the left side (positive slope) of the parabolic coupling constant versus bond angle relationship.^[22b] Note that compound 3 shows a positive

dependence of the coupling constant with increasing water bridging angle at a bond angle limit of $\pm 8^{\circ}$ from its most stable position. Thus, we conclude that in comparison with complexes 1 and 2, the relatively small phenoxido-bridged Ni–O–Ni angle gains stability from the water bridging in complex 3.

The Mulliken spin population analysis (Tables S3 and S4) indicates that a significant spin (ca. 0.64 *e*) is delocalized through the ligand, whereas the rest of the spin (ca. 3.36 e) is carried by the central nickel atoms for the highspin state of **1** and **2**. Here, the spin carried by the phenoxido oxygen atom is ca. 0.80 e in the high-spin state and $\pm 0.01 e$ in the broken-symmetry state. Although in complex **3** the spin density on the phenoxido-bridged oxygen atoms is approximately the same as in complexes **1** and **2**, in the broken-symmetry state of complex **3**, a very small spin density (0.004 *e*) on the water-bridged oxygen atoms signifies polarization competition between the two nickel atoms with α and β spin density, respectively.

To know the magnetic couplings (J) in the optimized structures of all three compounds 1–3, we performed geometrical optimization at the B3LYP/TZVP level of DFT. The optimized geometrical parameters for the three complexes show good agreement with their corresponding X-ray crystallographic data (Table S5). The J values calculated from the optimized and X-ray structures are listed in Table 5. Comparison of the data clearly shows that the J values of the optimized structures are underestimated by ca. 28%, although it can be said that these values are in agreement with the experimentally obtained J values. These deviations from the corresponding experimental J values may be accounted for by slight differences in the bridging angles and also in the bridging bond lengths in the optimized structures.

In summary, the theoretical calculations corroborate well the experimental findings that the antiferromagnetic interaction between the Ni^{II} centers in complexes 1 and 2 takes place through the phenoxido bridges, whereas the ferromagnetic interaction in complex 3 occurs through the phenoxido and water bridges. We carried out calculations to



Figure 9. Dependence of (a) the calculated exchange coupling constant and (b) the relative energy on the Ni–OH₂–Ni bridging angle.

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Table 5. Comparison of experimental, theoretical, and optimized J values
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Complex	Experimental J values [cm ⁻¹]	Theoretical J values calculated from X-ray structure [cm ⁻¹]	Theoretical J values calculated from optimized structure $[cm^{-1}]$
$[Ni_2L_2(NO_3)_2]$ (1)	-20.34	-19.994	-14.073
$[Ni_2L_2(NO_2)_2]$ (2)	-25.25	-24.192	-17.326
$[Ni_2L_2(CH_3COO)_2(H_2O)]$ (3)	+19.11	+18.811	+13.88

determine the influence of the Ni–O(phenoxido)–Ni bridging angles in complex 1 by varying the Ni···Ni distance. The results show a parabolic dependence of the values of J on the Ni···Ni distance or the phenoxido bridging angle. The relative stability calculations show that these kinds of compounds are stable when the phenoxido-bridged Ni–O–Ni angle is larger, and consequently the coupling becomes antiferromagnetic. However, in the case of complex 3, due to the presence of water-bridging, stability is achieved at relatively small Ni–O(phenoxido)–Ni angles. The dependence of the coupling constant on the water bridging angle shows that the most stable structure lies in the positive slope region of an unsymmetrical parabolic curve. Thus, the value of J increases with the bond angle in this region.

Conclusions

Three new dinuclear Ni^{II} complexes have been synthesized by using a tridentate N,N,O donor Schiff base ligand, 2-({[3-(dimethylamino)propyl]imino}methyl)phenol, and an anionic co-ligand, NO₃⁻, NO₂⁻, or CH₃COO⁻. Compounds 1 and 2 present diphenoxido-bridged complexes whereas in compound 3, as well as the diphenoxido bridges from the Schiff base ligand, a water molecule acts as a bridge between the two Ni^{II} ions. The strong hydrogen bond between the bridging water molecule and the uncoordinated oxygen atom of the acetate group seems to stabilize the structure of 3. The magnetic study revealed that compounds 1 and 2 are antiferromagnetically coupled, as is expected from the Ni-O-Ni bridging angles [99.31(8) and 100.01(7)°]. However, compound 3 is ferromagnetically coupled, as indicated by the smaller bridging angles [86.71(12), 86.30(11), and 87.18(10)°]. The experimental magnetic behavior of complexes 1-3 was corroborated by DFT calculations, which serve as an efficient tool for understanding the magnetic interaction pathways of the complexes. A combination of DFT calculations and magnetic studies have allowed us to deduce the dependence of the exchange coupling constant J on the bridge identity, the metal-metal separation, and the bond angles subtended at the bridging atoms in the dinuclear nickel complexes having either μ_2 -phenoxido or both μ_2 -phenoxido and μ_2 -water bridges. However, from the relative energy point of view, the diphenoxido-bridged complexes are highly unstable in the lower bond angle range, whereas in the triple-bridged Ni^{II} complexes such small angles can be obtained easily, which indicates the importance of the additional bridge in making them stable in the lower bridging angle region and consequently the coupling ferromagnetic.

Experimental Section

Materials: The diamine and salicylaldehyde were purchased from Lancaster Chemical Co. All other reagents were reagent-grade and used without further purification.

Physical Measurements: Elemental analyses (C, H, and N) were performed with a 2400 series II CHN analyzer. IR spectra (4500– 500 cm^{-1}) in KBr pellets were recorded with a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra (1400–350 nm) in CH₃OH (for 1–3) were recorded with a Hitachi U-3501 spectrophotometer. The magnetic measurements were carried out at the "Servei de Magnetoquimica (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL susceptometer in applied fields of 7000 and 400 G in the temperature ranges of 2–300 and 2–30 K, respectively. The field dependence of the magnetization measurements were performed with the same instrument at 2 K. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables^[37a] and sample holder calibration.

Synthesis of the Schiff Base Ligand 2-($\{[3-(Dimethylamino)-propy|]imino\}methyl)phenol (HL)$: The Schiff base was prepared by the condensation of salicylaldehyde and *N*,*N*-dimethyl-1,3-propanediamine in methanol as reported earlier.^[20]

Synthesis of $[Ni_2L_2(NO_3)_2]$ (1): Ni(NO₃)₂·6H₂O (1.455 g, 5 mmol) dissolved in methanol (10 mL) was added to a methanolic solution (10 mL) of the ligand HL (5 mmol) with constant stirring followed by the addition of triethylamine (0.70 mL, 5 mmol). The color of the solution turned deep green. The solution was left to stand in air until plate-shaped green X-ray quality single crystals of complex 1 appeared at the bottom of the vessel on slow evaporation of the solvent. Yield: 1.14 g; 70%. IR (KBr pellet): $\tilde{v} = 1644$ (vC=N), 1289 (vNO₃⁻) cm⁻¹. UV/Vis (CH₃OH): $\lambda_{max} = 365, 637, 1012$ nm. C₂₄H₃₄N₆Ni₂O₈ (651.99): calcd. C 44.21, H 5.26, N 12.89; found C 44.10, H 5.20, N 12.97.

Synthesis of $[Ni_2L_2(NO_2)_2]$ (2): Ni(ClO₄)₂·6H₂O (1.828 g, 5 mmol), dissolved in methanol (10 mL) was added to a methanolic solution (10 mL) of the Schiff base HL (5 mmol) with constant stirring followed by the addition of triethylamine (0.70 mL, 5 mmol). Then a methanol/water solution (9:1, v/v) of NaNO₂ (0.345 g, 5 mmol) was added with slow stirring. The solution was left to stand overnight in air in which time block-shaped light-green X-ray quality single crystals of complex **2** appeared. Yield: 1.16 g; 75%. IR (KBr pellet): $\tilde{v} = 1644$ (vC=N), 1290 (v_sNO₂), 1200 (v_{as}NO₂) cm⁻¹. UV/Vis (CH₃OH): $\lambda_{max} = 366$, 640, 1025 nm. C₂₄H₃₄N₆Ni₂O₆ (619.99): calcd. C 46.50, H 5.53, N 13.56; found C 46.31, H 5.25, N 13.12.

Synthesis of $[Ni_2L_2(CH_3COO)_2(H_2O)]$ (3): Ni(OAc)₂·4H₂O (1.240 g, 5 mmol) dissolved in hot methanol (10 mL) was added to a methanolic solution (10 mL) of the ligand HL (5 mmol) and the mixture stirred for ca. 10 min. Triethylamine (0.70 mL, 5 mmol) was added, the color of the solution turned deep green, and a green precipitate separated within 1 h. The green solid was then removed by filtration, washed with diethyl ether, and redissolved in CH₃CN. The solution was left to stand overnight in the air, which resulted

in the precipitation of deep-green, X-ray-quality single crystals of complex **3**. Yield: 1.09 g; 65%. IR (KBr pellet): $\tilde{v} = 3400$ (br., vOH), 1635 (vC=N), 1580 (vasC=O), 1450 (vsC=O) cm⁻¹. UV/Vis (CH₃OH): $\lambda_{max} = 367$, 644, 1022 nm. C₅₆H₈₆N₈Ni₄O₁₅ (1346.18): calcd. C 49.97, H 6.44, N 8.32; found C 49.55, H 6.38, N 8.16.

Crystallographic Data Collection and Refinement: Suitable single crystals of each complex were mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and $Mo-K_{\alpha}$ $(\lambda = 0.71073 \text{ Å})$ radiation. The structures were solved by the Patterson method by using SHELXS97.^[38] Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. The non-hydrogen atoms were refined with independent anisotropic displacement parameters. All the hydrogen atoms were placed in idealized positions, and their displacement parameters were fixed at 1.2 times larger than those of the attached non-hydrogen atoms except for the hydrogen atoms on C(6) in 1 and 2, and on C(7) and C(21) in 3 and on the water oxygen atoms O(3) and O(8) in 3, which were located in the difference Fourier map. Successful convergence was indicated by a maximum shift/error of 0.001 for the last cycle of the leastsquares refinement. All calculations were carried out by using SHELXS97,^[38] SHELXL97,^[39] PLATON99,^[40] ORTEP-32,^[41] and WinGX systemVer-1.64.^[42] Data collection and structure refinement parameters as well as the crystallographic data for the three complexes are given in Table 6. CCDC-852926 (for 1), -852927 (for 2), and -852928 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Table 6. Crystallographic data for complexes 1–3.

	1	2	3
Empirical formula	C ₂₄ H ₃₄ N ₆ Ni ₂ O ₈	C ₂₄ H ₃₄ N ₆ Ni ₂ O ₆	C ₅₆ H ₈₆ N ₈ Ni ₄ O ₁₅
M^{-}	651.95	619.95	1346.09
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 1 (No. 2)	C2/c (No. 15)	C2/c (No. 15)
a [Å]	8.736(5)	20.780(5)	18.746(4)
b [Å]	9.403(5)	17.503(5)	12.756(3)
<i>c</i> [Å]	9.964(5)	7.915(5)	28.761(8)
a [°]	109.039(5)	90	90
β [°]	94.159(5)	111.980(5)	107.871(3)
γ [°]	112.664(5)	90	90
V [Å ³]	695.3(6)	2670(2)	6546(3)
Z	1	4	4
$D_{\text{calcd.}} [\text{g cm}^{-3}]$	1.557	1.542	1.366
$\mu [{\rm mm}^{-1}]$	1.412	1.461	1.199
F(000)	340	1296	2840
R(int)	0.030	0.075	0.057
Total reflections	10577	19228	21975
Unique reflections	3241	2873	5731
$I > 2\sigma(I)$	2832	2115	4271
<i>R</i> 1, <i>wR</i> 2	0.0504, 0.1472	0.0340, 0.0737	0.0523, 0.1579
T [K]	293	293	293

Computational Methodology: To calculate the coupling constant (*J*) of the dinuclear nickel complexes, we calculated two energy levels corresponding to the high-spin (E_{hs}) and broken-symmetry (E_{bs}) states. Subsequently, the *J* values were obtained from Equation (3) proposed by Ruiz et al. with $S_1 \ge S_2$.^[43] The hybrid B3LYP functional^[44-46] and TZVP^[47] basis set was used in all calculations as implemented in the ORCA package.^[48] Relativistic effects were incorporated into the computations with the zeroth-order regular approximation (ZORA) to describe scalar relativistic effects. All the energy calculations were performed by including a tight SCF

convergence criterion (Grid4).^[49] The "resolution of identity" (RI) approximation with auxiliary TZV/J coulomb fitting basis sets were also used to increase the speed of the calculations.^[50] For the SCF calculations, we have taken into account all the experimental structures without further geometrical optimization. In the DFT calculations on angle dependence we modified the angle keeping the rest of the structure frozen and then performed the SCF calculations. To check the changes in J in the optimized structures, we performed a geometrical optimization at the B3LYP/TZVP level of theory. Then the SCF calculations of the optimized structure and J value extraction were performed by using the same method as used in previous calculations.

$$J = \frac{E_{\rm bs} - E_{\rm hs}}{2S_1 S_2 + S_1}$$
(3)

Supporting Information (see footnote on the first page of this article): Results of DFT calculations, given in Tables S1, S3 and S4, hydrogen bonding in complex **3**, shown in Table S2; selected bond lengths and angles of **1–3** in Table S5, Figures S1 and S2 with $\chi_{\rm M}$ vs. *T* plots of complexes **1–3**.

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Antiferro- and Ferromagnetic Dinuclear Nickel(II) Complexes



Dinuclear Nickel(II) Complexes

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One Ferromagnetic and Two Antiferromagnetic Dinuclear Nickel(II) Complexes Derived from a Tridentate N,N,O-Donor Schiff Base Ligand: A Density Functional Study of Magnetic Coupling

Keywords: Nickel / Schiff bases / O ligands / Magnetic properties / Density functional calculations



Of the three dinuclear Ni^{II} complexes synthesized, the two double-phenoxidobridged complexes are antiferromagnetically coupled, whereas the third with an



additional water bridge is ferromagnetic. A theoretical study has been performed to show the influence of the Ni–O–Ni bond angle on the exchange coupling constants.