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PAPER

The importance of an additional water bridge in making the exchange coupling of bis(μ-phenoxo)dinickel(II) complexes ferromagnetic†

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Two new nickel(II) complexes $[Ni_2L_2(PhCOO)_2(H_2O)]$ (**1**), $[Ni_2L_2(PhCH_2COO)_2(H_2O)]$ (**2**) have been synthesized using a tridentate Schiff base ligand, HL (2-[(3-dimethylamino-propylimino)-methyl]-phenol) and the carboxylate monoanions, benzoate and phenylacetate, respectively. The complexes have been characterized by spectral analysis, variable temperature magnetic susceptibility measurement and crystal structure analysis. The structural analyses reveal that both complexes are dinuclear in which the distorted octahedral Ni^{2+} ions share a face, bridged by one water molecule and two μ_2-phenoxo oxygen atoms. A monodentate benzoate or phenylacetate anion and two nitrogen atoms of the chelating deprotonated Schiff base (L) complete the hexa-coordination around the metal ion.
Variable-temperature magnetic susceptibility studies indicate the presence of dominant ferromagnetic exchange coupling in complexes **1** and **2** with J values of 11.1(2) and 10.9(2) cm^{-1} respectively. An attempt has been made to rationalize the observed magneto-structural behavior considering the importance of the additional water bridge in the present two complexes and also in other similar species.

Introduction

Dinuclear transition metal complexes and ligands facilitating their formation have been extensively investigated due to their potential applications in bioinorganic chemistry, magnetochemistry, materials chemistry and catalysis.[1–5] Multidentate ligands containing N, O donors, especially phenoxo O donor, have been widely used to form such dinuclear species.[6] In particular, the dinuclear Ni(II) species are of continuing interest mostly because of the occurrence of a pair of nickel(II) centers in the active site of the hydrolytic enzyme urease that catalyzes the hydrolysis of urea to ammonia and carbamate[7,8] or the ethanolysis of urea to ethyl carbamate.[9] The variable temperature magnetic behavior of urease is intriguing[10–12] and several synthetic models have addressed ligand environment and magnetic and electronic properties of the nickel(II) pair. However, recent interest in the magnetic study of polynuclear Ni(II) complexes with various bridging groups emerges from their potential use as molecular magnetic materials.[13,14] Among them, the carboxylates and the μ-1,1-azido bridged Ni(II) complexes deserve special mention as they are capable of transmitting ferromagnetic interactions.[15,16] Unlike hydroxo-, alkoxo- and phenoxo-bridged Cu(II) dinuclear complexes[6a,17,18] structural modeling and magneto-structural correlations are limited in nickel(II) complexes, due to fewer numbers of known complexes and to the large number of structural parameters that affect the superexchange mechanism in these systems. The major factor controlling the exchange coupling is observed to be the bridging Ni–O–Ni angle.[19] It has been established that for Ni–O–Ni angles close to 90°, the magnetic coupling is ferromagnetic. As the Ni–O–Ni angle increases from 90°, the ferromagnetic coupling decreases and becomes antiferromagnetic at values *ca.* 93.5–99°, depending upon the μ_2 and μ_3 bridging modes of phenoxo oxygen atoms. To design ferromagnetic phenoxo bridged Ni(II) complexes, it is thus imperative to understand what factors make the bridging angle less than this critical value. Most of the dinickel(II) complexes involving a Ni_2O_2-bridging moiety that are reported in the literature, are antiferromagnetically coupled.[20–22] Some ferromagnetic phenoxo-bridged polynuclear Ni(II) complexes are reported but in most cases they contain single phenoxo-bridge along with carboxylate bridge.[20,23] To the best of our knowledge, among the structurally characterized diphenoxo- bridged dinuclear nickel(II) complexes, only two show ferromagnetic coupling.[24] From a careful look into the structures of these two complexes, one can find that in both of them there is a water bridge in addition to the di-phenoxo bridge, which may be an important factor for the lower bridging angle.

In this paper we report the synthesis, crystal structure and magnetic properties of two new di-phenoxo bridged dinickel(II) complexes, $[Ni_2L_2(PhCOO)_2(H_2O)]$ (**1**), $[Ni_2L_2(PhCH_2COO)_2(H_2O)]$ (**2**) using a tridentate Schiff base ligand, 2-[(3-dimethylamino-propylimino)-methyl]-phenol (HL) and the carboxylate ion, benzoate (for **1**) or phenylacetate (for **2**). Both compounds contain an additional bridging water to form a face shared bi-octahedron.

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Face-sharing systems are of special importance in understanding overlapping magnetic orbitals, since both dx^2-y^2 and dz^2 orbitals are involved in bridging.[25] The observed moderately strong ferromagnetic coupling in both complexes has been rationalized with the help of the low bridging angles.

Experimental

Materials

The reagents and solvents used were of commercially available reagent quality, unless otherwise stated.

Synthesis of the Schiff-base ligand 2-[(3-dimethylamino-propylimino)-methyl]-phenol (HL). The Schiff base was prepared by the condensation of salicylaldehyde (1.05 mL, 10 mmol) and *N*,*N*-dimethyl-1,3-propanediamine (1.26 mL, 10 mmol) in methanol (10 mL) under reflux for an hour. The Schiff base ligands were not isolated and the yellow colored methanolic solution was used directly for complex formation.

Synthesis of [$Ni_2L_2(PhCOO)_2(H_2O)$] (1). $Ni(ClO_4)_2\cdot 6H_2O$ (1.828 g, 5 mmol), dissolved in 10 mL of methanol, was added to a methanolic solution (10 mL) of the Schiff base (HL) (5 mmol) with constant stirring. After *ca.* 15 min a methanolic solution of benzoic acid, PhCOOH (0.610 g, 5 mmol) was added with slow stirring followed by addition of triethylamine (0.70 mL, 5 mmol). Slow evaporation of the resulting green solution gave a dark green microcrystalline compound. The green solid was then filtered and washed with diethyl ether and dissolved in CH_3CN. X-ray quality deep-green single crystals of compound **1** were obtained by slow evaporation of the acetonitrile solution. (Yield: 1.57 g; 80%). Anal. Calcd. For $C_{38}H_{46}N_4Ni_2O_7$: C, 57.91; H, 5.88; N, 7.11. Found: C, 57.82; H, 5.69; N, 7.06. IR (KBr pellet, cm^{-1}): 3438(broad) ν(OH), 1634 ν(C=N), 1544 ν_{as}(C=O), and 1466 ν_s(C=O). λ_{max}(CH_3CN), 645 and 1046 nm.

Synthesis of [$Ni_2L_2(PhCH_2COO)_2(H_2O)$] (2). The procedure was the same as that for complex **1**, except that a methanolic solution of phenyl acetic acid, $PhCH_2COOH$ (0.680 g, 5 mmol) was added instead of benzoic acid. Needle-shaped deep-green X-ray quality single crystals of compound **2** were obtained by slow evaporation of the acetonitrile solution. (Yield: 1.53 g; 75%). Anal. Calcd. For $C_{40}H_{50}N_4Ni_2O_7$: C, 58.86; H, 6.17; N, 6.86. Found: C, 58.80; H, 6.09; N, 6.76. IR (KBr pellet, cm^{-1}): 3423(broad) ν(OH), 1632 ν(C=N), 1580 ν_{as}(C=O), and 1458 ν_s(C=O). λ_{max}(CH_3CN), 643 and 1043 nm.

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 using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra (1400–350 nm) in CH_3CN (for **1** and **2**) were recorded in a Hitachi U-3501spectrophotometer. The magnetization data were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer with an external magnetic field of 2000 Oe in the temperature ranges of 1.8–300 K. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables and sample holder calibration.

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

	1	**2**
Formula	$C_{38}H_{46}N_4Ni_2O_7$	$C_{40}H_{50}N_4Ni_2O_7$
M	788.17	816.22
Crystal System	Monoclinic	Triclinic
Space Group	$P21/c$	$P\bar{1}$
a/Å	8.4851(11)	10.351(3)
b/Å	21.865(3)	18.545(5)
c/Å	20.453(3)	22.502(6)
α (°)	90	68.265(7)
β (°)	98.113(2)	87.141(8)
γ (°)	90	83.820(7)
V/Å^3	3756.6(9)	3988.8(19)
Z	4	4
D_c/g cm^{-3}	1.394	1.359
μ/mm^{-1}	1.055	0.997
F(000)	1656	1720
R(int)	0.044	0.042
Total Reflections	25199	43562
Unique reflections	6241	15762
$I > 2\sigma(I)$	4745	11199
R_1, wR_2	0.0352, 0.0920	0.0596, 0.2177,
T/K	293	296

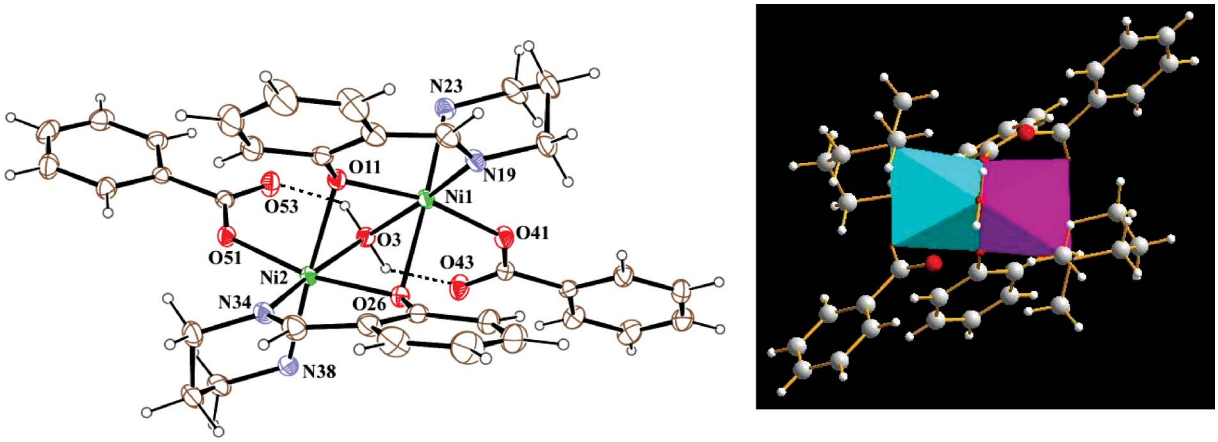
Crystallographic Data Collection and Refinement

Suitable single crystals of each complexes were mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved using Patterson method by using the SHELXS97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. All calculations were carried out using SHELXS 97,[26] SHELXL 97,[27] PLATON 99,[28] ORTEP-32[29] and WinGX systemVer-1.64.[30] Data collection and structure refinement parameters and crystallographic data for the two complexes are given in Table 1.

Results and discussion

Formation of the complexes

The complexes were synthesized simply by allowing the Schiff base to react with $Ni(ClO_4)_2\cdot 6H_2O$ in a methanol solution followed by the addition of benzoic acid (for **1**) or phenyl acetic acid (for **2**) in 1 : 1 : 1 molar ratios. Equimolar amount of triethyl amine was added for deprotonation of the respective carboxylic acid. The crystal field stabilization energy of the Schiff base ligands those are derived from the 1,3-propanediamine derivatives and salicylaldehyde is usually lower due to the longer M–N bond distances compared to their ethylenediamine analogue[31] and consequently hexa-coordinated Ni(II) is stabilized.[20,32] The mono-negative tridentate Schiff base ligand along with a benzoate or phenylacetate anion balance the charge of the complex species but the metal ion remains coordinately unsaturated. In such a situation, the phenoxo oxygen and or the carboxylate group can



(a)

(b)

Fig. 1 (**a**) Perspective view of the complex **1** (25% thermal probability ellipsoids). Methyl groups of amine nitrogen atoms (N(23) and N(38)) are omitted for clarity. The intramolecular hydrogen bonds are shown as dashed lines. (**b**) The face sharing bi-octahedron structure of compound **1**.

exploit their well known bridging properties to complete the hexacoordination in Ni(II) to result in polynuclear complexes. The solvent molecules have also been found to be coordinated in some cases.[33] In the present complexes, a solvent water molecule bridges the two Ni(II) along with phenoxo oxygen while carboxylate ion remains as monodentate. A strong H-bond between the uncoordinated oxygen atom of the carboxylate and the bridged water molecule may have important role in stabilizing the structures. Therefore, it is very difficult to predict the structure of such self-assembled species as various other parameters such as the steric and electronic requirements of the Schiff base ligand, different coordination modes of the anion, weak non-covalent forces etc play important role in stabilization of the resulting structure in the solid state.

IR and UV-VIS spectra of complexes. In the IR spectra of complexes **1** and **2**, a strong and sharp band due to azomethine ν(C═N) appears at 1634 cm^{-1}and 1632 cm^{-1}. The appearance of a broad band near 3400 cm^{-1} indicates the presence of water molecule in both of them. The IR spectral bands in the 1300–1650 cm^{-1} region are difficult to assign due to the appearance of several absorption bands both from the Schiff base and the carboxylate ligands. Nevertheless, by comparing the IR spectra of the Ni(II) complexes of the same ligand but with other anions (azide and halides), the strong bands at 1544 and 1580 cm^{-1} are likely to be due to the antisymmetric stretching mode of the carboxylate group, whereas the bands at 1460 and 1458 cm^{-1} may be attributed to the symmetric stretching modes of the carboxylate ligands in complexes **1** and **2** respectively. The absorption bands in the electronic spectra, taken in acetonitrile solution are very similar for the two complexes. Both of them exhibit a distinct band at 645 and 643 nm for **1** and **2** respectively which can be assigned to the spin-allowed d-d transition $^3T_{1g}(F) \leftarrow {}^3A_{2g}$. Another weaker broad band which is centered at 1046 and 1043 nm for **1** and **2** respectively and is well-separated from the first band is assignable to the transition $^3T_{2g} \leftarrow {}^3A_{2g}$. These values are in agreement with the literature values for octahedral Ni(II) compounds.

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

Ni(1)–O(11)	2.011(2)	Ni(2)–O(11)	2.163(2)
Ni(1)–O(26)	2.175(2)	Ni(2)–O(26)	2.017(2)
Ni(1)–O(3)	2.096(2)	Ni(2)–O(3)	2.108(2)
Ni(1)–O(41)	2.033(2)	Ni(2)–O(51)	2.059(2)
Ni(1)–N(19)	2.003(2)	Ni(2)–N(34)	1.998(3)
Ni(1)–N(23)	2.161(3)	Ni(2)–N(38)	2.146(3)
O(11)–Ni(1)–N(19)	91.48(9)	O(26)–Ni(2)–N(34)	91.52(9)
O(11)–Ni(1)–N(23)	100.61(8)	O(26)–Ni(2)–N(38)	99.51(8)
O(11)–Ni(1)–O(41)	167.51(7)	O(26)–Ni(2)–O(51)	167.76(7)
O(41)–Ni(1)–N(23)	89.83(8)	O(51)–Ni(2)–N(38)	90.64(8)
O(26)–Ni(1)–N(19)	99.53(9)	O(11)–Ni(2)–N(34)	97.99(9)
O(26)–Ni(1)–O(41)	90.01(7)	O(11)–Ni(2)–O(51)	90.10(7)
O(26)–Ni(1)–N(23)	174.74(8)	O(11)–Ni(2)–N(38)	174.38(9)
O(3)–Ni(1)–O(11)	80.21(7)	O(3)–Ni(2)–O(11)	76.58(7)
O(3)–Ni(1)–O(41)	91.60(7)	O(3)–Ni(2)–O(51)	92.22(7)
Ni(1)–(O3)–Ni(2)	85.83(7)	O(3)–Ni(2)–O(26)	79.71(7)
O(3)–Ni(1)–O(26)	76.48(7)	O(51)–Ni(2)–N(34)	95.76(9)
O(41)–Ni(1)–N(19)	96.17(9)	N(34)–Ni(2)–N(38)	87.48(10)
N(19)–Ni(1)–N(23)	85.71(10)	O(11)–Ni(2)–O(26)	79.14(7)
O(11)–Ni(1)–O(26)	78.96(7)	Ni(2)– O(11)–C(12)	123.54(17)
Ni(1)– O(11)–C(12)	127.96(18)	O(3)– Ni(2)–N(34)	170.38(9)
Ni(1)– O(11)–Ni(2)	86.53(7)	O(3)– Ni(2)–N(38)	97.82(9)
Ni(1)– O(26)–Ni(2)	86.03(7)		
O(3)– Ni(1)–N(19)	171.29(8)		
O(3)– Ni(1)–N(23)	98.27(8)		

Description of structure of [Ni$_2$L$_2$(PhCOO)$_2$(H$_2$O)] (1). The structure of **1** is shown in Fig. 1a together with the atomic numbering scheme. Selected bond lengths and angles are summarized in Table 2. The crystal structure of **1** consists of a discrete dinuclear unit of formula [Ni$_2$L$_2$(PhCOO)$_2$(H$_2$O)]. The dinuclear unit is formed by two independent nickel atoms, labeled Ni(1) and Ni(2), bridged by one water molecule O(3) and two μ_2-phenoxo oxygen atoms O(11) and O(26). Each of the two metal centers, Ni(1) and Ni(2) present distorted octahedral environment, being coordinated to the deprotonated chelating Schiff base ligand through the secondary amine nitrogen atoms N(23), N(38), the imine nitrogen atoms N(19), N(34) and the phenoxo oxygen atoms O(11) and O(26) respectively in facial configuration with usual bond distances (Table 2).[20,24a,34] The carboxylate oxygen atoms O(41) and O(51) of the terminally coordinated monodentate benzoate ions, the oxygen atom O(3) of the water molecule and the bridging phenoxo atoms O(26) and O(11) complete the hexacoordination of Ni(1) and Ni(2) respectively. Thus two nickel atoms are linked through a triple oxygen bridge to form a face shared bi-octahedron (Fig. 1b), leading to a Ni–Ni distance of 2.862 Å, which is slightly shorter to those found in other similar dinuclear nickel(II) complexes having a diphenoxo bridge only.[19,21,35,36] The two phenoxo bridging angles, Ni(1)–O(11)–Ni(2) and Ni(1)–O(26)–Ni(2) are 86.53(7)° and 86.03(7)° respectively, and the water bridge angle, Ni(1)–O(3)–Ni(2) is 85.83(7)°. Each bridging phenoxo oxygen atom is asymmetrically bound, with one Ni–O bond slightly longer [Ni(1)–O(26) 2.175(2) Å; Ni(2)–O(11) 2.163(2) Å] than the other [Ni(1)–O(11) 2.011(2) Å; Ni(2)–O(26) 2.017(2) Å]. The bridging water molecule is also asymmetrically bonded between the two metal atoms [Ni(1)–O(3) 2.096(2) Å; Ni(2)–O(3) 2.108(2) Å]. These distances are comparable to those found in some aqua-bridged dinuclear Ni(II) complexes,[37] in the range 2.09–2.25 Å reported for a few other known examples of water bridges in Ni(II) structures.[24,38] The sets of four donor atoms O(11), N(19), O(41), 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 −0.060(2), 0.053(3), −0.051(2), 0.058(2) Å, respectively. Ni(1) atom is displaced 0.114(1) Å from the same plane in the direction of N(23) atom. The basal bond lengths around the Ni(1) atom are in the range of 2.003(2)–2.096(2) Å. The apical bond lengths are Ni(1)–O(26) 2.175(2) Å and Ni(1)–N(23) 2.161(3) Å, the bond angle O(26)–Ni(1)–N(23) being 174.74(8)°. Similarly in the coordination sphere of Ni(2) the basal plane consists of O(3), O(26), O(51) and N(34) with bond lengths in the range of 1.998(3)–2.108(2) Å. The apical bond lengths are Ni(2)–O(11) 2.163(2) Å and Ni(2)–N(38) 2.146(3) Å, the bond angle O(11)–Ni(2)–N(38) being 174.38(9)°. Deviations of the coordinating atoms O(3), O(26), O(51), N(34) from the least-square mean plane through them are −0.045(2), 0.046(2), 0.039(2), −0.040(3) Å, respectively, and that of Ni(2) atom from the same plane is −0.126(1) Å in the direction of N(38) atom. The two hydrogen atoms H(3A) and H(3B) of the bridging water molecule participate in strong intramolecular hydrogen bonding to the oxygen atoms O(43) and O(53) respectively of the terminally coordinated benzoate anions within the dimeric unit with $D\cdots A$ bond distances of 2.574(3) Å and 2.554(3) Å. (Table 4)

Table 3 Selected bond lengths (Å) and bond angles (°) for complex **2**

Bond	A	B
Ni(1)–O(11)	2.014(3)	2.024(3)
Ni(1)–O(26)	2.159(4)	2.156(3)
Ni(1)–O(3)	2.096(3)	2.107(3)
Ni(1)–O(41)	2.018(4)	2.052(4)
Ni(1)–N(19)	2.004(4)	2.002(4)
Ni(1)–N(23)	2.148(6)	2.132(5)
Ni(2)–O(11)	2.203(3)	2.211(3)
Ni(2)–O(26)	2.013(3)	2.006(3)
Ni(2)–O(3)	2.084(4)	2.069(4)
Ni(2)–O(51)	2.010(4)	2.015(3)
Ni(2)–N(34)	2.014(4)	1.999(4)
Ni(2)–N(38)	2.151(4)	2.163(4)
O(11)–Ni(1)–N(19)	90.83(15)	86.59(14)
O(11)–Ni(1)–N(23)	102.89(16)	102.46(16)
O(11)–Ni(1)–O(41)	166.29(13)	165.09(15)
O(41)–Ni(1)–N(23)	88.30(17)	90.67(17)
O(26)–Ni(1)–N(19)	96.87(15)	98.59(15)
O(26)–Ni(1)–O(41)	88.68(14)	86.85(14)
O(26)–Ni(1)–N(23)	176.02(17)	173.86(16)
O(3)–Ni(1)–O(11)	79.20(13)	78.69(13)
O(3)–Ni(1)–O(41)	91.11(13)	92.61(14)
Ni(1)–(O3)–Ni(2)	86.59(14)	87.04(13)
O(3)–Ni(1)–O(26)	76.94(13)	76.37(13)
O(41)–Ni(1)–N(19)	97.89(15)	96.36(16)
N(19)–Ni(1)–N(23)	86.12(18)	87.26(17)
O(11)–Ni(1)–O(26)	79.75(13)	79.38(13)
Ni(1)–O(11)–C(12)	127.9(3)	126.8(3)
Ni(1)–O(11)–Ni(2)	85.51(12)	85.42(12)
O(3)–Ni(1)–N(19)	169.01(16)	169.48(15)
O(3)–Ni(1)–N(23)	100.52(17)	98.15(15)
Ni(1)–O(26)–Ni(2)	86.73(13)	87.32(13)
O(26)–Ni(2)–N(34)	90.28(15)	90.46(15)
O(26)–Ni(2)–N(38)	101.23(15)	101.55(14)
O(26)–Ni(2)–O(51)	167.51(16)	167.57(15)
O(51)–Ni(2)–N(38)	89.43(17)	89.15(16)
O(11)–Ni(2)–N(34)	100.25(16)	101.82(15)
O(11)–Ni(2)–O(51)	89.87(15)	90.03(14)
O(11)–Ni(2)–N(38)	172.41(19)	171.56(18)
O(3)–Ni(2)–O(11)	75.30(13)	75.42(13)
O(3)–Ni(2)–O(51)	91.83(15)	92.06(14)
O(3)–Ni(2)–O(26)	80.49(14)	80.61(14)
O(51)–Ni(2)–N(34)	96.77(16)	96.53(16)
N(34)–Ni(2)–N(38)	87.3(2)	86.6(2)
O(11)–Ni(2)–O(26)	78.71(12)	78.46(12)
Ni(2)–O(11)–C(12)	118.1(3)	119.8(3)
O(3)–Ni(2)–N(34)	170.34(15)	171.00(15)
O(3)–Ni(2)–N(38)	97.17(18)	96.22(18)

Description of structure of [$Ni_2L_2(PhCH_2COO)_2(H_2O)$] (2). The molecular structure of complex **2** is very similar to that of complex **1**. The only difference between the two structures is that the terminally coordinated carboxylate group is phenyl acetate in **2** in stead of benzoate in complex **1**. The asymmetric unit of **2** contains two independent Ni(II) dimers denoted as **A** and **B**. The structures of the two dimers are very similar to each other, except for a slight difference in the bond parameters, so we limit the description to only one dimer **2B** which is shown in Fig. 2 together with the atomic numbering scheme. The structural description of **2A** is given in Supporting Information.† Selected bond lengths and angles both are summarized in Table 3. Like complex **1**, the dinuclear structure of complex **2** consists of a face sharing bi-octahedron having triple oxo bridge. All the donor atoms in the coordination spheres of the Ni centers are bonded in similar fashion as that of **1**. The two Ni atoms are separated by 2.876 Å with two phenoxo bridging angles, Ni(1B)–O(11B)–Ni(2B) of 85.42(12)° and Ni(1B)–O(26B)–Ni(2B) of 87.32(13)° and the water bridge angle Ni(1B)–O(3B)–Ni(2B) of 87.04(13)°. The Ni–Ni distance and the bridging angles slightly differ from those in **1**. Moreover we note that in **1** the phenoxo oxygen atoms and the water molecule bridge the two Ni centers asymmetrically which is maintained in complex **2** also [Ni(1B)–O(26B) 2.156(3) Å; Ni(2B)–O(11B) 2.211(3) Å, Ni(1B)–O(11B) 2.024(3) Å; Ni(2B)–O(26B) 2.006(3) Å] and [Ni(1B)–O(3B) 2.107(3) Å; Ni(2B)–O(3B) 2.069(4) Å]. It is apparent that the basal planes around the metal centers consist of three oxygen atoms and one imine nitrogen atom as that of **1**. The deviations of the four basal donor atoms O(3B), O(11B), O(41B), N(19B) of Ni(1B) from their mean planes are 0.073(3), −0.076(3), −0.063(4), 0.066(4) Å. Similarly the deviations of the four basal donor atoms O(3B), O(26B), O(51B), N(34B) of Ni(2B) from their mean planes are 0.075(3), −0.077(3), −0.066(4), 0.068(4) Å. The two metal atoms Ni(1B) and Ni(2B) deviate from the mean plane by 0.151(1) Å and 0.106(1) Å in the direction of N(23B) and N(38B) atoms. The Ni–O and Ni–N distances in the basal planes are in the ranges 2.002(4) Å-2.024(3) Å and 1.999(4) Å-2.069(4) Å respectively. The apical bond lengths are

Table 4 Hydrogen bonding distances (Å) and angles (°) for the complex **1** and **2**

Compound	D–H···A	D–H	D···A	A···H	∠D–H···A
1	O3–H3A···O43	0.97	2.574(3)	1.76	139
	O3–H3B···O53	0.97	2.554(3)	1.74	139
2B	O3B–H3B1···O43B	0.97	2.520(6)	1.69	141
	O3B–H3B2···O53B	0.97	2.582(5)	1.78	138
2A	O3A–H3A1···O53A	0.97	2.526(5)	1.72	139
	O3A–H3A2···O43A	0.97	2.573(6)	1.73	142

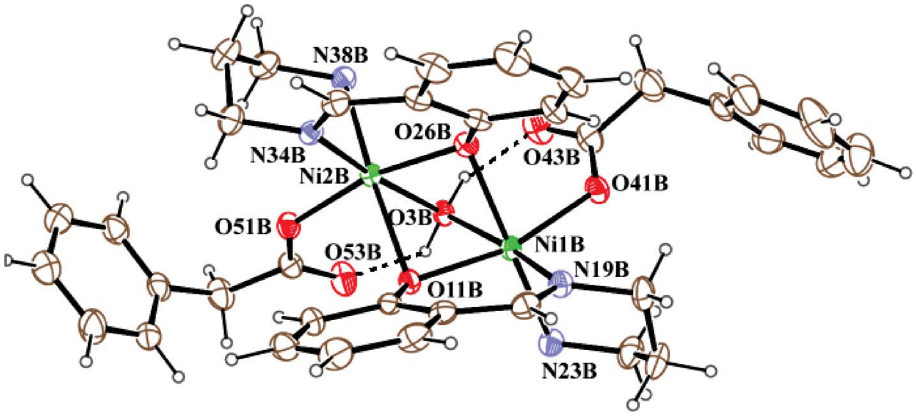


Fig. 2 Perspective view of the complex **2B** (25% thermal probability ellipsoids). Methyl groups of amine nitrogen atoms (N(23B) and N(38B)) are omitted for clarity. The intramolecular hydrogen bonds are shown as dashed lines.

Ni(1B)–O(26B) 2.156(3) Å and Ni(1B)–N(23B) 2.132(5) Å and Ni(2B)–O(11B) 2.211(3) Å and Ni(2B)–N(38B) 2.163(4) Å. The bond angles are O(26B)–Ni(1B)–N(23B) 173.86(16)° and O(11B)–Ni(2B)–N(38B) 171.56(18)°. All these bond distances and angles show only minor variations from those in **1**. In **2** also a strong intradimer H-bonding is observed between the non-coordinating oxygen atoms of phenylacetate ligand and bridging water with D···A bond distances of 2.520(6) Å and 2.582(5) Å which are very close to those of complex **1**. (Table 4)

Magnetic properties

The variable-temperature magnetic properties of **1** and **2** in the forms of $\chi_M T$ *vs.* T plots are illustrated in Fig. 3 and Fig. 4 respectively (χ_M is the molar susceptibility for two Ni(II) ions). As can be seen, the two compounds show room temperature $\chi_M T$ values of ca, 2.514 and 2.560 cm^{-1}mol^{-1}K which are slightly higher than the expected value for two non-interacting Ni(II) S = 1 ions (the expected spin only value is 2.0 cm^{-1}mol^{-1}K). When the temperature is lowered compounds **1** and **2** show very similar behavior: $\chi_M T$ increases gradually to reach a maximum value of 3.431 and 3.410 cm^{-1}mol^{-1}K at 9 K and 16 K respectively followed by a pronounced drop to reach values of 2.952 and 2.527 cm^{-1}mol^{-1}K respectively at 1.8 K.

This behavior is typical of a system exhibiting dominant intramolecular ferromagnetic exchange coupling and at lower temperature region; the drop of $\chi_M T$ is due to ZFS of ground state (S = 2) or due to possible interactions between the dimers. Because the evaluation of all the possible contributions at low temperatures in a simultaneous way is difficult and little reliable, we have proceeded in the following ways for both complexes. In the first step, we have fitted the magnetic properties of compounds **1** and **2** to a simple $S = 1$ dimer model (the Hamiltonian is always written as $H = -JS_1S_2$)

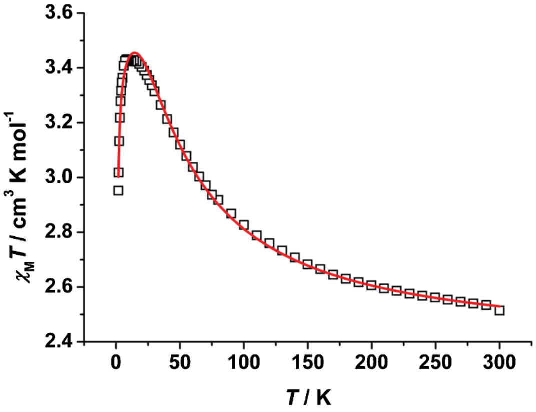


Fig. 3 Plot of $\chi_M T$ *vs.* T for complex **1**. The solid line is generated from the best-fit magnetic parameters.

$$\chi = \frac{2Ng^2\beta^2}{kT} \times \frac{e^{2J/kT} + 5e^{6J/kT}}{1 + 3e^{2J/kT} + 5e^{6J/kT}} \qquad (1)$$

In the second step, we have used the molecular field approximation expression to reproduce the interdimer antiferromagnetic coupling.[20,39]

$$\chi_M = \frac{\chi}{1 - (2zj'/Ng^2\beta^2)\chi} \qquad (2)$$

where j' is the interdimer exchange interaction and χ_{dim} is the expression for an S = 1 dimer (eqn (1)). For both compounds,

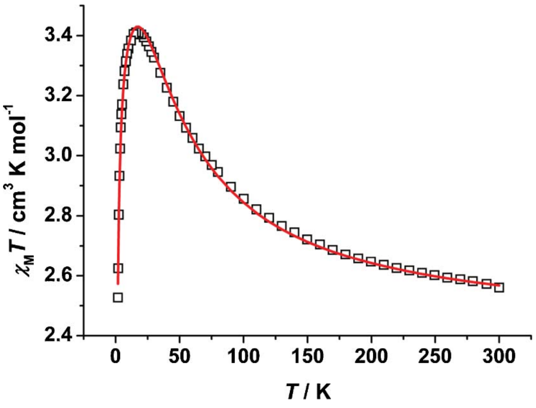


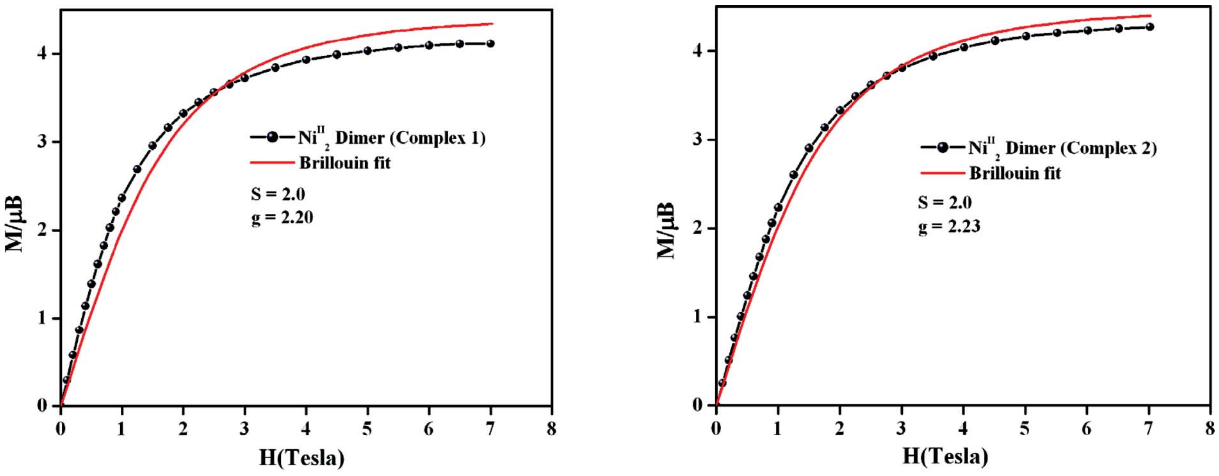
Fig. 4 Plot of $\chi_M T$ *vs.* T for complex **2**. The solid line is generated from the best-fit magnetic parameters.

this model reproduces satisfactorily the magnetic data in the whole temperature range with the following parameters J = 11.1(2) cm^{-1}, g = 2.176(3), zj' = –0.057(2) cm^{-1} with R = 4.25 × 10^{-5} {R is the agreement factor defined as: $R = \Sigma[(\chi_M T)_{\text{exp.}} - (\chi_M T)_{\text{calcd.}}]^2/\Sigma(\chi_M T)_{\text{exp.}}{}^2$} for complex **1** and J = 10.9(2) cm^{-1}, g = 2.195(2), zj' = –0.126(2) cm^{-1} with R = 2.52 × 10^{-5} for complex **2**.

The inclusion of a ZFS does not improve significantly the fit because the interdimer magnetic coupling and the D parameter are very closely related and their independent contributions cannot be easily accounted for. This result indicates that, besides the intradimer coupling, the ZFS and the interdimer coupling are present but their correct evaluation is not possible given their close relation as was also found in various Ni(II) complexes.[20,40] The fit of the isothermal magnetization measurements at 1.8 K (Fig. 5) to a S = 2 Brillouin function yielded g = 2.20 (for **1**) and 2.23 (for **2**). The results confirm a ferromagnetic coupling within the dimers with S = 2 ground state.

Dinuclear nickel(II) complexes in which one or two phenoxo groups act as bridges are generally found to be antiferromagnetic.[19,22,41,42] To the best of our knowledge, ferromagnetic behavior has been found only in seven μ_2-phenoxo bridged complexes[24,38,43,44] which have also been structurally characterized. Among them in two complexes, the two Ni(II) ions are linked by a carboxylate (acetate or benzoate) and a phenoxo bridge. The ferromagnetic behavior of these compounds has been tentatively ascribed to the 5-fold coordination of one of the Ni(II) ions. However, the authors' caution "Since it is hard to prove the conservation of the dinuclear structure as resulting from X-ray structure analysis under the experimental conditions of the magnetic measurements, we abstain from further explanations" should be noted as ferromagnetic coupling through such wide Ni–O–Ni angles that has been found (128.2 and 129.1°) in these compounds is unsupported by any other example. The bridging mode between the two Ni(II) of three other ferromagnetic compounds (two of which are dinuclear and the third one is hexanuclear) is the same as the present two complexes, *i.e.* a triple bridge is formed by the oxygen atoms of two phenoxo groups and a molecule of water. The rest two compounds are heterometallic cubic clusters of $[Ni_3(OH)(L)_3]^-$ and Na^+ or K^+ (L = 2-[(2-hydroxy-3-methoxy-benzylidene)-amino]-ethanesulfonate).[45] Selected parameters relevant to the magnetic properties of both μ_2 phenoxo and water bridge complexes have been shown in Table 5. The coupling in the complexes may be interpreted in terms of two different bridges, the phenoxo and the H_2O (Fig. 6).

In the present two complexes, both type of bridging angles (phenoxo and water) are comparable but in two of the other reported complexes, the phenoxo bridging angle(s) is considerably greater than that of water bridge. For di-[46] and tetranuclear[47] nickel(II) complexes magneto-structural correlations have been put forward. These correlations indicate Ni–O–Ni border line angles of about 93.5 and 99.08 for the corresponding μ_2-O and μ_3-O bridged di- and tetranuclear systems, respectively below which a ferromagnetic interaction is observed. In all five compounds (Table 5), all three bridging angles are well below the critical value of 93.5° and hence ferromagnetic exchange through the accidental orthogonality of the orbitals with the unpaired electrons (magnetic orbitals) is expected. In this context, the role of the additional water bridge



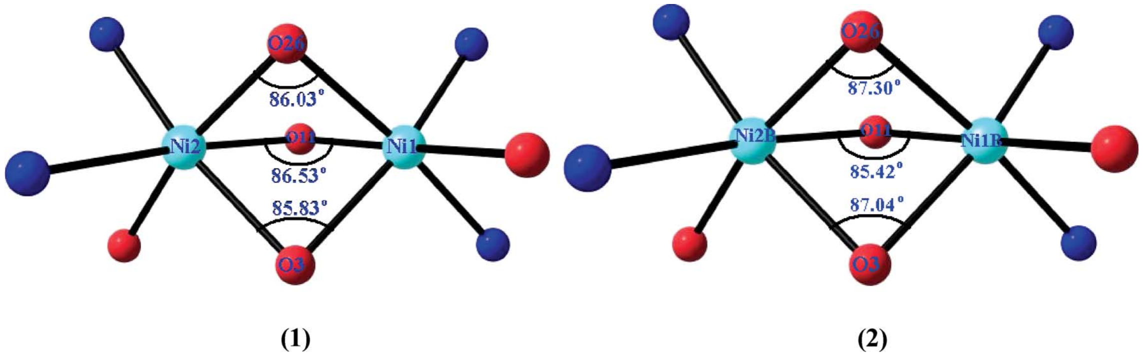
(a) (b)

Fig. 5 Isothermal magnetizations for compounds **1** and **2** at 1.8 K.

Table 5 Magnetic and structural parameters of compounds **1** and **2** and of other known Ni(II) complexes presenting both μ_2 phenoxo and water bridge

Complex	Magnetic coupling	*J* value in cm^{-1}	Ni–$\mu_2$phenoxo–Ni angles and distances	Ni–μH_2O–Ni angles and distances	Ni···Ni distances
$[Ni_2(H_2L^1)_2(H_2O)]\cdot H_2O$	Ferromagnetic	9.9	91.7(2)°, 91.2(3)° 1.983(5) Å, 2.088(6) Å, 2.076(5) Å, 1.987(6) Å	81.0(2)° 2.253(7) Å, 2.232(7) Å	2.913
$[Ni_2(L^2)_2(H_2O)(NCS)_2]\cdot 3H_2O$	Ferromagnetic	3.1	91.5(4)°, 91.5(4)° 1.990(10) Å, 2.131(9) Å	82.2(4)° 2.240(11) Å	2.953
$[Ni_6(HL^3)_4$-$H_2O(C_5H_5N)_4]$ _ 2DMF	Ferromagnetic	5.14	87.25(18)°, 2.032(6) Å, 2.266(5) Å	86.7(2) ° 2.164(4) Å	2.970
$[Ni_2(L^4)_2(PhCOO)_2(H_2O)]$	Ferromagnetic	11.1	86.53(7)°,86.03(7) ° 2.011(2) Å, 2.175(2) Å, 2.163(2) Å, 2.017(2) Å	85.83(7) ° 2.096(2) Å, 2.108(2) Å	2.862
$[Ni_2(L^4)_2(PhCH_2COO)_2(H_2O)]$	Ferromagnetic	10.9	85.42(12)°, 87.32(13)° 2.024(3) Å, 2.156(3) Å, 2.211(3) Å, 2.006(3) Å	87.04(13)° 2.107(3) Å, 2.069(4) Å	2.876

H_2L^1 = *N*,*N*-bis(3,4-dimethyl-2-hydroxybenzyl)-*N*′,*N*′-dimethylethylenediamine, L^2 = *N*-(3-aminopropyl)salicylaldimine, HL^3 = N-(3-t-butylbenzoyl)-5-bromosalicylhydrazide, L^4 = 2-[(3-dimethylamino-propylimino)-methyl]-phenol.



(1) **(2)**

Fig. 6 Ni(II) environments in compounds **1** and **2** with the two different bridging (phenoxo and water) angles (deg).

in making the exchange coupling ferromagnetic deserves special mention. Comparison of the structural parameters of these triple bridged compounds with that of the solely diphenoxo bridged species reveals that the Ni–Ni distance decreases due to the additional water bridge. As a consequence the average Ni–O–Ni bridging angle becomes lower and in general shorter is the Ni–Ni distances, lower is the average Ni–O–Ni angles. However, Table 5 shows that there are deviations from this linear relationship because of the variation in the bond distances. It is obvious that longer bond distances lower the bridging angle further and this explains the difference in bridging angles between the two types of bridges in the first two compounds of Table 5. In general, it may be assumed that any additional bridge other than water should also bring down the Ni–O(phenoxo)–Ni angle to a value lower than the critical one in diphenoxo bridged complexes to make the exchange coupling ferromagnetic. The presence of overall ferromagnetic interaction in a recently reported trinuclear isosceles Ni_3 core, bridged by μ_3-alcoholate O3 oxygen atoms[44] is consistent with this proposition.

Conclusions

The NNO donor Schiff base ligand, derived from the condensation of *N*,*N*-dimethyl-1,3-propanediamine and salicylaldehyde has been used to synthesize two neutral dinuclear complexes with Ni(II) having benzoate or phenylacetate ion as coligand. In both structures, in addition to the di-phenoxo bridges from the Schiff base ligand, a water molecule acts as a bridge between the two Ni(II) ions. An unusual feature of the structures is that the carboxylate ions, which are well known for their various bridging modes, remain monodentate in both complexes whereas the water molecule acts as a bridging ligand. The strong H-bond between the bridging water and the uncoordinated oxygen atom of the carboxylate group seems to stabilize the resulted structure. The majority of the reported di-phenoxo-bridged dinickel complexes enforce a planarity geometry about the bridging oxygen donor and result in strong antiferromagnetic interactions ($-20 > J > -100$ cm^{-1}) as the bridging angle is higher than the critical value. On the contrary, the face sharing octahedron created by triple oxo-bridges (two phenoxo and one water) between the Ni(II) ions like the present complexes are very rare. The magnetic study of these complexes reveals that such bridges favor moderate ferromagnetic coupling between the Ni(II) ions as the additional water bridge brings the Ni(II) ion closer in the dinuclear entity, causing the average bridging angle to be lower than the critical value of 93.5°.

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