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Novel nickel(II) complexes with diazamesocyclic ligands functionalized by additional phenol donor pendant(s): synthesis, characterization, crystal structures and magnetic properties

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The formation of two unique μ-phenoxo-bridged nickel(II) complexes with 1,5-diazacyclooctane (DACO) ligands functionalized by additional phenol donor pendants has been achieved and the complexes have been characterized by IR, elemental analyses, conductivity, thermal analysis, and UV-Vis techniques. Single-crystal X-ray diffraction analyses reveal that **HL^1** forms a phenoxo-bridged binuclear complex (in the presence of N_3^- anions) $[NiL^1(N_3)]_2\cdot 0.5H_2O$ **1**, **H$_2$L^2** a phenoxo-bridged edge-sharing linear trinuclear complex $[Ni_3(L^2)_2(C_2H_5OH)_2Cl_2]$ **2**, where **HL^1** = 1-(2-hydroxybenzyl)-1,5-diazacyclooctane and **H$_2$L^2** = 1,5-bis(2-hydroxybenzyl)-1,5-diazacyclooctane. In **1** the two Ni^{II} are in five-coordinated distorted square-pyramidal environments with a intramolecular Ni···Ni distance of 3.1232(13) Å. However in **2** the two terminal Ni^{II} are in nearly ideal square-pyramidal coordination environments and the central Ni^{II} takes an octahedral configuration by axial coordination of two ethanol molecules, the adjacent intramolecular Ni···Ni distance being 3.132(2) Å. Such a trinuclear nickel(II) complex with square-pyramidal/octahedral/square-pyramidal coordination is unprecedented. These results also indicate that the coordination chemistry of the nickel(II) complexes with DACO ligands can be controlled by altering the pendant donors. Variable-temperature magnetic data show that both complexes display modest intramolecular antiferromagnetic coupling between adjacent nickel(II) centers, which is unusual for such linear trinuclear nickel(II) complexes. The magneto-structural correlation has been investigated for both complexes, and a rough correlation between the exchange coupling and the Ni–O–Ni angle of phenoxo-bridged binuclear nickel(II) complexes obtained and discussed.

Introduction

1,5-Diazacyclooctane (DACO) is one of the most typical examples of the diazamesocycles, which offers several attractive features as a framework for ligand developments with exceptionally strong ligand fields,[1] unique conformational requirements[2] and the potential ability for further functionalization.[3] Since DACO has only two nitrogen donors, two or more of this ligand are required to complete the coordination geometry for a metal center, such as Ni^{II} or Cu^{II}.[1,4,5] However, the incorporation of one or two functional donor groups onto the nitrogen atom(s) of DACO could lead to a rational design of such ligands with well defined structure as well as tailored functions. DACO and its derivatives show an interesting "boat/chair" configuration when they form transition metal complexes. A hydrogen atom of the central methylene on the backbone of the DACO ring effectively blocks the sixth coordination site of the metal center to form complexes with five-coordination.[6,7] Furthermore, the flap-over ring could provide a sterically protected metal coordination site capable of supporting interactions of small molecules, such as H_2 or CO_2, or a highly reactive metal hydride functionality, especially for its nickel(II) complexes.[8]

The interesting work by Darensbourg and co-workers[3,9] and our previous successful results[10] have shown that the coordinating ability of DACO may be controlled and enriched through attaching donor pendants to it. As a continuation of our previous work, we report herein two novel nickel(II) complexes of DACO ligands functionalized by additional phenol donor(s) (see Chart 1). These tri- and tetra-dentate ligands can form stable phenoxo-bridged binuclear or trinuclear complexes with Ni^{II}. The influence of the pendant groups on the configurations of the complexes has been studied in detail based on X-ray crystal structural analysis. The magnetic properties of both complexes have been investigated by variable-temperature magnetic susceptibility measurements in the solid state, and unexpected magnetic coupling has been found to exist in the trinuclear nickel(II) complex. The magneto-structural correlation has been further analysed.

Experimental

Materials and general methods

The starting materials, DACO·2HBr[11] and 2-bromomethylphenyl acetate,[12] were prepared according to the literature methods. All other reagents for syntheses and analyses were of analytical grade and used without further purification. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer and electronic absorption spectra on a Hitachi UV-3010 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Conductivities of the complexes were measured at room temperature using a DDS 11A conductometer. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer. The variable temperature magnetic susceptibilities were measured on a SQUID magnet-

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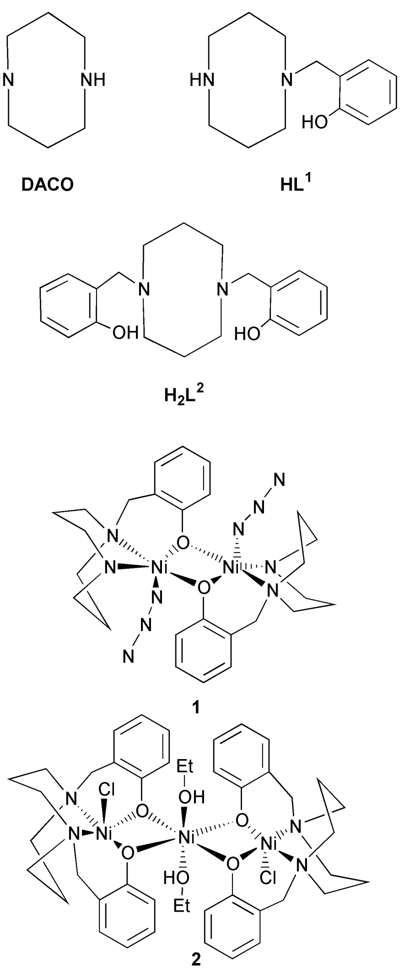

Chart 1

ometer at 5.0–300 K. The susceptibilities were corrected for diamagnetism with Pascal's constants for all the constituent atoms, and magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$.

Syntheses

The ligands, 1-(2-hydroxybenzyl)-1,5-diazacyclooctane (**HL^1**) and 1,5-bis(2-hydroxybenzyl)-1,5-diazacyclooctane (**H_2L^2**), were synthesized according to our previous work.[10e]

$[NiL^1(N_3)]_2\cdot 0.5H_2O$ 1. Complex **1** was synthesized by mixing a 1 : 1 molar ratio of $Ni(ClO_4)_2\cdot 6H_2O$ (72 mg, 0.2 mmol) and **HL^1** (42 mg, 0.2 mmol) in acetone–water (20 mL : 10 mL), followed by addition of nearly one equivalent of NaN_3 (14 mg, 0.2 mmol). The reaction mixture was filtered and green single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent. Yield 26 mg, 50% (Found: C, 47.92; H, 6.24; N, 21.65%. Calc. for $C_{26}H_{39}N_{10}Ni_2O_{2.5}$: C, 48.09; H, 6.05; N, 21.56%). IR (KBr pellet, cm^{-1}): 2930w, 2047vs, 1593s, 1481vs, 1454s, 1268m, 1120s, 988w, 756s and 629w. Λ_M (DMF): 8.9 Ω^{-1} cm^2 mol^{-1}. λ_{max}/nm (ε/M^{-1} cm^{-1}) (DMF) 690 (100), 512 (250), 276 (4990) and 260 (5000).

$[Ni_3(L^2)_2(C_2H_5OH)_2Cl_2]$ 2. Complex **2** was prepared by mixing a 3 : 2 molar ratio of $NiCl_2\cdot 6H_2O$ (50 mg, 0.3 mmol) and **H_2L^2** (59 mg, 0.2 mmol) in acetone–ethanol (15 mL : 15 mL). The green solution was filtered and left to stand at room temperature. Green single crystals were obtained by slow evaporation of the solvent. Yield 49 mg, 50% (Found: C, 53.18; H, 6.21; N, 5.50%. Calc. for $C_{44}H_{60}Cl_2N_4Ni_3O_6$: C, 53.49; H, 6.12; N, 5.67%). IR (KBr pellet, cm^{-1}): 2970m, 1596s, 1485vs, 1455s, 1338w, 1266vs, 1132s, 1114m, 1094m, 994s and 760s. Λ_M (methanol): 64 Ω^{-1} cm^2 mol^{-1}. λ_{max}/nm (ε/M^{-1} cm^{-1}) (methanol) 546 (340), 366 (1260), 276 (10800), 238 (24700) and 214 (23900).

CAUTION: although we have experienced no problems in handling perchlorate and azide compounds, these should be handled with great caution due to the potential for explosion.

X-Ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements of 11834 (for complex **1**) and 9655 (for **2**) reflections, respectively. The structures were solved by direct methods and semi-empirical absorption corrections were applied. The Ni atoms in each complex were located from *E*-maps, and the other non-hydrogen atoms and the H(3B) atom in **2** in successive Fourier difference syntheses. The final refinement was performed by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were added theoretically (except H(3B)), riding on the concerned atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

CCDC reference number 186/2314.

See http://www.rsc.org/suppdata/dt/b0/b008297j/ for crystallographic files in .cif format.

Results and discussion

Syntheses and general characterizations

Complexes **1** and **2** were synthesized by reaction of the corresponding ligands (**HL^1** and **H_2L^2**) with $Ni(ClO_4)_2\cdot 6H_2O$ (with additional NaN_3) or $NiCl_2\cdot 6H_2O$ salts. Both are neutral due to deprotonation of **HL^1** and **H_2L^2** upon complexation with Ni^{II} and coordination of counter anions (N_3^- or Cl^-). The uncharged nature results in very low solubility in some general solvents including water. The electrical conductance values of the complexes indicate that both behave as non-conductors,[13] implying that they are neutral and stable in solution. Their IR spectra show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600 cm^{-1} region. Complexes **1** and **2** exhibit broad bands centered around 3400 cm^{-1}, which are assignable to the ν_{O-H} stretch of coordinated water or ethanol, and a weak but sharp band at 3277 cm^{-1} for **1** due to the ν_{N-H} stretch of **L^1**. In addition, the ν_{N-N} stretch of N_3^- appears at 2047 cm^{-1} and its bending frequency at 629 cm^{-1} for **1**.

The electronic spectra exhibit two d–d transition bands at 512 and 690 nm for complex **1** and one strong band at 546 nm for **2**. The solution spectra of both complexes in the 200–300 nm range also show $\pi \longrightarrow \pi^*$ ligand transitions. In addition the absorption at 366 nm may be due to a metal to ligand charge transfer (MLCT) band for **2**.

Both complexes **1** and **2** are air stable at room temperature, however decomposition occurred at elevated temperature. Thermal analyses (from room temperature to 800 °C) show that decomposition starts when they are heated to above 241 *vs.* 341 °C and stops at above 505 *vs.* 508 °C, respectively. The TGA data indicate that the total weight losses (1.18% for **1** at 90–129 °C, and 8.70% for **2** at 147–190 °C, respectively) are consistent with losses of one crystal water (for **1**) and two coordinated ethanol molecules (for **2**) (the theoretical weight losses are 1.39% for **1** and 9.32% for **2**, respectively).

Description of the crystal structures

The binuclear complex 1. An ORTEP[14] view of complex **1** including the atomic numbering scheme is given in Fig. 1, and

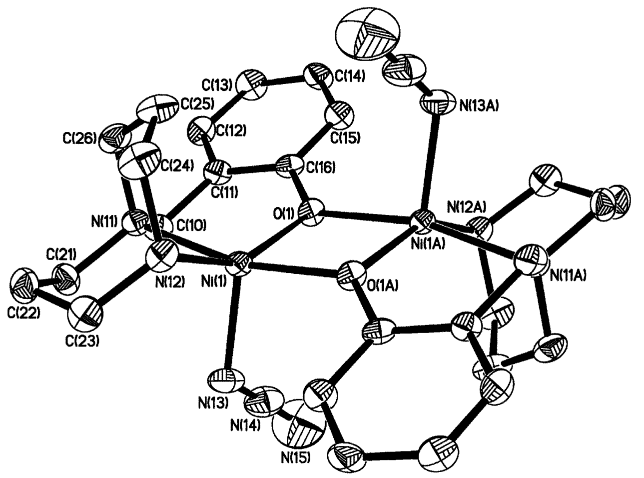

Fig. 1 ORTEP structure of the binuclear unit of complex **1** with 30% thermal ellipsoids.

Table 1 Crystallographic data and structure refinement summary for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{26}H_{39}N_{10}Ni_2O_{2.5}$	$C_{44}H_{60}Cl_2N_4Ni_3O_6$
Formula weight	649.35	987.99
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	13.311(2)	11.0715(16)
b/Å	16.542(3)	14.343(2)
c/Å	13.407(2)	14.691(2)
β/°	98.851(4)	109.052(3)
V/Å^3	2916.8(9)	2205.2(5)
T/K	293(2)	293(2)
Z	4	2
μ/cm^{-1}	13.84	14.41
R	0.0567	0.0671
R_w	0.0133	0.1337

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

Ni(1)–O(1)	2.004(3)	Ni(1)–O(1)#1	2.028(3)
Ni(1)–N(11)	2.105(4)	Ni(1)–N(12)	2.065(4)
Ni(1)–N(13)	2.017(5)	Ni···Ni	3.1232(13)
Ni(1)–O(1)–Ni(1)#1	101.57(13)	O(1)–Ni(1)–O(1)#1	78.43(13)
N(13)–Ni(1)–N(12)	104.2(2)	O(1)–Ni(1)–N(11)	93.07(14)
O(1)#1–Ni(1)–N(11)	165.78(15)	N(12)–Ni(1)–N(11)	84.58(17)

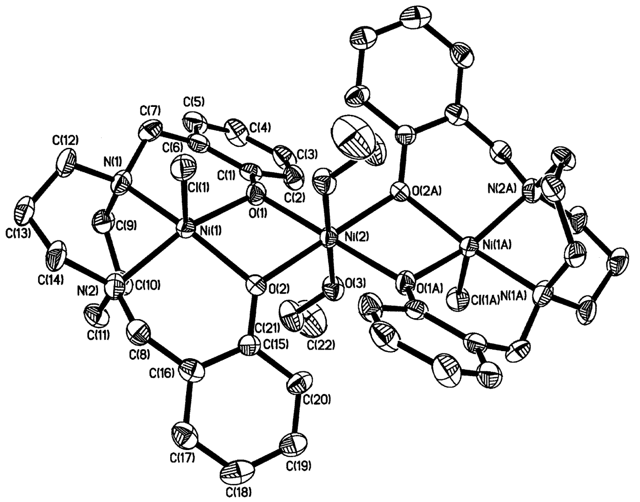

Fig. 2 ORTEP structure of the trinuclear complex **2** with 30% thermal ellipsoids.

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

Ni(1)–O(1)	2.026(5)	Ni(1)–O(2)	2.016(5)
Ni(1)–N(1)	2.108(6)	Ni(1)–N(2)	2.087(7)
Ni(1)–Cl(1)	2.336(2)	Ni(2)–O(1)	2.070(5)
Ni(2)–O(2)	2.058(5)	Ni(2)–O(3)	2.105(5)
O(2)–Ni(1)–O(1)	79.1(2)	O(2)–Ni(1)–N(2)	94.8(2)
O(1)–Ni(1)–N(1)	93.2(2)	N(2)–Ni(1)–N(1)	86.3(3)
O(2)–Ni(1)–N(1)	160.7(2)	O(2)–Ni(2)–O(1)	77.11(19)
O(2)#1–Ni(2)–O(1)	102.89(19)	Ni(1)–O(1)–Ni(2)	99.7(2)
Ni(1)–O(2)–Ni(2)	100.5(2)		

selected bond distances and angles are listed in Table 2. The structure consists of neutral binuclear entities and an uncoordinated disordered water molecule. Each molecule results from the pairing of two mononuclear units related by a crystallographic center of symmetry. Each Ni^{II} is bound by five donor atoms occupying the vertices of a distorted square-pyramidal coordination environment (with $\tau = 0.27$).[15,16] Two bridging oxygen atoms of the deprotonated pendant phenol groups and two nitrogen donors of the DACO ring of **L**^{1} comprise the basal plane, and each axial coordination site is occupied by one nitrogen atom of the azide anion. The Ni^{II} deviates from the basal mean equatorial plane of the square pyramid towards the apical N(13) by *ca.* 0.39 Å.

The two Ni are equivalently bridged by two phenoxo oxygen anions, which are bound asymmetrically at slightly different distances of 2.004(3) *vs.* 2.028(3) Å, respectively. The former lies in the range 1.93–2.01 Å (mean 1.98 Å)[17,18] reported for a selection of high-spin Ni^{II}–O (phenolate) bonds while the latter is a little longer. The Ni–O–Ni bridging angle is 101.57(13)° and the two phenol rings of the two **L**^{1} ligands in **1** are parallel to each other. The two Ni^{II} are separated by 3.1232(13) Å, which is similar to data for other binuclear nickel(II) complexes with phenoxo bridges at the two equatorial positions.[19]

The Ni–N$_{DACO}$ bond distances lie well within the reported range of secondary or tertiary amine to high-spin Ni^{II} bonds (mean 2.11 Å).[20] The axial azide anion is almost linear with the N(13)–N(14)–N(15) bond angle of 177.3(8)°. The N(13)–N(14) and N(14)–N(15) bond lengths (1.180(7) and 1.148(8) Å, respectively) are almost identical with the longer bond involving the nitrogen atom bound to the Ni^{II}. This is consistent with the structural results obtained with other azide complexes.[21]

In addition, it should be noted that two similar but different configurations were found to exist in each unit cell of this complex. They have similar DACO configurations but only slight differences in bond distances and angles.

The linear trinuclear complex 2. The ORTEP structure of complex **2** is shown in Fig. 2, and selected bond lengths and angles are listed in Table 3. Complex **2** is also neutral in which each ligand is doubly deprotonated and forms a square-pyramidal/octahedral/square-pyramidal linear trimeric complex. The asymmetric unit is formed by half the complex which shows an inversion center in the middle of the rhombus plane, which is similar to the linear trimeric nickel(II) complexes reported previously.[22] The central Ni, Ni(2), is located on a crystallographic inversion center and coordinated and bridged by four oxygen donors of the phenol groups of the two **L**^{2} ligands and two oxygen atoms of coordinated ethanol molecules, forming a nearly ideal octahedral environment. Atoms Ni(1) and Ni(1A), which occupy the terminal positions, are centrosymmetrically related to each other, hence Ni(1), Ni(2) and Ni(1A) lie in a straight line. Ni(1) is five-coordinated with a N_2O_2Cl donor set and the polyhedron may be best described as a genuine square pyramid with $\tau = 0.02$.[15,16] It is bound to the ligand by two oxygen atoms of the pendant groups and a pair of nitrogen donors of the DACO ring. A chloride anion occupies the axial position. The structure is entirely symmetric due to its position on an inversion center and the distance Ni(1)···Ni(2) in the dimer is 3.132(2) Å, which is consistent with those in other related complexes.[22c,23] The two phenoxo-bridged angles, Ni(1)–O(1)–Ni(2) and Ni(1)–O(2)–Ni(2), are 99.7(2) and 100.5(2)°, respectively. The folding angle between the perfect square plane [Ni(2), O(1), O(2), O(1A) and O(2A)] and the best plane calculated for N(1), N(2), O(1) and O(2) is only 5.3°, and the dihedral angle between the two phenol planes of **L**^{2} is 60.43°. Ni(1) is 0.3517° above the mean plane formed by N(1), N(2), O(1) and O(2) towards the apical Cl$^-$ anion. The apical position is occupied by a Cl$^-$ donor with axial [Ni(1)–Cl(1)] bond distance of 2.336(2) Å, which is similar to the Ni–Cl bond distance in a five-coordinate nickel(II) complex.[10a]

Examples of linear trinuclear homometallic complexes with oxygen or sulfur bridges are common, and their specific structural properties tend to be mediated mainly by the structural preferences of the metal (such as stereochemistry and coordination number, *etc.*) rather than by the ligand. This tendency leads to gross structural differences in a series of metal complexes.[23] Commonly, linear trinuclear nickel(II) complexes possess trinuclear units in a chair conformation with square-planar or octahedral environments for the terminal and central nickel(II) atoms.[24] To our knowledge a trinuclear nickel(II) complex with square-pyramidal/octahedral/square-pyramidal coordination is unprecedented.

As a common feature of the complexes with DACO, in both **1** and **2**, each DACO ring of the ligands adopts a boat/chair configuration, which can inhibit axial coordination to the metal, preventing the formation of a six-coordinated complex.[25] The central methylene C–H group of the boat form of the metalladiazacyclohexane rings shields the metal centers in the complex with a H···Ni distance of 2.511 Å for **1** (2.489 Å for **2**) and a H–Ni-apex angle of 14.6° for **1** (13.6° for **2**). The two complexes have approximately the same Ni–N$_{DACO}$ bond distances, indicating that the influences of the pendant groups on them are small, possibly negligible. However, the pendant arms significantly influence the coordination geometry of Ni^{II}, forming binuclear or trinuclear complexes, respectively.

Magnetochemistry

In the 300–5 K range investigated the molar magnetic susceptibility for complex **1** increases with temperature, and the magnetic moment decreases on cooling as shown in Fig. 3(a), which indicates a typical binuclear complex presenting intramolecular antiferromagnetic interaction. The similar curve obtained for **2** is shown in Fig. 3(b).

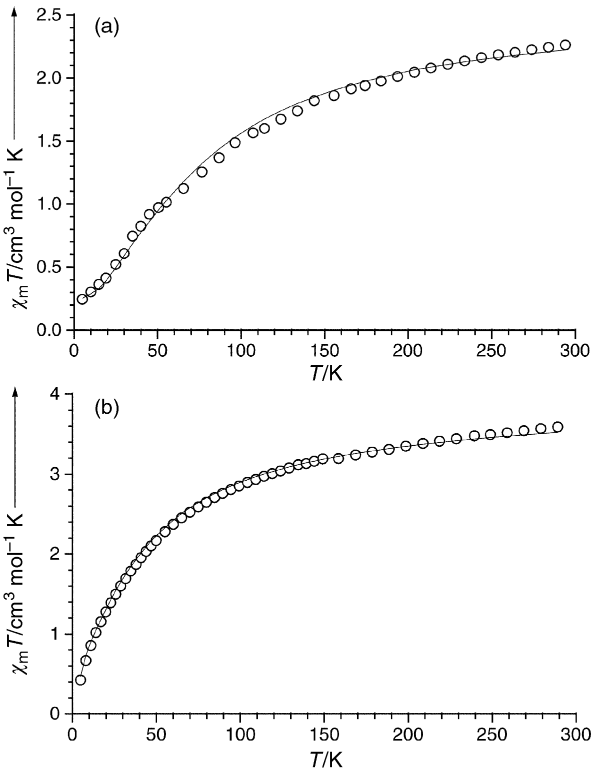

Fig. 3 Magnetic coupling diagram of the phenoxo-bridged binuclear complex **1** (a) and of the phenoxo-bridged linear trinuclear complex **2** (b).

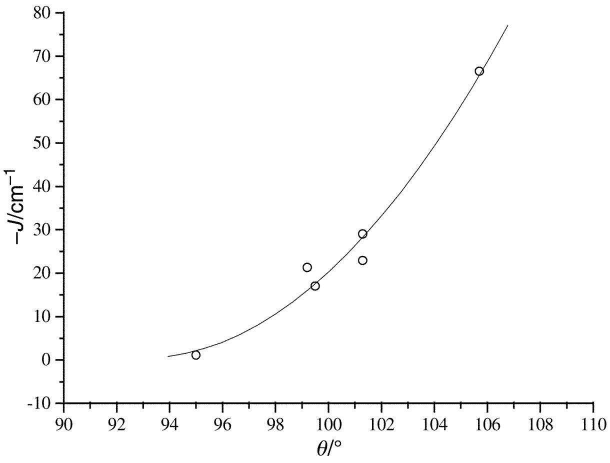

Fig. 4 Variation of the magnetic coupling parameter (J) *vs.* the Ni–O–Ni angle (θ) for some phenoxo-bridged binuclear nickel(II) complexes.

For **1**, magnetic analyses were carried out by using the magnetic susceptibility expression containing the correction term Θ for intermolecular interactions,[26] ρ for the fraction of paramagnetic impurity, and N_α for the temperature-independent paramagnetism based on the isotropic magnetic exchange Heisenberg model ($H = -2JS_1S_2$, $S_1 = S_2 = 1$).[27] A good fit as indicated in Fig. 3(a) was obtained using the parameters $g = 2.18$, $J = -22.9$ cm^{-1}, $\Theta = -1.2$ K, $\rho = 0.5\%$ and the agreement factor $F = 9.7 \times 10^{-4}$, where F is defined as $\Sigma[(\chi_m)_{obs} - (\chi_m)_{calc}]^2/\Sigma(\chi_m)_{obs}{}^2$. Magnetostructural correlations have extensively been studied for phenoxo-bridged binuclear copper(II) complexes.[28] Nevertheless, the similar correlation for nickel(II) complexes has not successfully been investigated because a large number of structural parameters seem to affect the super-exchange mechanism in these systems, such as the Ni–O–Ni bridging angle, Ni–O bond distance and dihedral angle between the Ni–O–Ni plane and the remaining coordination plane. In order to demonstrate the bridging-angle dependence graphically, the J values are plotted against the bridging angles in Fig. 4 for some phenoxo-bridged binuclear nickel(II) complexes.[29] A rough correlation emerges: the magnetic coupling becomes less antiferromagnetic as the angles diminish, and this effect is rather important. The shape of the correlated J (θ) curve suggests the possibility to obtain complexes with very weak ferromagnetic behavior at small θ angles (about 93.5°). A more definitive correlation between J and θ would be expected if more structural data of bisphenoxo-bridged nickel(II) complexes were available. A variety of co-operative factors affecting the J value in such compounds should be considered to explain individual differences shown, such as the metal–metal separation, the metal–bridge atom bond length and angle, and the terminal ligand basicity, *etc.*

For the linear trinuclear complex **2** the effective magnetic moment at room temperature is about 5.31 μ_B, slightly higher than the spin-only value of 4.90 μ_B expected for three non-interacting d^8 nickel(II) ions. As is shown in Fig. 3(b), the effective magnetic moment declines slowly with decreasing temperature. The susceptibility data were fitted using an expression for a linear trinuclear nickel(II) complex, based on the spin Hamiltonian $H = -2J(S_1S_2 + S_2S_3) - 2j(S_1S_3)$ $(S_1 = S_2 = S_3 = 1)$. The theoretical equation for χ_m can be expressed by eqn. (1) where $A = 42\exp[2(2x + y)] + 15\exp[2(y - x)] +$

$$\chi_m = \frac{2Ng^2\beta^2}{3kT}\left(\frac{A}{B}\right) \tag{1}$$

$15\exp[2(x - y)] + 3\exp[2(y - 3x)] + 3\exp[-2(x + y)] + 3\exp[-4y]$, $B = 7\exp[2(2x + y)] + 5\exp[2(y - x)] + 5\exp[2(x - y)] + 3\exp[2(y - 3x)] + 3\exp[-2(x + y)] + 3\exp[-4y] + \exp[-2(2x + y)]$, $x = J/kT$ and $y = j/kT$. The best fit parameters are $J = -7.9$ cm^{-1}, $j = -5.6$ cm^{-1}, $g = 2.23$, with $F = 9.7 \times 10^{-6}$. This indicates the existence of weak antiferromagnetic interactions between the adjacent two nickel(II) ions and the two terminal nickel(II) ions of **2**. The weak antiferromagnetic interactions may be attributed to the deviation of the metal atoms (0.3517 Å) from the basal plane, which reduces the overlap of the magnetic orbitals of the nickel(II) ions through the phenolate bridges. Compared to the magnetic interaction between the adjacent Ni^{II}, the antiferromagnetic interaction is weaker than that found in **1** (−22.9 *vs.* −7.9 cm^{-1}). The weaker antiferromagnetic interaction observed for **2** may be caused by the dihedral angle of 5.7° between Ni(1)–O(1)–O(2) and Ni(2)–O(1)–O(2), which results in less effectiveness to transmit the magnetic interaction due to the reduced spin overlap. Comparing the structure with those of other phenoxo-bridged trinuclear nickel(II) complexes, an interesting feature is that the terminal Ni^{II} are five-coordinated and the central Ni^{II} is six- rather than four-coordinated. To our knowledge, this is the first phenoxo-bridged trinuclear nickel(II) complex with such a coordination mode for which the magnetic properties have been investigated. Owing to the lack of magnetic data for related complexes with similar structures, we are forced to make a comparison with other trinuclear complexes bridged by phenolates. The antiferromagnetic interaction between the adjacent nickel(II) ions is unexpected and different from the ferromagnetic interaction (J = 12–15 cm^{-1}) found in similar complexes reported previously.[30] The weaker antiferromagnetic interaction between the terminal nickel(II) ions is similar in the range −4 to −6 cm^{-1}.[31] The unprecedented antiferromagnetic interaction for a linear pyramidal/octahedral/pyramidal trinuclear system is an open question.

In the light of these results it should also be noted that the Ni–O–Ni angle and the nickel(II) coordination geometry exert a remarkable influence on the magnetic exchange interaction. Small bridging Ni–O–Ni angles tend to yield a ferromagnetic interaction due to near orthogonality of the magnetic orbitals. Further study on such linear trinuclear systems is in progress.

Conclusion

Two novel nickel(II) complexes with unique structures involving diazamesocyclic ligands functionalized by phenol pendants have been synthesized and fully characterized. By attaching one or two phenol donor pendants to the framework of DACO the formation of unique binuclear and trinuclear nickel(II) complexes has been achieved. The interesting coordination modes of Ni^{II} with these ligands have been elucidated by X-ray structural analyses. From the structures of our complexes and those of other reported metal complexes with DACO ligands, we can conclude that DACO derivatives are good model ligands for the formation of metal complexes whose geometry usually can not be greater than five-coordinate due to the stereochemical effect (boat/chair configuration of DACO). With respect to their magnetic properties, the magneto-structural correlation has been investigated for both complexes and a rough correlation between the exchange coupling and the Ni–O–Ni angle obtained: the magnetic coupling becomes less antiferromagnetic as the angles diminish, and the effect is rather important.

Acknowledgements

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