1	Triangular Nickel Complexes Derived from 2-
2	Pyridylcyanoxime: An Approach to the Magnetic
3	Properties of the [Ni ₃ (µ ₃ -OH) {pyC(R)NO} ₃] ²⁺ Core
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23 Abstract

A series of nickel complexes with nuclearity ranging from Ni3 to Ni6 have been obtained by treatment of a variety of nickel salts with the 2-pyridylcyanoxime ligand. The reported compounds have as a common structural feature the triangular arrangement of nickel cations bridged by a central µ3-oxo/alkoxo ligand. These compounds are simultaneously the first nickel derivatives of the 2-pyridylcyanoxime ligand and the first examples of isolated, µ3-O triangular pyridyloximate nickel complexes. Magnetic measurements reveal antiferromagnetic interactions promoted by the µ3-O and oximato superexchange pathways and comparison of the experimental structural and magnetic data with DFT calculations give an in-depth explanation of the factors that determine the magnetic interaction in this kind of system.

48 **1. INTRODUCTION**

Triangular arrangement of paramagnetic cations is a significant topology in cluster 49 chemistry either on account of their intrinsic properties or as common fragments in larger 50 cages or extended structures such as Kagome networks. Equilateral triangular systems 51 exhibit spin frustration^[1] and become adequate systems for the study of subtle phenomena 52 such as the antisymmetric exchange interaction^{.[1]} A particular class of triangles are those 53 that contain a central µ3-O donor (oxo, hydroxo or alkoxo groups) and bridging oximato 54 55 ligands that define the sides of the triangle (Scheme 1). Most of the reported complexes with the $[M_3(\mu_3-O)-\{pyC(R)NO\}_3]^{n+}$ core (in which $pyC(R)NO^-=pyridyloximate$ ligands) are 56 Cu^{II} derivatives^[2] in contrast with the very rare examples of isolated triangular clusters 57 reported with manganese.^[3] iron^[4] or cobalt^{.[5]} It is surprising that similar triangular units 58 can only be found as a recognisable fragment in a few larger-nuclearity nickel clusters.^[6] 59 Related [Mn₃ (μ ₃-O) (R-salox)]ⁿ⁺ (salox=salicyloxime) complexes derived from 60 salicyloximate ligands and that include trivalent manganese cations have been widely 61 studied in the search for single-molecule magnets (SMMs) in recent years.^[7] 62

In recent years, nickel–oximato clusters derived from 2-pyridyloximes, (py)C(R)NOH,^[8] have yielded a surprisingly rich chemistry: clusters with a large variety of nuclearities and topologies have been reported for R=H,^[9] Me,^[6a, 9d, 10] Ph^[6a, 9d,e, 10, 11] or py;^[9h, 12] nuclearities of up to Ni14 ^[9g,h] have been reached by employing the ligands summarised in Scheme 1.

In the search for new properties in pyridyloxime chemistry, the choice of the ligand plays a fundamental role, and the properties induced by the R group of (py)C(R)NOH-type ligands is far from negligible. Coordination chemistry of 2-pyridylcyanoxime remains unexplored and only some copper derivatives with unusual μ_3 -O and μ_4 -O bridges have been recently reported by the authors.^[2g] Following our work with the 2-pyridylcyanoxime ligand, we report the syntheses and structural characterisation of the first series of nickel complexes derived from 2-pyridylcyanoxime with the formulas [Ni₃ (MeOH)₂ (BzO)(OH) 75 {pyC(CN)NO}4] (1), (NEt₃H) { $\mu_{1,5}$ -N(CN)₂} [Ni₆ (H₂O) (MeOH) (3-ClBzO)₂(OH)₂-{pyC(CN)NO}8] (2), [Ni4 (MeOH)2 (tfacac)2 (MeO)2-{pyC(CN)NO}4] (3), [Ni5 (MeOH)4] 76 $(3-ClBzO)_4(OH)_2-\{pyC(CN)NO\}_4$ (4) and [Ni5 (BzO)2(OH)2-77 $(H_2O)_4(N_3)_2$ {pyC(CN)NO}4] (5) in which pyC(CN)NO is the deprotonated form of 2-78 79 pyridylcyanoxime, BzO⁻ is benzoate and tfacac is trifluoroacetylacetonate. Complexes 1-5 exhibit a variety of topologies that are composed of different combinations of µ3-O 80 81 triangular subunits (Scheme 2).

Bearing in mind that the magnetic properties for this kind of nickel triangular topology system have not been established, we have devoted our attention to elucidating their magnetic response by combining experimental magnetic susceptibility measurements and DFT calculations, from which a complete description of the magnetic response of the µ3-O nickel–oximate system is proposed.

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92 2. RESULTS AND DISCUSSION

Synthetic comments: In the search for ligands that can induce new structural 93 features, the adequate addition of one R function to ligands that have previously proved to 94 be adequate for the syntheses of cluster compounds becomes a rational way to design new 95 ligands. The influence of the added R function can be effective in several aspects, the steric 96 hindrance or the electronic effects being among the most relevant. We have taken 2-97 pyridylaldoximate (paoH) as a reference ligand; an adequate position to place additional R 98 99 groups is on the carbon atom in the vicinity of the oximato function. With this idea in mind, we started a systematic exploration of the 2-pyridylcyanoxime ligand. When R = -CN, the 100 acidity of the cyanoxime function becomes $10^3 - 10^5$ times greater than that of common 101 oximes in which R is an aliphatic or aromatic $group^{[8b]}$ and thus it can induce strong 102 electronic effects. Very recently, we reported the first derivatives of the 2-pyridylcyanoxime 103 ligand in copper chemistry and the rare coordination of deprotonated µ3-O and µ4-O oxo 104 donors was characterised,^[2g] thereby suggesting that the strong increase in acidity of the 105 donors enhances the properties of clusters with divalent cations to those typical of the 106 trivalent ones. For Ni^{II}, this ligand easily promotes µ₃-OH coordination into triangular units, 107 which is extremely rare when employing other pyridyloximato ligands. 108

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110 Structural descriptions

[Ni3 (MeOH)2 (BzO)(OH) {pyC(CN)NO}4]·3MeOH (1·3MeOH): A view of the core 111 of complex 1 is illustrated in Figure 1. Selected interatomic distances and angles for 1 are 112 listed in Table 1. The core of this neutral compound can be described as a distorted trinuclear 113 isosceles arrangement of octahedrally coordinated Ni^{II} atoms linked by one µ3-OH ligand 114 115 with its oxygen atom placed 0.621(2) Å out of the plane defined by the three nickel atoms. Two sides of the triangle are defined by single oximato bridges, which link Ni(2) with Ni(1) 116 and Ni(3), and the third side is defined by one oximato and one syn-syn carboxylato bridge 117 between Ni(1) and Ni(3). Coordination spheres for Ni(1) and Ni(3) contain the µ3-OH 118 ligand, one O atom from the syn-syn benzoato ligand, one oximato bridge with Ni(2), one 119 pyC(CN)NO⁻ ligand and one methanol solvent molecule, whereas Ni(2) links two 120

pyC(CN)NO⁻ ligands, the central OH⁻ group and one O-oximato atom, thereby resulting in an N₂O₄ environment for Ni(1) and Ni(3) and an N₄O₂ environment for Ni(2). Bond angles that involve the central μ_3 -OH group are 116.28(8)° for Ni(1)-O(1)-Ni(2), 115.11(7) ° for Ni(3)-O(1)-Ni(2) and 102.16(7) ° for Ni(1)-O(1)-Ni(3); the corresponding Ni…Ni distances are 3.465(2), 3.494(2) and 3.199(2) Å, respectively.

126 The four oximato ligands are deprotonated, but one of them, which is coordinated to Ni(2), acts as a terminal ligand and interacts by means of one strong hydrogen bond with 127 one of the coordinated solvent molecules; there is an $O(3) \cdots O(9)$ distance of 2.682(3) Å. Ni-128 O-N-Ni torsion angles are moderate (close to 17°) for two of them and close to planar for 129 130 Ni(1)-O(2)-N(3)-Ni(2) (Table 1). One of the crystallization solvent molecules is involved in a set of hydrogen bonds and interacts with one of the coordinated methanol molecules to 131 Ni(3) (O(11)...O(8) 2.797(3) Å) and with the OH⁻ ligand (O(11)...O(1) 3.190(3) Å). An 132 additional intermolecular hydrogen bond links the nitrile groups of one neighbouring 133 trinuclear molecule (O(11)····N(2) 2.925(4) Å). 134

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136 $(NEt_3H){\mu_{1,5}-N(CN)_2}[Ni_6(H_2O)(MeOH)(3-ClBzO)_2(OH)_2-$

 $\{pyC(CN)NO\}$ 8]·3.5MeOH·0.5H2O (2·NEt3H·3.5MeOH·0.5H2O): The structure of 2 137 consists of two triangles, closely related to complex 1, in which two labile methanol donors 138 have been substituted by one dicyanamide bridging ligand. The extra negative charge is 139 140 compensated by one triethylammonium countercation. A view of the core of both triangles of complex 2 is shown in Figure 2. Selected interatomic distances and angles for 2 are listed 141 in Table 2. Bond parameters inside each triangular unit are very similar to those found in 1 142 without significant differences in the parameters related to the central OH⁻ groups, which 143 144 are placed 0.612(3) and 0.644(3) Å out of the plane defined by Ni(1,2,3) and Ni(4,5,6), respectively. The main nickel planes are quasi-parallel, with an angle between the planes of 145 $1.47(2)^{\circ}$. The only differences as a result of the coordination of the dicyanamide ligand are 146 related to the Ni-N-O-Ni torsion angles, which take values around 9, 11 and 25° (Table 2). 147 The dicyanamide ligand is coordinated in the $\mu_{1,5}$ mode with an Ni(1)...Ni(5) distance of 148 8.552(3) Å. In a similar manner to 1, solvent molecules are involved in hydrogen bonds with 149 the uncoordinated O-oximato and hydroxo groups. Intercluster hydrogen bonds are provided 150

through one of the solvent molecules that links the tri-ethylammonium cation and two cyanogroups of neighbouring molecules.

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[Ni4 (MeOH)₂ (tfacac)₂ (MeO)₂{pvC(CN)NO}4]·2MeOH (3·2MeOH): The neutral 154 core of the tetranuclear compound 3 can be described as a butterfly arrangement of four Ni^{II} 155 156 atoms, or alternatively, as two µ3-methoxo-centred triangles that share one side. A labelled plot and selected interatomic distances and angles for 3 are reported in Figure 3 and Table 157 3, respectively. Ni(1) and its equivalent Ni(1') atoms are placed in the wing sites of the 158 butterfly and their N2O4 coordination sphere is defined by one pyC(CN)NO⁻ ligand 159 160 coordinated by its two N atoms, two O atoms from one bidentate tfacac ligand, one O atom from one oximato bridge and the central methoxo group. The N4O2 environment of Ni(2) is 161 162 defined by two pyC(CN)NO⁻ ligands coordinated by its N atoms and the two methoxo groups, whereas Ni(3) coordinates six O atoms from two oximato bridges, the two methoxo 163 groups and two methanol molecules. The four pyC(CN)NO ligands are deprotonated. Bond 164 angles that involve the central μ_3 -OMe donor group are 115.0(2)° for Ni(1)-O(1)-Ni(2), 165 10°.1(2)° for Ni(1)-O(1)-Ni(3) and 96.2(2) ° for Ni(2)-O(1)-Ni(3), the corresponding 166 Ni···Ni distances being 3.523(1), 3.3554(9) and 3.097(2) Å, respectively. Ni-O-N-Ni torsion 167 angles show moderate values around 20°. Oxygen atoms of the µ3-OH groups are placed 168 169 0.785(4) Å out of the planes defined by Ni (1,2,3). No significant hydrogen bonds or intercluster interactions could be found. 170

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172 $[Ni5 (MeOH)4 (3-ClBzO)4(OH)_2\{pyC(CN)NO\}4] \cdot 7MeOH (4 \cdot 7MeOH):$ The 173 centrosymmetric molecule of 4 consists of two vertex-sharing µ3-OH-centred triangles 174 (bowtie topology). The oxygen atom of the µ3-OH ligand is placed 0.707(2) Å out of the 175 plane defined by the three nickel atoms. A labelled plot and selected interatomic distances 176 and angles for 4 are reported in Figure 4 and Table 4, respectively. In a similar manner to 1 177 and 2, the sides of the triangles are defined by single oximato bridges between the central 178 Ni(1) atom and the peripheral Ni(2) and Ni(3). These latter nickel atoms are bridged by one 179 oximato, one O-carboxylato and one syn-syn carboxylato bridge. The NiO₆ environment of 180 the central Ni(1) atom is formed by four O-oximato atoms and the two hydroxo groups, whereas the NiN2O4 environment of the remaining nickel atoms include the two N atoms of 181 182 one pyC(CN)NO⁻ ligand, the hydroxo ligand, two O atoms from the carboxylato ligands and one methanol molecule. Each diatomic oximate group links the central Ni^{II} atom and one 183 peripheral metallic ion with Ni-N-O-Ni torsion angles close to zero. The base of the triangles 184 is bridged by one µ3-OH group, one O-carboxylato atom with an Ni(2)-O(6)-Ni(3) bond 185 angle of 89.61(7)° and one syn-syn carboxylato. Each triangle is nearly isosceles, with the 186 187 Ni(1)…Ni(2), Ni(1)…Ni(3) and Ni(2)…Ni(3) distances being 3.3894(8), 3.3906(8) and 2.9609(7) Å, respectively. These intermetallic distances reflect the different Ni-O-Ni bond 188 189 angles with the central µ3-OH ligand: Ni(1)-O(1)-Ni(2) and Ni(1)-O(1)-Ni(3) are similar (114.43(8) and 114.71(7)°) and much larger than Ni(2)-O(1)-Ni(3) (95.13(7)°). 190

The O(1) atom from the μ3-OH groups and the uncoordinated O(7) atom of the
carboxylato ligands are connected by means of hydrogen bonds to ten crystallisation
methanol molecules, which define an (MeOH)8 ring. This "drop" of methanol connects four
Ni5 molecules (Figure 5).

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 $(H_2O)_4$ $(N_3)_2$ $(BzO)_2$ $(OH)_2$ {pyC (CN) NO}4]·2MeCN·10H₂O 196 [Ni₅ 197 (5.2MeCN.10H2O): A labelled plot and selected interatomic distances and angles for compound 5 are reported in Figure 6 and Table 5, respectively. The neutral core of this 198 199 centrosymmetric pentanuclear compound can be described as a bowtie arrangement of five Ni^{II} ions. The structure of 5 is very similar to that reported for compound 4, but the O-200 carboxylato bridge is changed for one $\mu_{1,1}$ -N₃-ligand with a similar Ni(1)-N(7)-Ni(3) bond 201 202 angle of 89.20(6)°. The complete description and bond parameters are very similar to 4 with 203 minor changes in the out-of-plane Ni(1,2,3) deviation of the O atom of the hydroxo group (0.720(1) Å) and slightly larger Ni-N-O-Ni torsion angles. 204

Magnetic measurements and fit procedure: Oxo-, hydroxoor methoxo-centred 206 triangles of Cu^{II} or Mn^{III} with oximato bridges have been previously studied and it has been 207 stated from the experimental work and DFT calculations that their magnetic properties 208 209 exhibit a strong dependence upon the bond parameters inside the triangular core. Oxo or methoxo Cu₃-centred triangles are always strongly antiferromagnetically coupled with -J210 coupling constants typically greater than 500 cm^{-1.[2]} For these systems, it has been 211 demonstrated that the main contribution to the antiferromagnetic coupling is correlated with 212 the out-of-plane displacement of the central µ3-O atom (or alternatively to the related Cu-213 O-Cu bond angles) with a minor contribution of the torsion of the oximato bridges^{.[2g]} In 214 contrast. for R-salox⁻/Mn^{III} triangles, ferro- or antiferromagnetic coupling has been reported 215 216 as a function of the Mn-N-O-Mn torsion angles, with the ferro-/antiferromagnetic boundary around torsion angles of 30°.^[3, 7] Studies of triangular nickel systems have not been reported 217 up to now and compounds 1-5 provide enough experimental data to propose their magneto-218 structural trends on the basis of their different kinds of magnetic responses as a function of 219 220 their topologies and nuclearity.

As has been described above, complexes 1 to 5 have key structural common features that provide us with the possibility to establish a detailed study of the superexchange pathways. The five complexes consist of isolated or linked isosceles or quasi-isosceles μ_3 -O-centred triangles in which the equivalent sides are defined by one diatomic oximato bridge and the base of the triangle is formed by a variety of bridging ligands (Scheme 3).

As can be observed in Table 6, the described complexes cover all combinations of Ni-O-Ni bond and Ni-N-O-Ni torsion angles including a third oximato bridge in the base of the triangle for 1 and 2. In addition, complexes 4 and 5 provide a nice comparison of the influence on the superexchange interaction of one O-carboxylato or one end-on azido bridge with the same Ni-X-Ni bond angle of 89°.

The numbering of all the spin carriers in the Hamiltonians applied to 1–5 and in the subsequent discussion is provided in Scheme 4. Compounds 1 and 2 show a very similar magnetic response that agrees with antiferromagnetic interactions inside one triangular arrangement of three *S*=1 local spins (Figure 7). Room-temperature $\chi_{M}T$ values (by the Ni3 unit) are 3.05 and 2.92 cm³K⁻¹mol⁻¹ for **1** and **2**, respectively. Upon cooling, $\chi_{M}T$ plots gradually decrease down to a plateau below 50 K and after a final decrease at low temperature (greater for compound **2**) reach values of 1.05 and 0.51 cm³K⁻¹mol⁻¹. On the basis of the data summarized in Table 7, which shows different bond parameters for the three interactions inside the triangle, the fit of the experimental data for compound 1 was initially performed on the basis of the superexchange pathways indicated in Scheme 4 using the CLUMAG program^[13] and by applying the Hamiltonian [Eq. (1)]:

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$$H = -J_1(S_1 \cdot S_3) - J_2(S_1 \cdot S_2) - J_3(S_2 \cdot S_3)$$
(1)

The fit was performed by discarding the low T values (<8 K) to avoid intercluster or zero-field splitting (ZFS) deviations. Best-fit parameters indicate a quasi-isosceles response with values of -14.5, -52.9 and -49.7 cm⁻¹, which indicate a similar value for J_2 and J_3 and clearly a lower value for the J_1 coupling constant.

Assuming that the two greater coupling constants are practically undistinguishable ($J_2=J_3$), a new fit was performed by including all data in the 2–300 K range with the conventional analytical equations, including a θ parameter to correct the low T decay, derived from the Hamiltonian [Eq. (2)]:

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$$H = -J_1(S_1 - S_3) - (J_2(S_1 \cdot S_2 + S_2 \cdot S_3))$$
(2)

252 Best-fit parameters were J_1 =-16.8(8) cm⁻¹, J_2 =-55.2(5) cm⁻¹, g=2.322(5) and θ =-0.53(2) 253 K.

In light of the results obtained for 1, the fit for compound 2 was performed by applying the Hamiltonian in Equation (2). Best-fit parameters were $J_1 = -19.8(4) \text{ cm}^{-1}$, $J_2 = -53.9(4) \text{ cm}^{-1}$, g = 2.280(5) and $\theta = -2.80(3)$ K, which are fully consistent with compound 1. The greater θ value and the more pronounced low-temperature decay should be attributed to the typically very weak interaction mediated between both triangular units by the dicyanamide bridge^[14] (Figure 7). Compound **3** shows an $\chi_M T$ value of 4.27 cm³K⁻¹mol⁻¹ at room temperature, which decreases upon cooling and tends toward zero at low temperature. The χ_M plot exhibits a broad maximum at 80 K, which is in good agreement with an even number of local *S*=1 spins antiferromagnetically coupled (Figure 8). Structural data show two sets of Ni-O-Ni bond angles for the wing–body interactions. The fit of the experimental data was then performed on the basis of Scheme 4 and by applying the Hamiltonian [Eq. (3)]:

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$$H = -J_1(S_2 \cdot S_3) - J_2(S_2 \cdot S_1 + S_2 \cdot S_{1a}) - J_3(S_3 \cdot S_1 + S_3 \cdot S_{1a})$$
(3)

Best-fit parameters obtained with the CLUMAG program^[13] were J_1 =+1.6 cm⁻¹, J_2 =-63.1 cm⁻¹, J_3 =-26.9 cm⁻¹ and g=2.352 with paramagnetic impurities of 1%.

As is explained below, the DFT-calculated values differ strongly from the above fit. To have a complete overview of the response of the fit procedure, we performed an additional fit and assumed that $J_2=J_3$. Under these conditions, a new excellent fit was obtained for $J_1=+0.3$ cm⁻¹, $J_2=J_3=-37.1$ cm⁻¹, and g=2.00. The g value seems too low but J_2 and J_3 agree very well with the DFT-calculated values. These fits indicate that the system has multiple analytical solutions and that the most reliable values should be assumed to be the calculated ones.

The calculated value for J_1 has a high degree of uncertainty because of the dominant strong antiferromagnetic coupling promoted by J_2 and J_3 that leads to the S=0 ground state independently of J_1 when J_2 , $J_3 \gg J_1$. This feature was checked by performing a set of simulations, which have shown that the quality of the fit is practically constant, even when changing the fixed J_1 value by one order of magnitude. Therefore we can only conclude that J_2 and J_3 indicate moderately strong antiferromagnetic coupling; for the body interaction J_1 we can only propose a weak coupling, probably ferromagnetic.

283 Complexes 4 and 5 exhibit a similar shape with an $\chi_{\rm M}$ T decrease from the room-284 temperature values of 4.74 and 5.28 cm3K⁻¹mol⁻¹ down to minimum values of 3.00 and 4.33 285 cm3K⁻¹mol⁻¹ at 44 K for 4 and 80 K for 5, respectively (Figure 9). Below the minimum, the

two plots increase up to maximum $\chi_M T$ values of 3.20 and 5.46 cm3K⁻¹mol⁻¹ placed at 13 286 287 K (for 4) and 14 K (for 5), thereby suggesting a ferrimagnetic response with greater antiferromagnetic components for 4. At low temperature, the $\chi_{M}T$ value decreases and 288 reaches 2.07 and 3.90 $\text{cm}^3\text{K}^{-1}\text{mol}^{-1}$ for 4 and 5, respectively, due to intercluster interactions 289 or ZFS effects. These compounds exhibit the guasi-isosceles core; a fit of the experimental 290 data was performed by applying the interaction (Scheme 4) and by assuming only two 291 coupling constants with the conventional analytical equation derived from the Hamiltonian 292 [Eq. (4)]: 293

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$$H = -J_1(S_1 \cdot S_3 + S_{1a} \cdot S_{3a}) - J_2(S_2 \cdot S_1 + S_2 \cdot S_3 + S_2 \cdot S_{1a} + S_2 \cdot S_{3a})$$
(4)

Best-fit parameters were $J_1 = -13.4(2)$ cm⁻¹, $J_2 = -27.2(4)$ cm⁻¹, g = 2.084(3) for 4 and 295 $J_1 = +10(2)$ cm⁻¹, $J_2 = -24.5(8)$ cm⁻¹, g = 2.13(1) for 5. Dominant antiferromagnetic 296 interactions between the central and peripheral S=1 spins in a bowtie topology led to an S=3 297 298 ground state for both compounds. As expected from the structural data, J_2 values are similar, whereas the replacement of an oxo bridging ligand by one end-on azido bridge switches the 299 300 sign of J_1 and introduces ferromagnetic components into the core of this pentanuclear system. Some of the coupling constants obtained in the above fits are unreliable (as J_1 in 301 302 compound 3), are indistinguishable by symmetry (J_2 and J_3 also in compound 3) or have been assumed to be equivalent to minimise the number of variables in the fit process. To 303 304 have a more precise picture of the coupling constant values and to rationalise the effect of 305 the main structural parameters, DFT calculations were performed.

306 The calculated J values by using DFT methods for complexes 1, 3 and 5 (see the computational details in the Experimental Section) show a good agreement with the 307 experimentally fitted J values (Table 7). In Figure 10, the comparison between the 308 experimental susceptibility curves and those obtained directly using the calculated J values 309 also confirms the accuracy of the employed methodology to reproduce the magnetic 310 properties of such complexes. The analysis of the J values indicates that cases with one 311 oximato bridging ligand combined with one hydroxo or alkoxo bridging ligand result in a 312 313 moderate antiferromagnetic coupling. To analyse the effect of the presence of alkoxo or hydroxo bridging ligand, the Ni4 complex (3) was calculated again by replacing the methoxo 314

group with a hydroxo ligand. The three calculated J_1 – J_3 values are -31.7, -27.6 and +17.2 cm⁻¹. The inverse procedure was followed for the Ni₅ complex (**5**) by replacing the original hydroxo group with a methoxo ligand to give the following J_1 – J_3 values: -32.7, -39.0 and +38.7 cm⁻¹. The results for both systems confirm that the presence of the methoxo group slightly enhances the strength of the exchange interactions relative to the hydroxo ligand.

Traditionally, for the oximato transition-metal complexes, the M-O-N-M torsion 320 angle was proposed to be the key structural parameter that primarily controls the magnetic 321 properties.^[15] To analyse the effect of such a geometrical parameter in our family of 322 complexes, the Ni₃ complex (1) was selected and we focused in the $J_{2,3}$ interaction (Scheme 323 4). We prepared some model complexes by changing the Ni(2)-O-N-Ni(3) torsion angle but 324 keeping all the remaining bond parameters of the triangular complex. The dependence of 325 $J_{2,3}$ on such a torsion angle is shown in Figure 11. The obtained results indicate that the 326 increase of the Ni-O-N-Ni torsion angle induces a slightly larger antiferromagnetic coupling. 327 At first glance, this result seems surprising, because for single oximato bridges between two 328 nickel centres a decrease in the antiferromagnetic interaction has recently been proposed^[16] 329 for large torsion angles. For the well-studied equivalent Mn^{III} triangles, the opposite 330 behaviour was found. In the case of the Mn3 complexes, there is a "magic" 331

Mn-N-O-Mn torsion angle. Thus if the value is larger than 31°, the coupling is 332 ferromagnetic, whereas smaller values lead to antiferromagnetic couplings.^[7, 15] To explain 333 the difference between the Mn^{III} and Ni^{II} complexes, we have to keep in mind the different 334 nature of the orbitals that bear the unpaired electrons. Thus, for the Ni^{II} complexes, those 335 orbitals are d_{z^2} and $d_{x^y-y^2}$, whereas for d⁴ Mn^{III} there is one unpaired electron on each d 336 orbital with the exception of the $d_{x^y-y^2}$ that remains empty. Assuming the validity of the 337 Kahn–Briatt model, we can expect that for Ni^{II} complexes the maximum coupling should be 338 reached for a perfect octahedral coordination sphere of the two involved Ni^{II} cations. This 339 fact can be easily understood because for a perfect octahedral coordination, the lobes of d_{z^2} 340 and $d_{x^y-y^2}$ orbitals will have the maximum overlap with those of the bridging ligand that 341 favours the interaction between the two paramagnetic centres. To measure the degree of 342

distortion of the coordination sphere of the Ni^{II} cations from a perfect octahedron, we have employed the continuous shape measures (S(Q); see the computational details in the Experimental Section).

346 This approach allows us to quantify the distortion. Thus a S(OC6) value equal to zero 347 indicates a perfect octahedral coordination. The smaller the S(OC6) value is, the smaller the structural distortion from the perfect octahedron. In Figure 12, there is the dependence of the 348 calculated $J_{2,3}$ value upon changing the Ni(2)-O-N-Ni(3) torsion angle (the same as those 349 represented in Figure 11) with the sum of the S(OC6) values for the two Ni^{II} cations involved 350 in the $J_{2,3}$ exchange interaction. The curve nicely corroborates the fact that the larger Ni-O-351 352 N-Ni torsion angle values lead to coordination spheres closer to the perfect octahedron (smaller S(OC6) values) and consequently larger antiferromagnetic couplings for a better 353 354 overlap with the bridging ligands that facilitate the interaction between the paramagnetic centres. The complete analysis of the magnetic response of this kind of triangular system 355 356 allows us to propose a behavior closer to the copper triangles than to the manganese ones and to confirm the Ni-O-Ni bond angle that involves the central hydroxo or alkoxo ligand as 357 358 a major factor. The amount of experimental data is still limited, but to check the validity of 359 the above conclusions and to compare the coupling constants in larger clusters, we have selected the previously reported hexanuclear systems [Ni₆ (SO₄)₄ (OH) - {pyC(R)NO}₃ 360 {pyC(R)NOH}3 (MeOH)2 (H2O)] (R=Me, Ph),^[6a] which are the only ones with available 361 magnetic data that contain the fragment [Ni₃ (μ ₃-OH) {pyC(R)NO}₃]³⁺ in a quasi-362 equilateral arrangement. These complexes exhibit Ni-O-Ni bond angles around 1108 (lower 363 than those found in 1–5) and medium Ni-O-N-Ni torsion angles around 25°. From the above 364 365 calculations we would expect moderately weak antiferromagnetic coupling and in excellent agreement, the reported J values were -20.5 and -17.0 cm⁻¹, which are lower than those 366 found in 1–5 for similar torsions and larger Ni-O-Ni bond angles. 367

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370 **3. CONCLUSION**

The employment of the relatively acidic 2-pyridylcyanoxime ligand in nickel 371 372 chemistry has allowed us to synthesise a series of Ni₃, Ni₄ and Ni₅ complexes that can be described as topologically derived from isolated, side- or vertex-sharing µ3-OR isosceles 373 triangles. Analysis of the experimental and DFT-calculated sign and magnitude of the 374 375 coupling constants gives a complete description of the magnetic properties of this kind of system, which can be summarised as follows. 1) Moderate antiferromagnetic interactions 376 should be expected in all cases for the [Ni₃ (μ 3-O) {pyC(R)NO}3]ⁿ⁺ core. 2) 377 Antiferromagnetic interactions are enhanced for -OR=alkoxo relative to hydroxo bridges. 3) 378 In contrast to isolated single oximato bridges, the effect of the torsion angle in the case of µ-379 OR-centred triangles is a minor effect and the magnitude of the antiferromagnetic interaction 380 should be attributed to the Ni-O-Ni bond angles. d) The structural dependence of the J value 381 for the double oximato and hydroxo exchange pathway on the torsion Ni-N-O-Ni angle is 382 rather small and an opposite trend is found to that of the equivalent Mn^{III} systems. For the 383 Ni^{II} systems, the increase of the Ni-N-O-Ni angle enhances the antiferromagnetic coupling. 384 Such a difference can be explained by the different magnetic orbitals of the Ni^{II} and Mn^{III} 385 cations involved in the exchange interactions. 386

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392 4. EXPERIMENTAL SECTION

General: Magnetic susceptibility measurements were carried out on 393 polycrystalline samples using a Quantum Design DSM5 susceptometer 394 working in the range 2–300 K under magnetic fields of 0.3 T. Diamagnetic 395 corrections were estimated from Pascal tables. Infrared spectra (4000-400 cm⁻ 396 ¹) were recorded from KBr pellets. 2-Pyridylacetonitrile, sodium azide and 397 sodium dicyanamide were purchased from Sigma-Aldrich and used without 398 further purification. Ni (BzO)2·3H2O and Ni (3-Cl-BzO)2·xH2O were 399 synthesised by dissolving equimolar quantities (40 mmol) of NaOH and 400 benzoic acid or 3-chlorobenzoic acid, respectively, in water (40 mL). The final 401 solution was filtered and mixed with a commercial source of Ni (NO₃)₂·6H₂O 402 (20 mmol) in water (20 mL). The resulting salts were obtained in good yields 403 (>80%). Ni (tfacac)₂·xH₂O was synthesised by mixing trifluoroacetylacetonate 404 (40 mmol), Ni (NO₃)₂·6H₂O (20 mmol) and NaAcO·3H₂O (40 mmol) in water 405 (100 mL). The precipitate was filtered, dissolved in ethanol (40 mL) and 406 recrystallized by the addition of water (100 mL). The resulting salt was 407 obtained in low yield (≈30%). The py-(CN)NOH ligand was prepared 408 according to the literature.^[17] 409

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Single-crystal X-ray structure analyses: Details of crystal data, data collection and refinement are given in Table 8. X-ray data were collected using a MAR345 diffractometer with an image-plate detector for 1, 2 and 4 and using a Bruker Kappa ApexII CCD diffractometer for 3 and 5 with Mo_{Ka} radiation (λ =0.71073 Å). The structures were solved by direct methods using the SHELXS computer program^[18] and refined by fullmatrix least-squares methods with the SHELXS97 computer program^{.[19]}

Three hydrogen atoms for 1 and one for 3, respectively, were located from difference 417 synthesis, whereas all the remaining hydrogen atoms were computed and refined by using a 418 riding model, using in all cases a temperature factor equal to 1.2 times the equivalent 419 temperature factor of the atom which was linked. Lorentz polarisation and absorption 420 421 corrections were applied. CCDC-844624 (1), 844625 (2), 844626 (3), 844627 (4) and 422 844628 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 423 www.ccdc.cam.ac.uk/data request/cif. 424

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[Ni3 (MeOH)2 (BzO)(OH){py-(CN)NO}4]·3MeOH (1): py-(CN)NOH (0.073 g, 0.5 426 427 mmol), Ni (BzO)2·3H2O (0.301 g, 1 mmol) and NaN(CN)2 (0.089 g, 1 mmol) were dissolved in MeOH (20 mL) and then NEt₃ (0.101 g, 1 mmol) was added. The solution was 428 stirred for 2 h, filtered and crystallised by layering with diethyl ether (10 mL). Relevant IR 429 bands: $\tilde{v} = 3446$ (br), 2210 (w), 1601 (s), 1558 (m), 1460 (s), 1416 (m), 1399 (m), 1296 (w), 430 1266 (w), 1225 (m), 1154 (w), 1102 (w), 1057 (w), 1037 (m), 780 (w), 712 cm⁻¹ (m); 431 elemental analysis calcd (%) for 1 (C₃₇H₃₀N₁₂Ni₃O₉): C 46.16, H 3.14, N 17.46; found: C 432 46.87, H 3.04, N 17.11. 433

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435 (NEt3H)[Ni6(H2O)(MeOH)(3-ClBzO)2{N(CN)2}(OH)2{py-

(CN)NO}8]·0.5H2O·3.5MeOH (2): py-(CN)NOH (0.073 g, 0.5 mmol), Ni(3-436 ClBzO)2·xH2O (0.369 g, 1 mmol) and NaN(CN)2 (0.089 g, 1 mmol) were added to MeOH 437 (20 mL) together with NEt₃ (0.101 g, 1 mmol). The solution was stirred for 2 h, filtered and 438 439 crystallised by layering with diethyl ether. Relevant IR bands: $\tilde{v} = 3412$ (br), 2294 (w), 2217 440 (m), 2187 (s), 1601 (s), 1558 (s), 1460 (s), 1422 (s), 1390 (s), 1302 (m), 1264 (m), 1227 (s), 1155 (m), 1107 (m), 1062 (w), 1036 (s), 1005 (w), 777 (m), 741 (w), 712 cm1 (m); elemental 441 442 analysis calcd (%) for 2 · (NEt₃H) (C₇₉Cl₂N₂₈Ni₆O₁₆H₆₄): C 45.62, H 3.08, N 18.86; found: C 45.94, H 2.98, N 18.38. 443

[Ni4 (MeOH)2 (MeO)2{py-(CN)NO}4(tfacac)2]·2MeOH (3): py-(CN)NOH

446 (0.073 g, 0.5 mmol), Ni (tfacac)2·xH2O (0.362 g, 1 mmol) and NaN(CN)₂ (0.089 g, 1 mmol) 447 were added to MeOH (20 mL) together with NEt3 (0.101 g, 1 mmol). The solution was 448 stirred and after a couple of hours filtered and layered by using diethyl ether (10 mL). 449 Relevant IR bands: $\tilde{v} = 3411$ (b), 2220 (w), 1626 (s), 1602 (m), 1521 (w), 1464 (s), 1428 450 (m), 1299 (s), 1266 (w), 1223 (s), 1190 (m), 1141 (m), 1108 (w), 1038 (m), 777 (m), 713 451 cm⁻¹ (m); elemental analysis calcd (%) for **3** (C4₂H₄₀F₆N₁₂Ni₄O₁₂): C 40.24, H 3.22, N 452 13.41; found: C 40.61, H 3.09, N 13.56.

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[Ni5 (MeOH)4 (3-ClBzO)4(OH)2{py-(CN)NO}4]·7MeOH (4): py-(CN)NOH (0.073 g, 0.5 mmol) and Ni (3-ClBzO)2·xH2O (0.369 g, 1 mmol) were dissolved in commercial MeOH (20 mL) and NEt3 (0.101 g, 1 mmol). The solution was stirred for 2 h, filtered and crystallised by layering with diethyl ether. Relevant IR bands: $\tilde{\nu}$ =3417 (br), 2219 (w), 1602 (s), 1559 (s), 1456 (s), 1428 (m), 1392 (s), 1341 (m), 1217 (m), 1036 (m), 766 (m), 739 (m), 711 cm⁻¹ (m); elemental analysis calcd (%) for 4 (C₆₀Cl₄N₁₂Ni₅O₁₈H₅₀): C 43.35, H 3.03, N 10.11; found: C 42.98, H 2.94, N 10.12.

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462 [Ni5(MeOH)4(BzO)2(N3)2(OH)2{py-(CN)NO}4]·2CH3CN·10H2O (5): py-(CN)NOH

463 (0.073 g, 0.5 mmol), Ni(BzO)₂·3H₂O (0.301 g, 1 mmol) and NaN₃ (0.065 g, 1 mmol) were 464 dissolved in MeOH (20 mL) together with NEt₃ (0.101 g, 1 mmol). The solution was stirred 465 for a couple of hours and filtered. Crystals were obtained by layering the final solution with 466 diethyl ether (10 mL). Relevant IR bands: \tilde{v} =3400 (br), 2221 (w), 2063 (s), 1601 (s), 1553 467 (s), 1463 (s), 1400 (s), 1299 (w), 1214 (m), 1104 (w), 1035 (m), 778 (w), 711 cm⁻¹ (m); 468 elemental analysis calcd (%) for 5·6H₂O (C4₂N₁₈Ni₅O₂₀H₄₈): C 35.56, H 3.41, N 17.78; 469 found: C 35.74, H 3.35, N 17.46.

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Computational details: Electronic structure calculations based on density functional 472 473 theory provide an excellent estimation of the exchange coupling constants in polynuclear transition-metal complexes when taking into account the tiny involved energy 474 differences.^[20] Since a detailed description of the computational strategy used to calculate 475 the exchange coupling constants in polynuclear complexes is outside the scope of this paper, 476 we will focus our discussion here to its most relevant aspects. Previously, we published a 477 series of papers devoted to such a purpose and in which more details can be found.^[21–23] 478 479 For the studied Ni₃ complex 1, there are three exchange interactions, and we employed four spin configurations to estimate these three J values: the high spin solution (S=3) and three 480 481 S=1 wave functions obtained with the spin inversion of each nickel centre. In the case of the Ni4 complex 3, with three J values, they were obtained by fitting the equations that involved 482 the following spin configurations: the high-spin S=4, two S=1 spin configurations for the 483 inversion of Ni(1) and Ni(3) and three S=0 for the inversion of the following pairs: {Ni(1), 484 485 Ni(2)}, {Ni(1), Ni(3)} and {Ni(2), Ni(3)}. Finally, the Ni5 complex 5, with three different J values, the high-spin S=5, one S=3 spin configuration for the inversion of Ni(1) and three 486 487 S=1 for the inversion of the following pairs {Ni(1), Ni(2)}, {Ni(2), Ni(2a)} and {Ni(3), Ni(3a)} were employed. 488

In previous papers, we have analysed the effect of the basis set and the choice of the 489 functional on the accuracy of the determination of the exchange coupling constants.^[22-24] 490 Thus, we found that the hybrid B3LYP functional,^[25] together with the all electron basis set 491 proposed by Schaefer et al., provide J values in excellent agreement with the experimental 492 493 ones. The hybrid character of the B3LYP, which is due to the inclusion of some contribution 494 of exact exchange, reduces the self-interaction error and improves the calculated J values relative to non-hybrid functionals. We have employed a basis set of triple- ζ quality as 495 proposed by Schaefer et al.^[26] The calculations were performed with the Gaussian 09 496 code^[27] by using guess functions generated with the Jaguar 7.0 code^[28] and introducing the 497 ligand-field effects^[29] to control the local charge and multiplicity of each atom. 498

A brief description of continuous shape measures is presented in this section. More detailed information on this stereochemical tool and its applications to transition-metal compounds can be found in previous publications^{.[30]} Continuous shape measures were

proposed by Avnir and coworkers to provide a quantitative evaluation of the degree of 502 distortion of a set of atoms (e.g., the coordination sphere of a transition metal) from a given 503 ideal polyhedral shape.^[31] In short, the proposed method consists of finding the ideal 504 505 structure that has the desired shape that is closest to the observed structure. The ideal and 506 real polyhedra are superimposed in such a way as to minimise the expression in Equation (5),^[20] the value of which is the shape measure of the investigated structure Q relative to the 507 ideal shape P, in which \vec{q}_i are N vectors that contain the 3N Cartesian coordinates of the 508 problem structure Q, \vec{p}_i contain the coordinates of the ideal polyhedron P, and \vec{q}_0 is the 509 position vector of the geometric centre that is chosen to be the same for the two polyhedra: 510

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$$S(P) = min\left[\frac{\sum_{i=1}^{N} |\vec{q}_i - \vec{p}_i|^2}{\sum_{i=1}^{N} |\vec{q}_i - \vec{p}_0|^2}\right] \times 100$$
(5)

513 S(P)=0 corresponds to a structure Q fully coincident in shape with the reference polyhedron 514 P, regardless of size and orientation. Thus, in this case this approach was employed to 515 estimate the distortion of the quasioctahedral coordination of the Ni^{II} cations with respect to 516 a perfect octahedron by using the S(OC6) value. Shape measures were calculated with 517 version 2.0 of the SHAPE program.[32]

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Table 1 Selected distances [Å] and angles [°] of the core of compound **1**.

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Ni(1)-O(1)	2.060(2)	Ni(1)-O(1)-Ni(2)	116.28(8)
Ni(2)-O(1)	2.053(2)	Ni(2)-O(1)-Ni(3)	115.11(7)
Ni(3)-O(1)	2.052(2)	Ni(1)-O(1)-Ni(3)	102.16(7)
Ni(1)-O(2)-N(3)	117.5(1)	Ni(1)-N(9)-O(5)	123.7(1)
Ni(2)-O(4)-N(12)	116.2(1)	Ni(2)-N(3)-O(2)	126.9(1)
Ni(3)-O(5)-N(9)	110.5(1)	Ni(3)-N(12)-O(4)	125.3(1)
Ni(1)…Ni(2)	3.465(2)	Ni(1)-O(2)-N(3)-Ni(2)	3.3(2)
Ni(2)…Ni(3)	3.494(2)	Ni(2)-O(4)-N(12)-Ni(3)	17.0(2)
Ni(1)…Ni(3)	3.199(2)	Ni(3)-O(5)-N(9)-Ni(1)	16.7(2)

Ni(1) - O(1)			
	2.043(3)	Ni(1)-O(1)-Ni(2)	103.3(1)
Ni(2) - O(1)	2.052(3)	Ni(2)-O(1)-Ni(3)	116.3(2)
Ni(3)–O(1)	2.052(3)	Ni(1)-O(1)-Ni(3)	114.6(2)
Ni(4)–O(2)	2.071(3)	Ni(4)-O(2)-Ni(5)	102.7(1)
Ni(5)-O(2)	2.051(3)	Ni(4)-O(2)-Ni(6)	115.6(2)
Ni(6)-O(2)	2.066(3)	Ni(5)-O(2)-Ni(6)	113.7(2)
Ni(1)-O(4)-N(8)	108.2(2)	Ni(1)-N(5)-O(3)	124.9(3)
Ni(2)-O(5)-N(11)	116.3(3)	Ni(2)-N(8)-O(4)	124.4(3)
Ni(3)-O(3)-N(5)	117.3(3)	Ni(3)-N(11)-O(5)	127.2(3)
Ni(4)-O(11)-N(20)	117.2(3)	Ni(4)-N(17)-O(10)	124.1(2)
Ni(5)-O(10)-N(17)	108.9(2)	Ni(5)-N(23)-O(12)	125.5(3)
Ni(6)-O(12)-N(23)	116.1(3)	Ni(6)-N(20)-O(11)	127.3(3)
Ni(1)…Ni(2)	3.212(1)	Ni(1)-O(4)-N(8)-Ni(2)	26.5(4)
Ni(2)…Ni(3)	3.487(1)	Ni(2)-O(5)-N(11)-Ni(3)	8.4(5)
Ni(1)…Ni(3)	3.445(1)	Ni(3)-O(3)-N(5)-Ni(1)	9.5(5)
Ni(4)…Ni(5)	3.200(1)	Ni(4)-O(11)-N(20)-Ni(6)	10.7(5)
Ni(4)…Ni(6)	3.500(1)	Ni(5)-O(10)-N(17)-Ni(4)	24.9(4)
Ni(5)…Ni(6)	3.446(1)	$N_{i}(6) = O(12) = N(23) = N_{i}(5)$	12 0(1)

Table 2. Selected distances [Å] and bond and torsion angles $[\circ]$ of the core of compound 2.

Table 3 Selected distances [Å] and bond and torsion angles [°] of the core of compound **3**.

Ni(1)-O(1)	2.082(4)	Ni(1)-O(1)-Ni(2)	115.0(2)
Ni(2)-O(1)	2.095(4)	Ni(2)-O(1)-Ni(3)	96.2(2)
Ni(3)-O(1)	2.064(4)	Ni(1)-O(1)-Ni(3)	108.1(2)
Ni(1)-O(3)-N(5)	117.2(4)	Ni(1)-N(2)-O(2)	125.1(4)
Ni(3)-O(2)-N(2)	113.8(4)	Ni(2)-N(5)-O(3)	126.0(4)
Ni(1)Ni(2)	3.523(1)	Ni(1)-O(3)-N(5)-Ni(2)	19.2(6)
Ni(2)…Ni(3)	3.097(2)	Ni(3)-O(2)-N(2)-Ni(1)	20.8(6)
Ni(1)…Ni(3)	3.3554(9)		

Table 4 Selected distances [Å] and bond and torsion angles [°] of the core of compound **4**.

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Ni(1)-O(1)	2.023(2)	Ni(1)-O(1)-Ni(2)	114.43(8)
Ni(2)-O(1)	2.008(2)	Ni(2)-O(1)-Ni(3)	95.13(7)
Ni(3)-O(1)	2.003(2)	Ni(1)-O(1)-Ni(3)	114.71(7)
Ni(1)-O(2)-N(3)	114.7(1)	Ni(2)-N(3)-O(2)	125.9(1)
Ni(1)-O(3)-N(6)	114.6(1)	Ni(3)-N(6)-O(3)	126.0(1)
Ni(1)…Ni(2)	3.3894(8)	Ni(2)-O(6)-Ni(3)	89.61(7)
Ni(2)…Ni(3)	2.9609(7)	Ni(1)-O(3)-N(6)-Ni(3)	1.0(2)
Ni(1)…Ni(3)	3.3906(8)	Ni(1)-O(2)-N(3)-Ni(2)	0.5(2)

Table 5 Selected distances [Å] and bond and torsion angles [8] of the core of compound **5**.

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Ni(1)-O(6)	2.017(1)	Ni(1)-O(6)-Ni(2)	113.71(6)
Ni(2)-O(6)	2.023(1)	Ni(2)-O(6)-Ni(3)	114.41(6)
Ni(3)-O(6)	2.022(1)	Ni(1)-O(6)-Ni(3)	95.23(6)
Ni(2)-O(3)-N(2)	114.9(1)	Ni(1)-N(2)-O(3)	125.8(1)
Ni(2)-O(5)-N(5)	114.7(1)	Ni(3)-N(5)-O(5)	126.4(1)
Ni(1)…Ni(2)	3.3825(3)	Ni(1)-N(7)-Ni(3)	89.20(6)
Ni(2)…Ni(3)	3.3999(2)	Ni(2)-O(3)-N(2)-Ni(1)	2.6(2)
Ni(1)…Ni(3)	2.9835(3)	Ni(2)-O(5)-N(5)-Ni(3)	7.3(2)

Table 6 Core parameters for compounds 1 to 5. Data for 2 corresponds to the triangle defined
by Ni (1,2,3).

	1	2	3	4	5
α	116.28(8)	116.3(2)	115.0(2)	114.71(7)	113.71(6)
β	115.11(8)	114.6(2)	108.1(2)	114.43(8)	114.41(6)
γ	102.16(7)	103.3(1)	96.2(2)	95.13(7)	95.23(6)
τ_1	3.3(2)	8.4(5)	19.2(6)	1.0(2)	7.3(2)
τ_2	17.0(2)	9.5(5)	20.8(6)	0.5(2)	2.6(2)
τ_3	16.7(2)	26.5(4)	-	-	-

Table 7 Structural parameters [Å and 8] and calculated exchange coupling constants [cm⁻¹] corresponding to the Ni₃ (1; see Figure 1), Ni₄ (3; see Figure 3) and Ni₅ (5; see Figure 6) complexes. The subscript numbers for the calculated coupling constants corresponds to the numbering employed in Scheme 4 and structural data. Two sets of values are indicated for complex 3 (see fit procedure).

	Bridges	d(Ni…Ni)	Ni-O-Ni	Ni-O-N	Ni-N-O-Ni	$J_{\rm exptl}$	$J_{ m calcd}$
Ni ₃ c	complex 1						
J_{12}	NO, OH	3.465	116.3	117.5	3.3	-52.9	-40.4
J_{23}	NO, OH	3.494	115.1	116.2	17.0	-49.7	-34.4
J_{13}	NO, RCOO, OH	3.199	102.2	110.5	16.7	-14.5	-13.3
Ni ₄ c	complex 3						
J_{12}	NO, OCH ₃	3.523	115.0	117.2	19.2	-63.1 (-37.1)	-38.5
J_{13}	NO, OCH ₃	3.355	108.1	113.8	20.8	-26.9(-37.1)	-32.7
J_{23}	2 OCH ₃	3.097	96.2	_	_	+1.6(+0.3)	+18.1
Ni ₅ c	complex 5						
J_{12}	NO, OH	3.382	113.7	114.9	2.7	-24.5	-28.2
J_{23}	NO, OH	3.400	114.4	114.7	7.3	-24.5	-32.1
$J_{1,3}$	RCOO, N ₃ , OH	2.984	95.2	-	-	+10.1	+34.3

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- **Table 8** Crystal data, data collection and structure refinement details for the X-ray structure
- 709 determination of compounds 1–5.

	1	2	3	4	5
formula	C40H42N12Ni3O12	C83H20Cl2N28Ni6O20	C444H48F6N12Ni4O14	C67H78Cl4N12Ni5O25	C46H52N20Ni5O24
M_r [g mol ⁻¹]	1058.99	2202.83	1317.78	1889.76	1562.63
space group	triclinic	triclinic	monoclinic	monoclinic	monoclinic
crystal system	$P\bar{1}$	PĪ	C2/c	P21/n	P21/n
a [Å]	11.093(6)	13.718(4)	22.622(1)	14.369(3)	13.8290(3)
b [Å]	14.064(5)	13.886(2)	15.945(1)	15.814(2)	13.8139(3)
c [Å]	15.945(6)	14.229(4)	16.0496(8)	19.039(3)	19.3703(4)
a [°]	90.07(3)	75.67(2)	90	90	90
β [°]	72.72(2)	85.08(2)	90.944(2)	92.68(2)	101.534(1)
γ [°]	89.20(3)	79.20(2)	90	90	90
$V[Å^3]$	2375(2)	2577(1)	5788.6(8)	4321(1)	3625.6(1)
Z	2	1	4	2	2
T [K]	293(2)	293(2)	100(2)	293(2)	100(2)
$D_{\text{caled}} [\text{gcm}^{-3}]$	1.481	1.419	1.512	1.450	1.416
F(000)	1092	1126	2696	1944	1568
$\mu(Mo_{Ka}) [mm^{-1}]$	1.248	1.202	1.369	1.269	1.356
measured reflns	24 989	18625	5670	35134	11132
unique reflns	12836	16224	5670	10978	11 132
R _{int}	0.0344	0.0364	0.0000	0.0641	0.0324
$\theta_{\min}/\theta_{\max}$ [°]	2.65/32.33	1.48/28.93	1.56/26.02	1.67/29.93	1.66/30.61
$R(F^2)$	0.0424	0.0397	0.0609	0.0535	0.0356
$wR(F^2)$	0.1198	0.1260	0.1797	0.1507	0.1038
variables	622	1323	372	563	460
$\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}} [e \text{ Å}^{-3}]$	0.577/-0.525	0.666/-0.723	1.596/-1.091	1.570/-0.573	1.200/-0.722

715 Figures Captions

716 Scheme 1. Top: 2-Pyridyloxime ((py)C(R)NOH) and salicyloxime (R-salox) ligands 717 referenced in the text. Bottom: Equilateral arrangement of an $\{M_3 \ (\mu_3-O) \ (L-NO)_3\}$ 718 fragment.

719 Scheme 2. Triangular-based core for the Ni₃ (1), (Ni₃)₂ (2), Ni₄ (3) and Ni₅ (4, 5) 720 compounds reported in this work.

Figure 1 Partially labelled molecular structure of the triangular compound 1. Hydrogen atoms of the organic ligands and the central OH group and solvent molecules have been suppressed for clarity.

Figure 2. Top: Partially labelled molecular structure of the triangular units of compound 2.
Bottom: Plot of the linkage of the two triangles by means of the dicyanamido bridging ligand.

The hydrogen atoms of the organic ligands and the central OH group, solvent molecules and

727 NEt_3H^+ countercation have been suppressed for clarity.

Figure 3. Partially labelled molecular structure of the tetranuclear structure of compound 3.
Hydrogen atoms of the organic ligands and solvent molecules have been suppressed for clarity.

- Figure 4. Partially labelled molecular structure of the pentanuclear structure of compound
 4. Hydrogen atoms of the organic ligands and the central OH groups and solvent molecules
 have been suppressed for clarity.
- **Figure 5.** Plot of the hydrogen bonds promoted by the ten methanol molecules found between four pentanuclear units of 4. Only three nickel atoms of each molecule and the OH or 3-Cl-benzoate ligands directly involved in the hydrogen-bonding network have been plotted.
- Figure 6. Partially labelled molecular structure of the pentanuclear structure of compound 5.
 Hydrogen atoms of the organic ligands and the central OH groups and solvent molecules have been suppressed by clarity.
- **Scheme 3**. Common triangular-based core for compounds 1–5. Symbols α , β and g represent
- the Ni-O-Ni bond angles and τ_1 and τ_2 the corresponding Ni-N-O-Ni torsion angles. For 1
- and 2, a third oximato bridge is present in the base of the triangle and in this case the torsion
- 744 is labelled as τ_3
- Scheme 4. Coupling schemes applied in the fit procedure of compounds 1–5. Different
 coupling constants in the corresponding Hamiltonians are indicated as dotted lines, bold lines
- and solid lines, corresponding in all cases J_1 to the base of the triangles.

Figure 7. Product of $\chi_M T$ versus *T* for compounds **1** (dot-centred circles) and **2** (triangles). Solid lines show the best obtained fit.

Figure 8. Product of χ_M (squares) and $\chi_M T$ (dot-centred circles) versus *T* for compound **3**. Solid lines show the best fit.

- **Figure 9.** Product of $\chi_{M}T$ versus *T* for compounds **4** (triangles) and **5** (dot-centred circles). Solid lines show the best obtained fit.
- **Figure 10**. Magnetic-susceptibility curves for the Ni₃ (1), Ni₄ (3), Ni₅ (5) complexes. Squares represent the experimental data, whereas the solid line was calculated with DFT *J* values.
- Figure 11. Dependence of the J_{2,3} value for some model systems on the Ni₃ complex (1) changing
 the Ni(2)-O-N-Ni(3) torsion angle.
- **Figure 12**. Dependence of the $J_{2,3}$ value for some model systems on the Ni₃ complex (1) changing
- the Ni(2)-O-N-Ni(3) torsion angle with the sum of the continuous shape measurement parameter S(OC6) corresponding to the two Ni^{II} cations involved in the $J_{2,3}$ interaction.
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839 Scheme 3.



845 Scheme 4.



851 Figure 7



857 Figure 8



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863 Figure 9
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869 Figure 10















Figure 12

