# Variation of nuclearity in $Ni^{II}$ complexes of a Schiff base ligand: crystal structures and magnetic studies

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## IR spectra of complexes

In the IR spectra of all four complexes, there are a band around 3200 $cm^{-1}$ due to the presence of the N−H group[1] and another broad band around 3400 $cm^{-1}$ assignable to the stretching vibration of the hydroxyl group.[1] A strong and sharp band due to the azomethine ν(C=N) group of the Schiff base ligand appears around 1620 $cm^{-1}$ in the IR spectra of all four complexes. A strong and sharp band around 1384 $cm^{-1}$ is clearly detected in the IR spectra of complexes **1**−**4** indicating the presence of the nitrate anion.

## H−bonding

In complex **1**, the mononuclear units are linked to each other through several hydrogen bonds (Table S5) involving the three solvent water molecules, the oxygen atoms (O4, O5, O6) of the nitrate co-anion and five amine hydrogen atoms (H2A, H2B, H3AA, H3AB, H3BA) to form a one-dimensional chain as shown in S2. In complex **2**, the two mononuclear units are connected to each other *via* several intermolecular hydrogen bonding interactions to form a three dimensional network as shown in Fig. S3. The solvent water molecule shows strong hydrogen bonding interactions with the amine hydrogen (H6A) and oxygen atoms (O11, O12) of non-coordinating nitrate ion. The other hydrogen atom (H6B) attach to nitrogen atom (N6) forms intramolecular hydrogen bond with the oxygen atom (O8) of other nitrate anion. The amine hydrogen (H5A) forms an intramolecular hydrogen bonding with the oxygen atom (O10) of nitrate ion. The pheoxo hydrogen (H2) forms a bifurcated hydrogen bond with the oxygen atoms (O7, O8) of nitrate ion. The hydrogen (H2A) attached to nitrogen (N2) shows bifurcated hydrogen bonding interaction with the symmetry related phenoxo oxygen ($O2^{e}$) atom and a symmetry related oxygen ($O7^{e}$) atom of nitrate annion (e = 1-x,1/2+y,1/2-z). Details of the hydrogen bonding interactions are given in Table S5. In complex **3**, the hydrogen atom (H2) attach to the nitrogen atom (N2) forms intermolecular bifurcated

hydrogen bonding interactions with two oxygen atoms O14 and O15 of non–coordinating nitrate ion. The hydrogen atom H5 attached to the amine nitrogen N5, forms intermolecular hydrogen bond with one oxygen atom O16$^{g}$ (g = -1+x,3/2-y,-1/2+z) of symmetry related nitrate anion (Fig. S4). Details of the hydrogen bonding interactions are given in Table S5. In complex **4,** the hydrogen atom (H2) attached to the nitrogen atom (N2) forms a hydrogen bond with oxygen atom (O12) of nitrate ion. The another hydrogen atom (H8) attached to the oxygen atom (O8) forms a hydrogen bond with the methoxy oxygen atom O4$^{h}$ (h = 1-x,y,3/2-z) (Fig. S5).

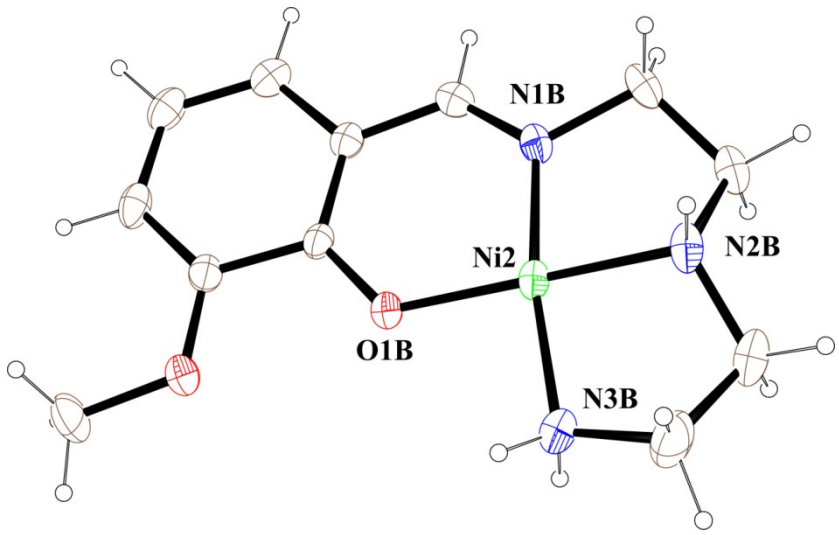


**Fig. S1:** ORTEP diagram of complex **1B** with 20% ellipsoid probability. Nitrate anions and solvent waters are not shown for clarity.

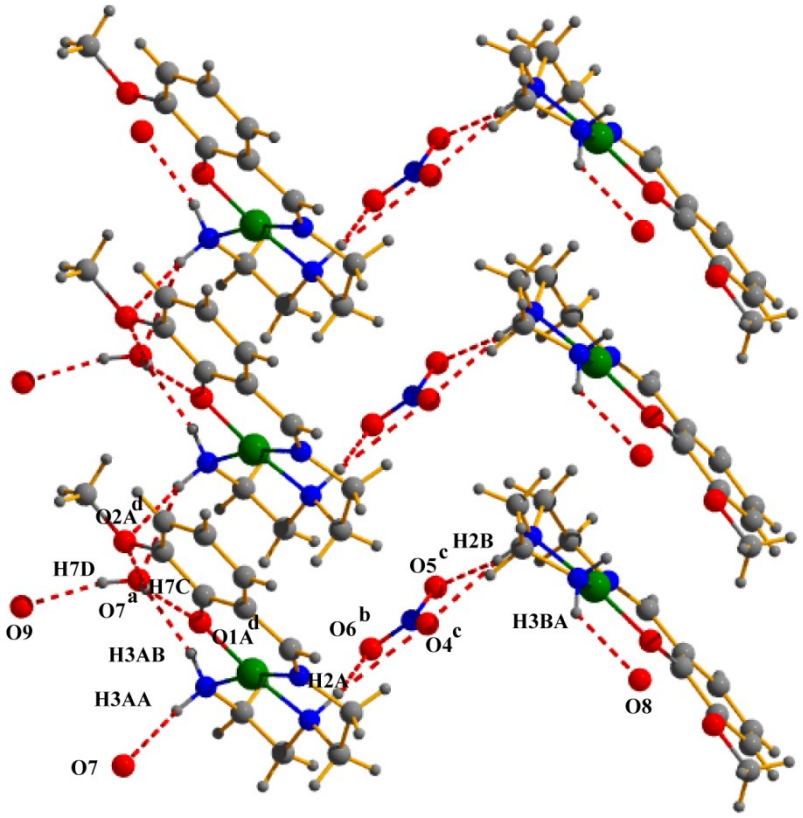


**Fig. S2:** H-bonded structure of complex **1**. H-bonds are shown by dotted lines.

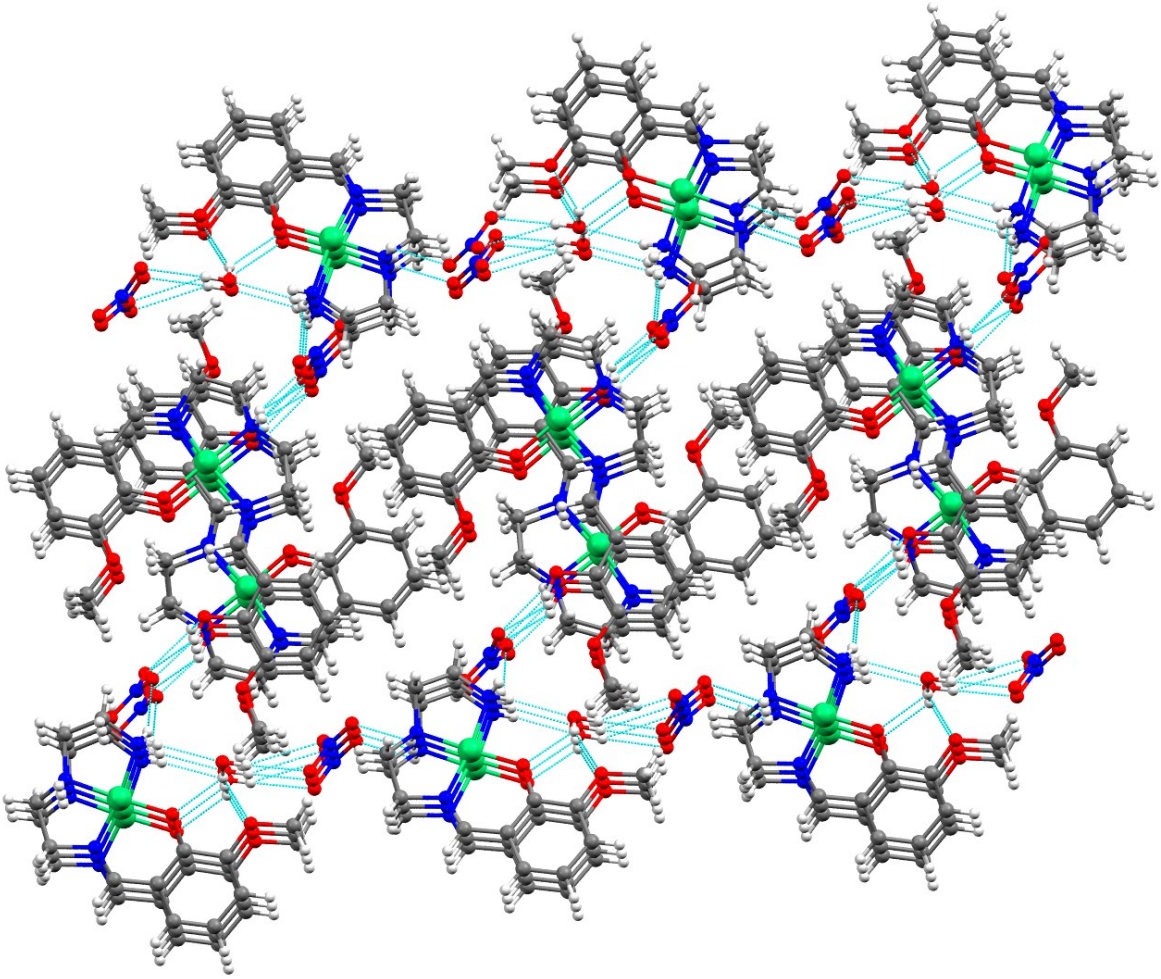

**Fig. S3**: H-bonded structure of complex **2**. H-bonds are shown by dotted lines.

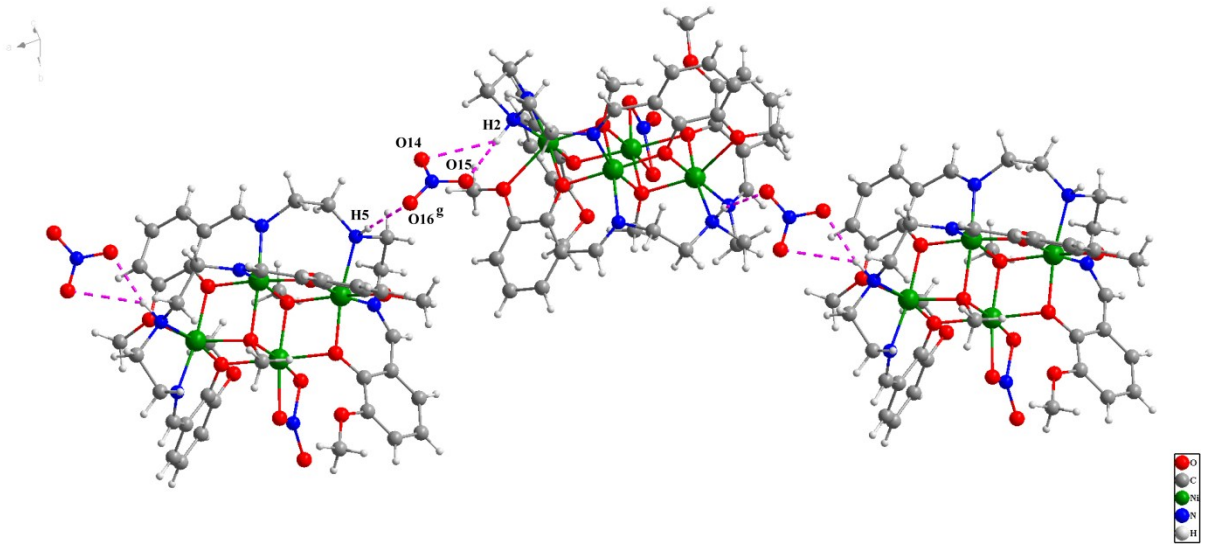


**Fig. S4**: H-bonded structure of complex **3**. H-bonds are shown by dotted lines.

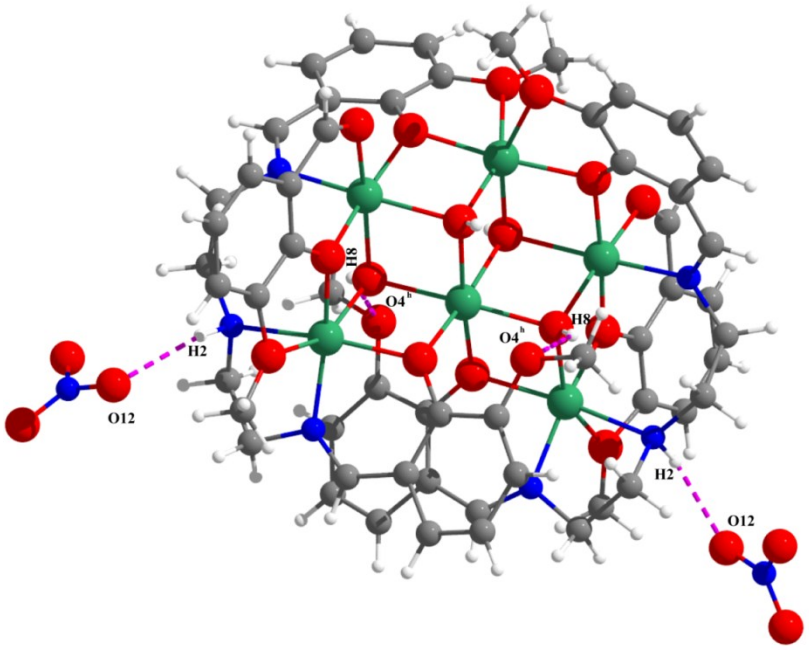


**Fig. S5**: H-bonded structure of complex **4**. H-bonds are shown by dotted lines.

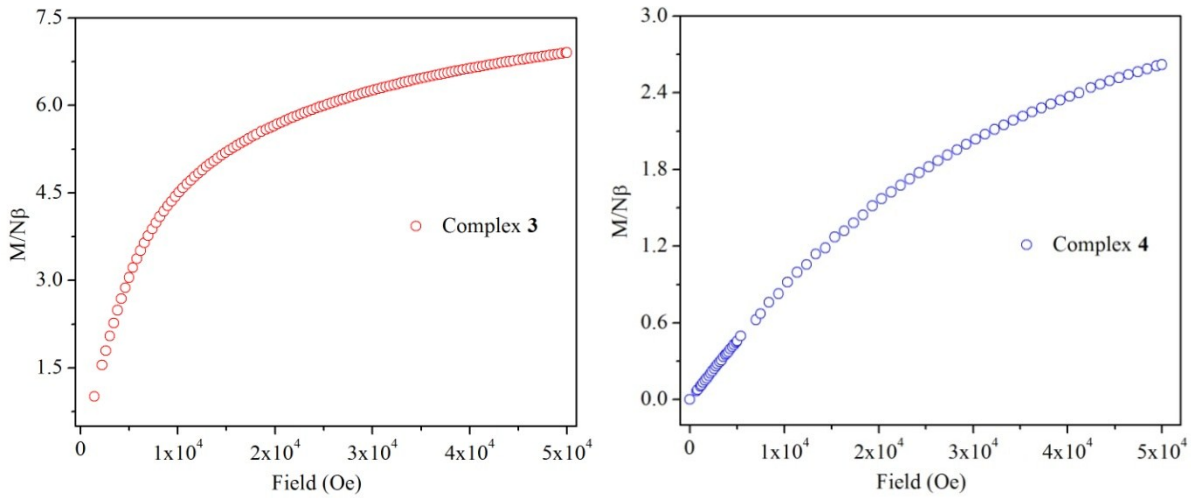


**Fig**. **S6**: Field dependence of molar magnetizations for complex **3** at 2 K (left) and complex **4** at 2.5 K (right).

**Table S1:** Selected bond lengths (Å) and angles (°) of complexes **1**.

| Bond lengths (Å) | | | |
|---|---|---|---|
| Ni(1)–O(1A) | 1.826(3) | Ni(2)–O(1B) | 1.830(4) |
| Ni(1)–N(1A) | 1.845(4) | Ni(2)–N(1B) | 1.829(4) |
| Ni(1)–N(2A) | 1.888(4) | Ni(2)–N(2B) | 1.889(5) |
| Ni(1)–N(3A) | 1.918(4) | Ni(2)–N(3B) | 1.903(6) |
| Bond angles (°) | | | |
| O(1A)–Ni(1)–N(1A) | 96.35(16) | O(1B)–Ni(2)–N(1B) | 96.49(18) |
| O(1A)–Ni(1)–N(2A) | 172.66 (15) | O(1B)–Ni(2)–N(2B) | 173.97(19) |
| O(1A)–Ni(1)–N(3A) | 91.64(16) | O(1B)–Ni(2)–N(3B) | 91.5(2) |
| N(1A)–Ni(1)–N(2A) | 86.40(17) | N(1B)–Ni(2)–N(2B) | 86.2(2) |
| N(1A)–Ni(1)–N(3A) | 169.58(18) | N(1B)–Ni(2)–N(3B) | 170.1(2) |
| N(2A)–Ni(1)–N(3A) | 86.49 (17) | N(2B)–Ni(2)–N(3B) | 86.4(2) |

**Table S2:** Selected bond lengths (Å) and angles (°) of complex **2**.

| Bond lengths (Å) | | | |
|---|---|---|---|
| Ni(1)–O(1) | 1.824(2) | Ni(2)–O(5) | 1.828(2) |
| Ni(1)–N(1) | 1.841(2) | Ni(2)–N(4) | 1.837(2) |
| Ni(1)–N(2) | 1.887(2) | Ni(2)–N(5) | 1.891(2) |
| Ni(1)–N(3) | 1.914(2) | Ni(2)–N(6) | 1.922(2) |
| Bond angles (°) | | | |
| O(1)–Ni(1)–N(1) | 95.75(10) | O(5)–Ni(2)–N(4) | 96.56(9) |
| O(1)–Ni(1)–N(2) | 177.80(10) | O(5)–Ni(2)–N(5) | 177.13(9) |
| O(1)–Ni(1)–N(3) | 92.02(9) | O(5)–Ni(2)–N(6) | 90.50(9) |
| N(1)–Ni(1)–N(2) | 86.20(10) | N(4)–Ni(2)–N(5) | 86.31(10) |
| N(1)–Ni(1)–N(3) | 171.55(10) | N(4)–Ni(2)–N(6) | 171.62(10) |
| N(2)–Ni(1)–N(3) | 86.10(9) | N5–Ni(2)–N(6) | 86.63(10) |

**Table S3:** Selected bond lengths (Å) and angles (°) of complex **3**.

| Bond lengths (Å) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni(1)–O(1) | 1.925(8) | Ni(2)–O(2) | 2.037(7) | Ni(3)–O(1) | 1.968(7) | Ni(4)–O(2) | 2.133(8) |
| Ni(1)–O(5) | 1.949(8) | Ni(2)–O(5) | 1.979(6) | Ni(3)–O(3) | 2.324(9) | Ni(4)–O(6) | 2.103(8) |
| Ni(1)–O(9) | 2.130(6) | Ni(2)–O(7) | 2.282(8) | Ni3–O(6) | 2.033(6) | Ni(4)–O(9) | 2.029(6) |
| Ni(1)–O(10) | 2.134(6) | Ni(2)–O(9) | 2.026(7) | Ni(3)–O(10) | 2.049(7) | Ni(4)–O(10) | 2.025(6) |
| Ni(1)–N(1) | 2.065(8) | Ni(2)–N(2) | 2.115(8) | Ni(3)–N(5) | 2.142(9) | Ni(4)–O(11) | 2.091(8) |
| Ni(1)–N(4) | 2.067(9) | Ni(2)–N(3) | 1.972(9) | Ni(3)–N(6) | 1.973(9) | Ni(4)–O(12) | 2.086(6) |
| Bond angles (°) | | | | | | | |
| O(1)–Ni(1)–O(5) | 172.9(3) | O(2)–Ni(2)–O(5) | 97.1(3) | O(1)–Ni(3)–O(3) | 74.1(3) | O(2)–Ni(4)–O(6) | 177.8(3) |
| O(1)–Ni(1)–O(9) | 94.5(3) | O(2) –Ni(2)–O(7) | 85.3(3) | O(1)–Ni(3)–O(6) | 95.6(3) | O(2)–Ni(4)–O(9) | 80.0(3) |
| O(1)–Ni(1)–O(10) | 81.1(3) | O(2)–Ni(2)–O(9) | 82.4(3) | O(1)–Ni(3)–O(10) | 82.3(3) | O(2)–Ni(4)–O(10) | 98.7(3) |
| O(1)–Ni(1)–N(1) | 89.2(4) | O(2)–Ni(2)–N(2) | 169.9(4) | O(1)–Ni(3)–N(5) | 89.3(3) | O(2)–Ni(4)–O(11) | 92.1(3) |
| O(1)–Ni(1)–N(4) | 94.8(3) | O(2)–Ni(2)–N(3) | 89.9(3) | O(1)–Ni(3)–N(6) | 172.8(4) | O(2)–Ni(4)–O(12) | 89.2(3) |
| O(5)–Ni(1)–O(9) | 80.5(3) | O(5)–Ni(2)–O(7) | 73.1(3) | O(3)–Ni(3)–O(6) | 87.9(3) | O(6)–Ni(4)–O(9) | 97.8(3) |
| O(5) –Ni(1)–O(10) | 92.9(3) | O(5)–Ni(2)–O(9) | 82.4(3) | O(3)–Ni(3)–O(10) | 153.4(2) | O(6)–Ni(4)–O(10) | 81.0(3) |
| O(5)–Ni(1)–N(1) | 95.8(3) | O(5)–Ni(2)–N(2) | 89.1(3) | O(3)–Ni(3)–N(5) | 86.6(4) | O(6)–Ni(4)–O(11) | 90.1(3) |
| O(5)–Ni(1)–N(4) | 89.0(3) | O(5)–Ni(2)–N(3) | 171.9(3) | O(3)–Ni(3)–N(6) | 103.2(4) | O(6)–Ni(4)–O(12) | 91.2(3) |
| O(9)–Ni(1)–O(10) | 79.9(2) | O(7)–Ni(2)–O(9) | 151.1(2) | O(6)–Ni(3)–O(10) | 82.2(3) | O(9)–Ni(4)–O(10) | 84.9(2) |
| O(9)–Ni(1)–N(1) | 89.7(3) | O(7)–Ni(2)–N(2) | 88.7(3) | O(6)–Ni(3)–N(5) | 171.3(3) | O(9)–Ni(4)–O(11) | 171.9(4) |
| O(9)–Ni(1)–N(4) | 164.4(3) | O(7)–Ni(2)–N(3) | 103.3(4) | O(6)–Ni(3)–N(6) | 91.0(3) | O(9)–Ni(4)–O(12) | 99.3(3) |
| O(10)–Ni(1)–N(1) | 165.1(3) | O(9)–Ni(2)–N(2) | 106.5(3) | O(10)–Ni(3)–N(5) | 105.7(3) | O(10 )–Ni(4)–O(11) | 97.9(4) |
| O(10)–Ni(1)–N(4) | 89.3(2) | O(9)–Ni(2)–N(3) | 102.8(3) | O(10)–Ni(3)–N(6) | 101.6(4) | O(10)–Ni(4)–O(12) | 171.6(3) |
| N(1)–Ni(1)–N(4) | 102.9(3) | N(2)–Ni(2)–N(3) | 83.4(3) | N(5)–Ni(3)–N(6) | 83.8(3) | O(11)–Ni(4)–O(12) | 79.0(4) |

**Table S4:** Selected bond lengths (Å) and angles (°) of complex **4**.

| Bond lengths (Å) | | | |
|---|---|---|---|
| Ni(1)–O(1) | 1.954(8) | Ni(3)–O(2) | 2.033(7) |
| Ni(1)–O(3) | 2.223(8) | Ni(3)–O(6) | 1.987(5) |
| Ni(1)–O(9) | 2.008(5) | Ni(3)–O(7) | 2.403(7) |
| Ni(1)–O(1*) | 1.954(8) | Ni(3)–O(8) | 2.033(5) |
| Ni(1)–O(3*) | 2.223(8) | Ni(3)–N(2) | 2.121(9) |
| Ni(1)–O(9*) | 2.008(5) | Ni(3)–N(3) | 1.959(9) |
| Ni(2)–O(1) | 1.962(5) | Ni(4)–O(2) | 2.126(6) |
| Ni(2)–O(5) | 2.111(8) | Ni(4)–O(8) | 1.998(7) |
| Ni(2)–O(6) | 1.977(5) | Ni(4)–O(9) | 2.084(5) |
| Ni(2)–O(8) | 2.064(7) | Ni(4)–O(2*) | 2.126(6) |
| Ni(2)–O(9) | 2.072(7) | Ni(4)–O(8*) | 1.998(7) |
| Ni(2)–N(1) | 2.043(11) | Ni(4)–O(9*) | 2.084(5) |
| Bond angles (°) | | | |
| O(1)–Ni(1)–O(3) | 75.3(3) | O(2)–Ni(3)–O(6) | 92.6(2) |
| O91)–Ni(1)–O(9) | 81.5(2) | O(2)–Ni(3)–O(7) | 104.5(3) |
| O(1)–Ni(1)–O(1*) | 175.0(2) | O(2)–Ni(3)–O(8) | 81.2(3) |
| O(1)–Ni(1)–O(3*) | 101.2(3) | O(2)–Ni(3)–N(2) | 167.6(3) |
| O(1)–Ni(1)–O(9*) | 102.3(3) | O(2)–Ni(3)–N(3) | 88.0(4) |
| O(3)–Ni(1)–O(9) | 156.1(3) | O(6)–Ni(3)–O(7) | 70.8(2) |
| O(3)–Ni(1)–O(3*) | 95.3(3) | O(6) –Ni(3)–O(8) | 82.2(2) |
| O(3)–Ni(1)–O(9*) | 94.4(2) | O(6)–Ni(3)–N(2) | 98.2(3) |
| O(9) –Ni(1)–O(9*) | 85.3(2) | O(6)–Ni(3)–N(3) | 159.9(3) |
| O(1)–Ni(2)–O(5) | 88.1(3) | O(7)–Ni(3)–O(8) | 152.4(2) |
| O(1)–Ni(2)–O(6) | 170.8(3) | O(7)–Ni(3)–N(2) | 84.9(3) |
| O(1)–Ni(2)–O(8) | 103.9(2) | O(7)–Ni(3)–N(3) | 89.7(3) |
| O(1)–Ni(2)–O(9) | 79.7(3) | O(8)–Ni(3)–N(2) | 94.1(3) |
| O(1)–Ni(2)–N(1) | 89.7(3) | O(8)–Ni(3)–N(3) | 117.7(3) |
| O(5)–Ni(2)–O(6) | 85.8(3) | N(2)–Ni(3)–N(3) | 84.0(4) |
| O(5)–Ni(2)–O(8) | 167.0(3) | O(2)–Ni(4)–O(9) | 89.4(2) |
| O(5)–Ni(2)–O(9) | 96.9(3) | O(2)–Ni(4)–O(2*) | 99.7(2) |
| O(5)–Ni2–N(1) | 94.2(4) | O(2)–Ni(4)–O(8*) | 99.2(2) |
| O(6)–Ni(2)–O(8) | 81.6(2) | O(2)–Ni(4)–O(9*) | 170.9(2) |
| O(6)–Ni(2)–O(9) | 94.2(2) | O(8)–Ni(4)–O(9) | 82.0(2) |
| O(6)–Ni(2)–N(1) | 97.6(3) | O(8)–Ni(4)–O(8*) | 178.5(2) |
| O(8)–Ni(2)–O(9) | 80.7(2) | O(8)–Ni(4)–O(9*) | 99.2(2) |
| O(8)–Ni(2)–N(1) | 90.9(3) | O(9)–Ni(4)–O(9*) | 81.1(2) |
| O(9)–Ni(2)–N(1) | 164.4(3) | O(2*)–Ni(4)–O(8*) | 79.8(3) |

Symmetry transformation * = 1-x,y,3/2-z

**Table S5: G**eometrical features of hydrogen bonding interactions (distances (Å) and angles (°)) of complexes **1–4**.

| **Complex** | **D−H···A** | **D–H** | **H···A** | **D···A** | **∠D−H···A** |
|---|---|---|---|---|---|
| **1** | N(3A)−H(3AA)···O(7) | 0.89 | 2.42 | 3.165(6) | 141 |
| | N(3A)−H(3AB)···O(7)[a] | 0.89 | 2.09 | 2.918(6) | 155 |
| | N(2A)−H(2A)···O(6)[b] | 0.98 | 2.00 | 2.904(7) | 152 |
| | N(2B)−H(2B)···O(4)[c] | 0.98 | 2.19 | 3.141(7) | 162 |
| | N(2B)−H(2B)···O(5)[c] | 0.98 | 2.37 | 3.203(9) | 143 |
| | N(3B)−H(3BA)···O(8) | 0.89 | 2.37 | 3.09(2) | 138 |
| | O(7)−H(7C)···O(1A)[d] | 0.85 | 2.12 | 2.910(5) | 154 |
| | O(7)−H(7C)···O(2A)[d] | 0.85 | 2.29 | 2.906(5) | 130 |
| | O(2)−H(2)···O(7) | 0.87 | 2.57 | 3.081(3) | 122 |
| | O(2)−H(2)···O(8) | 0.82 | 1.92 | 2.695(3) | 157 |
| | N(2)−H(2A)···O(2)[e] | 0.98 | 2.31 | 3.153(3) | 143 |
| | N(2)−H(2A)···O(7)[e] | 0.98 | 2.19 | 2.912(3) | 130 |
| | N(5)−H(5A)···O(10) | 0.98 | 2.32 | 2.989(5) | 125 |
| | N(6)−H(6A)···O(13)[f] | 0.89 | 2.23 | 3.003(3) | 145 |
| | N(6)−H(6B)···O(8) | 0.89 | 2.23 | 3.039(3) | 152 |
| | O(13)−H(13A)···O(11) | 0.85 | 2.24 | 3.186(7) | 177 |
| **3** | N(2)−H(2)···O(14) | 0.98 | 2.13 | 3.07(2) | 162 |
| | N(2)−H(5)···O(16)[g] | 0.98 | 2.19 | 3.13(2) | 161 |
| **4** | N(2)−H(2)···O(12) | 0.98 | 2.18 | 3.08(2) | 151 |
| | O(8)−H(8)···O(4)[h] | 0.98 | 2.08 | 2.855(8) | 134 |

(D, donor; H, hydrogen; A, acceptor, symmetry transformation [a] = 1+x,y,z, [b] = 1/2+x,3/2-y,1/2+z, [c] = 1-x,1-y,1-z, [d] = -1+x,y,z, [e] = 1-x,1/2+y,1/2-z, [f] = x,3/2-y,-1/2+z, [g]= -1+x,3/2-y,-1/2+z, [h]= 1-x,y,3/2-z)

**Table S6:** List of some reported $\mu$-phenoxido/$\mu_3$-OR (R = Me/H) bridged and double $\mu_3$-OR (R = Me/H) bridged average Ni–O–Ni angles with their corresponding *J* values.

| Average $\mu$-phenoxido/$\mu_3$-OR (R = Me/H) bridged Ni–O–Ni angle (°) | *J* ($cm^{-1}$) | Average double $\mu_3$-OR (R = Me/H) bridged Ni–O–Ni angles (°) | *J* ($cm^{-1}$) | References |
|---|---|---|---|---|
| 93.685 | +6.32 | 97.1 | +0.22 | 20e |
| | | 97.34 | –8.8 | 20a |
| | | 97.63 | –4.6 | 20a |
| | | 97.92 | –4.6 | 20a |
| 92.26 | +4.28 | 100.255 | +10.51 | 20d |
| 92.995 | +14.56 | 98.67 | +7.57 | 20d |
| 93.105 | +12 | | | 21b |
| 98.085 | –6.2 | 98.055 | –1.2 | 23b |
| 98.09 | –6.4 | 98.45 | –0.71 | 23b |
| 90.955 | +5.5 | 101.49 | –8.6 | 23b |
| 99.99 | –5.2 | | | 23b |
| 100.245 | –3.7 | | | 23b |
| 91.2275 | +8.3 | 101.76 | –12.0 | 23b |
| 100.57 | –0.56 | | | 23b |
| 100.545 | +0.37 | | | 23b |
| 95.9525 | +5.87 | 97.47 | +12.3 | 21c |
| 89.7 | +0.66 | 101.88 | –0.51 | 21c |
| 101.74 | +4.20 | 97.22 | +11.50 | 24b |
| 94.29 | –4.80 | | | 24b |
| 98.3 | +0.64 | 97.57 | +8.41 | Complex **3** |
| 98.13 | –5.60 | 96.79 | +3.72 | Complex **4** |
| 99.56 | –9.39 | 98.62 | –5.18 | Complex 4 |

## Reference

1 (a) A. Biswas, M. G. B. Drew, C. Diaz, A. Bauzá, A. Frontera and A. Ghosh, *Dalton Trans*., 2012, **41**, 12200–12212; (b) B. Sarkar, M. S. Ray, Y.-Z. Li, Y. Song, A. Figuerola, E. Ruiz, J. Cirera, J. Cano and A. Ghosh, *Chem. Eur. J*., 2007, **13**, 9297–9309.