



Synthesis and Crystal Structure of Binuclear and Pentanuclear Nickel(II) Complexes Containing 4-salicylaldiminato)antipyrine Schiff base

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Abstract: The new title binuclear Ni (II) compound $[\text{Ni}_2 \text{L}_2(\mu - \text{OAc})(\text{H}_2\text{O})_2](\text{BPh}_4)$ (**1**) and the novel pentanuclear Ni (II) cluster $\{[\text{Ni}_5 \text{L}_8(\mu - \text{H}_2\text{O})_8](\text{BPh}_4)_2 \cdot 8\text{H}_2\text{O}\}$ (**2**) are formed from the reaction of an asymmetric Schiff base ligand **L** ($\text{L} = 4\text{-}(\text{salicylaldiminato})\text{antipyrine}$) with $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in the former or $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in presence of malonate in the later. Complex (**1**) consists of $([\text{Ni}_2 \text{L}_2(\mu - \text{OAc})(\text{H}_2\text{O})_2]^+$ cation) and one uncoordinated tetraphenylborate anion. The cation adopts a distorted octahedral arrangement around each metal center. In the binuclear unit both Ni(II) ions are linked through two phenolate ($\mu_2\text{-O}$) oxygen atoms of **L**, and two oxygen atoms of a bridging carboxylate group. Each Ni (II) coordinates to four oxygen atoms at the basal plane, two oxygen atoms from two bridging phenolate groups, one from pyrazolone ring and the last of an aqua molecule, and at the axial positions to a bridging carboxylate-O atom and an azomethine nitrogen atom. In the pentanuclear cluster (**2**) consisting of $[\text{Ni}_5 \text{L}_8(\mu - \text{H}_2\text{O})_8]^+$ cation and two tetraphenylborate anions, the core of the cation is assembled by four $[\text{Ni}(\text{N}_2\text{O}_2)]$ units, linked to the central Ni-ion by two bridging water molecules. The resulting coordination sphere for the external symmetry related nickel ions is a pseudo octahedron. The central Ni-atom unusually adopts dodecahedron geometry through its coordination to eight bridging water molecules. In complex (**1**) each Ni-atom is coordinated to one tridentate **L** ligand and in complex (**2**) each $[\text{Ni}(\text{N}_2\text{O}_2)]$ unit is coordinated to two bidentate **L** ligands. Inter- and intramolecular hydrogen bonds are present in both crystal structures.

Keywords: Ni(II) complex, Schiff base, dodecahedron, acetate, crystal structure

Introduction

Binuclear metal complexes have been an attractive area of researches in view of their significance as biomimetic catalyst in the process of oxygenation¹. In recent years, an increasing effort has been dedicated to the preparation of binuclear transition metal complexes containing Schiff base ligands.² Late transition elements complexes of this type have extensively been used as catalysts for a wide variety of reactions, including olefin polymerization³⁻⁶ and oxygen activation⁷⁻⁹. High nuclearity 3d-clusters derived from O- and N-donor ligands are currently of interest because of their magnetic properties. Pentanuclear Ni (II) complexes are very rare and the strategies for their synthesis are still under development. There are few pentanuclear Ni (II) clusters in the literature mainly concerning linear structures with Ni---Ni bonds¹⁰ or those cluster molecules which are placed in crystallographic

center and contain planar spirane metal core non-bonding metal---metal contacts.¹¹ The chemistry of nickel complexes derived from asymmetric multi-dentate Schiff base ligands has attracted particular interest because this metal can exhibit several oxidation states and such complexes have a wide role in bioinorganic chemistry and redox enzyme systems and may provide the bases of models for active sites of biological systems, or act also as catalysts^{12,13}. The Schiff base of 4-aminoantipyrine has anticancer and antibacterial properties as well as it is effective in enzymes simulation¹⁴⁻¹⁶, consequently, their important part for coordination chemistry¹⁷. The Schiff bases of 4-aminoantipyrine and their metal complexes have been widely investigated because of their biological, clinical and pharmaceutical applications^{18,19}. This type of Schiff base can in principle behave as both bidentate and tridentate ligand towards the metal center. However, few metal complexes containing 4-aminoantipyrine as a Schiff

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base ligand, have been structurally characterized and their coordination chemistry remains unexplored. Recently binuclear and tetranuclear cobalt complex containing 4-aminoantipyrine Schiff base were structurally characterized^{20,21}. Herein, we report the synthesis and crystal structure of the title complexes, which contain ligand L coordinating in a tridentate (1) or in a bidentate fashion (2).

Experimental Section

Materials and methods

All reagent grade chemicals used in this work were obtained commercially from Aldrich or BDH and used without any further purification. All manipulations were carried out under atmospheric pressure. Elemental analysis (C, H and N) was performed on a Vario El (III) elemental analyzer. FTIR spectra were recorded at room temperature with a Bruker IFS-25 OPUS/IR over the range from 400 to 4000 cm^{-1} with resolution of 4 cm^{-1} . The electronic absorption spectrum was recorded over the range 200 – 800 nm using Cary 5000 UV-VIS-NR spectrophotometer.

Synthesis

(4-Salicylaldiminato)antipyrine-EtOH (HL•EtOH)

Yellow crystals of Schiff base, HL, were prepared using previously described method^{22,2}. A mixture of 4-aminoantipyrine (2.0g, 9.8mmol) in 20 ml ethanol and salicylaldehyde (1.22g, 10.00mmol) in 10 ml ethanol were refluxed together. Complete reaction with near quantitative conversion to the product required a period of 2.0 h. After cooling to room temperature, the yellow precipitate formed was collected by suction filtration and recrystallized from hot ethanol as deep yellow microcrystals (yield 2.81g, 85%). The Schiff base was characterized by elemental analysis. Anal. Calc. for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_3$: C, 68.18; H, 6.25; N, 11.93; Found: C, 67.95; H, 6.25; N, 11.70.

$[\text{Ni}_2\text{L}_2(\mu - \text{OAc})(\text{H}_2\text{O})_2](\text{BPh}_4)_2$ (1)

A solution of HL (2.00mmol, 0.60g) in 15 ml ethanol and nickel(II) acetate (2.00mmol, 0.50 g) in 15 ml ethanol were refluxed together; after 2 h a green clear solution was formed. To the resulted solution was added a solution of sodium tetraphenylborate (2.00mmol, 0.68 g) in ethanol (5 ml) with stirring. Green solid was formed immediately, filtered and air dried. The green solid was dissolved in acetone and filtered; on slow

evaporation, green crystals were formed (yield 70%). The final product was characterized by elemental analysis, FTIR, UV-Vis and single crystal x-ray diffraction analysis. Anal. Calc. for $\text{C}_{62}\text{H}_{57}\text{BNi}_2\text{N}_6\text{O}_8$: C, 65.72; H, 5.00; N, 7.42; Found: C, 65.58; H, 5.40; N, 6.93. Suitable pale-green prismatic single crystals of (1) were obtained by slow diffusion of diethyl ether into an acetone solution at an ambient temperature within one day.

$\{[\text{Ni}_5\text{L}_8(\mu - \text{H}_2\text{O})_8](\text{BPh}_4)_2 \cdot 8\text{H}_2\text{O}\}$ (2)

A solution of HL (2.0mmol, 0.60g) and dithallium malonate (1.00mmol, 0.51g) in 15 ml ethanol and nickel(II) perchlorate (2.00mmol, 0.73 g) in 15ml ethanol were refluxed together, after 2 h, greenish-yellow clear solution was formed. To the resulted solution was added a solution of sodium tetraphenylborate (2.00mmol, 0.68g) in ethanol (5 ml) with stirring. Greenish-yellow solid was formed immediately, filtered and air dried. The greenish-yellow solid was dissolved in acetone and filtered; on slow evaporation of the solvent yellow-green crystals were formed (yield 40%). Suitable yellow-green prismatic single crystals of (1) were obtained by slow diffusion of diethyl ether into an acetone solution at an ambient temperature within one day.

Crystal structure determination

Crystals were obtained *via* diethyl ether diffusion into a solution of compound (1) or and (2) in acetone. The crystals were particularly well-formed pale green prisms for compound (1) and yellow green prisms for compound (2) which enabled the collection of a high-quality data set.

Data for the X-ray analysis of (1) were collected on an Oxford Diffraction Xcalibur3 four circles diffractometer equipped with CCD area detector and Mo K_α radiation (0.7107 Å) at 150 K. For complex (2) data collection was executed on an Oxford Diffraction XcaliburPX diffractometer equipped with CCD area detector and Cu K_α radiation (1.5418 Å) at 120 K. Collections and data reductions were carried out through the suite CrysAlisPro²⁴ together with the absorption correction implemented in the routine SCALE3 ABSPACK. The structures of the complexes were both solved by direct methods of the program SIR97²⁵ and then refined by full-matrix least squares against F^2 using all data (SHELX-2013)²⁶.

Geometrical calculations were performed with the program PARST²⁷ and molecular plots were produced with Ortep-3 for windows program (Farrugia, 1997)²⁸. The details of the crystallographic data and structure refinement for the complexes (1) and (2) are shown in Table 1.

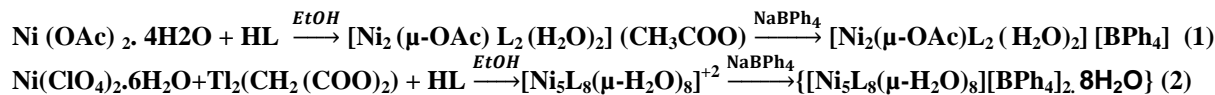
Table 1. Crystal data and structure refinement details for the complexes (**1** and **2**)

Empirical formula	C ₆₂ H ₅₇ BNi ₂ N ₆ O ₈ (1)	C ₁₉₂ H ₁₆₈ B ₂ Ni ₅ N ₂₄ O ₃₂ (2)
Formula weight	1142.37	3638.66
Temperature	150 K	120 K
Wavelength	0.71073	1.5418 Å
Crystal system	Monoclinic	Tetragonal
Space group (No.)	P2 ₁ /n(14)	P 4/n n c (126)
Unit cell parameters	a= 12.9117(7) Å b= 33.962(1) Å β = 108.09(6)° c= 13.4945(7) Å	a = 18.2627(3) Å, b = 18.2627(3) Å, c = 28.8467(9) Å
Cell volume	5625.1(5) Å ³	9621.1 (4) Å ³
Z	4	2
ρ _c	1.327Mg m ⁻³	1.693 Mg m ⁻³
μ	0.73mm ⁻¹	1.146 mm ⁻¹
F(000)	2384	3788
Crystal size	0.1x0.1x0.1mm	0.06× 0.05 × 0.02 mm
θ range for data collection	4.1-28.8°	4.6 – 66.6°
Reflections collected	20399	19886
Independent reflections	9887[R(int)=0.1071]	4218 [R(int) = 0.087]
Data / restraints / parameters	9934/0/724	4218 / 0 / 301
Goodness-of-fit on F ²	1.018	0.996
R indices (all data)	R ₁ =0.1594, wR ₂ =0.2062	R ₁ = 0.1514, wR ₂ = 0.2401

Results and Discussion

The new nickel title complex (**1**) was synthesized by the reaction of nickel acetate with HL Schiff base in ethanolic solution while, the novel

nickel title complex (**2**) was synthesized by the reaction of nickel perchlorate with HL Schiff base in presence of dithalium malonate in ethanol, where HL = 4-(salicylaldehydato) antipyrine, Scheme 1.



Scheme 1

The IR spectrum of the cationic complex exhibited strong absorptions at 1627 and 1565cm⁻¹ assignable to the carbonyl group of the pyrazolone ring, ν(C=O), and azomethine group (HC=N) of L, respectively. The first absorption band of the complex was shifted to the lower frequency for about 27cm⁻¹ relative to the free ligand (1654cm⁻¹) indicating that the ligand coordinates through the carbonyl oxygen of the pyrazolone ring. The second absorption was shifted to the lower frequency for about 26cm⁻¹ (for the free ligand 1591cm⁻¹) suggesting the involvement of the nitrogen atom of the azomethine group in the coordination. The absorptions appearing as shoulders at 1610 and 1457cm⁻¹ corresponds to the asymmetric and symmetric stretching of carboxyl group respectively.

The value of Δ [ν_{as}-ν_s] is 153cm⁻¹, comparatively smaller than 200cm⁻¹ indicating that the acetate group acts as a bidentate bridging ligand²⁹. The ν(OH) absorption at 3446cm⁻¹ indicates the presence of water molecules.

The UV-Vis spectrum of [Ni₂L₂(μ-OAc)(H₂O)₂](BPh₄) complex was obtained in acetone. The spectrum shows a broad band with a

shoulder at 413nm, the broadness may be attributed to the short contact between Ni-atoms.

Crystal Structure of

[Ni₂L₂(μ-OAc)(H₂O)₂](BPh₄) (**1**)

The crystal structure of the title complex (**1**) with atomic numbering scheme is presented as an ORTEP (Figure 1), while its crystal packing was shown in (Figure 2) and relevant bond distances and angles were given in (Table 2). From ORTEP presentation, the ligand L, acts as tris-chelate coordinating to the Ni atoms by two O and one N atom. Each, oxygen of the phenolate groups bridges the two Ni atoms (μ-O) so leading to Ni₂O₂ rhombic ring with Ni····Ni separation of 2.948(1) Å shorter than those reported by Koikawa³⁰. Each Ni atom has a distorted octahedral geometry with NiO₅ chromophore, the basal-planes, including two oxygen atoms from the bridging phenolate groups of two L ligands and another oxygen atom from the pyrazolone ring, while the fourth position is occupied by oxygen atoms of water molecules. The axial sites are occupied by one oxygen atoms from the bridging acetate group, and by an azomethine nitrogen atom of the ligand L. The acetate group acts

as a bidentate ligand bridging two Ni-atoms in the usual syn-syn fashion. The bridging (C37/O7/O8) carboxylate group features C-O bonds almost perfectly resonant [C37-O7 = 1.252(9) Å and C37-O8 = 1.257(8) Å] as already found in the related Ni (II) complexes^{31,32}. The central [Ni₂(μ-O)₂] moiety of the complex lies on an almost perfect plane, the molecule showing a virtual C₂ axes of symmetry passing through the center of that plane and the carboxylate carbon of the acetate group. The Ni-O-Ni bridging angles within this plane are 91.8(2) and 92.6(2)° for O2 and O4 respectively. The Ni1-O2-Ni2-O4 dihedral angle being 15.8(2)° and the mean planes of O6,O3,O2,O4 and O1,O5,O2,O4 are

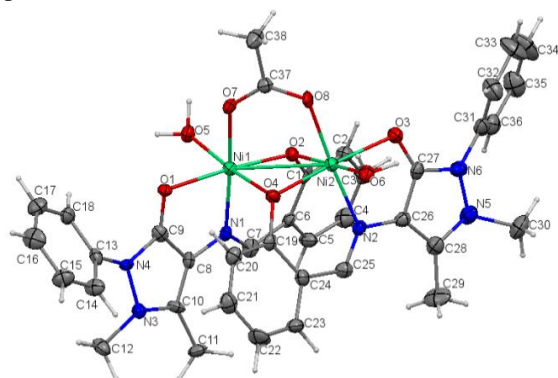


Figure 1. Molecular structure for the title complex (1) with the atomic numbering scheme (counterion omitted for clarity).

Further analysis of the crystal packing (Figure 2) reveals that this structure contains intermolecular hydrogen bond between coordinated water molecules of one molecule and the carboxylate oxygen atoms of the bridging acetate group and the oxygen atom of the pyrazolone ring of another molecule. The counter ion [BPh₄]⁻ exhibits its usual geometry.

almost coplanar and form angles of 4.42° and 8.13° respectively with the aromatic rings.

The di-(μ-phenoxo) and (μ-acetato) may have an effect in holding both nickel atoms very close to each other (2.948(1)Å), distance which is considered shorter than the sum of the van der Waals radii (3.26Å)³³, but still a little bit longer than 2.697 (2) and 2.814(2)Å reported by Elisabeth et al³⁴ and shorter than those reported for [Ni₂(bimp)(μ-OAc)₂]⁺ cation (3.422(4)) where Hbimp = 2,6-bis[(bis(1-methylimidazol-2-yl)methyl)-amino methyl]-4-methylphenol³⁵ and for [Ni₂(L1)(N₃)₄].CH₃CN (3.330(1)) where L1= N,N'-bis(3-aminopropyl)-ethylenediamine³⁶

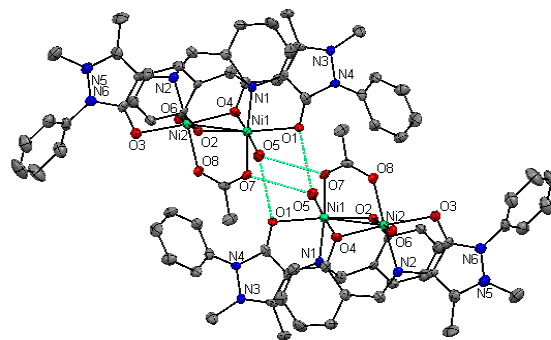


Figure 2. View of the crystal structure of complex (1) showing intermolecular hydrogen bonds.

Table 2: Some selected bond distances (Å°) and bond angles (°) of metal complex (1).

Bond	Length (Å°)	Bond	Angle (°)
Ni(1)–O(2)	2.006(4)	O(1)–Ni(1)–O(5)	86.8(2)
Ni(1)–N(1)	2.037(4)	N(1)–Ni(1)–O(4)	91.9(2)
Ni(1)–O(7)	2.034(4)	O(1)–Ni(1)–O(7)	91.0(2)
Ni(1)–O(4)	2.092(4)	N(1)–Ni(1)–O(5)	93.8(2)
Ni(1)–O(5)	2.093(4)	O(2)–Ni(1)–O(4)	85.4(1)
Ni(1)–O(1)	2.118(4)	N(1)–Ni(1)–O(7)	174.6(2)
Ni(1)–Ni(2)	2.948(1)	O(2)–Ni(1)–O(5)	94.0(2)
Ni(2)–O(2)	2.098(4)	O(1)–Ni(1)–O(2)	174.7(2)
Ni(2)–N(2)	2.038(4)	O(2)–Ni(1)–O(7)	94.3(2)
Ni(2)–O(4)	1.984(4)	O(1)–Ni(1)–O(4)	94.2(2)
Ni(2)–O(8)	2.044(4)	O(4)–Ni(1)–O(5)	174.3(2)
Ni(2)–O(6)	2.084(4)	O(4)–Ni(1)–O(7)	86.8(2)
Ni(2)–O(3)	2.129(4)	O(4)–Ni(2)–O(6)	91.1(2)
		O(3)–Ni(2)–O(8)	93.5(2)
		O(4)–Ni(2)–O(8)	91.0(2)
		O(3)–Ni(2)–O(6)	90.0(2)
		O(6)–Ni(2)–O(8)	88.5(2)
		O(3)–Ni(2)–O(4)	175.5(2)

Crystal Structure of

$\{[\text{Ni}_5 \text{L}_8(\mu - \text{H}_2\text{O})_8](\text{BPh}_4)_2 \cdot 8\text{H}_2\text{O}\} (2)$

According to the x-ray diffraction data, the pentanuclear nickel (II) cluster (2), forms planar metal core from four peripheral nickel atoms and a central nickel atom. The cluster is highly symmetric, featuring an-overall 422 (D_4) crystallographic point group symmetry, the central metal ion lying on the 4-fold crystallographic axes and the peripheral nickel ions lying on additional perpendicular 2-fold crystallographic axes. Each of the peripheral four nickel (II) atoms displays a pseudo octahedral $[\text{Ni}$

(N_2O_4) coordination, with identical bond lengths and angles. The non-bonding metal-metal separations are $\text{Ni1} \dots \text{Ni2} = 3.5296(9) \text{ \AA}$ and $\text{Ni1} \dots \text{Ni1} = 4.992(1) \text{ \AA}$. Each peripheral Ni (II) atom was ligated by two bidentate Schiff base ligands, through the azomethine nitrogen atom and the oxygen atom of the phenolate group. The coordination sphere is completed by two oxygen atoms from two water molecules bridging the central Ni (II) atom (Figure 3a).

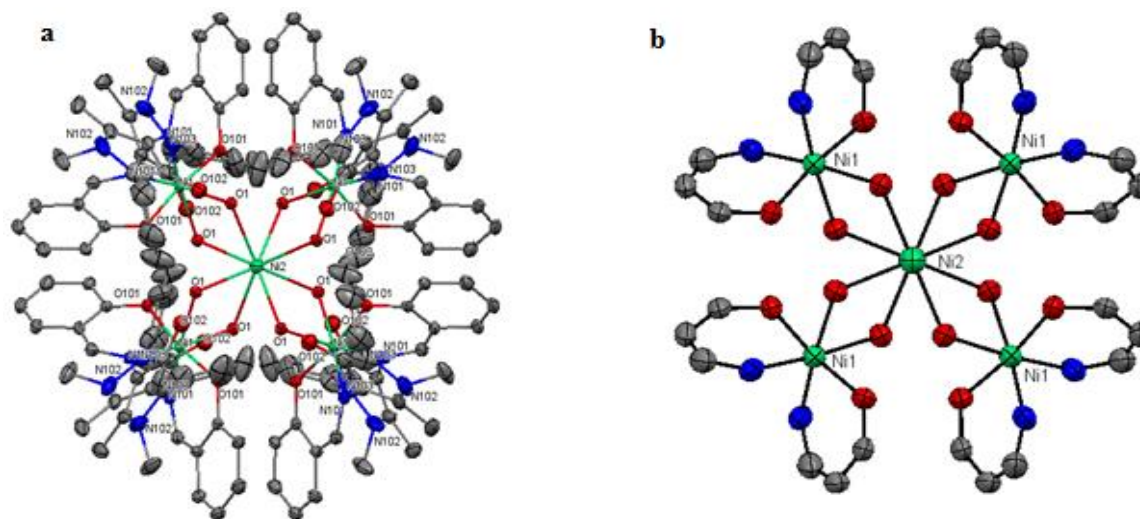


Figure 3. a. An ORTEP view of cationic complex 2 with the atom-numbering scheme. All hydrogen atoms, disordered water cluster and counterions have been omitted for clarity.

Displacement ellipsoids are plotted at the 20% probability level. b. Cationic complex.2 Showing the ligating atoms only.

The central nickel (II) atom unusually exhibits a coordination number-8 through its coordination to eight-bridging aqua molecules, with identical bond lengths ($\text{Ni2}-\text{O1} = 2.432(3) \text{ \AA}$) and different bond angles (Table 3), displaying a dodecahedron $[\text{NiO}_8]$ coordination sphere (Figure 3b). The two O-atoms of two phenolate groups [$\text{Ni1}-\text{O101} = 1.988(1) \text{ \AA}$] belonging to two Schiff base ligands, one O-atom of a bridging water molecule [$\text{Ni1}-\text{O1} = 2.147(2) \text{ \AA}$] and

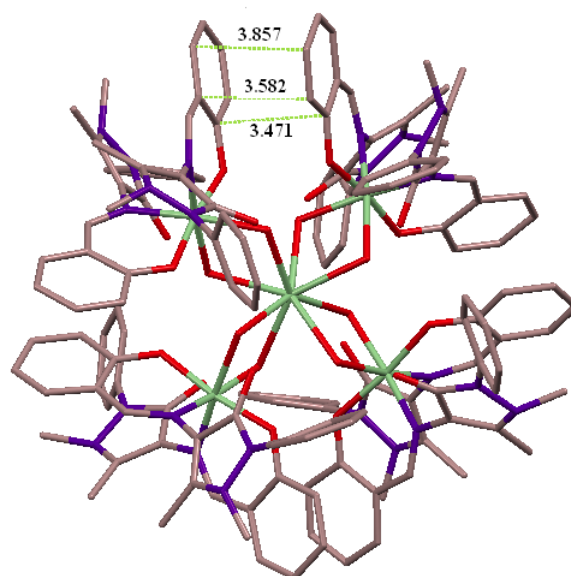
the N-atom of an azomethine group [$\text{Ni1}-\text{N101} = 2.0140(5) \text{ \AA}$] belonging to the Schiff base ligand are disposed at the basal-plane of an octahedron. These bond distances of Ni1 with L donor atoms are close to that reported for complex1 and that reported by Wasson³⁷. The axial sites of the octahedron were occupied by one O-atom from another bridging aqua molecule and N-atom of an azomethine group of another Schiff base ligand.

Table 3: Some selected bond distances (Å) and bond angles (°) of metal complex (2)

Bond	Length (Å)	Bond	Angle (°)
Ni1–O1	2.147(4)	N1–Ni1–O4	92.1(2)
Ni1–O1	1.985(4)	N1–Ni1–O5	93.7(2)
Ni1–N101	2.040(5)	N1–Ni1–O7	174.7(2)
Ni2–O1	2.432(3)	O1–Ni1–O2	174.6(2)
		O1–Ni1–O4	94.3(1)
		O4–Ni1–O7	86.6(2)
		O3–Ni2–O8	93.5(2)
		O3–Ni2–O6	90.0(2)
		O3–Ni2–O4	175.5(2)
		O4–Ni2–O6	91.2(2)
		O4–Ni2–O8	93.5(2)
		O6–Ni2–O8	88.5(2)

The remarkable difference in bond lengths between Ni1–O1 and Ni2–O1 bridged by an aqua molecule may due to the steric and / or electronic repulsion between the oxygen atoms of the water molecules. Donors that increase the electron density on the metal tend to reduce its acceptor properties, thus lowering the Ni–O bond order. To the best of our knowledge the title complex (2) is unique compared with known pentanuclear nickel (II) clusters, because it is the only reported pentanuclear cluster with a nickel atom featuring coordination number-8, and an overall 422 molecular symmetry. The packing structure of the title complex (2) reveals that the structure contains disordered water clusters

featuring H-bond contacts of O...O type as well as of CH...O type, involving the H-atoms of the benzene rings of the ligand **L**. Also, bridging water molecules form H-bonds with pyrazolone O-atoms (O1---O101 = 2.164 Å) and phenolate O-atoms (O1---O102 = 2.587 Å) of the **L** ligands. Adjacent Schiff base ligands are linked by π - π interactions through benzene rings. The shortest distances between C atoms of the neighboring benzene rings of the Schiff base ligands are 3.582 Å for C106...C102, 3.857 Å for C105...C103 and 3.471 Å for C101...C101. These values indicates a moderate to strong face-to-face π - π interactions (Figure 4).

**Figure 4. View of the crystal structure of complex 2 showing π - π interactions.**

Conclusion

We have reported herein two new transition metal complexes of Ni (II) prepared from the same

Schiff base ligand incorporating a *N,O,O* and *N,O* donor sets for complexes (1) and (2) respectively. The most striking result is the formation of a highly

symmetric pentanuclear cluster, featuring an overall 422 molecular symmetry and a central octa-coordinated nickel (II) ion. The remarkable difference in bond length between the peripheral Ni-O1 and the central Ni-O1 bridged by water molecules may be due to steric factors, but we could not rule out the electronic factors. We also conclude that the type of the counter ion of the metal salt plays an important role in tailoring the final product.

Supplementary Materials

Additional materials are available from the Cambridge Crystallographic Data Center comprises thermal parameters and remaining bond distances and angles (CCDC No. 921257 and 932926) for complexes 1 and 2 respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK (fax +44(0)1223-336033; e- mail: deposit@ccdc.cam.ac).

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