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Hydrogen-bond assisted stabilization of the less favored conformation of a tridentate Schiff base ligand in dinuclear nickel(II) complex: An experimental and theoretical study

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ABSTRACT

The Schiff base ligand, HL (2-[1-(3-methylamino-propylimino)-ethyl]-phenol), the 1:1 condensation product of 2-hydroxy acetophenone and N-methyl-1,3-diaminopropane, has been synthesized and characterized by X-ray crystallography as the perchlorate salt [H₂L]ClO₄ (**1**). The structure consists of discrete [H₂L]⁺ cations and perchlorate anions. Two dinuclear Ni^{II} complexes, [Ni₂L₂(NO₂)₂] (**2**), [Ni₂L₂(NO₃)₂] (**3**) have been synthesized using this ligand and characterized by single crystal X-ray analyses. Complexes **2** and **3** are centrosymmetric dimers in which the Ni^{II} ions are in distorted fac- and mer-octahedral environments, respectively, bridged by two μ_2 -phenolate ions of deprotonated ligand, L. The plane of the phenyl rings and the Ni₂O₂ basal plane are nearly coplanar in **2** but almost perpendicular in **3**. We have studied and explained this different behavior using high level DFT calculations (RI-BP86/def2-TZVP level of theory). The conformation observed in **3**, which is energetically less favorable, is stabilized via intermolecular non-covalent interactions. Under the excitation of ultraviolet light, characteristic fluorescence of compound **1** was observed; by comparison fluorescence intensity decreases in case of compound **3** and completely quenched in compound **2**.

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1. Introduction

Polynuclear metal complexes and ligands facilitating their formation have been extensively investigated due to their potential applications in many fields of chemistry [1–10]. The essential requirements for the formation of such polymeric complexes are an unsaturated coordination environment of the single-coordinated metal ion and the presence of bridging atoms or groups. The salicylaldehyde derived tridentate N,N,O donor Schiff bases that can bridge two metal ions through the phenolate oxygen and also with bridging anions (e.g. N₃⁻, R-CO₂⁻, NO₃⁻, NO₂⁻ etc.) are an excellent combination for the synthesis of such species [11-15]. It has been shown that the competitive as well as the cooperative role of the bridging anion and phenoxo group is very important in constructing the polymeric architecture [12,16–21]. However, the tridentate Schiff base can coordinate to metal ions either in meridional or facial configurations and this difference in configuration might be very important in building a desired polynuclear complex. We investigated the configurations of reported phenoxo bridged dinuclear Ni^{II} complexes of tridentate ligands [12,16–18,22–24]. The study of such compounds is of great interest in various aspects of chemistry since nickel compounds are present in the active sites of urease and they are used extensively in the design and construction of new magnetic materials [25,26]. It is interesting to note that in these complexes the ligand is meridionally coordinated when co-ligands are monodentate [16,27,28] and so can occupy the two trans positions. However, a chelating co-ligand (e.g. acetate, nitrate etc.), that must span cis positions, results in a facial coordination of the Schiff base ligand with a folded conformation [12,18]. Recently it has been shown that non-covalent interactions between the molecules in a supramolecular system are capable of directing the formation of a particular geometrical isomer [29] or even affecting the primary structure of the metallic building blocks to support the most-stabilized supramolecular architecture [30].

In this paper, we report the synthesis of a Schiff base ligand, 2-[1-(3-methylamino-propylimino)-ethyl]-phenol (HL) which is the 1:1 condensation product of 2-hydroxyacetophenone and N-methyl-1,3-diaminopropane (Scheme 1) and two dinuclear Ni^{II} complexes, $[Ni_2L_2(NO_2)_2]$ (2) and $[Ni_2L_2(NO_3)_2]$ (3). The perchlorate salt, of the ligand, $[H_2L]ClO_4$ (1) and the complexes have been characterized by single crystal X-ray crystallography. The structure of 3 shows a mer-coordination of the Schiff base in spite of the



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Conditions: a) MeOH/r.t/ 1h; b) 1.Ni(ClO₄).6H₂O/MeOH/r.t/ 10 min 2.NaNO₂ in MeOH/ : H₂O 9:1/ r.t; c) Ni(NO₃)₂.6H₂O/r.t/ 30 min

Scheme 1. Synthetic route to HL, 2 and 3.

presence of chelating nitrate as co-ligand. In addition, it shows an unusual disposition of the phenyl rings with respect to the bridging Ni_2O_2 plane which are unprecedented in Ni^{II} dinuclear complexes of tridentate Schiff base ligand. In order to explain these experimental observations, we have performed a theoretical study using DFT calculations. In particular, we have used the BP86 functional and the def2-TZVP basis set, using the resolution of the identity method (RI-BP86/def2-TZVP). The results establish that an intermolecular H-bond is responsible for the stabilization of the less favored conformation.

2. Experimental

2.1. Starting materials

All the chemicals were of reagent grade and were used without further purification.

2.2. Synthesis of the Schiff-base ligand 2-[1-(3-methylaminopropylimino)-ethyl]-phenol (HL)

The Schiff base ligand, HL, (Scheme 1) was prepared by the condensation of 2-hydroxyacetophenone (0.60 mL, 5 mmol) and Nmethyl-1,3-propanediamine (0.52 mL, 5 mmol) in methanol (10 mL) under reflux for an hour. The Schiff base ligands were not isolated and the yellow colored methanolic solution was used directly for complex formation.

2.3. Synthesis of $[H_2L]ClO_4(1)$

To prepare the perchlorate salt of the Schiff base, perchloric acid (1 mmol 0.06 mL) was added into the methanol solution of ligand HL, (1 mmol, 20 mL) and mixture was stirred for an hour. The solid obtained was dissolved in water. The block shaped pale yellow X-ray quality single crystals were obtained by diffusion of methanol to this aqueous solution. Yield: 0.4720 g (77%). *Anal.* Calc. for C₁₂H₁₉N₂O₅Cl (306.73): C, 46.99; H, 6.24; N, 9.13. Found: C, 46.72; H, 6.31; N, 9.24%. IR: v(N-H) = 3182, v(C=N) = 1614, $v(ClO_4) = 1108 \text{ cm}^{-1}$. ¹H NMR((DMSO-d₆, 300 MHz); 16.09 (s, 1H) OH; 6.77–6.71(m, 1H, 1H) C13-H and C14-H; 7.25 (dt, 3*J* = 8.1 Hz, 4*J* = 1.5 Hz, 1H) C15-H; 7.62(dd, 3*J* = 7.5 Hz, 4*J* = 1.5 Hz, 1H) C16-H; 2.97 (t, *J* = 10.5 Hz, 2H) C20-H; 3.58 (t, *J* = 6.6 Hz, 2H) C22-H; 2.00(p, *J* = 7.5 Hz, 2H) C21-H; 2.56 (s, 3H) 24CH₃; 2.32 (s, 3H) 181CH₃.

2.4. Synthesis of $[Ni_2L_2(NO_2)_2]$ (2)

 $Ni(ClO_4)_2 \cdot 6H_2O$ (0.582 g, 2 mmol), dissolved in 10 mL of methanol, was added to a methanolic solution (10 mL) of the ligand (HL) (2 mmol) with constant stirring. After 10 min, a methanol-water

solution (9:1, v/v) of NaNO₂ (0.138 g, 2 mmol) was added to it. The color of the solution turned to deep green. By slow evaporation of the resulting solution at room temperature, green colored X-ray quality, rectangular shaped, single crystals were obtained in 2 days. Yield: 0.444 g(72%). Anal. Calc. for $C_{24}H_{34}N_6Ni_2O_6(619.95)$: C, 46.50; H, 5.53; N, 13.56. Found: C, 46.64; H, 5.35; N, 13.61%. UV–Vis (methanol): λ_{max} (ϵ_{max}) = 650, 1003 nm (16.2, 12.4 dm³ mol⁻¹ cm⁻¹). IR: v(N-H) = 3256, v(C=N) = 1614, $v(NO_2)$ = 1319, 1159, 856 cm⁻¹, μ_{eff} = 2.89 B.M.

2.5. Synthesis of [Ni₂L₂(NO₃)₂] (3)

Compound **3** was obtained by similar procedure as **2**. Ni(-NO₃)₂·6H₂O (0.582 g, 2 mmol), dissolved in 10 mL of methanol, was added to a methanolic solution (10 mL) of the ligand (HL) (2 mmol). Green solution was appeared by constant stirring about 30 min. It was filtered and filtrate was left to stand in air. Overnight, the plate-shaped greenish-blue X-ray quality single crystals started to appear at the bottom of the vessel and were collected after 2 days. Yield: 0.4874 g (75%). Anal. Calc. for C₂₄H₃₄Ni₂N₆O₈ (651.95): C, 44.21; H, 5.26; N, 12.89. Found: C, 44.33; H, 5.15; N, 12.75%. UV-Vis (methanol): λ_{max} (ε_{max}) = 632, 1002 nm (21.2, 16.8 dm³ mol⁻¹ cm⁻¹). IR: v(N–H) = 3256, v(C=N) = 1612, v(NO₃) = 1287 cm⁻¹, μ_{eff} = 2.91 B.M.

2.6. Crystallographic studies

Crystal data and refinement details for **1–3** are given in Table 1. Independent data were collected with Mo K α radiation at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the CRYSALIS program [31]. The structures were solved using direct methods with the SHELXS-97 program [32]. The non-hydrogen

Table 1

Crysta	l data	and	refinement	details of	complexes	1 , 2 a	nd	3
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Compound	1	2	3
Formula Formula weight	C ₁₂ H ₁₉ ClN ₂ O ₅ 306.74	C ₂₄ H ₃₄ N ₆ Ni ₂ O ₆ 619.95	C ₂₄ H ₃₂ Ni ₂ O ₈ 649.93
T (K)	150	150	150
Space group	I2/a	P21/c	ΡĪ
Crystal system	monoclinic	monoclinic	triclinic
Crystal size (mm)	$0.05 \times 0.05 \times 0.30$	$0.03 \times 0.03 \times 0.27$	$0.05\times0.17\times0.19$
a (Å)	21.247(3)	12.6539(4)	9.1077(7)
b (Å)	8.394(14)	12.6656(4)	9.8769(8)
c (Å)	16.358(3)	16.6108(5)	16.1897(12)
α(°)	(90)	(90)	81.991(7)
β (°)	97.061(14)	96.405(3))	86.289(6)
γ(°)	(90)	(90)	71.385(7)
V (Å ³)	2895.3(8)	2645.58(14)	1366.39(18)
Ζ	4	4	2
D _{calc} (g/cm ³)	1.403	1.556	1.585
μ (mm ⁻¹)	0.284	1.474	1.437
F(000)	1288	1296	680
Total reflections	9617	18087	9630
Unique reflections	4176	7663	7509
Observed data ([I > 2σ(I)]	2072	4911	3060
Number of	parameters refined	183	347
362			
R _{int}	0.037	0.036	0.046
R indices (all	$R_1 = 0.0696$	$R_1 = 0.0305$	$R_1 = 0.0454$
data)	$WR_2 = 0.1695$	$WR_2 = 0.0634$	$WR_2 = 0.0556$

atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms bonded to N(19) and N(23) in **1** were located clearly in a difference Fourier map but then refined in calculated positions. Empirical absorption corrections were carried out using the ABSPACK program [33]. The structures were refined on F^2 using SHELXL-97 [32].

2.7. Theoretical methods

The geometries of all complexes studied in this work were fully optimized at the RI-BP86/def2-TZVP level of theory using the program TURBOMOLE version 5.7 [34]. The RI-DFT method applied to the study of weak interactions is considerably faster than the DFT and the interaction energies and equilibrium distances are almost identical for both methods [35]. The AIM analysis [36,37] of the dimer has been performed by means of the AIM2000 version 2.0 program [38] using the BP86/6-31+G^{*} wavefunction and the geometry obtained from the crystallographic coordinates. This lower theoretical level has been used in order to keep the calculation approachable

2.8. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm⁻¹) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1400– 200 nm) were recorded in a Hitachi U-3501 spectrophotometer. Magnetic susceptibility measurements at 300 K were carried out with a Sherwood Scientific Co., UK magnetic susceptibility balance and diamagnetic corrections were made using Pascal's constants. Fluorescence measurements were performed using a Perkin–Elmer LS55 spectrofluorimeter. The ¹H NMR spectra at 300 MHz were recorded in DMSO-d₆ on a Bruker DRX 300 Spectrometer. The numbers in parentheses after the H atoms in the NMR spectral data are the numbers of carbon atoms with which the hydrogen atoms are attached, as in respective Ortep-3 diagrams.

3. Results and discussion

3.1. Synthesis of the compounds

The tridentate ligand (HL) was synthesized in the usual way: reacting the diamine (N-methyl-1,3-propanediamine) with 2hydroxyacetophenone in 1:1 molar ratios in methanol medium [12]. We could not grow X-ray quality single crystals of this compound. However, we succeeded in obtaining single crystals of its perchlorate salt, $[H_2L]ClO_4$ (1) by adding one equivalent of perchloric acid. The Schiff bases derived from N-methyl-1,3-propanediamine and salicylaldehyde are expected to produce Ni^{II}-complexes with octahedral geometry as was found previously [12,39]. In the 1:1 complex, the mono-negative chelating ligand can coordinate only to three coordination sites and therefore, there is a high possibility of formation of different type polynuclear structures, bridged by the phenoxo- and/or anionic co-ligand to satisfy the coordination number of Ni^{II} [12,18]. In the present report, we synthesized two Ni^{II} complexes of Schiff base HL with nitrite (2) and nitrate (3) as anionic co-ligands. Both complexes were obtained readily by reacting HL with the respective Ni^{II} salt and both contain a phenolate oxygen bridged dimeric structure but the configurations around the metal centre and the position of phenyl rings relative to the Ni₂O₂ basal plane show interesting differences.

3.2. IR spectra of the compounds and magnetic moments

In the IR spectra there is a broad band at 3182 cm^{-1} for compound **1** and a sharp band at 3297 and 3256 cm^{-1} for complexes 2 and 3, respectively, characteristic of the N-substituted amine group in the Schiff base ligands. This lowering of frequency of N-H vibrations in 1 and 3 corroborates their participation in intermolecular hydrogen bonding. A strong and sharp band due to azomethine v(C=N) appears at 1614, 1614, and 1612, cm^{-1} for compounds 1–3, respectively. In the IR spectra of complex 1, the appearance of a broad single peak centering at 1108 cm⁻¹ indicates the presence of ionic perchlorate. In the spectra of complex 2, absorption bands at 1319, 1159, and 856 cm⁻¹ are tentatively assigned to $v_s(NO_2)$, $v_{as}(NO_2)$, and $\delta(NO_2)$, respectively. The separation of wave numbers between the v_{as} and v_s band are 160 cm⁻¹ which substantiates the symmetric chelating coordination of nitrite ion [21]. In complex 3, two sharp bands at 1470 and 1290 cm⁻¹ assigned to $v_{as}(NO_3)$ and $v_s(NO_3)$, respectively, indicate the presence of chelating coordination of NO_3^- ion.

The room temperature magnetic moment of complexes **2** and **3** are 2.89 and 2.91 BM which is close to 2.83 BM, fits well with the spin-only value for the discrete magnetically non-coupled nicke-l(II) system as was also observed in similar systems.

3.3. Photophysical properties of the compounds

The electronic spectra of these compounds are recorded in methanol solution. The electronic spectra show absorption bands at 632 and 1002 nm for compound 2 and 650 and 1003 nm for 3. These bands are assigned to the spin allowed transitions ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$, ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(P)$, respectively. The higher energy d-d bands are obscured by strong ligand to metal charge-transfer transitions. The electronic absorption spectrum of the protonated ligand (1) consists of two relatively intense bands centered at 250 and 320 nm assigned to the $\pi - \pi^{\uparrow}$ transitions of the benzene ring of acetophenone and the azomethine group, respectively. Upon coordination of the ligand, the absorption band at about 320 nm disappears from the UV-Vis spectra of complexes 2 and 3 indicating that the nitrogen atom of azomethine is involved in coordination to the metal ion. The intraligand $\pi - \pi^*$ transition of the benzene ring remains almost the same in the complexes and appears at 250 and 252 nm for complexes 2 and 3, respectively. Moreover, the new bands observed at 380, and 355 nm for complex **2** and **3**, respectively, are assigned to those of $L \rightarrow M$ charge-trans-



Fig. 1. Fluorescence spectra of compounds 1, 2 and 3.

fer transitions which are characteristic of the transition metal complexes with Schiff base ligands [40].

3.4. Fluorescence properties of the compounds

Fig. 1 shows the fluorescence emission spectra of protonated ligand (H_2L^+) with perchlorate anion and that of the two complexes. As can be seen, the ligand showed an emission maximum at \sim 433 nm in CH₃OH solution when excited at \sim 320 nm. This fluorescence behavior of the ligand is in agreement with the presence of the phenyl ring in the Schiff base ligand [40,41]. The nickel complex 3 with nitrate as co-ligand also exhibits an emission maximum at \sim 453 nm but the intensity is decreased compare to 1. However, in complex **2** where nitrite is the co-ligand, the fluorescence intensity is completely guenched under the same experimental conditions. Thus the fluorescence emission intensity of the ligand decreases depending upon the co-ligand in the metal complexes. The efficient quenching ability of the nitrite ion is well documented [42,43]. The red shift of band position of the complex **3** is observed (Fig. 1) compared with that of the ligand due to ligand to metal charge transfer. Evidently, the metal ion decreases the intensity of the fluorescence emission due to a consequent stabilization of the weak emissive $n\pi^*$ singlet excited state with respect to the strong emissive $\pi\pi^{T}$ state [44].

3.5. Description of the crystal structures of compounds 1-3

3.5.1. Compound 1

The structure of **1** consists of discrete $[H_2L]^+$ cations and perchlorate anions. The ORTEP view is shown in Fig. 2 and the bond distances and angles are given in Table S1 (supporting information). The secondary amine group of the compound, N(23) is protonated. The phenolic group and the imine nitrogen N(19) atom form a strong intramolecular hydrogen bond. The dimensions of this hydrogen bond from N(19)–H to O(11) are N–H···O = 142°, H···O = 1.79 Å and N···O = 2.525 Å. The C(12)–C(17)–C(18)–N(19) torsion angle is 1.0° clearly to facilitate the formation of the hydrogen bond. Interestingly, the hydrogen atom is located not on O11 but on N19. The C18–N19 bond distance of 1.292 Å indicates a double bond is retained between them. The C–O(11) bond length is 1.314(3) indicative of a C–O[–] bond so the overall charge on the cation is +1. The location of this hydrogen atom will be further described in the theoretical study.

Both hydrogen atoms on N(23) form hydrogen bonds to oxygen atoms, listed in Table 3, viz H(23A) to O(11) of another (3/2 - x, y, y)-z) molecule to form a $R_2^2(20)$ H-bonded dimer and H(23B) to O(31) (1 - x, -y, -z) of perchlorate ion with dimensions N-H···O = 159, 162°, H···O = 1.86, 2.19 Å and N···O = 2.720, 3.056 Å, respectively. The H-bonded dimers form a one-dimensional zigzag chain, (Fig. 2, bottom). The C-H/ π distance of 2.98 Å from C(181)–H(18C) of methyl group to the π -cloud of phenyl ring of other molecule (1.5 - x, 0.5 - y, 0.5 - z) with gamma angle = 23.16° may indicate that weak C–H/ π noncovalent interactions participate in the formation of the 1D chain. The other feature of note in the potentially terdentate ligand is that while O(11) and N(19) are in close proximity and could bind to a metal, N(23) is twisted well out of a possible third chelating site as is apparent in Fig. 2. Upon complex formation, there is a slight increase in the C-O(11) bond lengths (1.332(2), and 1.342(4) Å in 2 and **3**, respectively, compared to 1.314(3) Å in **1**). Other bond lengths remain similar.

3.5.2. Compounds 2 and 3

Both complexes consist of μ_2 -phenoxo bridged dimeric molecules (Fig. 3). In the structures of both **2** and **3** there are two centrosymmetric independent dimers, denoted as **A** and **B** with similar geometries which are compared in Table 2. The dimeric



Fig. 2. Top: The structure of the [HL]^{*} cation in 1 with ellipsoids at 30% probability. The intermolecular hydrogen bond is shown as a dotted line. Bottom: the 1D zig-zag chain structure formed by C-H/π and hydrogen bonding interactions in 1.



Fig. 3. The centrosymmetric dimeric structure of 2 (left) and 3 (right) with ellipsoids at 30% probability. There are two dimers in both 2 and 3 with equivalent structures, only one is shown.

Table 2	
Selected molecular dimensions in ${\bf 2}$ and ${\bf 3}$, distances (Å), angles (°).	

Complex	2 ª	2B	3A	3B
Ni(1)-O(11)	1.992(1)	1.998(1)	2 .002(2)	2.027(2)
Ni(1)-N(19)	2.017(1)	2.025(2)	2.054(3)	2.040(3)
Ni(1)-N(23)	2.101(2)	2.098(2)	2.065(3)	2.059(2)
$Ni(1) - O(11)^{a}$	2.085(1)	2.101(1)	2.044(2)	2.036(2)
Ni(1)-O(3)	2.157(1)	2.150(1)	2.233(2)	2.212(2)
Ni(1)-O(1)	2.123(1)	2.126(1)	2.118(2)	2.110(2)
O(11)-Ni(1)-N(19)	91.5(1)	91.6(1)	88.3(1)	87.4(1)
O(11)-Ni(1)-N(23)	96.9(1)	99.9(1)	172.9(1)	175.9(1)
N(19)-Ni(1)-N(23)	86.4(1)	86.0(1)	98.7(1)	96.7(1)
$O(11)-Ni(1)-O(11)^{a}$	81.1(1)	79.6(1)	82.3(1)	81.9(1)
N(19)-Ni(1)-O(11) ^a	172.4(1)	171.1(1)	88.3(1)	89.6(1)
N(23)-Ni(1)-O(11) ^a	92.9(1)	94.4(1)	98.6(1)	98.5(1)
O(11)-Ni(1)-O(3)	100.1(1)	99.9(1)	83.6(1)	84.4(1)
N(19)-Ni(1)-O(3)	91.8(1)	92.3(1)	162.7(1)	159.5(1)
N(23)-Ni(1)-O(3)	163.0(1)	160.2(1)	89.4(1)	89.7(1)
$O(3) - Ni(1) - O(11)^{a}$	91.0(1)	90.4(1)	105.7(1)	107.7(1)
O(11)-Ni(1)-O(1)	158.1(1)	158.0(1)	88.5(1)	89.1(1)
N(19)-Ni(1)-O(1)	94.5(1)	94.4(1)	104.9(1)	101.3(1)
N(23)-Ni(1)-O(1)	104.5(1)	101.6(1)	88.9(1)	89.7(1)
$O(1) - Ni(1) - O(11)^{a}$	93.1(1)	94.3(1)	163.7(1)	165.5(1)
O(3) -Ni(1)-O(1)	58.7(1)	58.7(1)	59.7(1)	59.9(1)

^a Represents symmetry element -x, 1 - y, -z in 2A, 1 - x, -y, -z in 2B, 1 - x, 2 - y, 1 - z in 3A and 1 - x, 1 - y, -z in 3B.

structures of **2A** and **3A** are shown in Fig. 4 and those of **2B** and **3B** in Fig. S2 (Supplementary information).

In both complexes the nickel atoms are six-coordinate with octahedral environments significantly distorted primarily by the small bite angle of 58.72(5)° and 58.74(5)° at the bidentate nitrite in **2A** and **2B** and of 59.7(1) and 59.9(1)° at the chelating nitrate in 3A and 3B, respectively. In addition the metal is bonded to the three donor atoms of L, the secondary amine nitrogen N(23), the imine nitrogen N(19) and the phenolate oxygen O(11) together with the oxygen atom O(11)' (' = -x, 1 - y, -z in 2A, 1 - x, -y, -z in 2B, 1 - x, 2 - y, -z in 3A and 1 - x, 1 - y, -z in 3B) of a second ligand to form the double μ_2 -phenolate bridged dimer. As usually found in this type of double oxo-bridged Ni(II) dimers, the bridging Ni–O(11)^y bond lengths are slightly longer than the corresponding chelating Ni–O(11) bond distances (Table 2) making the Ni₂O₂ core slightly asymmetric. The two Ni atoms are separated by 3.100(1) and 3.150(1) Å for **2A** and **2B** and 3.047(7) and 3.069(5) Å for **3A** and **3B**, respectively. The bridge angles are of 98.93(5) and

100.40(5)° for **2A** and **2B** and 98.11(8)° and 97.70(8)° for **3A** and **3B**, respectively.

Although the structures of 2 and 3 apparently look very similar, a comparison of the structures (Fig. 3) and the dimensions in Table 2, clearly show that the arrangement of the donor atoms around the metal is very different. The tridentate ligand coordinates to the metal ion in a facial configuration in 2 but in a meridional configuration in **3**. As a result, the bridging $O(11)^{\gamma}$ is trans to N(23) in **3** while in **2** it is trans to N(19) and this difference has a significant effect upon the bond lengths. First we note that Ni(1)–O(11) and Ni(1)–N(19) are the two shortest bonds in $\mathbf{2}$ and this is maintained in **3** (Table 2). It is apparent that bonds trans to N(19) are significantly lengthened in both structures. Thus in compound **2**, the trans bonds $Ni(1)-O(11)^{\gamma}$ are significantly longer than these bonds in compound 3 (Table 2). Moreover, in compound **3** the trans Ni(1)–O(3) bonds at 2.233(2), 2.212(2) Å are also considerably longer than the corresponding bonds in compound 2. The shortening of Ni–N(19) as well as the lengthening of the bond mutually trans, seems to stem from the better π -accepting ability of imine (C=N) functions which in turn weakens the bond mutually trans as both of them compete for the same metal d-orbital for back-bonding stabilization. On the other hand, in 3, the Ni(1)-N(23) bonds at 2.065(3), 2.059(2)Å and the Ni(1)-O(1)bonds at 2.118(2), 2.110(2) Å are significantly shorter than the equivalent bonds in 2 though whether the explanation is steric and/or electronic is not obvious. Another interesting difference between the two structures is the position of phenyl rings relative to the Ni₂O₂ basal plane. In both, one of the phenolate-rings is above and the other is below the Ni₂O₂ basal plane. However, this basal plane is nearly coplanar in 2 but is almost perpendicular in 3 with the benzene planes. In the Cambridge Crystallographic Database, both situations are known, as well as the intermediate ones. However, focusing only on the reported double phenolate-bridged Ni^{II} dimers with tridentate Schiff base ligands, it is found that the ligand coordination can be in a mer- or fac- configuration depending upon whether the co-ligand is monodentate or chelating bidentate but the benzene ring is nearly co-planar with Ni₂O₂ plane in both types of complex [12,16–21,27,28]. Complex 3 is unique in that the ligand coordination is meridional even with a chelating co-ligand. Additionally, the plane of the benzene ring is nearly perpendicular with the Ni₂O₂ core.

The difference in configuration and conformation can be explained by analyzing the supramolecular forces in the two compounds. In compound 2 there are no significant H-bonds and





Fig. 4. Top: $C-H/\pi$ interactions between the molecules in **2.** Bottom: Hydrogen bonding and $C-H/\pi$ interactions in **3**.

only the C–H/ π interactions [between H21A and Cg of phenyl ring of unit B with dimension $H \cdots Cg = 2.93(-x, 1-y, -z)$ and another between H22D and Cg of neighboring molecule with dimension $H \cdots Cg = 2.83(-x, -y, -z)$] are likely to have significant influence on the packing of the molecules (Fig. 4). However, in compound 3, both uncoordinated oxygen atoms of the nitrate ion are involved in N-H···O hydrogen bonds. The proton on N(23A) forms a single hydrogen bond, viz N(23A)–H(23A)····O(4A)(x, 1 + y, z) with dimensions N···O 3.018(3) Å, H···O 2.16, N-H···O 158°. By contrast N(23B)-H(23B) atom forms a bifurcated H-bond with the O(1A) and O(4A)(x, -1 + y, z) of the chelating nitrate ligand of the neighboring unit with dimensions: N···O 3.044(3), 3.284(3) Å, N–H···O angles 140° and 162°, and $0 \cdots$ H distances 2.29 and 2.41 Å (Table 3), which stabilize the unusual configuration of the complex as is substantiated by the theoretical study described in the following section. There is also a very weak $C-H/\pi$ interaction between the hydrogen atom (H24F) of methyl group and the phenyl ring of another molecule (x, -1 + y, z) along the H-bonded chain (Fig. 4, bottom). It should be mentioned that a single C-H/ π interaction

represents an energetic stabilization of approximately 1 kcal/mol in the gas phase and the distance from the ring plane to the inter-

Table 3			
Dimensions of hydrogen	bonding in	n compounds	1 and 3 .

D–H···A	D· · ·A (Å)	A· · ·H (Å)	$\angle D - H \cdots A$ (°)
$\begin{array}{l} In \ 1 \\ N(19)-H(19)\cdots O(21) \\ N(23)-H(23A)\cdots O(21)^a \\ N(23)-H(23B)\cdots O(11)^b \\ N(23)-H(23B)\cdots Cl(1)^b \end{array}$	2.522 2.720 3.056 3.505	1.79 1.86 2.19 2.82	142 159 162 134
In 3 N23A-H23A···O4B ^c N23B-H23B···O1A ^d N23B-H23B···O4A ^d	3.018(3) 3.044(3) 3.283(3)	2.15 2.29 2.41	158 140 162

^a 3/2 - x, y, -z.

^b 1 - x, -y, -z.

x, 1 + y, z

^d x, y - 1, z.



Fig. 5. Top: tautomeric dimers of the protonated ligand 1a and 1b. Bottom: X-ray structure of the dimer (left) and theoretically optimized structure (right), distances in Å.



Fig. 6. Comparison of the X-ray structures of compounds 2 and 3. Dihedral angles in degrees.

acting hydrogen atom varies from 2.5 to 3 Å depending on the orientation of the alkyl group [45]. Therefore a sufficient number of C–H/ π interactions working in concert can be important in the solid state, as is observed in compounds **1–3**. It should also be mentioned that in solution, the configuration having lowest energy should be stabilized. However, the electronic spectra of **3** in solid and in solution are identical and thus do not provide any evidence for isomerization on dissolution.

3.6. Theoretical study

Firstly, we have studied the structure of the protonated free ligand **1**. The crystal structure shows that the hydrogen atom is situated on nitrogen atom N(19) of the C=N group rather than the oxygen atom O(11). This proton participates in a strong intramolecular H-bond interaction with the phenolic oxygen atom. This structure has three separated charges, i.e. two at nitrogen atoms and one at the oxygen atom. It was interesting to study the other possible structure where this hydrogen atom is bonded to the phenolic oxygen atom and, consequently, only one positive charge located at the quaternary nitrogen atom is present in this tautomer form. We have analyzed both possibilities using theoretical calculations. We have optimized the dimeric form of **1** that is found in the crystal structure, locating the hydrogen atom bonded either at the nitrogen (**1a**) or the oxygen (**1b**) atoms (see Fig. 5, top). The optimized structure of **1a** is shown in Fig. 5 (bottom, right) and it is similar to the geometry found in the solid stare, which is also represented in Fig. 5 (bottom, left). Interestingly, the optimization of **1b** does not yield a stationary point. Instead, the optimization converges to **1a**, indicating that the tautomer **1b** is not stable. The result is therefore consistent with the experimental structure.

As aforementioned, from the inspection of the X-ray structures, it can be observed that in compound **3**, where the anion is nitrate, the phenyl rings are almost perpendicular to the plane defined by the two nickel atoms and the two phenolic oxygen atoms (Ni₂O₂ basal plane). This plane is represented in pink in Fig. 6.¹ In contrast,

¹ For interpretation of color in Fig. 6, the reader is referred to the web version of this article.



Fig. 7. RI-BP86/def2-TZVP optimized compounds 2a and 2b (top) and 3a and 3b (bottom).

when the anion is nitrite the phenyl rings are almost coplanar (compound **2**). This difference in the conformation of both compounds has a consequence on the spatial position of the N–H group. In compound **3**, the N–H group is *exo* (i.e. pointing to the external part of the molecule) and it is available to interact with neighboring molecules. In compound **2**, this group is *endo*. Therefore it is not available for establishing hydrogen bonding interactions with neighboring molecules in the solid state.

In order to give an explanation to these experimental observations, we have performed a theoretical study using DFT calculations. In particular, we have used the BP86 functional and the def2-TZVP basis set, using the resolution of the identity method (RI-BP86/def2-TZVP). Using this level of theory, we have computed compounds **2** and **3** in the two conformations observed in the solid state. That is, first the facial arrangement of **L** with the coplanar phenyl rings and second meridional **L** with perpendicular phenyl rings and the two corresponding conformers have been optimized (denoted with the letters "a" and "b", respectively). We have compared the energies of the two conformers in order to establish which conformation is more stable. The geometries of the optimized compounds and relative energies are included in Fig. 7.

First of all, it should be mentioned that the fully optimized structures are very similar to the experimental ones. The dihedral angles are in very good agreement, as can be deduced from the values indicated in Figs. 6 and 7. The theoretical and experimental Ni-O and Ni-N distances are also in good agreement. The experimental values for the Ni-N distances (basal plane) range from 2.050 to 2.163 Å and the theoretical ones range from 2.019 to 2.141 Å. Moreover, the experimental values for the Ni-O distances (basal plane) range from 2.004 to 2.112 Å and the theoretical ones range from 2.020 to 2.177 Å. These results give reliability to the theoretical level used in this study. From the energetic results, we learn that the conformation observed experimentally for nitrite is 1.0 kcal/mol more favorable than the conformation observed for nitrate. We should consider that this difference is too small to derive any absolute conclusion due to the intrinsic error of the theoretical method. However, a most likely explanation for the experimental results is that the more favorable conformation for both anions is achieved when the phenyl ring is disposed coplanar with the Ni₂O₂ basal plane. Obviously, the solid state structure observed for compound **3** is contrary to the theoretical prediction obtained through the energetic results. The explanation to this discrepancy comes from the intermolecular interactions, which are present in the crystal and have not been evaluated using this model. As previously indicated, in compound **3**, the N-H group is exo. In addition, the anion is nitrate, which uses two oxygen atoms to bind the nickel atom in a bidentate fashion. As a consequence, the third oxygen atom is available to interact with this group



Fig. 8. Supramolecular association of two dimeric units of compound 3. Distances in Å.



Fig. 9. Schematic representation of the critical points and bond paths observed between the dimers of compound **3**. Bond CPs are represented as red spheres and the ring CP as a yellow sphere. The bond paths are represented as grey lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(see Fig. 8). In compound **2**, the anion is nitrite and it is using both oxygen atoms to bind the nickel atom and thus the intermolecular $N-H\cdots O-N$ bond similar to nitrate is not possible.

We have computed the binding energy for the association of two dimers of compound **3** (see Fig. 8) with respect to each unit, which is -5.68 kcal/mol. This binding energy compensates the energy of conformation **3a** (observed in the crystal) which is 1.0 kcal/mol less favorable than conformation **3b**. In compound **2** these two intermolecular N-H···O-N hydrogen bonds can not be established. Consequently, conformation **2b** which is energetically more favorable is observed in the crystal structure.

Finally, we have performed an "atoms-in-molecules" (AIM) characterization of the non-covalent interactions observed between the dimers of compound **3**, which have been used to explain the conformation observed in the solid state. The AIM theory has been successfully used to characterize a great variety of interactions and provides an unambiguous definition of chemical bonding [46]. The critical points that characterize the intermolecular noncovalent interactions are shown in Fig. 9. The existence of critical points connecting the NO₃⁻ and the N-H group is a confirmation of the interactions. One hydrogen bond is characterized by the existence of one bond critical point (red sphere) that connects one oxygen atom of the anion with the hydrogen atom of the N-H group. The other hydrogen bond is characterized by two bonds and one ring (yellow sphere) CPs, indicating a bifurcate hydrogen bond between the N-H group and two oxygen atoms of the anion. In addition, a weak C–H/ π noncovalent interaction is established between the CH₃ group belonging to one dinuclear unit and the aromatic ring of the other one. This interaction is characterized by only one bond CP that connects one hydrogen atom of the CH₃ group with one carbon atom of the aromatic ring. The distance between the hydrogen atom and the carbon atom is 3.30 Å, which is typical for this type of non-covalent interaction.

4. Concluding remarks

Two new dinuclear Ni^{II} complexes have been synthesized using a tridentate Schiff base ligand and characterized by single crystal X-ray analyses. Complexes 2 and 3 are centrosymmetric dimers where the Ni^{II} ions are in distorted facial and meridional octahedral environment, respectively, bridged by two μ_2 -phenolate ions of the deprotonated ligand. Interestingly, the plane of the phenyl rings and the Ni_2O_2 basal plane are nearly coplanar in 2 but approximately perpendicular in **3**. The theoretical results demonstrate that the coplanar arrangement is approximately 1.0 kcal/mol more favorable than the perpendicular one. In addition, the theoretical study is useful to explain the experimental conformation observed in 3, which is energetically less favorable. It is stabilized in the solid state via intermolecular noncovalent interactions, which compensate the energy for unfavorable meridional configuration with perpendicular arrangement of the phenyl ring. The complexes are therefore very good examples to demonstrate that the facial and meridional arrangements of a tridentate ligand can be dictated by the supramolecular forces such as H-bonds and the stabilization of energetically less favored isomers in the solid state can occur with the help of weak intermolecular interactions specially when the isomers differ only slightly in energy. However, it should be noted that both the isomers are probably present in solution as the difference in energy between them is very small and that the solubility of a particular product and/or the kinetics of crystallization are also the important factors for separation of it in the solid state.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.058.

CCDC 753475, 753476 and 753477 contains the supplementary crystallographic data for compounds **1**, **2** and **3** (excluding structure factors). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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