

Spectral characterization and theoretical interpretation of a new bis- μ -phenoxo-bridged heterodinuclear nickel(II)-sodium(I) complex

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Abstract : Doubly phenoxo bridged heterometallic dinuclear Ni(II)-Na(I) complex [NiNaL(ClO₄)(CH₃OH)], **1** (H₂L = [(OCH₃)C₆H₃(OH)CH=N(CH₂CH)(CH₃)N=CH(OH)C₆H₃(OCH₃)] has been synthesised and characterized by infrared, electronic spectra, electrochemistry and single crystal X-ray diffraction study. In complex **1**, Ni(II) centre is distorted square-planar while the sodium(I) centre possesses pentagonal bipyramidal geometry. In the dimeric unit, the nickel and sodium atoms are held together by two distinct μ_2 -phenoxo oxygen of the Schiff base ligand. The Ni-Na distance is 3.354(2) Å and the Ni-O-Na angles are found to be 107.4(5)° and 108.2(4)°. Density functional theory (DFT) calculation results for the complex **1** are also reported and compared with the experimental data.

Keywords : Ni(II)-Na(I) heterometallic dimer, double phenoxo bridging, crystal structure, DFT calculations.

Introduction

Heteronuclear and/or polynuclear complexes are interesting materials due to their structures and properties : especially electrochemical and magnetic properties. A number of groups have been investigating the magnetic interaction between metal ions in heterometallic complexes¹. Transition metal ions in redox centres can change the electronic state of the binding molecule, making an increased selectivity against metal ions². Furthermore, binding property of some guest species has been changed dramatically depending on the oxidation state of the redox active site. So study on this redox switching process is really important because of its mechanistic aspects and is the essential point to develop the electrochemical sensor materials³.

Asymmetric or symmetric Schiff base compartmental ligands bearing an adjacent bidentate [NO], tridentate [N₂O] donor set, generally synthesize the homotrimeric nickel(II) complexes like [Ni₃(L)₂(OAc)₂(NCS)₂] in which

the metallic core is supported by acetato groups⁴⁻⁶. Oligonuclear 3d-metal complexes derived from O- and N-donor ligands are currently of interest because of their important magnetic properties⁷, and these complexes generally exhibit antiferromagnetic properties. Many oligonuclear cluster complexes arise from serendipitous assemblies and so the rational synthesis of such complexes is definitely a desirable target⁸.

On the other hand, coordination chemistry of alkali metal ions has attracted great interest since the fact was discovered that macrocyclic polyethers have been found to act as efficient ligands for alkali metals⁹ possessing high coordination numbers¹⁰. Metal-salicylaldimines with *o*-phenoxo group(s) are fascinating ligands that can coordinate with not only p- and d-block metal elements but also alkali-metal ions¹¹. Recently, some transition metal complexes of compartmental Schiff bases are used as popular complexing agents to bind alkali metals^{12,13}. One of the strategies in making the heterometallic coordination

polymers containing alkali metals is that the transition metal ions are placed in the N_2O_2 compartment of the ligand, and sodium(I) is placed in the O_4 compartment of the complexes^{14,15}. Some copper(II)-sodium(I) and nickel(II)-sodium(I) complexes with salen-type compartments Schiff bases has been reported where structural determination has revealed a new coordination mode of such kind of heterometallic complexes^{11,16,17}.

In the above scenario, we take an attempt to synthesise heterometallic complex of nickel(II) and sodium(I) by using the symmetric tetradentate Schiff base ligand with $[N_2O_2]$ donor set. Interestingly, we obtained one heterometallic dimer of nickel(II) and sodium(I) formed by double phenoxo bridge between the metal centres. In the present report, we describe synthesis, spectroscopic characterization, structural aspects and density functional theory (DFT) calculation of the titled dimeric complex $[NiNaL(ClO_4)(CH_3OH)]$, ($H_2L = [(OCH_3)C_6H_3(OH)CH=N(CH_2CH)(CH_3)N=CH(OH)C_6H_3(OCH_3)]$). Here the Schiff base itself behaves as terminal as well as bridging ligand.

Experimental

Materials :

All the reagents used were of reagent grade. $Ni(ClO_4)_2 \cdot 6H_2O$, *o*-vanillin, 1,2-diamino propane (Fluka) and sodium sulphate (Aldrich) were of reagent grade and used as received. All the solvents were of reagent grade and used as received.

Physical measurements :

Fourier Transform Infrared spectrum ($4000-400\text{ cm}^{-1}$) of the complex **1** was recorded on a Perkin-Elmer SPECTRUM-2 FT-IR spectrophotometer in solid KBr matrices. An electronic spectrum of the titled complex was recorded at 300 K on a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer in acetonitrile medium. Elemental analyses were carried out with a Perkin-Elmer 2400 II elemental analyzer. Electrochemical studies were carried out in acetonitrile with a CH 660E cyclic voltammeter using saturated calomel electrode (SCE) as a reference in a three electrodes system and using tetrabutylammonium perchlorate as a supporting electrolyte at a scan rate of 50 mV s^{-1} . Nitrogen gas was passed through sample solution at a constant rate for 1 min.

Preparation of the ligand and complex :

(a) Synthesis of the Schiff base ligand :

The Schiff base ligand $[(OCH_3)C_6H_3(OH)CH=N(CH_2CH)(CH_3)N=CH(OH)C_6H_3(OCH_3)]$ (H_2L) was obtained by refluxing methanolic solution (25 ml) of *o*-vanillin (2 mmol) and 1,2-diamino propane (1 mmol) for 30 min. The resulting orange-yellow solution containing the ligand was used without further purification.

(b) Synthesis of the complex **1** :

A methanolic solution of Schiff base ligand (1 mmol) was added to methanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1 mmol). The solution was cooled to $0\text{ }^\circ\text{C}$. Then, an aqueous solution (10 ml) of Na_2SO_4 (0.142 g, 1 mmol) was added slowly to it and the resulting solution was kept at $5\text{ }^\circ\text{C}$. The brown-red coloured crystals suitable for X-ray analysis appeared after one day.

Yield : 45%. Analytical results : $C_{16}H_{16}Cl_{0.80}N_{1.60}Na_{0.80}Ni_{0.80}O_{7.20}$: C, 43.67; H, 3.64; N, 5.09; Ni, 10.68%; Found : C, 43.63; H, 3.59; N, 5.07; Ni, 10.65%.

Caution! Perchlorate salts are potentially explosive and should be used in small quantity with much care.

X-Ray crystallographic analysis :

The X-ray single crystal data for the complex **1** (size $0.10 \times 0.08 \times 0.05\text{ mm}$) were collected on a Picker-Stoe diffractometer. Crystallographic data, the conditions for data collection, and some features of the structural refinements are listed in Table 1. Graphite-monochromatised (Cu-K α) radiation ($\lambda = 1.54184\text{ \AA}$) and the ω -scan technique were used to collect the data sets. The structure was solved by direct methods using the SHELXTL PLUS¹⁸ system and refined by a full-matrix least-squares methods based on F^2 using SHELXL-93¹⁹. All the non-hydrogen atoms were refined anisotropically.

Computational details :

The geometry of the ligand was optimized at the B3LYP/6-31+G* level of theory without symmetry constraints. The geometry of compound **1** in its singlet ground state (S_0) was optimized by DFT and time-dependent DFT (TDDFT)^{20,21} methods with the B3LYP functional approach associated with the conductor-like polarizable continuum model (CPCM)²²⁻²⁴. The geometry of the complex in its ground S_0 was optimized in solution phase. We calculated 40 singlet-singlet transitions using its ground

S_0 state geometry and using the conductor-like polarizable continuum model. For all atoms we have used 6-

31+G* as the basis set. The calculated electronic density plots for the frontier molecular orbitals were prepared by using the GaussView 5.0 software. All the calculations were performed with the Gaussian 09 software package²⁵.

Empirical formula	$C_{16}H_{16}C_{10.80}N_{1.60}Na_{0.80}Ni_{0.80}O_{7.20}$
Formula weight	439.62
Temperature	293(2) K
Crystal system, space group	monoclinic, P 21/c
Unit cell dimensions	$a = 16.3380(9) \text{ \AA}$ $b = 7.3210(3) \text{ \AA}$ $c = 23.1939(10) \text{ \AA}$ $\alpha (^{\circ}) = 90$ $\beta (^{\circ}) = 123.349(3)$ $\gamma (^{\circ}) = 90$
Volume	2317.4 (2) \AA^3
Z, Calculated density	4, 1.575 Mg/m^3
Absorption coefficient	2.940 mm^{-1}
$F(000)$	1128
Crystal size	0.1 × 0.08 × 0.05 mm
Theta range for data collection	3.24 to 42.73 deg.
Reflections collected/unique	3331/1493 [R(int) = 0.0773]
Completeness to theta = 42.73	89.5%
Data/restraints/parameters	1493/0/313
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0812$, $wR2 = 0.2095$
R indices (all data)	$R1 = 0.1076$, $wR2 = 0.2365$
Extinction coefficient	0.0024(6)
Largest diff. peak and hole	0.418 and -0.366 e. \AA^{-3}

Results and discussion

Crystal structure of the complex :

The ORTEP view of the dimeric complex is shown in Fig. 1 and bond lengths and angles are given in Table 2. In the dimeric unit, the nickel(II) centre adopts a square-planar geometry while sodium atom possesses pentagonal bipyramidal geometry. The nickel and sodium atoms are held together by doubly μ_2 -phenoxo oxygen atoms of the Schiff base ligand. In this case the Ni-Na distance is 3.354(5) \AA and Ni-O2-Na and Ni-O3-Na angles are 107.4(5) and 108.2(4) $^{\circ}$ respectively.

The geometry around nickel(II) centre is distorted (NNOO) square planar. The two imine nitrogens (N1 and N2) and two phenolic oxygen atoms (O2 and O3) of the Schiff base form the square plane. The nickel atom is displaced by 0.08 \AA out of the basal plane. In the square plane, the bond lengths are Ni-N(1) : 1.836(11), Ni-O(3) : 1.820(9), Ni-N(2) : 1.842(11), Ni-O(2) : 1.857(8) \AA . The deviation from the ideal square planar geometry is also indicated by the bond angles involving the atoms in the *cis*-positions which vary from 81.5(4) to 96.4(5) $^{\circ}$, as well as the angles involving the atoms in the *trans*-posi-

Table 2. Selected geometric parameters from X-ray analysis and theoretical calculations using the hybrid DFT (B3LYP/6-31+G*) method for the title compound

Bond lengths (\AA)					
Bond	Experimental	Calculated	Bond	Experimental	Calculated
Ni-N(1)	1.836(11)	1.838	Ni-O(3)	1.820(9)	1.838
Ni-N(2)	1.842(11)	1.852	Ni-O(2)	1.857(8)	1.839
Na-O(3)	2.306(10)	2.314	Na-O(1)	2.480(9)	2.404
Na-O(4)	2.515(10)	2.619	Na-O(2)	2.293(9)	2.379
Na-O(6)	2.436(17)	2.618	Na-O(5)	2.383(10)	2.322
Bond angles ($^{\circ}$)					
Bond angles	Experimental	Calculated	Bond angles	Experimental	Calculated
N(1)-Ni-O(3)	178.4(5)	173.3	O(2)-Na-O(3)	62.9(3)	62.3
N(1)-Ni-N(2)	85.1(6)	87.0	O(2)-Na-O(1)	64.1(3)	63.4
O(3)-Ni-N(2)	96.4(5)	95.0	O(3)-Na-O(1)	127.0(4)	124.2
ON(1)-Ni-O(2)	97.0(5)	94.0	O(2)-Na-O(4)	127.7(4)	125.0
O(3)-Ni-O(2)	81.5(4)	84.7	O(3)-Na-O(4)	64.8(3)	62.7
N(2)-Ni-O(2)	177.5(5)	173.2	O(1)-Na-O(4)	167.9(4)	168.1
Ni-O(3)-Na	108.2(4)	106.8	Ni-O(2)-Na	107.4(5)	105.7

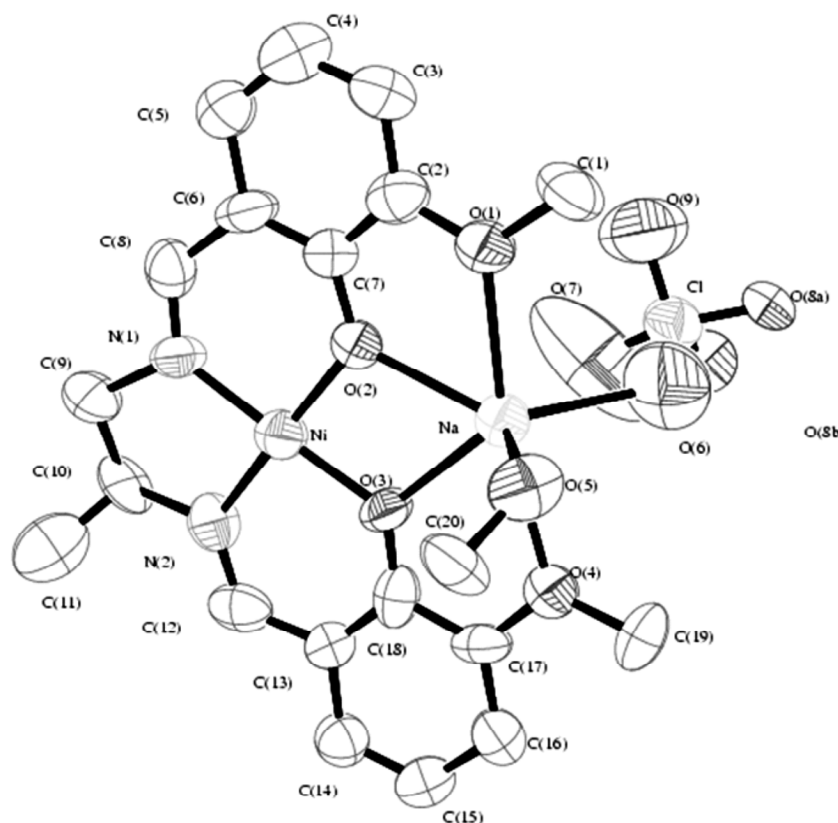


Fig. 1. ORTEP view of complex **1** with displacement ellipsoids drawn at 50% probability level (H-atoms are omitted for clarity).

tions that vary from $177.5(5)$ to $178.4(5)^\circ$. All the values are more or less comparable to similar Ni-centres in the literature^{17,26,27}.

The geometry of Na(I) centre is best described as distorted pentagonal bipyramid. The five atoms constituting the basal plane are two phenolic oxygen atoms (O2 and O3), two methoxy oxygen (O1 and O4) from the Schiff base, and O6 from coordinated ClO_4 anion. The O5 atom of the coordinated methanol molecule and O7 from perchlorate occupies the apical sites with O5-Ni-O7 angle $145.0(10)^\circ$. Na atom lies not in the basal plane but slightly out of it, at a distance of 0.178 \AA . In the basal plane, the average bond distances are Na-O(2) : $2.293(9)$, Na-O(3) : $2.306(10)$, Na-O(6) : $2.436(17)$, Na-O(1) : $2.480(9)$, Na-O(4) : $2.515(10) \text{ \AA}$. One axial length Na-O(7) is $2.82(4) \text{ \AA}$ which is much higher than the basal bond lengths. The Na-O distances fall within the range from $2.260(4)$ to $2.460(4) \text{ \AA}$ similar to other sodium complexes^{28,29}.

Infrared spectrum :

The infrared spectrum of complex **1** is very much consistent with the structural data presented in this paper. The bands in the range 3450 cm^{-1} for complex **1** is attributable to O-H stretching³⁰. The band at 2935 and 2838 cm^{-1} are due to the imine stretching frequency for complex **1**. The phenolic C=O stretching band is present at 1250 and 1318 cm^{-1} indicating the presence of phenoxo-bridge in the complex²⁵. Bands in agreement with coordinated perchlorate anion are also observed for at, 1172 , 1161 – 1086 , 979 , 673 , 488 , 435 cm^{-1} ^{31,32}. Ligand coordination to the nickel centre is substantiated by two bands appearing at 455 and 386 cm^{-1} , for complex **1**, attributable to $\nu(\text{Ni-N})$ and $\nu(\text{Ni-O})$, respectively³³.

Electronic spectrum :

Electronic spectrum of the title complex showed a broad d-d band at 541 nm and some closely spaced charge transfer (LMCT) bands at 402 , 340 , 246 and 207 nm . These charge transfer bands are assigned to the LMCT bands from the coordinated oxygen atoms to the Ni(II) ion³⁴.

Electrochemical study :

Electrochemical study of the complex **1** was performed using acetonitrile as solvent and tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 50 mV s⁻¹. Two distinct irreversible peaks at 0.67 and 0.91 V are observed in the cyclic voltammogram of the complex **1** (as shown in Fig. 2). This may be due to Ni(II) to Ni(III) oxidation, and/or coordinated ligand oxidation which implies that Ni(III) is unstable in solution and undergoes rapid decomposition.

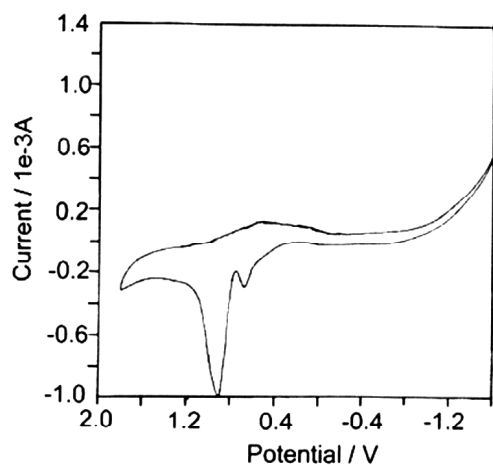


Fig. 2. Cyclic voltammogram of complex **1**.

Theoretical calculations and TDDFT study :

The DFT optimized structure of the ligand is given in Fig. 3a. It presents an extended conformation where two intramolecular OH...N bonds are established. The HOMO and LUMO plots are also included in Fig. 3b and 3c. The HOMO-LUMO gap of the ligand is 4.093 eV. Both orbitals are located at the aromatic π -systems. Compared to the HOMO, the HOMO-1 is close in energy (-5.847 eV) and located at the other aromatic ring of the ligand.

The DFT optimized structure of complex **1** is given in Fig. 4. The gas phase geometry of the heterometallic Ni(II) and Na(I) complex was optimized without any symmetry restrictions at the B3LYP/6-31+G(d) level of theory. A comparison of the theoretical and experimental values in Table 2 shows a good agreement giving reliability to the level of theory used herein.

In the ground state (S_0) of complex **1** the energies of HOMO, HOMO-1 and HOMO-2 are -5.508, -5.880 and

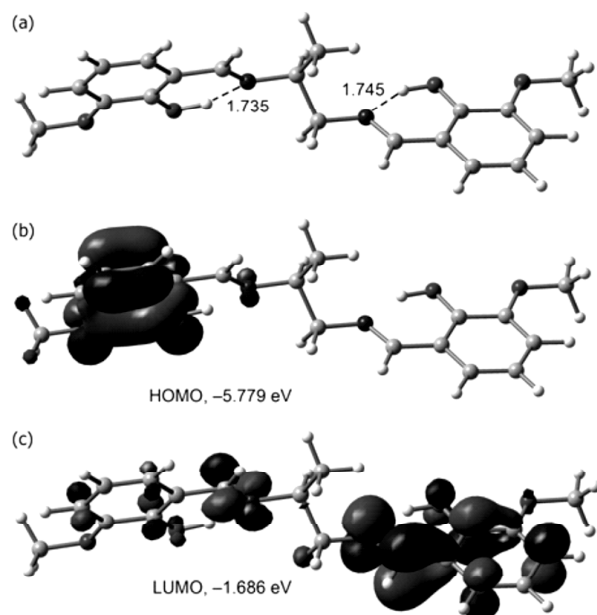


Fig. 3. (a) DFT optimized structure of the ligand. Distances in Å. (b,c) HOMO-LUMO plots and energies.

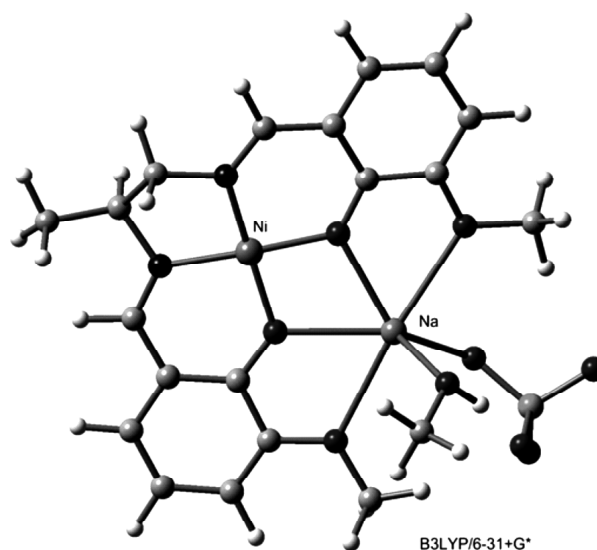


Fig. 4. DFT optimized structure of complex **1**.

-6.512 eV, respectively. They are basically composed by the aromatic moieties, the phenoxide atoms and the conjugated C=N bonds (see Fig. 5). Similarly the LUMO and LUMO+1 (-1.921 and -1.842 eV respectively) are also basically composed by the aromatic moieties and the conjugated C=N bonds. The energy difference between the HOMO and LUMO is 3.586 eV, considerably smaller than that of the free ligand (Fig. 3). To get better insight

into the experimental absorption values TDDFT calculations were done for the complex on the basis of the optimized geometry at the B3LYP/6-31+G* level of theory. The calculated absorption energies associated with their oscillator strengths, the main configurations and their assignments of the complex are given in Table 3. Here the lowest lying distinguishable singlet \rightarrow singlet absorption band can be mainly attributed to one excitation. It occurs at 2.3463 eV ($\lambda = 528$ nm and $f = 0.0008$) due to an HOMO \rightarrow LUMO transition with ILCT character, which can be assigned to a $\pi(L) \rightarrow \pi^*(L)$ transition (Fig. 5, highlighted in blue).

The following absorption band ($\lambda_{\text{exp}} = 402$ nm) consists of one excitation (3.0563 eV, 405 nm and $f = 0.0368$) that is attributed to a HOMO-1 \rightarrow LUMO, transition which can be assigned to $\pi(L) \rightarrow \pi^*(L)$ with basically ILCT character (Fig. 5). Finally, the third experimental excitation that we have studied ($\lambda_{\text{exp}} = 340$ nm) also consists of one excitation (3.5106 eV, 353 nm and $f = 0.1046$) that is attributed to a HOMO-2 \rightarrow LUMO+1, transition which can be assigned to $\pi(L) \rightarrow \pi^*(L)$ with basically ILCT character (Fig. 5). The experimental values are in good agreement with the theoretical ones, giv-

Table 3. Selected parameters for the vertical excitation (UV-Vis absorptions) of complex **1**, electronic excitation energies (eV) and oscillator strengths (f), configurations of the low-lying excited states of **1**; calculation of the S_0 - S_n energy gaps based on optimized ground-state geometries (UV-Vis absorption) (MeOH used as solvent)

Process	Electronic transitions	Composition	Excitation energy (λ)	Oscillator strength (f)	λ_{exp} (nm)
Absorption	$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO	2.3463 eV (528 nm)	0.0008	541
Absorption	$S_0 \rightarrow S_6$	HOMO-1 \rightarrow LUMO	3.0563 eV (405 nm)	0.0638	402
Absorption	$S_0 \rightarrow S_8$	HOMO-2 \rightarrow LUMO+1	3.5106 eV (353 nm)	0.1046	340

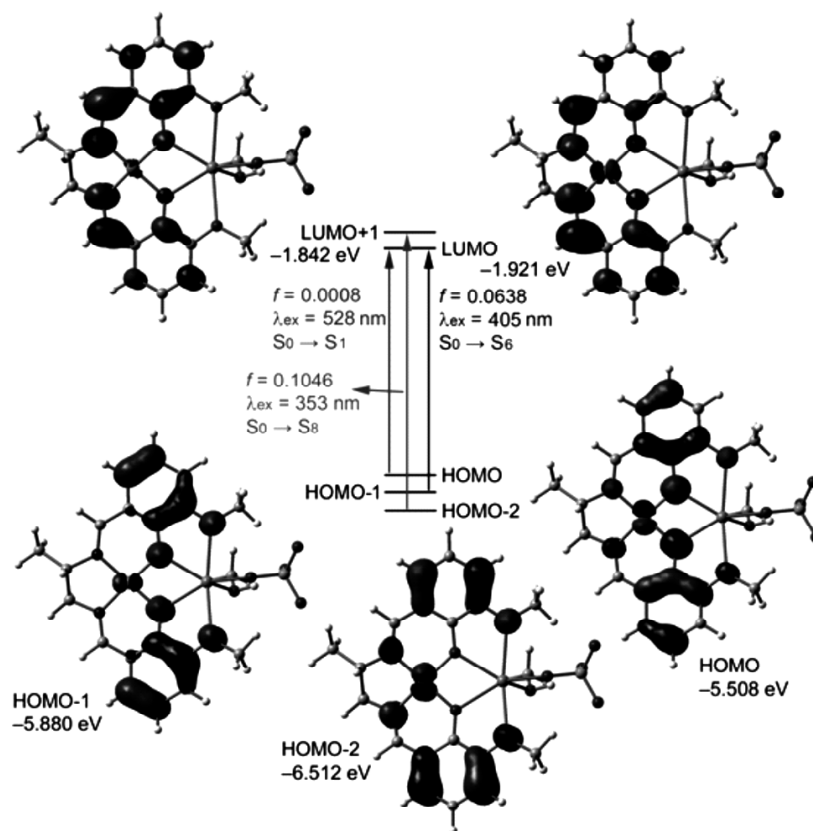


Fig. 5. Frontier molecular orbitals involved in three observable UV-Vis absorption bands of complex **1**.

ing reliability to the optimized geometry and the level of theory.

Conclusion

In the present study we have isolated a new doubly phenoxo bridged heterometallic dinuclear Ni(II)-Na(I) complex with a tetradentate Schiff base ligand with [N₂O₂] donor set. The complex was characterised by infrared, electronic spectra, electrochemical study and single crystal X-ray diffraction study. Density functional theory (DFT) calculations were carried out in gas phase for the complex **1** and was optimized without any symmetry restrictions at the B3LYP/6-31+G(d) level of theory. The energy difference between the HOMO and LUMO for complex **1** is 3.586 eV, which is considerably smaller than the HOMO-LUMO gap of free ligand (4.093 eV). TDDFT calculations of the S₀-S_n energy gaps, oscillator strengths (*f*) based on optimized ground-state geometries (UV-Vis absorption) in methanol as solvent shows experimental values are in good agreement with the theoretical ones.

Supporting data

CCDC 606867 contains the supplementary crystallographic data for the complex **1**. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieval.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax : 44-1223/336 033. E-mail : deposit@ccdc.ac.uk.

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