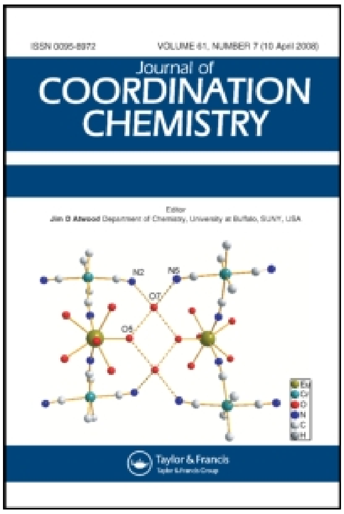

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Square-planar nickel(II) complexes with a tridentate Schiff base and monodentate heterocycles: self-assembly to dimeric and one-dimensional array via hydrogen bonding

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Square-planar nickel(II) complexes with a tridentate Schiff base and monodentate heterocycles: self-assembly to dimeric and one-dimensional array via hydrogen bonding

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Square-planar nickel(II) complex with tridentate ONO-donor 4-[(2-hydroxyphenyl)imino]-2-pentanone (H_2hpac) and imidazole (Himdz) are reported. The complex was synthesized in moderate yield by reacting $Ni(O_2CCH_3)_2 \cdot 4H_2O$, H_2hpac and imidazole in 1 : 1 : 1 mole ratio and characterized by elemental analysis, IR, ^{1}H NMR spectroscopy. An X-ray structure determination of the complex has been completed. In the solid state, a one-dimensional assembly of the [Ni(hpac)(Himdz)] molecules is formed via intermolecular hydrogen bonds between the imidazole N–H groups and the coordinated hydroxyphenyl-O atoms.

Keywords: Nickel(II) complex; Square-planar; Crystal structure; Hydrogen bonding; Self-assembly

1. Introduction

Extended arrays of metal ions and their applications have been reviewed [1]. The general strategies used for the self-assembly of transition metal complexes into such extended assemblies are coordination geometry, use of suitable ligands and weak intermolecular interactions such as hydrogen bonding and π–π interactions [2–4]. Tri- and higher dentate Schiff-base ligands are of interest [5–7], especially Schiff-base ligands derived from acetylacetone, which have immense applications, mostly due to acetylacetoneiminato being a very reactive nucleophilic center for easy incorporation of a variety of metal ions [8]. In the present work, we report a square-planar mixed-ligand nickel(II) complex with deprotonated 4-[(2-hydroxyphenyl)imino]-2-pentanone (H_2hpac, two H represent the dissociable enolic –OH and the hydroxyphenyl proton) coordinating through the enolate-O, the imine-N and the deprotonated hydroxyphenyl-O atoms; the neutral N-donor, imidazole (Himdz), has been used as

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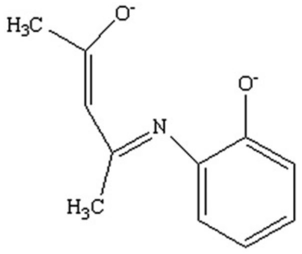
an ancillary ligand. In the following account, we describe the synthesis, characterization and solid state structure of the [Ni(hpac)(Himdz)]. The self-assembly of the complex molecules via intermolecular hydrogen bonds involving the heterocycle N–H group has been demonstrated.



hpac^{2-}

2. Experimental

The Schiff base, H_2hpac, was prepared as before [9]. All chemicals and solvents were of analytical grade, available commercially, and used as received.

2.1. *Physical measurements*

Elemental (C, H, N) analysis data were obtained with a Vario ELIII elemental analyzer. IR spectra were recorded by KBr pellets on a Bio-Rad FTIR spetrophotometer (in the 400–4000 cm^{-1} range). The EI mass spectrum was recorded on an Agilent 1100 Series ESI/MSD spectrometer. The electronic spectrum was recorded on a 8453 Value UV-Visible System. The ^1H NMR spectra of the compound were recorded on a JEOL ECX 500 MHz spectrometer.

2.2. *Synthesis of 4-[(2-hydroxyphenyl)imino]-2-pentanone (H_2hpac)*

An ethanol solution (20 mL) of acetylacetone (2.0 g, 0.02 mol) was added to another ethanol solution (60 mL) of 2-aminophenol (2.18 g, 0.02 mol). The solution was refluxed for 5 h, cooled, then the solvent removed partly under reduced pressure and the reaction mixture left overnight at room temperature in air giving yellow needle-like crystals. The crystals were collected by filtration and dried in air. Yield: 3.2 g (86%). Anal. Calcd for $C_{11}H_{13}NO_2$ (%): C, 69.09; H, 6.85; N, 7.32. Found: C, 69.25; H, 6.91; N, 7.34. Selected IR (cm^{-1}): 3479.7 [ν(O–H)], 3009, 2725 [$\nu_{as}(CH_3)$], 1729 [(ν(C=O)], 1599 [ν(C=N)]; ^1H NMR (DMSO-d_6): δ 1.955 (s, 3H, (CH_3)–C=O), 3.321 (s, 3H, CH_3–C=N), 5.185 (s, 1H, =CH– of hpac^{2-}), 6.756–7.161 (m, 4H, phenyl ring proton), 9.898 (1H, C=C–OH), 12.124(1H, Ar–OH).

2.3. *Preparation of [Ni(hpac)(Himdz)]*

An ethanol solution (10 mL) of $Ni(O_2CCH_3)_2 \cdot 4H_2O$ (125 mg, 0.5 mmol) was added to another ethanol solution (20 mL) of H_2hpac (95.5 mg, 0.5 mmol) and Himdz (34 mg, 0.5 mmol). The resulting solution was refluxed for 3 h. Slow evaporation of this reaction mixture at room temperature in air afforded the complex as dark brown crystalline material which was collected by filtration and dried in air. Yield: 82 mg (52%). Single crystal suitable for X-ray structure determination was selected from this material. Anal. Calcd for $C_{14}H_{15}N_3O_2Ni$ (%): C, 53.22; H, 4.75; N, 13.30. Found: C, 53.15; H, 4.71; N, 13.36. MS (EI) (m/z): 316 [(M^+) mol peak], 249 [M–(OAr–N=C(Me)CHC(Me)O]$^+$, 67[(imidazole)$^+$ mol peak]. Selected IR (cm^{-1}): 2831 [ν_{as}(CH)], 1569 [ν(C=N)]. Electronic spectrum [(λ_{max} (nm) (ε, $M^{-1} cm^{-1}$) ($CHCl_3$)]: 203 (25000), 235(20100), 386(10770), 535(450). ^{1}H NMR (DMSO-d_6): δ 2.30 (s, 3H, –(CH_3)C=O), 3.36 (s, 3H, –(CH_3)C=N), 5.24 (s, 1H, =CH– of hpac^{2-}), 6.24–6.28 (t, $J = 9.5$ Hz, 1H, phenyl ring proton), 6.396–6.442 (t, $J = 9.5$ Hz, 1H, phenyl ring proton), 6.631–6.668 (t, $J = 9.5$ Hz, 1H, phenyl ring proton), 7.247–7.266 (d, $J = 9.5$ Hz, 1H, phenyl ring proton), 6.67, 7.18, 7.63 (s, s, s, 3H, imidazole C–H protons), 12.71 (s, 1H, imidazole N–H proton).

2.4. *X-ray structure determination*

X-ray diffraction data were collected at room temperature with graphite monochromated Mo-Kα radiation on a Bruker Smart Apex single crystal diffractometer using the φ–ω scan method. Unit cell dimensions were obtained with least-squares refinements and multi-scan absorption corrections were applied by using SADABS. The structures were solved by direct methods using SHELXS86 in the winGX package [10]. H atoms were placed in calculated positions, with C–H distances of 0.93 ~ 0.96 Å and N–H = 0.86 Å, and refined using a riding model with $U_{iso}(H) = 1.2$–$1.5 U_{eq}(C)$. The ORTEP-3 [11] drawing of the molecule is shown in figure 1. Crystal and experimental data are listed in table 1, selected bond lengths and angles are given in table 2, and hydrogen bonding geometry is given in table 3.

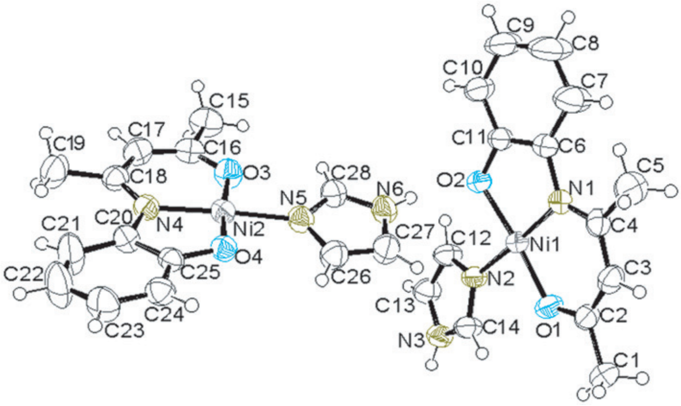


Figure 1. ORTEP drawing of [Ni(bhac)(Himdz)] with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles with arbitrary radii.

Table 1. Details of the X-ray crystal structure analysis for the [Ni(hpac)(Himdz)] molecule.

Empirical formula	$C_{14}H_{15}N_3O_2Ni$
Formula weight ($g\,mol^{-1}$)	315.69
Crystal color	Brown
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group (no.)	$P\bar{1}$
a (Å)	9.3673 (12)
b (Å)	9.6022 (13)
c (Å)	16.0534 (2)
α (°)	79.539 (5)
β (°)	85.862 (5)
γ (°)	75.097 (4)
V (Å^3)	1371.69 (3)
Density (calculated) ($mg\,m^{-3}$)	1.53
Z	2
Absorption coefficient (mm^{-1})	1.418
Crystal size (mm^3)	$0.53 \times 0.4 \times 0.2$
θ range (deg)	0.933–27.48°
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 12$, $-20 \leq 1 \leq 20$
Reflections collected	16119
Independent reflections	$5865[R(\mathrm{int}) = 0.021]$
Reflections with $I > 2\sigma(I)$	4974
Absorption correction	φ–ω scan
Refinement method	Full-matrix least-squares refinement on F^2
Data/restrains/parameters	5865/0/361
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0357$, $wR_2 = 0.099$
R indices (all data)	$R_1 = 0.0435$, $wR_2 = 0.10529$
Largest diff. peak, hole (e Å^{-3})	0.446 and −0.48

Table 2. Selected bond lengths (Å) and angles (°) for the Ni(hpac)(Himdz) with estimated standard deviations in parentheses.

Ni(1)–O(1)	1.8210(16)	Ni(2)–O(3)	1.8232(17)
Ni(1)–O(2)	1.8417(15)	Ni(2)–O(4)	1.8453(15)
Ni(1)–N(1)	1.8737(19)	Ni(2)–N(4)	1.873(2)
Ni(1)–N(2)	1.9165(19)	Ni(2)–N(5)	1.920(2)
O(1)–Ni(1)–O(2)	174.24(7)	O(3)–Ni(2)–O(4)	174.06(8)
O(1)–Ni(1)–N(1)	97.24(8)	O(3)–Ni(2)–N(4)	97.11(8)
O(2)–Ni(1)–N(1)	87.39(8)	O(4)–Ni(2)–N(4)	87.40(8)
O(1)–Ni(1)–N(2)	86.68(8)	O(3)–Ni(2)–N(5)	86.96(9)
O(2)–Ni(1)–N(2)	88.79(7)	O(4)–Ni(2)–N(5)	88.59(8)
N(1)–Ni(1)–N(2)	175.80(8)	N(4)–Ni(2)–N(5)	175.88(8)
C(4)–N(1)–Ni(1)	124.08(16)	C(6)–N(1)–Ni(1)	110.19(15)
C(14)–N(2)–Ni(1)	127.28(16)	C(12)–N(2)–Ni(1)	127.03(16)
C(18)–N(4)–Ni(2)	124.41(17)	C(20)–N(4)–Ni(2)	110.19(15)
C(28)–N(5)–Ni(2)	127.60(18)	C(26)–N(5)–Ni(2)	127.22(18)
C(2)–O(1)–Ni(1)	125.24(16)	C(11)–O(2)–Ni(1)	111.89(14)
C(16)–O(3)–Ni(2)	125.29(17)	C(25)–O(4)–Ni(2)	111.72(13)

Table 3. Data of hydrogen bond lengths (Å) and angles (°) of the complex.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry code
N(3)–H(3)···O(4)	0.86	1.964	2.786(3)	159.31	$x, y+1, z$
N(6)–H(6)···O(2)	0.86	1.918	2.756(3)	164.4	

3. Results and discussion

3.1. *Synthesis and characterization*

The dark brown complex was synthesized in moderate yield by reacting $Ni(O_2CCH_3)_2 \cdot 4H_2O$, H_2hpac and imidazole in 1 : 1 : 1 mole ratio in boiling ethanol. Elemental analyses are consistent with the molecular formula $C_{14}H_{15}N_3O_2Ni$ and fully characterized by IR, MS, ^{1}H NMR, UV–vis spectroscopy and X-ray structure analysis.

The IR spectral data (KBr pellet) are in accord with the structure determined by the X-ray diffraction. The IR spectra do not display any amide or secondary amine N–H stretch in the range 3300–3500 cm^{-1} [12]. Several sharp weak peaks observed in the range 2600–3200 cm^{-1} are likely to be due to the aromatic C–H stretches. The absence of any peak assignable to the heterocycle N–H group is consistent with its involvement in strong intermolecular hydrogen bonding (*vide infra*). The absorption bands of the C=O and O–H in free H_2hpac are also absent in the spectra of the complex. Thus, the Schiff base is completely deprotonated and is a dibasic enolate-O, imine-N and hydroxyphenyl-O donor ligand in the complex. A strong peak at 1569 cm^{-1} might involve the C=N stretches [13]. On coordination of the Schiff base, the C=N stretching frequency is at lower frequency indicating a decrease in the C=N bond order due to the coordinate bond of the nickel(II) with the azomethine nitrogen [14].

Electronic spectra of free H_2hpac in $CHCl_3$ appear at 206, 231(sh) and 322 nm. The strong absorption band at 206 nm is assigned to the π–π^* transition of the benzene. The shoulder at 322 nm is a π–π^* transition involving molecular orbitals localized on the C=N group and the benzene ring. For the complex, two strong absorptions are observed in the range 200–240 nm due to charge transfer and intra-ligand transitions. A weak absorption at ~535 nm is assigned to the spin-allowed d-d transition ($^1A_1g \rightarrow {}^1A_2g$) for a square-planar nickel(II) complex [15].

The ^{1}H NMR spectrum of the complex in DMSO-d_6 solution is also consistent with diamagnetic Ni(hpac)(Himdz). The spectrum of free H_2hpac displays two OH protons at δ 12.124 and 9.898, absent in the spectra of the coordinated ligand. For H_2hpac, the four phenyl protons appear in four groups at $\delta \sim 6.794$, ~6.910, ~7.027 and ~7.161, and for the complex at δ ~6.277, ~6.442, ~6.668 and ~7.266. The chemical shift of the =CH– proton of the free H_2hpac move downfield after coordination. The spectrum of free H_2hpac displays two methyl singlets at δ 1.955 and 3.321; protons of the two methyls on bound hpac^{2-} are singlets at δ 3.357 and 2.302. It is probable that the lower signal is due to the methyl groups adjacent to the C–O since these would be slightly less shielded than those near the C–N groups. The spectrum of free imidazole displays three C–H protons as two singlets at δ 7.12 and 7.71. The former corresponds to two protons and the latter to a single proton. However, the imidazole C–H protons in Ni(hpac)(Himdz) are three singlets at δ 6.668, 7.184 and 7.627. The heterocycle N–H proton is a singlet for the complex at δ 12.71.

3.2. *Molecular structure and self-assembly*

As shown in figure 1 the structure of the complex contains two independent mononuclear molecules in the unit cell, with intermolecular N6–H6↑O2^{i} hydrogen bonds (N–H = 0.86 Å (3), H↑O = 1.9178 Å, N–O = 2.758 Å, N–H↑O = 164.38°, symmetry codes: (i) (x, $1+y$, z) exist between the molecules. The tridentate hpac^{2-} coordinates the Ni(II) via the enolate-O, the imine-N and the deprotonated hydroxyphenyl-O atoms forming five- and six-membered chelate rings. Coordination of the imidazole with the nickel(II) occurs through the electron pair of N-3. There is no deviation of the metal center from the N_2O_2 plane. The N=C, C=C and C–O bond distances in $-N{=}C(CH_3)-CH{=}CH(CH_3)-(O^-)-$ of hpac^{2-} are consistent with the enolic form of acetylacetone [16]. The Ni–N$_{\text{imine}}$ and Ni–O$_{\text{enolate}}$ distances are similar to those reported for metal complexes, where the metal centers have the same coordinating atom [17]. The Ni(II)–N$_{\text{imidazole}}$ bond distance is normal, as observed in a similar square-planar Ni(II) complex with a tridentate ligand and imidazole [18].

Weak intermolecular interactions such as hydrogen bonding and π-overlapping can lead to an extended assembly of a complex molecule. For a π-stacked arrangement planarity of the whole molecule is a prerequisite [19]. In [Ni(hpac)(Himdz)], Ni, O(1), O(2), N(1), N(2), and C(1)–C(5) are satisfactorily planar. However, the phenyl ring and the imidazole plane are twisted with respect to the above mentioned plane in each molecule with dihedral angles of 15° and 14.8°, respectively. In addition to the twisting of the phenyl ring, the imidazole plane also has a different orientation with reference to the plane containing Ni, O(1), O(2), N(1), N(2) and C(1)–C(5) atoms. As a result of this non planarity, neither have intermolecular π–π interactions in the crystal lattice. However, the acidic imidazole N–H participates in strong intermolecular hydrogen bonding. The coordinated hydroxyphenyl-O atoms (O(2) and O(4)) act as acceptors in the hydrogen bonding and a one-dimensional assembly (figure 2) of the molecules is formed via N–H↑O interactions. The N(3)↑O(4) distance and N3–H3↑O4 angle are 2.786(3) Å and 159.31°, and the N(6)↑O(2) distance and N(6)–H(6)↑O(2) angle are 2.756(3) Å and 164.4° (table 3), respectively. The Ni↑Ni distances of adjacent molecules in the chain-like arrangement are 7.536 Å and 7.412 Å, respectively.

4. Conclusions

A new nickel(II) complex with hpac^{2-} and imidazole has been synthesized and characterized. The Ni^{2+} has square-planar N_2O_2 coordination geometry via the enolate-O, the imine-N and hydroxyphenyl-O atoms. However, the molecule is non-planar due

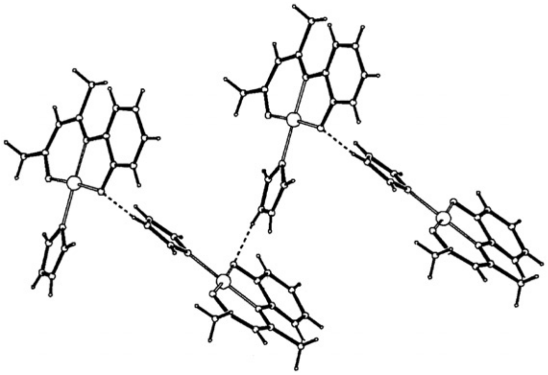


Figure 2. One-dimensional ordering of [Ni(bhac)(Himdz)] molecules via N–H↑O interactions.

to different orientations of the Schiff-base phenyl ring plane and the heterocycle (imidazole) plane with respect to the plane formed by the rest of the molecule. A one-dimensional assembly of the molecules is formed via intermolecular hydrogen bonding involving the acidic imidazole N–H in the solid state.

Supplementary material

Crystallographic data (excluding structure factors) for structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as deposition No. CCDC639265. Copies of the data can be obtained, free of charge, on application to the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 IEZ UK (Fax: +44(1223)336033; Email: deposit@ccdc.cam.ac.uk).

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