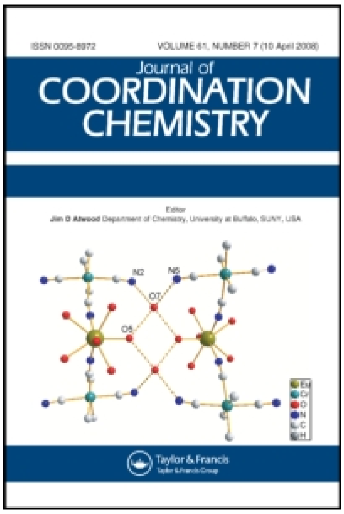

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Synthesis and crystal structure of Ni(II) complexes of 2'-(3,5-dibromo-2-hydroxybenzylidene)-3,5-dihydroxybenzoylhydrazide

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Synthesis and crystal structure of Ni(II) complexes of 2′-(3,5-dibromo-2-hydroxybenzylidene)-3,5-dihydroxybenzoylhydrazide

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A new mononuclear nickel(II) complex incorporating a Schiff-base ligand, $[NiL_2](DMF)_4$ (HL = 2′-(3,5-dibromo-2-hydroxybenzylidene)-3,5-dihydroxybenzoylhydrazide), has been synthesized and characterized by IR, UV-Vis, elemental analysis and X-ray crystal structure analysis. HL is an anionic tridentate ligand. The nickel atom is hexacoordinated with two oxygen atoms from keto group and two oxygen atoms from hydroxy group and two nitrogen atoms from amide, with the two nitrogen atoms occupying the axial positions forming a distorted octahedral coordination sphere.

Keywords: Nickel(II); 3,5-Dihydroxybenzoylhydrazide; Crystal structure; Synthesis

1. Introduction

Condensation of primary amines with carbonyl compounds yields Schiff bases [1]; chemistry of metal coordinated Schiff bases [2] are important because of their ability to serve as polymeric ultraviolet stabilizers [3], laser dyes [4] and molecular switches in logic or memory circuits [5]. Schiff-base complexes have also been employed as catalysts for many reactions and as biological models in understanding the structure of biomolecules and biological processes [6]. Several Schiff-base complexes have also been shown to inhibit tumor growth [7]. As a part of our study on the synthesis and characterization of Schiff-base complexes, a nickel complex was prepared and the crystal structure determined by X-ray diffraction.

2. Experimental

All chemicals were commercial reagents and used without further purification. Solvents were of analytical grade. Elemental analysis was performed on a Perkin-Elmer 2400/II instrument. IR spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer

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with KBr pellets in the range $4000 \sim 400\,\mathrm{cm}^{-1}$. UV-Vis measurements were carried out in DMF solution using a Shimadzu 2401PC UV-Vis spectrophotometer. ^{1}H NMR spectra were measured with a Varian XL200 nuclear magnetic resonance spectrometer using DMSO as solvent and TMS as internal standard. The melting point was determined on a WZ-1 melting point apparatus and uncorrected.

2.1. *Synthesis of HL (I)*

3,5-Dihydroxybenzoylhydrazine (5 mmol, 0.8408 g) was dissolved in anhydrous ethanol ($40\,\mathrm{cm}^3$) and 3,5-dibromo-2-hydroxybenzaldehyde (5 mmol, 1.3995 g) was added. The mixture was refluxed for 4 h and the yellow precipitate which formed was collected by filtration and washed with ethanol. The product was recrystallized from ethanol and dried under reduced pressure to give 2′-(3,5-dibromo-2-hydroxybenzylidene)-3,5-dihydroxybenzoylhydrazide. m.p. $266.1 \sim 266.9$°C. Yield: 88% (1.90 g). UV-Vis (EtOH, nm): $\lambda_{\max}$, 254, 337, 441. Anal. Calcd for $C_{14}H_{10}N_2Br_2O_4$: C 39.10; H 2.35; N 6.52. Found: C 39.20; H 2.22; N 6.56. IR(KBr, cm^{-1}): 3349 (m, ν(N–H)), 3209 (m, (O–H)), 3072 (m, (O–H)), 1649 (m, ν(C=O)), 1595 (s, ν(C=N)). ^{1}H NMR (200 MHz, DMSO, ppm). δ: 12.77 (s, 1H, OH), 12.23 (s, 1H, NH), 9.63 (s, 2H, OH), 8.50 (s, 1H, CH), $7.75 \sim 7.81$ (m, 2H, ArH), 6.77 (d, 2H, ArH), 6.43 (s, 1H, ArH).

2.2. *Synthesis of [NiL$_2$](DMF)$_4$ (II)*

A mixture of $NiAc_2 \cdot 4H_2O$ (1 mmol, 0.2488 g), HL (2 mmol, 0.8601 g) and distilled water ($30\,\mathrm{cm}^3$) was refluxed for 2 h. The green precipitate (yield about 92%) was filtered off, washed with ethanol and dried over P_2O_5 for 24 h. The compound is soluble in a range of common organic solvents like DMF and pyridine but insoluble in ethanol and water. The solid (0.1 mmol, 0.1209 g) was dissolved in DMF ($5\,\mathrm{cm}^3$) to give, with slow evaporation over 20 d at room temperature, green blocky crystals adequate for X-ray analysis. Yield: 42% based on Ni. Anal. Calcd for $C_{40}H_{46}Br_4N_8NiO_{12}$ (%): C 39.73; H 3.84; N 9.27. Found: C 39.66; H 3.72; N 9.35. UV-Vis (EtOH, nm): $\lambda_{\max}$, 272, 346, 418. IR(KBr, cm^{-1}): 3338 (m, υ(N-H)), 3059 (m, (O–H)), 1622 (m, ν(C=O)), 1580 (s, ν(C=N)), 444 (m, ν(Ni–N)), 413 (m, ν(Ni–O)).

2.3. *X-ray crystallography*

Crystallographic data were collected with a Bruker CCD Smart 1000 diffractometer equipped with graphite-monochromatized Mo-Ka X-ray radiation ($\lambda = 0.71073$ Å) using the ω-θ scan mode in the range $1.98 \leq \theta \leq 26.00°$ at 293 K. Raw frame data were integrated with the SAINT program [8]. The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares techniques (SHELXL-97) on F^2 [9]. An empirical absorption correction was applied with the SADABS program [10]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter.

2.3.1. Crystallographic data. $C_{40}H_{46}Br_4N_8NiO_{12}$, $M = 1209.20$, Monoclinic, $P2(1)/n$, $a = 11.2526(10)$ Å, $b = 32.430(3)$ Å, $c = 14.1136(13)$ Å, $\beta = 109.092(2)°$, $v = 4867.1(8)$ Å^3,

$Z = 4$, $Dc = 1.650\,\mathrm{Mg\,m^{-3}}$, crystal dimensions $0.495 \times 0.330 \times 0.237\,\mathrm{mm^3}$, $\mu = 3.748\,\mathrm{mm^{-1}}$, $F(000) = 2424$, $R_1 = 0.0525$, $wR_2 = 0.1088$ ($I \geq 2\sigma(\mathrm{I})$), goodness-of-fit is 0.994. A total of 26641 reflections were collected (9521 independent reflections with $R_{int} = 0.1088$). The largest peak and hole on the final difference Fourier map were 0.734 and $-0.633\,\mathrm{e\,Å^{-3}}$, respectively.

3. Results and discussion

3.1. *X-ray diffraction studies*

A diagram showing the structure and packing are shown in figures 1 and 2, respectively. The hexacoordinate Ni(II) is defined by the two keto oxygen atoms O(1) and O(5), by the two hydroxy oxygen atoms O(2) and O(6) and by the two amide nitrogen atoms N(1) and N(3). The two nitrogen atoms occupy axial positions forming a distorted octahedral coordination sphere. The O(1)–Ni–O(6), O(1)–Ni–O(5), O(5)–Ni–O(2) and O(2)–Ni–O(6) angles in the equatorial plane have values of 88.76(15)°, 90.18(14)°, 89.97(14)° and 93.51(14)°, respectively. The equatorial Ni–O distances are in the range 2.007(3)–2.124(3) Å, which are comparable with analogous hexacoordinated distorted Ni(II) complexes incorporating Schiff-base ligands [11], and appreciably longer than those of the square planar or tetrahedral complexes [12]. The axial Ni–N distances are in the range 1.979(4)–1.980(4) Å, comparable to corresponding values in similar systems [11]. The C(15)–O(5) and C(1)–O(1) bond lengths of 1.229(6) and 1.230(6) Å, respectively, are nearer to a C–O single bond than to a C–O double

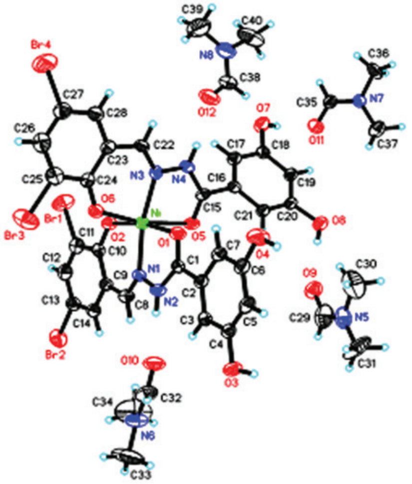

Figure 1. The structure of title complexes, showing the atomic numbering, Displacement ellipsoids are drawn at the 30% probalibity level. Selected bond distances (Å) and angles (°): Ni–N(1) 1.979(4), Ni–N(3) 1.980(4), Ni–O(2) 2.007(3), Ni–O(6) 2.042(4), Ni–O(1) 2.099(3), Ni–O(5) 2.124(3), O(1)–C(1) 1.230(6), O(5)–C(15) 1.229(6), N(1)–Ni–N(3) 168.98(17), (1)–Ni–O(2) 90.08(16), N(3)–Ni–O(6) 89.00(16) O(2)–Ni–O(6) 93.51(14), N(1)–Ni–O(1) 78.39(16), N(3)–Ni–O(1) 93.50(15), O(2)–Ni–O(1) 168.46(14), O(6)–Ni–O(1) 88.76(15), N(1)–Ni–O(5) 93.62(15), N(3)–Ni–O(5) 78.82(16), O(2)–Ni–O(5) 89.97(14), (6)–Ni–O(5) 167.68(14), O(1)–Ni–O(5) 90.18(14).

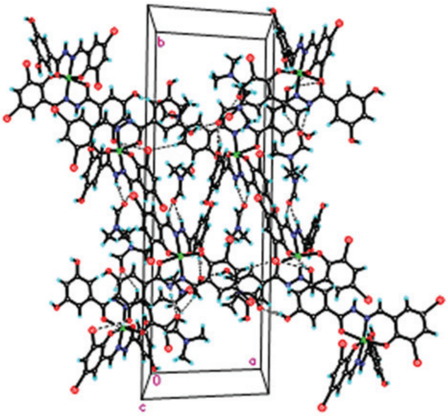

Figure 2. Packing of title complexes, viewed down the *c* axis.

bond distance. However, it is shorter than a classic C–O single bond 1.420 Å. Such shortening may be attributed to electron delocalization in the coordinated ligand [13]. The adjacent C(15)–N(4) and C(1)–N(2) bond lengths of 1.341(6) and 1.360(7) Å, respectively, are very close to the normal C=N length [14]. The Ni–O(6) and Ni–O(2) bond lengths of 2.042(4) and 2.007(3) Å, respectively, are slightly shorter than Ni–O(5) and Ni–O(1) indicating that the hydroxy oxygens coordinate slightly stronger than the oxygen atoms from keto.

Each unit has four DMF molecules of crystallization, involved in intra- and intermolecular hydrogen bonds, which are 3D in nature and thus not easy to describe (figure 2).

3.2. *IR spectra*

The IR spectrum of the ligand shows stretching bands at 3209 $\mathrm{cm^{-1}}$, attributed to phenyl O–H bonds [15] which disappears in the complex, indicating the phenyl O–H has been deprotoned and coordinated to the nickel. A band around 1649 $\mathrm{cm^{-1}}$, attributable to ν(C=O) in the ligand spectrum, is markedly shifted to lower energy at 1622 $\mathrm{cm^{-1}}$ in the complex indicating coordination in the enolate form. A sharp band at 1595 $\mathrm{cm^{-1}}$ in the spectrum of HL is shifted to lower frequencies by 15 $\mathrm{cm^{-1}}$ in the spectra of the complex indicating coordination via the amide nitrogen. Moreover, the Ni–N vibration is found at 444 $\mathrm{cm^{-1}}$ and the Ni–O at 413 $\mathrm{cm^{-1}}$ [12a]. These peaks are in agreement with related complexes regardless of the degree of distortion of the coordination environment.

3.3. *UV-Vis spectra*

The electronic spectra were recorded in ethanol solutions in the 200–500 nm range for the free ligand and the complex. The bands at 337 and 346 nm may be assigned to a n–π^* transition between lone-pair electron of p orbital of N atom in the C=N group and a conjugated Π bond of benzene. Peaks at 254 and 272 nm are assigned to a π–π^*

transition of the Schiff base [16]. Absorption spectra of the complex compared with HL exhibit reduced oscillator strengths and blue shifts versus HL with absorption maxima at 418 nm. This modification can be related to the molecular structure of the complexes with the planar geometry of the ligands hampered by steric hindrance in the complexes. The resulting lack of conjugation is consistent with the changes observed in intensity and energy of the charge transfer transition.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 632721. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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