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Synthesis and structural characterization of Ni(II) complexes containing a heterocyclic NO donor ligand

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1. Introduction

The heterocyclic NO donor Schiff base ligands play an important role in the development of coordination chemistry as they readily form complexes with most of the transition metal ions [1–4]. The synthesis, structure and properties of coordination complexes still arouse considerable research interests because of their potential applications in material science [5]. The Schiff base complexes of transition metals have acquired a special significance in the domain of coordination chemistry because of their diverse range of applications, such as in organic synthesis, photochemistry and heterogeneous catalysis, drug design and as models of biological systems [6–14]. Also the unsymmetrical Schiff bases are very important as they can bind one, two or more metal centers, involving various coordination modes, and allow successful synthesis of homo and/or heteronuclear metal complexes with interesting stereochemistries [15,16].

As part of our continued involvement in the coordination chemistry of NO donor Schiff bases, we have recently reported the metal-binding properties of the Schiff base Opdac to control the stereochemistry at cobalt(II) center [17]. So we were eager to explore the bonding features of this Schiff base Opdac with respect to nickel(II) center in the presence of various counter ions and herein we report the synthesis and characterization of its five novel Ni(II) complexes [Ni(Opdac)₂]Cl₂ (1), [Ni(Opdac)₂(CH₃OH)₂]Br₂(CH₃OH)₂ (2), [Ni(Opdac)₂]I₂ (3), [Ni(Opdac)₂NO₃]NO₃ (4) and [Ni(Opdac)₂-ClO₄]ClO₄ (5).

ABSTRACT

Five novel nickel(II) complexes have been successfully synthesized with a heterocyclic ligand, Opdac, $[Ni(Opdac)_2]Cl_2$ (1), $[Ni(Opdac)_2(CH_3OH)_2]Br_2(CH_3OH)_2$ (2), $[Ni(Opdac)_2]I_2$ (3), $[Ni(Opdac)_2NO_3]NO_3$ (4) and $[Ni(Opdac)_2ClO_4]ClO_4$ (5) where Opdac = 4-(1-H-1,3-benzimidazole-2-yl)-1,5-dimethyl-2-phenyl-1-2-dihydro-3-H-pyrazol-3-one. All the complexes were characterized by elemental analysis, molar conductivity, CHN analysis, magnetic susceptibility measurements, spectroscopic studies and TG/DTA methods. In all the complexes, Opdac acts as a bidentate ligand coordinating to Ni(II) ion via the benzimidazole imine nitrogen and the pyrazolone oxygen atoms. The complexes **1** and **3** have a tetrahedral geometry while **2**, **4** and **5** have an octahedral geometry around the Ni(II) center.

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2. Experimental

2.1. Materials and instrumentation

High purity 4-antipyrine carboxaldehyde (Aldrich, USA), O-phenylenediamine, nickel(II) nitrate hexahydrate, and nickel(II) chloride hexahydrate (E. Merck, India) were purchased from the respective concerns and used as such. Metal bromide, iodide and perchlorate salts were prepared by dissolving Analar BDH nickel carbonate in the respective 50% acids and crystallizing the salts after concentrating the respective solutions on a steam bath. All other chemicals and solvents were AR grade and used as such.

The carbon, hydrogen and nitrogen content in the synthesized compound was determined on a Perkin-Elmer 240 CHN elemental analyzer. All the complexes were analyzed for their metal, halide and perchlorate contents by standard methods [18,19]. Molar conductivities were measured using freshly prepared 10⁻³ M solutions in dimethylformamide, nitrobenzene and methanol at room temperature, using a Toshniwal conductivity bridge with a dip-type conductance cell (cell constant 0.9712) which was calibrated with 0.01 M KCl solution. The infrared spectra of the ligands and the complexes were recorded in the range 4000-400 cm⁻¹ on a Shimadzu IR 470 spectrophotometer. Solid state electronic spectra in the range 800-200 nm were recorded using a Shimadzu UV-Vis-2450 spectrophotometer and in the range 800-1500 nm on a Cary 2390 UV-Vis-NIR spectrophotometer. Magnetic susceptibility measurements were performed on pulverized samples at room temperature on a Sherwood Magway MSB Mk1 balance. The diamagnetic corrections were calculated by using Pascal's constants. Thermal studies were undertaken on Shimadzu DTG-60 thermal analyzer





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in nitrogen atmosphere in the temperature range 25–700 °C; heating rate: $10 \circ C \min^{-1}$.

The synthesis, structural and electronic features of 4-(1-H-1, 3-benzimidazole-2-yl)-1,5-dimethyl-2-phenyl-1-2-dihydro-3-H-pyrazol-3-one (Opdac) has already been published by the authors [17].

2.2. Synthesis of metal complexes

2.2.1. General procedure for synthesis of nickel(II) complexes

A solution of NiX₂· $6H_2O$ (X = Cl, Br, I, NO₃ and ClO₄) in acetonitrile (1 mmol, 10 mL) was added to a hot solution of Opdac (2 mmol, 20 mL) in ethyl acetate and refluxed for about 3 h. The precipitated complexes were filtered off, washed with ethyl acetate and dried under vacuum and kept in desiccator. All the complexes were recrystallized from methanol for single crystals by slow vapor diffusion of ethyl acetate from an adjacent container, but good quality single crystals, suitable for X-ray crystallography, of only complex **2** were obtained. The analytical, spectral and magnetic data are summarized below.

2.2.2. [Ni(Opdac)₂]Cl₂ (1)

Anal. Calc. for $C_{36}H_{32}N_8O_2Cl_2Ni$ (738.29): C, 58.57; H, 4.37; N, 15.18; Ni, 7.95; Cl, 9.60. Found: C, 58.54; H, 4.33; N, 15.16; Ni, 7.92; Cl, 9.56%. IR (cm⁻¹): 1620 [ν (C=O)], 1604 [ν (C=N)], 3320 [ν (N-H)], 446 [ν (Ni-N)], 556 [ν (Ni-O)]; (λ_M/Ω^{-1} cm² mol⁻¹): 152.37 (in DMF), 186.54 in MeOH), 53.81 (in C₆H₅NO₂); (λ_{max} , nm) 380 (n- π *), 260 (π - π *), 638, 1192 (d-d transitions), 290 (C-T transition); μ_{eff} = 3.39 BM.

2.2.3. [Ni(Opdac)₂(CH₃OH)₂]Br₂(CH₃OH)₂ (**2**)

Anal. Calc. for C₄₀H₄₈N₈O₆Br₂Ni (955.39): C, 50.29; H, 5.06; N, 11.73; Ni, 6.14; Br, 16.73. Found: C, 50.25; H, 5.02; N, 11.69; Ni, 6.11; Br, 16.71%. IR (cm⁻¹): 1622 [ν (C=O)], 1604 [ν (C=N)], 3320 [ν (N-H)], 450 [ν (Ni-N)], 555 [ν (Ni-O)]; (λ_{M}/Ω^{-1} cm² mol⁻¹): 164.58 (in DMF), 178.39 (in MeOH), 56.25 (in C₆H₅NO₂); (λ_{max} , nm) 378 (n- π *), 256 (π - π *), 420, 605, 1002 (d-d transitions), 318 (C-T transition); μ_{eff} = 3.08 BM.

2.2.4. $[Ni(Opdac)_2]I_2$ (**3**)

Anal. Calc. for $C_{36}H_{32}N_8O_2I_2Ni$ (921.19): C, 46.94; H, 3.50; N, 12.16; Ni, 6.37; I, 27.55. Found: C, 46.91; H, 3.47; N, 12.13; Ni, 6.34; I, 27.51%. IR (cm⁻¹): 1620 [ν (C=O)], 1602 [ν (C=N)], 3320 [ν (N-H)], 446 [ν (Ni-N)], 550 [ν (Ni-O)]; (λ_M/Ω^{-1} cm² mol⁻¹): 138.14 (in DMF), 172.36 (in MeOH), 54.72 (in C₆H₅NO₂); (λ_{max} , nm) 383 (n- π^*), 264 (π - π^*), 615, 1180 (d-d transitions), 292 (C-T transition); μ_{eff} = 3.49 BM.

2.2.5. [Ni(Opdac)₂NO₃]NO₃ (4)

Anal. Calc. for $C_{36}H_{32}N_{10}O_8Ni$ (791.40): C, 54.64; H, 4.08; N, 17.70; Ni, 7.42. Found: C, 54.60; H, 4.04; N, 17.67; Ni, 7.39%. IR (cm⁻¹): 1622 [ν (C=O)], 1604 [ν (C=N)], 3320 [ν (N-H)], 1435, 1240, 1052 [ν (NO₃coordinated)], 1384, 823 [ν (NO₃uncoordinated)], 443 [ν (Ni–N)], 550 [ν (Ni–O)]; (λ_M/Ω^{-1} cm² mol⁻¹): 69.37 (in DMF), 92. 14 (in MeOH), 24.52 (in C₆H₅NO₂); (λ_{max} , nm) 378 (n- π^*), 258 (π - π^*), 390, 600, 1006 (d-d transitions), 313 (C-T transition); μ_{eff} = 2.95 BM.

2.2.6. [Ni(Opdac)₂ClO₄]ClO₄ (**5**)

Anal. Calc. for $C_{36}H_{32}N_8O_{10}NiCl_2$ (886.29): C, 49.91; H, 3.72; N, 12.93; Ni, 6.78; ClO₄, 22.43. Found: C, 49.89; H, 3.68; N, 12.91; Ni, 6.75; ClO₄, 22.39%. IR (cm⁻¹): 1622 [ν (C=O)], 1602 [ν (C=N)], 320 [ν (N–H)], 1143, 1114, 1024, 945, 630 [ν (ClO₄coordinated)], 1089, 624 [ν (ClO₄uncoordinated)], 446 [ν (Co–N)], 550 [ν (Co–O)]. (λ_M/Ω^{-1} cm² mol⁻¹): 78.37 (in DMF), 110.25 (in MeOH), 27.41

Table 1

Crystal data and structure refinement parameters for complex 2.

CCDC No.	814713	
Formula	C40H48Br2N8NiO6	
Formula weight	955.39	
Crystal size (mm)	0.30 X 0.20 X 0.20	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions		
a (Å)	9.1391(2)	
b (Å)	13.1308(3)	
c (Å)	17.4313(4)	
β (°)	94.0830(10)	
V (Å ³)	2086.51(8)	
Ζ	2	
F(000)	980	
μ Mo K α (mm ⁻¹)	0.71073	
T (K)	293(2)	
R _{int}	0.0342	
Range of h, k, l	-13/14, -13/20, -26/26	
$\theta_{\min/\max}$ (°)	2.23 /33.17	
Reflections collected/unique/observed $[I > 2\sigma(I)]$	32657/7933/5408	
Data/restraints/parameters	7933/0/272	
Goodness-of-fit (GOF) on F^2	1.011	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0366$	
	$wR_2 = 0.0907$	
R indices (all data)	$R_1 = 0.0701$	
	$wR_2 = 0.1038$	

(in C₆H₅NO₂); (λ_{max} , nm) 380 (n– π^*), 256 (π – π^*), 426, 602, 1009 (d–d transitions), 323 (C–T transition); μ_{eff} = 2.96 BM.

Caution! Though we have not met with any incident while working with the perchlorate compound described here, care should be taken in handling them as the perchlorates are potentially explosive. They should not be prepared and stored in large amounts.

2.3. X-ray crystallographic study

The block pale green crystal of [Ni(Opdac)₂(CH₃OH)₂]Br₂(CH₃- OH_{2} (2) was directly picked up from the mother liquor, attached to a glass fiber and transferred for the data collection. X-ray single crystal data were collected using Mo K α (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Unit cell refinement (Bruker, 2006) [20] data reduction (SAINT) and structure solution as well as refinement (SHELXL97) [21] were carried out using the software package of SMART APEX. All structures were solved by direct method and refined in a routine manner. In most of the cases, nonhydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed. Molecular graphics were generated by using the softwares Mercury 2.3 [22] and ORTEP 3 [23]. The details of the X-ray crystal data and the structure solution as well as the refinement are given in Table 1.

3. Results and discussion

3.1. Properties

The crystalline complexes are soluble in common organic solvents such as methanol, ethanol, dimethylformamide and nitrobenzene, but insoluble in ethyl acetate, chloroform and acetone. The elemental analysis data suggest that the complexes can be formulated as Ni(Opdac)₂X₂ (X = Cl⁻, Br⁻, I⁻, NO₃⁻ or ClO₄⁻). The molar conductance data reveals that [Ni(Opdac)₂]Cl₂ (**1**), [Ni(Opdac)₂(-CH₃OH)₂]Br₂(CH₃OH)₂ (**2**) and [Ni(Opdac)₂]NO₃ (**4**) and the solution of the soluti $[Ni(Opdac)_2ClO_4]ClO_4$ (5) complexes behave as 1:1 electrolytic type [24].

3.2. Infrared spectra

The Infrared spectra of the complexes 1–5 are presented in Fig. 1. The strong bands observed at 1631 and 1612 cm⁻¹ in Opdac are attributed to the stretching vibrations of the pyrazolone carbonyl oxygen [17,25] and benzimidazole imine nitrogen [26], respectively. In the complexes 1–5 the v(C=O) and v(C=N) bands show a red shift with respect to those of the free ligand by 9-11 and 8–10 cm⁻¹, respectively. The N–H stretching frequency observed in Opdac around 3321 cm⁻¹ remains almost unchanged in all the complexes indicating that the N-H nitrogen of the benzimidazole moiety is not coordinated [26]. Thus the IR spectral data of the solid state complexes show that Opdac acts as a neutral bidentate ligand coordinating through the imine nitrogen and the pyrazolone oxygen forming a six membered ring around the central metal ion. The presence of additional non-ligand bands in the spectra of all the complexes around 443-450 and 550-556 cm⁻¹ are attributed to Ni–N and Ni–O stretching frequencies, respectively [27].

The nitrate complex exhibits vibrational frequencies characteristic of both uncoordinated and coordinated nitrate ions. A very strong band at 1384 cm^{-1} and a medium band at 823 cm^{-1} are attributed to the v_3 and v_2 vibrations, respectively, of ionic nitrate of D_{3h} symmetry [28]. The presence of coordinated nitrate is indicated by two bands at 1435 and 1240 cm⁻¹ due to the v_4 and v_1 vibrations, respectively, of the nitrate of C_{2v} symmetry [29]. Since $(v_4 - v_1) = 195 \text{ cm}^{-1}$, the nitrate ion is coordinated in a bidentate fashion [30].

In the perchlorate complex, the triply split band maxima at 1143, 1114 and 1024 cm⁻¹ are due to the v_8 , v_6 and v_1 vibrations, respectively, of the perchlorate ion of C_{2v} symmetry, indicating the coordination of the perchlorate ion in a bidentate fashion [31]. But the presence of a very strong band at around 1089 cm⁻¹ is attributed to the v_3 vibration of uncoordinated perchlorate ion of T_d symmetry [32]. The bands observed around 945 and 630 cm⁻¹ due to the v_2 and v_3 vibrations, respectively, of the coordinated perchlorate (C_{2v}) ion and the band at 624 cm⁻¹ due to the v_4 vibration of the uncoordinated perchlorate (T_d) ion also support the coexistence of both coordinated and uncoordinated perchlorate ion in the complex [31].

3.3. Electronic spectra and magnetism

The electronic spectra of the complexes 1-5 are presented in Figs. 2 and 3. The electronic spectrum of Opdac exhibits two main peaks at about 387 and 252 nm which are assignable to the $n-\pi^*$ and π - π ^{*} transitions, respectively [17]. In all the complexes, the $n-\pi^*$ band is blue-shifted to the 378–383 nm region while the π – π^* band is red-shifted to the 256–264 nm region compared to Opdac. The reflectance spectra of the complexes 1 and 3 show bands in the region 615–638 nm attributable to the ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ transition which is consistent with a tetrahedral geometry around the nickel(II) ion. The low-energy band expected for the ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(F)$ transition in tetrahedral nickel(II) complexes is observed in the region 1118–1192 nm. The observed μ_{eff} values of 3.39 BM for 1 and 3.49 BM for 3 are in good agreement with the tetrahedral nickel(II) complexes [27].

The diffuse reflectance spectra of complexes 2, 4 and 5 are characterized by three main bands in the regions $v_1 = 1002 - 1009$ nm ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F), \quad v_{2} = 600-605 \text{ nm} \quad {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and $v_3 = 390-426$ nm ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ and these transitions are indicative of an octahedral geometry around the Ni(II) center. The room temperature magnetic moments of the complexes 2, 4 and 5 are







Fig. 2. UV-Vis spectra of the complexes 1-5.

3.4. Thermal studies (TG/DTA)

The TG and DTA curves of the complexes **1–5** are illustrated in Fig. 4. The assignment of each decomposition process was based on the chemical and IR spectral analyses of the intermediate products and the final residue.

The complex **1** undergoes a two stage decomposition process. There is no mass loss up to 191 °C indicating the absence of either water or solvent molecules in the complex. The first stage starts at 191 °C and ends at 454 °C with an exothermic DTA shoulder at 352 °C, corresponding to the removal of one Opdac molecule (observed weight loss 41.24%, calculated 41.08%). The second stage occurs between 455 and 627 °C, resulting the release of remaining Opdac (observed weight loss 41.24%, calculated 41.12%) with an exothermic DTA shoulder at 574 °C. The final residue (17.56%) above 627 °C corresponds to anhydrous NiCl₂.

The thermogram of the complex **2** shows that the decomposition occurs in three steps. During the first stage (52–145 °C) both the coordinated as well as uncoordinated methanol molecules are decomposed with an exothermic DTA peak at 98 °C (observed weight loss 13.41%, calculated 13.15%). Two bromide ions (observed weight loss 16.73%, calculated 16.08%) are decomposed in second step (146–365 °C) with an exothermic DTA peak at 336 °C. The third stage (366–602 °C) is due to the removal of the two Opdac molecule (observed weight loss 63.71%, calculated 63.29%) with an exothermic DTA peak at 565 °C leaving anhydrous NiO (7.81%) as the final residue above 602 °C.

The complex **3** is thermally stable up to 171 °C indicating the absence of either water or solvent molecules in the complex.



Fig. 3. UV–Vis–NIR spectra of the complexes 1–5.

Complex **2** undergoes a two stage decomposition process. During the first stage (171–315 °C) two iodide ions are decomposed with an exothermic DTA peak at 305 °C (observed weight loss 27.56%, calculated 26.96%). The second stage (316–460 °C) occurs with an exothermic DTA peak at 445 °C, corresponding to the release of both Opdac molecules (observed weight loss 66.11%, calculated 66.02%). The final residue (8.11%) above 460 °C corresponds to anhydrous NiO.

The complex **4** is stable up to 161 °C indicating the absence of either water or solvent molecules in the complex. Two nitrate ions are decomposed in the first step (161–302 °C) with an exothermic DTA peak at 236 °C (observed weight loss 15.67%, calculated 15.49%). The second stage (303–474 °C) occurs with an exothermic DTA peak at 446 °C, corresponding to the release of both Opdac molecules (observed weight loss 76.95%, calculated 76.19%) leaving anhydrous NiO (9.44%) as the final residue above 474 °C.

The complex **5** is stable up to 186 °C indicating the absence of either water or solvent molecules in the complex. The first stage (186–378 °C) with an exothermic DTA shoulder at 344 °C, corresponds to the decomposition of two perchlorate ions (observed weight loss 22.96%, calculated 22.15%). The second stage with a mass loss of 69.98% (calculated 70.30%) takes place in the range of 379–539 °C with an exothermic effect (DTA_{max} = 482 °C), corresponding to the decomposition of the two Opdac moiety. The final residue (8.62%) above 539 °C is anhydrous NiO.

Comparing the temperature ranges of the first weight loss for complexes **1–5**, it can be shown that within the series the bromide complex is the least stable and the chloride complex is the most



Fig. 4. TG and DTA curves of the complexes 1-5

stable. The thermal stability of the complexes is in the order: chloride > perchlorate > iodide > nitrate > bromide.

Based on the above observations the following tentative structures in Figs. 5–8 may be assigned to the complexes.

3.5. Crystal structure of [Ni(Opdac)₂(CH₃OH)₂]Br₂(CH₃OH)₂ (**2**)

The crystallographic data are summarized in Table 1. The crystal structure of the complex **2** with the atom numbering scheme is given in Fig. 9. The selected bond lengths and bond angles are given in Table 2.



Fig. 5. $[Ni(Opdac)_2]Cl_2$ (1) and $[Ni(Opdac)_2]I_2$ (3).



Fig. 6. [Ni(Opdac)₂(CH₃OH)₂]Br₂(CH₃OH)₂ (2).



Fig. 7. [Ni(Opdac)₂NO₃]NO₃ (4).



Fig. 8. [Ni(Opdac)₂ClO₄]ClO₄ (5).



Fig. 9. Molecular structure of complex **2** with atom labeling scheme. Atomic displacement parameters are shown at 50% probability level. Hydrogen atoms as well as solvated methanol molecules are omitted for clarity.

Table 2

Selected bond distances (Å) and angles (°) of complex 2.

Bond lengths (Å))	Bond angles (°)	
Ni(1)-O(1)	2.0192(12)	N(4)-Ni(1)-O(1)	89.22(5)
Ni(1)-N(4)	2.0996(13)	N(4)-Ni(1)-O(2)	91.00(5)
Ni(1)-O(2)	2.1122(13)	O(1)-Ni(1)-O(2)	89.68(5)
C(16)-O(1)	1.2566(19)	C(19)-O(2)-Ni(1)	122.09(13)
C(18)-N(4)	1.331(2)	C(7)-N(4)-Ni(1)	129.19(11)
C(7) - N(4)	1.400(2)	C(16)-O(1)-Ni(1)	121.85(11)
C(12)-N(3)	1.383(2)	C(16)-C(17)-C(18)	122.25(14)
C(17)-C(18)	1.443(2)	C(17)-C(18)-N(4)	123.27(14)
C(16)-N(2)	1.369(2)	N(3) - C(18) - N(4)	112.04(14)
C(13)-N(1)	1.332(2)	C(18) –N(3)–C(12)	107.32(14)
N(1)-N(2)	1.378(2)	C(16) - N(2) - N(1)	108.92(13)

The crystal structure of complex ${\bf 2}$ describes a methanol inclusion coordination complex of Ni(II). The Ni(II) center presents a six

coordination number, ligated through the benzimidazole imine nitrogen N(4) and pyrazolone oxygen atom (O1) atoms of two bidentate Opdac moieties as well as the oxygen atoms (O2) of two methanol molecules. The Ni–N4 bond distance value [2.0996(13) Å] conforms to those reported for the similar octahedral Ni(II) complexes with some Schiff bases [34]. The observed value for the Ni–O1 bond length 2.0191(12) Å is agreeable [1.987(5)–2.039(5) Å] to related octahedral Ni(II) complexes [35–37]. The Ni(II) center in the complex **2** is significantly distorted from the octahedral geometry as revealed from the corresponding $\angle O$ –Ni–O and $\angle O$ –Ni–N angles [89.67(5)–90.32(5)° and 89.22(5)–90.77(5)°, respectively] (Table 2 for details).

4. Conclusion

A series of mononuclear nickel(II) complexes $[Ni(Opdac)_2]Cl_2(1)$, $[Ni(Opdac)_2(CH_3OH)_2]Br_2(CH_3OH)_2(2)$, $[Ni(Opdac)_2]l_2(3)$, $[Ni(Op-dac)_2NO_3]NO_3(4)$ and $[Ni(Opdac)_2ClO_4]ClO_4(5)$ were prepared and characterized. In all the cases the Ni(II) ion is coordinated by the imine nitrogen and pyrazolone oxygen donor sites of the ligand. In the free ligand moiety Opdac, the imine nitrogen (N4) and pyrazolone oxygen (O1) are *trans* oriented to each other. During chelation, they rearrange to *cis* fashion in all the complexes. This *cis* conformation of the ligand is necessary for its participation as a bidentate NO chelate ligand. The complexes **1** and **3** have a tetrahedral geometry while **2**, **4** and **5** have an octahedral geometry around the Ni(II) center.

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Appendix A. Supplementary data

CCDC 814713 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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