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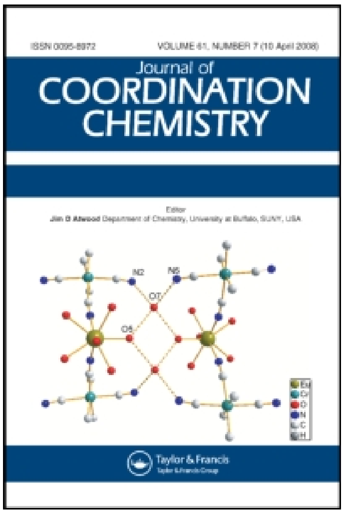

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Spectroscopic, thermal and X-ray crystal structure studies of some bis-(pyrazine-2-carboxylato) nickel(II) complexes

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Spectroscopic, thermal and X-ray crystal structure studies of some bis-(pyrazine-2-carboxylato) nickel(II) complexes

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Three nickel(II) complexes $[Ni(PC)_2(H_2O)_2]$, **1**, $[Ni(PC)_2(TU)_2]$, **2** and $[Ni(PC)_2(ABI)_2] \cdot 2(H_2O)$, **3**, PC = pyrazine-2-carboxylate, TU = thiourea and ABI = 2-aminobenzimidazole, were synthesized and characterized by elemental analysis, IR spectroscopy and thermal analysis. The complexes were also investigated by single crystal X-ray diffraction analysis. Structures of the monomeric complexes showed nickel(II) chelated to two PC ions from an oxygen atom of carboxylate ion and the adjacent hetero nitrogen atom. The three complexes were crystallized in a monoclinic system with $P2_1/c$ space group for **1**, while **2** and **3** had $C2/c$ space groups. The structure of **1** showed two coordinated water molecules occupying the *trans* positions of a slightly elongated octahedron. The structure of **2** consisted of two PC ions and two thiourea molecules in *trans* positions. The structure of **3** was different and showed a highly distorted octahedron with two ABI molecules chelated to the nickel ion in *cis* positions through their hetero nitrogen atoms. Two water molecules of crystallisation were shown in the structure of **3**.

Keywords: Nickel complexes; Pyrazine-2-carboxylic acid; Thiourea; 2-Aminobenzimidazole; X-ray analysis; Thermal analysis

1. Introduction

Pyridine and pyrazine carboxylic acids coordinate metal ions [1], as chelates through the hetero nitrogen atom and the carboxylate group. Reactions of bivalent transition metal ions with ligands containing heterocyclic carboxylic acids derived from pyridines, pyrazine and their homologous ring system have been extensively studied with respect to their bonding, electrochemical properties, thermal, and magnetic behaviour in

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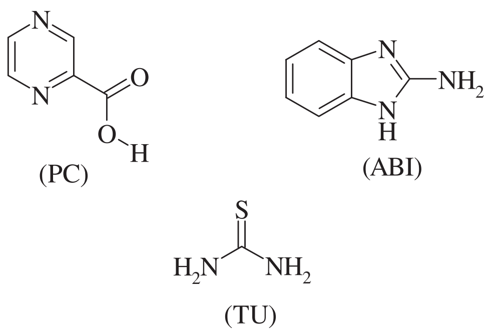

Scheme 1. Structures of the ligands.

addition to catalytic and photocatalytic processes [2–6]. In the last decade, complexes of pyrazines have found applications in the field of photochemistry and catalysis [7, 8]. Crystallographic study of a number of bivalent and trivalent metal complexes with NO-donor ligands such as pyrazine carboxylic acid derivatives have been reported [9–11]. The octahedral complexes $[M(PC)_2(H_2O)_2]$, M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), with pyrazine-2-carboxylate ion (PC^-) are characterized as monomeric molecules composed of a metal ion, two bidentate pyrazine-2-carboxylate moieties and two water molecules [9]. Crytallographic study of $[Mn(PC)_2(H_2O)_2]$ showed that pyrazine-2-carboxylate coordinated to the metal ion through the carboxyl oxygen and the adjacent nitrogen of the heterocyclic ring and the two water molecules were *cis*. In the remaining complexes, the two water molecules were found in a *trans* position [9].

In this article, we report the spectroscopic, thermal and X-ray crystal structure studies of $[Ni(PC)_2(H_2O)_2]$ and its thiourea and 2-aminobenzimidazole derivatives (scheme 1).

2. Experimental

2.1. *Materials*

$NiCl_2 \cdot 6H_2O$, pyrazine-2-carboxylic acid (PCA), thiourea (TU) and 2-aminobenzimidazole (ABZ) were purchased from Aldrich. All solvents were of analytical grade and were purified by distillation before use.

2.2. *Instrumentation*

Infrared measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Thermogravimetric analyses (TG) were performed under nitrogen with a heating rate of $10^\circ C\,min^{-1}$ using a Schimadzu DT-50 thermal analyser. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyser.

2.3. *Synthesis of $[Ni(PC)_2(H_2O)_2]$ (1)*

A mixture of pyrazine-2-carboxylic acid (0.50 g, 4.0 mmol) and KOH (0.23 g, 4.0 mmol) in *ca.* $20\,cm^3$ H_2O was stirred at room temperature for 10 min. An aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.48 g, 2.0 mmol) was added, and the mixture was then stirred for 5 min. The solvent was evaporated, and the residue was recrystallised from distilled water to give light blue crystals. The complex was washed with ethanol and then left to dry under vacuum (yield: 96%). $C_{10}H_{10}N_4O_6Ni$: M.wt. 340.91, Calcd (found): C, 35.2 (35.1); H, 3.0 (3.2); N, 16.4 (16.2).

2.4. *Synthesis of [Ni(PC)$_2$(TU)$_2$] (2)*

A mixture of 0.30 mmol (0.02 g) of ethanolic thiourea solution and 0.60 mmol (0.21 g) of $[Ni(PC)_2(H_2O)_2]$ aqueous solution was refluxed at 60°C for 30 h. The residue was isolated, filtered off and then washed several times with water. The complex was recrystallised from the ethanol : water mixture (1 : 1) to give deep-green crystals. The complex was left to dry *in vacuo* for several hours (yield 90%). $C_{12}H_{14}N_8O_4S_2Ni$: M.wt. 457.11, Calcd (found): C, 31.5 (31.3); H, 3.1 (3.3); N, 24.5 (24.4); S, 14.0 (13.7).

2.5. *Synthesis of [Ni(PC)$_2$(ABI)$_2$]·2H$_2$O (3)*

A similar procedure was employed as for $[Ni(PC)_2(TU)_2]$. Green crystals with a yield of 87% were obtained. $C_{24}H_{24}N_{10}O_6Ni$: M.wt. 607.22, Calcd (found): C, 47.5 (47.4); H, 4.0 (4.2); N, 23.1 (23.0).

2.6. *Single crystal X-ray structure determination*

The crystallographic data for X-ray analysis of complexes **1**, **2** and **3** are presented in table 1. Atomic positional parameters, bond lengths and angles, anisotropic temperature factors and the calculated and observed structure factors are given in supplementary tables (CCDC no for: (**1**) 257424; (**2**) 257425; (**3**) 257426). All diagrams

Table 1. Crystal parameters and X-ray diffraction data of complexes **1**, **2** and **3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{10}H_{10}N_4O_6Ni$	$C_{12}H_{14}N_8O_4S_2Ni$	$C_{12}H_{14}N_5O_4Ni$
Fw	340.922	457.134	350.985
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$
a (Å)	5.2515(2)	14.5147(4)	13.6533(3)
b (Å)	10.9933(4)	7.1486(2)	15.0594(5)
c (Å)	10.2851(4)	16.7491(5)	14.2461(4)
α (°)	90.00	90.00	90.00
β (°)	99.814(2)	90.7611(2)	113.448(2)
γ (°)	90.00	90.00	90.00
V (Å^3)	585.08(4)	1737.73(9)	2687.27(13)
Z	2	4	4
T (K)	298	298	298
ρ_{calc} (g cm^{-3})	1.935	1.747	0.868
μ (cm^{-1})	0.170	0.140	0.074
R^a	0.031	0.031	0.055
$R_w{}^b$	0.070	0.071	0.113
(Mo Kα) (Å)	0.71073	0.71073	0.71073

$^aR = \sum[|F_o| - |F_o| \sum |F_o|]$.
$^bR_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o)^2 + 0.10000(F_o)^2$.

and calculations were performed using the maXus crystallographic software package (Nonius, Delft & MacScience, Japan). The displacement factors of non-hydrogen atoms of the complexes were refined anisotropically, while the hydrogen atoms were refined isotropically.

3. Results and discussion

3.1. *IR spectra*

$NiCl_2$ interacts with pyrazine-2-carboxylic acid (PCA) to give the bis derivative, $[Ni(PC)_2(H_2O)_2]$, **1**. Reaction of **1** with thiourea (TU) resulted in the formation of the octahedral complex $[Ni(PC)_2(TU)_2]$; **1** reacted with 2-aminbenzimidazole (ABI) to give $[Ni(PC)_2(ABI)_2] \cdot 2(H_2O)$, **3**, with two waters of crystallisation. The IR spectra of pyrazine-2-carboxylic acid displayed stretching frequency bands at 1666, 1528, 1720 and 1273 cm^{-1} due to the ν(C=N), ν(C=C), ν(C=O) and ν(C–O). The three nickel complexes showed the ligand bands with the appropriate shifts, table 2. A separation by 21–60 cm^{-1} for the OCO^- stretching vibrations indicated monodentate carboxylate coordination. The complexes also showed positive shifts ($\Delta\nu \approx 24$–$56\ cm^{-1}$) from the free ligand C=N bond stretching frequency as well as from the out-of-plane ring deformation values suggesting coordination through heterocyclic nitrogen [12]. Furthermore, complexes **1**, **2** and **3** showed non-ligand ν(Ni–O) stretching frequency bands at 462, 535 and 530 cm^{-1}, respectively, indicating coordination of nickel via the carboxylate anion. Therefore, the nickel ion binds with PC through its hetero-nitrogen and hydroxyl oxygen atoms. Complexes **1** and **3** displayed strong and broad bands covering the 3000–3700 cm^{-1} range due to OH stretching vibration frequencies of water molecules indicating the hydrated nature of the complexes [12]. The broadness, however, cannot be used to determine whether the water molecules are coordinated or water of crystallisation.

3.2. *X-ray single crystal analysis*

X-ray measurements of the three nickel complexes were made at 298 K using suitable crystal sizes for data collection. The ORTEP representations of the complexes are

Table 2. Important IR data for the PCA, TU, ABI and complexes.

	IR data (cm^{-1})[a]					
Complex	ν(O–H)	ν(N–H)	ν(C=N)	ν(C=O)	ν(C–O)	ν(C=S)
PCA	3425	3062	1666(s)	1720(s)	1273(s)	–
1	3425	3063	1585(s) 1624(s)	1660(s)	1290(m)	–
TU	–	3383, 3278 3178, 3070	–	–	–	1619(m)
2	–	3358, 3288, 3160, 3057	1584(s) 1680(s)	1667(s)	1277(m)	1616(m)
ABI	–	3379, 3369	1651(s) 1558(s)	–	–	–
3	3449	3332	1600(s) 1569(s)	1628(s)	1269(s)	–

[a] s: strong; m: medium; w: weak.

illustrated in figures 1–3. Accurate lattice parameters were determined from least-squares refinements of well-centred reflections in the ranges $3.71 \leq \theta \leq 27.47$ for complex **1**, $3.04 \leq \theta \leq 27.49$ for complex **2** and $2.91 \leq \theta \leq 25.03$ for complex **3**. During data collection, three standard reflections were periodically observed and showed no significant intensity variations. The ranges of h, k and l are $-16 \leq h \leq 16$; $-16 \leq k \leq 17$ and $-16 \leq l \leq 16$ for **1**, and $0 \leq h \leq 18$; $0 \leq k \leq 9$; $-21 \leq l \leq 21$ for **2** and $-16 \leq h \leq 16$; $-16 \leq k \leq 17$; $-16 \leq l \leq 16$ for **3**. 2450 (complex **1**), 3647 (complex **2**) and 4371 (complex **3**) unique reflections were measured, of which 1317 (complex **1**), 2030 (complex **2**) and 1646 (complex **3**) had $I > 3.00\sigma(I)$. These observed reflections were used for structure determinations and refinements.

Single crystal X-ray analysis of $[Ni(PC)_2(H_2O)_2]$ showed that it has an identical structure to those reported in the literature [9, 10]. The analysis revealed that the complex crystallised in the monoclinic space group $P2_1/c$ with a Z value of 2. The X-ray study of **1** (figure 1) showed that the PC ligand uses one N,O-bonding moiety for coordination to the nickel(II) ion, leading to 2 : 1 stoichiometry and the appearance of monomeric molecules in the crystals. Two water molecules at the apices of the slightly elongated octahedron complete the coordination around the nickel ion (figure 1). This is apparent from the comparison of the respective Ni–O bond lengths, 2.095(13) and 2.069(11) Å. The nickel ion and both PC ligands lie in the equatorial plane. Selected bond lengths and bond angles within the complex are listed in table 3. The values obtained in this study are comparable with those obtained previously [9, 10]. The structure of a similar complex, $[Ni(PDC)_2(H_2O)_2]$, PDC = pyrazine-2,3-dicarboxylic acid, was also studied by X-ray diffraction [13] and has a slightly elongated octahedron with two water molecules in the axial positions at a distance of 2.0914(17) Å from the nickel(II) ion with an O–Ni–O angle of 88.17(7)°. Complex **1** showed a $Ni–O_3$ bond length of 2.095(13) Å, which is comparable with the corresponding one in $[Ni(PDC)_2(H_2O)_2]$. On the other hand, the bond angles around nickel(II) in complexes, $[Ni(PC)_2(H_2O)_2]$ and $[Ni(PDC)_2(H_2O)_2]$, are different, which could be due to the

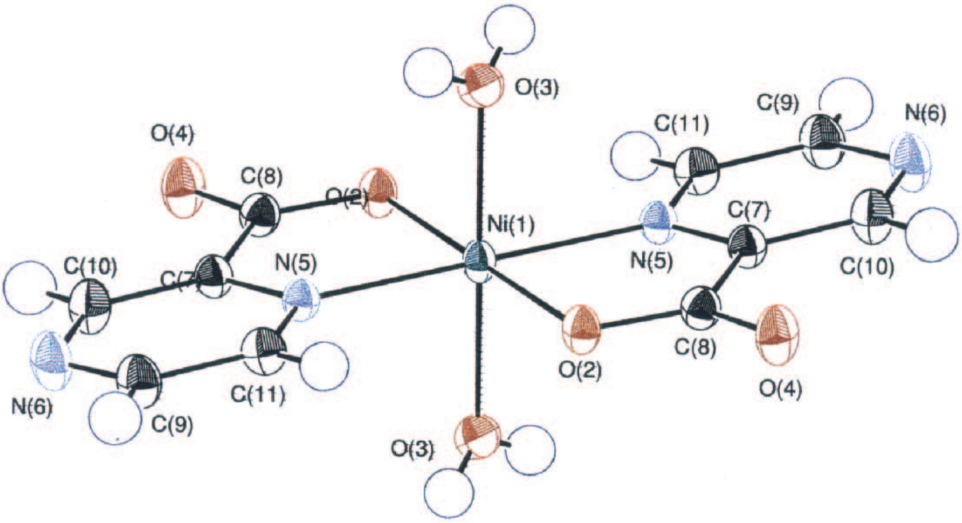

Figure 1. ORTEP representations of the $[Ni(PC)_2(H_2O)_2]$ complex.

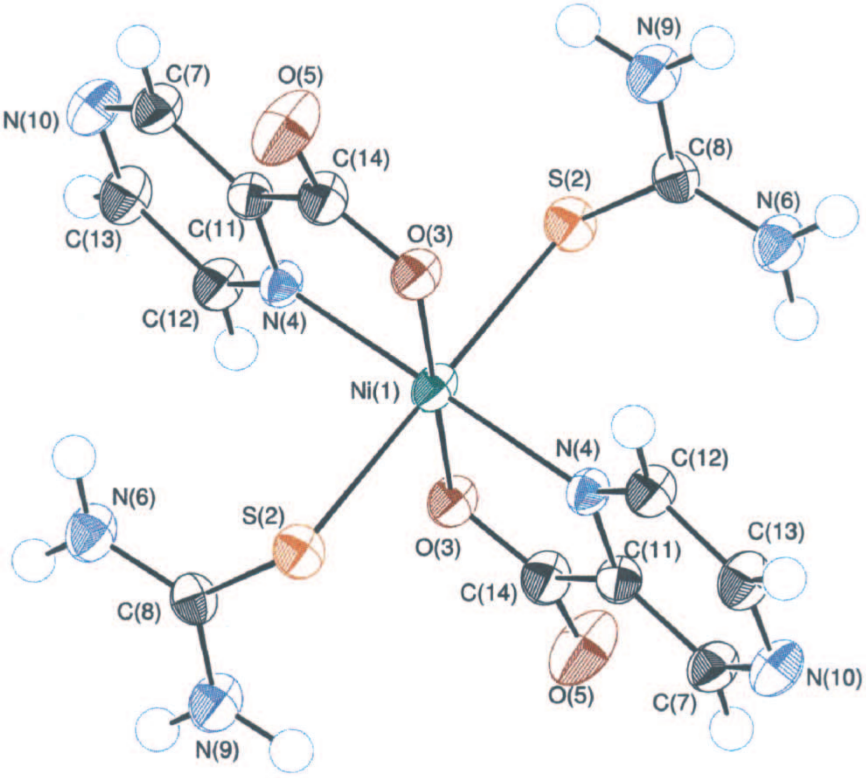

Figure 2. ORTEP representations of the $[Ni(PC)_2(TU)_2]$ complex.

presence of the additional carboxylic group in the latter complex. The contents of one unit cell showed that the chains of $[Ni(PC)_2(H_2O)_2]$ molecules are linked by N $\cdots$ H–O and O $\cdots$ H–O intermolecular hydrogen bonding. For example, bond distances of N_6–H_{3A} and O_4–H_{3B} are 3.28(2) and 2.95(2), respectively. This bonding occurred between the hydrogens of the coordinated water molecules and the uncoordinated nitrogen and oxygen of pyrazinecarboxylate moieties.

Complexes **2** and **3** crystallised in a monoclinic space group *C2/c* with a *Z* value of 4. Selected bond lengths and angles of the two complexes (**2** and **3**) are listed in tables 4 and 5. The X-ray study of the structure of **2** (figure 2) revealed that it has a highly distorted octahedron with the two water molecules of $[Ni(PC)_2(H_2O)_2]$ replaced by two thiourea molecules at the apices. Each thiourea molecule was bonded to nickel(II) via its sulphur atom with a distance of 2.559(3) Å. This value is higher than the bond lengths of Ni–O_3, 2.045(7) Å, and Ni–N_4, 2.0454(9) Å, indicating an elongated octahedral complex structure. The S–Ni–S bond angle is 180°, but the bond angles between the apical axis and the equatorial plane in both **1** and **2** $\neq 90°$, indicating distortion of the octahedral structure. As shown for complex **1**, the framework of $[Ni(PC)_2(TU)_2]$ molecules are linked with intermolecular hydrogen bonding of the type N–H $\cdots$ O with a bond distance of 2.89(2) for O_5–H_{6B}.

The X-ray crystal structure of $[Ni(PC)_2(ABI)_2] \cdot 2(H_2O)$, **3**, showed that it is a highly distorted octahedral complex with two waters of crystallisation (figure 3).

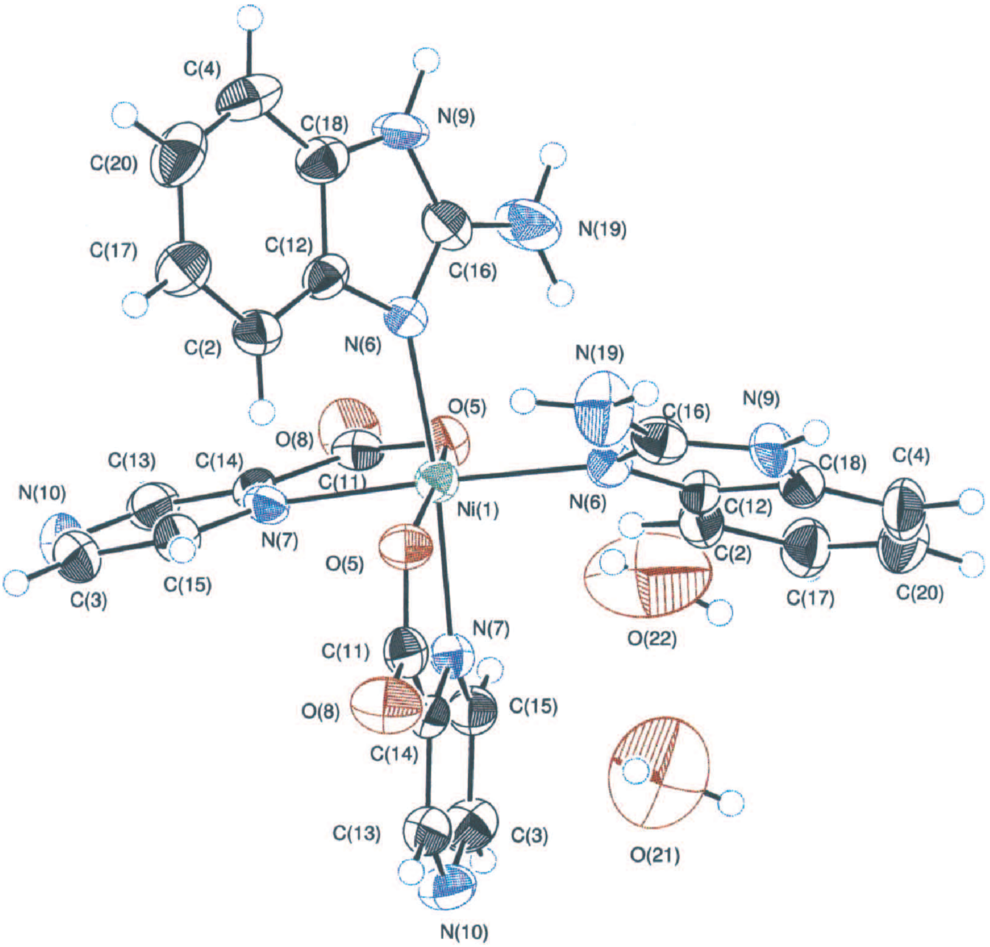

Figure 3. ORTEP representations of the [Ni(PC)$_2$(ABI)$_2$] · 2(H$_2$O) complex.

Table 3. Selected bond lengths (Å) and bond angles (°) for the [Ni(PC)$_2$(H$_2$O)$_2$] complex.

Bond lengths (Å)				
Ni–O$_3$	2.095(13)	C$_7$–C$_8$	1.516(2)	1.525(2)
Ni–O$_2$	2.069(11)	C$_8$–O$_4$	1.231(2)	1.225(2)
Ni–N$_5$	2.040(13)	C$_8$–O$_2$	1.282(2)	1.272(2)
N$_5$–C$_7$	1.342(2)	C$_{11}$–H$_{11}$	0.960(2)	0.880(4)
N$_5$–C$_{11}$	1.336(2)	C$_9$–H$_9$	0.960(2)	0.900(4)
N$_6$–C$_9$	1.333(2)	C$_{10}$–H$_{10}$	0.960(2)	0.940(4)
N$_6$–C$_{10}$	1.342(2)	O$_3$–H$_{3A}$	0.800(2)	0.780(4)
C$_9$–C$_{11}$	1.385(2)	O$_3$–H$_{3B}$	0.670(2)	0.750(4)
C$_7$–C$_{10}$	1.382(2)			
Bond angles (°)				
O$_3$–Ni–O$_3$	180	N$_5$–Ni–O$_2$	80.34(5)	80.30(1)
O$_2$–Ni–O$_2$	180	O$_3$–Ni–O$_2$	91.75(5)	92.00(1)
N$_5$–Ni–N$_5$	180	H$_{3A}$–O$_3$–H$_{3B}$	115.00(2)	110.00(2)
N$_5$–Ni–O$_3$	87.11(5)			

Table 4. Selected bond lengths (Å) and bond angles (°) for the [Ni(PC)$_2$(TU)$_2$] complex.

Bond lengths (Å)					
Ni–S$_2$	2.559(3)	C$_7$–H$_7$	0.960(10)	C$_{14}$–O$_5$	1.240(14)
Ni–O$_3$	2.045(7)	N$_{10}$–C$_{13}$	1.323(2)	C$_{14}$–O$_3$	1.274(14)
Ni–N$_4$	2.045(9)	C$_{12}$–C$_{13}$	1.389(2)	C$_{12}$–H$_{12}$	0.960(10)
N$_4$–C$_{11}$	1.338(13)	C$_7$–C$_{11}$	1.381(2)	C$_{13}$–H$_{13}$	0.960(12)
N$_4$–C$_{12}$	1.330(14)	C$_{11}$–C$_{14}$	1.504(2)		
S$_2$–Ni–S$_2$	180	N$_4$–Ni–S$_2$	85.72(3)	N$_9$–C$_8$–N$_6$	118.95(10)
O$_3$–Ni–O$_3$	180	N$_4$–Ni–O$_3$	81.40(3)	H$_6$–N$_6$–H$_6$	120.01(11)
N$_4$–Ni–N$_4$	180	S$_2$–Ni–O$_3$	87.94(3)	H$_9$–N$_9$–H$_9$	120.00(11)
Ni–S$_2$–C$_8$	102.26(4)				

Table 5. Selected bond lengths (Å) and bond angles (°) for the [Ni(PC)$_2$(ABI)$_2$] · 2H$_2$O complex.

Bond lengths (Å)					
Ni–O$_5$	2.063(13)	N$_{10}$–C$_3$	1.316(3)	C$_{11}$–O$_5$	1.267(2)
Ni–N$_7$	2.140(2)	N$_{10}$–C$_{13}$	1.351(3)	C$_3$–C$_{15}$	1.380(3)
Ni–N$_6$	2.082(2)	C$_{13}$–C$_{14}$	1.371(3)	C$_3$–H$_3$	0.960(2)
N$_7$–C$_{14}$	1.346(2)	C$_{14}$–C$_{11}$	1.513(3)	C$_{13}$–H$_{13}$	0.960(2)
N$_7$–C$_{15}$	1.317(2)	C$_{11}$–O$_8$	1.233(2)	C$_{15}$–H$_{15}$	0.960(2)
Bond angles (°)[a]					
N$_6$–Ni–N$_7^{i}$	171.75(6)	N$_6^{i}$–Ni–O$_5$	93.99(6)	N$_{19}$–C$_{16}$–N$_6$	124.50(2)
N$_6$–Ni–N$_7$	92.11(6)	N$_7$–Ni–N$_7^{i}$	84.16(8)	N$_{19}$–C$_{16}$–N$_9$	122.10(2)
O$_5$–Ni–O$_5^{i}$	168.06(7)	N$_6$–Ni–N$_6^{i}$	92.51(9)	H$_{19}$–N$_{19}$–H$_{19}$	120.00(2)
N$_7$–Ni–O$_5^{i}$	92.48(6)	C$_{16}$–N$_6$–C$_{12}$	104.10(2)	C$_{14}$–C$_{11}$–O$_8$	118.30(2)
N$_7^{i}$–Ni–O$_5^{i}$	78.60(5)	Ni–O$_5$–C$_{11}$	117.41(12)	C$_{14}$–N$_7$–C$_{15}$	116.90(2)
N$_6$–Ni–O$_5$	94.26(6)	O$_5$–C$_{11}$–O$_8$	125.90(2)	C$_3$–N$_{10}$–C$_{13}$	115.40(2)

[a] The superscript letter ‘i’ represents atoms of one set of ABI and PC in *cis* positions.

The coordination polyhedron around the metal ion consisted of atoms contributed by two PC molecules and two ABI molecules. The ABI molecules are monodentate, while the PC molecules are bidentate. In **3**, the two ABI molecules lie *cis* with one ABI molecule sited along the apical axis of the octahedron while the other molecule in the equatorial plane (figure 3). The bond lengths Ni–N$_6$, Ni–N$_7$ and Ni–O$_5$ are 2.082(2), 2.140(2) and 2.063(13), respectively (table 5). The bond angles O$_5$–Ni–O$_5^{i}$, N$_7$–Ni–N$_6$ and N$_6$–Ni–N$_7^{i}$ are 168.06(7), 92.11(6) and 171.75(6), respectively. These values indicate that the nickel centre [Ni(PC)$_2$(ABI)$_2$] · 2(H$_2$O) lies in a distorted octahedral coordination environment. Inter- and intramolecular hydrogen bonds in complex **3** of the type N–H · · · O are clearly observed from the contents of one unit cell.

3.3. *Thermogravimetric analysis*

Thermal studies of the nickel(II) complexes, [Ni(PC)$_2$(TU)$_2$], **2** and [Ni(PC)$_2$(ABI)$_2$] · 2H$_2$O, **3**, were carried out using thermogravimetry (TG). The TG plot of complex **2** displayed three resolved and well-defined decomposition steps. The first decomposition step was found in the temperature range 508–677 K, with a net weight loss of 33.32%, probably due to elimination of two thiourea moieties ($C_2H_8N_4S_2$). The second decomposition step occurred in the temperature range 677–764 K with a net weight loss of 38.10%, due to the loss of a $C_8H_6N_4O$ species. The third decomposition step (764–1050 K, 12.23%) was attributed to elimination of two CO molecules to leave the metal oxide, NiO (16.34%) as residue.

The TG plot of complex **3** displayed also three well-defined decomposition steps in the temperature range 304–1061 K. The first decomposition step is accompanied by the elimination of two water molecules and one NH_3 molecule. This step occurred in the temperature range 304–413 K with a net weight loss of 8.75%. The second decomposition peak occurred in the temperature range 532–687 K with a weight loss of 31.57% corresponding to elimination of a $C_7H_6N_5O_2$ moiety. However, the final decomposition step occurred in the temperature range 687–1061 K and corresponded to the material decomposition of $C_{17}H_{11}N_4O$ with a weight loss of 47.35% to leave the metallic residue NiO.

4. Conclusion

The crystal structure analysis of the two complexes $[Ni(PC)_2(H_2O)_2]$ and $[Ni(PC)_2(TU)_2]$ showed that they are isostructural. The water or thiourea molecules coordinated to the Ni ion in *trans* positions. Structural analysis of $[Ni(PC)_2(ABI)_2] \cdot 2H_2O$ indicated that the two ABI molecules coordinate *cis* to nickel. The molecules in the framework of the three complexes are linked together with inter- and intramolecular hydrogen bonding.

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