

Scientific paper

Synthesis, Characterization and Crystal Structure Studies of Nickel(II) Complexes With NO Donor Schiff Base Ligands

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Abstract

Four complexes of the type $[\text{Ni}(\text{N-substituted-salicydenaminato})_2]$, with bidentate Schiff base ligands ($\text{L}^1\text{--L}^4$), have been synthesized. The complexes were characterized by IR and elemental analysis methods. The solid state structures of three complexes (**1–3**) were determined by X-ray crystallography. The complexes show mononuclear, four-coordinate, slightly distorted square-planar $\text{trans-Ni}(\text{N}_2\text{O}_2)$ geometry. The angles around the Ni center deviate slightly from 90° indicating a rectangular distortion. The chelating N–Ni–O angles are larger than 90° whereas the non-chelating N–Ni–O angles are smaller than 90° . The crystallographic studies indicate that any steric/electronic effects due to CH_3 and Br moieties have had no significant impact on the coordination sphere.

Keyword: Nickel complexes; Schiff base; X-ray crystallography; disorder; bidentate

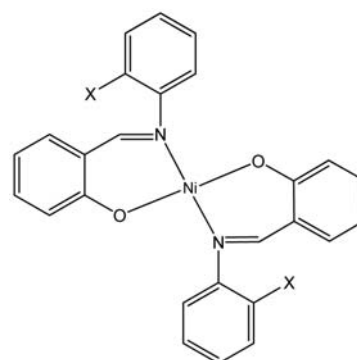
1. Introduction

The chemistry of transition-metal complexes with Schiff base ligands has played an important role in the development of coordination chemistry.^{1–3} Many of these complexes exhibit wide applications in biological and industrial systems.^{4–7} The nickel(II) complexes with Schiff base ligands have been regarded as models for enzymes such as urease.⁸ The nickel enzymes are involved in various biological reactions and consequently study of the coordination chemistry of nickel has been of significant interest in recent years.^{9–11}

Complexes of nickel(II) with Schiff bases derived from salicylaldehyde with various amines are known to show considerable structural flexibility.¹² Four coordinate bis(Schiff base bidentate) Cu(II) and Ni(II) complexes can have coordination environments ranging between square-planar and tetrahedral. Changing the N-imine group of the Schiff base ligand can alter the steric and electronic properties of the ligand and thus the coordination geometry

of Ni(II) complexes gives both square-planar and distorted tetrahedral structures.^{13–18}

In previous work we have reported the syntheses, crystal structures and electronic spectra of some



X = H, (**1**); X = CH_3 , (**2**); X = Br, (**3**); X = Cl, (**4**)

Scheme 1. The structure of Ni complexes

bis(N-substitutedsalicydenaminato)copper(II) complexes.¹⁹ In the present study, we describe the synthesis, crystal structures and structural changes arising from changes to the steric and electronic nature of the substituent on the Schiff base ligand in a series of the nickel(II) complexes (Scheme 1).

2. Experimental

2.1. Reagents

All chemicals were used as supplied by Merck and Fluka without further purification.

2.2. Physical Measurements

Elemental microanalysis (C, H, N) were performed by the microanalytical service of the Australian National University. Infrared spectra were taken with an Equinox 55 Bruker FT-IR spectrometer using KBr pellets in the 400–4000 cm⁻¹ range at 298 K.

2.3. X-ray Crystallography

Diffraction images were measured at 200 K on a Nonius Kappa CCD diffractometer using Mo K α , graphite monochromator ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods with the SIR92.²⁰ The structures

were refined on F² by full matrix least-squares techniques using the CRYSTALS program package.²¹ Atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Crystallographic data for the three crystals 1–3 are summarized in Table 1.

2.4. Syntheses of the Ligands, L¹–L⁴

All homologue Schiff base ligands were synthesized as reported in previous work by the condensation reaction of an equimolar amount of salicylaldehyde (10 mmol) and the related substituted- phenylamine (10 mmol) in methanol (20 ml) at room temperature to give yellow micro crystals after 30 min, yield 80%–90% (dependent on amines).¹⁹ The micro crystals were filtered off, and recrystallization has been performed in diethyl ether solution at room temperature.

2.5. Syntheses of Nickel(II) complexes (1–4)

The nickel(II) complexes were synthesized in a similar manner. To a solution of the Schiff base ligand (5 mmol) dissolved in ethanol (50 ml), nickel(II) acetate tetrahydrate (2.5 mmol, 0.622 g) was slowly added and the resulting solution was stirred for 2 h at room temperature. The resulting green precipitates were collected by filtration and dried in the air.

Table 1. Crystallographic data of the complexes 1–3

Compound	1	2	3
Chemical formula	C ₂₆ H ₂₀ N ₂ NiO ₂	C ₂₈ H ₂₄ N ₂ NiO ₂	C ₂₆ H ₁₈ Br ₂ N ₂ NiO ₂
Formula weight	451.17	479.22	608.96
Temperature (K)	200	200	200
Space group	Monoclinic, p2 ₁ /n, Z = 2	Monoclinic, p2 ₁ /n, Z = 2	Triclinic, P $\bar{1}$ Z = 2
Unit cell dimensions			
a (Å)	11.7732 (2)	10.6093 (8)	9.4458 (6)
b (Å)	7.5155 (2)	9.1509 (7)	10.5636 (7)
c (Å)	12.6762 (2)	12.4223 (8)	12.4184 (7)
α (°)	90	90	68.229 (4)
β (°)	111.9948 (11)	110.206 (5)	85.713 (4)
γ (°)	90	90	82.308 (4)
V (Å ³)	1039.98 (5)	1131.79 (15)	1139.96 (13)
F(000)	468	500	604
D _{calc} (g cm ⁻³)	1.441	1.406	1.774
Crystal size (mm)	0.40 × 0.34 × 0.22 mm	0.32 × 0.27 × 0.06 mm	0.20 × 0.09 × 0.08 mm
μ (mm ⁻¹)	0.96	0.89	4.38
θ range (°)	3–30	2.6–27.5	2.6–27.5
Limiting indices	-16 ≤ h ≤ 16 -10 ≤ k ≤ 10 -17 ≤ l ≤ 17	-13 ≤ h ≤ 13 -11 ≤ k ≤ 11 -16 ≤ l ≤ 16	-12 ≤ h ≤ 12 -13 ≤ k ≤ 13 -16 ≤ l ≤ 16
R ₁ (F ² > 2 σ (F ²), reflections)	0.026(2676)	0.044(1928)	0.045(4291)
R _w (all reflections)	0.069(3036)*	0.116(2597)**	0.107(5176)***
T _{min} /T _{max}	0.671/0.831	0.771/0.949	0.521/0.761

*w = 1/[\sigma²(F²) + (0.03P)² + 0.48P], where P = (max(F_o², 0) + 2F_c²)/3 **w = 1/[\sigma²(F²) + (0.06P)² + 0.64P], where P = (max(F_o², 0) + 2F_c²)/3 ***w = 1/[\sigma²(F²) + (0.04P)² + 2.45P], where P = (max(F_o², 0) + 2F_c²)/3

bis(N-phenyl-salicydenaminato)nickel(II), NiL¹, 1

Recrystallized from dichloromethane/ethanol (1:1 v/v). Yield 54%. Anal. Calc. for C₂₆H₂₀N₂NiO₂: C, 69.22; H, 4.47; N, 6.21. Found: C, 69.43; H, 4.50; N, 6.16%. IR (KBr, cm⁻¹): ν_{C=N} = 1604, ν_{C-O} = 1185.

bis(N-2-methylphenyl-salicydenaminato)nickel(II), NiL², 2

Recrystallized from dichloromethane/ethanol (1:1 v/v). Yield 53%. Anal. Calc. for C₂₈H₂₄N₂NiO₂: C, 70.18; H, 5.05; N, 5.85. Found: C, 70.35; H, 5.14; N, 5.76%. IR (KBr, cm⁻¹): ν_{C=N} = 1600, ν_{C-O} = 1175.

bis(N-2-bromophenyl-salicydenaminato)nickel(II), NiL³, 3

Recrystallized from dichloromethane/2-propanol (2:1 v/v). Yield 44%. Anal. Calc. for C₂₆H₁₈Br₂N₂NiO₂: C, 51.28; H, 2.98; N, 4.60. Found: C, 51.35; H, 3.04; N, 4.66%. IR (KBr, cm⁻¹): ν_{C=N} = 1601, ν_{C-O} = 1188.

bis(N-2-chlorophenyl-salicydenaminato)nickel(II), NiL⁴, 4

Several trials to prepare single crystals of X-ray quality were unsuccessful. Yield 48%. Anal. Calc. for

C₂₆H₁₈Cl₂N₂NiO₂: C, 60.05; H, 3.49; N, 5.39. Found: C, 60.22; H, 3.40; N, 5.46%. IR (KBr, cm⁻¹): ν_{C=N} = 1601, ν_{C-O} = 1188.

3. Result and Discussion

3. 1. Infrared Spectra

The IR spectra of the Schiff base free ligand shows no C=O band of salicylaldehyde at 1665 cm⁻¹ but exhibits a strong band at 1611–1619 cm⁻¹ due to νC=N of imine, which indicates that the Schiff base ligands have been produced.^{22–24} The C=N band in the Ni(Schiff base)₂ complexes exhibits a band at 1602–1612 cm⁻¹. The appearance of νC=N in these complexes at lower frequencies than in the free Schiff base ligands demonstrates that C=N has been coordinated to the metal center. The double bond order of the C=N is reduced as a result of coordination of the nitrogen of the imine to the nickel center which reduces the electron density in the azomethine link.^{25–27} In the free Schiff base ligand, the frequency of the hydroxyl

Table 2. Selected bond lengths (Å) and angles (°) in complexes 1–3^a

Complex 1			
Ni1–O1	1.8309 (9)	N9–Ni1–O1	92.76 (4)
Ni1–N9	1.9068 (10)	N9*–Ni1–O1	87.24 (4)
C2–O1	1.3070 (14)	Ni1–O1–C2	126.59 (8)
C8–N9	1.2986 (15)	Ni1–N9–C10	119.29 (7)
C10–N9	1.4430 (14)	Ni1–N9–C10–C11	70.4 (1)
		O1–Ni1–N9–C10	-161.17 (9)
Complex 2			
Ni1–O1	1.8170 (18)	N9–Ni1–O1	93.35 (8)
Ni1–N9	1.911 (2)	N9*–Ni1–O1	86.68 (8)
C2–O1	1.309 (3)	Ni1–O1–C2	130.60 (17)
C8–N9	1.299 (3)	Ni1–N9–C10	120.63 (17)
C10–N9	1.460 (4)	Ni1–N9–C10–C11	90.3 (1)
C15–C16	1.486 (5)	N9–C10–C15–C16	-4.4 (5)
		O1–Ni1–N9–C10	-177.5 (3)
Complex 3A			
Ni1–O1	1.836 (2)	N9–Ni1–O1	92.99 (12)
Ni1–N9	1.902 (3)	N9*–Ni1–O1	87.01 (12)
C2–O1	1.314 (4)	Ni1–O1–C2	126.6 (2)
C8–N9	1.308 (5)	Ni1–N9–C10	120.5 (2)
C10–N9	1.438 (4)	Ni1–N9–C10–C11	116.8 (3)
C15–Br16	1.888 (4)	N9–C10–C15–Br16	0.9 (4)
		O1–Ni1–N9–C10	159.0 (3)
Complex 3B			
Ni2–O51	1.831 (2)	N59–Ni2–O51	92.91 (12)
Ni2–N59	1.899 (3)	N59*–Ni2–O51	87.09 (12)
C52–O51	1.308 (4)	Ni2–O51–C52	128.0 (2)
C58–N59	1.298 (5)	Ni2–N59–C60	118.4 (2)
C60–N59	1.458 (5)	Ni1–N59–C60–C61	72.3 (4)
C65–Br66	1.897 (4)	N59–C60–C65–Br66	-2.5 (5)
		O51–Ni2–N59–C60	-162.0 (3)

^a symmetry codes indicated by *: for **1**, **2** and **3A**, -x + 1, -y + 1, -z + 1 and for **3B**, -x, -y, -z.

group is observed at about 2700–3000 cm^{-1} due to intramolecular hydrogen bonding between OH and the imine group in the Schiff base.^{27, 28} This band disappears for the nickel complexes which indicates that the OH group has been deprotonated and the oxygen is coordinated to the Ni center. A strong band observed at 1175–1188 cm^{-1} in the free Schiff base ligands due to phenolic C–O stretching is shifted to lower frequency upon complexation, also indicating coordination through the phenolic oxygen.²⁹

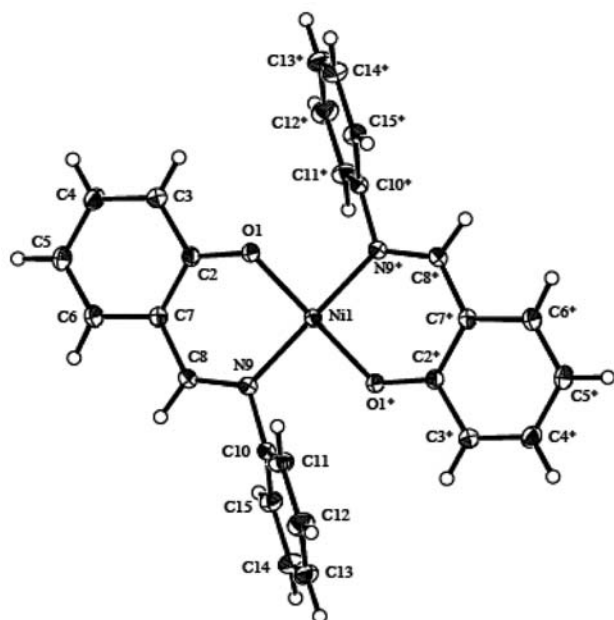


Fig. 1. The molecular structure of **1** with labelling of selected atoms, ellipsoids show 30% probability levels.

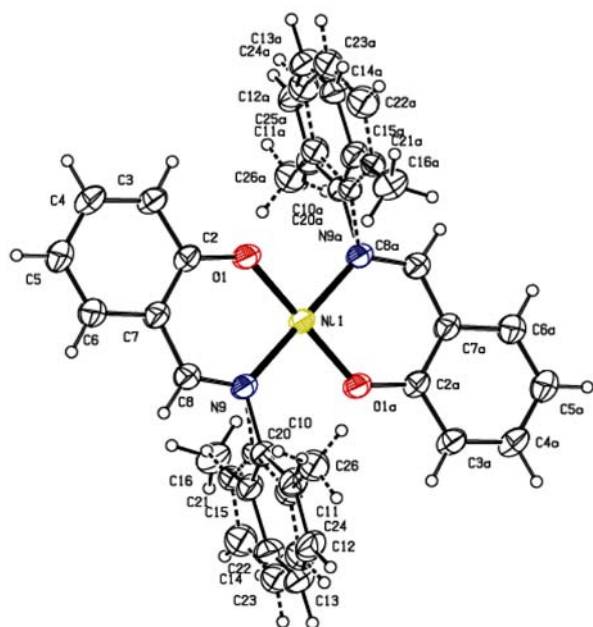


Fig. 2. The molecular structure of **2** with labelling of selected atoms, showing both orientations of the disordered group.

3. 2. Crystal Structures

The complexes **1** and **2** crystallized in the monoclinic space group $P2_1/n$ and complex **3** crystallized in the triclinic space group $P\bar{1}$. The molecular structure of the complexes with labelling of selected atoms is shown in Figures 1–5. Selected bond lengths and angles are listed in Table 2.

In each case, Ni atom is located on an inversion center and is surrounded by two nitrogen and the two oxygen atoms of two mono-deprotonated ligands. These four atoms around the Ni(II) form a slightly distorted square-planar trans- $\text{Ni}(\text{N}_2\text{O}_2)$ geometry.

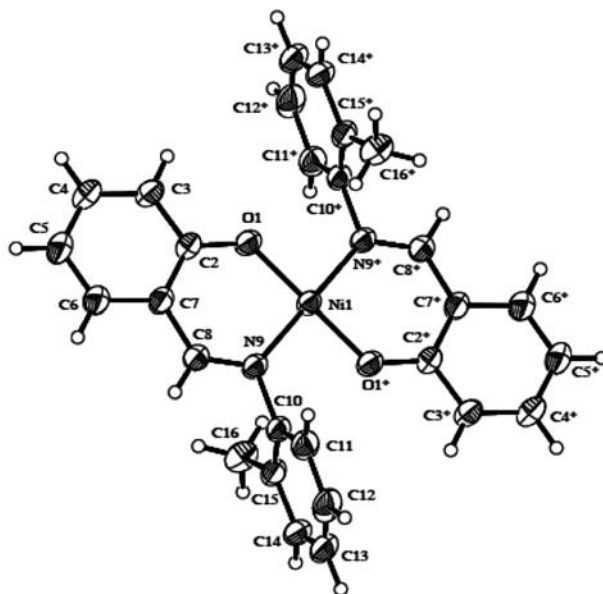


Fig. 3. The molecular structure of **2A** with labelling of selected atoms, showing the major sites of disordered atoms.

There are two independent molecules of the complex **3** in the structure (called **3A** and **3B** with labelling Ni1 and Ni2 for central Ni(II) atom, respectively), each centered on a crystallographic inversion symmetry point.

In complexes **2** and **3**, there is rotational disorder in the packing of the $\text{C}_6\text{H}_4\text{X}$ groups over two positions (**2A1** and **2A2** for complex **2** and **3A1**, **3A2**, **3B1** and **3B2** complex **3**), which have relative occupancies refined to 83%:17%, 98%:2% and 89%:11%, respectively. The major image of this group is represented in Figs. 3 and 5, and minor image of this group is represented in Figures S1 and S2. These latter sites have been refined with isotropic displacement parameters and restraints have been applied to their bond distances and angles. In addition, in **3A2** the C isotropic displacement factors were set all equal to the average of U_{eq} of the equivalent sites of **3A1**, and the C isotropic displacement factors of **3B2** were refined as one common parameter.

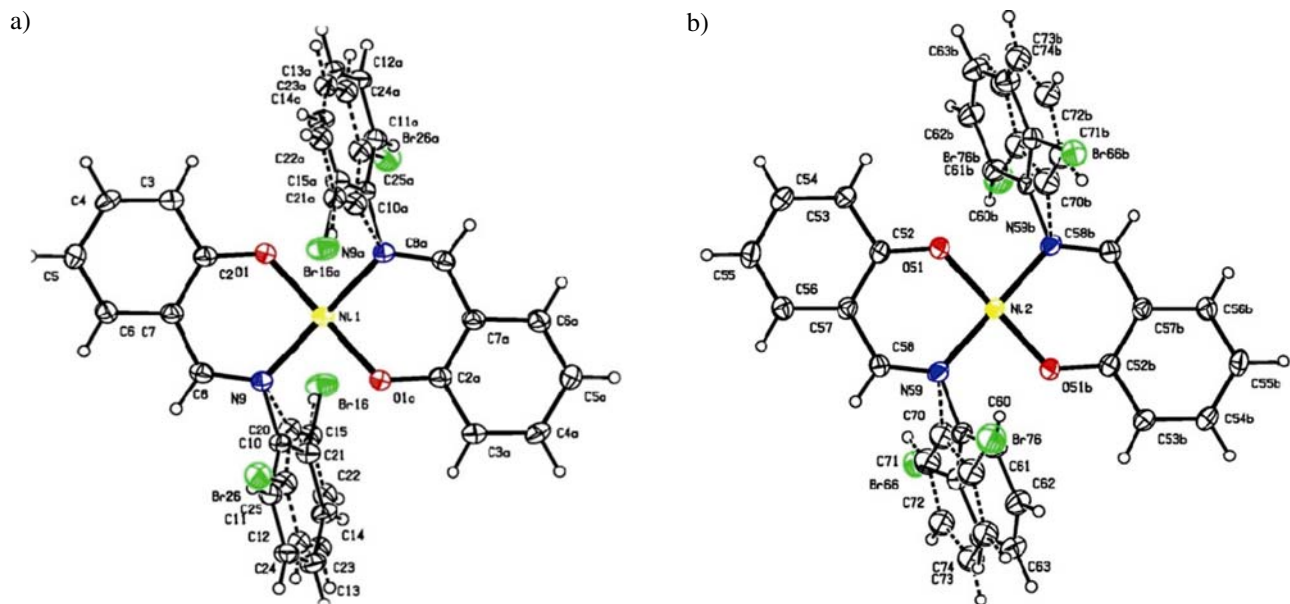


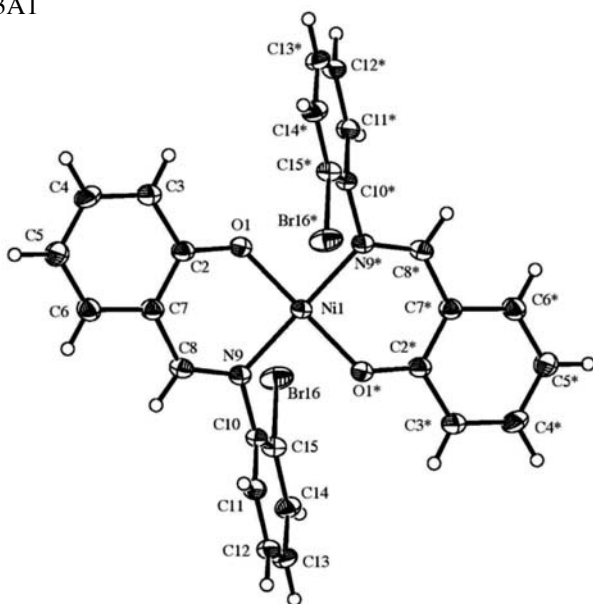
Fig. 4. Two independent molecular structure of **3** with labelling of selected atoms, showing both orientations of the disordered group.

In all of the complexes, the chelating N–Ni–O angles are larger than 90° whereas the non-chelating N–Ni–O angles are smaller than 90° . The chelating N–Ni–O angle in complexes **1**, **2**, **3A1** and **3B1** are $92.76(4)^\circ$, $93.35(8)^\circ$, $92.99(12)^\circ$ and $92.91(12)^\circ$, and the non-chelating O–Ni–N angle are $87.24(4)^\circ$, $86.65(8)^\circ$, $87.01(12)^\circ$ and $87.09(8)^\circ$, respectively. The Ni–O and Ni–N bond lengths in the complexes **1–3**, are in the range of 1.817–1.836 and 1.899–1.911 Å, respectively, which have good agreement with analogous square-planar Ni(II)

complexes observed in the literature.^{30–32} The imine C=N double-bond distance in the complexes **1–3** are in the range of 1.298–1.308 Å and are similar to values reported for other Schiff base nickel complexes.^{32–34} The pendant phenyl rings (C_6H_4X , $X=H$, CH_3 and Br) of the Schiff base ligands are on the opposite side of the molecular plane, which are similar to analogous nickel complexes.^{17, 30}

In the complexes **1–3**, there are no remarkable intramolecular interactions. However, in complexes **2** and **3**, there are the intermolecular interactions between the pen-

3A1



3B1

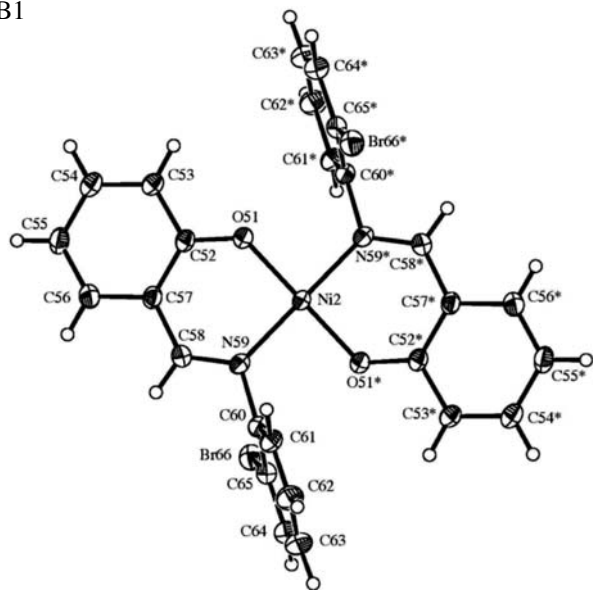


Fig. 5. Two independent molecular structures of **3** showing the major orientations of the disordered group.

dant phenyl rings and the salicydenaminato plane of adjacent molecules. The shortest intermolecular interaction distances in **2** and **3** (2.97(2) and 2.59(2) Å, respectively) are shorter than in complex **1** (3.482(2) Å). This structural feature in complexes **2** and **3**, suggests intermolecular interaction is sufficiently effective for C₆H₄X groups to be disordered.

4. Conclusion

New nickel complexes with the bidentate Schiff base were prepared. Elemental analysis of the complexes suggests a general formula [Ni(N₂O₂)]. The molecular structures of the three complexes were determined by single X-ray crystal analysis. The three Ni complexes **1–3** have slightly distorted square-planer coordination geometry. Comparison of the structure of the complexes **1–3**, shows that there are no significant variation in geometry, bonds length and angle of the complexes and they are similar to values in analogous square-planar Ni(II) complexes. Indeed, no structural features indicating steric/electronic effects can be observed due to CH₃ and Br moieties in these complexes. However, there is disorder in the packing of the C₆H₄X groups in the crystal structures when the CH₃ and Br moieties are present.

5. Supplementary Material

The deposition numbers of the studied complexes, **1–3** are CCDC 869785–869787, respectively. These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data-request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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Povzetek

Sintetizirali smo štiri koordinacijske spojine tipa $[\text{Ni}(\text{N-substiturani-salicidenaminato})_2]$ z bidentatnimi Schiffovimi bazami ($\text{L}^1\text{--L}^4$) kot ligandi. Komplekse smo okarakterizirali z IR spektri in elementno analizo. Z rentgensko strukturno analizo smo trem kompleksom (**1–3**) določili kristalno strukturo. Koordinacijske spojine imajo monojedrno zgradbo s koordinacijskim številom štiri in rahlo popačeno kvadratno-planarno *trans*- $\text{Ni}(\text{N}_2\text{O}_2)$ geometrijo. Koti okoli centralnega nikljevega atoma rahlo odstopajo od 90° , kar kaže na pravokotno pačenje. Kelatni koti N–Ni–O so večji od 90° , medtem ko so nekelatni koti N–Ni–O manjši od 90° . Analiza kristalnih struktur kaže, da sterični ali elektronski efekti zaradi prisotnosti CH_3 in Br skupin nimajo pomembnejšega vpliva na koordinacijsko sfero nikljevega atoma.