**Abstract**

The reactions of Ni(OAc)$_2$·2H$_2$O with Schiff base ligands 5-bromo-2-((cyclopentylimino)methyl)phenol (HL$_1$) and 5-bromo-2-(((2-(isopropylamino)ethyl)imino)methyl)phenol (HL$_2$) in methanol afforded two discrete trinuclear complexes \([\text{Ni}_3(\text{L}_1)_2(\mu_2-\eta^1:\eta^1-\text{OAc})_2(\text{DMF})_2(\text{BrSal})_2]\) (1) and \([\text{Ni}_3(\text{L}_2)_2(\mu_2-\eta^1:\eta^1-\text{OAc})_2(\mu_2-\eta^2:\eta^1-\text{OAc})_2]\) (2), where BrSal is the monoanionic form of 4-bromosalicylaldehyde. The complexes were characterized by elemental analysis, IR and UV-Vis spectroscopy. The crystal structures of the complexes have been determined by X-ray crystallography. In both complexes, the nickel atoms are in octahedral coordination geometries. The L$_1$ ligand coordinates to the nickel atoms through the phenolate O and imino N atoms, and the L$_2$ ligand coordinates to the nickel atoms through the phenolate O, imino N and amino N atoms. The antimicrobial activities of the complexes were assayed.

**Keywords:** Nickel complexes; schiff bases; crystal structures; trinuclear complexes; antimicrobial activity

**1. Introduction**

Studies on supramolecular interaction and the self-assembly resulting from them have attracted remarkable attention in recent years. Schiff bases and their metal complexes exhibit biological activity as antibiotics, antiviral, antibacterial and antitumour agents because of their specific structures.$^1$ Among Schiff bases, those derived from the mono-condensation of organic amines with carbonyl compounds, are a group of classical NO or NNO donor ligands.$^2$ These ligands react readily with nickel salts to occupy its equatorial coordination sites whereas several anionic or neutral ligands can be coordinated to the fourth coordination site of the square plane to yield different type of complexes.$^3$ Among the co-ligands, acetate has received remarkable attention because it can coordinate to the metal centers through versatile modes, such as monodentate, chelating, bidentate bridging, monoatomic bridging, chelating bridging, etc (Scheme 1).$^4$ To combine Schiff bases and acetate ligands together in the complexes, a number of nickel complexes have been prepared. The complexes show interesting structures, biological, magnetic, and catalytic properties.$^5$ However, it is still a great challenge to prepare acetate bridged multi-nuclear complexes with aiming structures. Herein, we report the synthesis and crystal structures of two new nickel(II) complexes, \([\text{Ni}_3(\text{L}_1)_2(\mu_2-\eta^1:\eta^1-\text{OAc})_2(\mu_2-\eta^2:\eta^1-\text{OAc})_2]\) and \([\text{Ni}_3(\text{L}_2)_2(\mu_2-\eta^1:\eta^1-\text{OAc})_2(\mu_2-\eta^2:\eta^1-\text{OAc})_2]\), where BrSal is the monoanionic form of 4-bromosalicylaldehyde.

**Scheme 1. Chelating modes of acetate ligand.**
\[ \eta^1\eta^1-\text{OAc}_2(\text{DMF})_2(\text{BrSal})_2 \] (1) and \[ [\text{Ni}_3(\text{L}^2_2)\eta^1\eta^1-\text{OAc}_2][\mu_2-\eta^1\eta^1-\text{OAc}_2] \] (2), where \( \text{L}^1 = 5\text{-bromo-2-}(\text{cyclopentylimino})\text{methyl}\text{phenolate}, \text{L}^2 = 5\text{-bromo-2-}(\text{2-isopropylamino}(\text{ethyl})\text{limino})\text{methyl}\text{phenolate} \). (Scheme 2), BrSal = 4-bromosalicylaldehyde.

### 2. Experimental Section

#### 2.1. Materials and Physical Measurements

4-Bromosalicylaldehyde, cyclopentylamine, \( N\)-isopropylethane-1,2-diamine and nickel acetate were purchased from Sigma-Aldrich. All other chemicals were commercially available and used as received. Elemental analysis was carried out using model 2400 Perkin-Elmer CHN analyzer. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. Electronic spectra were carried out with a Lambda 35 spectrometer.

#### 2.2. Preparation of Complex 1

4-Bromosalicylaldehyde (0.20 g, 10 mmol) and cyclopentylamine (0.085 g, 10 mmol) were dissolved and stirred at ambient temperature in methanol (30 mL). Thirty minutes later, nickel acetate tetrahydrate (0.50 g, 20 mmol) was added to the solution. The color turned from yellow to deep green. The reaction mixture was allowed to slow evaporate for a few days, generating green block shaped single crystals. Yield: 0.21 g (43%). Anal. Calcd for \( \text{C}_{32}\text{H}_{44}\text{Br}_2\text{N}_4\text{Ni}_3\text{O}_{10} \): C, 39.19; H, 4.52; N, 5.71. Found: C, 38.96; H, 4.61; N, 5.82. IR data (KBr; \( \nu_{\max} \text{ cm}^{-1} \): 3107, 3075, 2935, 2858, 1627, 1582, 1550, 1473, 1430, 1409, 1396, 1295, 1188, 1157, 1102, 987, 862, 785, 667, 610, 565, 463. UV-Vis data in methanol (\( \lambda \text{, nm} \left( \varepsilon, \text{L mol}^{-1} \text{cm}^{-1} \right) \)): 222 (1.56 \times 10^4), 240 (1.70 \times 10^4), 265 (5.32 \times 10^3), 335 (4.81 \times 10^3).

#### 2.3. Preparation of Complex 2

4-Bromosalicylaldehyde (0.20 g, 10 mmol) and \( N\)-isopropylethane-1,2-diamine (0.102 g, 10 mmol) were dissolved and stirred at ambient temperature in methanol (30 mL). Thirty minutes later, nickel acetate was added. Then, a few drops of DMF was added until the insoluble residue has disappeared. The reaction mixture was stirred for about 1 h and filtered. The filtrate was allowed to slow evaporate for a few days, generating green block shaped single crystals. Yield: 0.21 g (43%). Anal. Calcd for \( \text{C}_{12}\text{H}_{14}\text{BrCuN}_3\text{OS} \): C, 41.94; H, 3.96; N, 4.08. Found: C, 41.72; H, 4.11; N, 3.97. IR data (KBr; \( \nu_{\max} \text{ cm}^{-1} \): 4.416 3.588 2.646 2.452 1.980 1.809 1.763 1.712 1.588 1.243 1.203 1.183 1.066 0.987 0.862 0.785 0.667 0.610. UV-Vis data in methanol (\( \lambda, \text{nm} \left( \varepsilon, \text{L mol}^{-1} \text{cm}^{-1} \right) \)): 220 (1.71 \times 10^4), 230 (1.04 \times 10^4), 245 (1.08 \times 10^4), 265 (1.24 \times 10^4), 335 (2.09 \times 10^3).
3. Results and Discussion

3.1. Chemistry

Both complexes were readily prepared by reacting nickel acetate tetrahydrate with Schiff base ligands. The elemental analysis data are consistent with the general molecular formulae of the complexes. In complex 1, the acetate ligands act as bidentate bridging groups. In complex 2, two acetate ligands act as bidentate bridging groups, and the other two act as chelating bridging groups. The complexes are soluble in common organic solvents like dimethyl sulphoxide, dimethylformamide, methanol, and ethanol.

3.2. Infrared and Electronic Spectra of the Complexes

In the spectra of the free Schiff bases HL1 and HL2, the bands at 1650 and 1645 cm\(^{-1}\), respectively, are assigned to the azomethine groups, \(\nu_{C=N}\), and the broad and weak absorptions at about 3430 cm\(^{-1}\) are assigned to the hydroxyl groups, \(\nu_{O-H}\). In the complexes, the absence of the O–H bidentate bridging group. The Ni\(_2\) atom is located at the O and phenolate O atoms. The acetate ligand acts as a ylaldehyde coordinates to the Ni atoms through carbonyl stretching and bonding vibrations indicates coordination through the phenolate groups. The C=N stretches of the complexes are observed at lower frequencies (1643 and 1627 cm\(^{-1}\)) when compared to the free Schiff bases.\(^{10}\) The phenolic \(\nu(\text{Ar–O})\) in the free ligands exhibit bands at about 1270 cm\(^{-1}\). However, in the complexes it appears at about 1283 cm\(^{-1}\). The shift to higher wave number is an indication of C–O–M bond formation. The bands at about 1582 and 1408 cm\(^{-1}\) are assigned to the acetate ligands.\(^{4a,5b}\) The occurrence of new bands in the 450–670 cm\(^{-1}\) region confirms the presence of metal-nitrogen and metal-oxide bonds, respectively.\(^{11}\)

In the electronic spectra of the free Schiff bases and the complexes, the absorption frequencies ascribed to the aromatic \(\pi-\pi^*\) and \(n-\pi^*\) transitions are located in the region 240–290 nm.\(^{12}\) In the electronic spectra of the complexes, the absorption centered at 380 nm for complex 1 and 335 nm for complex 2 are assigned to ligand-to-metal charge transfer.\(^{13}\)

3.3. Structure Description of Complex 1

The molecular structure of complex 1 is depicted in Fig. 1. Bond parameters associated with the metal atom are listed in Table 2. The molecular structure is centrosymmetric with Ni2 atom on an inversion center. The structure shows a trinuclear complex consisting of three Ni atoms in a linear array, which is bridged by two acetate ligands and four phenolate groups. The Ni–Ni distance is 3.053(2) Å. The Schiff base ligand coordinates to the Ni atoms through phenolate O and imino N atoms. The ligand 4-bromosalicylaldehyde coordinates to the Ni atoms through carbonyl O and phenolate O atoms. The acetate ligand acts as a bidentate bridging group. The Ni2 atom is located at the inversion centre of the complex in an octahedral geometry. This atom is coordinated by four phenolate O atoms from the Schiff base and 4-bromosalicylaldehyde ligands that form a plane and, near-perpendicular to it, by two O atoms from two acetate bridging ligands that connect the central Ni atom to the outer Ni atoms. The greatest deviation of the bond angles from those expected for an ideal octahedral geometry is found for O1–Ni2–O3 with 79.3(3)° and O1–Ni2–O3A with 100.7(3)°. The remaining bond angles are close to the ideal values for the octahedral coordination. The cis and trans coordinate bond angles for Ni2 are in the region 79.3(3)°–100.7(3)° and 180°. The terminal Ni1 atom is in an octahedral environment and is coordinated by the four donor atoms of the Schiff base and 4-bromosalicylaldehyde ligands in the equatorial plane, and by two O atoms from one bridging acetate group and one coordinated DMF ligand in the axial positions. The greatest deviations from an ideal octahedral geometry are found in the O2–Ni1–O6 (84.9(3)°) and in N1–Ni1–O2 (100.8(4)°) angles. The remaining bond angles are close to the ideal values for the octahedral coordination. The cis and trans coordinate bond angles for Ni1 are in the region 84.9(3)°–100.8(4)° and 168.8(3)°–176.6(3)°. The Ni–O and Ni–N bond lengths are similar to those reported previously.\(^{14}\)

3.4. Structure Description of Complex 2

The molecular structure of complex 2 is depicted in Fig. 2. Bond parameters associated with the metal atom are listed in Table 2. The molecular structure is centrosymmetric with Ni2 atom on an inversion center. The structure shows a trinuclear complex consisting of three Ni atoms in a linear array, which are bridged by four acetate ligands and two phenolate groups. The Ni–Ni distance is 3.043(2) Å. The Schiff base ligand coordinates to the Ni atoms through phenolate O, imino N and amino N atoms. Two of the acetate ligands act as bidentate bridging groups, and the other
two act as chelating bridging groups. The Ni2 atom is located at the inversion centre of the complex in an octahedral geometry. This atom is coordinated by two phenolate O atoms from the Schiff base ligands and two O atoms from two bidentate bridging acetate groups that form a plane and, near-perpendicularly to it, by two O atoms from two chelating bridging acetate groups that connect the central Ni atom to the outer Ni atoms. The greatest deviation of the bond angles from those expected for an ideal octahedral geometry is found for O1–Ni2–O2 with 79.97(16)° and O1–Ni2–O2A with 100.03(16)°. The remaining bond angles are close to the ideal values for the octahedral coordination. The cis and trans coordinate bond angles for Ni2 are in the region 79.97(16)–100.03(16)° and 180°. The terminal Ni1 atom is in an octahedral environment and is coordinated by the three donor atoms of the Schiff base ligand and the O2 atom of the chelating bridging acetate group in the equatorial plane, and by O3 atom of the chelating bridging acetate group and O4 atom of the bidentate bridging acetate group in the axial positions. The greatest deviations from an ideal octahedral geometry are found in O2–Ni1–O3 (60.69(19)°) and in O2–Ni1–N2 (103.6(3)°) angles. The remaining bond angles are close to the ideal values for the octahedral coordination. The cis and trans coordinate bond angles for Ni1 are in the region 60.69(19)–103.6(3)° and 157.1(2)–174.1(2)°. The Ni–O and Ni–N bond lengths are comparable to those of complex 1.

3. 5. Antimicrobial Activity

The complexes were assayed against the bacteria Escherichia coli and Salmonella typhi, and the fungi Aspergillus niger and Candida albicans by MIC (Minimum Inhibitory Concentration) method with three different concentrations of 100, 50 and 25 μg.\textsuperscript{15} The activity was also assayed for the free Schiff bases, the pure solvent DMF and the standard gentamycin for each of antibacterial and fluconazole for antifungal cultures. Final adjustments were made using optical density measurement for bacteria (absorbance 0.05 at 580 nm). The zones of inhibition in millimeter for the compounds are presented in Table 3. The two complexes have similar activities against the bacteria and fungi, and they are more susceptible toward bacterial cells than fungicidal cells. In general, both complexes have better activities than the free Schiff bases. The trends are in

| Bond distances | Bond angles |
|---------------|-------------|
| Ni1–N1 | 2.035(10) | Ni1–O1 | 2.014(7) |
| Ni1–O2 | 2.062(9) | Ni1–O3 | 2.023(7) |
| Ni1–O4 | 2.023(7) | Ni1–O6 | 2.125(8) |
| Ni2–O5 | 2.022(7) | Ni2–O1 | 2.048(6) |
| Ni2–O3 | 2.071(6) | |
| O1–Ni1–O4 | 91.2(3) | O1–Ni1–O3 | 81.3(3) |
| O4–Ni1–O3 | 90.9(3) | O1–Ni1–N1 | 89.7(4) |
| O4–Ni1–N1 | 93.2(4) | O3–Ni1–N1 | 170.2(4) |
| O1–Ni1–O2 | 168.8(3) | O4–Ni1–O2 | 92.0(3) |
| O3–Ni1–O2 | 88.0(3) | O3–Ni1–O2 | 176.6(3) |
| O1–Ni1–O6 | 90.5(3) | O3–Ni1–O6 | 85.8(4) |
| O2–Ni1–O6 | 84.9(3) | O5–Ni2–O5A | 180 |
| O5–Ni2–O2A | 100.03(16) | O5–Ni2–O2A | 100.03(16) |
| O1–Ni2–O2A | 79.97(16) | O2–Ni2–O2A | 180 |

Symmetry operation for A: 1–x, 1–y, 1–z.

Figure 2. ORTEP diagram of complex 2 with thermal ellipsoids at 30% probability level. Selected bond lengths and angles are given in Table 2. Unlabeled atoms are related to the symmetry operation 1 – x, 1 – y, 1 – z.
accordance with the literature that metal complexes are more active in the biological potential than the ligands used in the synthesis.\textsuperscript{16} When comparing the antimicrobial activity of the studied complexes to those of reference antibiotics, the inhibitory ability is found to be good. For example, the two complexes have similar or even higher activity on the bacteria \textit{Escherichia coli} and \textit{Salmonella typhi} than gentamycin, and have effective activity on \textit{Aspergillus niger} and \textit{Candida albicans}, which is seldom seen in the literature. The results indicate that the two complexes can possibly be used in the treatment of diseases caused by the bacteria that were tested.

4. Conclusion

A pair of novel acetato-bridged nickel(II) complexes derived from the Schiff base ligands 5-bromo-2-(((cyclopentylimino)methyl)phenol and 5-bromo-2-(((2-isopropylamino)ethyl)iminomethyl)phenol were prepared. Single crystal structures of the complexes indicates that both complexes are trinuclear nickel(II) compounds. All of the nickel atoms in the complexes are in octahedral coordination geometries. The complexes have good antimicrobial activities against \textit{Escherichia coli}, \textit{Salmonella typhi}, \textit{Aspergillus niger} and \textit{Candida albicans}.

Supplementary Material

CCDC Nos. 1974759 (1) and 1974760 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data and details of the data collection and refinement for the complexes are collected in Table 1.

5. References

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Povzetek

Z reakcijo Ni(OAc)\(_2\)·2H\(_2\)O s Schiffovo bazo 5-bromo-2-((ciklopentilimino)metil)fenolom (HL\(_1\)) in 5-bromo-2-((2-(izopropilamino)etil)imino)metil)fenolom (HL\(_2\)) v metanolu smo izolirali dva diskretna trijedrna kompleksa \([\text{Ni}_3(\text{L}_1)_2(\mu_2-\eta_1:\eta_1-\text{OAc})_2(\text{DMF})_2(\text{BrSal})_2]\) (1) in \([\text{Ni}_3(\text{L}_2)_2(\mu_2-\eta_1:\eta_1-\text{OAc})_2(\mu_2-\eta_2:\eta_1-\text{OAc})_2]\) (2), kjer je BrSal monoanionska oblika 4-bromosalicilaldehida. Kompleksa sta bila okarakterizirana z elementno analizo, IR in UV-Vis spektroskojo. Strukture kompleksov so bile določene z rentgensko monokristalno difrakcijo. V obeh kompleksih je nikljev atom v oktaedrični koordinaciji. Ligand L\(_1\) se koordinira na nikljev atom preko fenolatnega O in imino N atoma, ligand L\(_2\) se koordinira na nikljev atom preko fenolatnega O, imino N in amino N atomov. Določena je bila tudi antimikrobna aktivnost kompleksov.

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