

NEW NICKEL(II) COMPLEXES INCORPORATING DISSYMMETRIC
TETRADENTATE SCHIFF BASE LIGANDS DERIVED FROM
AMINOTHIOETHER PYRIDINE WITH N₂OS CHROMOPHORES:
SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL
STRUCTURES OF [Ni(pytlSal)]ClO₄ and [Ni(pytAzosal)]ClO₄·H₂O

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Abstract

The synthesis of nickel (II) complexes with five dissymmetric Schiff base ligands (abbreviated pytlSalH, pytBrsalH, pytNO₂salH, pytOMesalH, and pytAzosalH) which were prepared from aminothioether pyridine and a salicylaldehyde derivative, are described. The ligands were characterized by ¹H, ¹³C NMR, FTIR and elemental analysis. The complexes of these ligands were synthesized by treating an ethanolic solution of appropriate ligand with equimolar amount of Ni(ClO₄)₂·6H₂O and methanolic NaOH or alternatively by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. The complexes were characterized by elemental analysis, FTIR, electronic spectra and molar conductivity. The complex [Ni(pytlSal)]ClO₄ (**6**) crystallizes in triclinic space group P $\bar{1}$ with a = 12.188(2) Å, b = 13.312(3) Å, c = 13.348(3) Å, α = 115.48(3)°, β = 90.78(3)°, γ = 90.90(3)°, Z = 4, R₁ = 0.0617 for 4276 reflections with I > 2 σ (I). The complex [Ni(pytAzosal)]ClO₄·H₂O (**10**) crystallizes in orthorhombic space group P2₁2₁2₁ with a = 7.093(5) Å, b = 9.277(6) Å, c = 34.62(3) Å, α = 90°, β = 90°, γ = 90°, Z = 4, R₁ = 0.0635 for 2185 reflections with I > 2 σ (I). The coordination geometry of nickel ions in the complexes with mixed N, S and O donor atoms is square planar with a slight tetrahedron distortion. All of the complexes were found to be 1:1 electrolyte systems in acetonitrile. Cyclic voltammetry studies indicates that the complexes [Ni(pytxSal)]ClO₄ (X = I and OMe) show quasi-reversible reduction to Ni(I) while this process for X = Azo and NO₂ is reversible and irreversible, respectively.

Introduction

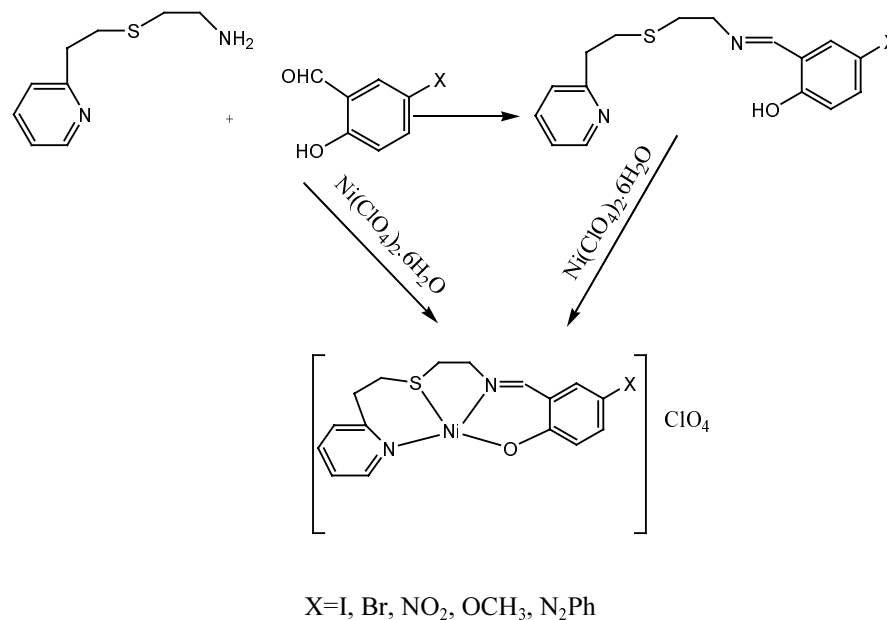
Low symmetry complexes are very important in biological systems as well as in industrial catalysis. From the theoretical point of view they are interesting, too.¹⁻⁵ Transition metals occur in metalloenzymes bound to a macrocycle such as heme ring or to donor atoms of peptide chains in a distorted environment, as in hemerythrin (Fe₂),

hemocyanin (Cu_2) and [Ni-Fe] hydrogenase enzymes.⁶⁻⁷ A great deal of work has been reported on the synthesis, structural investigations, various crystallographic features, mesogenic characteristics, structure-redox relationships and catalytic properties of different types of Schiff bases and their complexes with transition and non-transition elements.⁸ Dissymmetrical Schiff base ligands can clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of metal ions binding sites in metalloproteins, and selectivity of natural systems with synthetic materials.⁹ Dissymmetric Schiff base complexes as chiral analogues become more effective and prevalent in asymmetric catalysis.^{6,9-14} The synthesis of transition metal complexes containing thiolate ligand is an important area of study with implication in bioinorganic chemistry, catalysis and medical chemistry.¹⁵ The structural characterization of active site of the [Ni-Fe] hydrogenase, by which the catalytic site was revealed to contain a heterodimetallic nickel-iron cluster in a sulfur rich environment, has renewed interest in the chemical modeling of [Ni-Fe] hydrogenases.¹⁶ This hypothesis that the coordination environment of nickel in NiFe hydrogenase and CO-dehydrogenase contains sulfur, nitrogen and/or oxygen donors, resulted in a continuing effort to obtain nickel complexes with this kind of coordination environment.¹⁶⁻¹⁷ Herein, we describe the synthesis and spectroscopic characterization of five nickel(II) complexes with N_2OS co-ordination sphere as depicted in Scheme 1, and the crystal structures of 4-iodo-2-{[2-(2-pyridin-2-yl-ethylsulfanyl)-ethylimino]methyl}phenol-nickel(II) ($[\text{Ni}(\text{pytIsal})]\text{ClO}_4$) (**6**) and 4-phenylazo-2-{[2-(2-pyridin-2-yl-ethylsulfanyl)-ethylimino]methyl}phenol-nickel(II) ($[\text{Ni}(\text{pytAzosal})]\text{ClO}_4 \cdot \text{H}_2\text{O}$) (**10**) are reported.

Results and discussion

1-(2-Pyridyl)-3-thia-5-amino pentane (pyta) is a convenient starting material for the synthesis of dissymmetric ligands containing NSON coordination sphere. Schiff base condensation of pyta with several substituted salicylaldehydes yields the desired ligand in a facile manner and with good purity. Nickel(II) complexes of these ligands depicted in Scheme 1 have been prepared using an ethanolic solution of the suitable ligand with equimolar amounts of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of methanolic NaOH or alternatively by a more direct route in which two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. The same

products obtained in both routes but the latter was less time consuming and gave higher yields.



Scheme 1. The formation of Schiff base ligands and Ni(II) complexes.

The Schiff base ligands and complexes were characterized by the usual methods: elemental analysis, absorption electronic spectroscopy, molar conductivity, FTIR, ¹H and ¹³C NMR and also crystal structure determinations of the two of the complexes. The measurement of molar conductivities at 10⁻³ M concentration carried out in acetonitrile, the obtained Λ_M values for monocationic complexes, indicating a behavior attributable to 1:1 electrolytes.²² These complexes display good stability in the air at room temperature and are soluble in acetonitrile, methanol, dimethyl formamide and dimethyl sulfoxide. The structures of the ligands confirmed by the ¹H and ¹³C NMR spectra data. The signal for proton of the –NH group was not found in the ¹H NMR spectra and it is suggested that the Schiff base ligands do not undergo keto-enol tautomerism.²³⁻²⁴ A signal at 59.33 ppm in the ¹³C NMR spectrum of pytOMesalH can be attributed to the carbon atom of the methoxy group.²⁴ FTIR spectra of the Ni(II) complexes are all fairly similar, and not very different from the free ligands spectra. The ligands show strong bands at 1634-1655 cm⁻¹ characteristic of the ν (C=N) stretching mode. The shift of these strong bands towards lower frequencies by 16-35 cm⁻¹, compared to free ligands

spectra, are consistent with the iminic nitrogen coordination. The disappearance of the OH bands of the free ligands in the complexes show that the OH group has been deprotonated and bonded to metal ion. The spectra of $[\text{Ni}(\text{pytNO}_2\text{sal})]\text{ClO}_4$ and its free ligand show two bands at 1325 and 1557 cm^{-1} attributable to the nitro group, $\nu(\text{N}=\text{O})$.²⁴ The complexes display very strong band for perchlorate anion at 1086-1094 cm^{-1} .²⁵ A relatively medium broad absorption band with maximum at 3600 and 3531 cm^{-1} indicates the presence of crystal water or methanol as the elemental analyses of $[\text{Ni}(\text{pytAzosal})]\text{ClO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Ni}(\text{pytOMesal})]\text{ClO}_4 \cdot 0.5\text{CH}_3\text{OH}$ show the presence of one mole of water and half mole of methanol in the one mole of the complex, respectively. The electronic spectra of the Ni(II) complexes, which give light brown reddish solutions in acetonitrile, were obtained. The $[\text{Ni}(\text{PytXsal})]\text{ClO}_4$ (X=I, Br, NO_2 , Azo, OMe) complexes show a low energy band as a shoulder at 538, 535, 530 and 540 nm, respectively, with the exception of $[\text{Ni}(\text{PytOMesal})]\text{ClO}_4$ which shows a broad low energy band at 579 nm. The relatively intense bands at 314-417 nm may be assigned to ligand to metal charge transfer or metal to ligand charge transfer bands.^{6,17,21,26,27} The absorption spectra of all the complexes are similar despite the changes of nature of the salicylaldehyde substituents. This is not surprising since the d-d bands occur as a shoulder on the intense UV band, which can be expected to obscure changes in the d-d band positions brought about by small changes in the environment of the nickel atom. The low energy band is typical of d-d transition in square planar Ni(II) complexes with mixed coordination sphere containing nitrogen, oxygen and sulfur atoms.^{6,17,21,26, 27}

Crystal Structures of $[\text{Ni}(\text{PytIsal})]\text{ClO}_4$ (6) and $[\text{Ni}(\text{PytAzo sal})]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (10)

Compounds **6** and **10** are both cationic and have been crystallized as the perchlorate salt. The complex **6** does not include any solvent molecule, but the complex **10** includes one water molecule. Details of data collection procedures and structures are given in Table 1. The crystal structures of complexes **6** and **10** and their unit cell diagrams are shown in Figs. 1-4. The relevant distances and angles are listed in Table 2. The complex **6** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two independent molecules (molecule **I** and **II**) of $[\text{Ni}(\text{PytIsal})]\text{ClO}_4$. The complex **10** crystallizes in the orthorhombic space group $P2_12_12_1$, with one asymmetric unit

constituted by a molecule of complex and a molecule of water. The nickel ion in both complexes has N_2OS coordination sphere, bound by deprotonated phenolic oxygen, imine and pyridine type nitrogens and the thioether sulfur atoms. Bond lengths of both independent molecules in complex **6** are similar, with only significant difference occurring in the Ni-S distance that is 0.01 Å longer in molecule **II** compared to molecule **I**. While the O-Ni-N(2), O-Ni-N(1), N(2)-Ni-S bond angles are similar in both molecules, the O-Ni-S and N(1)-Ni-N(2) bond angles are smaller and the N(1)-Ni-S bond angle is larger in molecule **I** than in molecule **II** (Table 2). In the complex **6** the Ni-O (1.843 Å) and Ni-N(1) (1.922 Å) bond lengths are slightly longer while Ni-N(2) (1.866 Å) and Ni-S (2.1775 Å) are slightly shorter than related Schiff base complexes.^{15,17,21} In complex **10**, Ni-O (1.821 Å), Ni-N(2) (1.884 Å) and Ni-N(1) (1.911 Å) bond lengths are in the range found for similar Ni-O (phenolate), Ni-N (imine) and Ni-N (pyridine) interactions, but Ni-S (2.158 Å) distance is slightly shorter than related Schiff base complexes.^{15,17,21} Apparently, the double bonds in the chelate ring Ni(1)-N(2)-C(10)-C(11)-C(16)-O(1) in both complexes are delocalized. In the complexes of **6** and **10** the C(10)-C(11) distance of 1.428 Å and 1.383 Å, respectively, is much shorter than the normal $C(sp^2)-C(sp^2)$ single bond (1.51 Å),⁹ the C(10)-N(2) distance of 1.286 Å and 1.293 Å, respectively, are a little longer than normal imine C=N double bond (1.28 Å)⁹ and the C(16)-O(1) bond lengths of 1.306 Å and 1.297 Å, respectively, are shorter than the normal $C(sp^2)-O$ single bond (1.34 Å).⁹ All these changes in bond lengths indicate delocalization of the donating ring of aromatic Schiff base portion, so this chelating ring tends to remain planar as a result of this delocalization to form a stable conjugation structure.⁹ Within the ligand-metal fragment, the four adjacent bond angles around the Ni center are unevenly distributed from the ideal 90°. The comparison of bond angles of complexes of **6** and **10** with similar tetradentate Schiff base complexes show that in both independent molecules of complex **6** the angles of N(1)-Ni(1)-S(1) and O(1)-Ni(1)-N(2) are larger, but the angles of N(2)-Ni(1)-N(1), O(1)-Ni(1)-N(1) and O(1)-Ni(1)-S(1) are smaller.²¹ The main difference observed in molecule **I** is that the angles of N(2)-Ni(1)-N(1) and O(1)-Ni(1)-S(1) are 6° and 4.35° smaller, respectively, and N(1)-Ni(1)-S(1) angle is 3.99° larger than the obtained values for earlier known compounds.²¹ On the other hand, in complex **10** the N(1)-Ni(1)-S(1) and N(2)-Ni(1)-S(1) angles are larger, but the angle of O(1)-Ni(1)-N(1) is smaller, and the only

significant difference observed for N(1)-Ni(1)-S(1) angle which is 2.5° larger than reported values.²¹ It is emphasized that the bond angles of O(1)-Ni(1)-N(2), N(2)-Ni(1)-S(1), N(1)-Ni(1)-S(1), O(1)-Ni(1)-N(1), O(1)-Ni(1)-S(1) and N(2)-Ni(1)-N(1) obtained for, already reported nickel Schiff base complexes are 94.8° , 87.5° , 87.6° , 87.6° , 176.5° and 176.5° , respectively.²¹ In complex **6** the weak interactions are observed between hydrogen atom of C(6) and iodine atom of another independent molecule with a distance of 2.98 \AA , also weak interaction between the nickel atom and iodine atom from the

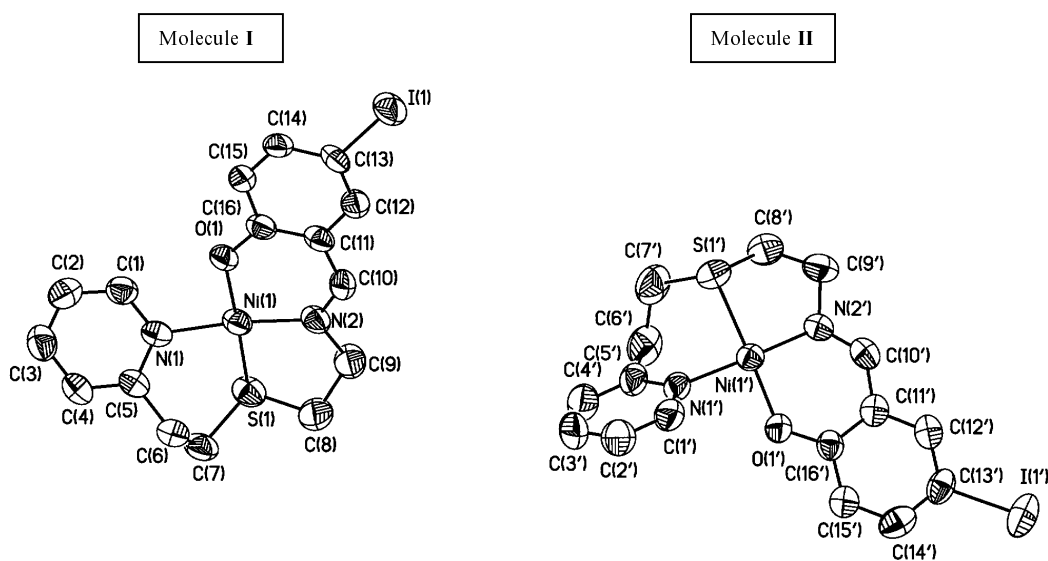


Fig. 1. The structure of $[\text{Ni}(\text{pytlSal})]\text{ClO}_4$.

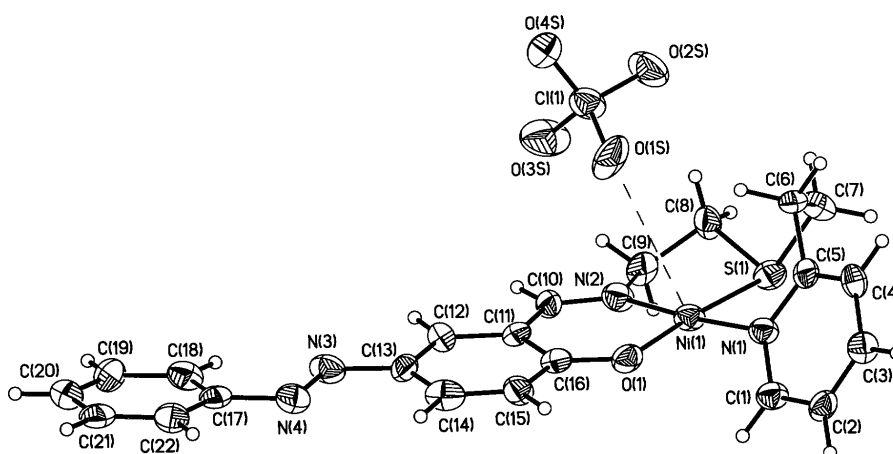


Fig. 2. The structure of $[\text{Ni}(\text{pytlAzosal})]\text{ClO}_4 \cdot \text{H}_2\text{O}$.

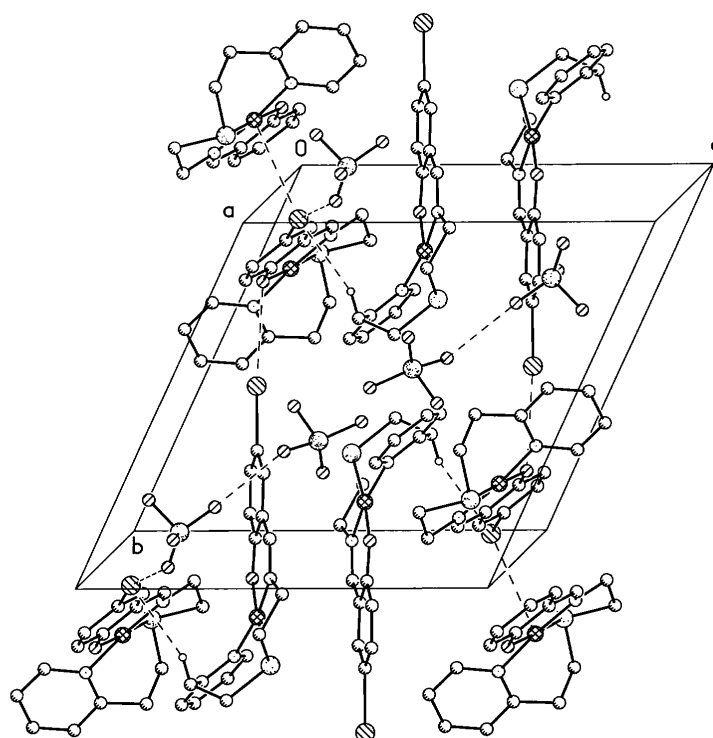


Fig. 3. Stereoview of the $[\text{Ni}(\text{pytlSal})]\text{ClO}_4$.

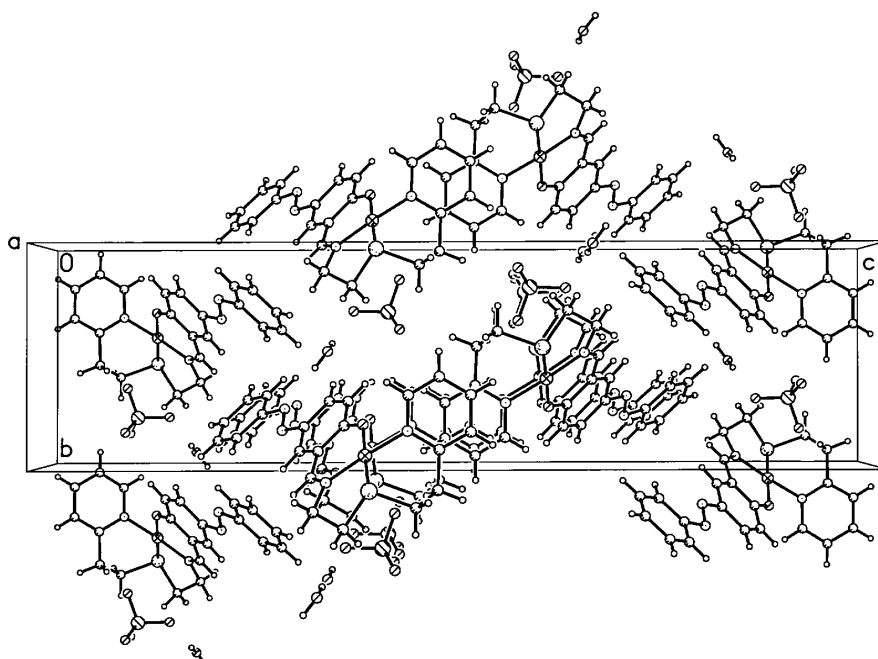


Fig. 4. Stereoview of the $[\text{Ni}(\text{pytlAzosal})]\text{ClO}_4 \cdot \text{H}_2\text{O}$.

Table 1. Crystal and structure refinement data for the nickel complexes.

| | [Ni(pytlal)]ClO ₄ | [Ni(pytlazol)]ClO ₄ ·H ₂ O |
|---|--|---|
| Empirical formula | C ₁₆ H ₁₆ ClIN ₂ NiO ₅ S | C ₂₂ H ₂₃ ClN ₄ NiO ₆ S |
| Formula weight | 569.43 | 565.66 |
| Temperature (K) | 293(2) | 110(2) |
| Space group | P-1 | P2 ₁ 2 ₁ 2 ₁ |
| Crystal system | Triclinic | Orthorhombic |
| Unit cell | | |
| a (Å) | 12.188(2) | 7.093(5) |
| b (Å) | 13.312(3) | 9.277(6) |
| c (Å) | 13.348(3) | 34.62(3) |
| α (°) | 115.48(3) | 90.0 |
| β (°) | 90.78(3) | 90.0 |
| γ (°) | 90.90(3) | 90.0 |
| Volum (Å ³) | 1945.2(7) | 2278(3) |
| Z | 4 | 4 |
| Density (Calc.) (Mgm ⁻³) | 1.935 | 1.649 |
| Absorption Coefficient (mm ⁻¹) | 2.846 | 1.110 |
| F(000) | 1120 | 1168 |
| Crystal Size (mm) | 0.2×0.08×0.02 | 0.08×0.08×0.4 |
| θ Range for data collection (°) | 2.40 to 27.06 | 2.27 to 26.02 |
| Index ranges | 0 ≤ h ≤ 15, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17 | -8 ≤ h ≤ 6, -10 ≤ k ≤ 7, -42 ≤ l ≤ 30 |
| Reflections collected | 11038 | 6614 |
| Independent reflections | 8759 | 4365 |
| Reflection observed | 4276 | 2158 |
| Data/ restraints/ parameters | 8579/0/479 | 4265/0/317 |
| Goodness-of-fit on F ² | 1.010 | 0.929 |
| Final R indices [I > 2σ (I)] | R ₁ = 0.0617, wR ₂ = 0.1124 | R ₁ = 0.0635, wR ₂ = 0.1072 |
| R indices (all data) | R ₁ = 0.1364, wR ₂ = 0.1282 | R ₁ = 0.1330, wR ₂ = 0.1215 |
| Largest difference peak and hole (e Å ⁻³) | 0.649 and -0.801 | 0.834 and -0.568 |

same molecule with a distance of 3.565 Å, and between one of the O atoms of ClO₄⁻ anion with iodine atom with a distance of 3.01 Å, and between two O atoms from two separated perchlorate anions with a distance of 2.85 Å are observed. The crystal structure of complex **10** consists of discrete complex mononuclear cation and perchlorate anion with no significant intermolecular interactions. In regard to the bond angles of O(1)-Ni(1)-S(1) (175.77°) and N(1)-Ni(1)-N(2) (176°) in complex **10** and in the molecule **II** which are 176 and 174.5°, respectively, we conclude that the coordination geometry

Table 2. Selected bond lengths (Å) and angles (°) for complexes.

| | [Ni(pytlSal)]ClO ₄ | | [Ni(pytlAzosal)]ClO ₄ |
|-----------------|-------------------------------|-------------|----------------------------------|
| | Molecule I | Molecule II | |
| Ni(1)–O(1) | 1.843(4) | 1.845(4) | 1.821(6) |
| Ni(1)–N(2) | 1.866(5) | 1.866(5) | 1.884(7) |
| Ni(1)–N(1) | 1.922(5) | 1.914(5) | 1.911(6) |
| Ni(1)–S(1) | 2.1775(19) | 2.1878(19) | 2.158(3) |
| N(2)–C(10) | 1.286(7) | 1.277(8) | 1.293(9) |
| N(2)–C(9) | 1.485(8) | 1.472(8) | 1.478(9) |
| O(1)–C(16) | 1.306(7) | 1.303(7) | 1.297(9) |
| C(10)–C(11) | 1.428(8) | 1.422(9) | 1.383(11) |
| O(1)-Ni(1)-N(2) | 95.35(19) | 95.1(2) | 94.60(3) |
| O(1)-Ni(1)-N(1) | 86.641(18) | 87.59(19) | 86.60(3) |
| N(2)-Ni(1)-N(1) | 170.5(2) | 174.5(2) | 176.0(3) |
| O(1)-Ni(1)-S(1) | 172.15(15) | 176.10(14) | 175.77(18) |
| N(2)-Ni(1)-S(1) | 87.65(15) | 87.75(17) | 88.80(2) |
| N(1)-Ni(1)-S(1) | 91.59(15) | 89.80(16) | 90.10(2) |

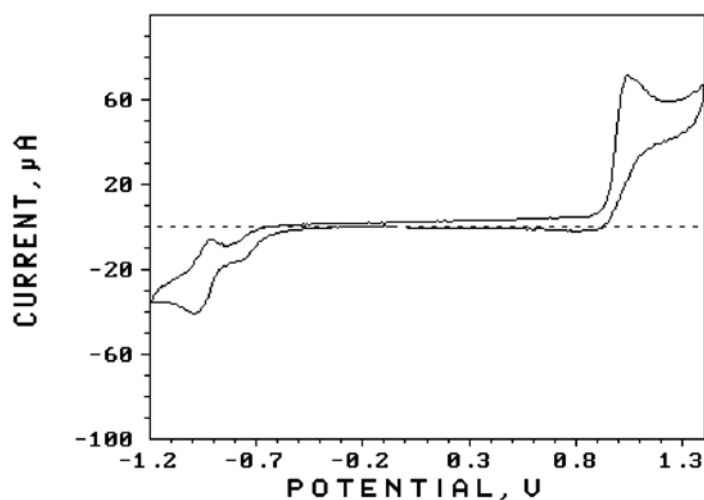
around nickel in complex **10** and molecule **II** is near to square planar in comparison to molecule **I** which has corresponding values of 172.15 and 170.5°, respectively. The nickel center resides on the basal ONSN plane, however in the independent molecule **I** the atoms of O(1) and S(1) are, respectively, 0.131 and 0.153 Å above the mean plane, and the N(1) and N(2) atoms are 0.141 and 0.143 Å below the same plane, respectively. But this situation in molecule **II** is reversed and the atoms of O(1) and S(1) are 0.068 and 0.060 Å below this plane, respectively, and the atoms of N(1) and N(2) with a value of 0.065 and 0.063 Å are placed above the same plane, respectively. Donor atoms situations in complex **10** are the same as molecule **II**, in which the atoms of O(1) and S(1) are, respectively, 0.055 and 0.047 Å below the plane and the atoms of N(1) and N(2) are respectively, 0.056 and 0.053 Å above the same plane. Comparison of these data shows that the tetrahedral distortion for molecule **I** respect to ideal square planar arrangement is larger than complex **10** and molecule **II**.

Cyclic voltammetry

The electrochemistry data obtained for the Ni(II) complexes are given in Table 3. Moreover, one of the voltammograms of the complexes is shown in Fig. 5. On the basis

Table 3. Cyclic voltammetry data for Ni(II) complexes.

| Copmlex | $E_{pc}(I)$, mV | $E_{pa}(I)$, mV | $\Delta E(I)$, mV | $i_{pc}(I)/i_{pa}(I)$ | $E_{pc}(II)$, mV | $E_{pa}(II)$, mV | $\Delta E(II)$, mV | $i_{pc}(II)/i_{pa}(II)$ |
|--|---------------------|---------------------|-----------------------|-----------------------|----------------------|----------------------|------------------------|-------------------------|
| [Ni(pytno ₂ sal)]ClO ₄ | -912 | – | – | – | – | 1375 | – | – |
| [Ni(pyta _z osal)]ClO ₄ | -994 | -917 | 77 | 0.9 | – | 1025 | – | – |
| [Ni(pytl _s sal)]ClO ₄ | -1015 | -886 | 129 | 0.75 | 627 | 1002 | 375 | 0.2 |
| [Ni(pyto _m sal)]ClO ₄ | -1086 | -962 | 124 | 0.85 | 707 | 964 | 257 | 0.57 |

**Fig. 5.** The voltammogram of the [Ni(pytaZosal)]ClO₄.

of the voltammetric data, the complex of [Ni(pytno₂sal)]ClO₄ undergoes irreversible reduction process in potential range of -1200 - +1500 mV, as no anodic wave is observed. For other three complexes reduction waves are observed in the range of -1086 - -912 mV. The peak separation ΔE ($= E_{pc} - E_{pa}$) for complexes [Ni(pytxsal)]ClO₄ (X= OMe, I, Azo) are 124, 129, and 77 mV, respectively at scan rate of 100 mVs⁻¹, thus the redox process for complexes of [Ni(pyto_msal)]ClO₄ and [Ni(pytl_ssal)]ClO₄ is quasi reversible and for complex of [Ni(pyta_zosal)]ClO₄ is reversible. The voltammetric responses are assignable to the Ni(II)/Ni(I) couple. For dissymmetric Schiff base complexes herein studied, E_{pc} becomes less negative in the sequence of OCH₃ < I < Azo < NO₂ with increasing electron-withdrawing effects of the substituent at para position respect to phenolic hydroxyl group, and this has been interpreted by assuming that the strong electron withdrawing effects stabilise the lower oxidation state.²⁸ On the other hand, the complexes of [Ni(pytxsal)]ClO₄ (X=NO₂, Azo) show similar irreversible oxidation waves while complexes of (X= OMe, I) show quasi reversible oxidation waves

with the peak separation (ΔE) 254 and 375 mV, respectively, implying that a stable Ni(III) is inaccessible, most probably due to oxidation of the ligands.

Conclusions

In this paper, we could synthesize Ni(II) tetradentate dissymmetric Schiff base complexes containing sulfur, nitrogen and oxygen donor atoms. The structure determinations of two of these complexes were established by single crystal X-ray diffraction study. In both complexes the geometry around the nickel ions are square planar with a slight tetrahedron distortion. Crystallographic identification of molecules with two different geometries in the case of the $[\text{Ni}(\text{pytIsal})]\text{ClO}_4$ (molecules **I** and **II**) is interesting from a structural point of view. Electrochemistry data show reversible and irreversible reductions for $[\text{Ni}(\text{pytXsal})]\text{ClO}_4$ ($X = \text{Azo}$ and NO_2), respectively, while this process for $[\text{Ni}(\text{pytXsal})]\text{ClO}_4$ ($X = \text{OMe}$ and **I**), respectively, is quasireversible.

Experimental

Materials

All solvents used in the preparations were reagent grade. Chemicals for the preparations were reagent grade and commercially available, and were used without further purification. The solvents were purified by standard methods.¹⁸ 5-Phenylazo salicylaldehyde, 5-iodosalicylaldehyde, and 1-(2-pyridyl)-3-thia-5-amino pentane (pyta) were synthesized according to the known procedures¹⁹⁻²¹ and 2-vinyl pyridine distilled in vacuum before using.

Physical Measurements

Elemental analyses (C, H, N) were performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared (FTIR) spectra were recorded using KBr discs on a FTIR Unicam 4600. ^1H and ^{13}C spectra were taken in CDCl_3 on a Bruker spectropin 400 MHz ultrashield spectrometer and chemical shifts were indicated in ppm relative to tetramethylsilane(TMS). The electronic spectra in 200-900 nm range were obtained in acetonitrile on a Shimadzu UV-265 FW spectrophotometer. The conductivity measurements were carried out in acetonitrile at room temperature using a Hanna conductometer HI 8828N instrument. Cyclic voltammograms were performed using an AMEL instrument Model 2053 as potentiostat connected with a function generator

(AMEL Model 568). All solutions were deoxygenated by passing a stream of Ar into the solution for at least 10 min prior to recording the voltammogram. All potentials reported herein were measured at room temperature and referenced to the saturated calomel electrode (SCE) with ferrocene as an internal standard. A platinum wire was used as counter electrode and a glassy carbon disc with a diameter of 3 mm was used as working electrode. Before each experiment the working electrode was cleaned perfectly by polishing with alumina and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 M LiClO₄ in acetonitrile. Under these conditions the ferrocenium - ferrocene couple was located at 371 mV with a peak separation of 89 mV.

X-ray Crystallography

Crystallographic data for complexes of [Ni(PytlSal)]ClO₄ (**6**) and [Ni(PytAzosal)]ClO₄.H₂O (**10**) are given in Table 1. Suitable single crystals for both complexes were acquired by slow evaporation from of the methanol solution of related complexes at room temperature and mounted in sealed glass capillaries. Diffraction data were collected on a Bruker Smart CCD diffractometer at 110 K for complex **10** and on a Siemens P3/PC diffractometer at 293 K for complex **6** and the ω and π scan modes were used. Intensity data were obtained using Mo K α radiation (0.7107Å) monochromatized from graphite. The data were reduced and the structures were solved by direct methods using the program SHELXTL version 5.1,²⁹ and refined by the full-matrix least-squares on F², using all the unique data and the weighting scheme $w=[\sigma^2(F_0)^2+(0.0554P)^2+1.944P]^{-1}$ for complex **6** and $w=[\sigma^2(F_0)^2+(0.0300P)^2]^{-1}$ for complex **10** where $P=(F_0^2+2Fc^2)/3$.

Synthesis of Schiff base ligands

The procedure for preparation of the 4-X-2- {[2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino]methyl}-phenol [X=I, Br, NO₂, OMe and N₂ph] which will abbreviated as pytlSalH, pytBrsalH, pytNO₂salH, pytOMesalH and pytAzosalH, respectively, is the same. Pyta (1 mmol) dissolved in ethanol (5 mL), was added with constant stirring to a solution of appropriate salicylaldehyde (1 mmol) in ethanol (5 mL). The mixture was allowed to stir magnetically at reflux for about 60 min. After cooling,

the resulting precipitate was collected on a filter and washed with cooled ethanol and recrystallized from ethanol-chloroform (2:1,v/v) with the exception of pytAzosalH which gave viscous oily liquid.

4-iodo-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol, (1)

pytIisalH. Yield 70%, Anal. Calcd for C₁₆H₁₇IN₂OS: C 46.61, H 4.15, N 6.79. Found: C 46.70, H 4.20, N 6.80. ¹H NMR (400 MHz CDCl₃) δ 13.35 (br s, 1H, OH), , 8.23 (s, 1H, iminic), [8.54 (d, 1H), 7.64 (t, 1H), 7.17-7.55 (m, 4H), 6.74 (d, 1H) (total 7H, ArH)], 3.78-2.84 (t, 8H, 4×CH₂). ¹³C NMR (400 MHz CDCl₃) δ 31.84, 32.97, 38.36, 58.93, 79.15, 119.57, 120.79, 121.60, 123.31, 136.52, 139.56, 140.68, 149.33, 159.67, 160.90, 164.55 (16 C). FTIR (KBr) ν 3485, 3053, 2853-2930, 1634 cm⁻¹. mp 71 °C. Yellow microcrystal.

4-bromo-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol (2),

pytBrsalH. Yield 83%, Anal. Calcd for C₁₆H₁₇BrN₂OS: C 52.60, H 4.69, N 7.66. Found: C 52.50, H 4.70, N 7.60. ¹H NMR (400 MHz CDCl₃) δ 13.20 (br s, 1H, OH), 8.26 (s, 1H, iminic), [8.55 (d, 1H), 7.67 (t, 1H), 7.21-7.39 (m, 4H), 6.85 (d, 1H) (total 7H ArH)] 3.80-2.86 (t, 8H, 4×CH₂). ¹³C NMR (400 MHz CDCl₃) δ 31.82, 32.94, 38.36, 58.93, 109.95, 119.02, 119.96, 121.56, 123.25, 133.46, 134.92, 136.45, 149.32, 159.66, 160.16, 164.61 (16 C). FTIR(KBr) ν 3447, 3015- 3050, 2850-2930, 1634 cm⁻¹. mp 69 °C. Yellow microcrystal.

4-nitro-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol (3),

pytNO₂salH. Yield 78%, Anal. Calcd for C₁₆H₁₇N₃O₃S: C 57.99, H 5.17, N 12.67. Found: C 57.70, H 5.20, N 12.50. ¹H NMR (400 MHz CDCl₃) δ 14.55 (br s, 1H, OH), 8.35 (s, 1H, iminic), [8.55 (d, 1H), 8.16-8.22 (m, 2H), 7.65 (t, 1H), 7.19 (m, 2H), 6.96 (d, 1H) (total 7H ArH)], 3.84-2.88 (t, 8H, 4×CH₂). ¹³C NMR (400 MHz CDCl₃) δ 31.70, 32.72, 38.21, 57.04, 116.65, 119.02, 121.69, 123.35, 128.21, 128.41, 136.62, 138.72, 149.25, 159.48, 164.98, 169.22 (16 C). FTIR (KBr) ν 3447, 3053, 2922-2940, 1655, 1325-1557 cm⁻¹. mp 90 °C. Orange microcrystal.

4-methoxy-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol (4),

pytOMesalH. Yield 75%, Anal. Calcd for C₁₇H₂₀N₂O₂S: C 64.50, H 6.37, N 8.85. Found: C 64.00, H 6.30, N 8.70. ¹H NMR (400 MHz CDCl₃) δ 12.75 (br s, 1H, OH), 8.29 (s, 1H, iminic), [8.52 (d, 1H), 7.58 (t, 1H), 7.11-7.20 (m, 4H), 6.76(d, 1H) (total 7H ArH)], 3.77-2.83 (m, t, CH₃ and 4×CH₂). ¹³C NMR (400 MHz CDCl₃) δ 31.90, 33.09,

38.44, 55.93, 59.33, 114.95, 117.23, 118.30, 119.38, 121.54, 123.27, 136.48, 149.29, 152.00, 155.21, 159.77, 165.55 (17 C). FTIR (KBr) ν 3447, 3053, 2850-2937, 1641 cm^{-1} . mp 59-60 °C. Orange microcrystal.

4-phenylazo-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol (5), pytAzosalH. Yield 65%, Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{OS}$: C 67.70, H 5.67, N 14.35. Found: C 67.35, H 5.85, N 14.50. ^1H NMR (400 MHz CDCl_3) δ 13.80 (br s, 1H, OH), 8.39 (s, 1H, iminic), [8.54 (d, 1H), 7.98 (d, 1H), 7.86-7.89 (m, 3H), 7.61(t, 1H), 7.41-7.51 (m, 3H), 7.13-7.18 (m, 2H), 7.05 (d, 1H) (total 12H ArH)], 3.80-2.85 (t, 8H, $4\times\text{CH}_2$). ^{13}C NMR (400 MHz CDCl_3) δ 31.83, 32.94, 38.24, 58.38, 118.05, 118.27, 121.71, 122.53, 122.53, 123.45, 126.96, 127.50, 129.09, 129.09, 130.45, 136.77, 145.02, 149.12, 152.56, 159.54, 164.94, 165.67 (22 C). FTIR (KBr) ν 3400, 3069, 2850-2930, 1641 cm^{-1} . Dark brown liquid.

Synthesis of Schiff base complexes

The Ni(II) complexes were prepared using similar method. A solution of the appropriate ligand was prepared by either dissolving the required amount (1 mmol) of the ligand in absolute ethanol (10 mL) or by preparing the ligand in situ from its precursors as follow, a solution of 1 mmol of pyta in 5 mL absolute ethanol was added to solution of 1 mmol required salicylaldehyde in 5 mL absolute ethanol and the mixture was refluxed for 40 min and then 1 mL of 1 M methanolic NaOH was added and reflux and stirring were continued for a further 5 min. Then 1 mmol of $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ in 5 mL absolute ethanol was added to the ligand solution with stirring and the reaction mixture was stirred under reflux for 25 min. The obtained colored solution was left at room temperature. The product was removed by filtration, washed with cooled absolute ethanol, recrystallized from acetonitrile or methanol and dried in vacuum.

4-iodo-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol nickell(II) (6), [Ni(pytIisal)] ClO_4 . Yield 58%, Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{ClIN}_2\text{NiO}_5\text{S}$: C 33.75, H 2.83, N 4.92. Found: C 34.30, H 2.83, N 5.00. FTIR (KBr) ν 3007-3115, 2850-2950, 1618, 1086 cm^{-1} . mp 274 °C dec. UV (CH_3CN) λ_{max} (log ϵ) 538 nm (sh). Mol. Conductivity 138 μS . Dark brown crystal.

4-bromo-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol Nickell(II) (7), [Ni(pytBrsal)] ClO_4 . Yield 60%, Anal. Calculated for

$C_{16}H_{16}BrClN_2NiO_5S$: C 36.78, H 3.08, N 5.36. Found: C 36.90, H 3.10, N 5.50. FTIR (KBr) ν 3030-3076, 2850-2937, 1618, 1094 cm^{-1} . mp 271 °C dec. UV (CH_3CN) λ_{max} (log ϵ) 535 nm (sh). Mol. Conductivity 140 μS . Light brown crystal.

4-nitro-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol

nickell(II) (8), [Ni(pytno₂sal)]ClO₄. Yield 53%, Anal. Calcd for $C_{16}H_{16}ClN_3NiO_7S$: C 39.33, H 3.30, N 8.60. Found: C 39.40, H 3.30, N 8.40. FTIR (KBr) ν 3022-3107, 2945, 1620, 1325-1557, 1094 cm^{-1} . mp 298 °C dec. UV (CH_3CN) λ_{max} (log ϵ) 530 nm (sh). Mol. Conductivity 136 μS . Dark brown crystal.

4-methoxy-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol

nickell(II) (9), [Ni(pytmesal)]ClO₄·0.5CH₃OH. Yield 54%, Anal. Calcd for $C_{17.5}H_{21}ClN_2NiO_{6.5}S$: C 42.93, H 4.32, N 5.72. Found: C 43.10, H 4.20, N 5.80. FTIR (KBr) ν 3531, 3059, 2850-2930, 1611, 1094 cm^{-1} . UV (CH_3CN) λ_{max} (log ϵ) 579 nm (201). mp 220 °C dec. Mol. Conductivity 150 μS . Black crystal.

4-phenylazo-2-{{2-(2-pyridin-2-yl-ethylsulfanyl)ethylimino}methyl}phenol

nickell(II) (10), [Ni(pyta_zosal)]ClO₄·1 H₂O. Yield 55%, Anal. Calcd for $C_{22}H_{23}ClN_4NiO_6S$: C 46.67, H 4.09, N 9.90. Found: C 46.10, H 3.90, N 9.60. FTIR (KBr) ν 3600, 3050, 2937-2991, 1618, 1094 cm^{-1} . UV (CH_3CN) λ_{max} (log ϵ) 540 nm (sh). mp 251 °C dec. Mol. Conductivity 133 μS . Light reddish crystal.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive! only small quantities of material should be prepared, and should be handled with great caution.

Supplementary data

Supplementary crystallographic data are available from the CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax. +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition number CCDC 198418 for complex **6** and CCDC 198419 for complex **10**.

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Povzetek

Pripravili smo nikeljeve(II) komplekse s petimi novimi Shiffovimi bazami kot ligandi z reakcijo med etanolno raztopino liganda, Ni(ClO₄)₄·6H₂O in metanolno raztopino NaOH. Ligande smo preiskali s ¹H in ¹³C NMR spektroskopijo, FTIR in elementno analizo, komplekse pa z elementno analizo, FTIR, UV-vidno spektroskopijo, ciklično voltometrijo in meritvami prevodnosti. Z uklonom rentgenskih žarkov na monokristalu smo določili kristalno strukturo [Ni(pyIsal)]ClO₄ in [Ni(ptyAzosal)]ClO₄·H₂O. Koordinacijska geometrija nikeljevega iona v obeh kompleksih je kvadratno-planarna s tetraedričnim popačenjem.