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Ru(III) Complexes and Their Ligands Derived from Salicylaldehyde and Halogenated Anilines: Synthesis, Characterisation, and Antioxidant Activity

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Abstract

This work aimed to describe the synthesis and characterisation of two anionic Ru(III) complexes of the general formula Na[Ru-Cl_2(*N*-4-Cl-Ph-salim)$_2$] and Na[$RuCl_2$(*N*-3-Br-Ph-salim)$_2$, their associated ligands, and determine their antioxidant activity. The ligands *N*-4-Cl-phenylsalicylidenimine (*N*-4-Cl-Ph-salimH, HL[a]) and *N*-3-Br-phenylsalicylidenimine (*N*-3-Br-Ph-salimH, HL[b]), Schiff bases, were synthesised from salicylaldehyde and chloroaniline or bromoaniline. The compounds were characterised using IR spectroscopy and ESI ToF mass spectrometry. The following was confirmed: coordination of ligands on the Ru(III) centre, the molecular formulas, and the corresponding M^- ions: $[C_{26}H_{18}N_2O_2Cl_4Ru]^-$ ion, (m/z: 631.9173) and $[C_{26}H_{18}N_2O_2Cl_2Br_2Ru]^-$ ion, (m/z: 719.8283). The antioxidant activity was determined by the ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) and DPPH (1,1-diphenyl-2-picrylhydrazyl) assays. In contrast to the ligands, both complexes proved to be strong scavengers of the ABTS and DPPH radicals with IC_{50} (half maximal inhibitory concentration) values comparable to those of Trolox. As such, they present valuable candidates for further research related to their biological properties.

Keywords

Ru(III) complexes, Schiff bases, IR spectroscopy, ESI ToF mass spectrometry, antioxidant activity

1 Introduction

Over the last decades, transition metal complexes have gained much attention as attractive candidates in drug development. Among the transition-metal complexes, ruthenium represents a superior choice in biological applications considering its specific biophysical properties and advantages. The safety profile of ruthenium complexes has been extensively researched leading to the conclusion that these agents are generally characterised by low *in vivo* toxicity, which is a precondition for medical use. Ruthenium binds easily to biomolecules as it mimics iron in its mode of action,[1] the metal ion is generally hexacoordinated, and its different oxidative states facilitate redox reactions and DNA binding.[2] In addition, the reactivity of Ru complexes can be fine-tuned by using labile or kinetically inert ligands.[1]

Until today, a wide range of different ligands has been chelated to ruthenium, such as Schiff bases, hydrazones, thiosemicarbazones, succinimidato, and phthalimidato ligands, and even flavonoids, as the pharmacological properties of metal complexes depend on both the metal ion and the ligand.[3,4] Schiff bases are widely used due to their thermal and chemical stability, and their simple synthesis.[5] Alone, or bound to metal-ions, Schiff bases are used in many branches of chemistry, including inorganic, organic, polymer chemistry, industrial chemistry, but also in material science and pharmacological studies. The quest for novel pharmacological agents with advanced properties is a never-ending process, where Schiff bases and their metal complexes could play a significant role as they have been reported to exhibit important biological activities, such as antiproliferative, antimicrobial, anti-inflammatory, antioxidant, and cytotoxic activities.[6,7] Oxidative stress, caused by excessive free radicals and the redox imbalance, is implicated in the majority of diseases. New antioxidant compounds capable of protecting cells and tissues from oxidative stress-induced damage are receiving much attention since they are often multi-modal, exhibiting anticancer, anti-inflammatory, and other biological activities.[8] Recently, several *in vitro* studies have investigated ruthenium complexes containing diverse ligands for their radical scavenging activity, and compared to a range of standard antioxidant substances, such as ascorbic acid, alpha-tocopherol or butylated hydroxytoluene.[4,6–12] A few *in vivo* studies have also been performed, reporting excellent antioxidant properties of ruthenium complexes that reduced intracellular levels of reactive oxygen species.[13] Mechanistic studies have shown that Ru(III) complexes are more inert in physiological conditions but are, nevertheless, readily reduced to Ru(II) in the acidic, glutathione-rich environment of cancerous cells, thus making water-soluble Ru(III) complexes the preferred targets for the synthesis of bioactive metallodrugs.[14] Ionic, water-soluble Ru(III) complexes with strategically placed chloride ligands as labile coordination sites are of particular interest for anticancer

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research.[15] These complex species are exploiting the well-known fact that the hydrolysis of Ru-Cl bonds, usually after Ru(III) reduction in the cellular medium, is a major activation pathway for their subsequent cytotoxicity.[16]

Therefore, this study aimed to describe the synthesis and characterisation of two Ru(III) complexes, containing the anionic $[RuCl_2(\kappa^2\text{-}N,O\text{-}L^{a/b})_2]^-$ species, with salicylaldehyde-derived Schiff base ligands, and determine their radical scavenging ability against the DPPH and ABTS free radicals.

2 Experimental

2.1 Chemicals

All reagents used in this study were of analytical grade, obtained from commercial sources, and used as received without further purification. All solvents were distilled prior to use.

2.2 Methods

Infrared spectra were recorded on a Perkin Elmer spectrum BX FTIR System in the range of 4000–400 cm^{-1} as KBr pellets. Mass spectra of the synthesised complexes were recorded on a 6210 Time-of-Flight LC/MS system (Agilent Technologies, Santa Clara, California, USA) equipped with an ESI interface (ESI–ToF–MS. Mass spectra were recorded in the range 100–2000 m/z in negative ESI ionisation mode (capillary voltage 4000 V, fragmentor voltage 140 V, skimmer voltage 60 V, OCT RF voltage 250 V); atomising gas (nitrogen): pressure 45 psi, temperature 350 °C, flow 12 l min^{-1}). The mobile phase consisted of 0.2 % formic acid in water (v/v) (A) and acetonitrile (B) in a 1 : 1 ratio. The flow of the mobile phase was 0.20 ml min^{-1}, the temperature of the column compartment 25 °C, and the injection volume of the samples dissolved in acetonitrile 5 µl, $c \approx 1$ mg ml^{-1}. Absorption spectra were measured on a Perkin Elmer lambda 35, ranging from 240–800 nm in quartz cells of path length 1 cm. Melting points were measured on a BÜCHI Melting Point B-545 apparatus.

2.2.1 Synthesis of Schiff base ligands HL^a and HL^b

To an ethanolic solution (20 ml) containing 1 mmol of the appropriate halogenated aniline (128 mg of 4-Cl-aniline; 109 µl of 3-Br-aniline) and one drop of formic acid was added 1 mmol (105 µl) of salicylaldehyde. The resulting yellow solution was heated in a water bath kept at 50 °C for 1 h. After completion of the reaction, the resulting mixtures were cooled in an ice bath, and the precipitated products were filtered by suction. The crude products were recrystallised from aqueous ethanol, and the obtained crystals were dried in a vacuum desiccator overnight.

N-4-Cl-phenylsalicylidenimine(HL^a): yellow-orange crystalline solid; yield (82 %). M. p. 104 °C. FT-IR (KBr, cm^{-1}): 3010 w [ν(O−H)], 1610 s [ν(C=N)], 1584 m [$\nu(C=C)_{arom.}$], 1568 s [δ(C−O−H) + (C=N) + (H−C=N)], 1458 s [ν(C−N)] 1272 m [ν(C−O)], 758 s [$\delta(C-H)_{arom.}$], 698 s [ν(C–Cl)]. UV/Vis (DCM) λ_{max}/nm (log ε): 272 (4.15), 320 (4.12), 343 (4.15).

N-3-Br-phenylsalicylidenimine(HL^b): orange crystalline solid; yield (87 %). M. p. 106 °C. FT-IR (KBr, cm^{-1}): 3010 w [ν(O−H)], 1616 s [ν(C=N)], 1589 m [$\nu(C=C)_{arom.}$], 1569 s [δ(C−O−H) + (C=N) + (H−C=N)], 1457 s [ν(C−N)] 1279 m [ν(C−O)], 753 s [$\delta(C-H)_{arom.}$], 650 m [ν(C−Br)]. UV/Vis (DCM) λ_{max}/nm (log ε): 272 (4.22), 319 (4.09), 342 (4.13).

2.2.2 Synthesis of complexes

A warm ethanolic solution (40 ml) of the appropriate Schiff base ligand HL^a or HL^b (1 mmol; 232 mg or 276 mg, respectively) was added to a freshly prepared solution of $RuCl_3 \cdot 3\,H_2O$ (0.5 mmol, 131 mg) in 10 ml of absolute ethanol. The resulting dark green solution was stirred magnetically and heated in a water bath maintained at 70 °C for 3 h. The reaction mixture was allowed to cool to room temperature, and then treated with an equimolar amount of a saturated, aqueous NaCl solution (0.5 mmol, 58 mg in 170 µl deionised water). After 24 h at room temperature, the mixture was cooled in an ice bath for 3 h. The fine precipitated solids were vacuum filtered, washed with deionised water, ethanol, and finally three 10 ml portions of ether. The crude products were recrystallised from dichlormethane/ethanol DCM/EtOH (1 : 1), filtered, and dried in a vacuum desiccator overnight.

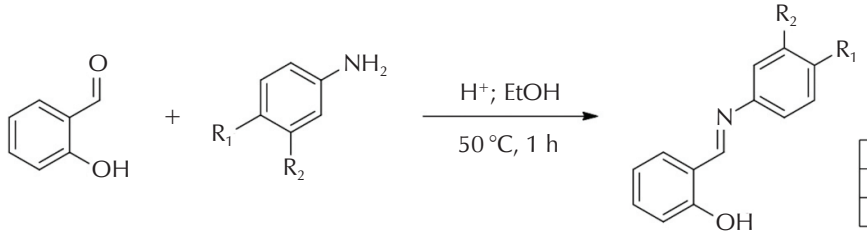
$Na[RuCl_2(L^a)_2]$: black solid; yield (37 %). M. p. > 200 °C. FT-IR (KBr, cm^{-1}): 1602 s [ν(C=N)], 1584 m [$\nu(C=C)_{arom.}$], 1532 s [(C=N) + (H−C=N)], 1434 m [ν(C−N)] 1294 m [ν(C−O)], 760 s [$\delta(C-H)_{arom.}$], 700 m [ν(C−Cl)], 531 m [ν(Ru−N)], 432 m [ν(Ru−O)]; ESI-ToF MS for $[C_{26}H_{18}N_2O_2Cl_4Ru]^-$ Found (Calc.): 631.9173 (631.9166). UV/Vis (DCM) λ_{max}/nm (log ε): 252 (4.33), 322 (3.98), 622 (3.85).

$Na[RuCl_2(L^b)_2]$: black solid; yield (21 %). M. p. > 200 °C. FT-IR (KBr, cm^{-1}): 1603 s [ν(C=N)], 1585 s [$\nu(C=C)_{arom.}$], 1529 s [(C=N) + (H−C=N)],1437 m [ν(C−N)] 1300 m [ν(C−O)], 756 s [$\delta(C-H)_{arom.}$], 646 m [ν(C−Br)], 537 m [ν(Ru−N)], 422 m [ν(Ru−O)]; ESI-ToF MS for $[C_{26}H_{18}N_2O_2Cl_2Br_2Ru]^-$ Found (Calc.): 719.8283 (719.8156). UV/Vis (DCM) λ_{max}/nm (log ε): 252 (4.33), 319 (3.96), 549 (3.76).

2.2.3 ABTS and DPPH assay

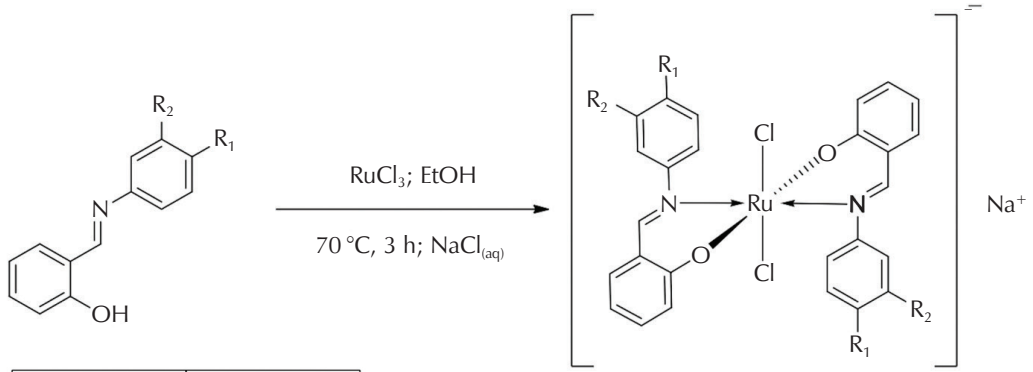
For both assays, samples were prepared in various concentrations, dissolved in dichloromethane, and then in methanol. The ABTS assay was carried out using the method by *Re et al.*[17] Briefly, $ABTS^{\cdot+}$ reagent (1200 µl) was mixed with sample or negative control (30 µl) and the absorbance at 734 nm was measured 6 min after the initial mixing, using 95 % ethanol as the blank.

The DPPH assay was performed following the method described by *Blois*.[18] 1000 µl of DPPH solution (0.05 mmol l^{-1} in methanol) were added to 100 µl of sample solution or negative control. The reaction mixture was allowed to stand for 30 min at room temperature in the dark, and



Ligand	R_1	R_2
HL^a	Cl	H
HL^b	H	Br

Fig. 1 – Synthesis of *N*-salicylidene-X-halogenated anilines
Slika 1 – Sinteza *N*-saliciliden-X-halogeniranih anilina



Complex	Ligand
$Na[RuCl_2(L^a)_2]$	HL^a
$Na[RuCl_2(L^b)_2]$	HL^b

Fig. 2 – Synthesis of Ru(III) complexes
Slika 2 – Sinteza Ru(III) kompleksa

thereupon the absorbance was measured at 517 nm, using methanol as the blank.

For both assays, the radical scavenging ability was expressed as IC_{50} (μg ml^{-1} and mg ml^{-1}) and calculated using the Eq. (1).

$$\text{scavenging activity (\%)} = [(A0 - A1)/A0] \cdot 100 \qquad (1)$$

where A0 is the absorbance of the control, and A1 is the absorbance of the sample/standard solution. Trolox, with a final concentration range of 10–80 μg ml^{-1}, was prepared as a standard.

3 Results and discussion

The ligands HL^a and HL^b, imines of halogenated anilines and salicylaldehyde were prepared by the usual procedure for the synthesis of such Schiff bases (Fig. 1) *via* acid-catalysed condensation of salicylaldehyde with an equimolar amount of the appropriate aniline in ethanol.[19,20]

The complexes, proposed as sodium dichlorido-bis[(*N*-(3-bromophenyl)-2-oxy-κ*O*-ben-zilidenimine-κ*N*-(1-)]ruthenate(III) and sodium dichlorido-bis[(*N*-(4-chlorophenyl)-2-oxy-κ*O*-benziliden-imine-κ*N*-(1-)]ruthenate(III), abbreviated as $Na[RuCl_2(L^a)_2]$ and $Na[RuCl_2(L^b)_2]$, respectively, were synthesised according to literature with slight modifications.[21] The starting $RuCl_3 \cdot 3\,H_2O$ and the corresponding Schiff base ligand were reacted in a 1 : 2 molar ratio in absolute ethanol, and the resulting anionic complexes precipitated as their sodium salts by the addition of aqueous NaCl solution (Fig. 2).

ESI-ToF mass spectrometry confirmed the formulated complexes by detection of the corresponding $[C_{26}H_{18}N_2O_2Cl_4Ru]^-$ and $[C_{26}H_{18}N_2O_2Cl_2Br_2Ru]^-$ anions with the observed peaks at 631.9173 m/z and 719.8283 m/z, respectively (Fig. 3, Table 1). Both spectra showed the authentic isotopic pattern characteristic of stable ruthenium isotopes.[22]

The infrared spectra of the synthesised complexes showed a high degree of similarity, suggesting an identical structure.

Both Schiff base ligands functioned as *O*- and *N*-donating phenolates, indicated by the band shifts in the phenolic and azomethine groups of the complexes as opposed to the free ligands (Figs. 4 and 5).

Coordination *via* the azomethine nitrogen was confirmed by a shift of the C=N stretching vibration to lower wavenumbers for 8–13 cm^{-1} in the spectra of the prepared complexes (1602–1603 cm^{-1}) compared to the spectra of the free ligands (1610–1613 cm^{-1}). Both free ligands showed a prominent band at around 1568 cm^{-1}, which

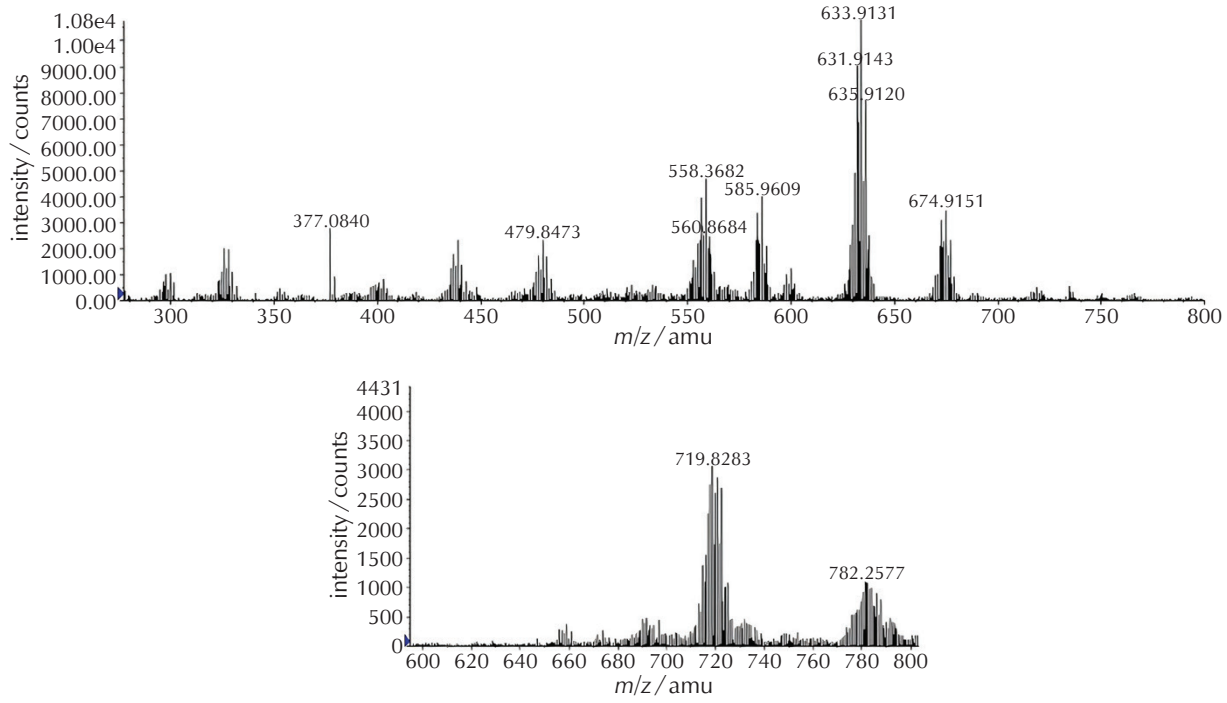


Fig. 3 – Mass spectrum of $Na[RuCl_2(L^a)_2]$ (top), and $Na[RuCl_2(L^b)_2]$ (bottom)
Slika 3 – Maseni spektri $Na[RuCl_2(L^a)_2]$ (gore) i $Na[RuCl_2(L^b)_2]$ (dolje)

Table 1 – ESI ToF MS data for molecular ions of the complex compounds
Tablica 1 – ESI ToF MS podatci za molekularne ione kompleksnih spojeva

Complex compounds	Molecular ion	Ion mass / m/z	Measured mass / m/z	Error / ppm
$Na[RuCl_2(L^a)_2]$	$[C_{26}H_{18}N_2O_2Cl_4Ru]^-$	631.9166	631.9173	1.11
$Na[RuCl_2(L^b)_2]$	$[C_{26}H_{18}N_2O_2Cl_2Br_2Ru]^-$	719.8156	719.8283	17.63

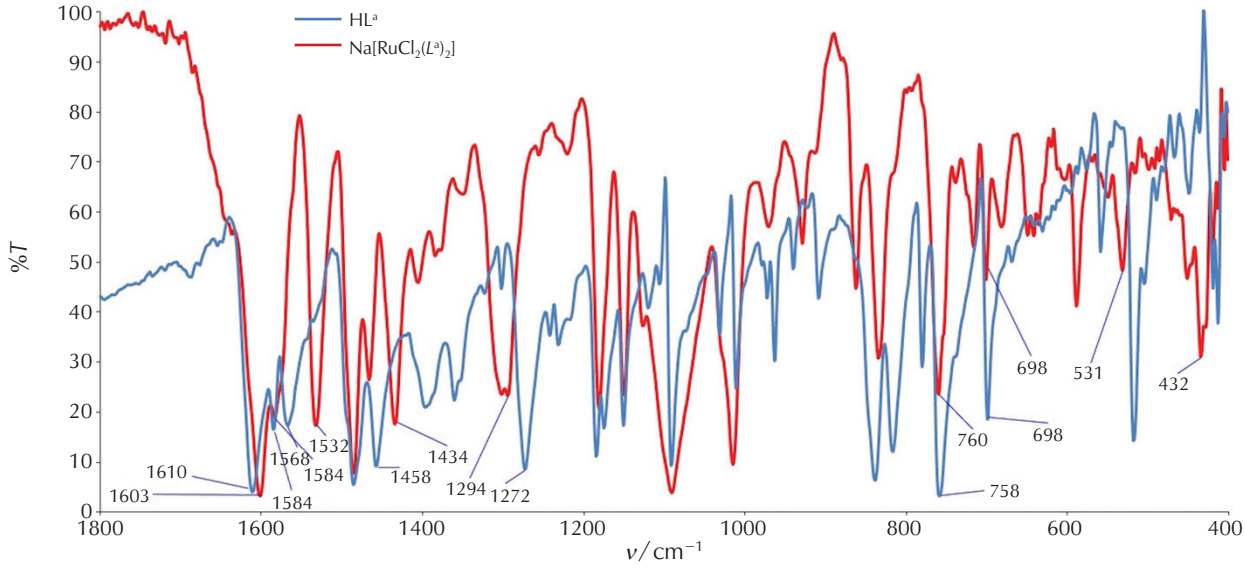


Fig. 4 – FT-IR spectra of ligand HL^a (blue line), and complex $Na[RuCl_2(L^a)_2]$ (red line)
Slika 4 – FT-IR spektri liganda HL^a (plava linija) i kompleksa $Na[RuCl_2(L^a)_2]$ (crvena linija)

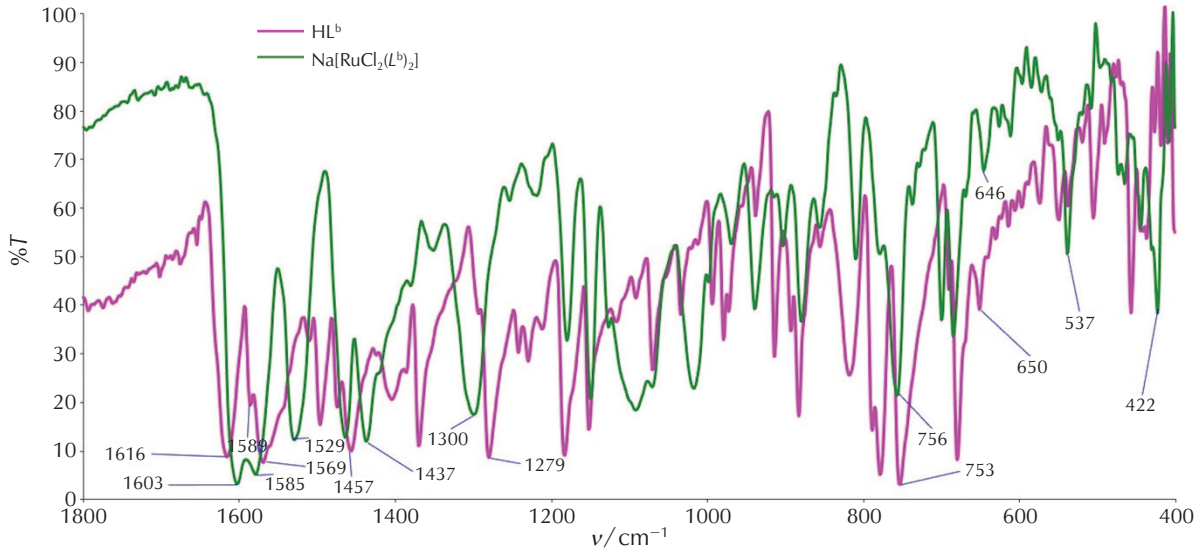


Fig. 5 – FT-IR spectra of ligand HL^b (pink line), and complex $Na[RuCl_2(L^b)_2]$ (green line)
Slika 5 – FT-IR spektri liganda HL^b (ružičasta linija) i kompleksa $Na[RuCl_2(L^b)_2]$ (zelena linija)

Table 2 – Characteristic IR vibrations of the ligands and complexes
Tablica 2 – Karakteristične IR vibracije liganada i kompleksa

Vibration / cm^{-1}	HL^a	$Na[RuCl_2(L^a)_2]$	HL^b	$Na[RuCl_2(L^b)_2]$
ν(C=N)	1610	1602	1616	1603
$\nu(C=C)_{arom.}$	1584	1584	1589	1585
[δ(C−O−H) + ν(C=N) + δ(H−C=N)]	1568	–	1569	–
[ν(C=N) + δ(H−C=N)]	–	1532	–	1529
ν(C−N)	1458	1434	1457	1437
ν(C−O)	1272	1294	1279	1300
$\delta(C-H)_{arom.}$	758	760	753	756
ν(C−Cl)	698	700	–	–
ν(C−Br)	–	–	650	646
ν(Ru−N)	–	531	–	537
ν(Ru−O)	–	432	–	422

Turbeville and Dutta (1990)[23] assigned to a mode centred on the conjugated HOCCCN region due to its high sensitivity to isotopic effect (both deuteration and ^{15}N substitution). This band disappeared from the spectra of the ruthenium complexes and was replaced by a less intense band at around 1530 cm^{-1} owing to the coordination of the azomethine nitrogen, as well as the deprotonation and subsequent coordination of the phenolic oxygen.

This conclusion is furthermore indicated based on the shift of the phenolic ν(C−O) vibration to higher wavenumbers for ≈ 21 cm^{-1} in the spectra of the complexes (1272–1279 cm^{-1}) *versus* the spectra of free the ligands (1294–1300 cm^{-1}), and a regular decrease in band intensities following this increase in band wavenumbers. Additionally, the aniline ν(C−N) vibration of the free ligands found at around 1457 cm^{-1} decreased in intensity and shifted to lower wavenumbers for 20–24 cm^{-1} in the spectra of the complexes (1434–1437 cm^{-1}). The mentioned observations are consistent with substituted salicylidene anilines figuring as phenolate ligands.[24] Bands ascribed to stretching vibrations of the aromatic skeleton at around 1585 cm^{-1}, and the out-of-plane C−H bending vibration of ortho-substituted benzene rings at around 755 cm^{-1}, as well as the carbon halogen stretching vibrations (650 and 698 cm^{-1} for C−Br and C−Cl, respectively), remained almost identical between the spectra of the ligands and complexes. The infrared spectra of the complexes displayed increased complexity in the region below 600 cm^{-1}, most likely caused by new ruthenium-heteroatom bonds. The most interesting, new bands in both the complexes appeared at 531–537 cm^{-1} and 422–432 cm^{-1}, which may have arisen due to Ru−N and Ru−O stretching vibrations, respectively.[25]

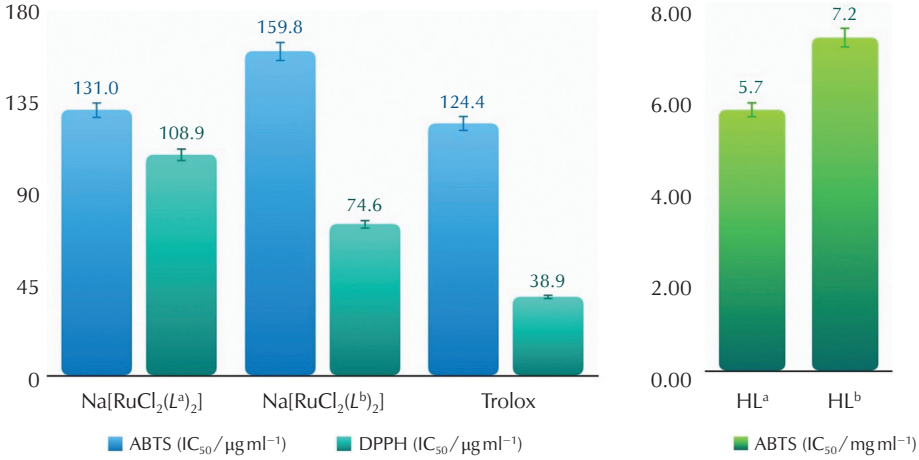


Fig. 6 – Antioxidant activity of the complexes and ligands in comparison to Trolox, determined using the ABTS and DPPH assays and expressed as IC_{50} values

Slika 6 – Antioksidativna aktivnost kompleksa i liganada u usporedbi s Troloxom, određena primjenom ABTS i DPPH testova i izražena kao IC_{50} vrijednosti

The electronic absorption spectra of the ligands and complexes were taken in DCM in the spectral range of 240–800 nm. Ligand-centred transitions ranged from 250 to 400 nm, and are attributable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the aromatic ring and the double bond of the azomethine group, the letter being affected by coordination to ruthenium. Broad bands of low-intensity peaking at 600 nm arose from spin-allowed d–d transitions of the t_{2g}^5 Ru(III) centre and can be denoted as $(^2t_{2g} \rightarrow {}^2A_{2g})$.[25]

The antioxidant activity of ligands and their transition metal complexes is most commonly determined using free radicals scavenging assays, metal chelating assays, and by evaluating their reducing power. There are numerous studies describing various ruthenium complexes as effective antioxidants.[9,11,26] In the present study, the antioxidant activity of the synthesised complexes and ligands was analysed using the ABTS and DPPH assay. The DPPH and ABTS free radicals can easily accept an electron or hydrogen to become stable diamagnetic molecules.[27] The obtained IC_{50} values revealed a high radical scavenging ability of both complexes, which closely resembled the antioxidant activity of Trolox. This is particularly well illustrated by the IC_{50} value of $Na[RuCl_2(L^a)_2]$ (131.00 μg ml^{-1}) in comparison to the standard antioxidant (124.35 μg ml^{-1}) in the ABTS assay. The ligands were found to be less effective as antioxidants with IC_{50} values in the mg ml^{-1} range. According to the ABTS assay, the IC_{50} values ranged between 5.67 mg ml^{-1} (HL^a) and 7.24 mg ml^{-1} (HL^b). The IC_{50} values in the DPPH assay were experimentally found to be above 8 mg ml^{-1}.

The results presented in Fig. 6 clearly suggest a strong antioxidant activity of the complexes and a low antioxidant activity of the ligands. Similar results were described by *Soh et al.*[9] who found the arene Ru(II) complexes to be more effective in the neutralisation of free radicals than their free ligands or even positive controls as in the case of azo-containing Schiff base Ru(II) complexes.[26] The better scavenging activity of the complexes may be due to chelation of the metal ions with the ligands; however, this cannot be considered a general rule. The biological activity of metal complexes depends on a number of factors, including the nature of the metal ion and its oxidation state, the type and number of chelated ligands and isomers present.[28,29]

In conclusion, the finding of this study is in line with several other studies of ruthenium complexes with different Schiff bases suggesting their strong antioxidant activities.[11,26,30] The synthesised complexes could be valuable candidates in future *in vitro* and *in vivo* research that would extend to their antimicrobial, antiproliferative, and other biological activities.

4 Conclusion

In the present study, we describe the synthesis of two Ru(III) complexes with Schiff base ligands derived from substituted anilines and salicylaldehyde. The synthesised complexes were characterised by FT-IR spectroscopy, UV/Vis spectrometry, and ESI ToF mass spectrometry, based on which we propose their structures to be sodium dichlorido-bis[(*N*-(3-bromophenyl)-2-oxy-κ*O*-benzilidenimine-κ*N*-(1-)]ruthenate(III) and sodium dichlorido-bis[(*N*-(4-chlorophenyl)-2-oxy-κ*O*-benzilidenimine-κ*N*-(1-)]ruthenate(III). The antioxidant activity was evaluated using the ABTS and DPPH assays, and the results clearly showed the radical scavenging ability of the complexes to be manifold stronger than those of ligands. The IC_{50} values showed that both complexes are comparable to Trolox in terms of scavenging the ABTS and DPPH free radicals. These compounds represent attractive candidates for further research of their biological properties and potential applications.

Popis kratica
List of abbreviations

ABTS – 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid
– 2,2′-azino-bis(3-etilbenzotiazolin-6-sulfonska kiselina

DPPH – 1,1-diphenyl-2-picrylhydrazyl
– 1,1-difenil-2-pikrilhidrazil

HL^a – *N*-4-Cl-phenylsalicylidenimine
– *N*-4-Cl-fenilsalicilidenimin

HL^b – *N*-3-Br-phenylsalicylidenimine
– *N*-3-Br- fenilsalicilidenimin

$Na[RuCl_2(L^a)_2]$ – sodium bis[*N*-4-Cl-phenylsalicyliden iminato-*N,O*]dichloridoruthenate(III)
– natrij bis[*N*-4-Cl-fenilsalicilideniminato-*N,O*] dikloridorutenat(III)

$Na[RuCl_2(L^b)_2]$ – sodium bis[*N*-3-Br-phenylsalicyliden iminato-*N,O*]dichloridoruthenate(III)
– natrij bis[*N*-3-Br-fenilsalicilideniminato-*N,O*] dikloridorutenat(III)

DCM – dichloromethane
– diklormetan

EtOH – ethanol
– etanol

IR – infrared
– infracrveno

ESI ToF – electrospray ionisation time-of-flight
– elektrosprej ionizacija vrijeme leta

MS – mass spectrometry
– spektormetrija masa

FT-IR – Fourier-transform infrared spectroscopy
– infracrvena spektroskopija s Fourierovom transformacijom

IC_{50} – half maximal inhibitory concentration
– koncentracija koja postiže 50 % inhibicije

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SAŽETAK

Ru(III) kompleksi i njihovi ligandi izvedeni iz salicilaldehida i halogeniranih anilina: sinteza, karakterizacija i antioksidativno djelovanje

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Ovaj rad je imao cilj opisati sintezu i karakterizaciju dvaju anionskih Ru(III) kompleksa općenite formule Na[$RuCl_2$(*N*-4-Cl-Ph-salim)$_2$] i Na[$RuCl_2$(*N*-3-Br-Ph-salim)$_2$, njihove pridružene ligande i odrediti njihovu antioksidacijsku aktivnost. Ligandi *N*-4-Cl-fenilsalicilidenimin (*N*-4-Cl-Ph-salimH, HL[a]) i *N*-3-Br-fenilsalicilidenimin (*N*-3-Br-Ph-salimH, HL[b]), Schiffove baze, sintetizirani su iz salicilaldehida i kloranilina ili bromoanilina. Spojevi su karakterizirani primjenom IR spektroskopije i ESI ToF spektrometrije masa. Potvrđena je koordinacija liganada na Ru(III) centru, molekulske formule i odgovarajući M^- ioni: $[C_{26}H_{18}N_2O_2Cl_4Ru]^-$ ion, (m/z: 631.9173) i $[C_{26}H_{18}N_2O_2Cl_2Br_2Ru]^-$ ion (m/z: 719.8283). Antioksidacijska aktivnost određena je metodama ABTS (2,2'-azino-bis(3-etilbenzotiazolin-6-sulfonska kiselina) i DPPH (1,1-difenil-2-pikrilhidrazil). Za razliku od liganda, oba kompleksa pokazala su se jakim hvatačima ABTS i DPPH radikala s IC_{50} vrijednostima (koncentracija koja postiže 50 % inhibicije) usporedivim s onima od Troloxa. Kao takvi, vrijedni su kandidati za daljnja istraživanja vezana uz njihova biološka svojstva.

Ključne riječi
Ru(III) kompleksi, Schiffove baze, IR spektroskopija, ESI ToF spektrometrija masa, antioksidativno djelovanje

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