Synthesis, Characterization and Antimicrobial Studies of Ruthenium(II) Carboxylates with 3-Hydroxypyridine

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Received: January 18, 2011   Accepted: February 10, 2011   doi:10.5539/ijc.v3n2p3

This research is financed by Bowen University, Iwo through award of Senate Research Grant

Abstract
Four new complexes, [Ru(O_2CCCH_3)_2(3-pyOH)_2]_2 (1), [Ru_2(O_2CCCH_3)_4(3-pyOH)_2]_2 (2), [Ru(O_2CC_6H_5)_2(3-pyOH)_2]_n (3) and [Ru(O_2(CH_2)_4CH_3)_2(3-pyOH)_2]_n (4) (where pyOH = hydroxypyridine) have been prepared by reacting 3-hydroxypyridine with ruthenium carboxylates. The complexes were characterized by IR spectra, elemental analyses, electronic absorption spectroscopy and single crystal X-ray crystallography. The X-ray diffraction study results revealed that the crystal structures of the complexes are triclinic, for 1; orthorhombic, for 2; and monoclinic, for both 3 and 4. Antimicrobial studies revealed that the four complexes are potential antimicrobial agents.

Keywords: 3-Hydroxypyridine, Ruthenium carboxylates, Distorted octahedral, Dimers, Antimicrobial

1. Introduction

Many metal ions carboxylates of both first and second roles of transition series have been complexed with different ligands (Bera et al, 2009, Anjani et al, 2006, Naceur et al, 2010 and Vishnu et al, 2006). Ligands with N-donor atom(s) have frequently been used to model the active site in metal proteins molecules with aim to obtain insight into the correlation between structures, the spectroscopic and magnetic behaviors (Pernark et al, 2002, Sheela et al, 2010, Carissa et al, 2003). Researchers have made efforts to design new synthetic routes for preparation of transition metal carboxylates with additional N-donor ligands (Sheela et al 2010, Sweetina et al, 2005).

Ligands with nitrogen bond and functionality could lead to the formation of useful inorganic materials with interesting physical properties. Synthesis of [Cu(O_2CCF_3)_2(3-pyOH)_2](THF)_2 in which two dimensional network linked by hydrogen bonds between the trifluoroacetate ligands and the (3-pyOH) has been reported recently (Hong-Ling et al, 2001). It was found that 3-pyOH ligands has two functions: capable of forming both metal-ligand and hydrogen bonds. This results in extended two-dimensional sheet structures also in [Cu(O_2CF_3)_2(3-pyOH)_2]_n. [Cu(ox)(3-pyOH)_2]_n has been reported to have be an extended one-dimensional complex (Hong-Ling et al, 2001).

Despite such interesting exhibitions, only few coordination compounds of M^{n+} carboxylates with 3-hydroxypyridine (3-pyOH) have been fully characterized so far.

Research to find platinum and iridium containing anti-cancer drugs is actively being pursued (Jens et al, 2010,
Tetrazine complexes of tin and zinc ions are known to have anti-fungical and anti tumor activities (Okabe et al, 2000, Motohashi et al, 2000). Some have been used in the treatments of fungi skin diseases, bladder and cervical tumors, ovarian and testicular cancers (Young-Jae et al, 2000, Violeta et al, 2010).

Unfortunately, their side effects are serious: cause of skin irritation, nausea and kidney damage (Anjani et al, 2006, Kovala et al, 1997 and Naceur et al, 2010). Therefore need for clinically active with fewer side-effect new compounds is being vigorously pursued.

Due to the increase number of immuno-compromised individuals, fungal infections have increase steadily in the last two decades, affecting millions of people worldwide (Vishunu et al, 2006). Opportunistic systemic mycoses are associated to high rates of deaths; and skin fungal infections, although not life threatening, debilitate patients’ quality of life, with additional danger that can spread to other areas of the body and other individuals (Motohashi et al, 2000, Jens et al, 2010). Although several drugs have been developed for the treatment of systemic an superficial mycoses, there are, in fact, a limited number of efficacious antifungal drugs. Many of the currently available drugs have undesirable side-effects or are very toxic, produce reoccurrence or lead to the development of resistance (Carissa et al, 2003, Okabe et al, 2000, Sweetina et al, 2005) As a consequence, there is a real need for a next generation of antifungal agents. Therefore need for clinically active with fewer side-effect new compounds is being vigorously pursued.

We present, in this work, synthesis, characterization and antibiocidal activities of ruthenium carboxylates complexed with 3-pyOH. It also includes our efforts to find new synthesis routes for preparation of transition metal carboxylates with additional N-donor ligands.

2. Experimental

2.1 Physico-chemical measurements

All chemicals used were analytical reagent grade purchased from Aldrich and used without further purification. Micro analytical data were obtained on a Perkin Elmer model 2400 elemental analyzer. IR spectra were obtained as KBr disks on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range of 400 - 4500 cm⁻¹. Electronic spectra were recorded in CH₂Cl₂ and MeOH solutions with a Spectronic, Genesys 2, spectrophotometer. Single crystal data were collected at room temperature on a Bruker Smart CCD diffractometer equipped with graphite monochromated Mo Kα radiation (λ: 0.71073 Å). Absorption corrections were performed using the multi scan method. SHELXL9712 were used for the structure resolution. The magnetic susceptibility data were determined for the power samples over the temperature range 200-300 K by using a SQUID magnetometer (QUANTUM DESING MODEL MPMS-XL5 instrument). All susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constant. EPR spectra were recorded on JEOL JES RE2X spectrometer using a rectangular cavity with a 50 KHz field modulation. Bacterial and fungal strains: Staphylococcus aureus, Bacillus cereus, Pseudomonas aeruginosa, Salmonella enteritidis, Escherichia coli, Klebsiella pneumonia, Agaricus bisporus, Agrocyte arvalis and Actinocorallia herbida used in this study are property of the Department of Biological Sciences, Bowen University, Iwo, Nigeria.

The standardized disc agar diffusion method was followed to determine the activities of the synthesised compounds against the sensitive organisms (Bera et al, 2009). Staphylococcus aureus, Bacillus cereus and Pseudomonas aeruginosa as Gram positive bacteria, Salmonella enteritidis, Escherichia coli and Klebsiella pneumonia as Gram negative bacteria and three species of fungi namely, Agaricus bisporus, Agrocyte arvalis and Actinocorallia herbida used in this study are property of the Department of Biological Sciences, Bowen University, Iwo, Nigeria.

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2.2 Preparation of complexes

2.2.1 [Ru(O2C(CH3)2)(3-pyOH)2] (1)

20 mL of 0.26 g of well filtered solution of [Ru(O2C(CH3)2CH3)(H2O)2], prepared in absolute ethanol was mixed with 13.00 mL of 2.26 g (0.22 mmol) of 3-hydroxypyridine in 6.5 mL absolute ethanol, stirred thoroughly, then heated gently on a hotplate to a temperature of 50 °C and kept at this temperature for 5 hrs.
The reaction mixed was then allowed to cool to room temperature and further cooled to 5°C in ice bath. The violet crystals precipitate was filtered off. Re-crystalized twice in n-heptane and then dried in desiccator over KOH for 3 days.

2.2.2 [Ru$_2$(O$_2$CCH$_3$)$_4$(3-py OH)$_2$]$_2$ (2)

1.20 g (3 mmol) of 35 mL of absolute ethanolic solution of Ru$_2$(O$_2$CCH$_3$)$_4$ were added to 0.56 g (5 mmol) of 3-py OH in 10 mL of absolute ethanol and then heated gently on a hotplate to a temperature of 55 ºC. The temperature was maintained for 17 hours. Allowed to cool to room temperature and then further cooled in a water bath to +8 ºC. The crystals formed were filtered off and re-crystalised twice in n-heptane.

2.2.3 [Ru(O$_2$CC$_6$H$_5$)$_2$(3-py OH)$_2$]n (3)

0.33 g (0.5mmol) of Ru(O$_2$CC$_6$H$_5$)$_2$ dissolved in 30 mL of hot CH$_3$CN was mixed with 0.58 g (7 mmol) of 3-pyOH dissolved in 15 mL of absolute ethanol. The mixture was thoroughly stirred and then placed on a hotplate with magnetic stirrer, heated for 2 hours. The violet plate-like crystals precipitated was filtered off while still hot, and then re-crystallised from n-heptane. The product was washed with very small portions of cold methanol and dried over KOH.

2.2.4 [Ru(O$_2$C(CH$_2$)$_4$CH$_3$)$_2$(3-pyOH)$_2$]n (4)

Hot 5.5 mL of 0.42 g (0.6 mmol) of Ru(O$_2$C(CH$_2$)$_4$CH$_3$)$_2$ dissolved in a hot mixture of 10 mL of CH$_3$OH and CH$_3$CN (1:1, v/v) were filtered into a solution of 0.22 g (1.1 mmol.) of 3-py OH in 4.0 mL of the same mixture of solvents., stirred thoroughly then placed on a hot plate with magnetic stirrer, heated and refluxed for 2 hrs. The resulting solution was allowed to cool to room temperature and stored in a refrigerator for 2 weeks.

The blue-violet crystals formed were then filtered off. The crystals were purified by recrystallisation with n-heptane. Then dried in desiccator over KOH for 5 days.

3. Results and Discussion

All reactions of 3-pyOH with metals ions are strongly dependent on the pH of the solution because it is an organic ampholyte which is acidic medium can attract easily a proton to its pyridine nitrogen atom, while in basic medium its O- hydrogen group can easily dissociate. The equation for the preparation of compound 1 is written below:

$$\text{Ru(O}_2\text{C(CH}_2\text{)}\text{CH}_3)_2\text{(H}_2\text{O)}_2\text{]} + \text{Ethanol, 50 ºC}$$

Table 1 shows the percentage yields, colour, melting points and other determined properties of the complexes prepared. The micro-elemental analyses, presented in Table 1 agree with the X-ray results.

Significant frequencies were selected by comparing the IR spectra of the free ligands and its metal complexes.

A strong band typical of C=C stretching frequency, $\nu$, are found in all the complexes in the region of 1632-1638 cm$^{-1}$ and 1622 cm$^{-1}$ in the free ligand. The observed shifts on the $\nu$(C=N) stretch regions after complexation indicate that they have been affected upon co-ordination to metal ion which also indicate the formation of Ru-N bonds whose IR stretching frequencies are all in the range of 602 - 608 cm$^{-1}$. The $\nu$(C=N) bond is shifts to a lower region in the complexes. This indicates that N must be involved in the coordination in the complexes. Additionally, the characteristic carbonyl stretching frequency observed in the IR spectra of the free ligand is shifted to around 1680 in all the complexes. The occurrence of new bands in the 738 - 748 cm$^{-1}$ region in the IR spectra of the metal complexes confirm the presence of Ru-N. The IR spectrum of the ligand shows broad bands at 3446 - 3553 cm$^{-1}$,
which are attributed to the phenolic OH group. These bands are not found in all the complexes. The absence of the O-H stretching bonding vibrations from the spectra of the complexes indicates deprotonation of the O-H group.

The υ(C=N) stretching band in the free ligand is observed at 1690 cm⁻¹. This band is shifted to lower 1678 - 1684 cm⁻¹ upon complexation suggesting coordination via the N atom of the pyridyl group. Other details are shown in Table 2.

The electronic absorption spectrum of each of the complexes recorded in EtOH and DMF solutions shows four bands at 211 – 234, 244 – 258, 262 – 294 and 368 – 415 nm which were attributed to the ϒ → π* and n → π* transitions. The uv spectra of the complexes also show other bands at 474 -483, 510 -522, 532 -539, 711 – 719, assignable to 4T1g → 6A1g, 4T2g (G) → 6A1g, 4T1g (D) → 6A1g and 5T2g → 5Eg transitions, respectively, which lie in the same range as reported for octahedrally coordinated Ru(II) ion. The uv spectra revealed a band of medium intensity at 528 -537 nm which is assigned to the transition 4T1g (F) → 4T1g (P)υ3. The band 320 -329 nm is assigned to the charge transfer transition (L-MCT).

The magnetic susceptibility values of the complexes which are all in the range 5.2 -5.7 B. M. point toward that they are paramagnetic and also evidence of high spin octahedral structures. The low values of the molar conductance data listed in Table 1 indicate that the complexes are non-electrolytes.

The ORTEP drawings of complexes 1 - 4 molecules are presented in Figures 1 to 4. The bond lengths and angles of complexes are presented in Table 5. Complexes 1 and 2 have similar structures at 150 K and room temperature (about 298 K). The unit cells are smaller at room temperature, as expected. There is contraction of contact distances which are less affected by changes in the geometrical parameters of the complex molecules. The asymmetric unit of 1 consists of two half-units of [Ru(O2C(CH2)7CH3)2(3-pyOH)2]. RuO2+ ion lies on inversion centre and is coordinated by two 3-pyOH ligands, trans coordinated through N atom and two a distances are 2.566 Å and 2.631 (2) Å and O32 … O31 i – Hi …O2b ii and O32- H … O2a ii angles 174(2) and 171(3) ° respectively, i: -x, -y + 1, -z+1; ii: -x, -y, -z. The Ru …Ru contact distance within the chain is 5.436(4) Å. The crystal packaging is also stabilizes by π …π and π …σ interactions among stacked heteroaromatic rings. Distance among ring centroids is 3. 686 (1) Å. Dihedral between planes of these rings is 0 ° and the angle between centroid vector and normal to ring plane is 24.9 °. The conformation of complex molecules of 2 is of a paddle-wheel type. The molecules are centrosymmetric dimmers with four syn-syn bridging acetonato and two apical 3-pyOH ligands coordinated through N atoms. The coordination polyhedron of Ru is slightly distorted square pyramid. The apical Ru-N distance 2.146(3) Å is significantly longer thanRu-O distances.

The Ru … Ru separation within a dimer is 2.646 (4) Å. Hydroxyl group is uncoordinated. It forms intermolecular hydrogen bond with O21 atom of symmetry related acetonato ligand linking the dimeric complex molecule in a two dimensional layer structure perpendicular to c edge. Compounds 3 and 4 contain 3-pyOH ligand and besides also benzonato of heptanato ligand which is larger in comparison with the acetonato ligand in 1 and 2. This is probably the reason that they have similar structures which differs completely from that of 1 or 2. In both structures, N and hydroxyl O atom form coordinated bond, resulting in a two-dimensional covalently bonded extended structure analogous to the trifluoroacetonato coordination compounds, with the same linkage pattern.15 Hydroxyl O atom in the two complexes forms additionally an intramolecular hydrogen bond with uncoordinated O atom of carboxylato ligand which has the consequence that also the coordination sphere is very similar. In the two cases, there is a distorted octahedral arrangement of bonded ligands. Detailed are contained in Tables 3 - 5.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC no. 7217563).

Antimicrobial activities of these complexes at different concentrations were tested on *Staphylococcus aureus, Bacillus cereus, Pseudomonas aeruginosa, Salmonella enteritidis, Escherichia coli, Klebsiella pneumonia, Agaricus bisporus, Agrocybe arvalis and Actinocorallia herbida*. After incubation for 48 h at 26 °C, in the case of bacteria and for 48 h at 24 °C, in the case of fungi, inhibition of the organisms was measured and used to calculate mean of inhibition zones. Activity index of all the synthesized compounds was also calculated against the corresponding standard drug (Table 6). The products showed various activities against all species of microorganisms, which suggest the variations in the structures affect on the growth of the microorganisms. Complex 2 is the most effective against gram-positive *S. aureus, B. cereus,* and *P. aerugiosa,* while complex 4 is the most effective against gram-negative *E. coli,* and *K. pneumonia.* Thus, we can conclude from these results: The prepared compounds have been fully characterised and they showed a moderate to high antimicrobial activity towards the species of bacteria and fungi. Therefore, these compounds may be considered promising for the development of new antimicrobial agents. However, there is still need for us to investigate their toxicity and selectivity to animals and human beings.
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Table 1. Physical properties and elemental analysis of the complexes

| Empirical formula | Yield (%) | M. Pt (˚C) | N   | C     | H     | µeff (B.M.) | λ m (Ω⁻¹ cm² Mol⁻¹) |
|-------------------|-----------|------------|-----|-------|-------|-------------|---------------------|
| [Ru(O₂CCH₃)₂(3-py-OH)₂] | 38.43 | 234 – 235 | 7.12 (7.05) | 43.40 (42.38) | 2.84 (2.78) | 5.6 | 8.46 |
| (377.15)          |          |            |     |       |       |             |                     |
| [Ru₂(O₂CCH₃)₂(3-py-OH)₂]₂ | 43.05 | 287 - 289 | 6.25 (6.27) | 36.86 (36.88) | 2.36 (2.37) | 5.2 | 9.22 |
| (1128.31)         |          |            |     |       |       |             |                     |
| [Ru(O₂CCH₆H₅)₂(3-pyOH)₂]n | 32.22 | 373-375 | 6.74 (6.72) | 39.56 (39.58) | 2.74 (2.73) | 5.7 | 7.78 |
| (477.13)          |          |            |     |       |       |             |                     |
| [Ru(O₂C(CH₂)₄CH₃)₂)(3-pyOH₂)] | 25.72 | 343-345 | 5.38 (5.37) | 43.21 (43.23) | 2.41 (2.39) | 5.3 | 6.37 |
| (489.12)n         |          |            |     |       |       |             |                     |

Table 2. Selected infrared band (cm⁻¹) of synthesized typical monomeric and polymeric ruthenium compounds

| Compd | υ(C – H) | υ(C-H₂, asy.) | υ(CH₂, sym.) | υ(C=C) ar, sym.) | υ(C– C, ar, sym.) | υ(C = O) | υ(Ru – O) | υ(Ru-N) | υ(C = N) |
|-------|----------|---------------|--------------|------------------|-------------------|----------|-----------|---------|----------|
| 3pyOH | 3102, m  | 2990, s       | 2902, s      | 1622, m          | 1472, s           | 1578, m  | -         | -       | 1690, s  |
| 1     | 2955, s  | 2920, s       | 2852, m      | 1606, m, 1514,s  | 1433, m           | 1560, m  | 795, s    | 746, m  | 1684, m  |
| 2     | 2962, s, 2913, s 2924, m | 2856,s | 1615, m 1524, s | 1428, s | 1564, s | 802, m | 730, s | 1680, s |
| 3     | 2954, m | 2919, s       | 2858,s       | 1600, m 1522, s | 1438, s           | 1558, m  | 796, s    | 738,s   | 1678, m  |
| 4     | 2955, m | 2922, s       | 2865, m      | 1608, m 1519, s | 1440, m           | 1557, m  | 796, m    | 736, s  | 1676, s  |
Table 3. Crystallographic data and structure refinements details of the complexes

| Complex | Empirical Formula       | Formula weight | Temperature (K) | Wavelength (Å) | Crystal system       | Space group          | Unit cell Dimensions | Refinement method | Data/restraints/parameters | Goodness-of-fit on F² |
|---------|-------------------------|----------------|-----------------|----------------|----------------------|----------------------|----------------------|----------------------|---------------------------|----------------------|
| 1       | RuC₂N₉H₁₉O₉             | 377.07         | 120(1)          | 0.73423        | Triclinic            | P-1                  | a (Å) 8.862 (2)       | F2                   | 1, 143/7/138            | 1.065                  |
| 2       | Ru₃C₁₈N₁₂H₂₂O₁₈          | 1128.31        | 120(1)          | 14.9983 (2)    | orthorhombic         | Pca2₁               | b (Å) 14.9983 (2)     | F2                   | 1, 237/6/163            | 1.170                  |
| 3       | [RuC₂₂N₁₂H₂₀O₆]ₙ        | [477.13]n      | 120(1)          | 9.74827        | monoclinic           | P 2₁/n               | c (Å) 23.040 (1)      | F²                   | 1, 156/7/172            | 1.085                  |
| 4       | RuC₂₂N₁₃H₃₂O₆[       | [489.12]n      | 120(1)          | 10.684 (2)     | monoclinic           | P 2₁/n               | α 90.00 (1)           | F²                   | 1, 145/7/149            | 1.028                  |

Z 2 8 2 2
ρ (calculated) gcm⁻³ 1.256 1.756 1.476 1.486
Absorption coefficient (mm⁻¹) 1.053 1.067 1.305 1.285
F(000) 348 359 360 339
Crystal size (mm) 0.5 x 0.1 x 0.5 0.5 x 0.1 x 0.5 0.5 x 0.1 x 0.5 0.5 x 0.1 x 0.5
Reflection collected/unique 18636/10831 19488/13126 17495/18321 19432/16932

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Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for 1, [Ru(O₂CCH₃)₂(3-pyOH)₂]

| Atom       | X       | Y       | Z       | U(eq)’  |
|------------|---------|---------|---------|---------|
| Ru         | 7746(1) | 5667(1) | 5319(1) | 18(1)   |
| O (1a)     | 6458(2) | 4721(1) | 5690(1) | 17(1)   |
| O (1b)     | 5532(2) | 3489(1) | 5563(1) | 17(1)   |
| O (2a)     | 1423(2) | 2427(2) | 7453(1) | 24(1)   |
| O (2a’)    | 1216(3) | 1211(2) | 7532(1) | 22(1)   |
| O (2b)     | 6542(3) | 7217(2) | 7564(1) | 23(1)   |
| C (1b)     | 6747(3) | 3876(2) | 5991(2) | 16(1)   |
| C (2a)     | 7668(4) | 3164(2) | 6512(2) | 16(1)   |
| C (21)     | 9444(4) | 3309(2) | 6718(2) | 17(1)   |
| C (22)     | 10275(4)| 2578(2) | 7140(2) | 19(1)   |
| C (31)     | 9430(4) | 1718(2) | 7369(2) | 20(1)   |
| C (52)     | 7528(4) | 3309(2) | 6718(2) | 17(1)   |
| C (62)     | 6707(4) | 2308(2) | 6751(2) | 19(1)   |
| O (1a)     | 5268(2) | 6342(1) | 6176(1) | 17(1)   |
| O (2a)     | 2932(2) | 5191(2) | 6036(1) | 16(1)   |
| O (2a’)    | 4863(2) | 8461(2) | 9142(1) | 23(1)   |

U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor, X, Y, and Z are fractional atomic coordinates.

Table 5. Selected bond lengths (Å) and bond angles (°) for complexes 1-4

| Complex 1 | Bond Lengths          | Bond Angles            |
|-----------|-----------------------|------------------------|
| Ru-O(1a)  | 1.527 (16)            | O(1a)-Ru1-N(11)        | 89.96 (5)               |
| Ru2-O(1b) | 1.863 (5)             | O(1a)-Ru1-O(2a)        | 56.374 (3)              |
| Ru1-N(11) | 2.0333 (1)            | O(1b)-Ru2-N(12)        | 88.98(6)                |
| Ru2-N(12) | 1.968(3)              | O(1b)-Ru2-O2b(11)      | 90.23 (3)               |
| Ru1-O(2a) | 2.613 (3)             | O(2a)-Ru1-O2b         | 90.15 (3)               |
| Ru2-O2b   | 2.5962 (2)            | O(2b)-Ru-N12          | 87.03 (3)               |

| Complex 2 | Bond Lengths          | Bond Angles            |
|-----------|-----------------------|------------------------|
| Ru-O11    | 1.874(2)              | O11-Ru-O21i            | 168.47(4)               |
| Ru-O12    | 1.968(2)              | O11-Ru-O22i            | 89.45(5)                |
| Ru-O21i   | 1.996(4)              | O11-Ru-O12             | 89.66(6)                |
| Ru-O22    | 1.978(2)              | O11-Ru-O12             | 96.96(6)                |
| Ru-N1     | 2.231(3)              | O21-Ru-O12             | 90.58(3)                |
| O12-Ru-N1 | 96.47(5)              | O21-Ru-O22i            | 88.13(6)                |

| Complex 3 | Bond Lengths          | Bond Angles            |
|-----------|-----------------------|------------------------|
| Ru-N11    | 2.130(3)              | N11-Ru-O31iv           | 84.39(6)                |
| Ru-N12    | 2.014(2)              | N11-Ru-O31iv           | 177.87(6)               |
| Ru-O13    | 1.893(2)              | N11-Ru-O32iv           | 98.04(8)                |
| Ru-O14    | 1.956(6)              | N11-Ru-O13             | 89.56(6)                |
| Ru-O31iv  | 2.656(7)              | N11-Ru-O14             | 87.66(7)                |
| O31iv-Ru-O14 | 86.875(6)            | N12-Ru-O13             | 90.67(6)                |
| O32iv-Ru-O13 | 84.700(6)            | N12-Cu-O14             | 91.22(6)                |
| O32ii-Ru-O14 | 95.83(6)            | O31ii-Ru-N12           | 94.98(5)                |

| Complex 4 | Bond Lengths          | Bond Angles            |
|-----------|-----------------------|------------------------|
| Ru-N1     | 2.070(3)              | N1-Ru-O11              | 89.4(4)                 |
| Ru-O3iv   | 2.601(4)              | N1-Ru-O3iv             | 96.03(6)                |
| Ru-O11    | 1.943(6)              | O3iv-Ru-O11            | 88.23(2)                |

Symmetry transformation used to generate equivalent atoms: (i) –x, 1 – y, - z.
Table 6. Antimicrobial activities of the complexes at 1.50 mg L\(^{-1}\)

| Complex No. | Gram positive bacteria | Gram negative bacteria | Fungal strains |
|-------------|------------------------|------------------------|----------------|
|             | \(S.\) aureus | \(B.\) cereus | \(P.\) aeruginosa, \(S.\) enteritidis | \(E.\) coli | \(K.\) pneumonia | \(A.\) bisporus | \(A.\) arvalis | \(A.\) herbida |
| 1           | 15 (0.37) | 12 (0.28) | 13 (0.83) | 7 (0.47) | 9 (0.78) | 8 (0.67) | 8 (0.73) | 10 (0.73) | 12 (0.33) |
| 2           | 24 (0.66) | 19 (0.64) | 22 (0.67) | 17 (0.61) | 4 (0.33) | 6 (0.52) | 12 (0.62) | 14 (0.84) | 9 (0.69) |
| 3           | 6 (0.58)  | 7 (0.56)  | 10 (0.62) | 8 (0.72) | 11 (0.53) | 9 (0.41) | 7 (0.38) | 15 (0.66) | 13 (0.74) |
| 4           | 8 (0.52)  | 11 (0.58) | 11 (0.22) | 7 (0.94) | 13 (0.41) | 10 (0.84) | 9 (0.24) | 13 (0.32) | 13 (0.31) |

Cephalothin | 27 | 30 | 28 | - | - | - | - | - |
Chloramphenicol | - | - | - | 25 | 29 | 30 | - | - |
Cycloheximide | - | - | - | 27 | 29 | 30 | - | - |

\(a\)Calculated from 3 values; \(b\)Identified depending on morphological and microscopical characteristics. Low activity = mean of zone diameter \(\leq 0.33\) of mean zone diameter of reference. Moderate activity = mean of zone diameter \(0.33 \leq 0.66\) of the reference compound. High activity = mean of zone diameter \(\geq 0.67\) of the mean zone diameter of the reference compound; \(c\) Activity index: inhibition zone of the sample / inhibition zone of the reference compound.

Figure 1. Crystal structure of the monomeric complex molecule of \([\text{Ru}(O\text{CCH}_3)_2(\text{py-OH})_2]\),1, with labelling of nonhydrogen atoms of asymmetrical unit.
Figure 2. Crystal structure of dimeric molecule of [Ru₂(OC₆H₄)₂(3-py-OH)]₂ with labelling of the non-hydrogen atoms of asymmetrical unit

Figure 3. A view of the complex [Ru₂(OCC₆H₅)₂(3-py-OH)]₆
Figure 4. Crystal structure of complex molecule of [Ru(O2)CCH3(CH2)4]2(3-pyOH)2].