

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

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Abstract

Four new complexes, $[\text{Ru}(\text{O}_2\text{CCH}_3)_2(3\text{-pyOH})_2]$ (1), $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(3\text{-pyOH})_2]$ (2), $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_5)_2(3\text{-pyOH})_2]_n$ (3) and $[\text{Ru}(\text{O}_2(\text{CH}_2)_4\text{CH}_3)_2(3\text{-pyOH})_2]_n$ (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 rows 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*, 200, 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 $[\text{Cu}(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2](\text{THF})_2$ 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 $[\text{Cu}(\text{O}_2(\text{CF}_3)_2(3\text{-pyOH})_2)]_n$. $[\text{Cu}(\text{ox})(3\text{-pyOH})_2]_n$ 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,

Na-Xu *et al*, 2008, Antony *et al*, 1992, Ljerka *et al*, 2003, Antonio *et al*, 2001).

Tetrazine complexes of tin and zinc ions are known to have anti-fungicidal 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 systematic 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 antibioidal 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 CH_2Cl_2 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 $\text{K}\alpha$ 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*. The antibiotic, chloramphenicol was used as reference in the case of Gram negative bacteria, while cephalothin as used in the case of Gram positive bacteria and cycloheximide was used as antifungal reference. The compounds were dissolved in DMF which has no inhibition activity to get concentration of 1.50 mg mL^{-1} . The test was performed on medium potato dextrose agars which contain infusion of 200 g potatoes, 6 g dextrose and 15 g agar. Uniform size filter paper disks were impregnated with equal volume (10 μL) from specific concentration of dissolved tested compounds and carefully placed on inoculated agar surface. These were incubated for 48 h at 26 °C in the case of bacteria and for 48 h at 24 °C in the case of fungi.

2.2 Preparation of complexes

2.2.1 $[\text{Ru}(\text{O}_2\text{CCH}_3)_2(3\text{-pyOH})_2]$ (1)

20 mL of 0.26 g of well filtered solution of $[\text{Ru}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}_3)_4(\text{H}_2\text{O})_2]$, 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 mixture 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-crystallized twice in n-heptane and then dried in desiccator over KOH for 3 days.

2.2.2 $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(3\text{-py OH})_2]_2$ (**2**)

1.20 g (3 mmol) of 35 mL of absolute ethanolic solution of $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4$ 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 °C. The temperature was maintained for 17 hours. Allowed to cool to room temperature and then further cooled in a water bath to +8 °C. The crystals formed were filtered off and re-crystallised twice in n-heptane.

2.2.3 $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_5)_2(3\text{-py OH})_2]_n$ (**3**)

0.33g (0.5mmol) of $\text{Ru}(\text{O}_2\text{CC}_6\text{H}_5)_2$ dissolved in 30 mL of hot CH_3CN was mixed with 0.58g (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 $[\text{Ru}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CH}_3)_2(3\text{-pyOH})_2]_n$ (**4**)

Hot 5.5 mL of 0.42 g (0.6 mmol) of $\text{Ru}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CH}_3)_2$ dissolved in a hot mixture of 10 mL of CH_3OH and CH_3CN (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 in 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:

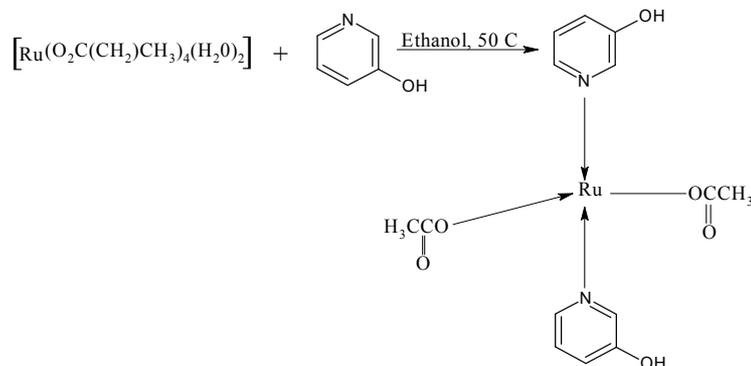


Table 1 shows the percentage yields, colour, melting points and other determined properties of the complexes prepared. The micro-elemental analyses, presented in Table 1 agree with the X-ray results.

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, ν , 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 $\nu(\text{C}=\text{N})$ 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 $\nu(\text{C}=\text{N})$ bond is shifted 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 $\nu(\text{C}=\text{N})$ stretching band in the free ligand is observed at 1690 cm^{-1} . This band is shifted to lower $1678 - 1684\text{ cm}^{-1}$ 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 $368 - 415\text{ nm}$ which were attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The uv spectra of the complexes also show other bands at $474 - 483$, $510 - 522$, $532 - 539$, $711 - 719$, assignable to $4T_{1g} \rightarrow 6A_{1g}$, $4T_{2g}(\text{G}) \rightarrow 6A_{1g}$, $4T_{1g}(\text{D}) \rightarrow 6A_{1g}$ and $5T_{2g} \rightarrow 5E_g$ 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 $528 - 537\text{ nm}$ which is assigned to the transition $4T_{1g}(\text{F}) \rightarrow 4T_{1g}(\text{P})\nu_3$. The band $320 - 329\text{ nm}$ is assigned to the charge transfer transition (L-MCT).

The magnetic susceptibility values of the complexes which are all in the range $5.2 - 5.7\text{ B. M.}$ 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 $[\text{Ru}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}_3)_2(3\text{-pyOH})_2]$. Ru^{2+} ion lies on inversion centre and is coordinated by two 3-pyOH ligands, trans coordinated through N atom and two a distances are $2.566(3)$ and $2.631(2)\text{ \AA}$ and $\text{O}32 \dots \text{O}31^i - \text{H}^i \dots \text{O}2b^{ii}$ and $\text{O}32 - \text{H} \dots \text{O}2a^i$ angles $174(2)$ and $171(3)^\circ$ respectively, i: $-x, -y + 1, -z + 1$; ii: $-x, -y, -z$. The $\text{Ru} \dots \text{Ru}$ contact distance within the chain is $5.436(4)\text{ \AA}$. The crystal packaging is also stabilizes by $\pi \dots \pi$ and $\pi \dots \sigma$ interactions among stacked heteroaromatic rings. Distance among ring centroids is $3.686(1)\text{ \AA}$. 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 $2.146(3)\text{ \AA}$ is significantly longer than Ru-O distances.

The $\text{Ru} \dots \text{Ru}$ separation within a dimer is $2.646(4)\text{ \AA}$. 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 aceonato 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 trifluoroacetato 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*, *Agrocyte 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. aeruginosa*, 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 (formula weight)	Colour	Yield (%)	M. Pt (°C)	Analysis % found (calculated)			μ_{eff} (B.M.)	λ_m (Ω^{-1}) $\text{cm}^2 \text{Mol}^{-1}$
				N	C	H		
[Ru(O ₂ CCH ₃) ₂ (3-py-OH) ₂] (377.15)	Green	38.43	234 – 235	7.12 (7.05)	43.40 (42.38)	2.84 (2.78)	5.6	8.46
[Ru ₂ (O ₂ CCH ₃) ₂ (3-py-OH) ₂] ₂ (1128.31)	Green	43.05	287 -289	6.25 (6.27)	36.86 (36.88)	2.36 (2.37)	5.2	9.22
[Ru(O ₂ CC ₆ H ₅) ₂ (3-pyOH) ₂] _n (477.13)n	Grenish-yellow	32.22	373-375	6.74 (6.72)	39.56 (39.58)	2.74 (2.73)	5.7	7.78
[Ru(O ₂ C(CH ₂) ₄ CH ₃) ₂ (3-pyOH) ₂] _n (489.12)n	Yellowish	25.72	343-345	5.38 (5.37)	43.21 (43.23)	2.41 (2.39)	5.3	6.37

Table 2. Selected infrared band (cm^{-1}) of synthesized typical monomeric and polymeric ruthenium compounds

Compd	$\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{H}_2, \text{asy.})$	$\nu(\text{CH}_2, \text{sym.})$	$\nu \text{C}=\text{C}$ ar, sym)	$\nu(\text{C}-\text{C}, \text{ar, sym.})$	$\nu(\text{C}=\text{O})$	$\nu(\text{Ru}-\text{O})$	$\nu(\text{Ru}-\text{N})$	$\nu(\text{C}=\text{N})$
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, s 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, s	796, m	736, s	1676, s

Table 3. Crystallographic data and structure refinements details of the complexes

	Complex 1	Complex 2	Complex 3	Complex 4
Empirical Formula	RuC ₉ NH ₉ O ₉	Ru ₂ C ₁₈ N ₂ H ₂₂ O ₁₈	[RuC ₂₂ N ₂ H ₂₀ O ₆] _n	RuC ₂₂ N ₂ H ₃₂ O ₆] _n
Formula weight	377.07	1128.31	[477.13] _n	[489.12] _n
Temperature (K)	120(1)	120(1)	120(1)	120(1)
Wavelength (Å)	0.73423	0.63828	0.74827	0.70428
Crystal system	Triclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell Dimensions				
<i>a</i> (Å)	8.862 (2)	8.474 (2)	9.765 (2)	10.684 (2)
<i>b</i> (Å)	9.9983 (2)	14.9983 (2)	9.9983 (2)	9.9983 (2)
<i>c</i> (Å)	10.0634 (2)	23.040 (1)	10.8360 (2)	10.0481 (2)
α	99.264(1)°	90.00(1)°	90.00(1)°	90.00(1)°
β	92.245 (1)°	90.00(1)°	90.00 (1)°	90.00 (1)°
γ	114.623 (4)°	90.00 (1)°	104.682 (1)°	100.415 (1)°
Vol., (Å ³)	793.35 (2)	853.35 (2)	883.35 (2)	863.35 (2)
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
Refinement method	F ²	F ²	F ²	F ²
Data/restraints/parameters	1, 143/7/138	1, 237/6/163	1, 156/7/172	1, 145/7/149
Goodness-of-fit on F ²	1.065	1.170	1.085	1.028

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)^p for **1**, [Ru(O₂CCH₃)₂ (3-pyOH)₂]

Atom	X	Y	Z	U(eq) ^y
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)
O (2b)	4212(1)	7123(2)	7821 (1)	15 (1)

^pU (eq) is define as one third of the trace of the orthogonalized U_{ij} tensor, X,Y, and Z are fractional atomic coordinates

Table 5. ^kSelected bond lengths (\AA) and bond angles ($^\circ$) for complexes **1- 4**

Complex 1			
Ru 1- 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			
Ru-O11	1.874(2)	O11- Ru-O 21 ⁱ	168.47(4)
Ru-O12	1.968(2)	O11-Ru-O22 ⁱ	89.45(5)
Ru-O21 ⁱ	1.996(4)	O11-Ru-O12	89.66(6)
Ru-O22	1.978(2)	O-11-Ru-N1	96.96(6)
Ru-Ni	2.231(3)	O21 ⁱ -Ru-O12	90.58(3)
O12-Ru-N1	96.47(5)	O21 ⁱ -Ru-22 ⁱ	88.13(6)
Complex 3			
Ru-N11	2.130(3)	N11-Ru-O31 ⁱⁱ	84.39(6)
Ru-N12	2.014(2)	N11-Ru-N12	177.87(6)
Ru-O13	1.893(2)	N11-Ru-O32 ⁱⁱⁱ	98.04(8)
Ru-O14	1.956(6)	N11-Ru-O13	89.56(6)
Ru-O31 ⁱⁱ	2.656(7)	N11-Ru-O14	87.66(7)
O31 ⁱⁱ -Ru-O14	86.875(6)	N12-Ru-O13	90.67(6)
O32 ⁱⁱ -Ru-O13	84.700(6)	N12-Cu-O14	91.22(6)
O32 ⁱⁱⁱ -Ru-O14	95.83(6)	O31 ⁱⁱ -Ru-N12	94.98(5)
Complex 4			
Ru-N1	2.070(3)	N1-Ru-O11	89.4(4)
Ru-O3 ^{iv}	2.601(4)	N1-Ru-O3 ^{iv}	96.03(6)
Ru-O11	1.943(6)	O3 ^{iv} -Ru-O11	88.23(2)

^kSymmetry 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.	Diameter of the inhibition zone in mm ^{a,b} (activity index) ^c								
	Gram positive bacteria			Gram negative bacteria			Fungal strains		
	<i>S. aureus</i>	<i>B. cereus</i>	<i>P. aeruginosa</i>	<i>S. enteritidis</i>	<i>E. coli</i>	<i>K. pneumonia</i>	<i>A. bisporus</i>	<i>A. arvalis</i>	<i>A. herbida</i>
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

^aCalculated from 3 values; ^bIdentified depending on morphological and microscopical characteristics. Low activity = mean of zone diameter ≤ 0.33 of mean zone diameter of reference. Moderate activity = mean of zone diameter $\square 0.33 \leq 0.66$ of the reference compound. High activity = mean of zone diameter ≥ 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.

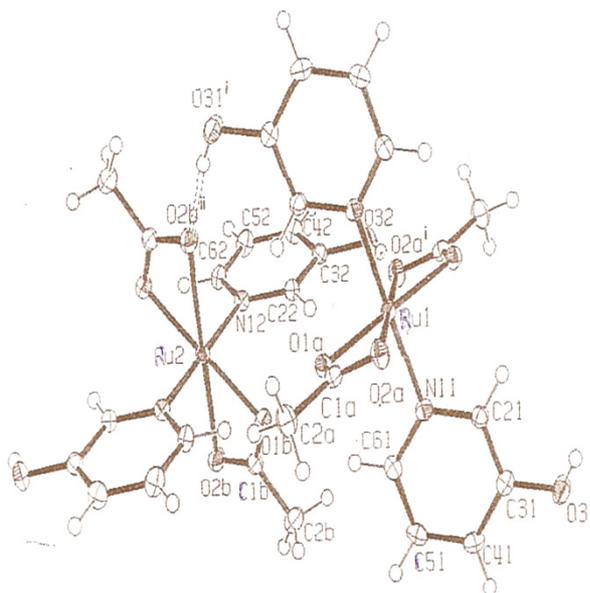


Figure 1. Crystal structure of the monomeric complex molecule of [Ru(O₂CCH₃)₂(py-OH)₂], 1, with labelling of nonhydrogen atoms of asymmetrical unit

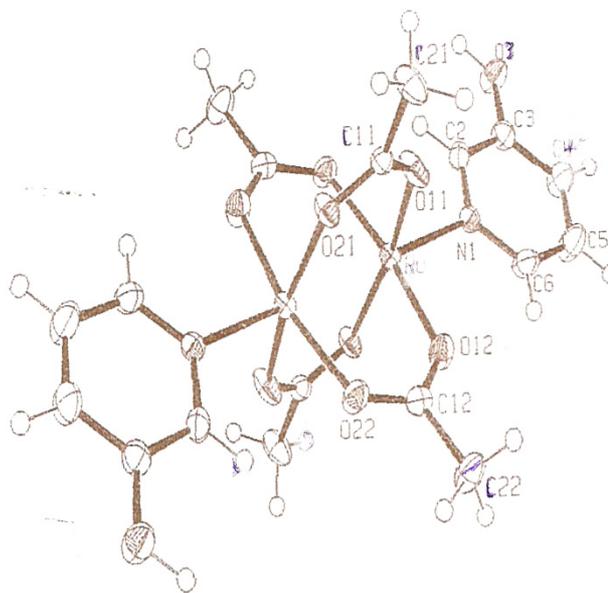


Figure 2. Crystal structure of dimeric molecule of $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(3\text{-py-OH})_2]_2$ with labelling of the non-hydrogen atoms of asymmetrical unit

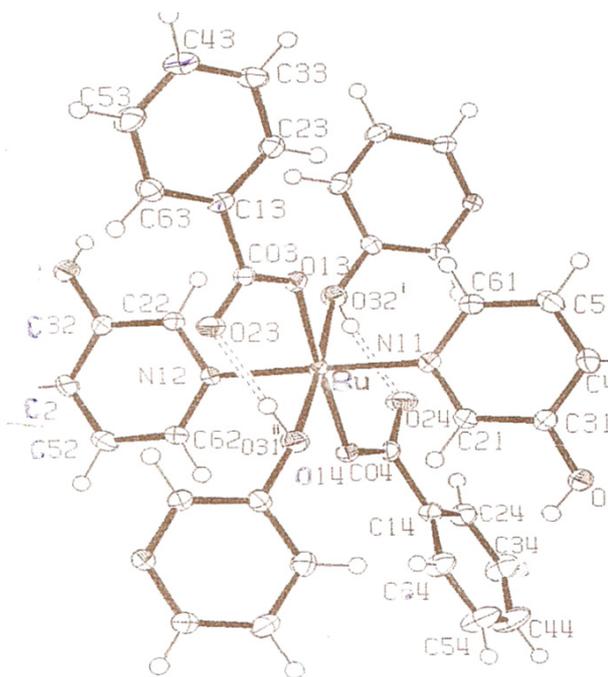


Figure 3. A view of the complex $[\text{Ru}_2(\text{O}_2\text{CC}_6\text{H}_5)_2(3\text{-py-OH})]_n$

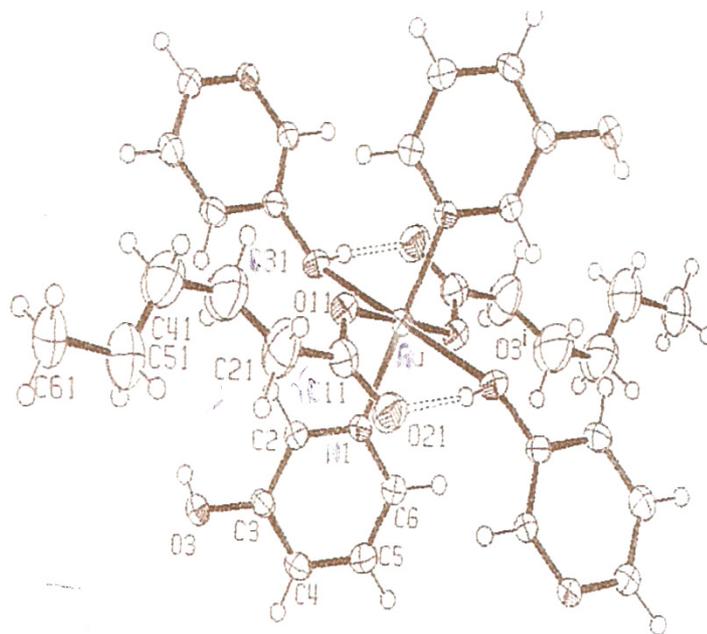


Figure 4. Crystal structure of complex molecule of $[\text{Ru}(\text{O}_2)\text{CCH}_3(\text{CH}_2)_4)_2(3\text{-pyOH})_2]_n$, **4**