PERGAMON

Polyhedron 20 (2001) 975–980

POLYHEDRON

www.elsevier.nl/locate/poly

A new route for the synthesis of bis(pyridine dicarboxylato)bis(triphenylphosphine) complexes of ruthenium(II) and X-ray structural characterisation of the biologically active *trans*-$[Ru(PPh_3)_2(L^1H)_2]$ (L^1H_2 = pyridine 2,3-dicarboxylic acid)

Parbati Sengupta [a], Saktiprosad Ghosh [a,*], Thomas C.W. Mak [b]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India*
[b] *Department of Chemistry, Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China*

Received 28 September 2000; accepted 31 January 2001

Abstract

Ruthenium(II) complexes of the general formula $Ru(LH)_2(PPh_3)_2$, (LH_2 = pyridine 2,3-; 2,4-; 2,5- and 2,6-dicarboxylic acid) are synthesised by a new method. All the pyridine dicarboxylic acids are found to behave as bidentate, monobasic chelating donors, with one carboxyl group remaining idle. The electrochemical behaviour of the compounds is explored with the help of cyclic voltammetry. The antibacterial activities of these compounds were examined against *Escherichia coli* in nutrient broth in order to check their potential for antitumour activity. Single-crystal X-ray analysis of the complex involving pyridine 2,3-dicarboxylic acid (L^1H_2) revealed that the coordination environment consists of a centrosymmetric, axially elongated $N_2P_2O_2$ octahedron with a pair of coordinated L^1H ligands occupying the equatorial plane.

Keywords: Ruthenium complexes; Pyridine dicarboxylic acids; X-ray structures; Antibacterial activity

1. Introduction

Pyridine-2,6-dicarboxylic acid or dipicolinic acid ($DPAH_2$) forms stable chelates with simple metal ions and oxometal cations [1–6] and can display widely varying coordination demeanour, functioning as a bidentate [7–10], tridentate [11–13], meridian [14,15] or bridging ligand [16]. Along with picolinic acid, dipicolinic acid can stabilise unfamiliar oxidation states [17,18] and is found to be useful in corrosion inhibition [19] and decontamination of nuclear reactors [20]. The other isomeric pyridine dicarboxylic acids like pyridine 2,3-, 2,4- and 2,5- dicarboxylic acids behave like picolinic acid and act as chelating bidentate N–O donors, the second carboxyl group remaining idle.

A very important characteristic of these ligands is their diverse biological activity [21,22]. Dipicolinic acid, along with its 2,4- and 2,5-isomers, is found to inhibit the enzyme GA 2β-hydroxylase and its mechanistically related enzyme proline 4-hydroxylase [23]. Dipicolinic acid complexes of iron are found to play the role of electron carriers in some model biological systems [24–26] and are recognised as specific molecular tools in DNA cleavage [27]. The heat resistance property of the spores of several gram-positive eubacteria during sporulation is attributed to the presence of the calcium salt of DPA [28].

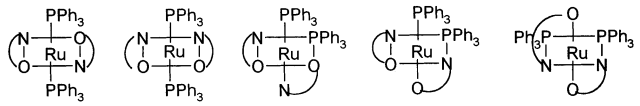
Ru(III) complexes with the proposed formulae $Na[Ru(DPA)_2]\cdot 2H_2O$ and [Ru(DPA)(L)] (LH = picolinic acid, nicotinic acid, isonicotinic acid, glycine, orthoamino phenol) have been reported [10], but none of them has its strucuture uneqivocally established. Moreover, no report on Ru(II) complexes of the other pyridine dicarboxylic acids is available till now. The present work describes the synthesis of ruthenium(II) complexes of the general formula $Ru(LH)_2(PPh_3)_2$ (LH_2 = pyridine-2,3-, 2,4-, 2,5- and 2,6-dicarboxylic acids). They were characterised by elemental analysis, spectro-

* Corresponding author. Tel: +91-33-4734971, ext. 3372; fax: +91-33-4732805.
E-mail address: icspg@mahendra.iacs.res.in (S. Ghosh).

0277-5387/01/$ - see front matter
PII: S0277-5387(01)00736-7

scopic techniques (UV–Vis, IR, NMR), measurement of magnetic susceptibility at room temperature and conductance in solution. Their chemical reactivity and electrochemical behaviour were also explored. The molecular structure of $Ru(L^1H)_2(PPh_3)_2$ (L^1H_2 = pyridine 2,3-dicarboxylic acid) was determined by single-crystal X-ray crystallography.

As all four pyridine dicarboxylic acids (2,3-, 2,4-, 2,5- and 2,6- designated as L^1H_2, L^2H_2, L^3H_2, L^4H_2, respectively) behave as a bidentate chelating N–O donor like picolinic acid, an octahedral complex of the general formula $[Ru(LH)_2(PPh_3)_2]$ (where LH_2 = a pyridine dicarboxylic acid) can exist in five geometrical isomers **I**–**V** shown below.



(I)	(II)	(III)	(IV)	(V)
P-P *trans*	P-P *trans*	P-P *cis*	P-P *cis*	P-P *cis*
O-O *trans*	N-O *trans*	N-O *trans*	N-N *trans*	O-O *trans*
N-N *trans*	N-O *trans*	P-O *trans*	P-O *trans*	P-N *trans*
		P-N *trans*	P-O *trans*	P-N *trans*

In order to identify the actual form in which the complex $[Ru(LH)_2(PPh_3)_2]$ exists, we tried to prepare good single crystals of all the four complexes but succeeded only in the case of the pyridine 2,3-dicarboxylic acid complex. X-ray crystallography enabled us to establish that the isomer **I** was produced in the synthetic procedure adopted in this study. ^{31}P NMR spectra of this complex exhibit only one signal at δ 45.5 ppm. The spectra of the other $[Ru(LH)_2(PPh_3)_2]$ complexes also exhibit a similar characteristic feature (single signal $\delta \sim 45.5$ ppm) that is consistent with the *trans* disposition of the two triphenylphosphines groups. However, whether each of them exists as the form **I** or **II** cannot be ascertained in the absence of X-ray structural data for the other complexes. We have explored various methods to prepare good single crystals of these three complexes, but so far success has eluded us.

2. Experimental

2.1. Materials

Commercial ruthenium trichloride, $RuCl_3 \cdot xH_2O$, purchased from Arora Matthey (Calcutta, India) was processed by repeated evaporation to dryness with conc. HCl. $Ru(PPh_3)_3Cl_2$ was prepared using a previously published procedure [29]. All four pyridine dicarboxylic acids (pyridine 2,3-, 2,4-, 2,5- and 2,6-dicarboxylic acids) used as ligands were purchased from Aldrich, and $AgNO_3$ from BDH. All other chemicals were of reagent grade and used without further purification. Tetraethylammonium perchlorate (TEAP) used for electrochemical work was prepared as reported in the literature [30].

2.2. Physical measurements

Elemental analyses were performed with a Perkin–Elmer 240 CHNS/O analyser. IR and electronic spectra were recorded on a Perkin–Elmer 783 spectrophotometer (as KBr pellets) and on a Shimadzu UV–Vis recording spectrophotometer, respectively. Solution conductance was measured on a Systronics direct reading conductivity meter (Model 304) and magnetic susceptibility was measured with a PAR vibrating sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. Electrochemical data were collected with a BAS CV-27 electrochemical analyser and a BAS Model *X*–*Y* recorder at 298 K. Cyclic voltammetry experiments were carried out with a platinum working electrode, platinum auxiliary electrode and Ag | AgCl reference electrode. The ^1H NMR spectra was recorded with a Bruker 300-MHz NMR spectrometer relative to $SiMe_4$, and ^{31}P NMR with a UNITY-400 NMR spectrometer relative to external 85% H_3PO_4 using $(CD_3)_2SO$ as solvent.

2.3. Synthesis of complexes

2.3.1. $Ru(PPh_3)_2(L^1H)_2$ (1) (L^1H_2 = pyridine 2,3-dicarboxylic acid)

Preparation of Ag-salt of pyridine 2,3-dicarboxylic acid. Pyridine 2,3-dicarboxylic acid (167 mg, 1 mmol) was dissolved in hot water and solid $NaHCO_3$ added to it pinch by pinch until the pH of the solution is ~ 5. An aqueous solution of $AgNO_3$ (169 mg, 1 mmol) was added to it and stirred for about 3 h. The silver salt was separated out, filtered and washed with water. It was dried in vacuum.

To the methanolic (60 ml) suspension of the Ag-salt of pyridine 2,3-dicarboxylic acid, $Ru(PPh_3)_3Cl_2$ (960 mg, 1 mmol) was added and the reaction mixture was refluxed for 6 h and filtered hot. The AgCl residue was rejected. The resultant deep violet solution deposited shiny blue crystals of **1** on standing, which were filtered washed with a little benzene and then with methanol and dried in vacuum over fused $CaCl_2$. Yield: 82%. *Anal.* Found: C, 62.4; H, 4.02; N, 2.81. Calc. for $RuC_{50}H_{38}N_2P_2O_8$: C, 62.6; H, 3.96; N, 2.92%. IR (KBr pellet, cm^{-1}): 3420[b], 3090, 2930[b], 1715, 1635, 1475[b], 1420, 1355, 750, 685, 630, 585, 490 (b = broad). ^1H NMR spectral data (DMSO-d_6, 300 MHz, 22°C δ ppm): 17.6 (br, s, 1H), 7.0–8.6 (m, 36H) (aromatic). ^{31}P (DMSO-d_6, 400 MHz, 22°C, δ ppm): 45.5 (s, 2P).

*2.3.2. $Ru(PPh_3)_2(L^2H)_2$ (**2**) (L^2H_2 = pyridine 2,4-dicarboxylic acid)*

The compound was prepared as a crystalline dark brown solid by the same procedure as described above through the Ag-salt method using pyridine 2,4-dicarboxylic acid instead of pyridine 2,3-dicarboxylic acid. Yield: 65%. *Anal*. Found: C, 62.32; H, 4.0; N, 2.8. Calc. for $RuC_{50}H_{38}N_2P_2O_8$: C, 62.6; H, 3.96; N, 2.92%. IR (KBr pellet, cm^{-1}): 3470[b], 3050, 2680[b], 1720, 1645, 1475, 1415, 1365, 1330, 750, 695, 610, 535, 505 (b = broad). ^1H NMR spectral data (DMSO-d_6, 300 MHz, 22°C, δ ppm): 17.4 (br, s, 1H), 6.9–8.4 (m, 36H). ^{31}P (DMSO-d_6, 400 MHz, 22°C, δ ppm): 46.2 (s, 2P).

*2.3.3. $Ru(PPh_3)_2(L^3H)_2$ (**3**) (L^3H_2 = pyridine 2,5-dicarboxylic acid)*

The compound was prepared as a crystalline dark reddish–brown solid by the same procedure as described above using pyridine 2,5-dicarboxylic acid in place of pyridine 2,3-dicarboxylic acid. Yield: 78%. *Anal*. Found: C, 61.92; H, 4.1; N, 2.85. Calc. for $RuC_{50}H_{38}N_2P_2O_8$: C, 62.6; H, 3.96; N, 2.92%. IR (KBr pellet, cm^{-1}): 3440[b], 3060, 2620[b], 1730, 1625, 1480, 1435, 1390, 1330, 755, 705, 615, 530, 508, 500 (b = broad). ^1H NMR spectral data (DMSO-d_6, 300 MHz, 22°C, δ ppm): 16.9 (br, s, 1H), 6.8–8.6 (m, 36H). ^{31}P (DMSO-d_6, 400 MHz, 22°C, δ ppm): 45.2 (s, 2P).

Table 1
Crystal data and structure refinement for [$Ru(PPh_3)_2(L^1H)_2$] (**1**)

Empirical formula	$C_{50}H_{38}N_2O_8P_2Ru$
Formula weight	478.92
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	
a (Å)	10.8275(5)
b (Å)	15.7721(7)
c (Å)	12.2599(6)
α (°)	90
β (°)	94.610(1)
γ (°)	90
Volume (Å^3)	2086.9(2)
Z	2
D_{calc} (Mg m^{-3})	1.524
Absorption coefficient (mm^{-1})	0.513
F(000)	980
Crystal size (mm)	0.26 × 0.20 × 0.18
θ Range for data collection	1.89–28.30°
Index ranges	$-12 \le h \le 14$, $-20 \le k \le 21$, $-11 \le l \le 16$
Reflections collected	14 889
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5190/0/362
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0264$, $wR_2 = 0.0673$
R indices (all data)	$R_1 = 0.0385$, $wR_2 = 0.0727$
Largest difference peak and hole (e Å^{-3})	0.649 and −0.254

*2.3.4. $Ru(PPh_3)_2(L^4H)_2$ (**4**) (L^4H_2 = pyridine 2,6-dicarboxylic acid):*

The compound was prepared as an orange crystalline solid by the same procedure as described above using the respective acid in place of pyridine 2,3-dicarboxylic acid. Yield: 72%. *Anal*. Found: C, 61.86; H, 4.05; N, 2.91. Calc. for $RuC_{50}H_{38}N_2P_2O_8$: C, 62.6; H, 3.96; N, 2.92%. IR (KBr pellet, cm^{-1}): 3570, 3440[b], 3060, 2630[b], 1725, 1620, 1475, 1430, 1350, 740, 695, 605, 535, 520 (b = broad). ^1H NMR data: (DMSO-d_6, 300 MHz, 22°C, δ ppm): 17.1 (br, s, 1H), 6.9–7.8 (m, 36H). ^{31}P (DMSO-d_6, 400 MHz, 22°C, δ ppm): 45.5 (s, 2P).

2.4. X-ray crystallography

Dark blue prismatic crystals of **1** were isolated by slow cooling of the mother liquor obtained by refluxing the silver salt of pyridine 2,3-dicarboxylic acid with $Ru(PPh_3)_3Cl_2$ in methanol medium after filtering out the precipitated AgCl. A single crystal of dimensions $0.26 \times 0.20 \times 0.18$ mm^3 was chosen for diffraction study. As the compound crystallised in the monoclinic space group $P2_1/c$ with $Z = 2$, the molecule is located at a centre of symmetry. Intensity data were collected at 296 Kon a Bruker Smart CCD area detector system using graphite-monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å). The intensities were corrected for empirical absorption effects using the SADABS program ($R_{int} = 0.0233$) [31]. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares, with a riding model for the hydrogen atoms, using the SHELXTL package [32]. The crystal data and refinement parameters are summarised in Table 1.

3. Results and discussion

*3.1. Crystal structure of $Ru(PPh_3)_2(L^1H)_2$ (**1**) (L^1H_2 = Pyridine 2,3-dicarboxylic acid)*

The molecule is centrosymmetric, and its *trans*-octahedral Ru(II) centre is coordinated by a pair of monodeprotonated pyridine 2,3-dicarboxylic acid ligands (L^1H) acting in a bidentate chelating manner in the equatorial plane, and the PPh_3 groups fill up the two axial positions. Each L^1H ligand is chelated to the Ru(II) centre through its pyridyl nitrogen atom and one oxygen atom of the α-carboxylate group while the other carboxyl group remains idle. Fig. 1 shows the ORTEP [33] plot of **1**, and selected bond lengths and bond angles are given in Table 2. The bite angle of the L^1H ligand at the Ru(II) centre is 76.64(5)°. The equatorial Ru–N [2.069(1) Å], equatorial Ru–O [2.070 (1) Å] and axial Ru–P [2.4168(4) Å] bond lengths indicate an axially elongated octahedral $N_2P_2O_2$ coordination envi-

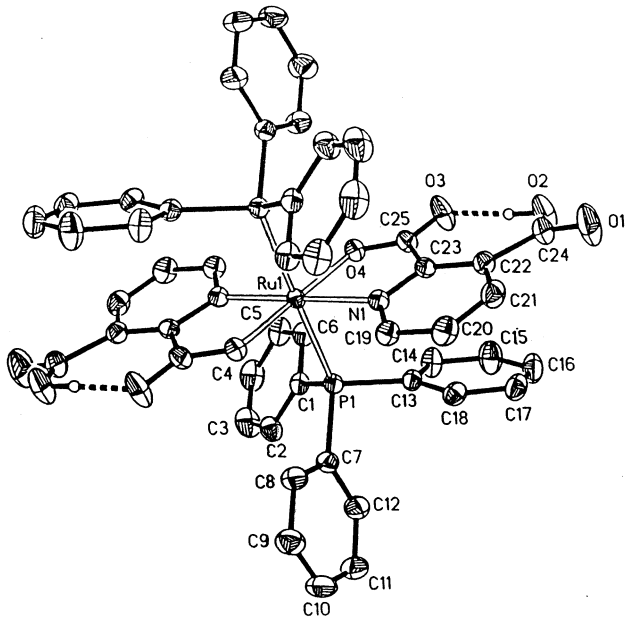


Fig. 1. ORTEP plot of the molecular structure of $Ru(L^1H)_2(PPh_3)_2$ (**1**).

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Ru(PPh_3)_2(L^1H)_2]$ (**1**)

Bond lengths			
Ru(1)–N(1)	2.069(1)	O(3)–C(25)	1.253(2)
Ru(1)–P(1)	2.4168(4)	O(1)–C(24)	1.198(3)
Ru(1)–O(4)	2.070 (1)	O(4)–C(25)	1.267(2)
		O(2)–C(24)	1.282(3)
Bond angles			
N(1)–Ru(1)–O(4)	76.64(5)	C(13)–P(1)–Ru(1)	113.02(5)
N(1)–Ru(1)–P(1)	89.02(4)	C(7)–P(1)–Ru(1)	120.88(6)
O(4)–Ru(1)–P(1)	95.11(3)	C(23)–N(1)–Ru(1)	117.3 (1)
C(1)–P(1)–Ru(1)	111.58(6)	C(19)–N(1)–Ru(1)	123.2(1)

Table 3
Electronic spectra and cyclic voltammetric data

Complexes	Absorption in DMF maxima (nm); $\varepsilon \times 10^{-3}$ ($M^{-1}\,cm^{-1}$) [a]	Oxidation [b] $E_{1/2}$ (V) [c], ΔE_p (mV) [d]
1	305, 8235; 358, 5650	0.49, 40
2	306, 4034; 356, 6530	0.43, 50
3	311, 6873; 353, 5778	0.45, 60
4	329, 3916; 380, 7355	0.37, 60

[a] Electronic spectral data (absorption in DMF).
[b] Cyclic voltammetric data (298 K).
[c] Conditions: solvent, DMF; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, Ag | AgCl; solute concentration, 10^{-3} M; scan rate, 0.4 V s^{-1}; and temperature, 298 K. $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potential.
[d] $\Delta E_p = E_{pa} - E_{pc}$

ronment around the Ru(II) centre. The hydrogen atom of the free carboxylic acid group is found to be hydrogen bonded with the carbonyl oxygen of the adjacent coordinated carboxylate moiety. The C=O bond of the coordinated carboxylate moiety [1.253(2) Å] is longer than the corresponding C=O bond [1.198(3) Å] in the free carboxyl group. Also, the C–O bond length in the coordinated carboxylate [1.267(2) Å] is shorter than the corresponding bond length in the free carboxylic group [1.282(3) Å]. Such a difference is definitely due to the participation of the carboxylate moiety in coordination to Ru(II).

3.2. Infrared spectra

The IR spectra of the free ligands (LH_2) exhibit the ν(C–O) stretch of the free –COOH group in the 1700–1730 cm^{-1} range [18,34]. The presence of the –COOH group involved in the intramolecular hydrogen bonding is evident by a broad and irregularly shaped band in the 3340–2500 cm^{-1} region. In the IR spectra of the complexes the ν(C–O) bands observed in the spectra of the free ligand are found to decrease in intensity significantly and new bands appeared in the 1650–1610 and 1390–1350 cm^{-1} regions corresponding to the ν_{as}(C–O) and ν_s(C–O) modes of the coordinated carboxyl group. The considerable difference between ν_{as} and ν_s indicates strong coordination of the $-COO^-$ oxygen to the Ru(II) acceptor centre [35–37]. The presence of a rather weak band in the 1730–1710 cm^{-1} region suggests that both the carboxyl groups of the pyridine dicarboxylic acids are not involved in coordination. This is corroborated by the fact that each of the $Ru(LH)_2(PPh_3)_2$ complexes liberates CO_2 when put in a saturated aqueous solution of $NaHCO_3$. However, we failed to isolate the corresponding sodium salt, $Na_2[Ru(L)_2(PPh_3)_2]$. Coordination from the pyridine nitrogen is indicated by the red shift of the pyridine ring in plane and out of plane deformation vibrations observed near 630–600 and 430–400 by 15–20 cm^{-1} [38,39]. The characteristic bands of coordinated PPh_3 are present in all the complexes.

3.3. Magnetic moment and conductance

All these complexes are diamagnetic and hence contain the Ru(II) acceptor centre. Measurement of conductance in DMF solution indicates the non-electrolyte nature of all the compounds.

3.4. Electronic spectra

In the absence of any d–d transition, the electronic spectra of such low spin d^6 complexes are usually dominated by metal to ligand charge transfers in the visible region [40–42]. All the complexes exhibit two well-resolved MLCT transitions around 350–380 nm (Band-I) and 300–330 nm (Band-II) (Table 3).

3.5. Electrochemistry

As the complexes are fairly soluble only in DMF, the electron transfer behaviour of the complexes was studied in DMF solution by cyclic voltammetry and the data are presented in Table 3. A reversible ruthenium (II)–ruthenium (III) couple is observed in the range 0.37–0.49 V. The one-electron nature of the couple is substantiated by comparing its current height with those of the standard ferrocene–ferrocinium couple under exactly the same experimental conditions. The ΔE_p values lie around 60 mV and do not change with scan rate, and the i_{pa}/i_{pc} ratio is nearly 1, indicating the reversible nature of all the complexes.

3.6. Study of biological activity

Inhibition of cell division (associated with cell elongation) is a characteristic property of anticarcinogenic compounds like *cis*-platin and its analogues [43,44]. In one of our previous works we selected some ruthenium complexes as potential antitumour agents due to their antibacterial activity against *Escherichia coli*, studied their antitumour activity on two tumour models (Mca mammary carcinoma and TLX5 lymphoma) transplanted on CBA mice and got quite encouraging results [45,46]. The ruthenium complexes reported in this work were also tested against *E. coli* (10 536) to find out whether they can significantly inhibit the bacterial growth with the final objective of testing them against selected tumour models. Activities of the four complexes against *E. coli* (10 536) were examined in a nutrient broth. A culture was grown from a single colony of *E. coli* in the nutrient broth (Difco) kept in an Erlenmeyer flask and incubated at 37°C in a B.O.D. incubator shaker. Standard solutions of all the four complexes were prepared in a 1:1 DMSO–ethanol mixture and requisite quantities of these solution were added to 10 ml of the medium kept in 20ml sterilised test tubes. Cell suspension (0.1 ml, 5×10^5 cfu ml^{-1}) from an 18 h old culture was added for each 5 ml of the sterilised medium and incubated at 37°C for 24 h. The result of the bacterial growth inhibition study is reported below in terms of minimum inhibitory concentration (MIC).

Compound	MIC	
	(μg ml^{-1})	(μM ml^{-1})
$[Ru(PPh_3)_2(L^1H)_2]$ (**1**)	20	0.0214
$[Ru(PPh_3)_2(L^2H)_2]$ (**2**)	100	0.107
$[Ru(PPh_3)_2(L^3H)_2]$ (**3**)	200	0.214
$[Ru(PPh_3)_2(L^4H)_2]$ (**4**)	250	0.268

The value of MIC indicates that the antibacterial activity of compound **1** is very high, that of **2** is quite good and those of **3** and **4** are rather low. We intend to pursue further studies on compound **1** and to examine it for possible antitumour activity against selected tumour models both in vitro and in vivo.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 148937 for $[Ru(PPh_3)_2(L^1H)_2]$ (**1**). Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to Profèssor A.K. Guha, Head of the Department of Biological Chemistry, I.A.C.S., for the antibacterial activity data. We are also indebted to Dr P.K. Bhattacharyya, IICB, Calcutta, for ^{1}H NMR data and Dr A.C. Kunwar, NMR Centre, IICT, Hyderabad, for ^{31}P NMR data. We thank Dr S.K. Chattopadhyay, B.E. College, Howrah, for fruitful discussions. A part of this work is supported by the Hong Kong Research Grants Council (Earmarked grant CUHK 4022/98P).

References

[1] R.L. Dutta, S. Ghosh, J. Inorg. Nucl. Chem. 28 (1966) 247.
[2] R.L. Dutta, S. Ghosh, J. Indian Chem. Soc. 44 (1967) 273.
[3] U. Casellato, P.A. Vigato, Coord. Chem. Rev. 26 (1978) 85.
[4] S. Ghosh, T.K. Banerjee, P.K. Ray, J. Ind. Chem. Soc. 55 (1978) 610.
[5] T.E. Erikson, I. Grenthe, I. Puigdomenech, Inorg. Chim. Acta. 126 (1987) 131.
[6] Y. Ducommun, L. Helm, G. Laurenezy, A. Merbach, Inorg. Chim. Acta. 158 (1989) 3.
[7] D. Ventur, K. Wieghardt, J. Weiss, Z. Anorg. Allg. Chem. 524 (1985) 40.
[8] X.Y. Zhou, N.M. Kostic, Inorg. Chem. 27 (1998) 4402.
[9] A.M. Herring, L. Henling, J.A. Labinger, J.E. Bercaw, Inorg. Chem. 30 (1991) 851.
[10] S.K. Sengupta, S.K. Sahni, R.N. Kapoor, Polyhedron 2 (1983) 317.
[11] M. Chatterjee, S. Ghosh, Bo-Mu Wu, T.C.W. Mak, Polyhedron 17 (1998) 1369.
[12] M. Chatterjee, M. Maji, S. Ghosh, T.C.W. Mak, J. Chem. Soc., Dalton. Trans. (1998) 3641.
[13] M. Chatterjee, S. Ghosh, A.K. Nandi, Trans. Met. Chem. 24 (1999) 183.
[14] M.G.B. Drew, G.W.A. Fowles, R.W. Matthews, R.A. Walton, J. Am. Chem. Soc. 91 (1969) 7769.

[15] W. Fürst, P. Gouzerth, Y. Jeannin, J. Coord. Chem. 8 (1979) 237.
[16] G. Nardin, L. Randaccio, R.P. Bonomo, E. Rizzaretti, J. Chem. Soc., Dalton. Trans. (1980) 369.
[17] D.L. Hoof, D.G. Tisley, R.A. Walton, J. Chem. Soc., Dalton. Trans. (1973) 200.
[18] S. Ghosh, P.K. Ray, T.K. Bandyopadhyay, A.K. Deb, Z. Naturforsch, Teil B 36 (1981) 1270.
[19] R.L. Every, O.L. Riggs Jr, Mater. Prot. 3 (1964) 46.
[20] C.G. Pope, E. Matijevic, R.C. Patel, J. Colloid Interface Sci. 80 (1981) 874.
[21] G.F. Bailey, S. Karp, T.E. Sacks, J. Bacteriol. 89 (1965) 984.
[22] B. Setlow, P. Setlow, Appl. Environ. Microbiol. 59 (1993) 640.
[23] D.L. Griggs, P. Heden, K.E. Temple Smith, W. Rademacher, Phytochemistry 30 (1991) 2513.
[24] P. Laine, A. Gourdon, J.P. Launay, Inorg. Chem. 34 (1995) 5129.
[25] A.G. Mauk, C.L. Coyle, E. Bardingnon, H.B. Gray, J. Am. Chem. Soc. 101 (1979) 5054.
[26] P.C. Harrington, R.G. Wilkins, J. Inorg. Biochem. 12 (1980) 107.
[27] J.T. Groves, I.O. Kady, Inorg. Chem. 32 (1993) 3868.
[28] T. Hasimoto, S.H. Black, P. Gerhardt, Can. J. Microbiol. 6 (1960) 203.
[29] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem 28 (1966) 945.
[30] D.T. Sawyer, J.L. Roberts, Experimental Electrochemistry for Chemists, Wiley, New York, 1974, p. 212.
[31] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, 1996.
[32] G.M. Sheldrick, SHELXTL 5.10, Structure Determination Software Package, Bruker Analytical X-Ray Systems, Madison, WI, 1998.
[33] C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
[34] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd ed., Wiley Interscience, New York, 1970, p. 230.
[35] J. Michel, R.A. Walton, J. Inorg. Nucl. Chem. 37 (1975) 71.
[36] V. Kumari, S.K. Sahni, S. Kher, R.N. Kapoor, Synth. React. Inorg. Met. Org. Chem. 9 (1979) 409.
[37] A.B.P. Lever, J. Lewis, R.S. Nyholm., J. Chem. Soc. (1962) 5262.
[38] R.J.H. Clark, C.S. Williams, Inorg. Chem. 4 (1965) 350.
[39] N.S. Gill, R.H. Nuttal, D.E. Scaife, D.W.A. Sharp, J. Inorg. Nucl. Chem. 18 (1961) 79.
[40] M. Haga, E.S. Dodsworth, A.B.P. Lever, Inorg. Chem. 25 (1986) 447.
[41] E.S. Dodsworth, A.B.P. Lever, Chem. Phys. Lett. 124 (1986) 152.
[42] M.A. Greaney, C.L. Coyle, M.A. Harmer, A. Jordan, E.I. Stifel, Inorg.Chem. 28 (1989) 912.
[43] D.R. Williams, Inorg. Chim. Acta Rev. (1972) 132.
[44] S. Resolva, A.J. Thomson, R.J.P. Willams, Struct. Bonding (Berlin) 11 (1972) 1.
[45] S.K. Chattopadhyay, S. Ghosh, Inorg. Chim. Acta 163 (1987) 246.
[46] F. Bregant, S. Pacor, S. Ghosh, S.K. Chattopadhyay, G. Sava, Anticancer Res. 13 (1993) 1007.