Pergamon

Polyhedron Vol. 14, No. 10, pp. 1307–1314, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

0277–5387(94)00403–X

SYNTHESIS, CRYSTAL STRUCTURE, ELECTROCHEMICAL AND SPECTROSCOPIC PROPERTIES OF $[Ru(BBPEN)][PF_6]\cdot H_2O$. CRYSTAL STRUCTURE OF THE H_2BBPEN [H_2BBPEN = *N*,*N*′-BIS(2-HYDROXYBENZYL)-*N*,*N*′-BIS(2-METHYLPYRIDYL)ETHYLENEDIAMINE]

ADEMIR NEVES* and **MARCOS A. DE BRITO**

Departamento de Química, Universidade Federal de Santa Catarina, CEP 88049
Florianópolis SC, Brazil

GLAUCIUS OLIVA, OTACIRO R. NASCIMENTO, EZEQUIEL H. PANEPUCCI and DULCE H. F. SOUZA†

Instituto de Física de São Carlos, Universidade de São Paulo, CEP 13561-200,
São Carlos SP, Brazil

ALZIR A. BATISTA*

Departamento de Química, Universidade Federal de São Carlos, CEP 13565-905,
São Carlos SP, Brazil

(*Received* 12 *July* 1994; *accepted* 12 *October* 1994)

Abstract—The X-ray crystal structures of *N*,*N*′-bis(2-hydroxybenzyl)-*N*,*N*′-bis(2-methylpyridyl)ethylenediamine (H_2BBPEN) and the complex $[Ru(BBPEN)][PF_6]\cdot H_2O$ have been determined. In this complex the two phenolate oxygens, the two aliphatic nitrogens and the pyridine rings lie in *cis* positions. Two reversible processes at $E_{1/2}+0.854$ V (Ru^{IV}/Ru^{III}) and -0.056 V (Ru^{III}/Ru^{II}) versus Fc^+/Fc, consistent with one-electron transfer, were detected by cyclic voltammetry. The EPR measurements for the Ru^{III} complex in solid state at room temperature have shown three *g*-tensor values: $g_x = 2.4503$, $g_y = 2.2077$ and $g_z = 1.19131$, which are in agreement with the distortion of the structure for the complex determined by X-ray diffraction.

Within a wide program to investigate complexes which can have biological relevance, we have published a paper[1] reporting the synthesis of *N*,*N*′-bis(2-hydroxylbenzyl(2-methylpyridyl)ethylenediamine) (H_2BBPEN), a heterotrifunctional ligand which can offer considerable scope for the preparation of useful complexes. This molecule presents relatively soft centres at the pyridine rings (borderline base), with predisposition to combination with soft metals, i.e. "late" transition metals or metals in low oxidation states. Juxtaposed to them, there are two hard π-base centres at the oxygens of the hydroxylbenzyl groups, which are predisposed to combination with "early" transition metals in high oxidation states. In addition, σ-bonds can be achieved between the metal and nitrogen atoms from amine groups which present no π effects. This unique balance of properties makes H_2BBPEN a very interesting ligand for reactions with different kinds of metals in different oxidation states, forming transition metal complexes which can be useful as models for several biological processes. In our previous papers we reported on $[Mn^{III}(BBPEN)][PF_6]$[1]

---

* Authors to whom correspondence should be addressed.

† Permanent address: UNESP, Departmento de Química, Ilha Solteira, SP, Brazil.

and $[V^{III}(BBPEN)][PF_6]^2$ which are good models in order to help the understanding of the chemistry of these elements in bioinorganic processes. Here we describe the X-ray structure of the free ligand H_2BBPEN and the synthesis and structure of the complex $[Ru^{III}(BBPEN)][PF_6]$ which was obtained from the $[RuCl_2(DMSO)_4]^3$ compound. Despite the fact that this Ru^{III} complex by itself does not show major bioinorganic interest, since the ruthenium metal is not an essential element, it may be useful to know better the reactivity and chemical properties of the interesting H_2BBPEN ligand. Besides the X-ray structure the ruthenium complex was characterized by IR and UV–vis spectroscopies, cyclic voltammetry, EPR and magnetic moment.

EXPERIMENTAL

Materials

Salicylaldehyde, 2-picolyl chloride hydrochloride, NH_4PF_6, $RuCl_3 \cdot 3H_2O$, dimethyl sulphoxide and tetra-n-butylammonium hexafluorophosphate (TBAH) were used as obtained from Aldrich Chemical Co. Ethylenediamine and 1,3-propanediamine were obtained from Merck. For the electrochemical and spectroscopic studies high purity solvents were used as received from Merck. High-purity argon was used to deoxygenate solutions. All other chemicals and solvents were reagent grade.

Syntheses

H_2BBPEN. This compound was prepared as reported before[1] through the intermediates H_2SALEN[4] and H_2BBEN [*N,N'*-bis(2-hydroxybenzyl)ethylenediamine].[5] ^1H NMR ($CDCl_3$): δ 10.6 (s, two phenolic protons), 6.7–8.5 (m, 16 H, phenyl and py), 3.6–3.8 (d, 8H,N—CH_2—R), 2.8 (s, 4H, N—CH_2CH_2—N). MS: *m/z* 455. Found: C, 74.2; H, 7.0; N, 12.4. Calc. for $C_{28}H_{30}N_4O_2$: C, 74.0; H, 6.7; N, 12.3%. Crystals of this ligand suitable for X-ray crystallography were formed by slow evaporation of a CH_2Cl_2—ether solution of the white solid obtained.

$[Ru(H_2BBPEN)(DMSO)_2]Cl_2$. *Cis*-$[RuCl_2(DMSO)_4]$ (0.94 g, 1.31 mmol) and 0.94 g (2.07 mmol) of H_2BBPEN were dissolved in 50 cm^3 of ethanol, the solution was refluxed for 1 h and the resulting yellow precipitate was filtered. Yield: 82%. Found: C, 50.2; H, 5.5; N, 7.3. Calc. for $[C_{32}H_{42}N_4O_4S_2Ru]Cl_2$: C, 49.1; H, 5.4, N, 7.2%. The magnetic susceptibility of this complex shows that the Ru^{II} is low-spin. IR: ν(SC) 1055 and 1109 cm^{-1}; $\nu(OH^-)$ (non-coordinated phenol) 1366 cm^{-1}.

$[Ru(BBPEN)][PF_6] \cdot H_2O$ $[Ru(H_2BBPEN)(DMSO)_2]Cl_2$ (0.5 g, 0.319 mmol) was dissolved in 50 cm^3 of water and 1.0 g (7.3 mmol) of $CH_3COONa \cdot 3H_2O$ was added to this solution. After refluxing for 1 h under air, NH_4PF_6 in excess (0.57 g, 3.5 mmol) was added and the mixture was stirred for 30 min. The solution was cooled and the formed blue solid was collected by filtrating. Yield: 90%. Found: C, 47.0; H, 4.5; N, 7.7. Calc. for $[C_{28}H_{30}N_4O_3Ru][PF_6]$: C, 46.9, H, 4.2; N, 7.8%. The magnetic susceptibility of this complex using the Faraday method showed spin-only value of μ_{eff} 2.13 μ_B for the Ru^{III} (d^5) complex. IR: PF_6^- 820 cm^{-1}.

Crystal structure determination and refinement

Experimental details on X-ray diffraction are given in Table 1. Data were corrected for Lorentz and polarization effects and, for the ruthenium complex, for absorption following the procedure of Walker and Stuart.[6] The structure determinations and refinements were performed with the SHELX-76[7] and MolEN[8] systems of programs. Figures 1 and 2 were drawn with the ORTEP[9] program. Bonded hydrogen-atom scattering factors[10] and complex scattering factors[11,12] for the remaining atoms were employed. In the H_2BBPEN structure, the aromatic rings were treated as rigid groups. In both structures all non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were located at calculated positions and included as fixed contributors, with one common isotropic temperature factor of 4 $Å^2$. The corresponding interatomic bond distances and angles are given in Tables 2 and 3. Atomic coordinates, equivalent isotropic temperature factors for all non-hydrogen atoms, listings of anisotropic thermal parameters, hydrogen atom coordinates, fractional atomic coordinates, a complete list of bond distances and angles for both structures reported in this paper have been deposited with the Editor as supplementary material.

Spectroscopic measurements

IR spectra. Pellets were prepared from crystalline powder samples diluted in CsI. Measurements were performed on a Bomen-Michelson 102 spectrometer in the region 4000–190 cm^{-1}.

UV–vis spectra. The electronic spectra were measured in CH_2Cl_2 solution (10^{-4} mol dm^{-3}) on a Varian DMS-100 spectrophotometer.

Table 1. Crystal data, data collection details and structure refinement results for $C_{28}H_{30}N_4O_2$ and [$RuC_{28}H_{28}N_4O_2$]PF_6·H_2O

Formula	$C_{28}H_{30}N_4O_2$	[$RuC_{28}H_{28}N_4O_2$]PF_6·H_2O
Formula weight	454.58	716.61
Space group	*Pbca*	*C2c*
Lattice parameters		
a (Å)	12.645 (4)	17.220 (4)
b (Å)	17.232 (5)	15.126 (3)
c (Å)	22.319 (8)	22.198 (4)
β (°)	—	99.25 (2)
V (Å^3)	4863 (3)	5706 (2)
Z	8	8
D_{calc} (g cm^{-3})	1.242	1.668
Sample dimensions (mm)	0.08 × 0.10 × 0.50	0.25 × 0.25 × 0.60
Radiation (Å)	Cu-K_α, λ = 1.54056	Mo-K_α, λ = 0.71073
T (°C)	25	25
Linear abs. coeff. (μ) (mm^{-1})	0.596	6.684
Transmission factors (max, min)		1.089 0.884
Scan technique	ω–2θ	ω–2θ
Scan speed range (° min^{-1})	6.7–20	6.7–20
θ range for data collect (°)	0–55	0–25
F(000)	912	2848
No. of indepentant reflections	2487	4628
No. of reflections above 3σ (I)	1317	3834
No. of refined parameters	259	385
Minimized function	$\Sigma w(\lvert F_0\rvert-\lvert F_c\rvert)^2$	$\Sigma w(\lvert F_0\rvert-\lvert F_c\rvert)^2$
Weighting scheme	$w = [\sigma^2(\lvert F_0\rvert(+0.0017\lvert F_0\rvert^2]^{-1}$	$w = [\sigma^2(\lvert F_0\rvert)+0.001\lvert F_0\rvert^2]$
$R = \Sigma\lVert F_0\rvert-\lvert F_c\rVert/\Sigma\lvert F_0\rvert$	0.082	0.037
$R_w = [\Sigma w(\lvert F_0\rvert-\lvert F_c\rvert)^2/\Sigma w\lvert F_0\rvert^2]^{1/2}$	0.091	0.043
$S = [\Sigma w(\lvert F_0\rvert-\lvert F_c\rvert)^2/(M-N)]^{1/2}$	1.97	1.56
$h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}$	0, 13; 0, 18; 0, 23	−20, 20; 0, 17; 0, 26
Max, min residual ρ (e Å^{-3})	0.398, −0.312	−0.611, 0.522

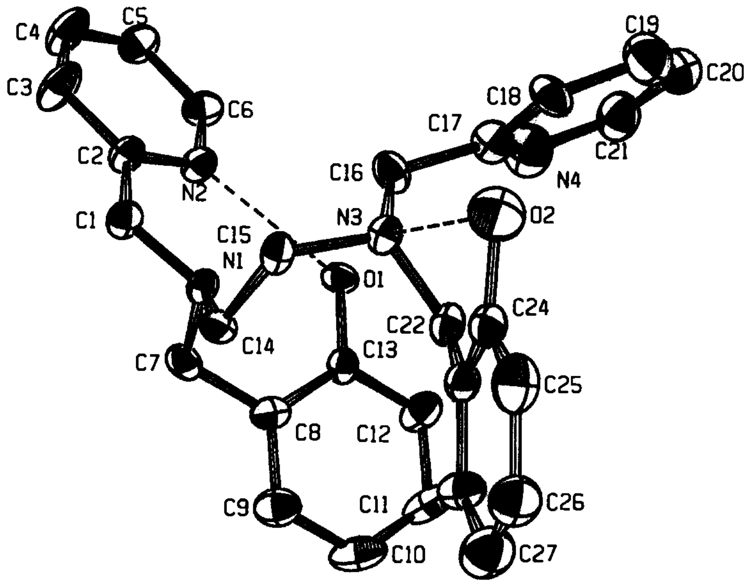

Fig. 1. Perspective view of the molecule of H_2BBPEN showing the atom labelling (except hydrogen atoms).

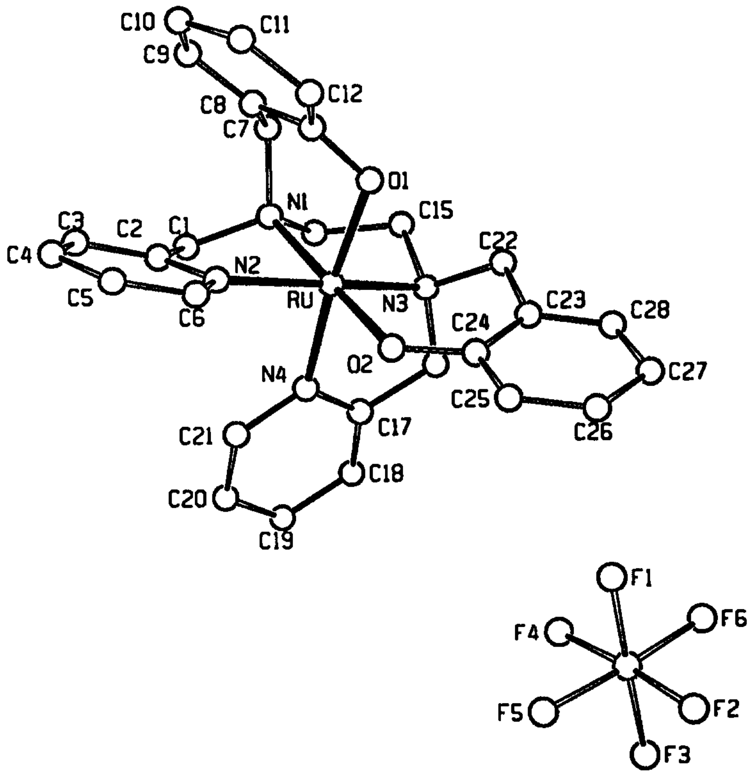

Fig. 2. Molecular structure and atom labelling scheme for $[Ru(BBPEN)][PF_6] \cdot H_2O$.

Electrochemistry

Electrochemical experiments were performed with a Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat equipped with an X–Y–T recorder (ECB Equipamentos Cientificos do Brasil). Cyclic voltammograms (CVs) were performed in dimethylformamide solutions containing 0.1 M $[TBA][PF_6]$ as supporting electrolyte and were conducted at 25°C under argon. The electrochemical cell employed was a standard three-electrode configuration: a platinum working electrode, a platinum-wire auxiliary electrode and an SCE reference. Electrode performance was monitored by observing the ferrocene (Fc^+/Fc) couple. The half-wave potentials were taken as the average of the anodic and cathodic peak potentials of reversible or quasi-reversible cyclic voltammograms. Diagnostic criteria for reversibility of electron-transfer processes were employed in the usual manner.[13]

RESULTS AND DISCUSSION

The X-ray structure of H_2BBPEN ligand, depicted in Fig. 1, shows that the species crystallized has two aliphatic nitrogen chiral centres with the same configuration, named *RR* (or *SS* as the molecule crystallizes in a centrosymmetric space group). The relatively compact conformation adopted by the molecule in the solid state is achieved through two strong internal hydrogen bonds between the phenolate protons and the aliphatic N(3) atom in one half of the molecule and the pyridine N(2) atom in the other [O(1)—N(2) = 2.682(8) and N(3)—O(2) = 2.67(1) Å]. The crystal structure of the $[Ru(BBPEN)][PF_6]$ complex is built up of monomeric units in the space group *C*2/*c* (Fig. 2). in contrast with the free ligand structure, the molecule coordinating the metal is of the *RS* enantiomeric species, adopting a distorted octahedral arrangement around the ruthenium centre.

It is interesting to note that the two previously reported crystal structures of complexes presenting the H_2BBPEN ligand with metal ions of the first transition series (MN^{III} and V^{III})[1,2] have the coordinated ligand in the *RR* (*SS*) enantiomeric form, with the two pyridine nitrogens bonded to the metal centre in a *trans* configuration and two phenolate oxygen and two aliphatic nitrogen atoms of ethylenediamine forming the equatorial plane. As the syntheses of all three complexes were conducted with racemic mixtures of the ligand (*RR*, *SS*, *RS*), the selection of the enantiomeric species complexed is determined by the metal centre, manganese and

Table 2. Interatomic bond distances (Å) and angles (°) of $[C_{28}H_{30}N_4O_2]$ for all non-hydrogen atoms, excluding the aromatic rings, which were treated as rigid groups

O(1)—C(13)	1.340(9)
O(2)—C(24)	1.38(1)
N(1)—C(1)	1.43(1)
N(1)—C(7)	1.47(1)
N(1)—C(14)	1.47(1)
N(3)—C(15)	1.47(1)
N(3)—C(16)	1.48(1)
N(3)—C(22)	1.45(1)
C(1)—C(2)	1.47(1)
C(7)—C(8)	1.49(1)
C(8)—C(9)	1.39(1)
C(14)—C(15)	1.54(1)
C(16)—C(17)	1.46(1)
C(22)—C(23)	1.49(1)
C(1)—N(1)—C(7)	111.1(7)
C(1)—N(1)—C(14)	109.7(6)
C(7)—N(1)—C(14)	110.4(6)
C(15)—N(3)—C(16)	112.1(6)
C(15)—N(3)—C(22)	115.1(6)
C(16)—N(3)—C(22)	112.4(6)
N(1)—C(1)—C(2)	114.9(7)
C(1)—C(2)—N(2)	117.7(6)
C(1)—C(2)—C(3)	122.2(6)
N(1)—C(7)—C(8)	112.3(7)
C(7)—C(8)—C(9)	120.0(6)
C(7)—C(8)—C(13)	120.0(6)
O(1)—C(13)—C(8)	123.4(5)
O(1)—C(13)—C(12)	116.5(5)
N(1)—C(14)—C(15)	112.7(7)
N(3)—C(15)—C(14)	117.7(7)
N(3)—C(16)—C(17)	111.3(7)
C(16)—C(17)—C(18)	118.8(6)
C(16)—C(17)—N(4)	121.1(6)
N(3)—C(22)—C(23)	111.8(6)
C(22)—C(23)—C(28)	120.1(6)
C(22)—C(23)—C(24)	119.6(6)
O(2)—C(24)—C(23)	120.7(6)
O(2)—C(24)—C(25)	119.2(6)

vanadium, showing preference for the *RR* (*SS*) forms, whereas Ru^{III} prefers the *RS* form. Thus, the larger radius of the latter would possibly present steric hindrance to the formation of the $[Ru(H_2BBPEN)]^+$ complex with the ligand in the *RR* (*SS*) form. Data from Table 4 support this hypothesis, showing that in the *RR* (*SS*) complexes (Mn^{III} and V^{III}) the octahedral angles around the metal centres are quite distorted, suggesting that if Ru^{III}, which has a larger ionic radius, was to be complexed with the *RR* (*SS*) ligand the distortion would be even greater, making the complex unstable. It is also possible that the mechanisms of formation of these complexes are different. So, the hard ions Mn^{III} and V^{III} probably bite the hard oxygen atoms first then the pyridine nitrogen, forming in this way the equatorial plane of the complexes with the aliphatic nitrogens. In this case the pyridine rings lie in *trans* positions. Since in the intermediate complex $[Ru(H_2BBPEN)(DMSO)_2]Cl_2$ obtained during the synthesis of $[Ru(BBPEN)][PF_6]$ the phenolate groups are free, as indicated by IR data, and the pyridine rings are coordinated, it is possible that due to steric effects in the end all coordinating points are in *cis* positions in the Ru^{III} complex, making its structure more stable than in the case where the pyridine rings are in *trans* positions.

The Ru^{III}—$N(sp^3)$ bonds, which are of σ character, have distances 2.104 Å as found in $[Ru(NH_3)_6]Cl_3$[14]. Since the pyridine ligand is a weak π-acceptor[15] and forms essentially a σ bond, it is not surprising to find that in our complex the Ru—N(py) distances are essentially the same as the ones for ruthenium and alphatic nitrogens. In the $pyH[RuCl_4(py)_2]$ complex the Ru—N(py) distance was found to be 2.08 Å.[16]

The electronic spectrum of $[Ru(BBPEN)][PF_6]$ in acetonitrile shows two bands. The lowest energy band at 652 nm ($\varepsilon = 3250\ M^{-1}\ cm^{-1}$), analogously to the similar Mn^{III} complex,[1] can be assigned as LMCT from a $p\pi$-orbital on the phenolate oxygen to the unfilled Ru^{II} $d\pi^*$ orbitals. A second transition is observed at 380 nm ($\varepsilon = 3700\ M^{-1}\ cm^{-1}$) and is suggested to originate from a second LMCT to a $d\sigma^*$ orbital of the Ru^{III}. In this case the energy difference, 10978 cm^{-1} between the two transitions is a measurement of 10 Dq for this octahedral complex, which is red-shifted when compared with the 10 Dq found for the manganese complex (7260 cm^{-1}).[1] These data are in accordance with expected results, as the ligand field splitting for the same ligand is higher for metals from the second transition series compared with those from the first transition series. The H_2BBPEN ligand spectrum in CH_3CN does not show any absorption maximum above 300 nm.[1]

The magnetic moment for $[Ru(BBPEN)][PF_6]$ was found to be 2.13 μB, which is characteristic of one unpaired electron. Paramagnetic Ru^{III} complexes with μ_{eff} in the range 1.78–2.30 μ_B have been reported.[17]

The redox properties of $[Ru(BBPEN)][PF_6]$ in dimethylformamide have been investigated by cyclic voltammetry (Fig. 3) and two reversible processes involving one-electron transfer were detected: the first at $E_{1/2}$ of $+0.854$ V and the second at -0.056 versus Fc^+/Fc. These data are consistent with the processes Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II}, respectively.[18] It is interesting to point out that

Table 3. Interatomic bond distances (Å) and angles (°) of [RuBBPEN]$PF_6 \cdot H_2O$

Ru—O(1)	2.005(3)	C(8)—C(13)	1.410(6)
Ru—O(2)	1.974(3)	C(9)—C(10)	1.383(7)
Ru—N(1)	2.100(4)	C(10)—C(11)	1.371(7)
Ru—N(2)	2.061(4)	C(11)—C(12)	1.390(6)
Ru—N(3)	2.080(4)	C(12)—C(13)	1.391(6)
Ru—N(4)	2.091(4)	C(14)—C(15)	1.529(6)
O(1)—C(13)	1.341(5)	C(16)—C(17)	1.520(6)
O(2)—C(24)	1.333(5)	C(17)—C(18)	1.365(6)
N(1)—C(1)	1.496(6)	C(18)—C(19)	1.372(6)
N(1)—C(7)	1.499(6)	C(19)—C(20)	1.382(7)
N(1)—C(14)	1.501(5)	C(20)—C(21)	1.384(7)
N(2)—C(2)	1.365(5)	C(22)—C(23)	1.496(7)
N(2)—C(6)	1.341(6)	C(23)—C(24)	1.412(6)
N(3)—C(15)	1.499(5)	C(23)—C(28)	1.403(7)
N(3)—C(16)	1.487(6)	C(24)—C(25)	1.415(6)
N(3)—C(22)	1.499(6)	C(25)—C(26)	1.372(7)
N(4)—C(17)	1.335(6)	C(26)—C(27)	1.409(9)
N(4)—C(21)	1.351(6)	C(27)—C(28)	1.379(9)
C(1)—C(2)	1.491(6)	P—F(1)	1.566(5)
C(2)—C(3)	1.371(6)	P—F(2)	1.567(4)
C(3)—C(4)	1.385(7)	P—F(3)	1.578(5)
C(4)—C(5)	1.370(7)	P—F(4)	1.595(4)
C(5)—C(6)	1.379(6)	P—F(5)	1.581(5)
C(7)—C(8)	1.510(6)	P—F(6)	1.542(5)
C(8)—C(9)	1.366(6)		
O(1)—Ru—O(2)	90.5(1)	C(7)—C(8)—C(13)	116.6(4)
O(1)—Ru—N(1)	87.9(1)	C(9)—C(8)—C(13)	120.6(4)
O(1)—Ru—N(2)	94.2(1)	C(8)—C(9)—C(10)	120.5(4)
O(1)—Ru—N(3)	92.1(1)	C(9)—C(10)—C(11)	119.0(4)
O(1)—Ru—N(4)	172.9(1)	C(10)—C(11)—C(12)	121.9(5)
O(2)—Ru—N(1)	178.0(1)	C(11)—C(12)—C(13)	118.9(4)
O(2)—Ru—N(2)	98.3(1)	O(1)—C(13)—C(8)	119.5(4)
O(2)—Ru—N(3)	93.7(1)	O(1)—C(13)—C(12)	121.7(4)
O(2)—Ru—N(4)	88.8(1)	C(8)—C(13)—C(12)	118.8(4)
N(1)—Ru—N(2)	80.6(1)	N(1)—C(14)—C(15)	108.6(3)
N(1)—Ru—N(3)	87.6(1)	N(3)—C(15)—C(14)	111.1(3)
N(1)—Ru—N(4)	93.0(1)	N(3)—C(16)—C(17)	111.9(4)
N(2)—Ru—N(3)	166.4(1)	N(4)—C(17)—C(16)	116.3(4)
N(2)—Ru—N(4)	92.9(1)	N(4)—C(17)—C(18)	122.6(4)
N(3)—Ru—N(4)	80.9(1)	C(16)—C(17)—C(18)	121.1(4)
Ru—O(1)—C(12)	129.9(2)	C(17)—C(18)—C(19)	119.8(4)
Ru—O(1)—C(13)	116.4(3)	C(18)—C(19)—C(20)	118.7(4)
Ru—O(2)—C(24)	122.9(3)	C(19)—C(20)—C(21)	118.7(4)
Ru—N(1)—C(1)	104.1(3)	N(4)—C(21)—C(20)	122.2(4)
Ru—N(1)—C(7)	115.4(3)	N(3)—C(22)—C(23)	114.1(4)
Ru—N(1)—C(14)	103.1(2)	C(22)—C(23)—C(24)	126.0(4)
Ru—N(2)—C(2)	112.8(3)	C(22)—C(23)—C(28)	115.4(4)
Ru—N(2)—C(6)	127.9(3)	C(24)—C(23)—C(28)	118.5(4)
Ru—N(3)—C(15)	104.0(2)	O(2)—C(24)—C(23)	126.4(4)
Ru—N(3)—C(16)	111.0(3)	O(2)—C(24)—C(25)	114.9(4)
Ru—N(3)—C(22)	109.2(3)	C(23)—C(24)—C(25)	118.7(4)
Ru—N(4)—C(17)	115.5(3)	C(24)—C(25)—C(26)	121.7(4)
Ru—N(4)—C(21)	126.5(3)	C(25)—C(26)—C(27)	119.6(5)
C(1)—N(1)—C(7)	108.5(3)	C(26)—C(27)—C(28)	119.3(6)
C(1)—N(1)—C(14)	115.8(3)	C(23)—C(28)—C(27)	122.2(5)
C(7)—N(1)—C(14)	109.9(3)	F(1)—P—F(2)	90.0(3)
C(2)—N(2)—C(6)	119.1(4)	F(1)—P—F(3)	179.8(3)
C(15)—N(3)—C(16)	111.2(3)	F(1)—P—F(4)	91.4(2)

continued

Table 3—*continued.*

C(15)—N(3)—C(22)	111.7(3)	F(1)—P—F(5)	88.9(2)
C(16)—N(3)—C(22)	109.6(3)	F(1)—P—F(6)	90.2(3)
C(17)—N(4)—C(21)	118.0(4)	F(2)—P—F(3)	89.8(3)
N(1)—C(1)—C(2)	109.2(4)	F(2)—P—F(4)	176.6(3)
N(2)—C(2)—C(1)	115.3(4)	F(2)—P—F(5)	89.6(3)
N(2)—C(2)—C(3)	120.6(4)	F(2)—P—F(6)	94.2(3)
C(1)—C(2)—C(3)	124.1(4)	F(3)—P—F(4)	88.8(2)
C(2)—C(3)—C(4)	119.9(4)	F(3)—P—F(5)	91.0(3)
C(3)—C(4)—C(5)	119.4(4)	F(3)—P—F(6)	89.8(3)
C(4)—C(5)—C(6)	118.8(4)	F(4)—P—F(5)	87.4(2)
N(2)—C(6)—C(5)	122.2(4)	F(4)—P—F(6)	88.8(2)
N(1)—C(7)—C(8)	115.1(4)	F(5)—P—F(6)	176.1(3)
C(7)—C(8)—C(9)	122.5(4)		

Table 4. Selected angles (°) for [Ru(BBPEN)][PF_6] (I) [Mn(BBPEN)][PF_6] (II) and [V(BBPEN)][PF_6] (III)[a]

I	II	III[a]
pyN(4)—Ru—O(1)	pyN(4)—Mn—pyN(1)	pyN(2)—V—pyN(4)
172.9(1)	168.8(2)	168.6(1)
amN(1)—Ru—O(2)	amN(1)—Mn—O(2)	amN(1)—V—O(2)
178.0(1)	169.9(2)	153.1(1)
pyN(2)—Ru—amN(3)	amN(3)—Mn—O(1)	amN(3)—V—O(2)
166.4(1)	167.5(2)	151.5(1)

[a] The mentioned atoms of the ligands are *trans* to each other.

our ligand H_2BBPEN is able to stabilize ruthenium in the II and IV oxidation states, besides the species in oxidation state III, in which the complex was synthesized.

The EPR measurements for [Ru(BBPEN)][PF_6] in the solid state at room temperature show three g-tensor values, $g_x = 2.4503$, $g_y = 2.2077$ and $g_z = 1.9131$, which confirm the distortion of the complex found by X-ray data.

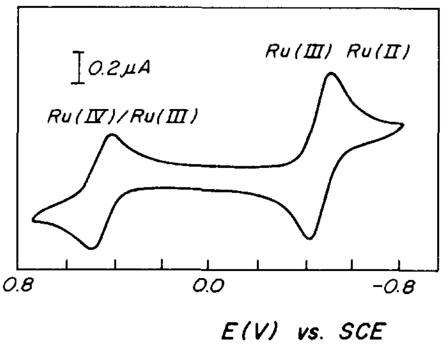

Fig. 3. Cyclic voltammogram (scan rate 50 mV s^{-1}) of *ca* 10^{-3} M solution of the [Ru(BBPEN)][PF_6]·H_2O complex in dimethylformamide (0.1 M [TBA][PF_6] at a platinum electrode with the internal standard ferrocene).

Acknowledgements—This work was supported by grants from the FAPESP, CNPq, CAPES, FINEP and PADCT.

REFERENCES

1. A. Neves, S. M. D. Erthal, I. Vencato, A. S. Ceccato, Y. P. Mascarenhas, O. R. Nascimento, M. Hörner and A. A. Batista, *Inorg. Chem.* 1992, **31**, 4749.
2. A. Neves, A. S. Ceccato, S. M. D. Erthal, I. Vencato, B. Nuber and J. Weiss, *Inorg. Chim. Acta* 1991, **187**, 119.
3. I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 1973, 204.
4. H. Diehl and C. C. Hach, *Inorg. Synth.* 1950, **3**, 196.
5. A. Funke and J. P. Fourneau, *Bull. Soc. Chim. Fr.* 1942, **9**, 806.
6. N. Walker and D. Stuart, *Acta Cryst.* 1983, **158**, A39.
7. G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination. University of Cambridge, Cambridge, U.K. (1976).
8. MolEN, Structure Determination System, Enraf–Nonius, Delft, The Netherlands (1990).

9. C. K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee U.S.A. (1965).
10. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* 1965, **42**, 3175.
11. D. T. Cromer and J. B. Mann, *Acta Cryst.* 1968, **24A**, 321.
12. D. T. Cromer and D. Liberman, *J. Chem. Phys.* 1970, **53**, 1891.
13. R. S. Nicholson and I. Shain, *Analyt. Chem.* 1964, **36**, 706.
14. H. C. Stynes and J. A. Ibers, *Inorg. Chem.* 1971, **10**, 2304.
15. Ch. Elschenbroich and A. Salzer, *Organometallics, A Concise Introduction*, 1st edn, p. 230. VCH, Weinheim, Germany (1989).
16. G. Oliva, personal communication.
17. E. Seddon and K. Seddon, *The Chemistry of Ruthenium*, 1st edn, Ch. 8. Elsevier, New York (1984).
18. R. Contreras, G. A. Heath, A. J. Lindsay and T. A. Stephenson, *J. Organomet. Chem.* 1979, **179**, C55.