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## Supramolecular Chemistry

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### Synthesis, Structural, Spectroscopic and Electrochemical Characterization of New Ruthenium(II) Tetramer Complexes Containing 1,4-Bis(diphenylphosphine)butane and Alterdentate Ligands

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# Synthesis, Structural, Spectroscopic and Electrochemical Characterization of New Ruthenium(II) Tetramer Complexes Containing 1,4-Bis(diphenylphosphine)butane and Alterdentate Ligands

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In this work a series of  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-N-N})\}_4$  complexes were synthesized and characterized by elemental analysis, cyclic voltammetry and differential pulse voltammetry and UV–Vis and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies; [ $\mu\text{-}4,4'\text{-N-N}$  = pyrazine (pz), 4,4'-bipyridine = (4,4'-bipy), 1,2-bis-*trans*-(4-pyridyl)ethane = (pyeta) and 1,2-bis-*trans*-(4-pyridyl)ethylene = (pyetil) as bridging alterdentate ligands (alterdentate ligands are molecules (or ions), with two equivalent ligating atoms or ligating sites that do not simultaneously bind to a metallic center [Zelewsky von A. in *Stereochemistry of Coordination Compounds, Inorganic Chemistry, A Textbook Series*; John Wiley & Sons, Inc.: New York, 1995: p. 45] [1]) and 1,4-bis(diphenylphosphino)butane = dppb]. Electrochemical experiments (cyclic voltammetry and differential pulse voltammetry) suggest that for longer ligands the interaction between two ruthenium atoms is weak and for short ligands like pyrazine the corresponding interaction is strong. The analysis of the X-ray structure of the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$  complex showed that the molecular squares obtained are stacked on top of each other along the  $\alpha$  axis forming infinite columns and that the formation of central tunnels is prevented by the bulky character of the phenyl groups of the diphenylphosphine ligands.

**Keywords:** Supramolecular square tetramers; Ruthenium; Bis(diphenylphosphino)butane; Alterdentate ligands

## INTRODUCTION

There is currently considerable interest in the study of macromolecules of nanoscopic dimensions. The preparation of chemical compounds of

nanometer size (1 nm to 1  $\mu\text{m}$ ) is a challenge for those who deal with chemical synthesis to achieve ordered structures. Some of the possible applications of these types of molecules involve molecular and chiral recognition, host–guest chemistry and catalysis. A review was recently published on this subject describing many geometrical forms of some of these species and a variety of ways to synthesize them [2]. The molecular architecture or the self-assembly arrangement to be attained in the syntheses of these complexes depends on the goal one is looking for. The five-coordinate, mixed-phosphine complex  $[\text{RuCl}_2(\text{dppb})(\text{PPh}_3)]$  has been used for the preparation of mono- and dinuclear complexes [3–6]. Thus, in this paper we would like to present a simple methodology using this complex as a precursor to obtain a symmetric square type of self-assembled structure of ruthenium–phosphine complexes containing alterdentate ligands [1] [pyrazine (pz), 4,4'-bipyridine (4,4'-bipy), 1,2-bis-*trans*-(4-pyridyl)ethane (pyeta) and 1,2-bis-*trans*-(4-pyridyl)ethylene (pyetil) as bridging (N-N) ligands]. The complexes with the general formula  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-N-N})\}_4$  were characterized by elemental analysis, cyclic voltammetry and differential pulse voltammetry and UV–Vis and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies. The structure of the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$  complex was established by X-ray crystallographic analysis.

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## EXPERIMENTAL

## General Considerations

All manipulations involving solutions of the complexes were performed under argon. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was purchased from Degussa and the ligands 1,4-bis(diphenylphosphine)butane, pyrazine, 4,4'-bipyridine, 1,2-bis-*trans*-(4-pyridyl)ethane, and 1,2-bis-*trans*-(4-pyridyl)ethylene were purchased from Aldrich. The  $[\text{RuCl}_2(\text{dppb})]_2 \{\mu\text{-dppb}\}$  was synthesized according to the literature procedure [7,8].

Tetrabutylammonium perchlorate (Fluka purum) was recrystallized from ethanol–water and dried overnight, under vacuum, at 80°C. Reagent grade solvents (Merck) were appropriately distilled, dried and stored over Linde 4 Å molecular sieves. Purified argon used in all procedures described here was used for the removal of dissolved oxygen.

Microanalyses were performed by Microanalytical Laboratory of Universidade Federal de São Carlos, São Carlos (SP).

## Measurements

Crystals of the complex  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$  were grown by slow evaporation of a dichloromethane–diethyl ether solution. Single crystals were used for data collection and cell parameter determination on an Enraf-Nonius Kappa-CCD diffractometer, using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection was made using the COLLECT program [9]; integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [10]. Absorption corrections were carried out using the multi-scan method [11]. The structure was solved by direct methods with SHELXS-97 [12]. The models were refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [13]. All the hydrogen atoms were stereochemically positioned and refined with the riding model [14]. Experimental details are summarized in Table I. Relevant interatomic bond lengths and bond angles are listed in Table IV. The UV–Vis spectra were recorded in  $\text{CH}_2\text{Cl}_2$  on a Varian spectrophotometer, model 450 and are given as  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ , in  $\text{mol}^{-1} \text{cm}^{-1}$ ).

Cyclic voltammetry was carried out at room temperature in freshly distilled dichloromethane containing  $0.1 \text{ mol l}^{-1}$  of  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$  (TBAP), using an EG&G/PARC electrochemical system consisting of a 273A potentiostat or BAS Electrochemical Analyzer. A three-electrode system with resistance compensation was used throughout. The working and auxiliary

TABLE I Crystal data and structure refinement for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$  complex

Empirical formula	$[\text{C}_{152}\text{H}_{154}\text{N}_8\text{P}_8\text{Cl}_8\text{Ru}_4] \cdot 1.2 \text{ H}_2\text{O}$
Formula weight	3061.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.1820(6) \text{ \AA}$ $\alpha = 104.663(4)^\circ$ $b = 19.295(2) \text{ \AA}$ $\beta = 98.258(5)^\circ$ $c = 22.931(2) \text{ \AA}$ $\gamma = 99.079(5)^\circ$
$V$	$3808.7(6) \text{ \AA}^3$
$Z$	1
Density (calculated)	$1.335 \text{ mg m}^{-3}$
Absorption coefficient	$0.665 \text{ mm}^{-1}$
$F(000)$	1568
Crystal size	$0.22 \times 0.10 \times 0.03 \text{ mm}^3$
$\theta$ range for data collection	$1.64$ to $22.00^\circ$
Index ranges	$0 \leq h \leq 9, -20 \leq k \leq 20,$ $-24 \leq l \leq 23$
Reflections collected	17707
Independent reflections	9347 [R(int) = 0.0705]
Completeness to $\theta = 22.00^\circ$	99.9%
Max and min transmission	0.969 and 0.838
Refinement method*	Full-matrix least-squares on $F^2$
Data/parameters	9347/742
Goodness-of-fit on $F^2$	1.138
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0611, wR2 = 0.1543$
$R$ indices (all data)	$R1 = 0.1279, wR2 = 0.2117$
Largest diff. peak and hole	$0.779$ and $-1.007 \text{ e \AA}^{-3}$

\*Data collection, data processing, structure solution and structure refinement respectively.

electrodes were a stationary platinum foil and a wire, respectively. The reference electrode was Ag/AgCl in a Luggin capillary,  $0.1 \text{ mol l}^{-1}$  TBAP in  $\text{CH}_2\text{Cl}_2$ , a medium in which ferrocene is oxidized at 0.43 V ( $\text{Fc}^+/\text{Fc}$ ); all potentials are referred to this electrode.

The infrared spectra of the complexes were measured from powder samples diluted in CsI on an FTIR Bomem-Mechelson 102 spectrometer in the  $4000\text{--}200 \text{ cm}^{-1}$  region. The  $^{31}\text{P}\{^1\text{H}\}$  spectra were recorded in  $\text{CH}_2\text{Cl}_2$  on a Bruker 400 MHz spectrometer, with  $\text{H}_3\text{PO}_4$  (85%) as external reference, and the  $^{13}\text{C}$  and the  $^1\text{H}$  NMR data for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})\}_4$  complex were obtained in deuterated chloroform.

Preparation of the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-N-N})\}_4$  Complexes

Typical syntheses of the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-N-N})\}_4$  complexes are described below:

**Tetakis[trans-dichloro[1,4-bis(diphenylphosphino)butane]- $\mu$ -(4,4'-bipyridine)ruthenium (II)];  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$** 

$[\text{RuCl}_2(\text{dppb})]_2(\mu\text{-dppb})$  (0.200 g; 0.123 mmol) was dissolved in benzene (8 ml), and 4,4'-bipyridine

(0.0962 g, 0.616 mmol) was added to produce a reddish orange solution. This solution was stirred at room temperature for 30 min after which its volume was reduced to approximately 1 ml, and diethyl ether was added to precipitate an orange solid which was filtered, washed well with diethyl ether and dried under vacuum. Yield: 85%. Calcd for  $C_{152}H_{144}Cl_8N_8Ru_4P_8$ : C, 60.48; H, 4.81; N, 3.71. Found: C, 60.81; H, 5.02; N, 4.07.  $\nu_{Ru-Cl}$  308  $cm^{-1}$ ;  $\nu_{Ru-N}$  431  $cm^{-1}$ ;  $\nu_{Ru-P}$  513  $cm^{-1}$ .

This synthesis was reproduced using  $[RuCl_2(dppb)]_2(\mu-dppb)$  (0.100 g; 0.062 mmol) dissolved in benzene (5 ml) and 4,4'-bipyridine (0.114 g; 0.070 mmol). The results of this procedure were essentially the same as above.

**Tetrakis(trans-dichloro[1,4-bis(diphenylphosphino)butane]- $\mu$ -(pyrazine)ruthenium(II)); Trans- $\{[RuCl_2(dppb)](\mu-pz)\}_4$  II**

$[RuCl_2(dppb)]_2(\mu-dppb)$  (0.100 g, 0.062 mmol) was dissolved in benzene (5 ml), and pyrazine (0.006 g, 0.075 mmol) was added to produce a reddish brown solution. This solution was stirred at room temperature for 40 min after which its volume was reduced to approximately 1 ml and acetone was added to precipitate a brown solid which was filtered, washed well with acetone and dried under vacuum. Yield: 87%. Calcd for  $C_{128}H_{128}Cl_8N_8Ru_4P_8$ : C, 56.64; H, 4.75; N, 4.13. Found: C, 56.71; H, 4.86; N, 3.95.  $\nu_{Ru-Cl}$  321  $cm^{-1}$ ;  $\nu_{Ru-N}$   $cm^{-1}$ ;  $\nu_{Ru-P}$  510  $cm^{-1}$ .

Compounds III and IV were obtained by methods similar to those described above using the approximate proportion 1:1. Their microanalysis and infrared data areas follow:

**Tetrakis(trans-dichloro[1,4-bis(diphenylphosphino)butane]- $\mu$ -[1,2-bis-trans-(4-pyridyl)ethane]ruthenium(II)), Trans- $\{[RuCl_2(dppb)](\mu-pyeta)\}_4$  III**

Yield: 83%. Calcd for  $C_{160}H_{160}Cl_8N_8Ru_4P_8$ : C, 61.38; H, 5.15; N, 3.58. Found: C, 61.51; H, 5.32; N, 3.95.  $\nu_{Ru-Cl}$  321  $cm^{-1}$ ;  $\nu_{Ru-N}$  423  $cm^{-1}$ ;  $\nu_{Ru-P}$  510  $cm^{-1}$ .

**Tetrakis(trans-dichloro[1,4-bis(diphenylphosphino)butane]- $\mu$ -[1,2-bis-trans-(4-pyridyl) Ethylene] ruthenium(II)), Trans- $\{[RuCl_2(dppb)](\mu-pyetil)\}_4$  IV**

Yield: 78%. Calcd for  $C_{160}H_{152}Cl_8N_8Ru_4P_8$ : C, 61.54; H, 4.91; N, 3.59. Found: C, 61.50; H, 5.17; N, 3.69.  $\nu_{Ru-Cl}$  321  $cm^{-1}$ ;  $\nu_{Ru-N}$  416  $cm^{-1}$ ;  $\nu_{Ru-P}$  508  $cm^{-1}$ .

## RESULTS AND DISCUSSION

The  $[RuCl_2(dppb)(PPh_3)]$  complex has been shown to be a useful precursor for the preparation

of mono- and dinuclear complexes containing the ' $RuCl_2(dppb)$ ' moiety which have been used for catalytic hydrogenation and epoxidation of unsaturated organics [3–6,15]. Less obvious is the utility of this five-coordinated complex as a precursor for the synthesis of supramolecular species. However, this present paper reports that  $[RuCl_2(dppb)(PPh_3)]$  is useful for the preparation of  $\{[RuCl_2(dppb)](\mu-4,4'-N-N)\}_4$  complexes, where N-N is an alterdentate ligand.

Thus the synthesized complexes with general formula  $\{[RuCl_2(dppb)](\mu-4,4'-N-N)\}_4$  containing the pyrazine (pz), 4,4'-bipyridine (4,4'-bipy), 1,2-bis-trans-(4-pyridyl) ethane (pyeta) or 1,2-bis-trans-(4-pyridyl)ethylene (pyetil) ligand show IR bands close to 320  $cm^{-1}$  and are tentatively assigned to  $\nu_{Ru-Cl}$ . The spectra in this region are complex but the values are reasonable for Ru(II)-phosphine species [6,16,17]. The presence of only one  $\nu_{Ru-Cl}$  stretch in the IR spectra of the complexes suggests a *trans*-isomer where one chlorine is *trans* to the other chlorine. Absorption peaks at 1433  $cm^{-1}$  indicated the aromatic 4,4'-bipyridine and phosphine ligands [18,19] and  $\nu_{Ru-N}$  and  $\nu_{Ru-P}$  stretches are close to 420 and 500  $cm^{-1}$ , respectively [16,17].

In the UV-Vis region, intense bands below 300 nm are present in the free ligands and are assigned to  $\pi \rightarrow \pi^*$  transitions from the aromatic rings which are found in the spectra of the complexes. Moderately intense bands are observed in the complexes which could be assigned to charge transfer (Ru(II)  $d\pi \rightarrow p\pi^*$ ) [20–23]. Transitions of the metal ion ( $d-d$  transitions) can be obscured by charge transfer transitions at lower energies in these complexes [24]. The two bands observed for the  $[RuCl_2(PPh_3)_2(\text{pyrazole})_2]$  complex with low energy were attributed as  $d-d$  transitions ( $^1A_1 \rightarrow ^1T_1$  and  $^1A_1 \rightarrow ^1T_2$ ) and the other two bands with high energy were attributed as  $\pi \rightarrow \pi^*$  [18]. In our complexes only two bands were observed, and in this case probably the other two bands (one  $d-d$  and one  $\pi \rightarrow \pi^*$ ) are covered by the broad band observed, close to 400 nm.

The  $^{31}P\{^1H\}$  NMR spectra for all four complexes studied in this work in  $CH_2Cl_2$  solution displayed just one sharp singlet as expected for the equivalent P atoms located in highly symmetrical structures [25,26]. The chemical shifts of the  $^{31}P\{^1H\}$  NMR are close to 40 ppm (Table II) which is consistent with a geometry where the phosphorus atoms are *trans* to the nitrogen atoms as detected for other ruthenium complexes with general formula  $[RuCl_2(dppb)(N-N)]$  (N-N = N-heterocyclic ligands) [6,25] or for the  $[RuCl_2(PPh_3)_2(\text{pyrazole})_2]$  [18].

Particularly revealing are the  $^1H$  and the  $^{13}C$  NMR spectra of the complex with the pyrazine ligand (Table III). Thus the singlet at 8.80 ppm  $\{^1H\}$  and at 146.5 ppm ( $^{13}C$ ) in the NMR spectra of the complex

TABLE II Spectroscopic and electrochemical parameters for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-N-N})\}_4$  complexes

(N-N)	$^{31}\text{P}\{^1\text{H}\}^*$ (ppm)	$E_{1/2} \text{V}^\dagger$	$\lambda$ (nm); (log $\epsilon$ )	$\text{p}K_a$
pz	38.0	0.65; 0.82	234(4.70), 428(3.91) <sup>b</sup>	0.65
4,4'-bipy	36.7	0.55	236(5.07), 392(4.35) <sup>b</sup>	4.82
pyeta	41.4	0.45	236(4.52), 418(3.97) <sup>b</sup>	
pyetil	41.3	0.53	286(5.44), 412(5.27) <sup>b</sup>	5.6


\* $\text{H}_3\text{PO}_4$ (85%);  $^\dagger$ in  $\text{CH}_2\text{Cl}_2$ , (vs. Ag/AgCl); <sup>b</sup>(broad).

in  $\text{CDCl}_3$  solution show that the pyrazine ligand is coordinated as a bridge comprising *cis* bridging metal centers connected by the ligands. Thus taking in to consideration the above microanalysis data and the spectroscopic data (IR;  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR) and considering that the phosphorus NMR data mainly suggest the presence of highly symmetrical geometries for the complexes it is possible to derive a structure for the pyrazine compound which is consistent with a square configuration also in solution (Fig. 1).

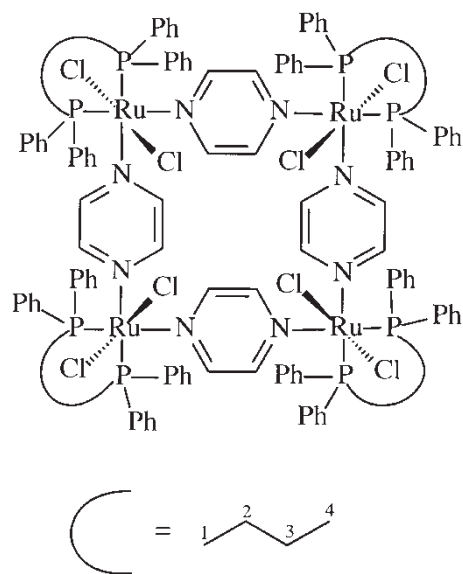
The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the complexes with the 4,4'-bipyridine, 1,2-bis-*trans*-(4-pyridyl)ethane and 1,2-bis-*trans*-(4-pyridyl)ethylene ligands reveal more complicated data since the hydrogen and the carbon atoms are not equivalent and probably there are subtle differences in the environment surrounding these atoms in the complexes in solution.

It is interesting to point out that the self-assembled two-dimensional Pd(II) complex derived from the 1,2-bis-*trans*-(4-pyridyl)ethylene ligand and  $[(\text{en})\text{Pd}(\text{NO}_3)_2]$  in  $\text{D}_2\text{O}$  showed concentration dependency [27]. Thus while the trimeric assembly was induced at very low concentration, the tetrameric assembly was induced in less dilute solution. The equilibrium between these two species in  $\text{D}_2\text{O}$  solution was followed by monitoring a  $^1\text{H}$  NMR

TABLE III  $^{13}\text{C}$  and  $^1\text{H}$  NMR data ( $\text{CDCl}_3$ ) for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})\}_4$  complex

Assignment	$\delta^1\text{H}$	$J^1\text{H} \times ^1\text{H}$	$\delta^{13}\text{C}$	$J^1\text{H} \times ^{13}\text{C}$
C1, C4	1.67 s*	–	32.5 d	13.8
C2, C3	2.79 s	–	22.92	–
C5	–	–	138.4 d	19.2
			138.2 d	19.2
C6, C10	7.45 d <sup>†</sup>	7.81	127.3 d	3.8
			127.2 d	3.8
C7, C9	7.07 t <sup>‡</sup>	7.81	133.7 s	–
C8	6.96 t	7.31	129.0 s	–
	8.80 s	–	146.5 s	–

\*Singlet; <sup>†</sup>Doublet; <sup>‡</sup>Triplet.

FIGURE 1 Suggested structure for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})\}_4$  complex in solution.

experiment. Thus the major component at higher concentration was assigned as the most stable, strainless molecular square by analogy with the structure of a bipyridyl based complex and the other structure which could be stable at lower concentration was assigned as the second most stable molecular triangle [28–31]. In our work no detectable change in the  $^1\text{H}$  NMR experiments in  $\text{CDCl}_3$  was observed, suggesting the presence of just one structure in solution, independent of the concentration of the pyrazine complex (0.2–100 mM). The same was observed for the 4,4'-bipyridine, 1,2-bis-*trans*-(4-pyridyl)ethane and 1,2-bis-*trans*-(4-pyridyl)ethylene complexes. However in these cases, we do not absolutely exclude the possibility of the presence of more than one polymer in solution since their spectra are more complex as mentioned above, and small changes in the spectra might not be perceptible.

The reaction of  $[\text{RuCl}_2(\text{dppb})]_2(\mu\text{-dppb})$  with the 4,4'-bipyridine ligand produced a tetramer, as can be seen in the X-ray molecular structure of the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-4,4'-bipy})\}_4$  complex (Fig. 2), confirming our above suggestion. This complex crystallizes in the *P*-1 space group and the tetramer is sited on a crystallographic symmetry center. In this case, both nitrogen atoms of the 4,4'-bipy ligand are *trans* to the phosphorus atoms of the biphosphine. As suggested by spectroscopic data (IR and  $^{31}\text{P}\{^1\text{H}\}$  NMR data) the geometry about the Ru(II) metal center is octahedral with small deviations from the 90 or 180° angles. Thus the chlorines are *trans* to each other and the angles N(22)–Ru(1)–N(11) and N(11)–Ru(1)–P(2) are 80.8(3) and 170.2(2)°,

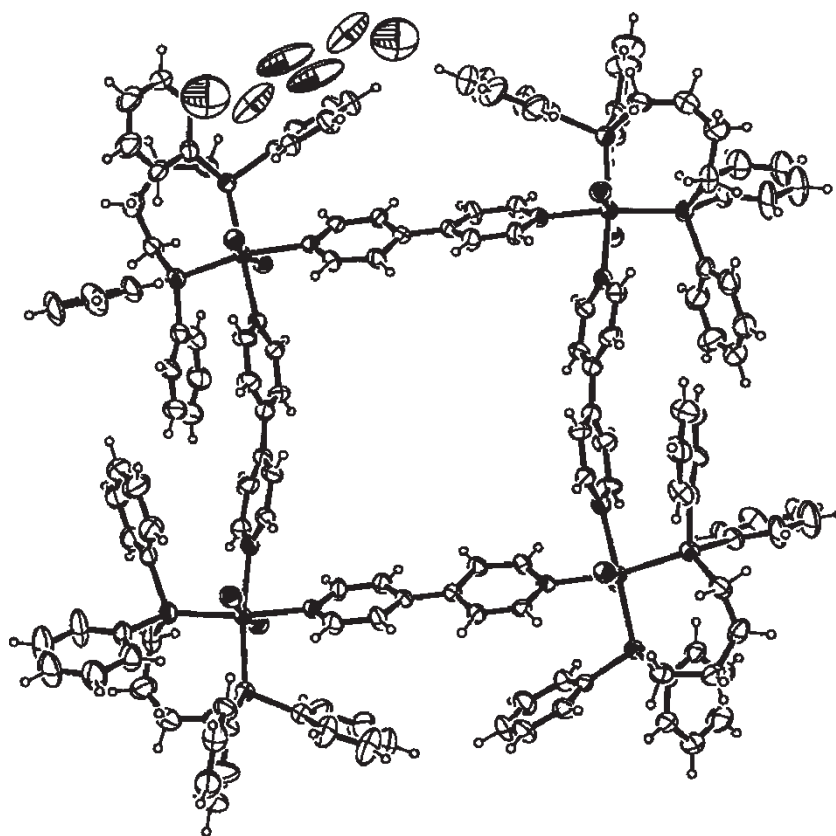


FIGURE 2 ORTEP view of the asymmetric unit of the complex  $[[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})]_4$ , showing the atom labeling and the 30% probability ellipsoids.

respectively (Table IV). The long carbon-carbon chain  $\text{P}-(\text{CH}_2)_4\text{-P}$  in the phosphine group allows the angle  $\text{P}-\text{Ru}(\text{II})-\text{P}$  to be as large as  $94.7^\circ$  (average). Due to the P-phenyl rings stacking with the 4,4'-bipyridine, the  $\text{N}-\text{Ru}(\text{II})-\text{N}$  angle is reduced to  $82.5^\circ$  (average). To accommodate this deviation from planarity, the entire molecule is puckered. The  $\text{Cl}(1)-\text{Ru}-\text{Cl}(2)$  angle is  $172.74(10)^\circ$ . The  $\text{N}(21)-\text{Ru}(2)-\text{P}(4)$ ,  $165.7(2)^\circ$ ;  $\text{N}(12)^i-\text{Ru}(2)-\text{P}3$ ,  $174.7(3)^\circ$ ;  $\text{Cl}(4)-\text{Ru}(2)-\text{Cl}(3)$ ,  $169.74(10)^\circ$  angles show that the four Ru(II) atoms are not in a perfect planar square configuration, but the shape of the molecule is undoubtedly that of a square. The Ru-Cl, Ru-N and Ru-P bond lengths (av. 2.425, 2.190 and 2.313 Å, respectively) are within the well-established range for Ru(II) complexes [3,16,18,32]. The edge-to-edge distance in the structure is of 11.493(8) Å for  $\text{Ru}(1)-\text{Ru}(2)$  and 11.382(8) Å for  $\text{Ru}(1)-\text{Ru}(2)^i$ . The diagonal Ru(II)-Ru(II) distance is 15.554(8) Å for  $\text{Ru}(1)-\text{Ru}(1)^i$  and 16.773(8) Å for  $\text{Ru}(2)-\text{Ru}(2)^i$ .

The analysis of the supramolecular organization of the complex shows that the molecular squares are stacked on top of each other along the  $a$  axis forming infinite columns. Unfortunately, the formation of the corresponding internal tunnels is prevented by

the bulky character of the phenyl groups of the diphenylphosphine ligands. As it turns out, the centers of the squares are shifted from each other by 6.473(2) Å along the (0 - 11) direction, preventing the formation of perfect channel-like cavities (Fig. 3). Each molecule is linked to the molecule just above or below it through four hydrogen bonds (Table V), two of them subtended between the Cl4 and a hydrogen atom of the dipyrindyl group and the other two between the Cl2 and another hydrogen of the dipyrindyl group. The connection between the columns is made through hydrogen bonds involving the chlorines and aromatic hydrogen atoms.

The cyclic voltammograms of the complexes (except for those with the pyrazine ligand) present only one quasi-reversible process, which was attributed to the four electrons for the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couples as suggested by pulse differential voltammetry experiments. The oxidation potentials of the tetramers follow the  $\text{p}K_a$  of the ligands (Table II) as expected. Unlike those of the other complexes, the pyrazine ligand compound presents two electrochemical processes involving two electrons ( $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couples, Fig. 4). This is consistent with a strong

TABLE IV Bond lengths (Å) and angles (°)\*

Ru(1)–N(22)	2.177(8)
Ru(1)–N(11)	2.194(8)
Ru(1)–P(2)	2.312(3)
Ru(1)–P(1)	2.315(3)
Ru(1)–Cl(1)	2.420(3)
Ru(1)–Cl(2)	2.430(3)
Ru(2)–N(21)	2.190(8)
Ru(2)–N(12) <sup>i</sup>	2.197(8)
Ru(2)–P(3)	2.311(3)
Ru(2)–P(4)	2.316(3)
Ru(2)–Cl(4)	2.421(3)
Ru(2)–Cl(3)	2.431(3)
P(1)–C(111)	1.850(7)
P(2)–C(231)	1.821(12)
P(4)–C(421)	1.909(7)
N(11)–C(10)	1.320(13)
N(11)–C(19)	1.349(13)
N(12)–C(16)	1.340(13)
N(12)–Ru(2) <sup>i</sup>	2.197(8)
N(21)–C(20)	1.312(12)
N(22)–Ru(1)–N(11)	80.8(3)
N(22)–Ru(1)–P(2)	92.1(2)
N(11)–Ru(1)–P(2)	170.2(2)
N(22)–Ru(1)–P(1)	173.3(2)
N(11)–Ru(1)–P(1)	92.4(2)
P(2)–Ru(1)–P(1)	94.56(10)
N(22)–Ru(1)–Cl(1)	88.0(2)
N(11)–Ru(1)–Cl(1)	86.9(3)
P(2)–Ru(1)–Cl(1)	99.75(11)
P(1)–Ru(1)–Cl(1)	92.01(11)
N(22)–Ru(1)–Cl(2)	88.1(2)
N(11)–Ru(1)–Cl(2)	86.5(3)
P(2)–Ru(1)–Cl(2)	86.49(11)
P(1)–Ru(1)–Cl(2)	91.18(11)
Cl(1)–Ru(1)–Cl(2)	172.74(10)
N(21)–Ru(2)–N(12) <sup>i</sup>	84.2(3)
N(22) <sup>i</sup> –Ru(2)–P(3)	174.7(3)
N(21)–Ru(2)–P(3)	94.8(2)
N(21)–Ru(2)–P(4)	165.7(2)
N(12) <sup>i</sup> –Ru(2)–P(4)	87.1(2)
P(3)–Ru(2)–P(4)	94.84(10)
N(21)–Ru(2)–Cl(4)	84.7(2)
N(12) <sup>i</sup> –Ru(2)–Cl(4)	92.8(3)
P(3)–Ru(2)–Cl(4)	92.31(10)
P(4)–Ru(2)–Cl(4)	84.46(11)
N(21)–Ru(2)–Cl(3)	85.4(2)
N(12) <sup>i</sup> –Ru(2)–Cl(3)	88.8(3)
P(3)–Ru(2)–Cl(3)	85.93(10)
P(4)–Ru(2)–Cl(3)	105.76(11)
Cl(4)–Ru(2)–Cl(3)	169.74(10)
C(111)–P(1)–C(131)	100.5(5)
C(111)–P(1)–C(121)	96.6(4)
C(131)–P(1)–C(121)	104.9(5)
C(111)–P(1)–Ru(1)	125.4(3)
C(131)–P(1)–Ru(1)	115.3(4)

\*Symmetry transformations used to generate equivalent atoms:  
 $i - x + 2, -y + 1, -z + 1.$

interaction between the ruthenium atoms in this complex, which is made possible because of the small size of the pyrazine molecule. Our suggestion is that each electrochemical process involves the oxidation of the metal centers sited on opposite positions in the square, as illustrated in Scheme 1.

One of the most relevant manifestations of metal–metal interaction is the separation of electrochemical couples [33–35]. In complexes

with similar donor atoms coordinated to both metal centers this separation is related to the comproportionation constant ( $K_c$ ). Thus measurements of  $K_c$  permitted evaluation of the degree of electronic coupling between the metal centers. In the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})\}_4$  complex the separation of the half-wave potentials is 0.17 V which gives  $K_c = 721$  much lower than the comproportionation constant of the classical Creutz-Taube mixed valence  $[(\text{NH}_3)_5\text{Ru-pz-Ru}(\text{NH}_3)_5]^{5+}$  complex where  $K_c$  is  $4.6 \times 10^6$  and belongs to class III [33]. Thus according to the Robin and Day classification the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})\}_4$  complex belongs to the class II [36].

## CONCLUSIONS

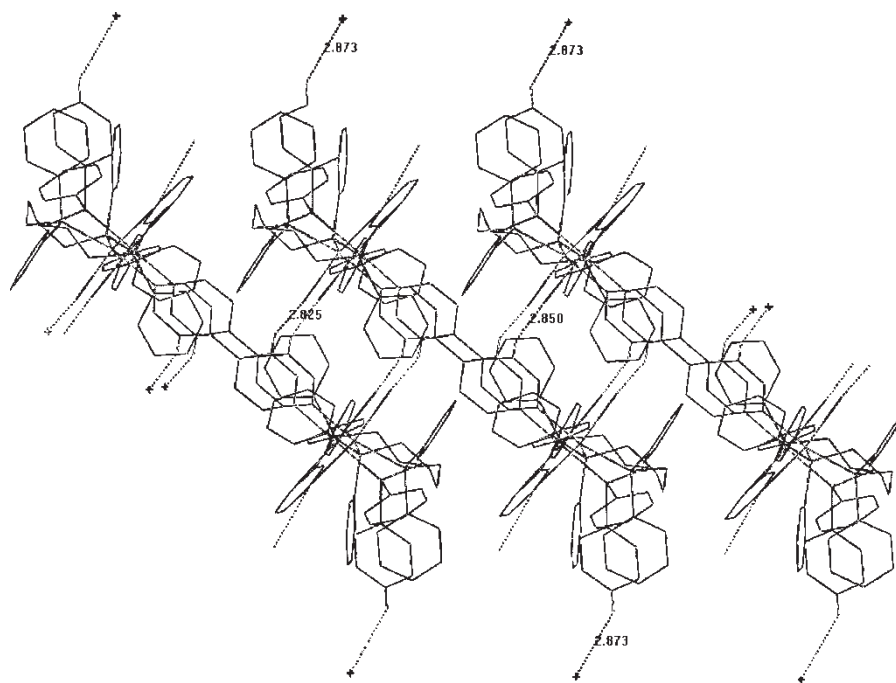
This study has demonstrated the synthetic utility of the five-coordinate complex  $[\text{RuCl}_2(\text{dppb})(\text{PPh}_3)]$  for the preparation of supramolecular species containing alterdentate ligands. Spectroscopic data (IR and  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR) suggest tetrameric structures for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-N-N})\}_4$  complexes  $[(\mu\text{-}4,4'\text{-N-N} = \text{pyrazine, } 4,4'\text{-bipyridine, } 1,2\text{-bis-}trans\text{-}(4\text{-pyridyl})\text{ethane, and } 1,2\text{-bis-}trans\text{-}(4\text{-pyridyl})\text{ethylene}]$ . The  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$  complex has been characterized by X-ray crystallography confirming the tetrameric structure for the 4,4'-bipyridine ligand. Electrochemical experiments (cyclic voltammetry and differential pulse voltammetry) show only one redox potential for the complexes containing the 4,4'-bipyridine, 1,2-bis-*trans*-(4-pyridyl)ethane and 1,2-bis-*trans*-(4-pyridyl)ethylene ligands suggesting a 4-electron process while the complex with the two pyrazine ligand redox processes was observed. Thus the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-pyrazine})\}_4$  complex can be classified as belonging to the class II according to the Robin and Day classification.

## SUPPLEMENTARY MATERIAL

Coordinates and other crystallographic data have been deposited with the deposition code CCDC 201320 for the  $\{[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})\}_4$  complex.

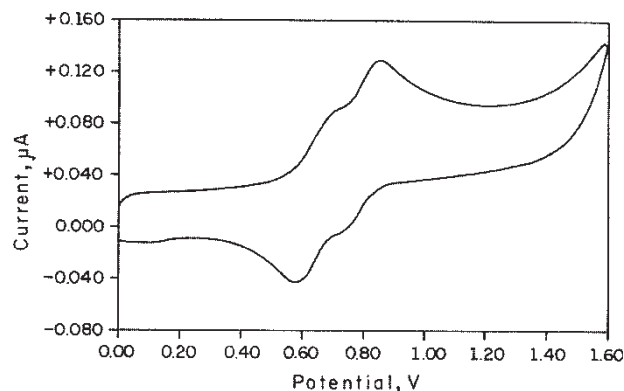
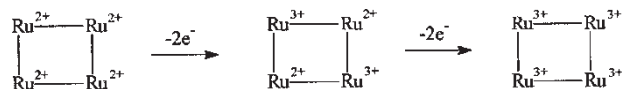
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FIGURE 3 Supramolecular organization of the  $[[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})_4$  complex.TABLE V Intermolecular interaction (Å) in the complex  $[[\text{RuCl}_2(\text{dppb})](\mu\text{-}4,4'\text{-bipy})_4$ 

Interaction*	A...H	A...D	H-D	A...H-D
$\text{Cl}4 \cdots \text{H}24^i - \text{C}24^i$	2.825(9)	3.665(9)	0.93	150.6(2)
$\text{Cl}2 \cdots \text{H}28^{ii} - \text{C}28^{ii}$	2.850(9)	3.737(9)	0.93	159.7(3)
$\text{Cl}2 \cdots \text{H}14^{iii} - \text{C}14^{iii}$	2.873(2)	3.628(2)	0.93	139.3(3)

\*Sym. Operation:  $i - x - 1, -y - 1, -z - 1$ ;  $ii x + 1, y, z$ ,  $iii - x + 1, -y, -z + 1$ .

FIGURE 4 Cyclic voltammogram of the  $[[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})_4$  complex in  $\text{CH}_2\text{Cl}_2$ ,  $0.1 \text{ mol l}^{-1}$  TBAP; measured at platinum foil electrode; reference electrode Ag/AgCl.SCHEME 1 Withdrawal of 4 electrons from the  $[[\text{RuCl}_2(\text{dppb})](\mu\text{-pz})_4$  complex via cyclic voltammetry:  $2e^-$  at  $E_{1/2} = 0.65 \text{ V}$  and  $2e^-$  at  $E_{1/2} = 0.82 \text{ V}$ .

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