

Universidade Federal de São Carlos  
Departamento de Química

**Espectroscopia Paramagnética**  
**Eletrônica:**  
**Conceitos Fundamentais e Aplicações**



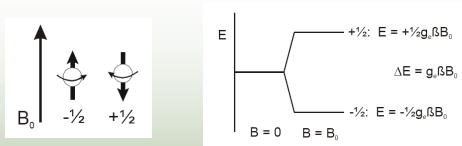
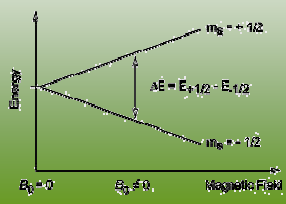
Prof. Alzir Azevedo Batista

**Introdução**

Um elétron desemparelhado pode mover-se entre os dois níveis de energia absorvendo, ou emitindo energia de radiação eletromagnética de energia  $\epsilon = h\nu$  de forma que a condição de ressonância,  $\epsilon = \Delta E$ , seja observada. A substituição de  $\epsilon = h\nu$  em  $\Delta E = g_e \beta B_0$  conduz à equação fundamental da espectroscopia de EPR, que é:

$$h\nu = g_e \beta B_0$$

- $h$  - Planck's constant  $6.626196 \times 10^{-34}$  Joule.sec
- $\nu$  - frequency (GHz or MHz)
- $g_e$  - g-factor ( $\sim 2.0$  for radicals)
- $\beta$  - Bohr magneton ( $9.2741 \times 10^{-21}$  erg.Gauss $^{-1}$ )
- $B_0$  - magnetic field (Gauss or mT)

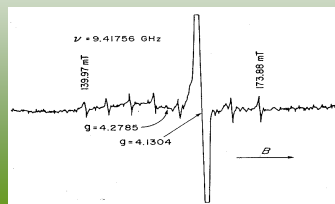



**DETERMINAÇÃO EXPERIMENTAL DE VALORES DE g**





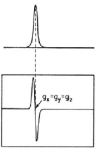



$\Delta E = h\nu = g \beta B$   $\nu = \text{cte}$  em todo experimento

$$g = \frac{h\nu}{\beta B} = \frac{(6.626076 \times 10^{-34} \text{ Js})(9.41756 \times 10^9 \text{ s}^{-1})}{(9.27402 \times 10^{-24} \text{ JT}^{-1}) \times B}$$

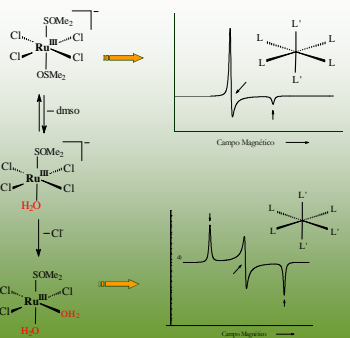
Espectro de  $\text{Fe}^{3+}$  e  $\text{Co}^{2+}$  em MgO a 4.2 K.  
Para  $\text{Fe}^{3+}$   $B = 162.906 \text{ mT}$   $g = 4.1304$   
Para  $\text{Co}^{2+}$   $g = 4.2785$   $^{59}\text{Co}$  ( $I = 7/2$ )

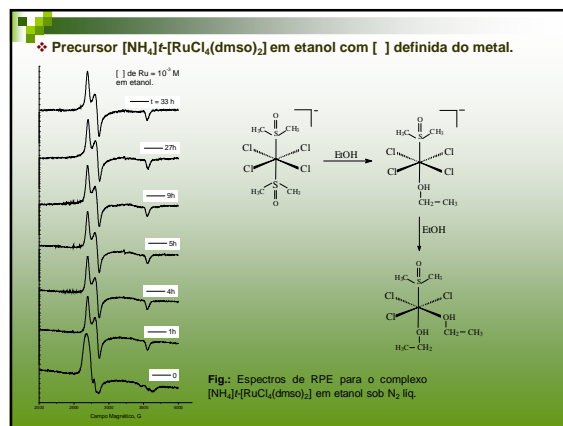
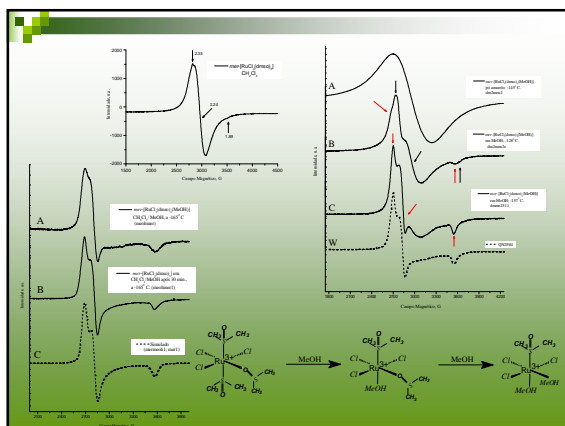
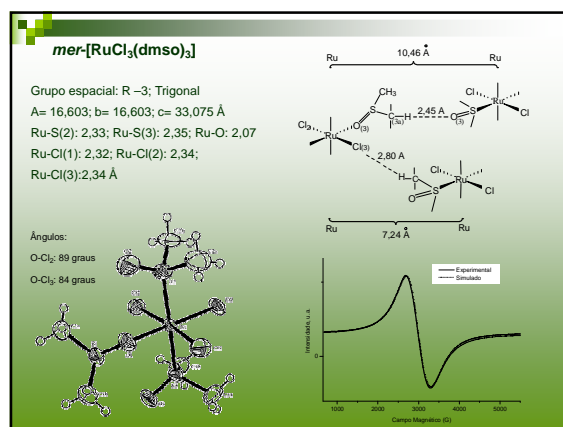
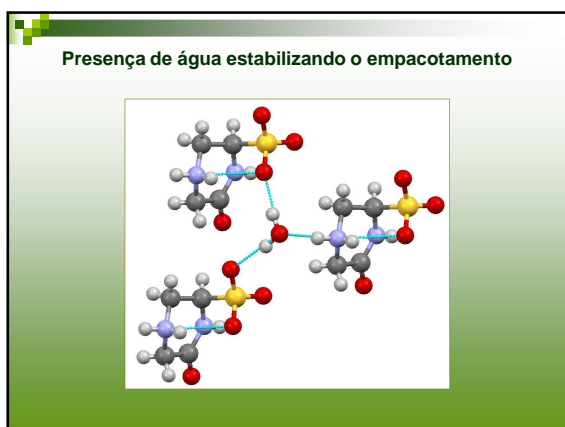
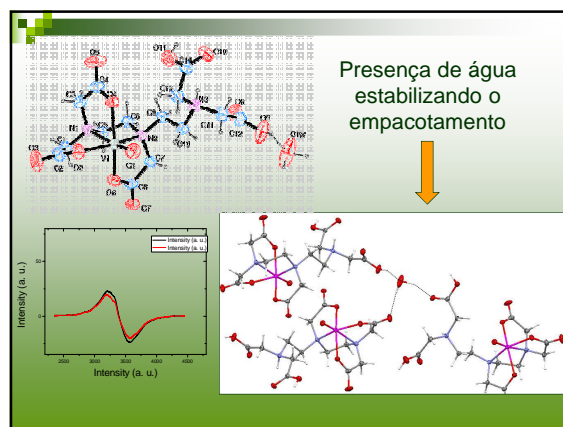
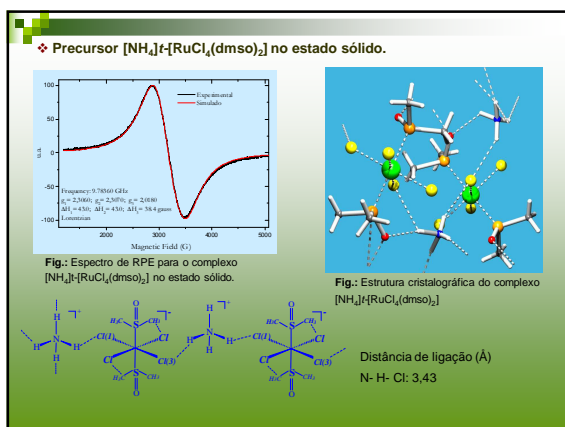


**Interações Anisotrópicas**

(a) ISOTROPIC	(b) AXIAL	(c) AXIAL	(d) RHOMBIC
$g_x = g_y = g_z$	$g_x = g_y < g_z$	$g_x = g_y > g_z$	$g_x \neq g_y \neq g_z$
			
			
MAGNETIC FIELD $\rightarrow$			

❖ Precursor  $[\text{NH}_4][\text{r-RuCl}_4(\text{dmsO})_2]$  em solução.





**Síntese da espécie  $t\text{-}[\text{RuCl}_4(\text{dmsol})(\text{im})]$  a partir do complexo  $t\text{-}[\text{RuCl}_4(\text{dmsol})_2]$**

Acetona  
DMSO  
imidazol

Com cátion  $[(\text{DMSO})_2\text{H}]$  ou  $(\text{CH}_3\text{CH}_2)_2\text{NH}_2\text{Cl}$ , a espécie cristaliza com imH.  
Com  $\text{Na}^+$  e im em excesso, a cristalização ocorre com o  $\text{Na}^+$ .

Distâncias de ligação (Å)

Ru(1)-N(1)	2.098(3)
Ru(1)-S(1)	2.2924(9)
Ru(1)-Cl(4)	2.3297(10)
Ru(1)-Cl(2)	2.3730(10)
Ru(1)-Cl(3)	2.3763(10)
S(1)-O(1)	1.489(3)

Sist. Cristalino: Triclinico

Fig.: Produto da reação entre o complexo  $t\text{-}[\text{RuCl}_4(\text{dmsol})_2]$  e o ligante imidazol.

**Estrutura do  $[\text{RuCl}_3(\text{dppb})\text{H}_2\text{O}]$  e Espectros de EPR do  $[\text{RuCl}_3(\text{dppb})\text{L}]$  (DMSO,  $\text{H}_2\text{O}$ , MeOH), em estado sólido, -160°C**

L = DMSO, py, MeOH

Inorganic Chemistry, Vol. 38, No. 23, 1999

**Caracterização de compostos paramagnéticos**

0.5 mol 4,4'-Bipy  
1.1 mol 4,4'-Bipy

$\text{CH}_2\text{Cl}_2$

$g_1 = 2.893$   
 $g_2 = 2.124$   
 $g_3 = 1.685$

JBCS, v. 17, p. 1634-1641, 2006.

**O que é ESR?**

- Resonance position (g-factor)
- Multiplet structure (hyperfine interaction)
- Lineshape (width, symmetry,...)
- Intensity (amplitude/area)

"Fingerprint" to identify the paramagnetic species

**O que é ESR?**

**Zeeman Effect**

Energy

$M_s = +\frac{1}{2}$   
 $M_s = -\frac{1}{2}$

$\Delta E = h\nu = g\beta B$

$B = 0$   $B > 0$

**Electron Paramagnetic Resonance (EPR)**  
**Electron Spin Resonance (ESR)**  
**Electron Magnetic Resonance (EMR)**  
EPR - ESR - EMR

$h$  Planck's constant  $6.626196 \times 10^{-34}$  Joule.sec  
 $\nu$  frequency (GHz or MHz)  
 $g$  g-factor ( $\sim 2.0$  for radicals)  
 $\beta$  Bohr magneton ( $9.2741 \times 10^{-21}$  erg.Gauss $^{-1}$ )  
 $B$  magnetic field (Gauss or mT)

ESR: resonant absorption of microwaves by paramagnetic systems subjected to an external magnetic field

$h\nu = g\beta B$  (g-factor)  
 $\nu = (g\beta/h)B = 2.8024 \times B$  MHz

$\nu/B = 3480$ G	$\nu = 9.75$ GHz (X-band)
$\nu/B = 420$ G	$\nu = 1.2$ GHz (L-band)
$\nu/B = 110$ G	$\nu = 300$ MHz (Radiofrequency)

**Hyperfine Interaction**

Elétron  $S(1/2)$  Nucleus  $I(1/2)$

$M_s = \pm 1/2$   $M_I = \pm 1/2$

$\Delta E_1$   $\Delta E_2$

"doublet"

$E = g\beta BS_z + (hA_0)S_zI_z$   
 $E = g\beta BS_z + (a)S_zI_z$   
( $hA_0$  (Hz)  $\rightarrow$  a (G) via g-factor)

**Selection Rule**  
 $\Delta M_s = \pm 1$  (electron)  
 $\Delta M_I = 0$  (nuclear)

$\Delta E_1 = g\beta B + a/2$   
 $\Delta E_2 = g\beta B - a/2$   
 $\Delta E_1 - \Delta E_2 = a$

### Hyperfine Interaction

Electron  
S (½)

↑

Nucleus  
I (1)

↓

$M_S$

+½

-½

$M_S = \pm ½$

$M_I$

+1

+0

-1

-1

+0

+1

triplet

Selection rule  
 $\Delta M_S = \pm 1$  (electron)  
 $\Delta M_I = 0$  (nuclear)

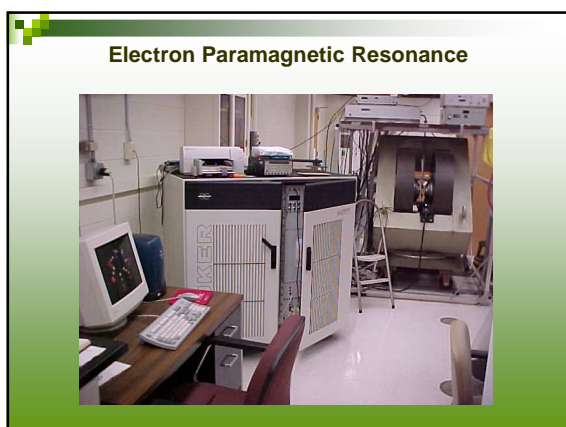
$\Delta E_1 = g\beta B + a$   
 $\Delta E_2 = g\beta B$   
 $\Delta E_3 = g\beta B - a$

$E = g\beta B S_z + (hA_n) S_z I_z$   
 $E = g\beta B S_z + (a) S_z I_z$   
( $hA_n$  (Hz)  $\rightarrow$  a (G) via g-factor)

### The EMR Experiment

A few numbers:

- experiments at several temperatures
- solid- or liquid-state samples



### Fe(III) – d<sup>5</sup> and Fe(II) – d<sup>6</sup>

High spin  
Fe<sup>III</sup> – d<sup>5</sup>

Total spin,  $S = \frac{5}{2}$

Low spin  
Fe<sup>III</sup> – d<sup>5</sup>

Total spin,  $S = \frac{1}{2}$

High spin  
Fe<sup>II</sup> – d<sup>6</sup>

Total spin,  $S = 2$

### Glyoxalase II – é uma enzima hidrolítica responsável pela desintoxicação do metilgloxal empregando glutamina.

**Fe(III) – S=5/2**

**Mn(II) – S=1/2, I=5/2**

**GLXII + SLG**

**GLXII + GSH**

**Fe(III)/Fe(II) – Antiferro coupling**  
Fe(III) S=5/2 and Fe(II) S=2 giving S=1/2

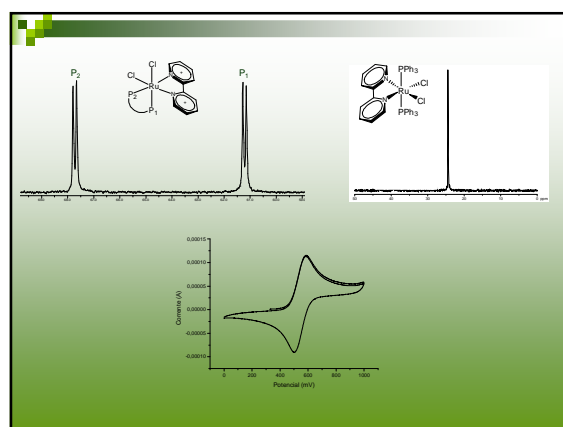
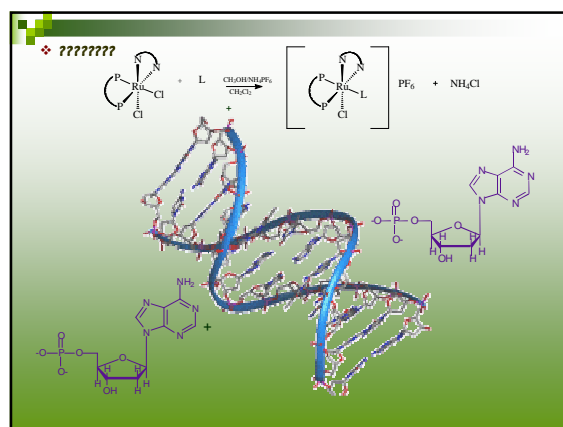
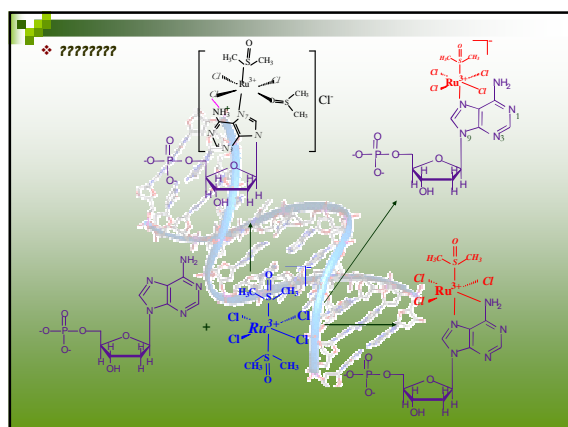
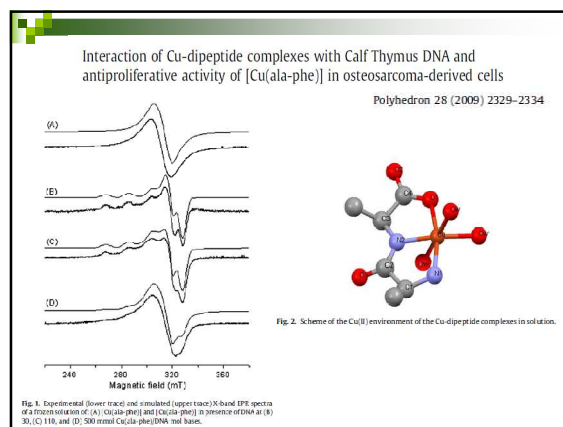
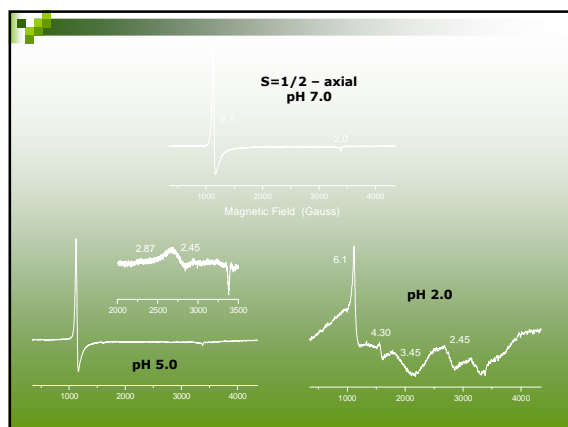
Magnetic field (mT)

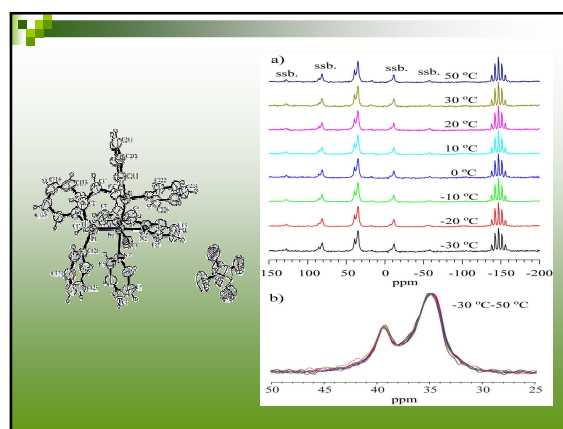
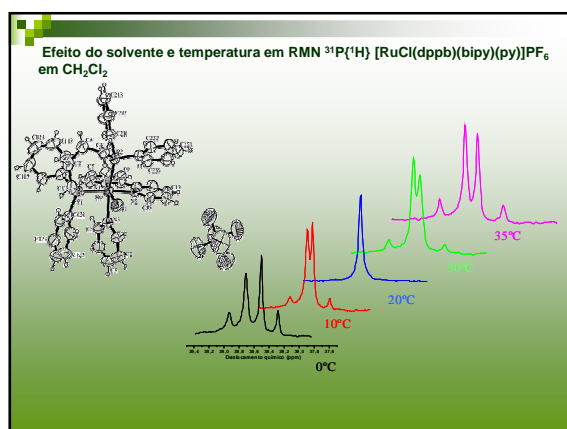
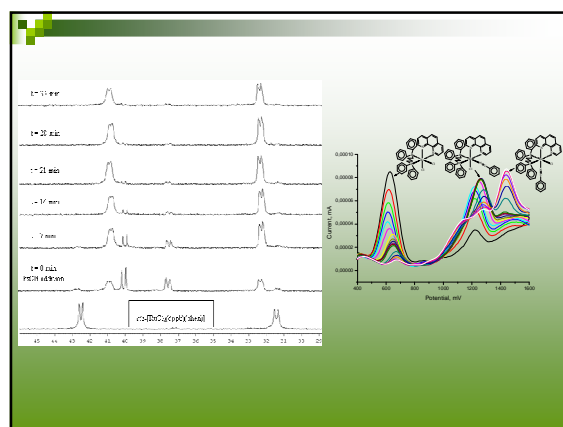
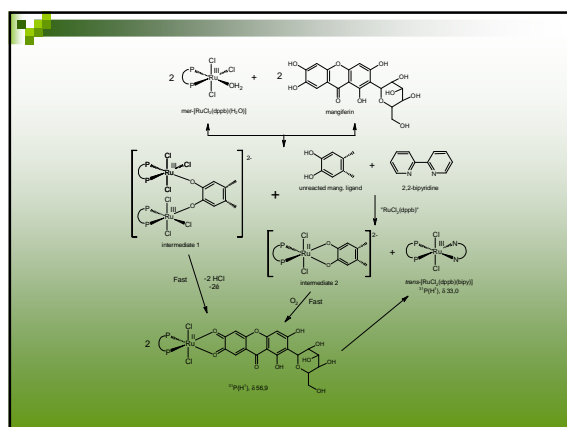
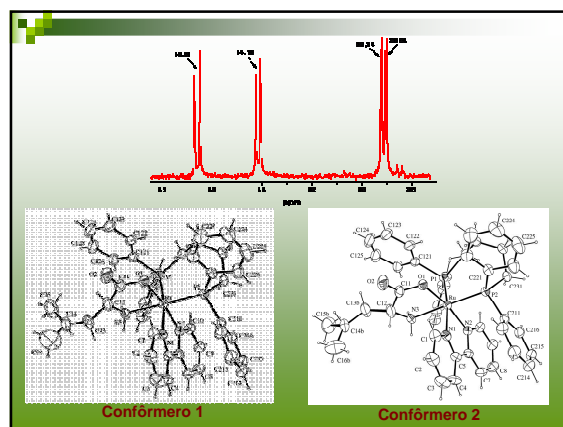
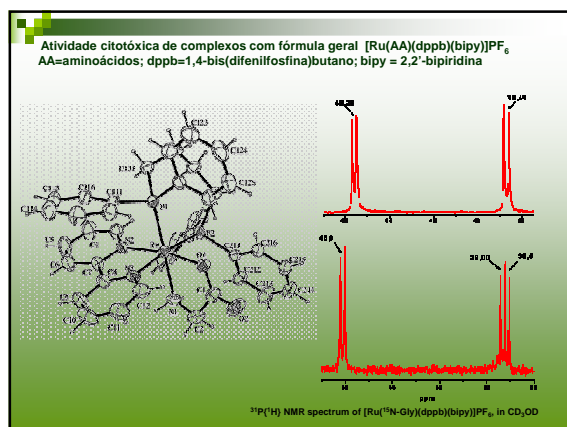
Campos et al. Biochemistry (2007)

### Hemoglobina

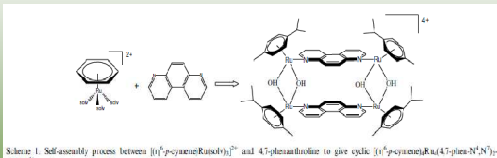
#### Equilíbrio entre espécies de ferro (III) em função do pH da hemoglobina

Moreira et al. Biophys. Chem. (2005)

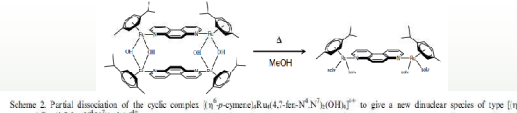




**Cyclic tetranuclear half-sandwich ruthenium(II) complexes with 4,7-phenanthroline and hydroxo bridges: Crystal structure, solution behaviour and binding to nucleosides**  
 Journal of Inorganic Biochemistry 102 (2008) 1025–1032



Scheme 1. Self-assembly process between  $[Ru(p\text{-cymene})Ru(OH)_2]^{2+}$  and 4,7-phenanthroline to give cyclic  $[Ru(p\text{-cymene})_2Ru(4,7\text{-phen-}N^2,N^3)]^{2+}(OH)_2$  species (sol = solvent).



Scheme 2. Partial dissociation of the cyclic complex  $[Ru(p\text{-cymene})_2Ru(4,7\text{-phen-}N^2,N^3)]^{2+}(OH)_2^+$  to give a new dinuclear species of type  $[Ru(p\text{-cymene})Ru(4,7\text{-phen-}N^2,N^3)]^{2+}$ .

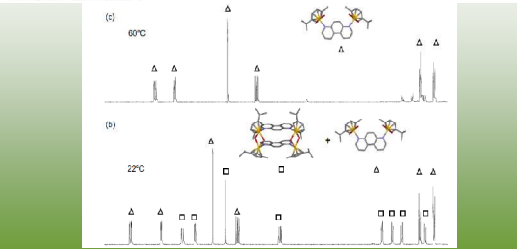
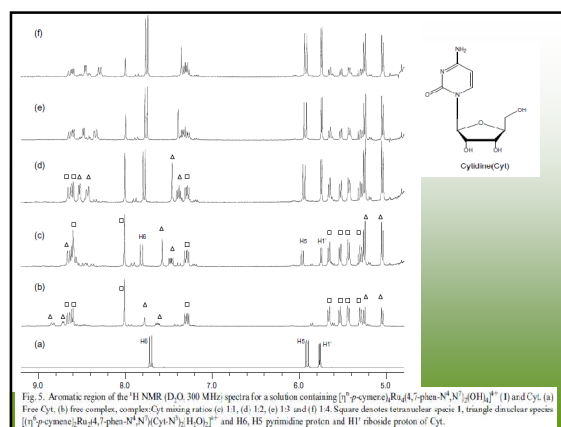
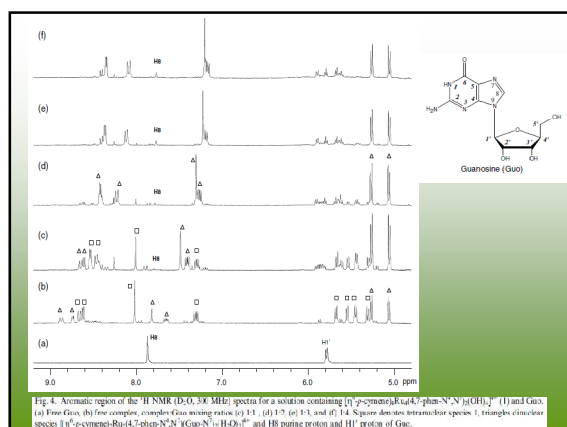
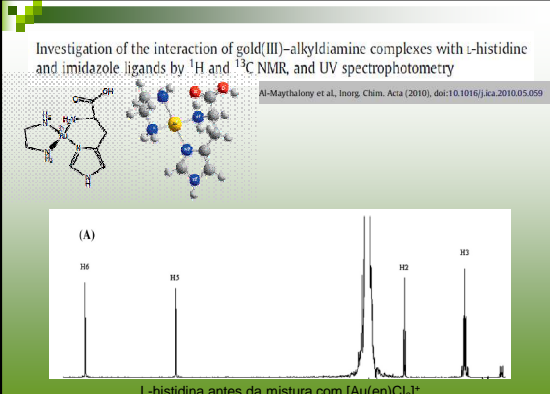


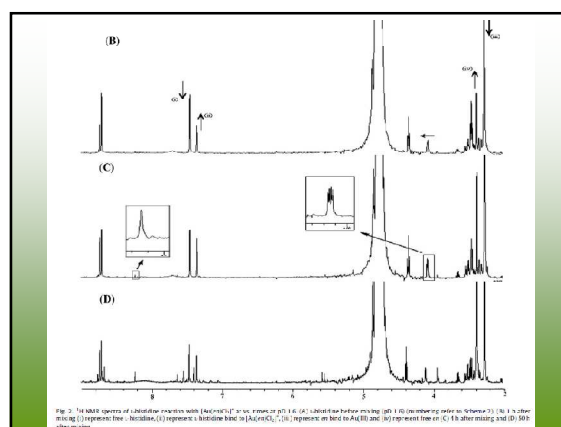
Fig. 3.  $^1H$  NMR spectrum in MeOD of (a) free 4,7-phenanthroline, (b) complex 1a at 22°C, and (c) at 60°C. It should be noted that this dissociation process is reversible upon cooling.



**Investigation of the interaction of gold(III)-alkyldiamine complexes with L-histidine and imidazole ligands by  $^1H$  and  $^{13}C$  NMR, and UV spectrophotometry**  
 Al-Maythaly et al., Inorg. Chim. Acta (2010), doi:10.1016/j.ica.2010.05.059



(A) L-histidine antes da mistura com  $[Au(en)Cl_2]^+$



### Referências Bibliográficas

A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Wiley, New York, 1979.

A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Clarendon, Oxford, 1970.

W. Weltner, Jr., "Magnetic Atoms and Molecules," Van Nostrand Reinhold, New York, 1983.

J. Weil, Ed., "Electronic Magnetic Resonance of the Solid State," Canadian Society for Chemistry, Ottawa, 1987.

J. R. Pilbrow, "Transition Ion Paramagnetic Resonance," Clarendon, Oxford, 1990.

L. Kevan and R. N. Schwartz, Eds., "Time Domain Electron Spin Resonance," Wiley, New York (1979).