

**CALCULATION OF BOND LENGTH, BOND ANGLE AND  
DISTORTION DEGREE IN RU(III) COMPLEXES  
DERIVED FROM FORMYLHYDRAZINE (L)  
BY MOLECULAR MECHANICS**

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**ABSTRACT**

Structural studies of transition metal complexes by crystallographic method need the obtaining of monocrystals which are not always possible. Molecular mechanics calculations help to avoid this difficulty. Indeed, with the powerful logical and powerful computer one can study the structure of the transition metal complexes and determine their most common conformations. In this work, structural studies of Ru(III) complexes derived from formylhydrazine (L) are studied by molecular mechanics calculations. The complexes were previously synthesised and characterised by spectroscopic methods and elemental analysis (C, H, N). On the basis of these results the structural formulae were proposed. We applied the molecular mechanics calculations to determine the more stable geometry of the complex which is less steric energy. The bond length and bond angle are determined for this geometry and for which the charges on atoms and the atomic coordinates using the extended Huckel theory were calculated. The data obtained are in good agreement with the experimental studies and that reported in literature. Degrees of distortion were evaluated for the complexes and the iodide complexes have more distortion structures. These complexes are studied for biological, pharmacological and medicinal interests.

## INTRODUCTION

In the last twenty years molecular mechanics method becomes essential to experimental chemists. Powerful software associated with powerful computers put the practical representation of many aspects of chemical structure and reactivity. The molecular mechanics calculation allows to calculate the energy of the molecule [Williams et al., (1968); Altona & Faber (1974); Engler et al., (1973); Allinger (1976); Ermer (1976); Niketic & Rasmussen (1977); Mislou et al., (1978); Ermer (1981); Boyd & Lipkowitz (1982), Cox (1982); Osawa & Musso (1983); Osawa & Musso (1983) and Burbert & Allinger (1982)]. This energy is mainly the sum of three contributions [Kearley & Nicolai (2000)]. An internal contribution with brings in; bond lengths, deformation angles and torsion angles, and an external contribution bringing in a Van Der Waals term and a coulomb interaction.

Molecular mechanic was successfully applied to organic compounds [Burkert & Allinger (1982); Rameau et al., (1998); Rameau et al., (1998) and Bierbach & Farrell (1997)]. However, this method obtained a bigger interest after its use in inorganic systems [Saito (1985); Hancock & Martell (1989); Pozigun et al., (1990); Zinelabidine et al., (1993); Coelho et al., (1999); Blaive et al., (1995); Jemmis & Sharma (2001) and Sternberg et al., (2001)].

In this paper we report, a structural study of Ru(III) complexes derived from formyl- hydrazine (L), using molecular mechanics calculations. These compounds were synthesized because of their biological and pharmacological activities and they can serve as eventual medicinal drugs and probes. Also, formyl hydrazine presents a big cytostatic activity [Weitzel et al., (1967)]. It reduces of tumor more than 60% in eight cases among eleven alive animals. This activity is emphasized on complexation. Transition metal complexes with ligands containing nitrogen and oxygen have recently received great attention because of their role in carcinogenesis and chemotherapy.

Sliocik et al series of work have been done on ruthenium(III) complexes as antitumour agents [Sliocik et al., (2000)].

Ruthenium has received an even poorer interest and besides the use in histology, neither ruthenium ions nor ruthenium compounds have a clear role in medicine and biology. In this way, many studies have been published, showing the role of ruthenium complexes in cancer therapy and tumor growth control [Zorzet et al., (2001); Sava & Bergamo



(2000); Magnarin et al., (2000); Alessio et al., (2000); Cocchietto & Sava (2000) and Sava & Cocchietto (2000)].

As the complex activity depends on its geometry, we have used molecular mechanics calculation to the different conformers of these complexes in order to determine the most stable geometry. And then for each complex we determined the important bond distances and bond angles and we calculated the degrees of distortion, charges on atoms and atomic coordinates.

## EXPERIMENTAL

The complexes  $[\text{Ru}_2(\text{L})_2\text{Cl}_6\text{EtOH}]\text{EtOH}$ ,  $[\text{Ru}(\text{L})_2\text{I}_3\text{EtOH}]2\text{EtOH}$  and  $[\text{Ru}(\text{L})_2\text{Br}_3\text{EtOH}] 3/2\text{EtOH}$  were synthesised [Mostafa et al., (2002)]. The formulae and structures of these complexes have been suggested on the basis of the spectroscopic analysis (IR, UV), elemental analysis and magnetic susceptibility measurements.

We applied these complexes to molecular mechanics calculation using hyperchem (Hypercube, Inc. Canada). The geometry optimisation and energy minimisation for these complexes were performed by Fletcher Reeves conjugate gradient algorithm [Fletcher (1980)]. The residual gradient did not go beyond  $0.01 \text{ Kcal.mol}^{-1}.\text{\AA}^{-1}$ . For each complex, the calculation was done using an MM+ force field.

We determine the most stable conformer which is the one with the less steric energy. For this conformer we calculate bond lengths and bond angles.

After the optimisation of the geometry and minimisation of the energy, we applied to the optimise geometry semi empirical calculation using extended Huckel theory in order to calculate the charges on atoms and atomic coordinates.

Either in molecular mechanics or semi empirical calculations; the solvent effects (solvent existing out side of the coordination sphere) are not included. The freedom from lattice effects may allow a molecular mechanics calculation to generate a model of the structure superior to a structure determined by crystallography [Hancock et al., (1987)].

## RESULTS AND DISCUSSION

The optimized geometries of the different possible conformers of Ru(III) complexes (Figs.1a-3g) are represented with their respective

minimized steric energies and residual gradients. For each complex the most common conformation is the one with the less steric energy. We are interested by the geometry with the less steric energy. The steric energies calculated (Figs. 1a-3g) are higher than the values obtained by Lin et al for the Fe(III) complexes [Lin et al., (1994)].

The important bond distances and bond angles for the most stable geometries are summarized in Tables (1-6). These values indicate that Ru(III) complexes have an octahedral structure, which is in good agreement with the results found in literature [Mostafa et al., (2002)]. The Ru-O distance varies with the nature of oxygen. This phenomenon was observed by Hurthouse et al [Hurthouse et al., (1975)] for copper complexes.

Table 7 provides a comparison of the distortion degrees in the octahedral complexes. These degrees are evaluated using equation (1), mentioned in literature [Wang et al., (1993)].

$$\Delta t = (1/6)\Sigma[(R_i - R)/R]^2 \quad (1)$$

Where  $R_i$  is the individual Ru-X distance (X is the atom bonded to the metal ion) and R is the mean Ru-X distance.

The most stable geometry of  $[\text{Ru}_2(\text{L})_2\text{Cl}_6\text{EtOH}]\text{EtOH}$  shown in Figure 1 present one ligand and one chlorine atom in axial substitution and the equatorial chlorine are in trans position. In the case of  $[\text{Ru}(\text{L})_2\text{Br}_3\text{EtOH}]\text{3/2EtOH}$ , we have in axial position one bromine and the ethanol molecule, the  $\text{Br}_{\text{eq}}$  are trans (Fig.2). While for the complex  $[\text{Ru}(\text{L})_2\text{I}_3\text{EtOH}]\text{2EtOH}$  the most common conformation is the one with the ligand and one iodine in axial substitution and the two  $\text{I}_{\text{eq}}$  in cis position (Fig.3).

Ruthenium (III) complexes have octahedral structures. The principal bond angles and bond distances for Ru(III) complexes (Tables 1-6) show that these structures are distorted. Indeed, we observe that the axial bonds are in general shorter than the equatorial ones. Moreover, this distortion is confirmed by the degrees of distortion (Table 7) which indicate that the iodide complex has the higher distortion and the chloride complex has the less one. For these three complexes, Ru-N bond length is in good agreement with the values found in literature [Spasojevic-de Bire et al., (2001)]. the bond angles values about the coordinated nitrogen (tables 2, 4 and 6) indicate that the nitrogen is well kept in its  $\text{sp}^3$  configuration and therefore the ligand act in its keto form.

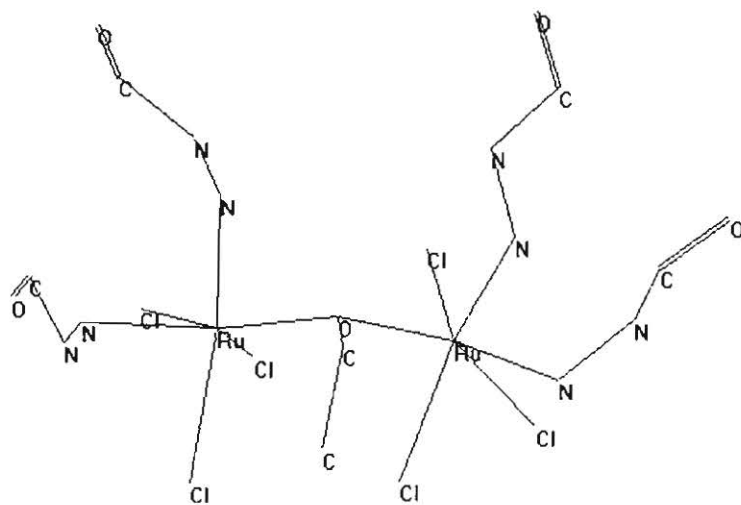


Fig.(1a)- Steric Energy=77.042801 Kcal/mol  
Residual Gradient=0.009506 Kcal/mol<sup>-1</sup>Å<sup>-1</sup>

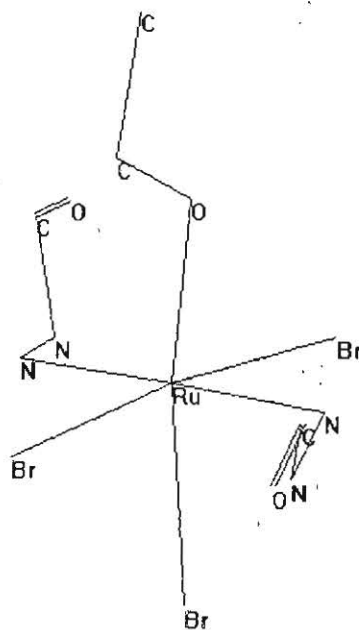
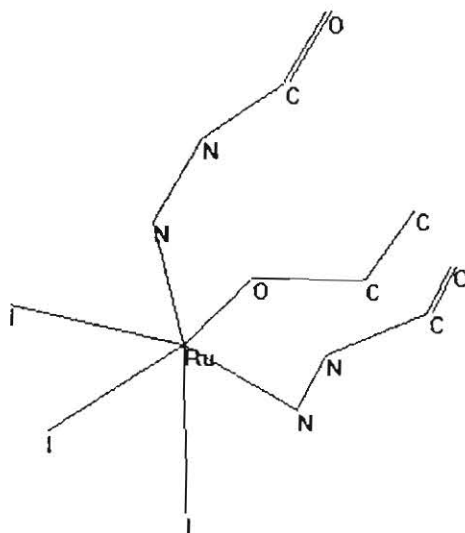


Fig.(2a)- Steric Energy=15.000175 Kcal/mol  
Residual Gradient=0.009983 Kcal/mol<sup>-1</sup>Å<sup>-1</sup>



**Fig.(3a)**- Steric Energy=13.021419 Kcal/mol  
Residual Gradient=0.007696 Kcal/mol<sup>-1</sup>Å<sup>-1</sup>

**Table 1.** Some bond lengths for [Ru<sub>2</sub>(L)<sub>2</sub>Cl<sub>6</sub> ETOH] ETOH

Atoms	Bond lengths(Å)	Atoms	Bond lengths(Å)
Ru(20)-Cl(37)	2.269	C(7)-C(6)	1.548
Ru(20)-N(36)	1.988	N(36)-N(3)	1.384
Ru(20)-Cl(19)	2.281	N(3)-C(39)	1.413
Ru(20)-Cl(5)	2.270	C(39)-O(2)	1.231
Ru(20)-N(18)	2.017	N(18)-N(17)	1.385
Ru(20)-O(8)	1.991	N(17)-C(16)	1.414
Ru(13)-Cl(35)	2.268	C(16)-O(15)	1.231
Ru(13)-N(38)	1.998	N(11)-N(14)	1.385
Ru(13)-O(8)	1.981	N(14)-C(10)	1.414
Ru(13)-N(11)	2.010	C(10)-O(9)	1.231
Ru(13)-Cl(12)	2.282	N(38)-N(44)	1.385
Ru(13)-Cl(4)	2.270	N(44)-C(45)	1.414
O(8)-C(7)	1.459	C(45)-O(1)	1.231



Table 2. Some bond angles for [Ru<sub>2</sub>(L)<sub>2</sub>Cl<sub>6</sub> ETOH] ETOH

Atoms	Bond angles (degrees)	Atoms	Bond angles (degrees)
Cl(37)-Ru(20)-Cl(5)	84.9675	Cl(35)-Ru(13)-O(8)	90.7279
Cl(37)-Ru(20)-O(8)	101.844	Cl(12)-Ru(13)-N(11)	82.0344
Cl(37)-Ru(20)-N(36)	166.675	Cl(12)-Ru(13)-N(38)	82.4499
Cl(37)-Ru(20)-Cl(19)	89.4658	Cl(12)-Ru(13)-Cl(4)	159.751
Cl(37)-Ru(20)-N(18)	83.7839	Cl(12)-Ru(13)-O(8)	102.649
Cl(5)-Ru(20)-O(8)	102.189	N(11)-Ru(13)-N(38)	99.0028
Cl(5)-Ru(20)-N(36)	86.7751	N(11)-Ru(13)-Cl(4)	79.8612
Cl(5)-Ru(20)-Cl(19)	164.963	N(11)-Ru(13)-O(8)	169.712
Cl(5)-Ru(20)-N(18)	88.3752	N(38)-Ru(13)-Cl(4)	89.4697
O(8)-Ru(20)-N(36)	90.1068	N(38)-Ru(13)-O(8)	90.7432
O(8)-Ru(20)-Cl(19)	92.6148	Cl(4)-Ru(13)-O(8)	97.0509
O(8)-Ru(20)-N(18)	168.349	H(49)-N(38)-Ru(13)	109.196
N(36)-Ru(20)-Cl(19)	95.9222	N(44)-N(38)-Ru(13)	115.336
N(36)-Ru(20)-N(18)	85.5477	H(23)-N(11)-Ru(13)	109.248
Cl(19)-Ru(20)-N(18)	77.1243	N(14)-N(11)-Ru(13)	114.347
Cl(35)-Ru(13)-Cl(12)	84.6641	H(42)-N(36)-Ru(20)	109.658
Cl(35)-Ru(13)-N(11)	84.6641	N(3)-N(36)-Ru(20)	113.406
Cl(35)-Ru(13)-N(38)	167.04	N(17)-N(18)-Ru(20)	116.514
Cl(35)-Ru(13)-Cl(4)	103.124	H(26)-N(18)-Ru(20)	108.98

Table (3): Some bond lengths for  $[\text{Ru}(\text{L})_2\text{Br}_3\text{ ETOH}] \cdot 3/2\text{ ETOH}$ 

Atoms	Bond lengths(Å)
Ru(12)-Br(9)	2.410
Ru(12)-N(14)	1.978
Ru(12)-Br(11)	2.417
Ru(12)-Br(13)	2.414
Ru(12)-O(8)	1.934
Ru(12)-N(10)	1.979
N(14)-N(19)	1.382
N(19)-C(4)	1.413
C(4)-O(3)	1.231
N(10)-N(7)	1.382
N(7)-C(6)	1.413
C(6)-O(5)	1.231
O(8)-C(2)	1.436
C(2)-C(1)	1.547

Table (4): Some bond angles for  $[\text{Ru}(\text{L})_2\text{Br}_3\text{ ETOH}] \cdot 3/2\text{ ETOH}$ 

Atoms	Bond angles (degrees)	Atoms	Bond angles (degrees)
Br(9)-Ru(12)-Br(11)	86.0811	N(14)-Ru(12)-N(10)	173.847
Br(9)-Ru(12)-N(14)	89.172	O(8)-Ru(12)-Br(13)	101.958
Br(9)-Ru(12)-O(8)	168.08	O(8)-Ru(12)-N(10)	86.8326
Br(9)-Ru(12)-Br(13)	86.6177	Br(13)-Ru(12)-N(10)	94.2602
Br(9)-Ru(12)-N(10)	89.3856	H(16)-N(10)-Ru(12)	110.843
Br(11)-Ru(12)-N(14)	100.132	N(7)-N(10)-Ru(12)	115.923
Br(11)-Ru(12)-O(8)	86.5213	H(21)-N(14)-Ru(12)	112.126
Br(11)-Ru(12)-Br(13)	171.519	N(19)-N(14)-Ru(12)	109.423
Br(11)-Ru(12)-N(10)	85.966	C(4)-N(19)-N(14)	122.111
N(14)-Ru(12)-O(8)	94.3113	C(6)-N(7)-N(10)	122.134
N(14)-Ru(12)-Br(13)	79.5878		



**Table 5.** Some bond lengths for [Ru (L)<sub>2</sub> I<sub>3</sub> ETOH] 2 ETOH

Atoms	Bond lengths(Å)	Atoms	Bond lengths(Å)
Ru(12)-N(9)	1.976	C(2)-C(1)	1.546
Ru(12)-O(14)	1.933	O(14)-H(24)	0.979
Ru(12)-N(13)	1.976	N(13)-N(7)	1.382
Ru(12)-I(8)	2.602	N(7)-C(4)	1.413
Ru(12)-I(10)	2.603	C(4)-O(3)	1.231
Ru(12)-I(11)	2.607	N(9)-H(18)	1.020
N(9)-N(6)	1.383	C(5)-H(20)	1.051
N(6)-C(5)	1.413	N(6)-H(19)	0.998
C(5)-O(16)	1.231	O(14)-C(2)	1.435

**Table 6.** Some bond angles for [Ru (L)<sub>2</sub> I<sub>3</sub> ETOH] 2 ETOH

Atoms	Bond angles (degrees)	Atoms	Bond angles (degrees)
N(9)-Ru(12)-O(14)	93.8696	N(13)-Ru(12)-I(11)	165.563
N(9)-Ru(12)-N(13)	103.276	I(8)-Ru(12)-I(10)	87.5763
N(9)-Ru(12)-I(8)	170.115	I(8)-Ru(12)-I(11)	84.6944
N(9)-Ru(12)-I(10)	86.352	I(10)-Ru(12)-I(11)	84.0329
N(9)-Ru(12)-I(11)	86.9215	H(18)-N(9)-Ru(12)	109.375
O(14)-Ru(12)-N(13)	107.735	N(6)-N(9)-Ru(12)	112.505
O(14)-Ru(12)-I(8)	90.039	H(22)-N(13)-Ru(12)	109.357
O(14)-Ru(12)-I(10)	165.331	N(7)-N(13)-Ru(12)	112.897
O(14)-Ru(12)-I(11)	81.335	C(5)-N(6)-N(9)	122.12
N(13)-Ru(12)-I(8)	84.104	N(13)-N(7)-C(4)	122.238
N(13)-Ru(12)-I(10)	86.4208		

**Table 7 :** Degrees of distortion within the Ru(III) octahedral.

Compound	Central metal	Distortion ( $\Delta l \cdot 10^4$ )
[Ru <sub>2</sub> (FH) <sub>2</sub> Cl <sub>6</sub> ETOH] ETOH	Ru(13)	42.288
	Ru(20)	41.556
[Ru (FH) <sub>2</sub> I <sub>3</sub> ETOH] 2 ETOH	Ru(12)	198.335
[Ru(FH) <sub>2</sub> Br <sub>3</sub> ETOH] 3/2ETOH	Ru(12)	106.148

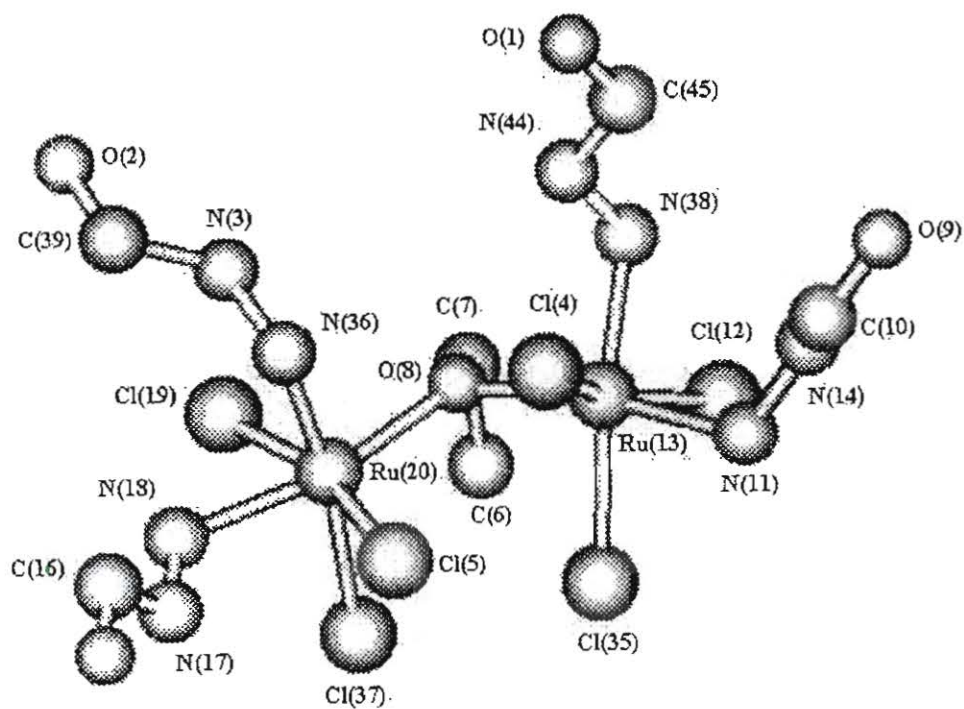


Fig. (1): The most stable geometry of  $[\text{Ru}_2(\text{L})_2\text{Cl}_6]\cdot 2\text{EtOH}$ , drawn by Hyperchem.

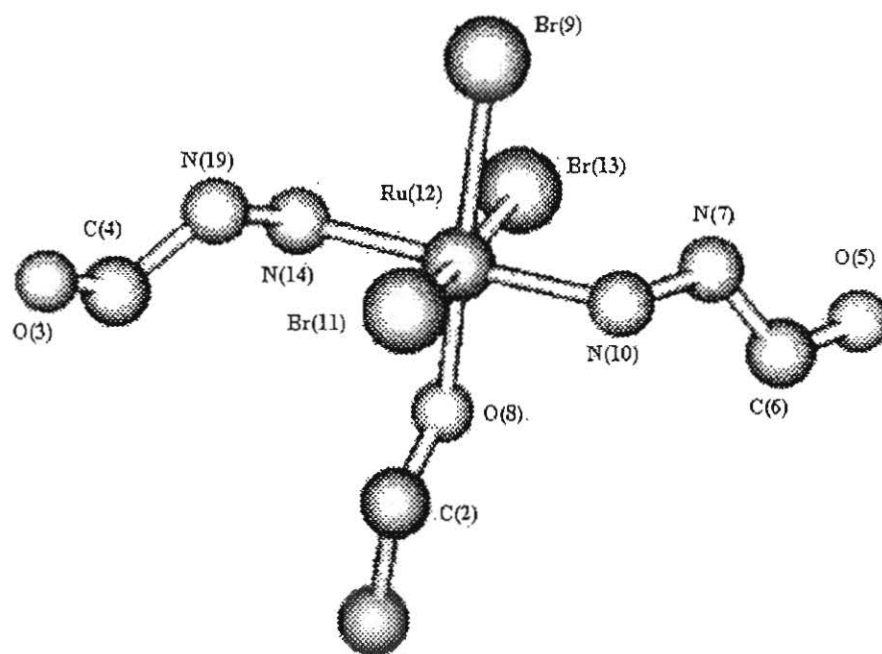


Fig. (2): The most stable geometry of  $[\text{Ru}(\text{L})_2\text{Br}_3\cdot\frac{3}{2}\text{EtOH}]$ , drawn by Hyperchem.



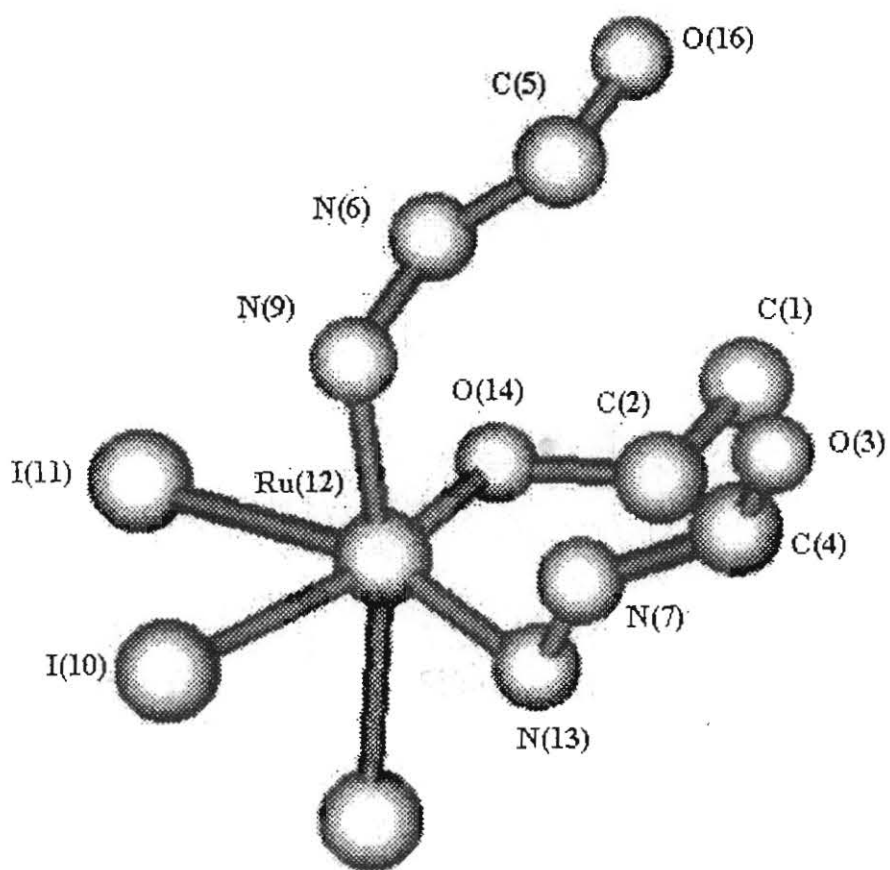


Fig. (3): The most stable geometry of  $[Ru(L)_2I_3] \cdot 2 EtOH$ , drawn by Hyperchem.

## CONCLUSION

It is often necessary to know the most stable geometry of a compound for eventual application in biological or pharmacological areas. In this paper the molecular mechanics calculations are efficient since they give a full information and good knowledge on the geometry and its features.

The data obtained by molecular mechanics calculation fall in the same range with those found in literature. We have determined the bond distances of Ru-O, Ru-Cl, Ru-Br, Ru-I and Ru-N. The degrees of distortion are different for the complexes. Indeed, the iodide complexes have the higher distortion while the chloride one are the less distorted. This is in good agreement with the fact that chlorine is smaller than bromine than iodine.

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حساب طول الرابطة و زاوية الرابطة و درجة التشوه لمتراكبات الريثنيوم (III) المشتقة  
من الفورميل هيدرازين بالميكانيكا الجزيئية

يتطلب تعيين تركيب متراكبات العناصر الانتقالية بلورات احادية وهذا صعب المنال في اغلب الاحيان ويمكن التغلب على ذلك بحسابات الميكانيكا الجزيئية وهذا يتطلب حسابات متقدمة لتعيين التركيب الجزيئي لهذه المتراكبات. في هذا البحث تم تعيين تركيب المتراكبات المشتقة من الفورميل هيدرازين مع الريثنيوم (III). تم تحليل المتراكبات لتعيين نسب الكربون ، الهيدروجين والنيتروجين. وعلى اساس النتائج تم وضع الصيغة التركيبية. كما تم استخدام حسابات الميكانيكا الجزيئية لتعيين طول الرابطة وزوايتها وكذلك درجة التشوه للمتراكبات. وقد وجد توافق بين النتائج والتجارب وماهو متواتر في الدوريات العلمية.

و هذا وقد تم دراسة الاثر البيولوجى والصيدلانى والدوائى لهذه المتراكبات.



