

## A Comparative MO Study of Three Dichlorodiamminedihydroxo Pt(IV) Isomers

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### Abstract

The electronic structure of the ground state of the title complexes is investigated by means of X $\alpha$ -MSW and EH calculations. The facile isomerization of the all-*trans* complex to the corresponding *cis,trans,cis* is explained in terms of total energy and atomic d level stabilization, as they emerge from the MO calculations. Furthermore, a qualitative prediction is made of the antitumor activity of the compounds provided that this is a consequence of their reduction to *cis*-dichlorodiammine Pt(II) by reductive elimination of their HO ligands.

### Introduction

Considerable interest has been placed upon platinum(II) diammine complexes since the discovery of the antitumor activity of *cis*-diamminodichloroplatinum(II) (*cis*-DDP). A number of novel Pt(II) complexes have been prepared, studied and tested in an effort to modify the activity of the complex by introducing either bulky or polyfunctional amines as ligands [1, 2]. The potential antitumor activity of Pt(II) complexes has been further studied in relation to their interaction toward certain DNA bases [3] or in connection with ground state electronic indices [4] describing the tendency of specific site coordination in an oxidative or reductive reaction scheme to DNA base sequence models. On the other hand, platinum(IV) diammine complexes have also proved to be at least equally active as their Pt(II) counterparts [5] in a number of tests, and have provoked several interesting antitumor activity investigations [6].

Dihydroxo-platinum(IV) compounds are particularly interesting as it is suspected that besides offering additional solubility to the complex, the hydroxyl groups are taking part in a reductive elimination procedure to afford the finally active Pt(II) diammine complexes. Recently, X-ray diffraction as well as spectroscopic data have been collected

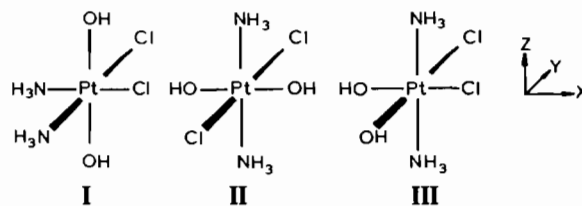


Fig. 1. The complex models in  $C_{2v}$  symmetry.

and presented [7, 8] for three dichlorodiamminedihydroxoplatinum(IV) isomers, namely the *cis*, *cis,trans*, *trans,trans,trans* and *cis,trans,cis*. The three complexes are presented in Fig. 1 and coded as **I**, **II** and **III** according to the notation already used [8].

### Computational Details

Though the three compounds possess nearly octahedral chromophores of the type  $PtCl_2N_2O_2$ , small changes were necessary in order to afford strictly symmetric species. The bond distances were set equal to 2.32 Å for Pt–Cl, 2.06 Å for Pt–N, 2.00 Å for Pt–O, 0.987 Å for N–H and 0.863 Å for O–H. The Pt–N–H angle was assumed to be 109° in all cases while the Pt–O–H angle was set equal to 105°, 109° and 103° for complexes **I**, **II** and **III** respectively. A strictly tetrahedral environment was assumed around the ammine nitrogen atoms. The overall symmetry was therefore  $C_{2v}$  for all the studied compounds. In order to ensure that no dramatic influence might be caused by the modifications induced, two series of iterative EH calculations [9, 10] were carried out on both the real and the idealized geometries by means of the FORTICON8 program [11]. Quadratic dependence of the diagonal matrix elements on the corresponding orbital electron population was assumed and the Wolfsberg–Helmholtz constant  $k$  was set to 1.75. No differences were observed in the ordering and the atomic partitioning of the molecular orbitals

TABLE I. Extended Hückel Parameters

	$\zeta_s$	$H_{ss}$	$\zeta_p$	$H_{pp}$	$\zeta_{d1}$	$\zeta_{d2}$	$H_{dd}$
Pt	2.554	-9.88	2.535	-6.09	6.013(0.633)	2.696(0.551)	-13.95
Cl	2.033	-23.09	2.033	-11.18			
N	1.950	-27.56	1.950	-14.56			
O	2.275	-27.41	2.275	-10.81			
H(N)	1.300	-16.68					
H(O)	1.300	-16.46					

TABLE II. MS-X $\alpha$  Parameters

	Outer sphere	Pt	Cl	N	O	H(N)	H(O)
Sphere radii	6.96	2.39	2.57	1.65	1.75	0.83	0.64
Max $l$ value	4	3	1	1	1	0	0

and the final two sets of parameters were essentially identical (Table I).

Calculations using the standard MS-X $\alpha$  method [12–15] were performed on the ground state of the idealized geometry of each compound. The atomic  $\alpha_{HF}$  parameters were taken from the tables of Schwarz [16, 17] and a weighted average of these values was adopted for both the interatomic region and the outer sphere. The hydrogen sphere radii were set to 10% greater than the touching sphere radii, because the overlap of O and H using Norman's procedure [18] was found greater than 40% leading to significant negative charges in the intersphere region. Relativistic mass and Darwin corrections

were applied to the Pt center [19, 20]. Table II provides details about the sphere radii and maximum  $l$  used in the computations.

## Results and Discussion

The symmetry, energy and percent charge distribution of the valence molecular orbitals are presented in Tables III to V (Fig. 2). For each wavefunction the intersphere and outer sphere charge is distributed among the radial functions according to the algorithm developed by Case and Karplus [21]. In all cases the HOMO has  $a_2$  symmetry ( $4a_2$

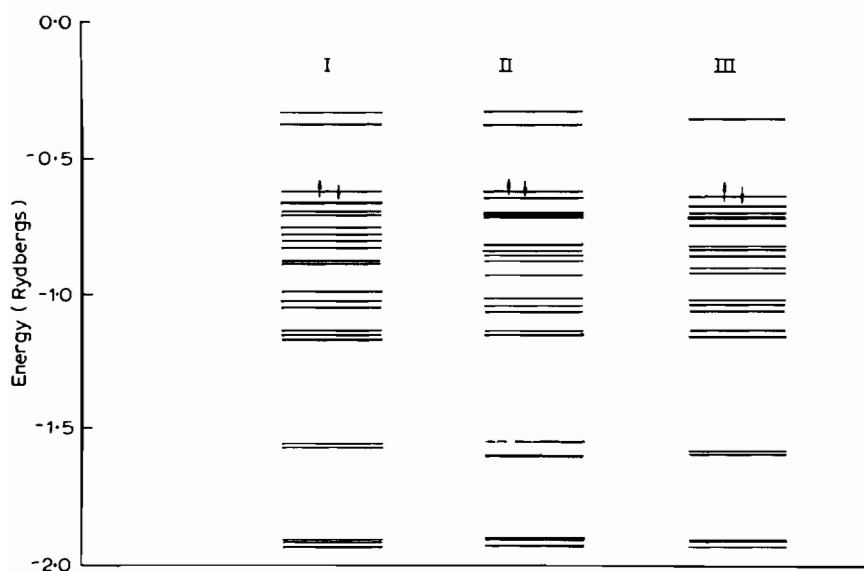


Fig. 2. Molecular orbital energies (MS-X $\alpha$ ) for the three complexes. Arrows indicate the highest occupied molecular level. The symmetry state of each orbital may be determined from Tables III, IV and V.

TABLE III. Energy Levels (Symmetry, Eigenvalue and Atomic Participation) for Complex I<sup>a</sup>

MO	Energy (Ry)	Pt				Cl		N		H	H	O		H
		s	p	d	f	s	p	s	p			s	p	
1a <sub>1</sub>	-1.938	2	0	0	0	0	0	32	0	2	5	50	1	3
2a <sub>1</sub>	-1.920	0	0	3	0	0	0	44	0	3	7	36	1	2
1b <sub>1</sub>	-1.918	0	0	1	0	0	0	77	0	6	13	0	0	0
1b <sub>2</sub>	-1.908	0	1	0	0	0	0	0	0	0	0	88	2	6
3a <sub>1</sub>	-1.571	1	0	1	0	95	0	0	0	0	0	0	0	0
2b <sub>1</sub>	-1.558	0	0	2	0	95	0	0	0	0	0	0	0	0
4a <sub>1</sub>	-1.173	0	0	4	0	0	0	0	66	19	8	0	0	0
2b <sub>2</sub>	-1.171	0	0	3	0	0	0	0	63	0	27	0	3	0
1a <sub>2</sub>	-1.155	0	0	3	0	0	0	0	67	0	28	0	0	0
3b <sub>1</sub>	-1.135	0	0	0	0	0	0	0	69	19	19	0	0	0
5a <sub>1</sub>	-1.050	1	0	34	0	0	1	0	2	0	0	0	53	6
4b <sub>1</sub>	-1.024	0	0	46	0	1	9	0	38	1	1	0	0	0
6a <sub>1</sub>	-0.992	15	1	7	0	1	8	0	45	1	2	0	13	2
3b <sub>2</sub>	-0.990	0	0	13	0	0	1	0	5	0	2	2	63	0
7a <sub>1</sub>	-0.886	7	0	7	0	0	5	0	2	0	0	3	68	3
1a <sub>2</sub>	-0.875	0	0	59	0	0	9	0	3	0	2	0	24	0
8a <sub>1</sub>	-0.828	0	0	59	0	0	30	0	4	2	0	0	2	0
4b <sub>2</sub>	-0.801	0	5	31	0	0	17	0	0	0	0	0	41	2
5b <sub>1</sub>	-0.779	0	8	4	0	0	49	0	18	0	0	0	16	0
9a <sub>1</sub>	-0.752	1	6	7	1	0	60	1	18	0	1	0	1	0
5b <sub>2</sub>	-0.709	0	4	25	1	0	4	0	0	0	0	0	63	1
6b <sub>1</sub>	-0.694	0	0	1	2	0	13	0	7	0	0	0	73	0
6b <sub>2</sub>	-0.668	0	0	23	0	0	72	0	0	0	0	0	2	0
3a <sub>2</sub>	-0.663	0	0	3	0	0	87	0	0	0	0	0	8	0
10a <sub>1</sub>	-0.662	0	0	29	0	0	68	0	0	0	0	0	0	0
7b <sub>1</sub>	-0.660	0	0	0	0	0	96	0	1	0	0	0	1	0
4a <sub>2</sub>	-0.620	0	0	34	0	0	1	0	0	0	0	0	64	0
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8b <sub>1</sub>	-0.372	0	0	45	0	2	28	2	20	0	0	0	0	0
11a <sub>1</sub>	-0.331	0	0	45	0	1	9	0	7	0	0	2	32	0

<sup>a</sup>The dotted line separates the occupied from the virtual levels. Hydrogen atoms next to N are NH<sub>3</sub> ones; the hydroxyl hydrogen is placed next to O.

TABLE IV. Energy Levels (Symmetry, Eigenvalue and Atomic participation) for Complex II<sup>a</sup>

MO	Energy (Ry)	Pt				Cl		Cl		N		H	H	O		H
		s	p	d	f	s	p	s	p	s	p			s	p	
1a <sub>1</sub>	-1.931	2	0	1	0	0	0	0	0	19	0	1	3	65	1	4
2a <sub>1</sub>	-1.909	0	0	3	0	0	0	0	0	57	0	4	9	22	0	1
1b <sub>2</sub>	-1.903	0	1	0	0	0	0	0	0	0	0	0	0	88	2	6
1b <sub>1</sub>	-1.901	0	1	0	0	0	0	0	0	77	1	6	13	0	0	0
3a <sub>1</sub>	-1.600	1	0	2	0	2	0	92	0	0	0	0	0	0	0	0
4a <sub>1</sub>	-1.547	0	1	1	0	93	0	3	0	0	0	0	0	0	0	0
2b <sub>1</sub>	-1.153	0	0	5	0	0	0	0	0	0	65	18	9	0	0	0
1a <sub>2</sub>	-1.150	0	0	6	0	0	0	0	0	0	65	0	27	0	1	0
5a <sub>1</sub>	-1.136	0	0	0	0	0	0	0	0	0	68	19	9	0	0	0
2b <sub>2</sub>	-1.133	0	0	0	0	0	0	0	0	0	68	0	29	0	0	0
6a <sub>1</sub>	-1.064	0	0	39	0	0	0	0	0	0	16	0	0	0	37	0
7a <sub>1</sub>	-1.038	8	0	25	0	0	0	0	0	0	32	0	2	0	25	3
3b <sub>2</sub>	-1.009	0	1	18	0	0	2	0	2	0	0	0	0	2	63	9
8a <sub>1</sub>	-0.924	8	0	29	0	1	21	1	26	0	1	0	0	0	8	1
9a <sub>1</sub>	-0.872	7	0	6	0	0	0	0	9	0	1	0	0	3	66	3

(continued)

TABLE IV. (continued)

MO	Energy (Ry)	Pt				Cl		Cl		N		H	H	O		H
		s	p	d	f	s	p	s	p	s	p			s	p	
3b <sub>1</sub>	-0.851	0	10	0	1	0	0	0	2	1	73	1	3	0	3	0
2a <sub>2</sub>	-0.835	0	0	60	0	0	0	0	0	0	6	0	4	0	28	0
4b <sub>1</sub>	-0.812	0	0	64	0	0	8	0	16	0	6	2	1	0	0	0
4b <sub>2</sub>	-0.809	0	4	32	0	0	1	0	17	0	0	0	0	0	38	2
5b <sub>2</sub>	-0.715	0	2	19	0	0	31	0	11	0	0	0	0	0	32	1
5b <sub>1</sub>	-0.713	0	0	4	2	0	17	0	41	1	7	0	0	0	26	0
10a <sub>1</sub>	-0.707	0	6	0	1	0	48	0	38	0	0	0	0	0	3	0
6b <sub>2</sub>	-0.702	0	2	0	2	0	2	0	51	0	0	0	0	0	41	0
6b <sub>1</sub>	-0.696	0	0	2	1	0	5	0	24	0	0	0	0	0	65	0
7b <sub>1</sub>	-0.641	0	0	22	0	0	65	0	11	0	0	0	0	0	0	0
7b <sub>2</sub>	-0.639	0	0	27	0	0	59	0	10	0	0	0	0	0	2	0
3a <sub>2</sub>	-0.615	0	0	32	0	0	0	0	0	0	0	0	0	0	67	0
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11a <sub>1</sub>	-0.374	0	0	43	0	1	19	1	14	1	13	0	0	0	2	0
12a <sub>1</sub>	-0.322	0	0	47	0	0	0	0	0	2	16	0	0	2	28	0

<sup>a</sup>The dotted line separates the occupied from the virtual levels.

TABLE V. Energy Levels (Eigenvalues and Atomic participation) for Complex III<sup>a</sup>

MO	Energy (Ry)	Pt				Cl		N		H	H	O		H		
		s	p	d	f	s	p	s	p			s	p			
1a <sub>1</sub>	-1.930	2	0	0	0	0	0	36	0	3	6	45	1	3		
1b <sub>2</sub>	-1.914	0	0	2	0	0	0	0	0	0	0	87	2	6		
2a <sub>1</sub>	-1.912	0	0	2	0	0	0	40	0	3	6	41	1	3		
1b <sub>1</sub>	-1.906	0	1	0	0	0	0	77	1	6	13	0	0	0		
3a <sub>1</sub>	-1.592	1	0	0	0	95	0	0	0	0	0	0	0	0		
2b <sub>2</sub>	-1.579	0	0	2	0	95	0	0	0	0	0	0	0	0		
1a <sub>2</sub>	-1.160	0	0	5	0	0	0	0	65	0	28	0	0	0		
2b <sub>1</sub>	-1.154	0	0	6	0	0	0	0	65	18	9	0	0	0		
3b <sub>2</sub>	-1.143	0	0	0	0	0	0	0	69	0	29	0	0	0		
4a <sub>1</sub>	-1.137	0	0	0	0	0	0	0	68	19	9	0	1	0		
5a <sub>1</sub>	-1.061	1	0	42	0	0	1	0	36	0	2	0	13	1		
6a <sub>1</sub>	-1.037	6	0	14	0	0	2	0	13	1	0	0	53	8		
4b <sub>2</sub>	-1.019	0	0	37	0	1	10	0	0	0	0	0	44	5		
7a <sub>1</sub>	-0.919	17	0	16	0	1	28	0	4	0	0	1	31	0		
5b <sub>2</sub>	-0.897	0	0	14	0	0	7	0	0	0	0	4	66	6		
3b <sub>1</sub>	-0.857	0	10	1	1	0	2	1	73	2	2	0	4	0		
2a <sub>2</sub>	-0.833	0	0	63	0	0	8	0	6	0	4	0	16	0		
4b <sub>1</sub>	-0.832	0	0	62	0	0	11	0	8	2	2	0	13	0		
8a <sub>1</sub>	-0.819	0	2	30	0	0	48	0	0	0	0	0	14	2		
6b <sub>2</sub>	-0.745	0	8	0	1	0	59	0	0	0	0	0	29	0		
5b <sub>1</sub>	-0.719	0	0	0	2	0	61	1	7	0	0	0	26	0		
9a <sub>1</sub>	-0.713	0	5	4	2	0	43	0	0	0	0	0	44	0		
3a <sub>2</sub>	-0.700	0	0	0	1	0	72	0	0	0	0	0	26	0		
7b <sub>2</sub>	-0.677	0	0	0	0	0	91	0	0	0	0	0	6	0		
10a <sub>1</sub>	-0.672	0	0	42	0	0	53	0	0	0	0	0	3	0		
6b <sub>1</sub>	-0.638	0	0	29	0	0	21	0	0	0	0	0	49	0		
4a <sub>2</sub>	-0.637	0	0	29	0	0	16	0	0	0	0	0	53	0		
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11a <sub>1</sub>	-0.355	0	0	48	0	0	7	3	28	0	0	0	9	0		
8b <sub>2</sub>	-0.355	0	0	43	0	3	22	0	0	0	0	1	29	0		

<sup>a</sup>The dotted line separates the occupied from the virtual levels.

for **I** and **III**,  $3a_2$  for **II**) mainly of oxygen  $p_\pi$  character with a smaller participation of metal d functions. The LUMO is of  $b_1$  symmetry in **I**, and  $a_1$  in **II** bearing significant metal d contribution, though it is to a degree delocalized in a bonding fashion toward the other atoms of the chromophore, mainly N and Cl. The LUMO in **III** is predicted to be degenerate ( $a_1$  and  $b_2$ ). A common feature of the virtual levels is the delocalization of the charge distribution in the interatomic and extramolecular regions, a feature observed in other complexes as well. Such an effect has been attributed [22, 23] to the diffuse nature of some virtual orbitals, or to the effect of the muffin-tin approximation which may lead to

rather unrealistic potentials for low lying unoccupied levels.

The three isomers lie in a zone of *ca.* 24 kcal/mol, **I** being the most stable. The *ca.* 3 kcal/mol separating **II** from **III** is a very narrow gap, in accord with the observed facile conversion of the former complex to the latter by means of a simple recrystallization from  $H_2O$ .

The mechanism for such a conversion of *trans* to *cis* complexes has been extensively investigated and discussed [24]. The initial step is proposed to be a reductive elimination of a hydroxyl group. Maybe an adduct with  $H_2O$  is formed (via some sort of hydrogen bond) but the intermediate state

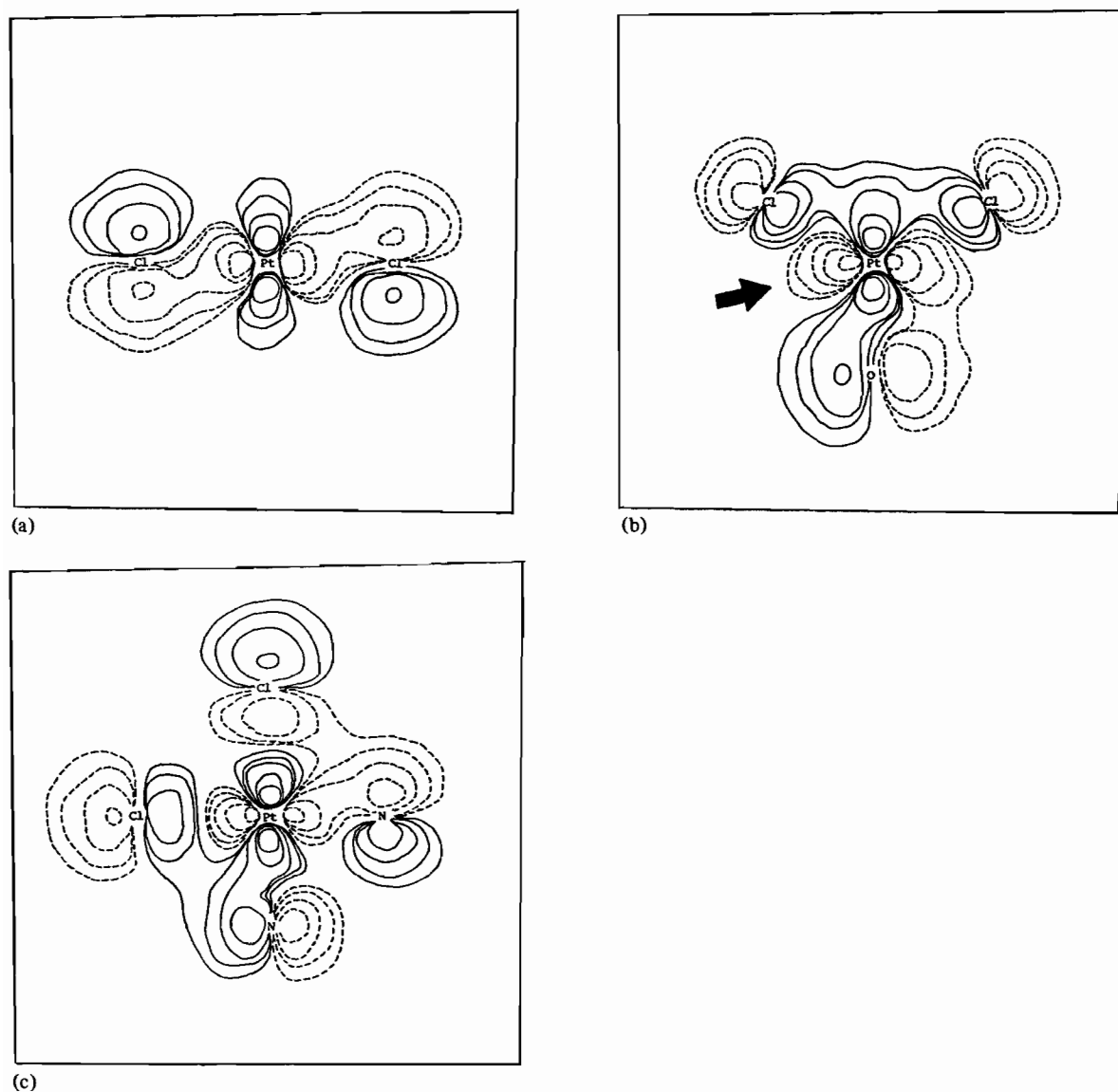


Fig. 3. LUMO contours (EH) for (a) complex **II**, (b) the trigonal bipyramid intermediate (see text) and (c) complex **I**. The outer contour value is  $0.0156 [e \text{ Bohr}^{-3}]^{1/2}$  and each inner one is scaled by a factor of 2. Positive contours are indicated by dashed lines, while the negative ones are presented by solid lines.

must be a trigonal bipyramid, the two chlorine atoms and the remaining  $-\text{OH}$  group occupying the basal plane. The re-entry of the second  $-\text{OH}$  group is affected by the stronger *trans*-effect of Cl, apparently leading to the *cis*-orientation of the four basal plane ligands.

The above assumption is confirmed to an extent by the  $X\alpha$  calculations reported hereby, since the HOMO partitioning in **II** hints at the enhanced electron donation character of the oxygen atoms. Furthermore, if one assumes that the compound should undergo a direct metal ion reduction, the LUMO constitution predicts that the  $\text{M}-\text{Cl}$  and the  $\text{M}-\text{N}$  bonds would be strengthened at the expense of the  $\text{M}-\text{O}$  ones, thus providing grounds for elimination of the hydroxyl group.

A separate EH calculation on the supposed trigonal bipyramidal species assuming the same bond distances as in the studied complexes produced a  $d_{x^2-y^2}$  LUMO for the 'intermediate' complex. It is apparent by inspection of Fig. 3(b) that a rearrangement of the approaching  $-\text{OH}$  and the existing ligands would result in a *cis*-structure of the final complex.

The preference for isomer **III** may also be understood in terms of EH obtained quantities, such as bond polarization, metal d orbital stabilization etc. A qualitative description of the isomerization procedure is that on going from **II** to **III** the actual chromophore symmetry is reduced from  $D_{2h}$  to  $C_{2v}$ , thus allowing considerable d-p mixing among Pt AOs. Consequently the  $d_{x^2-y^2}$  and  $d_{z^2}$  AOs will be present as participants in hybrid orbitals and will be lowered in energy, becoming more 'bonding'. In **III**, the platinum p population is lowered by 0.018 e while the d population is enhanced by 0.023 e with respect to **II**. At the same time the fractional electron populations of  $d_{x^2-y^2}$  and  $d_{z^2}$  are enhanced by 0.014 and 0.009 e respectively. A slight drop in the higher energy platinum d band of **III** with respect to that of **II** is observed in both the EH and the  $X\alpha$  calculations, though its width remains essentially the same. This fact provides evidence for the above mentioned diversity in the bonding ability of the ' $e_g$ ' set of platinum d AOs, in the two complexes of interest.

Owing to the *trans*-effect of Cl, an appreciable electron drift is evident (as encompassed by EH calculations) through the  $\text{HO}-\text{Pt}-\text{Cl}$  system in **III**. The result is a slight rise in the positive atomic charge on both hydroxyl hydrogen atom (0.4 pm) and platinum (2.0 pm), while a rise in the negative charge on Cl is also present (1.1 pm) when compared to **II**. The metal-ligand overlap populations are also depressed in value ( $\text{Pt}-\text{Cl}$  by 8.5 pm,  $\text{Pt}-\text{N}$  by 1.0 pm and  $\text{Pt}-\text{O}$  by 4.6 pm) thus predicting a 'more ionic structure' for the *cis*-complex. This electron delocalization toward the chlorine atoms

in **III** is also evident from the (EH derived) HOMO constitution. The differences in the percent electron distribution in the HOMO of **II** and **III** show that the metal participation is reduced from 8.7% to 7.1%, the oxygen participation is lowered from 95.6% to 89.2% while the contribution from the chlorine atoms increases from 0.1% to 7.1%. The almost oxygen-localized nature of the MO is not surprising in view of the well-established tendency of the EH wavefunctions to diminish the covalency of the system. The corresponding  $X\alpha$  results (Tables IV and V) parallel this observation though the individual contributions differ significantly in magnitude from the EH ones.

The oxygen participation in the HOMO is of interest since a reductive elimination of the hydroxyl groups is thought to occur in solution, leading to the formation of the antitumor Pt(II) diammine complex. To our knowledge such a hypothesis has not yet been fully confirmed, but is partly supported by the reduction of analogous Pt(IV) complexes by thioles under mild conditions. In this case the initial step is quite obvious and involves the approach of the labile thiol H atom to the oxygen center, provoking an electron drift through the  $\text{Pt}-\text{O}$  bond, consequently weakening this bond. Finally the  $\text{H}_2\text{O}$  molecules formed in this way are eliminated; the remaining part of the complex undergoing further geometrical rearrangements affords the final *cis*-DDP structure. An analogous mechanism may possibly apply in the present case assuming that the antitumor active species are Pt(II) diammine complexes, a fact that has yet to be confirmed by experimental findings.

However, if we suppose that in every case the reactive species is a Pt(II) diammine complex, we may attempt a prediction, our estimation based on the HOMO energy of each compound. Since a HOMO with higher energy would be a more preferable site for  $\text{H}^+$ , the compound with the higher HOMO eigenvalue should be the most susceptible substrate for such an electrophilic attack. It is therefore expected that such an initial  $\text{H}^+$  approach would be favoured in the sequence **II** > **I** > **III** (HOMO eigenvalues  $-0.615$  au,  $-0.620$  au and  $-0.677$  au respectively; au = Ry) as can be deduced from the results presented in Tables III, IV and V.

## Conclusions

In conclusion it could be stated that based on the frontier MO's energy eigenvalues and constitution, a qualitative estimation may be applied on the facile isomerization of *trans,trans,trans*-dichlorodiammine-dihydroxoplatinum(IV) to its *cis,trans,cis*-counterpart. The finding that this conversion is taking place in  $\text{H}_2\text{O}$  but not in  $\text{H}_2\text{O}_2$  strongly suggests that a

Pt(III) catalysed reaction mechanism is involved, leading to a trigonal bipyramidal  $\text{PtCl}_2(\text{NH}_3)_2\text{OH}$  complex intermediate. EH calculations on this complex account for the molecular structure of the final product of the isomerization.

EH-SCCC calculations parallel the results of the more sophisticated  $X\alpha$ -MSW as far as the ground state properties are discussed. The total energies of the two complexes involved in the isomerization are comparable and their overall electronic structure nearly identical except for small changes in the charge distribution and the metal d level stabilization, factors which allowed the 'quantification' of the observed reaction.

### Acknowledgement

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