

## Trans or (Unusual) Cis Geometry in d<sup>2</sup> Octahedral Dioxo Complexes. A DFT Study

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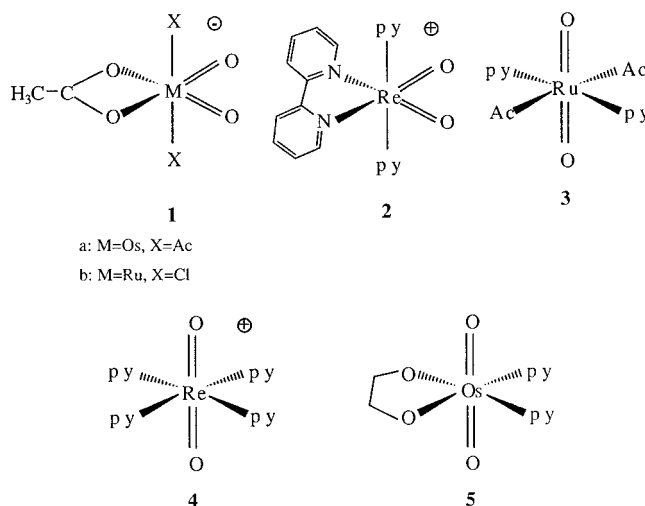
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Geometry optimization of the *cis* and the *trans* isomers of several octahedral dioxo complexes of d<sup>2</sup> electronic configuration are performed using the gradient-corrected density functional theory (B3LYP and, for some key structures, BP86). With only monodentate  $\sigma$  donor ligands (ReO<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub><sup>+</sup>, **7**), the usual energy order is found (i.e., the *trans* isomer is the most stable). Complexes with a chelating bidentate ligand, OsO<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>O)-(NH<sub>3</sub>)<sub>2</sub> (**10**) and ReO<sub>2</sub>(HN=CHCH=NH)(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> (**11**), are used as models for the experimental complexes **5** and **2** in which the arrangement of the O=M=O unit is *trans* and *cis*, respectively. Our calculations actually show an inversion of the relative energy of the two isomers in going from **10** to **11**: while the *trans* isomer is found to be the most stable in **10**, the unusual *cis* diamagnetic isomer is favored by about 29 kcal mol<sup>-1</sup> in **11**. This result is traced to the geometric and electronic properties of the bidentate ligand, in particular an acute bite angle and good  $\pi$  acceptor character. In complex **14** with a bipyridine chelating ligand (weaker  $\pi$  acceptor than diaza-1,4-butadiene in **11**), this energy difference is, however, reduced to 7.5 kcal mol<sup>-1</sup> (partial geometry optimization).

A *trans* arrangement of the O=M=O unit is most often found in octahedral dioxo transition metal complexes of d<sup>2</sup> electronic configuration.<sup>1–3</sup> This trend was rationalized on orbital grounds by Atovmyan and Porai-Koshits<sup>1a</sup> and by Mingos<sup>1b</sup> (EHMO calculations): in the *trans* isomer, one of the three orbitals deriving from the t<sub>2g</sub> block remains nonbonding, which is ideal to accommodate the two d electrons, while in the *cis* isomer the three d orbitals are destabilized by antibonding interactions with the oxygen lone pairs.

However, a few *cis* d<sup>2</sup> complexes are known and they are of great general interest.<sup>4,5</sup> A successful way to synthesize these unusual *cis* complexes has been to use some tridentate or tetradentate amines as ancillary ligands. The cavity size upon coordination to the metal is small enough to prevent the formation of the *trans* complex and favor the fabrication of complexes having a *cis*-dioxo unit.<sup>5</sup> However, three characterized (X-ray) *cis* complexes are of special interest since such a constraint is not at work: OsO<sub>2</sub>(O<sub>2</sub>CMe)<sub>3</sub><sup>-</sup> (**1a**),<sup>6</sup> RuO<sub>2</sub>Cl<sub>2</sub>(O<sub>2</sub>CMe)<sup>-</sup> (**1b**),<sup>7</sup> and ReO<sub>2</sub>(bpy)(py)<sub>2</sub><sup>+</sup> (bpy = 2,2'-bipyridine, py = pyridine) (**2**).<sup>8</sup> For the latter, however, it was suggested that the appearance of the *cis* structure might reflect a kinetic preference at some stage in the synthesis. It is noteworthy that, in very similar complexes, the usual *trans* structure is found

(X-ray): RuO<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>(py)<sub>2</sub> (**3**),<sup>9</sup> ReO<sub>2</sub>(py)<sub>4</sub><sup>+</sup> (**4**),<sup>10</sup> OsO<sub>2</sub>(py)<sub>2</sub>(OCR<sub>2</sub>CR'<sub>2</sub>O) (**5**),<sup>11</sup> and MO<sub>2</sub>(py)<sub>2</sub>X<sub>2</sub> (M = Ru, Os; X = Cl, Br, OH) (Raman, IR, and NMR spectroscopy).<sup>12</sup> Finally, the *diamagnetism* of the characterized *cis* complexes is also surprising, since, in a regular octahedral geometry, the two lowest d orbitals are close in energy.<sup>1b</sup>



The few X-ray characterized *cis* complexes carry a conjugated bidentate chelating ligand with the following acute bite angles: 59.2(3)<sup>∘</sup> in **1a**, 60.6(5)<sup>∘</sup> in **1b**, and 70.6(3)<sup>∘</sup> in **2**. In the similar complexes **3** and **4** with only monodentate ligands, the usual

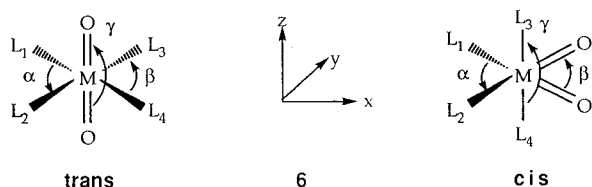
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*trans* structure is found. In a previous work,<sup>13</sup> qualitative extended Hückel (EH) calculations led us to suggest that a bidentate ligand with a small bite angle and good  $\sigma$  donor and  $\pi$  acceptor properties should reduce the energy difference between the two isomers. However, total energies given by EH calculations are not reliable enough to decide which isomer is actually the most stable. On the other hand, the study of the magnetic properties of the electronic ground state in the *cis* complexes was not feasible in the framework of mono-electronic calculations. This problem was discussed only in a qualitative way by looking at the HOMO–LUMO energy gap.

In this work, the geometries of the *trans* (**t**) and the *cis* (**c**) isomers of several octahedral dioxo d<sup>2</sup> complexes were optimized by means of DFT calculations. In the *cis* isomer, both the diamagnetic and the paramagnetic states were studied in order to determine which is the electronic ground state. The definition of the angles and the numbering of the ligands used in the following are given in structures **6** for both *trans* and *cis*



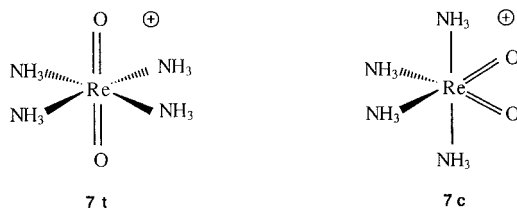
isomers. When a bidentate ligand is involved, the L<sub>1</sub> and L<sub>2</sub> sites are connected so that the bite angle is  $\alpha$ .

### Method of Calculation

Quasirelativistic pseudopotentials were used for the transition metal atoms (Re, Os) with the (8s/7p/6d) basis set contracted to a (6s/5p/3d) basis set for the valence orbitals (which include 5s and 5p).<sup>14a</sup> For the other atoms, 4-31G and/or 6-31G\* basis sets<sup>14b</sup> were used (basis sets I and II, respectively). Density functional theory (DFT) calculations were performed for all the complexes using the B3LYP functional implemented in the Gaussian 92/DFT package.<sup>15</sup> A few key structures were recalculated with the BP86 functional (basis set I). The nitrogen environment in the NH<sub>3</sub> ligands was kept tetrahedral, and the N–H bond lengths were held fixed to 1.0 Å.

### Complexes with Monodentate Ligands: ReO<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub><sup>+</sup> as an Example

The Mingos analysis for the geometry of d<sup>2</sup> dioxo complexes was supported by EH calculations with an idealized octahedral geometry for each isomer and monodentate  $\sigma$  donor ancillary ligands (PH<sub>3</sub>).<sup>1b</sup> The influence of geometry optimization was tested on the ReO<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub><sup>+</sup> complex (**7**), used as a model for this family of compounds.



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**Table 1.** Optimized Geometrical Parameters (Bond Lengths in Å, Angles in deg) for the *Trans* (**7t**) and the *Cis* (**7c**) Isomers of Complex **7** (ReO<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub><sup>+</sup>) with B3LYP Functional and Basis Sets I and II<sup>a</sup>

		<b>7t</b> (dia)	<b>7c</b> (dia)	<b>7c</b> (para)
Re=O	I	1.799	1.770	1.799
	II	1.778	1.744	1.774
Re–N <sub>1,2</sub>	I	2.231	2.381	2.391
	II	2.244	2.416	2.428
Re–N <sub>3,4</sub>	I	2.232	2.235	2.229
	II	2.244	2.243	2.237
$\alpha$	I	90.7	73.8	77.9
	II	90.0	72.9	76.9
$\beta$	I	90.8	125.8	107.8
	II	90.0	125.6	107.4
$\gamma$	I	180.3	167.4	173.9
	II	180.2	167.2	174.1
<i>E</i>	I	0	14.9	29.7
	II	0	11.3	28.9

<sup>a</sup> Relative energies are in kcal mol<sup>−1</sup>. The energy of the *trans* structure is −454.47491 au (basis set I) and −454.91728 au (basis set II).

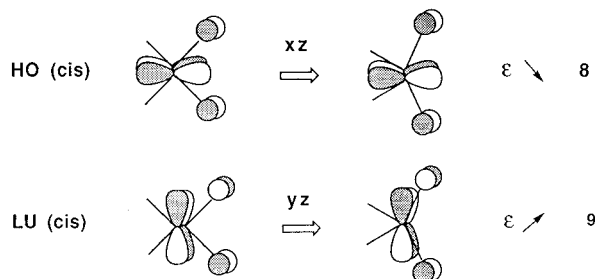
The results of the calculations are reported in Table 1. The diamagnetic *trans* isomer **7t** is found to be the most stable structure. This is in agreement with the Mingos conclusion and with the experimental structures determined by X-ray crystallography: to the best of our knowledge, all of the d<sup>2</sup> dioxo complexes with monodentate ancillary ligands (**3** and **4** for instance) exhibit a *trans* arrangement of the O=M=O unit.<sup>16</sup> The computed energy difference between the *trans* and the *cis* isomers (diamagnetic states) is 14.9 kcal mol<sup>−1</sup> with basis set I and 11.3 kcal mol<sup>−1</sup> with basis set II. In the *cis* isomer **7c**, the electronic ground state is diamagnetic, as in the few characterized *cis* complexes. The computed energy gap between the singlet and the triplet states is 14.8 kcal mol<sup>−1</sup> with basis set I and 17.6 kcal mol<sup>−1</sup> with basis set II.

From a geometrical point of view, almost ideal octahedral angle values are found for the *trans* isomer **7t**. It is in agreement with the experimental data on related complexes<sup>9b,10,17</sup> and with our previous qualitative analysis.<sup>13</sup> The optimized Re=O bond length is 1.799 Å with basis set I (i.e., only 0.025 Å longer than the average experimental value (1.765 Å) in *trans* d<sup>2</sup> complexes).<sup>10,18</sup> With basis set II, the theoretical value is even better (1.778 Å). Whatever the basis set, the Re–N bond lengths are about 0.09 Å longer than the average experimental ones (2.14 Å).<sup>10,18</sup> However, this later value corresponds either to pyridines<sup>10</sup> or to tetradentate amine ligands.<sup>18</sup> Therefore, the comparison between theoretical and experimental values may be less meaningful for Re–N bonds than for Re=O ones.

In the *cis* isomer **7c**, strong angular deviations from the octahedral geometry are found, in particular for  $\alpha$  and  $\beta$  angles (see **6**): in the diamagnetic electronic ground state, the equilibrium angle values for  $\alpha$  and  $\beta$  are about 73 and 125°, respectively. The O=M=O angle is much larger than in *cis* d<sup>0</sup>

- (16) One exception might be the OsO<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>(mes)<sub>2</sub> complexes, for which a *cis* structure has been proposed on the basis of <sup>1</sup>H NMR and IR data: McGilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465.
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complexes (105° (av))<sup>19</sup> because the two extra electrons lying in the HOMO (*xz*) are stabilized upon opening this angle (see **8**).<sup>13</sup> Although the *cis* isomer is not the lowest energy one in the ReO<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub><sup>+</sup> complex, it is noteworthy that its optimized geometry resembles that of the characterized *cis* complexes **1** and **2**: a large O=M=O angle (120–125°) and an acute opposite L<sub>1</sub>–M–L<sub>2</sub> angle (60–70°, imposed by a bidentate ligand). In the *cis* ground state, the Re=O bond lengths are found to be slightly shorter than those in the *trans* isomer (1.744 Å instead of 1.778 Å with basis set II), a trend in agreement with the experimental data (Re=O = 1.733(8) and 1.736(7) Å in complex **2**<sup>8a</sup> instead of 1.765 Å (av) in *trans* complexes). Finally, note that the Re–N<sub>1,2</sub> bond lengths in the *cis* isomer are longer than the Re–N<sub>3,4</sub> ones, a change which results, at least in part, from the *trans* influence of the oxo ligands.



The main geometrical change in going from the diamagnetic to the paramagnetic state in the *cis* isomer is the decrease of the O=Re=O equilibrium angle (125 vs 107°, Table 1). In the triplet state, both *xz* and *yz* are singly occupied. The former is stabilized upon O=M=O opening (see **8**), and the latter is destabilized (see **9**). On the whole, the effects of the two d electrons almost cancel. The equilibrium O=Re=O angle in the triplet state of *cis* d<sup>2</sup> complexes is thus in the range of that found for *cis* d<sup>0</sup> complexes (i.e., much smaller than in the diamagnetic ground state). On the other hand, the Re=O bond lengths are slightly longer in the triplet state than in the singlet state, by about 0.03 Å. As a matter of fact, for β > 90°, *yz* is more metal–oxo antibonding than *xz*, so that the promotion of one electron from *xz* to *yz* weakens the Re=O bonds. Finally, the electronic ground state of the *cis* isomer is diamagnetic. This result may be related, at least in part, to the rather large energy gap created between the frontier orbitals by the wide opening of the O=M=O angle.<sup>20,13</sup>

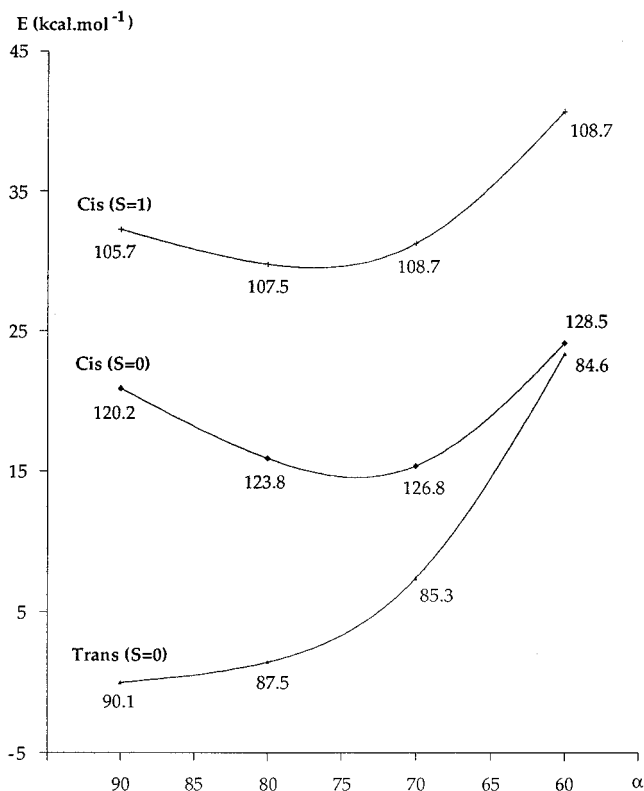
In Figure 1, the energy of the two isomers (basis set I) is given as a function of α which is varied from 90 to 60° by steps of 10°. At each point, the other geometrical parameters are optimized. Departure of α from 90° destabilizes the *trans* isomer and stabilizes the *cis* isomer. For small values of α, the steric repulsion between L<sub>1</sub> and L<sub>2</sub> ligands dominates and the total energy of both isomers strongly increases. These potential energy curves show how a bidentate ligand imposing an acute L<sub>1</sub>–M–L<sub>2</sub> bite angle (α) can make the two isomers closer in energy: it destabilizes the *trans* isomer and stabilizes the *cis* isomer by allowing it to reach its equilibrium geometry without developing steric repulsion between L<sub>1</sub> and L<sub>2</sub> ligands.

### Complexes with a Bidentate Ligand

Two complexes were studied, OsO<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub> and ReO<sub>2</sub>(HN=CHCH=NH)(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> (**10** and **11**, respectively).

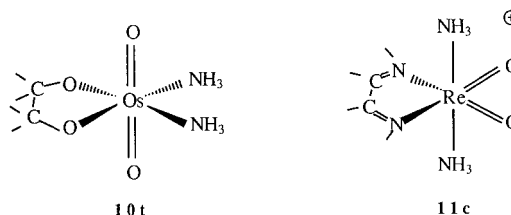
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(20) This interpretation has already been suggested for the related diamagnetic *cis*-Ru(bpy)<sub>2</sub>(O)<sub>2</sub><sup>2+</sup> complex<sup>4a</sup> (X-ray structure still unknown).



**Figure 1.** Optimized potential energy curves for the *trans* (**7t**) and the *cis* (**7c**, dia- and paramagnetic states) isomers of the complex **7** (ReO<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub><sup>+</sup>) as a function of α angle (see structures **6**). At each point, the optimized value of the β angle (O=Re=O angle in the *cis* isomer) is given.

These complexes were used as models for the experimental complexes **5**<sup>11</sup> and **2**<sup>8a</sup> which exhibit a *different* arrangement of the O=M=O unit (*trans* and *cis*, respectively). Geometry



optimizations were performed within the C<sub>2</sub> group, the *x* axis (**6**) being kept as symmetry element in both *trans* (**t**) and *cis* (**c**) isomers. The results are reported in Tables 2 (compound **10**) and 3 (compound **11**). Except when noted, only the complete set of B3LYP results will be discussed in the following.

In the OsO<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub> complex, the *trans* isomer (**10t**) is found to be more stable than the diamagnetic *cis* isomer **10c**, in agreement with the structure of the related experimental complex **5**.<sup>11</sup> The computed energy difference is large (20.7 kcal mol<sup>-1</sup>, basis set I), a value in the range of that reported in recent ab initio calculations (26 kcal mol<sup>-1</sup>).<sup>1e</sup> In the less stable (and experimentally unknown) *cis* isomer, the geometric results are in many aspects similar to those found for the rhenium complex **7c** (in particular for the angular distortions from the octahedral geometry). However, in marked contrast with complex **7c**, the electronic ground state of **10c** is paramagnetic. One may wonder whether this result might not come from the use of the B3LYP functional which contains a component of Hartree–Fock exchange favoring the high-spin state. Reoptimization using the BP86 functional actually reduces the singlet–

**Table 2.** Main Geometrical Parameters (Bond Lengths in Å, Angles in deg) Optimized for the *Trans* (**10t**) and the *Cis* (**10c**) Isomers of Complex **10** ( $\text{OsO}_2(\text{OCH}_2\text{CH}_2\text{O})(\text{NH}_3)_2$ )<sup>a</sup>

		<b>10t</b> (dia)	<b>10c</b> (dia)	<b>10c</b> (para)
Os=O	I <sup>b</sup>	1.791 (1.810)	1.785 (1.802)	1.809 (1.823)
	exptl <sup>c</sup>	1.728(5)		
Os—O	I	1.960 (1.969)	2.082 (2.097)	2.061 (2.075)
	exptl	1.983(5)		
Os—N	I	2.241 (2.231)	2.145 (2.144)	2.141 (2.139)
	exptl	2.128(7)		
$\alpha$	I	86.5 (87.3)	77.1 (76.7)	76.9 (76.8)
	exptl	81.9(2)		
$\beta$	I	98.7 (98.6)	117.6 (117.3)	105.8 (106.2)
	exptl	88.6(2)		
$\gamma$	I	153.7 (154.3)	179.2 (178.7)	182.5 (181.1)
	exptl	167.1(3)		
E	I	0 (0)	20.7 (19.0)	11.5 (15.3)

<sup>a</sup> Relative energies are in kcal mol<sup>-1</sup>. The energy of the *trans* structure is -582.78849 au (B3LYP) and -582.95411 au (BP86). <sup>b</sup> Basis set I was used with both B3LYP and BP86 functionals (values in parenthesis for the latter). <sup>c</sup> Experimental (exptl) data are taken from ref 11b.

**Table 3.** Main Geometrical Parameters (Bond Lengths in Å, Angles in deg) Optimized for the *Trans* and the *Cis* Isomers of Complexes **11** ( $\text{ReO}_2(\text{HN}=\text{CHCH}=\text{NH})(\text{NH}_3)_2^+$ ) and **14** ( $\text{ReO}_2(\text{bpy})(\text{NH}_3)_2^+$ ) with B3LYP Functional and Basis Sets I and/or II<sup>a</sup>

		<b>11t</b> (dia)	<b>11c</b> (dia)	<b>11c</b> (para)	<b>14t</b> (dia)	<b>14c</b> (dia)
Re=O	I	1.802	1.768	1.794	1.802	1.776
	II	1.781	1.742			
	exptl <sup>b</sup>		1.735(7)			1.735(7)
Re—N <sub>1,2</sub>	I	2.170	2.110	2.180	2.095	2.181
	II	2.183	2.135			
	exptl		2.20(1)			2.20(1)
Re—N <sub>3,4</sub>	I	2.235	2.217	2.216	2.263	2.215
	II	2.244	2.228			
	exptl		2.138(9)			2.138(9)
$\alpha$	I	74.5	70.7	70.3	74.5	71.1
	II	74.2	69.8			
	exptl		70.6(3)			70.6(3)
$\beta$	I	86.0	120.9	105.4	82.5	121.3
	II	86.3	120.9			
	exptl		121.4(4)			121.4(4)
$\gamma$	I	174.0	170.6	178.5	168.0	170.9
	II	173.3	170.3			
	exptl		169.0(3)			169.0(3)
E	I	28.7	0	30.2	7.5	0
	II	27.4	0			

<sup>a</sup> Relative energies are in kcal mol<sup>-1</sup>. The energy of **11c** is -529.36157 au (basis set I) and -529.91226 au (basis set II), and that of **14c** is -832.69789 au (basis set I). <sup>b</sup> Experimental (exptl) values are taken from ref 8a.

triplet energy gap in **10c** from 9.2 to 3.7 kcal mol<sup>-1</sup> (Table 2), a value too small to allow a definite conclusion.

Optimized geometrical parameters for the *trans* isomer compare rather well with the experimental data.<sup>11b,c</sup> The optimized Os—O bond length is close to the average experimental one (1.960 vs 1.983(5) Å) while the Os=O one is overestimated (1.791 Å instead of 1.728(5) Å, Table 2). The bite angle of the glyoxalate ligand is not very different from 90° (86.5° (exptl 81.9(2)°)), and the O=Os=O unit is bent away from the bidentate ligand ( $\gamma = 153.7^\circ$ ). This bending is however found to be larger than that in the related experimental complex ( $\gamma = 167.1(3)^\circ$ ), but in excellent agreement with recent ab initio calculations on the same model complex ( $\gamma = 151.3^\circ$ ).<sup>1e</sup> A reason for this discrepancy between theoretical and experimental values might be the size of the pyridine ligands which could reduce the ability of the O=Os=O unit to bend in complex **5**. Although some of these values could be improved

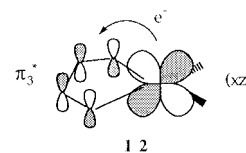
by using the extended basis set II (in particular the Os=O distance), no further optimizations were performed on this complex. In fact, (i) the calculations with basis set I reproduce the usual *trans* arrangement of the O=M=O unit found in the experimental complex **5**<sup>11</sup> and (ii) the energy difference between the *cis* and the *trans* isomers is large enough to make us confident that no inversion would occur with the basis set II (in complex **7**, the change in the relative energies was at most 3.6 kcal mol<sup>-1</sup> in going from basis set I to basis set II, Table 1).

Similar calculations were performed on the complex  $\text{ReO}_2(\text{HN}=\text{CHCH}=\text{NH})(\text{NH}_3)_2^+$  (**11**), the results being reported in Table 3. In marked contrast with the other complexes, the diamagnetic *cis* isomer is now the most stable structure. The computed energy difference between the *cis* and the *trans* isomers is 28.7 kcal mol<sup>-1</sup> (basis set I).<sup>21</sup> We checked the influence of the basis set by reoptimizing both isomers in their diamagnetic state with the extended basis set II. The energy difference remains almost unchanged (27.4 kcal mol<sup>-1</sup>). Therefore, there is no doubt that the *cis* isomer is more stable than the *trans* isomer in complex **11**. In the former, the triplet state is located well above the diamagnetic state (30.2 kcal mol<sup>-1</sup>, basis set I).

Let us compare the geometrical parameters optimized with the extended basis set II with the data on the related experimental complex **2** (Table 3). The optimized Re=O bond lengths (1.742 Å) are in good agreement with the experimental ones (1.733(8) and 1.736(7) Å) while the Re—N (bidentate) bond lengths are underestimated by about 0.07 Å. As in the preceding complexes, the Re—NH<sub>3</sub> bond length is found to be longer than the Re—py ones (2.228 Å instead of 2.138 Å). The optimized values for  $\alpha$  (bite angle),  $\beta$  (O=Re=O angle), and  $\gamma$  angles all fall very close the experimental ones: 69.8° (70.6(3)°), 120.9° (121.4(4)°), and 170.3° (169.0(3)°), respectively.

## Discussion

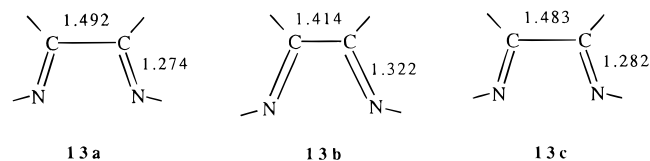
These results on the model complexes  $\text{OsO}_2(\text{OCH}_2\text{CH}_2\text{O})(\text{NH}_3)_2$  (**10**) and  $\text{ReO}_2(\text{HN}=\text{CHCH}=\text{NH})(\text{NH}_3)_2^+$  (**11**) account for both the geometry and the magnetic properties of the related experimental complexes **5** and **2**, respectively: in the former, the arrangement of the O=M=O unit is *trans* while in the latter it is *cis*, and both complexes are diamagnetic. The inversion of the stability order may be traced to the smaller bite angle and to the  $\pi$  acceptor properties of the bidentate ligand in **11** (instead of  $\pi$  donor in **10**). The later factor may be exemplified as follows: the stabilization of the HOMO ( $xz$ ) by a bonding interaction with the vacant  $\pi_3^*$  orbital of the diaza-1,4-butadiene (**12**) populates  $\pi_3^*$  which is N—C antibonding and C—C bonding.



Comparison of the optimized geometries (basis set II) of the isolated (**13a**) and the complexed (**13b**) diaza-1,4-butadiene actually shows significant lengthening of the N—C bonds and shortening of the C—C one. Therefore, the stabilizing d— $\pi$  interaction in the *cis* isomer is expected to be large. In the *trans* isomer, the overlap between the HOMO ( $x^2 - y^2$ ) and the  $\pi$  system of the bidentate ligand vanishes by symmetry: the

(21) Using the BP86 functional, the relative energies were found (without reoptimizing the geometries): 0, 38.1, and 35.4 kcal mol<sup>-1</sup> for **11c** (dia), **11t** (dia), and **11c** (para), respectively.

geometries of the complexed (**13c**) and the free (**13a**) bidentate ligands are almost identical.

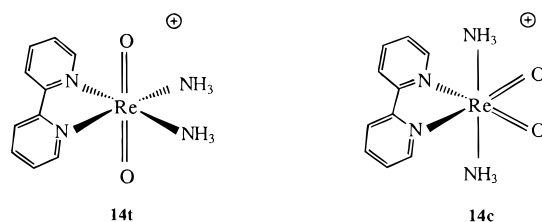


Another interesting result concerns the electronic ground state of the *cis* isomer. In **11c**, the diamagnetic state is located well below the triplet state (30.2 kcal mol<sup>-1</sup>) while in **10c** the triplet state is more stable (B3LYP) or at least competitive in energy (BP86) with the diamagnetic state. With pure  $\sigma$  donor ligands (see **7c**), the energy gap is intermediate between the values found for **10c** and **11c** (14.8 kcal mol<sup>-1</sup> in favor of the diamagnetic state). These results first show that a large O=M=O equilibrium angle in the *cis* isomer does not necessarily prevent the ground state from being paramagnetic. The  $\pi$  properties of the bidentate ligand should contribute to this large change in the following way: with respect to pure  $\sigma$  donor ligands such as NH<sub>3</sub> (**7c**), the HOMO ( $xz$ ) is destabilized by a  $\pi$  donor ligand in **10c** and stabilized by a  $\pi$  acceptor in **11c**, thus making the diamagnetic state more favored, which is in agreement with the series **10c**, **7c**, and **11c**.<sup>22</sup>

Although our results on the model complexes OsO<sub>2</sub>(OCH<sub>2</sub>-CH<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub> (**10**) and ReO<sub>2</sub>(HN=CHCH=NH)(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> (**11**) nicely account for the structures and the magnetic properties of the related experimental complexes **5** and **2**, one must recall that the formation of the *cis* complex **2** has been suggested to reflect a *kinetic* preference.<sup>8a</sup> Since **11c** is found to be definitely more stable than **11t**, it remains to determine if **11** is a good enough model for complex **2** to conclude that the *cis* complex **2** is the thermodynamically most stable isomer. In the characterized *cis* complex **2**, the pyridines are *trans* to each other (no steric repulsion). Therefore, we see no obvious reasons for which the replacement of pyridines by smaller NH<sub>3</sub> groups would strongly favor the *cis* isomer. Moreover, the model (diaz-1,4-butadiene) and the actual (bpy) bidentate ligand properties are similar for the  $\alpha$  bite angle (69.8 and 70.6(3)<sup>o</sup>, respectively) and for the  $\sigma$ -donating character ( $sp^2$  nitrogen lone pairs in both cases). Finally, both these ligands act as  $\pi$  acceptors with respect to the metal fragment. However, test calculations using the EH method showed that the electron transfer to the vacant  $\pi^*$  orbital(s) is 0.40 electron with the diaza-1,4-butadiene ligand and only 0.10 electron with the bipyridine ligand.<sup>13b</sup> Therefore, the model complex **11** is questionable with respect to the *cis* vs *trans* problem in complex **2** because the  $\pi$  acceptor properties of the bidentate ligand are overestimated. According to our previous analysis, the *cis* isomer should be less favored in **2** than in **11**.

Further calculations were thus performed on the more realistic ReO<sub>2</sub>(bpy)(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complex (**14**) with basis set I. Since full geometry optimization was not feasible, the geometrical pa-

rameters associated with the bipyridine ligand were held fixed at their experimental values.<sup>8a</sup> Bond lengths and bond angles around the metal center were then optimized in both *trans* (**14t**) and *cis* (**14c**) isomers. The optimized parameters in **14c** (Table



3) are in good agreement with the experimental data for complex **2**: 1.776 Å for Re=O (exptl 1.735(7) Å); 2.181 Å for Re-N-(bpy) (exptl 2.20(1)); 71.1, 121.3, and 170.9<sup>o</sup> for  $\alpha$ ,  $\beta$ , and  $\gamma$  angles, respectively (exptl 70.6(3), 121.4(4), and 169.0(3)<sup>o</sup>). The Re-NH<sub>3</sub> bond lengths are, as in the other complexes, longer than the Re-py ones. While there are no significant changes in the optimized geometrical parameters in going from complex **11** to complex **14**, the energy difference between the two isomers strongly decreases from 28.7 to 7.5 kcal mol<sup>-1</sup> (basis set I, Table 3). The same trend is found using the BP86 functional: without reoptimizing the geometries, this energy difference decreases from 38.1 to 13.2 kcal mol<sup>-1</sup>. Strictly speaking, these calculations do not prove the *cis* complex **2** to be the thermodynamic isomer, but make this possibility not to be excluded. As a matter of fact, the expected (thermodynamic?) *trans* isomer of complex **2** is still unknown. We still however have to remember that (1) the bipyridine geometry is not optimized in our calculations (we have used the experimental values reported for the *cis* complex **2** for both *cis* and *trans* isomers of **14**) and (2) the pyridine ligands are replaced by NH<sub>3</sub> groups. On the other hand, from an experimental point of view, a linear MO<sub>2</sub> arrangement has been proposed from IR data for RuO<sub>2</sub>(bpy)X<sub>2</sub> complexes (X = mesityl, Cl)<sup>17,23a</sup> and the X-ray structure of OsO<sub>2</sub>(phen)-(mes)<sub>2</sub> (phen = 1,10-phenanthroline, mes = mesityl)<sup>23b</sup> also reveals a *trans* structure of the O=Os=O unit. These experimental data suggest that the energy difference between *cis* and *trans* isomers might be rather small in this family of d<sup>2</sup> MO<sub>2</sub>-(L-L)X<sub>2</sub> complexes and also depend on the metal and the ancillary ligands X. DFT calculations are in progress to clarify these points.

## Conclusion

The main purpose of this work was to show that in some d<sup>2</sup> octahedral dioxo complexes the unusual *cis* isomer might be more stable than the *trans* isomer. The results actually suggest that the formation of unusual *cis* complexes can be made easier by tuning the geometric and the electronic properties of an ancillary bidentate ligand.

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(22) According to this reasoning, the diamagnetism of the *cis* complexes **1**, which contain a bidentate acetato ligand, may be surprising. However, EH calculations<sup>13b</sup> have shown that, due to the values of the M-O bond lengths (about 0.2 Å longer than in **5**), the d- $\pi$  interactions are almost negligible. DFT calculations on this complex are in progress.

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