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Favoring the *cis* Isomer in d^2 Octahedral Dioxo Complexes: Role of the Metal

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Introduction

Most of the octahedral dioxo transition metal complexes of d^2 electronic configurations exhibit a *trans* arrangement of the $O{=}M{=}O$ unit.[1−3] This trend was rationalized on orbital grounds[1a,b] (Chart 1): in the *trans* isomer, one of the three orbitals deriving from the t$_{2g}$ block ($x^2 - y^2$) remains nonbonding, which is ideal to accommodate the two d electrons. In the *cis* isomer the three d orbitals are destabilized by antibonding interactions with the oxygen lone pairs so that the HOMO (*yz*) is higher in energy than it is in the *trans* isomer.

However, a few diamagnetic *cis* d^2 complexes have been characterized (X-ray)[4−6] and they are of great chemical interest: compared to the usual *trans* isomers, they lead to new oxidation pathways and accelerate the kinetics of multielectron chemical reduction.[7]

In a previous theoretical study, we showed how tuning the geometrical and electronic properties of ancillary ligands may help to reverse the usual stability order of the two isomers.[8] In particular, a bidentate ligand imposing an acute bite angle destabilizes the *trans* isomer and stabilizes the *cis* isomer. Good π-acceptor properties of such a ligand also work in favor of the *cis* isomer: for instance, the HOMO (*yz*) can be stabilized by a bonding interaction with the LUMO π_3* of the diimine ligand (Chart 2b), while such an interaction is prevented by symmetry in the *trans* isomer because the HOMO ($x^2 - y^2$) is lying in the nodal plane of the ligand π system (Chart 2a). The usual energy ordering of the two isomers was actually found to be reversed in the $Re(HN{=}CHCH{=}NH)(NH_3)_2O_2^+$ complex in which the diimine ligand fulfills the geometrical and electronic conditions described above.

In this note, it is shown how, for a given set of ligands, the energy difference between *cis* and *trans* diamagnetic isomers may also strongly depend on the nature of the metal. The changes studied involve moving both in a row (Re, Os) and in a column (Ru, Os). Geometry optimizations were performed on the dioxo compounds $M(HN{=}CHCH{=}NH)(NH_3)_2O_2^{q+}$ (Chart 3), in which the diimine acts as a chelating bidentate ligand, while two monodentate NH$_3$ molecules complete the coordination sphere. A d^2 electronic count on the metal requires the rhenium complex to bear one positive charge ($q = 1$), while the ruthenium and the osmium complexes are dications ($q = 2$).

Chart 1

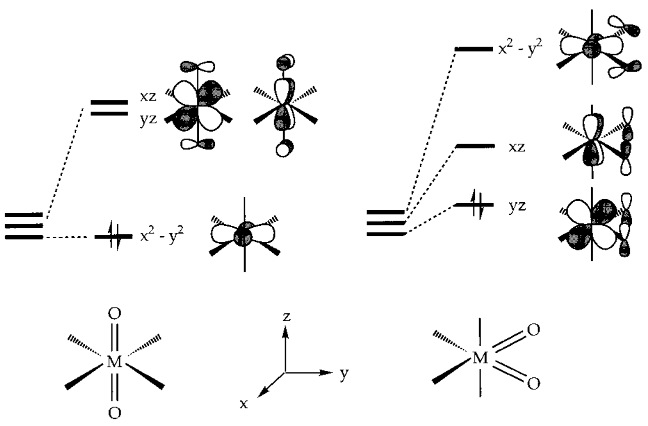
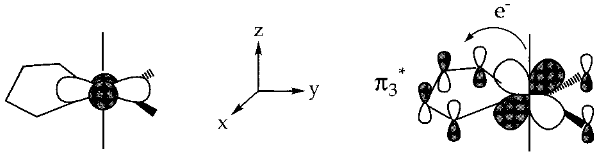
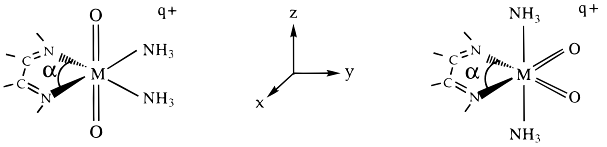


Chart 2



2 a **2 b**

Chart 3



3 t **3 c**

Computational Details

Quasirelativistic pseudopotentials were used for the transition metal atoms (Re, Os, Ru) with the (8s/7p/6d) basis set contracted to a (6s/5p/3d) basis set for the valence orbitals (which include 5s and 5p for Re and Os and 4s and 4p for Ru).[9a] For the other atoms, the 6-31G* basis set[9b] was used. DFT calculations were performed for all the complexes using the B3LYP functional implemented in the Gaussian 92/DFT package.[10] The *cis* and the *trans* isomers of each complex were optimized with the C_2 symmetry maintained; the nitrogen environment in the NH$_3$ ligands was kept tetrahedral, and the N−H bond lengths were held fixed to 1.0 Å.

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Table 1. Relative Energies (kcal/mol) of the *cis* and the *trans* Isomers in the M(HN=CHCH=NH)$(NH_3)_2O_2^{q+}$ Complexes (M = Re (q = 1), M = Os (q = 2), M = Ru (q = 2))[a]

	free diimine	Re complex		Os complex		Ru complex	
		cis	*trans*	*cis*	*trans*	*cis*	*trans*
ΔE		0	27.4	0	4.5	0	5.2
$\pi + \pi^*$ pop	4.00	4.62	4.04	4.16	4.01	4.08	4.00
N−M−N		69.8	74.2	69.8	75.4	70.0	75.9
M−N		2.135	2.184	2.180	2.145	2.212	2.142
N−C	1.274	1.322	1.282	1.289	1.283	1.282	1.282
C−C	1.492	1.414	1.484	1.467	1.491	1.481	1.490

[a] The π populations and the optimized geometrical parameters (bond lengths in angstroms; angles in degrees) are given for the diimine (free molecule and bidentate moiety in the *cis* and the *trans* geometries). B3LYP energies (au) of the *cis* structures are −529.912 26 (Re), −541.827 83 (Os), and −545.978 27 (Ru).

Results and Discussion

The energy differences between the *cis* and the *trans* diamagnetic isomers are reported in Table 1 for the three complexes under study (M = Re, Os, Ru). Due to the presence of the diimine ligand, the unusual *cis* isomer is always found to be more stable. However, the energy difference dramatically decreases in going from the rhenium to the osmium complex (27.4 and 4.5 kcal/mol, respectively). In marked contrast, replacing osmium by ruthenium leaves the energy difference small and almost unchanged (4.5 and 5.2 kcal/mol, respectively). The change between Re and Os or Ru complexes is so large that it can be concluded that, for this set of ligands, the rhenium complex is by far the best candidate for the formation of the unusual *cis* isomer.

This trend can be rationalized by analyzing the evolution of the geometrical and electronic factors recalled in the Introduction. Let us first note that in the three complexes the optimized bite angles NMN (α) are almost insensitive to the nature of the metal: they remain equal to 70 and 74−76° in the *cis* and the *trans* geometries, respectively (Table 1). Therefore, these small bite angles work in favor of the *cis* isomer in the three complexes, but the changes in the relative stability of the two isomers cannot be traced to this geometrical factor. The second factor is the back-donation interaction at work in the *cis* isomer between the HOMO on the d^2 metal center and the LUMO of the diimine ligand (Chart 2b). There are two ways to estimate the strength of this interaction: (i) it increases the π population on the bidentate ligand by populating the π_3^* orbital; (ii) due to the phase relationships in this orbital, this electron transfer results in a geometrical distortion of the bidentate chelating moeity, i.e. a shortening of the C−C bond and a lengthening of the N=C bonds. It is expected that the larger the electron transfer, the greater the bond length changes in the diimine ligand.

The π electron population, obtained from NBO analysis, and the main optimized parameters are given in Table 1. Let us first notice that diimine π populations in the *trans* isomers are close to 4 electrons, i.e. the value for the free diimine molecule. Comparison of the optimized bond lengths in the free and in the chelating diimine in the *trans* geometries shows no significant changes (Table 1). Both sets of results confirm the absence of any significant metal−diimine back-bonding interaction in this arrangement of the oxo groups. In marked contrast, there is a diimine π population excess in the *cis* isomers which results from the interaction depicted in Chart 2b. The electron transfer toward the diimine ligand is however much larger in the rhenium complex (0.62 e^-) than in the osmium (0.16 e^-) or ruthenium (0.08 e^-) complexes (Table 1). The optimized values for the N=C and C−C bond lengths in the *cis* compounds are consistent with the amplitude of the metal−diimine electron transfers.[11] Compared to those of the free diimine molecule, N=C bonds are lengthened by 0.048 Å and the C−C bond is shortened by 0.078 Å in the Re complex. Corresponding variations for the Os and Ru complexes are only 0.015, 0.025, and 0.008, 0.002 Å, respectively. These results afford a clear rationalization of the origin of the energy difference between the *cis* and the *trans* isomers depending on the nature of the metal center: in the rhenium complex, both the acute bite angle of the bidentate ligand and the large electron transfer toward this π-acceptor ligand make the *cis* isomer definitely more stable. In the osmium and ruthenium complexes, this transfer is much smaller and only the first geometrical factor works in favor of the *cis* isomer: as a matter of fact, the two isomers are close in energy.

Two questions remain to be answered: (i) Why is the back-donation interaction found to be much smaller in the Os and Ru complexes than in the Re complex? (ii) How could the preference for the *cis* isomer be increased for Os and Ru complexes?

The ability of a metal center to transfer electrons toward a given π-acceptor ligand (the diimine in our model complexes) is related to the d orbital energies and to their diffuseness. From the position of the three neutral metal atoms in the periodic table, one may expect a decrease of atomic radius in the order rhenium, osmium, ruthenium.[12] Although it is consistent with the ordering of the electron transfers (Re > Os > Ru), we believe this argument alone can hardly explain the dramatically different results found for the Re complex compared to the Os and Ru complexes. Another important factor which distinguishes the rhenium complex is the total charge: it is a monocation, while Ru and Os complexes are dications. This charge effect makes the d orbitals more diffuse and higher in energy in the rhenium complex than in the ruthenium and osmium complexes. Consequently, the back-bonding metal−diimine interaction is much stronger in the former.

According to the above analysis, one should expect the *cis* isomer in Os(VI) or Ru(VI) octahedral dioxo complexes to be favored by increasing the electron-donating ability of the metal center. One way could be to use neutral or negatively charged complexes instead of dicationic species. As a matter of fact, two among the three characterized *cis* dioxo d^2 complexes[4−6] actually involve Os and Ru metal centers in negatively charged complexes ($OsO_2(O_2CMe)_3^-$ and $RuO_2Cl_2(O_2CMe)^-$). In order to test the influence of the charge on the energy difference between the *cis* and the *trans* isomers, additional calculations were performed on the neutral Os(HN=CHCH=NH)O_2Cl_2 complex and compared to the results for the dicationic complex Os(HN=CHCH=NH)$O_2NH_3^{2+}$. The *cis* isomer was found to be favored by 9.1 kcal/mol, a value two times larger than that found for the related dicationic complex (4.5 kcal/mol, Table 1). As expected, the metal−diimine electron transfer is larger in the neutral complex (0.30 e^-) than in the dicationic complex (0.16 e^-). Note that the increased electron-donating ability of the metal in the neutral Os(HN=CHCH=NH)O_2Cl_2 complex is likely to be enhanced by the π-donating character of the chloride ligands, which will raise the energy of the HOMO (*yz*).

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(11) Note also the M−N bond evolution from *trans* to *cis* isomer. With osmium and ruthenium metal atoms, M−N distances increase as a geometrical consequence of NMN angle decrease. In spite of a similar NMN evolution in the rhenium complex, the M−N bond length decreases from *trans* to *cis* geometry. This trend results from the strong metal−diimine bonding interaction (Chart 2b) at work in the Re complex.

(12) This evolution is reflected by the decrease of the optimized M−O bond lengths (for instance in *trans* isomers: 1.781 Å (Re), 1.747 Å (Os), 1.722 Å (Ru)).

In conclusion of this study, the energy difference between the *cis* and the *trans* isomers in octahedral d^2 dioxo complexes with a π-acceptor bidentate ligand strongly depends on the electronic properties of the metal center: the better its electron-donating capability, the more favored the unusual *cis* isomer. Since we showed previously[8] that the same trend holds upon making the ligand π system more electron withdrawing, a good energy and overlap match between the filled d orbital and the ligand π-acceptor orbital seems to be required to favor the unusual *cis* isomer.

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Supporting Information Available: A table of optimized geometrical parameters for $M(HN{=}CHCH{=}NH)(NH_3)_2O_2^{q+}$ complexes ($M = Re$ ($q = 1$), $M = Os$ ($q = 2$), $M = Ru$ ($q = 2$)) in *cis* and *trans* geometries (1 page). Ordering information is given on any current masthead page.

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