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Quantum-Chemical Calculations of Ruthenium Nitrosyl Complexes with Tetradentate Macrocyclic Ligands

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Abstract—The geometric structure of the ground state and of metastable isomers of nitrosyl complexes *trans*-[Ru(P)(NO)(Cl)] (P = porphinate dianion) and *trans*-[Ru(NO)(salen)(X)]^q [salen = *N*,*N*'-ethylenebis(salicylideniminate) dianion; X = Cl^- (q = 0), H_2O (q = +1)] was optimized within the framework of the density functional method (SVWN/LanL2DZ+6-31G). The local minima corresponding to metastable isomers with a linear NO coordination through the oxygen atom and with a side η^2 NO coordination were found on the potential energy surfaces of these compounds. The second metastable states of all the three complexes have a lower energy. The difference in energies between the stable and metastable isomers is the least in the case of the complex *trans*-[Ru(NO)(salen)(Cl)].

Here we report on quantum-chemical calculations of nitrosyl complexes [Ru(P)(NO)(X)]^q with two tetradentate ligands: L = P (porphinate dianion) and L = salen [*N*,*N*'-ethylenebis(salicylideniminate) dianion $C_{16}H_{14}N_2O_2^{2-}$]. These compounds and their derivatives are actively studied in the context of a search for photoreactive NO donors with which the nitrogen oxide content in a living body could be controlled [1]. Previously [2] we calculated the structural characteristics of the nitrosyl complexes $[Ru(NO)(CN)_5]^{2-}$, $[Ru(NO)Cl_5]^{2-}$, and *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$ (L = NH_3, im, py, pyz, and nc) using the density functional method (DFT). Along with the stable structure with the η^1 coordination of the nitrosyl group through the nitrogen atom (GS), we have found two metastable isomers for each of the above complexes: with a linear η^1 NO cordination through the oxygen atom (MS1) and with a dihapto η^2 NO cordination (MS2). It was shown that, in the series of *trans*-$[Ru(NO)(NH_3)_4(L)]^{3+}$ ammine complexes, the difference in the energy between the η^1-NO and η^1-ON isomers is almost independent of the *trans* ligand, whereas the energy of the η^2-NO isomer decreases when the ligand has π-acceptor properties.

The formation of metastable coordination isomers η^1-ON and η^2-NO for the complexes $Ru^{III}(OEP)\cdot(NO)(L)$ (OEP = octaethylporphyrin), L = *O*-*iso*-C_5H_{11}, SCH_2CF_3) upon irradiation at low temperatures was detected by IR spectroscopy [3]. These metastable states were confirmed also by DFT calculations of [Ru(P)(NO)(Cl)] [4]. For the comparison of the calculated characteristics of [Ru(P)(NO)(Cl)] and other nitrosyl complexe to be possible, we included this complex in the set of compounds to be studied within the framework of a common calculation scheme.

The synthesis and properties of the nitrosyl complexes $[Ru(salen)(NO)(H_2O)]^+$ and [Ru(salen)(NO)Cl] have been described in [5–7]. It was found that, when the complexes [Ru(salen)(NO)Cl] (in organic solvents) and $[Ru(salen)(NO)(H_2O)]^+$ (in aqueous solutions) are irradiated by visible light, they lose the nitrosyl ligand in the form of nitrogen(II) oxide: $[Ru(salen)(X)(NO)]^q$ + Sol $\rightarrow$ $[Ru^{III}(salen)(X)(Sol)])]^q$ + NO (X = Cl^-, H_2O, Sol is a solvent molecule). Since the complex with X = H_2O is soluble in water, thermodynamically stable, and kinetically inert under physicochemical conditions characteristic for human body, it is considered as a potential photoreactive therapeutic preparation. The tetradentate ligand salen, like porphyrins, is a double-charged anion with an expanded system of π bonds. However, unlike porphyrins, it is asymmetric and coordinated through two pairs of nonequivalent atoms (N and O), and its atoms are not coplanar (Fig. 1).

All the calculations were performed using the GAMESS program [8]. As in [2], we used the DFT method with the local SVWN5 functional [9] in the LanL2DZ basis and effective core potential for Ru and Cl atoms [10] and in the 6-31G basis for H, C, N, and O atoms {the replacement of the LanL2DZ basis by the 6-31G basis for the chlorine atom in the case of [Ru(NO)(salen)(Cl)] does not noticeably affect the calculation results}. The geometry of the complexes was optimized without imposing restrictions

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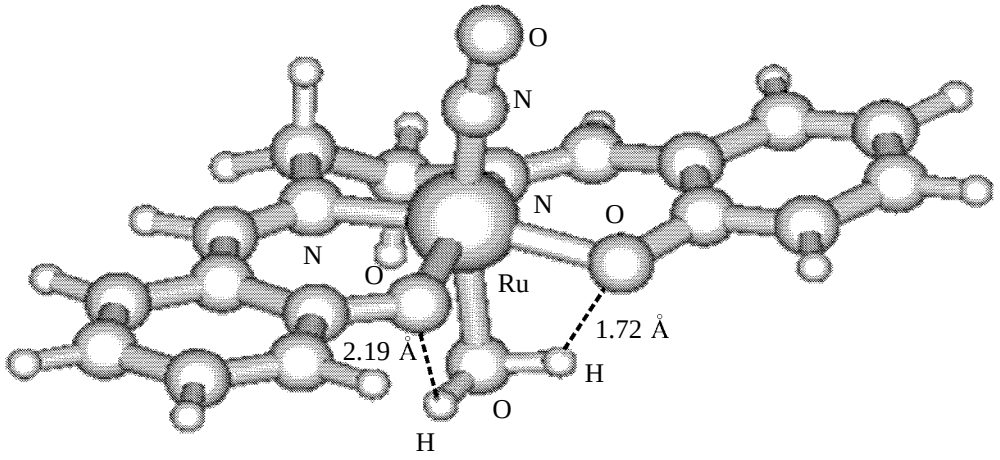

Fig. 1. Structure of the complex $[Ru(NO)(salen)(H_2O)]^+$.

on symmetry. The results were analyzed in two aspects: comparison of [Ru(L)(NO)(Cl)] complexes with L = P and L = salen and comparison of $[Ru(NO)(salen)(X)]^q$ complexes with X = H_2O and X = Cl^-.

The calculated characteristics of stable η^1 NO isomers of the complexes $[Ru(NO)(salen)(X)]^q$ (X = Cl^-, H_2O) reasonably agree with the experimental data (Table 1). Both these values suggest that, on passing from the complex [Ru(NO)(salen)(Cl)] to $[Ru(NO)\cdot(salen)(H_2O)]^+$, the frequency of the ν(N–O) stretching vibration increases, the lengths of the N–O and Ru–N bonds decrease, and the differences in the lengths of bonds in the equatorial plane become somewhat more pronounced. It should be noted that, in the optimized structure of the complex $[Ru(NO)\cdot(salen)(H_2O)]^+$, the twofold axis of the H_2O molecule does not coincide with the line of the Ru–OH_2 bond, H atoms are oriented toward the equatorial O atoms, the plane of the molecule is inclined in the same direction, and the H(H_2O)–O(salen) distances (2.19 and 1.72 Å) suggest possible interactions between these atoms (Fig. 1).

By varying the starting geometry, in addition to stable structures (GS) with a linear Ru–N–O group, for each of the complexes under consideration we obtained two more local minima on the potential energy surface of the ground state, corresponding to the metastable isomers MS1 and MS2. The results of calculations of the ground and metastable states of the complexes $[Ru(NO)(salen)X]^q$ and [Ru(P)(NO)(Cl)] are given in Table 2. In the isomers with the dihapto coordination of NO, the Ru–N bond (~1.9 Å) is considerably shorter than the Ru–O bond (~2.4 Å), and the N–O bond is weakened, as indicated by its length and stretching vibration frequency (Table 2). In the MS2 state, the nitrosyl nitrogen atom is inclined toward the equatorial ligands (∠NRuCl ~155°), and the oxygen atom is located closely to a perpendicular to the equatorial plane (∠ORuCl ~175°). The line of the N–O bond of the complex [Ru(P)(NO)(Cl)] is located in the diagonal plane relative to the bonds of the metal with equatorial ligands, whereas in the complexes [Ru(NO)(salen)X] it is turned so that its N atom is located closer to one of the equatorial O atoms (Fig. 2).

The optimized structures of the GS and MS1 states of the complex [Ru(P)(NO)(Cl)] have a symmetry close to C_{4v}: the RuNO group lies on a normal to the porphine plane, in contrast to the complexes with L = salen; all the four bonds with the porphine nitrogen atoms are equivalent, their lengths being 2.051 and 2.043 Å in the GS and MS1 states, respectively. In the MS2 isomer, the symmetry of the equatorial ligand is broken: both Ru–N bonds to which the nitro-

Table 1. Calculated and experimental bond lengths (*R*, Å), angles (deg), and ν(NO) frequencies (cm^{-1}) for stable isomers (GS) of *trans*-$[Ru(NO)(salen)X]^q$ complexes

Parameter	X = Cl^-		X = H_2O	
	calculation	experiment [7]	calculation	experiment [7]
R(N–O)	1.195	1.149	1.185	1.142
R(Ru–N)	1.769	1.728	1.753	1.718
R(Ru–N)salen	2.007	2.013	2.004	2.039
	2.008	2.012	1.994	2.000
R(Ru–O)salen	2.030	2.034	2.060	2.034
	2.021	2.030	2.026	2.020
R(Ru–X)	2.375	2.354	2.110	2.059
∠RuNO	174.3	173.7	174.2	176.3
ν(N–O)	1796	1838	1849	1855

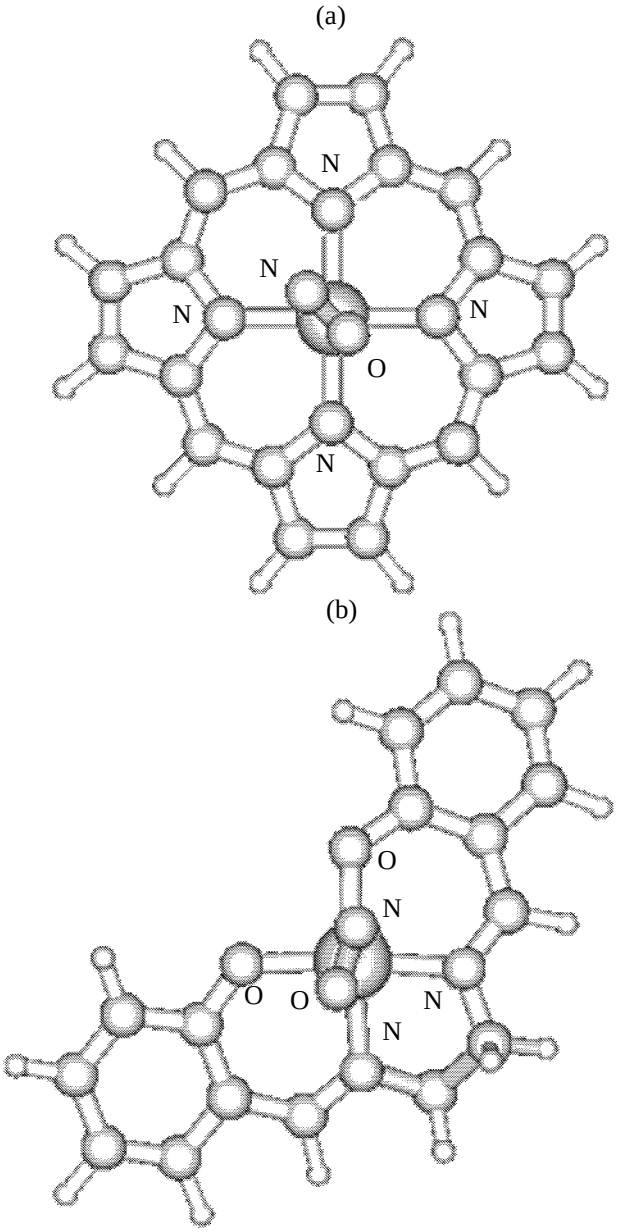

Fig. 2. Orientation in the η^2 isomers of the complexes (a) [Ru(P)(NO)(Cl)] and (b) [Ru(NO)(salen)(Cl)] (projection onto equatorial plane).

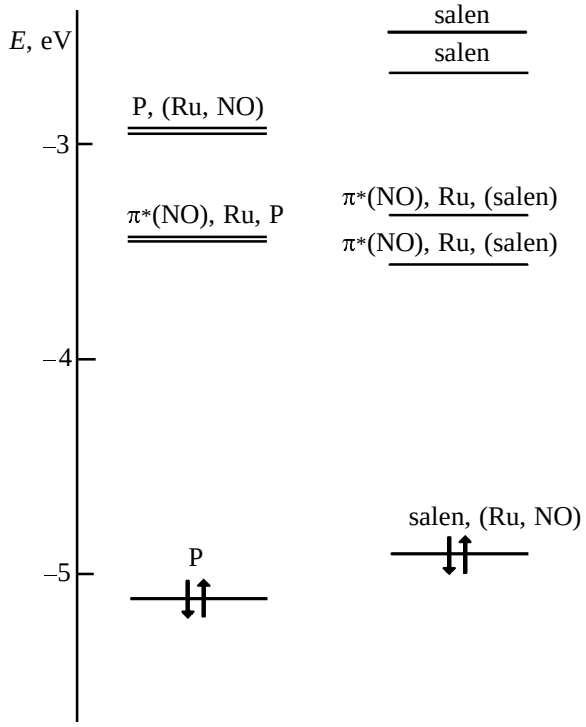

Fig. 3. Comparison of diagrams of Kohn–Sham frontier orbitals for [Ru(P)(NO)(Cl)] and [Ru(NO)(salen)(Cl)].

syl nitrogen atom is inclined are longer than the Ru–N bonds to which it is faced by the O atom (Table 2). In the complex with L = salen, the bonds of Ru with the atoms of the nitrosyl group are shorter than in the complex with L = P. In GS, the length of the N–O bond is somewhat longer than in the complex with L = salen. This difference remains and even increases in going to MS1 and MS2, which correlates with changes in the frequency of the NO stretching vibration, decreasing in the order GS > MS1 > MS2 for all the complexes under consideration. For [Ru(P)(NO)·(Cl)], $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS1})$ is 121 and $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS2})$, 396 cm^{-1}; for [Ru(salen)(NO)Cl)], $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS1})$ is 128 and $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS2})$, 419 cm^{-1}. In the complex [Ru(salen)(NO)(H_2O)], $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS1})$ is 147 and $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS2})$, 514 cm^{-1}. The experimentally determined changes in the frequency of the NO stretching vibrations for the complexes Ru^{III}(OEP)(NO)(L) (OEP = octaethylporphyrin, L = O-*iso*-C_5H_{11} and SCH_2CF_3) are as follows: $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS1})$ 146 and 128 cm^{-1}, $\Delta\nu(\mathrm{GS}\rightarrow\mathrm{MS2})$ 294 and 242 cm^{-1}, respectively [3].

Judging from total charges of equatorial ligands [q(P) –0.54 and q(salen) –0.30], the nitrosyl group in the complexes [Ru(L)(NO)(Cl)] (L = salen) proves to be a better electron donor; nevertheless, in [Ru(P)·(NO)(Cl)] and [Ru(NO)(salen)(Cl)] the charge of the nitrosyl group (Table 2) and the Ru–NO bond orders are almost equal: The linearly coordinated nitrosyl group forms a very strong bond with the metal, typical of such complexes, and shows a low sensitivity to variation of the composition of the isolated complex. The Ru–NO and N–O bond orders for the complexes are given below.

Complex	Bond order	
	Ru–NO	N–O
[Ru(P)(NO)(Cl)]	1.07	1.54
[Ru(NO)(salen)(Cl)]	1.06	1.51
$[Ru(NO)(salen)(H_2O)]^+$	1.12	1.55

Table 2. Bond lengths (R, Å), angles (deg), effective charges of atoms and fragments (q), bond orders (B), energies (ε, eV) of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, ν(NO) frequencies (cm^{-1}), and energies (E, eV) of the MS1 and MS2 states relative to GS for the complexes *trans*-[Ru(P)(NO)(Cl)], *trans*-[Ru(NO)(salen)(Cl)], and *trans*-$[Ru(NO)(salen)(H_2O)]^+$, as calculated by the SVWN5/LanL2DZ(Ru, Cl)+6-31G(N, O) method

Parameter	[Ru(P)(NO)(Cl)]			[Ru(NO)(salen)(Cl)]			$[Ru(NO)(salen)(H_2O)]^+$		
	GS	MS2	MS1	GS	MS2	MS1	GS	MS2	MS1
R(N–O)	1.190	1.235	1.194	1.195	1.246	1.200	1.185	1.255	1.193
R(Ru–N)	1.764	1.962	–	1.769	1.944	–	1.753	1.919	–
R(Ru–O)	–	2.425	1.854	–	2.359	1.863	–	2.214	1.842
R(Ru–X)	2.356	2.327	2.321	2.375	2.371	2.338	2.110	2.052	2.071
R(Ru–N_{cis})	2.051	2.077	2.043	2.007	1.994	1.991	2.004	1.995	1.996
		2.014		2.008	1.986	1.991	1.994	2.005	1.986
R(Ru–O_{cis})	–	–	–	2.030	2.008	2.021	2.060	2.018	2.048
				2.021	2.039	2.021	2.026	2.093	2.016
∠RuNO	180.0	96.0	–	174.3	92.8	–	174.2	85.7	–
∠RuON	–	53.0	180.0	–	55.4	178.6	–	59.8	174.6
∠N(O)RuX	(N) 180.0	(N) 153.1	(O) 180.0	(N) 175.5	(N) 157.0	(O) 179.1	(N) 167.8	(N) 146.4	(O) 170.6
		(O) 176.4			(O) 171.0			(O) 175.3	
q(Ru)	0.77	0.55	0.75	0.59	0.43	0.57	0.84	0.73	0.86
q(N)	0.00	0.02	0.11	–0.01	0.01	0.09	0.03	0.04	0.18
q(O)	–0.18	–0.12	–0.25	–0.19	–0.15	–0.27	–0.13	–0.13	–0.26
q(NO)	–0.18	–0.10	–0.14	–0.20	–0.14	–0.18	–0.10	–0.09	–0.08
q(L)	–0.54	–0.44	–0.59	–0.30	–0.23	–0.35	–0.04	0.05	–0.08
B(N–O)	1.54	1.38	1.54	1.51	1.33	1.51	1.56	1.27	1.53
ε(HOMO)	–5.09	–5.13	–5.10	–4.88	–4.97	–4.76	–8.51	–8.57	–8.34
ε(LUMO)	–3.41	–4.09	–3.92	–3.54	–4.05	–4.01	–7.01	–7.63	–7.53
ν(NO)	1820	1424	1699	1796	1377	1668	1849	1335	1702
ΔE, eV	0	1.627	1.685	0	1.342	1.655	0	1.558	1.853

The energies of the Kohn–Sham frontier orbitals responsible for the Ru–NO bonding and the energies of the lowest unoccupied orbitals are compared in Fig. 3, and changes in the diagram of Kohn–Sham frontier orbitals for the complex [Ru(NO)(P)(Cl)] on passing from GS to MS2 and MS1 are shown in Fig. 4. The two highest occupied orbitals of [Ru(P)(NO)·(Cl)], φ_{98} and φ_{99}, consist almost completely of porphine orbitals; the two lowest unoccupied orbitals, of π*(NO) with almost equal contributions of Ru and P orbitals; and the two following orbitals, of P orbitals with small contributions of Ru and NO orbitals. In [Ru(NO)(salen)(Cl)], the highest occupied molecular orbitals φ_{88} and φ_{89}, along with the salen orbital, include a small admixture of Ru and π*(NO) orbitals; the two lowest unoccupied orbitals are similar in composition to the corresponding orbitals of [Ru(P)·(NO)(Cl)]; and the two following orbitals consist almost exclusively of salen orbitals. The comparison of the energies of vacant π* MO localized on L suggests that salen is a weaker π* acceptor than porphine. The changes in diagrams of Kohn–Sham molecular orbitals on passing from GS to MS2 and then to MS1 mainly coincide with those found in [11] for the complex $[Ru(NH_3)_5(NO)]^{3+}$, but differ by the fact that π orbitals of the equatorial ligands make a dominating contribution to the highest occupied orbitals.

In spite of the fact that the above-considered characteristics of the electronic structure depend on the composition of the complex only slightly, the energies of the metastable states ΔE(MS) = E(MS) – E(GS) change significantly. For all the three complexes, the structure with the dihapto coordination of the nitrosyl group (MS2) has a lower energy than the structure

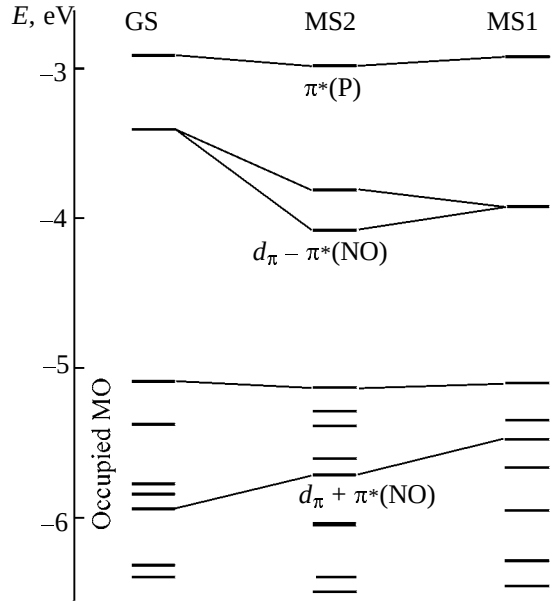

Fig. 4. Diagram of Kohn–Sham frontier orbitals for [Ru(P)(NO)(Cl)].

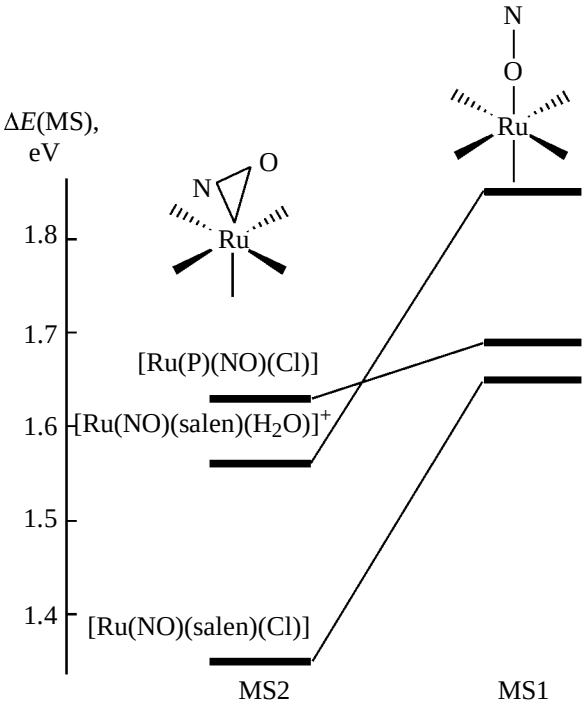

Fig. 5. Energies of metastable states MS2 and MS1 of [Ru(L)(NO)(Cl)] complexes.

with the linear NO coordination η^1-ON (MS1). As follows from [2, 12], the calculated ΔE(MS) values considerably depend on the basis set in use, the ΔE(MS2) values in the LanL2DZ basis being overestimated as compared to the DZVP basis containing all electronic shells. Therefore, we can assume that the transition to the DZVP basis will not change the obtained relationship between the energies of the metastable states. The replacement of the negatively charged σ-donor ligand Cl^- in [Ru(NO)(salen)(Cl)] by the weak σ-donor H_2O increases the energies of both metastable states (Fig. 5). As is the case with the complexes *trans*-$[Ru(NO)(NH_3)_4(X)]^{3+}$ and $[Ru(NO)X_5]^q$, the parameter ΔE(MS1) depends on the composition of the complex to a lesser extent than ΔE(MS2). For the complex [Ru(NO)(salen)(Cl)], we have obtained low energies of both metastable isomers, the energy of the isomer with the dihapto coordination of the nitrosyl group being the lowest among the related complexes considered so far.

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