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DFT Investigation of Metal Complexes Containing a Nitrosyl Ligand. 2. Excited States

**P. Boulet,[†,‡] M. Buchs,[§] H. Chermette,*[,‡] C. Daul,[§,$] E. Furet,[†,#] F. Gilardoni,[||] F. Rogemond,[⊥]
C. W. Schläpfer,[§] and J. Weber[†]**

*Université de Genève, département de Chimie Physique, 30 quai E-Ansermet, CH-1211 Genève 4, Switzerland,
Université Claude Bernard Lyon 1, Laboratoire de Chimie-Physique Théorique, Bât 201,
43 Bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France and Institut de Recherches sur la Catalyse,
CNRS UPR 5401, 69626 Villeurbanne Cedex, France, Institut de Chimie Inorganique, Université de Fribourg,
Pérolles, CH-1700 Fribourg, Switzerland, Avantium Technologies, zekeringstraat 29, 1000 CX Amsterdam,
The Netherlands, and Laboratoire du Traitement du Signal et Instrumentation, UMR CNRS 5516,
Université de Saint Etienne, 23 rue du Dr. P. Michelon, F-42023 Saint Etienne Cedex, France*

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The photochemical reactions of the nitroprusside and the CpNiNO complexes are explained on the basis of ΔSCF and time-dependent density functional theory (TD-DFT) calculations. Both similarities and differences in the photochemical processes are highlighted.

Introduction

Transition metal nitrosyl compounds have attracted chemists' interest for more than 30 years. The main reason for this interest is the existence of long-lived metastable states that are easily obtained by light irradiation. Complex systems, with long-living metastable states, are good candidates for optical information storage.

The most studied compound among those nitrosyl complexes is the sodium nitroprusside $Na_2[Fe(CN)_5NO]2H_2O$. The existence of its metastable states were predicted in 1977 on the basis of Mössbauer spectra.[1]

In the preceding paper in this issue,[2] we studied the ground state and the metastable states of two different metal complexes containing a nitrosyl ligand, namely, the nitroprusside and the cyclopentadienylnitrosylnickel(II) (CpNiNO) complexes. In this paper, we complete our theoretical investigation with a study of the excited states of those compounds. On the basis of our earlier results, we propose a photochemical mechanism for the transformation of the ground state (global minimum) into the various metastable states (local minima) and vice-versa.

Theoretical Approach

This aspect has already been widely described in the preceding joint paper in this issue.[2] Briefly, the density functional theory[3] within the Kohn−Sham methodology[4] has been used. The Becke's exchange functional[5] and the Perdew's correlation functional[6] (B88P86) have been used in the generalized gradient approximation (GGA). The calculations have been performed with the ADF99[7,8] program package. Computational details (basis set and integration accuracy) are the same as in the previous paper.[2]

TABLE 1: Lowest Excitation Energies of the Ground State $[Fe(CN)_5NO]^{2-}$ Complex[a]

symmetry	MO	character[b]	ΔSCF	TD-DFT[c]	exp[16]
^1E	$2b_2 \rightarrow 10e$	MLCT	2.30	1.91	2.49
$^1B_2$	$2b_2 \rightarrow 13a_1$	MC	4.05	3.92	
$^1A_2$	$2b_2 \rightarrow 5b_1$	MC	3.69	3.94	3.76
$^1A_1$	$9e \rightarrow 10e$	LC	3.69	2.66	
$^1A_2$			3.42	2.48	
$^1B_1$			3.69	2.57	
$^1B_2$			3.42	2.50	
$^1A_1$	$8e \rightarrow 10e$	MLCT	3.74	3.36	3.15
$^1A_2$			3.78	2.75	
$^1B_1$			3.74	2.93	
$^1B_2$			3.78	2.90	
^1E	$9e \rightarrow 13a_1$	LMCT	4.65	4.37	
^1E	$9e \rightarrow 5b_1$	LMCT	6.61	4.87	
^1E	$8e \rightarrow 13a_1$	MC	5.01	4.63	4.69
^1E	$8e \rightarrow 5b_1$	MC	5.47	5.03	5.21

[a] Values in eV. [b] LMCT: ligand−metal charge transfer; MC: metal centered transition; LC: ligand centered transition. [c] Calculation with the LB94//B88P86 scheme.

For the calculation of excited states, both the ΔSCF method[9,10] and the time-dependent density-functional theory (TD-DFT)[11−13] within the adiabatic approximation have been used. As first mentioned by Jamorski et al.,[14] the use of an asymptotically well-behaved potential functional is preferable to avoid the dramatic collapse of excitation energies calculated with an LDA potential. Therefore, such a potential, developed by van Leeuwen and Baerends (LB94),[15] has been used during the SCF procedure. The evaluation of the coupling matrix has been performed using the adiabatic local density approximation (ALDA).

Results and Discussion

Transition Energies from the Ground State. *$[Fe(CN)_5NO]^{2-}$*. A detailed description of the electronic structure of the ground-state nitroprusside can be found in our preceding paper in this issue.[2] As can be seen, the HOMO (highest occupied molecular orbital) is the $2b_2$ orbital and has a predominant iron $3d_{xy}$ character. The LUMO 10e (lowest unoccupied molecular orbital) is of NO π^* character.

Calculations of the excited-state energies of the nitroprusside ion are given in Table 1. For the lowest excitation due to the

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* To whom correspondence should be addressed: cherm@catalyse.univ-lyon1.fr.

[†] Université de Genève.

[‡] Université Claude Bernard Lyon 1 and Institut de Recherches sur la Catalyse, CNRS UPR 5401.

[§] Université de Fribourg.

[||] Avantium Technologies.

[⊥] Université de Saint Etienne.

[$] E-mail: Claude.Daul@unifr.ch.

[#] Present address: Ecole Nationale Supérieure de Chimie, av. Gl Leclerc, F-35042 Rennes, France.

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TABLE 2: Optical Absorption of the Ground State CpNiNO Complex

			LB94//B88P86			exp[18]	
sym	MO[a]	ΔSCF (eV)	energy (eV)	f (a.u.)[b]	%[c]	energy (eV)	intensity[d]
E_1	$9a_1 \rightarrow 7e_1$	3.25	3.08	0.0004	87	2.68 (2.85[e])	w
	$3e_2 \rightarrow 7e_1$				7		
E_1	$9a_1 \rightarrow 7e_1$	3.95	3.52	0.0004	13	3.22 (3.40[e])	w
	$3e_2 \rightarrow 7e_1$				86		
A_1	$6e_1 \rightarrow 7e_1$	3.69	4.24	0.4128	70	4.43 (4.27−4.77[e])	s
	$5e_1 \rightarrow 7e_1$				24		
E_1	$6e_1 \rightarrow 10a_1$	5.98	6.42	0.0012	94		
E_1	$3e_2 \rightarrow 4e_2$		6.41	0.0166	78		
	$8a_1 \rightarrow 7e_1$				10		
E_1	$8a_1 \rightarrow 7e_1$	6.39	5.97	0.0364	54	6.20	s
	$6e_1 \rightarrow 4e_2$				44		
E_1	$2e_2 \rightarrow 7e_1$		5.54	$\ll 10^{-4}$	100		

[a] Major molecular orbital transition. [b] Oscillator strength. [c] Percentage of the corresponding electron configuration in the total density. [d] w = weak and s = strong. [e] Hg lines used in ref 18 to study the wavelengh dependence of the GS → MS_{II} reaction.

TABLE 3: Geometric Parameters of Ground-, Metastable-, and Excited-States of the Nitroprusside and the CpNiNO Complexes[a]

parameters	MN[b] (pm)	MO[b] (pm)	NO (pm)	MNO[b] (pm)	MON[b] (pm)
		nitroprusside			
GS	164.2	281.2	117.0	180	0
r-ExSt$_{GS}$	183.7	286.7	119.1	141.5	23.5
MS_{II}	183.4	205.7	121.	82.2	62.1
r-ExSt $^{l}{}_{MSII}$	183.7	286.7	119.1	141.5	23.5
r-ExSt $^{r}{}_{MSII}$	303.2	202.5	119.	25.6	139.8
MS_{I}	289.4	173.1	116.3	0	180
r-ExSt$_{MSI}$	303.2	202.5	119.	25.6	139.8
		CpNiNO			
GS	162.9	344.	118.1	180.	0.
r-ExSt$_{GS}$	177.4	278.9	120.4	138.1	25.1
TS_{II}	167.6	251.7	119.4	121.7	34.6
MS_{II}	172.1	209.	123.	88.6	55.4
r-ExSt $^{l}{}_{MS_{II}}$	167.2	287.4	120.4	176.0	2.3
r-ExSt $^{r}{}_{MS_{II}}$	187.6	177.0	122.3	19.4	147.3
TS_{I}	265.	172.4	119.3	30.	129.7
MS_{I}	287.5	169.2	118.3	0.	180.
r-ExSt$_{MS_{I}}$	277.4	187.0	120.7	32.4	127.4

[a] GS = ground state. r-ExSt = relaxed excited state. r, l = “left” or “right” with respect to the position of MS_{II}. TS = transition state. MS = metastable state. [b] M = metal center (Fe for nitroprusside and Ni for CpNiNO).

promotion of one electron from the HOMO to the LUMO, the experimental transition energy is best reproduced by the ΔSCF procedure. In this case, the transition is of metal to ligand charge transfer (MLCT) type, and the TD-DFT method largely underestimates the excitation energy. For states lying at higher energy and for which the experimental transition energies are known, the TD-DFT method gives results in slightly better agreement with experiment.

Long-living metastable states of nitroprusside have been observed[16] when the molecule is excited below 150 K with a 514.5 nm (2.41 eV) Ar ion laser beam. The wavelength dependence of the formation of the metastable states indicates that the metastable state MS_{II} is a relaxed byproduct of the charge-transfer transition 3d → π*(NO). That experimental evidence combined with the results of our calculations on the electronic structure and transition energies of $[Fe(CN)_5NO]^{2-}$ clearly indicate that the metastable state appears after excitation of one electron from the $2b_2$ molecular orbital (MO) to the 10e one, i.e., the HOMO−LUMO excitation. The resulting state, $|9e^{4}2b_{2}^{1}10a^{1};\ ^{1}E\ >$, is Jahn−Teller, or pseudo Renner-Teller, active. It will then be split and will give rise to two nondegenerate states. Pressprich et al.[17] have predicted the higher energy state to have a linear Fe−N−O geometry and the lower energy state to have a bent Fe−N−O geometry. We computed the energy of both states resulting from this excited configuration in C_s symmetry, namely, the $|12a''^{1}13a''^{1};\ ^{1}A'>$ and the $|12a''^{1}26a'^{1};\ ^{1}A''>$ states. Note that the HOMO $2b_2$ in the ground-state geometry (C_{4v} symmetry) becomes 12a″ in the C_s symmetry, whereas the LUMO 10e splits into the 13a″ and 26a′ orbitals. We let the geometry of the excited-state relax and obtained the bent structure more stable than the other one. The calculated energy difference (Jahn−Teller stabilization energy) amounts to 0.26 eV, and the distorted FeNO angle is 119.1° (Table 3). Furthermore, it can be seen that the Fe−N bond length increases and is close to that of the MS_{II} species. As for the energetics, the geometrically relaxed excited state (r-ExSt$_{GS}$) is only 0.17 eV higher in energy than the TS_{II} species (Table 4).

CpNiNO. The experimental UV spectrum[18] features four bands located at 2.68, 3.22, 4.43, and 6.20 eV (see Table 2). The former two are about 100 times less intense than the latter two. According to the TD-DFT calculations, the electronic density of the first two excited states (E_1 symmetry) is a combination of the $9a_1 \rightarrow 7e_1$ and $3e_1 \rightarrow 7e_1$ excited determinants. One can notice that in both transitions the contribution of each determinant is reverse. As far as the transition energies are concerned, the ΔSCF procedure leads to similar positions for the bands. As compared with the TD-DFT formalism, which already overestimates the energies as compared with experiments, the ΔSCF method overestimates even more the excitation energies. The deviation is however acceptable, remaining less than 0.45 eV. On the other hand, the corresponding calculation of the intensities (not presented in Table 2) gives erroneous results. This is probably related to the mixture of determinants already mentioned. Despite the small intensities of these bands, experimentalists[18] have suggested that these transitions can be responsible of the formation of the metastable state MS_{II}.

The next two experimental bands emerging at 4.43 eV (A_1 symmetry) and 6.20 eV (E_1 symmetry) are well reproduced by the TD-DFT calculations. At most, the deviation amounts to only 0.23 eV. One should however note that whereas the TD-DFT calculation overestimates the transition energies in the case of the two former bands, the contrary is observed for these bands. Consequently, the spectrum is slightly shrunk. Such a trend is not observed in ΔSCF which underestimated the energy of the excited-state found at 4.43 eV and overestimated the energy of the excited state at 6.20 eV. The dramatic underestimation of the A_1 state (lowered by 0.74 eV as compared with experiment) by the ΔSCF procedure leads to an inversion of the ordering of the states. The calculated intensities of these

TABLE 4: Energetics of the Species Pertaining to the Photochemistry of the $[Fe(CN)_5NO]^{2-}$ and the CpNiNO Complexes (eV)[a]

	GS	r-ExSt$_{GS}$	TS$_{II}$	r-ExSt $^{l}_{MSII}$	MS$_{II}$	r-ExSt $^{r}_{MSII}$	TS$_{I}$	r-ExSt$_{MSI}$	MS$_{I}$
$Fe(CN)_5NO^{2-}$	0	1.98	1.81	1.98	1.42	2.75	2.80	2.75	1.61
CpNiNO	0	1.57	1.44	3.61	1.05	1.72	2.68	3.05	1.74

[a] r-ExSt = relaxed excited state. r,l = "left" or "right" with respect to the position of MS$_{II}$. TS = transition state. MS = metastable state.

transitions are roughly 1000 and 100 times greater than those of the small peaks, respectively, in agreement with experimental observations. The most intense band (4.43 eV) corresponds to the HOMO−LUMO transition, with a slight contribution from the $5e_1$(HOMO-3) → $7e_1$(LUMO) electron promotion. As this excitation is of ligand-to-ligand (from σ-Cp to π*-NO) charge transfer type, a strong intensity is expected. The next excited state (6.20 eV) is composed of a strong mixture between two excited Slater determinants, namely, the HOMO-2 → LUMO (55%) and the HOMO-1 → LUMO (44%) ones. On the basis of these results, we infer that the transition that is responsible for the formation of the MS$_{II}$ metastable state is the HOMO−LUMO one.

Similar to the nitroprusside complex, the electron promotion from the HOMO to the LUMO of the CpNiNO leads to a degenerate excited state, which induces a spontaneous symmetry breaking of the electronic density. This leads to a removal of the 2-fold degeneracy of the molecular orbitals, involving the so-called pseudo-Renner-Teller effect. Therefore, upon relaxation of the degenerate excited state, the molecular symmetry is also broken, leaving the complex in the C_s symmetry. The geometry of the relaxed HOMO−LUMO excited state has been calculated. As expected, the NiNO fragment of the complex is distorted, and the corresponding angle amounts to 138.1° (see Table 3). Therefore, the NiNO bending of TS$_{II}$ is largely initiated in the relaxed excited state (121.7° and 138.1°, respectively). The energetic relaxation due to the pseudo-Renner-Teller instability amounts to 1.09 eV which is significantly larger than for the nitroprusside. The relaxed excited state remains slightly higher in energy than the transition state TS$_{II}$ of the ground state potential energy curve. The difference in energy between both structures amounts only to 0.13 eV (Table 4).

In conclusion, we observe that the pseudo-Renner-Teller effect in the degenerate excited states of the two (nitroprusside and CpNiNO) complexes leads to relaxed excited states that are geometrically and electronically very similar to both the TS$_{II}$ transition states and the MS$_{II}$ metastable states of the corresponding species. It is therefore suggested that, by the HOMO−LUMO excitation, an excited state is formed, which decays not only to the ground state, but also at least partially into the MS$_{II}$ metastable state.

Excited States of MS$_{II}$ Metastable State. From the MS$_{II}$ state, both the forward reaction (toward MS$_{I}$) and the reverse reaction (toward the GS) are possible. The following sections compare the pathways and electronic excitations of both complexes to accomplish these reactions.

$[Fe(CN)_5NO]^{2-}$. It is experimentally known[16] that irradiation with visible light (350−600 nm) converts MS$_{II}$ to MS$_{I}$, as is the case for the GS → MS$_{II}$ reaction. The photoreaction of MS$_{II}$ to GS is activated by irradiation with light within the range 600−1200 nm as the MS$_{II}$ ← MS$_{I}$ reaction.

The electronic configuration of the MS$_{II}$ state is $10a''^{2}25a'^{2}11a''^{2}12a''^{2}13a''^{0}26a'^{0}$. According to Table 5 the promotion of one electron from the HOMO $12a''(d_{xy})$ into the $26a'(\pi^{*}_{dxz})$ orbital occurs at ca. 2.0 eV, which lies in the range 600−1200 nm as experimentally observed. According to Figure 2 of ref 2, the MO 26a′ is of π^{*}_{dxz} character and undergoes the strongest perturbation upon rotation of the NO ligand. The relaxation of the vertically excited state was performed. The results are given in Table 3 (structure r-ExSt $^{l}_{MSII}$). Comparison with the geometry of MS$_{II}$ indicates that the major change in the geometry of the relaxed excited state $|12a''^{1}26a'^{1};\ ^{1}A''>$ is the variation of the Fe−N−O angle. In MS$_{II}$, the nitrosyl ligand is (η^2) bonded sideway, whereas it is N-π bonded in the excited state. Hence, the ring opens upon excitation. Consequently, the $|12a''^{1}26a'^{1};\ ^{1}A''>$ state will decay on the ground-state potential energy surface near the TS$_{II}$ transition state and then relax either to the ground state or to the MS$_{II}$ species. The r-ExSt$_{GS}$ structure of Table 3, is very similar to the geometry of r-ExSt$^{l}_{MSII}$. Furthermore, their electronic configurations are identical. Therefore, we can ascertain that both the r-ExSt$_{GS}$ and the r-ExSt$^{l}_{MSII}$ are the same relaxation product of the excited state of both of the GS and MS$_{II}$. This unique excited-state allows for the backward and forward GS ↔ MS$_{II}$ reaction.

TABLE 5: Lowest Electronic Transitions from the Metastable States of the Nitroprusside Complex (eV)

symmetry	MO	ΔSCF	TD-DFT (LB94)
	MS$_{II}$ state		
$^{1}A'$	$12a'' \rightarrow 13a''$	1.37	1.08
$^{1}A'$	$11a'' \rightarrow 13a''$	1.76	2.08
$^{1}A''$	$12a'' \rightarrow 26a'$	1.97	2.02
$^{1}A''$	$25a' \rightarrow 13a''$	2.38	1.66
$^{1}A'$	$10a'' \rightarrow 13a''$	2.85	1.78
	MS$_{I}$ state		
^{1}E	$2b_2 \rightarrow 10e$	1.29	1.03

To complete the photochemistry description of MS$_{II}$, it remains to explain how the MS$_{I}$ state can be generated. As seen in Figure 2 of ref 2, the energy of the MO 26a′ reaches a maximum for angle Fe−N−O of 70°. Although this angle is close to that of MS$_{II}$, the excited state $|12a''^{1}26a'^{1};\ ^{1}A''>$ could also relax, at least to a small extent, to the geometry of TS$_{I}$ state and then reach upon relaxation the MS$_{I}$ species. The geometry of the corresponding relaxed excited state (r-ExSt $^{r}_{MSII}$) is depicted in Table 3. All excited molecules are relaxing from the $\pi^{*} - d_{yz}$ orbital into the MS$_{II}$ and subsequently can be excited toward the MS$_{I}$ isomer. According to experimental results, the range of excitation to generate the MS$_{I}$ complex is 350−600 nm. It is remarkable that the HOMO → LUMO+1 (12a″ → 26a′) excitation energy lies at the boundary of this range. As the structure of the excited-state relaxes, the Fe−O−N angle increases, reaching 139.8°. Therefore, the r-ExSt$^{r}_{MSII}$ state is located beyond the barrier. It can be seen in Table 4 that the energy of TS$_{I}$ is higher than that of r-ExSt$^{r}_{MSII}$. However, it must be stressed that some imprecision may be related to the geometry of TS$_{I}$ that could not be optimized. Therefore, the geometrical parameters of TS$_{I}$ are not reported in Table 3, and its energy is a crude estimate from a linear transit calculation. Furthermore, the energy of the r-ExSt$^{r}_{MSII}$ species does not correspond to the energy of a corresponding true state but rather to a monodeterminantal wave function one.

CpNiNO. The experimental UV−Vis spectrum[18] of the MS$_{II}$ species of CpNiNO features a broad absorption band at 1.46 eV, with low intensity, upon excitation at 3.96/4.10 eV (Hg lines). The calculated transition energies and intensities are given in Table 6. The configuration of MS$_{II}$ species near the Fermi level is $8a''^{2}17a'^{2}18a'^{2}9a''^{2}10a''^{0}19a'^{0}$. As compared with the

TABLE 6: Optical Absorption of the MS$_{II}$ Complex of CpNiNO

		LB94//B88P86			exp[18]
symmetry	MO[a]	energy (eV)	*f* (au)[b]	%[c]	energy (eV)
A′	9a″ → 10a″	1.66	0.0072	83	1.46
	18a′ → 19a′			14	
A′	8a″ → 10a″	2.77	0.0060	70	2.27[d]
	18a′ → 19a′			27	
A′	17a′ → 19a′	3.32	0.0420	37	
	18a′ → 19a′			26	
	16a′ → 19a′			21	
	8a″ → 10a″			9	
A′	7a″ → 10a″	4.00	0.0757	71	3.71[d]
	18a′ → 19a′			9	
	16a′ → 19a′			7	
	17a′ → 19a′			2	
A′	15a′ → 19a′	4.15	0.1510	26	3.96/4.10[d]
	17a′ → 19a′			18	
	18a′ → 19a′			13	
	16a′ → 19a′			12	
	8a″ → 10a″			11	
	7a″ → 10a″			11	

[a] Molecular orbitals. [b] Oscillator strength. [c] Percentage of the corresponding electron configuration in the total density. [d] Mercury lines used to excite the sample.

spectrum of the ground state (Table 2) the MS$_{II}$ spectrum features the same small peaks, with the same intensities, in which the electron density is given by two excited Slater determinants. However, the comparison stops here. First, these peaks are largely downshifted as compared with those of the CpNiNO ground state. Second, the first band mainly corresponds to the HOMO−LUMO transition, whereas the second one arises from the HOMO-3 → LUMO electron promotion. The fact that both the HOMO and HOMO-3 orbitals mainly accommodate the nickel d electrons probably explains the reason that these absorption peaks have a similar intensity. The next two peaks (3.32 and 4.00 eV) have higher intensity and correspond to HOMO-2 → LUMO+1 and HOMO-5 → LUMO excitations, respectively. Finally, the most intense band is calculated at 4.15 eV and corresponds to the HOMO-6 → LUMO+1 excitation.

The band at 4.15 eV falls exactly in the domain of the mercury lines of excitation (Table 6). Furthermore, it is in the same energy region as that of the ground state (see Table 2). One can therefore suggest that the absorption spectrum of the MS$_{II}$ metastable state features some bands in this region, although these peaks may be hidden by those of the ground-state CpNiNO. This last assumption can be justified by the relative proportion between the ground state and that of the metastable state in the sample. Comparing the Ni−N−O angle of the r-ExSt$_{GS}$ species with that of the TS$_{II}$ transition state, one can assume that the relaxation of the excited state can lead both to the ground-state itself or to the MS$_{II}$ metastable state. As the r-ExSt$_{GS}$ species is located before the barrier (i.e., the NiNO angle of r-ExSt$_{GS}$ is smaller than that of TS$_{II}$), one can suppose that the decay of the excited state will yield a greater proportion of ground-state molecules. Therefore, although the intensity of the 4.15 eV band of MS$_{II}$ is high (0.1510 au), this band can be hidden by the absorption of the ground state because the concentration of MS$_{II}$ remains always small. However, the vertical excitation is high enough to cross the barriers and to allow for the formation of either the ground state or the second metastable state MS$_{I}$. The calculation of structure relaxation has been performed. Two structures labeled r-ExSt$^{r}_{MSII}$ and r-ExSt$^{l}_{MSII}$, respectively, (see Table 3) are obtained. For the r-ExSt$^{l}_{MSII}$ species, the gain in energy upon geometry relaxation is as high as 2.07 eV, and the state is located close to the structure of the complex in the ground state (similar Ni−N−O angles). Therefore, the r-ExSt$^{l}_{MSII}$ structure relaxes toward the CpNiNO species. The r-ExSt$^{r}_{MSII}$ structure is higher in energy than the TS$_{I}$ complex (2.68 and 4.81 eV, respectively, in Table 4) and shows a structure similar to the latter (147.3° and 129.7°, respectively, for the NiON angle. See Table 3). Therefore, this structure can relax toward the second metastable state (MS$_{I}$).

As is the case with nitroprusside, a unique excitation is able to convert the MS$_{II}$ species into the ground state or into the second metastable state MS$_{I}$. However, the energetics for the MS$_{II}$ → MS$_{I}$ pathway is much more demanding in the case of CpNiNO. Therefore, the MOs involved in the transition are different. Whereas the HOMO → LUMO+1 transition is sufficiently effective in the case of nitroprusside, it is necessary to promote an electron from the HOMO-6 to the LUMO+1 to reach the MS$_{I}$ species in the case of CpNiNO.

Excited States of the MS$_{I}$ Metastable State. *[Fe(CN)$_5$NO]$^{2-}$*. Similarly to the ground-state nitroprusside, the MS$_{I}$ complex has a linear Fe−O−N group and is of C_{4v} symmetry. The NO ligand is reversed, i.e., O-bound to the Fe. Therefore, the electronic structure of the two systems are very close to each other. The ordering of the orbitals is identical ($8e^{4}9e^{4}2b_2^{2}10e^{0}$-$13a_1^{0}5b_1^{0}$). The main difference is the gap between the HOMO and the LUMO, which is smaller for the MS$_{I}$ state. This is in agreement with the maximum hardness principle which states that the higher the hardness (i.e., the gap), the more stable the compound is.[19−22] Consequently, the lowest electronic transition (HOMO → LUMO) of MS$_{I}$ appears red-shifted (see Tables 1 and 5). As is the case with the other nitroprusside isomers, the MLCT transition energies calculated with the TD-DFT methodology are significantly downshifted as compared with the ΔSCF results. As compared to the literature,[23] these kinds of transitions are better described by the ΔSCF method. For the MS$_{I}$ species, we only know from experiment that light irradiation in the range 600−1200 nm depopulates the metastable state. According to our results (Table 5), the HOMO−LUMO transition lies in this range.

As was also the case with the ground-state nitroprusside, the $|2b_2{}^{1}10e^{1}; {}^{1}E>$ state, which corresponds to the HOMO−LUMO excitation, is pseudo Renner-Teller active. As a consequence of the vibronic coupling the symmetry of the complex is broken (C_s) and the π*(NO) levels (10e) split, giving rise to two states with lower symmetries, namely, the $^{1}A'$ and the $^{1}A''$ ones. The excited state $|12a''^{1}26a'^{1}; {}^{1}A''>$ is the most stable one. Because of the pseudo Renner-Teller effect, the Fe−O−N angle deviates from linearity and amounts to 139.8° (Table 3) in the completely relaxed structure. The pseudo Renner-Teller energy stabilization amounts to 0.14 eV. The Fe−O bond length elongates in this excited state ($^{1}A''$) since the antibonding $\pi^{*} - d_{yz}$ orbital is populated. Even if it was not possible to optimize the structure of TS$_{I}$, the Fe−O−N angle is estimated to amount to ca. 140°. Hence, the excited state has a geometry very close to the transition state TS$_{I}$ (Table 3). Through relaxation, the $^{1}A''$ state should fall onto the ground-state potential energy surface around TS$_{I}$ and then populate MS$_{II}$. This corresponds to the reverse reaction MS$_{II}$ ← MS$_{I}$. Consequently, we assume that there exists a unique relaxed HOMO−LUMO excited state which allows for the MS$_{II}$ ↔ MS$_{I}$ reaction in both direction.

CpNiNO. Until recently, the MS$_{I}$ species was not experimentally detected, although its existence was predicted by both theoretical investigations and experimental studies on similar compounds.[1,24] Very recently, evidence of the existence of the MS$_{I}$ metastable state of the CpNiNO complex has been established from IR spectroscopy.[25]

TABLE 7: Optical Absorption of CpNiON ($\mathrm{MS_I}$)

		LB94//B88P86		
symmetry	MO[a]	energy(eV)	*f* (a.u.)[b]	%[c]
E_1	$9a_1 \rightarrow 7e_1$	2.47	0.0003	0.87
	$3e_2 \rightarrow 7e_1$			0.14
E_1	$3e_2 \rightarrow 7e_1$	2.83	0.0001	0.86
	$9a_1 \rightarrow 7e_1$			0.13
A_1	$6e_1 \rightarrow 7e_1$	3.73	0.4192	0.62
	$5e_1 \rightarrow 7e_1$			0.32
A_1	$4e_1 \rightarrow 7e_1$	5.46	0.4536	0.44
	$5e_1 \rightarrow 7e_1$			0.28
	$6e_1 \rightarrow 7e_1$			0.24

[a] Major molecular orbitals transitions. [b] Oscillator strength. [c] Percentage of the corresponding electron configuration in the total density.

The UV absorption spectrum of the CpNiON species has been calculated and is presented in Table 7. As compared with those of the ground state CpNiNO (Table 2), the spectrum of CpNiON is very similar although slightly downshifted. The absorption of the $\mathrm{MS_I}$ features two small peaks located at 2.47 and 2.83 eV, with the same intensities, and for which the same Slater's determinants enter in the composition of the electron density though with reverse contributions. These states correspond to the HOMO-2 → LUMO and HOMO-1 → LUMO excitations. Two strong peaks of A_1 symmetry appear at 3.73 and 5.46 eV. The first one is mainly composed of HOMO−LUMO excitation with a slight contribution of the HOMO-3 → LUMO electron promotion. Finally, the 5.46 eV peak is even more intense than the HOMO−LUMO peak and corresponds to a mixture of three transitions, namely, HOMO-6 → LUMO, HOMO-3 → LUMO and HOMO−LUMO ones.

Similar to the nitroprusside complex, the HOMO−LUMO transition is responsible for the backward reaction $\mathrm{MS_{II}} \leftarrow \mathrm{MS_I}$. This excitation induces a vibronic coupling (pseudo Renner-Teller effect) which results in the splitting of the HOMO and LUMO orbitals and a descent in symmetry. The energetic extent of this effect has been calculated by optimizing the geometry of the excited state. The relaxation energy is slightly higher than for the nitroprusside and amounts to 0.42 eV. However, the relaxed excited state is still higher in energy than the $\mathrm{TS_I}$ species of the CpNiNO ground-state energy potential curve of ref 2 (see Table 4). Furthermore, their geometries are very similar (see Table 3), the Ni−O−N angle of $\mathrm{r\text{-}ExSt_{MSI}}$ being slightly smaller than that of $\mathrm{TS_I}$. Therefore, upon geometric relaxation the $\mathrm{r\text{-}ExSt_{MSI}}$ excited state will populate the $\mathrm{MS_{II}}$ state leading to the reverse reaction. Finally, as compared with the nitroprusside complex, one can assume that the photochemical processes, from which the $\mathrm{MS_{II}} \leftrightarrow \mathrm{MS_I}$ equilibrium of CpNiNO originates, are different from those of nitroprusside. Although the same excited state is involved in the $\mathrm{MS_{II}} \leftarrow \mathrm{MS_I}$ reaction, namely, the HOMO−LUMO one, a different excited-state originates the MS $_{\mathrm{II}}$ → $\mathrm{MS_I}$ reaction.

Conclusion

The photochemical processes occurring upon excitation of the nitroprusside and the CpNiNO complexes have been explained with the help of ΔSCF and TD-DFT calculations. It has been shown that the excited states that are responsible for the forward reaction GS → $\mathrm{MS_{II}}$ and the backward reaction $\mathrm{MS_{II}} \leftarrow \mathrm{MS_I}$ are similar for both systems. They arise from the HOMO−LUMO excitation. The HOMO−LUMO gap is smaller for $\mathrm{MS_I}$ than for the ground state. As a consequence, it is possible to pump the system via $\mathrm{MS_{II}}$ to $\mathrm{MS_I}$ by blue light. The backward relaxation is not possible because $\mathrm{MS_I}$ does not absorb in this spectral region. The back reaction is induced by red light, where $\mathrm{MS_I}$ shows an absorption band. As the geometrically relaxed excited states are all higher in energy than the ground-state energy potential barrier, they can lead to the $\mathrm{MS_{II}}$ species. It is also noteworthy that the extent of the pseudo Renner-Teller effect is significantly higher in the case of CpNiNO.

On the contrary, the behavior of the $\mathrm{MS_{II}}$ species, and in particular their photochemistry, is drastically different if one considers the nitroprusside complex or the CpNiNO. This is closely related to the height of the barrier between $\mathrm{MS_{II}}$ and $\mathrm{MS_I}$. In the case of the nitroprusside complex, this barrier is lower than the relaxed HOMO−LUMO excited state. Consequently, this state can lead to either the ground state or the $\mathrm{MS_I}$ species. In the case of CpNiNO, this $\mathrm{MS_{II}} \rightarrow \mathrm{MS_I}$ barrier is higher than the relaxed HOMO−LUMO excited state. Therefore, this reaction is energetically more demanding. It has been shown that the backward reaction GS ← $\mathrm{MS_{II}}$ and the forward one $\mathrm{MS_{II}} \rightarrow \mathrm{MS_I}$ is enabled by the HOMO-6 → LUMO+1 transition.

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