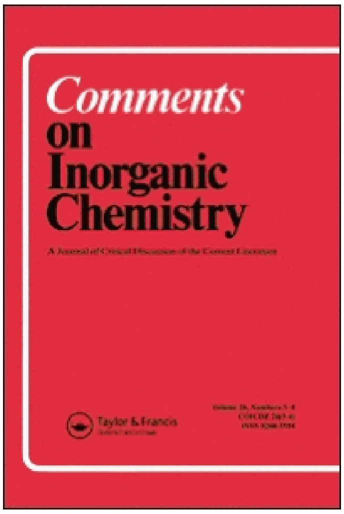

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Light-Induced Metastable Linkage Isomers of Transition Metal Nitrosyls

Dmitry V. Fomitchev[a]; Philip Coppens[a]
[a] Department of Chemistry Natural Sciences Complex, State University of New York at Buffalo, Buffalo, NY

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Light-Induced Metastable Linkage Isomers of Transition Metal Nitrosyls

DMITRY V. FOMITCHEV* and PHILIP COPPENS*

Department of Chemistry,
Natural Sciences Complex,
State University of New York at Buffalo,
Buffalo, NY 14260–3000

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Previously observed long-lived light-induced metastable states of transition metal nitrosyl complexes were identified as η^2 nitrosyl and isonitrosyl linkage isomers. A novel technique combining low temperature X-ray crystallography and photochemistry was used to determine the geometry of the new species. Light-induced side-bound nitrosyl ligands were observed in complexes with the electronic configurations $\{MNO\}^6$ and $\{MNO\}^{10}$, using the nomenclature introduced by Enemark and Feltham. The isonitrosyl binding mode was observed only in the $\{MNO\}^6$ complexes. The influence of the *trans* ligand, with respect to NO, on thermal stability of the isonitrosyls was studied in a series of complexes of Ru (II). In general, the isonitrosyl species were found to be more stable in complexes with the weak π-donor ligand in the *trans* position. Results of theoretical calculations based on density functional theory indicate that the new linkage isomers correspond to local minima on the electronic ground state potential energy surface.

Keywords: *light-induced metastable state, linkage isomer, transition metal nitrosyl, X-ray diffraction, photochemistry and photochromism*

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* Correspondence Authors.

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INTRODUCTION

The aim of this paper is to present experimental and theoretical evidence for the existence of two new binding modes of nitric oxide. Side-on (η^2) and O-bound nitrosyls can be generated upon irradiation of crystals of certain transition metal nitrosyls with light of an appropriate wavelength. These species have almost infinite lifetime at sufficiently low temperatures. Linkage isomers of this type have not been experimentally observed before, and the possibility of their existence has received little theoretical consideration in the past.

Nitric oxide has been of interest to inorganic chemists due to its ability to coordinate to a metal with either linear or bent MNO geometry [1]. The first molecular orbital models of the bonding in nitrosyls, based on results of extended Hückel calculations were constructed in the 1970s. At that time, the very useful and by now widely accepted notation $\{MNO\}^n$, where n is the number of electrons on the metal and in the π^* orbital of the nitrosyl, was introduced by Enemark and Feltham [2]. Approximately at the same time Hoffmann and co-workers [3] presented a general qualitative discussion of coordination modes of diatomic ligands in transition metal complexes. Their consideration was based on the Walsh diagram for the L_nMXY (n=4,5) complex, in which the geometry of the MXY fragment changes from linear, through bent and kinked conformations, to η^2 coordination. They concluded that there is a minimum on the potential energy surface for the η^2 bound diatomics in the case of $\{MXY\}^4$, $\{MXY\}^8$ and $\{MXY\}^{10}$. This explained the existence of well known η^2 five-coordinate dioxygen complexes, exemplified by $Ti(H_2O)_2(dipic)(O_2)$ [4a], $IrCl(CO)O_2(PPh_3)_2$ [4b], and many other compounds. The authors also formulated the conditions that might promote bending of CO in pentacoordinate $\{MCO\}^8$ complexes. However, neither at that time, nor later, have structures of mononuclear complexes with side-on bound nitrosyl been observed.

The photochemistry of transition metal nitrosyls has been an area of active research starting in the late 1960s. Since then, several intriguing observations have been reported concerning the action of light on these compounds. In 1977, the existence of a long-lived metastable state of sodium nitroprusside dihydrate ($Na_2[Fe(CN_5)(NO)]\cdot 2H_2O$, or SNP), produced by irradiation of a single crystal with coherent light at 100 K, was discovered by Mössbauer spectroscopy [5]. The lifetime of the new species was estimated to be at least 10^7s at 100 K. Similar long-lived states were found later in analogous nitrosyl complexes like $K_2[RuCl_5(NO)]$ [6], $K_2[Ru(NO_2)_4(NO)(OH)]$ [7], $Na_2[Ru(CN)_5(NO)]\cdot 2H_2O$ [8] and $Na_2[Os(CN)_5(NO)]\cdot 2H_2O$ [9]. It is noteworthy that all of these compounds belong to the $\{MNO\}^6$ class. The nature of the metastable states has been explored by different physical methods such as differential scanning calorimetry (DSC), infrared, Raman and Mössbauer spectroscopies, neutron and X-ray diffraction. The major results can be summarized as follows: (1) Two metastable states, MS_1 and MS_2, can be generated in all compounds cited above, with a total population below 50%. (2) Decay of the metastable states is a thermally or a light-induced process. (3) Frequencies of the stretching vibrations of NO are downshifted by approximately 100 cm^{-1}on formation of MS_1 and almost 200 cm^{-1} for MS_2. (4) Vibrational modes of the other ligands are affected much less upon formation of the metastable state. (6) There is evidence that both metastable states are diamagnetic [10].

Despite extensive investigations, the electronic configurations of MS_1 and MS_2, and the origin of their record long low-temperature lifetimes remained poorly understood.

In the same year as the discovery of light-induced metastable states of SNP, Rest and co-workers reported the results of their photochemical studies of $[Ni(NO)(\eta^5\text{-}Cp)]$, $[Mn(CO)(NO)_3]$, $[Cr(NO)_4]$ and $[Mn(CO)_4(NO)]$ [11–13]. According to the Enemark and Feltham nomenclature, the first three compounds have the $\{MNO\}^{10}$ and the last one the $\{MNO\}^8$ configuration. In all cases irradiation of a sample with ultraviolet light ($230 < \lambda < 280$ nm) causes a reduction of intensity of the band assigned to the stretching vibration of NO. It also generates a new intense band, downshifted by at least 400 cm^{-1}. In these experiments, samples were prepared as frozen glasses of CH_4, Ar or N_2. The photochemical changes were found to be reversible by heating or light exposure. Based only on the results of spectroscopic experiments (IR and UV/vis), the authors could not reach a definitive conclusion about the nature of the species produced.

In 1994 Chen and co-workers [14] reported the structures of $[Ni(NO)(\eta^5\text{-}Cp)]$ in the ground and light-induced states as derived from EXAFS data. The two major findings, regarding the structure of the light-induced state, were: (1) the elongation of the Ni-N bond by 0.123(3) Å and (2) bending of the Ni-N-O fragment from 180° to 160–133°. Unfortunately, the accuracy of the data was limited, and the experiments did not provide detailed insight into the nature of the metastable state. Based on the observation that the forward and reverse reactions could be induced by light with an energy difference of 2400 cm^{-1} (280 nm for the forward reaction vs. 300 nm for the reverse reaction), which was considered too small to separate any two electronic states, the authors suggested existence of at least one other intermediate state. Thus, the bent NiNO geometry results from the relaxation of an initially excited state.

The original aim of our research was to utilize X-ray diffraction for the study of the electron density distribution of molecules in light-induced electronically excited states. However, in the course of the work it became clear that the light-induced states are metastable linkage isomers with unprecedented NO coordination modes, rather than electronically excited states.

X-RAY DIFFRACTION STUDY OF $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ AND $K_2[Ru(NO_2)_4(NO)(OH)]$ IN THE LIGHT-INDUCED METASTABLE STATES

Our investigation of the light-induced metastable states started with the X-ray diffraction study of the MS_1 and MS_2 structures of SNP, and the MS_1 structure of $K_2[Ru(NO_2)_4(NO)(OH)]$. ORTEP plots of the two anions in the ground state are shown in Fig. 1. For each of the compounds, two light-induced metastable states had been found previously [5, 7]. The reported decay temperatures are 195 K (MS_1) and 151 K (MS_2) for SNP, and 200 K (MS_1) and 166 K (MS_2) for $K_2[Ru(NO_2)_4(NO)(OH)]$. According to vibrational spectroscopy, the NO ligand is most affected by the excitation, the frequencies of the stretching vibrations of NO being downshifted by about 115 cm^{-1} in MS_1 and by more than 260 cm^{-1} for MS_2 in both complexes. The vibrational frequencies of the other ligands are much less affected. For instance, the stretching frequency of the *trans* OH^- ligand of $K_2[Ru(NO_2)_4(NO)(OH)]$ decreases by only 29 and 61 cm^{-1} in MS_1 and MS_2, respectively. The reported maximum populations of the excited states due to direct excitation with 457 nm light are 50% (MS_1) and 5% (MS_2) for SNP, and 16% (MS_1) and 2% (MS_2) for $K_2[Ru(NO_2)_4(NO)(OH)]$.

In the following discussion we will focus on the results rather than on experimental details which have been published elsewhere [15]. We

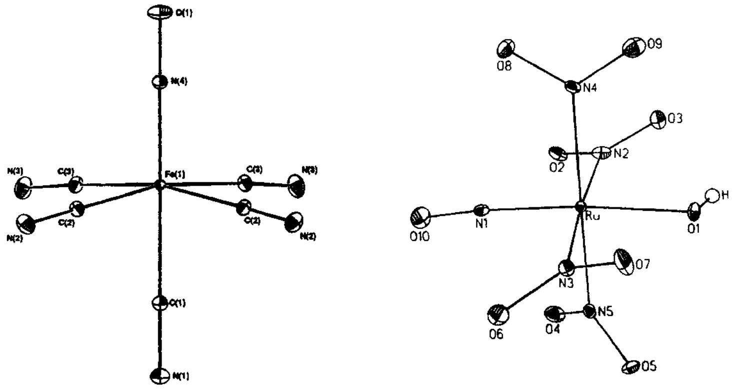


FIGURE 1 ORTEP of ground state SNP (left) and $[Ru(NO_2)_4(NO)(OH)]^{2-}$ (right) anions showing 50% probability ellipsoids

found that the changes which occur in the geometry of the anions $[Fe(CN)_5(NO)]^{2-}$ and $[Ru(NO_2)_4(NO)(OH)]^{2-}$ on transition to MS_1 are comparable. The elongation of the Ru-NO bond by 0.097(11) Å is twice that for SNP, for which values of 0.053(6) [16] and 0.049(8) Å [17] were observed. However, lengthening of the N-O bond, expected from the significant downshift of the stretching frequency of NO in MS_1, was observed neither for SNP, nor for $[Ru(NO_2)_4(NO)(OH)]^{2-}$.

A persistent inconsistency attracted our attention during the crystal structure analyses of the MS_1 containing crystals. When the isotropic temperature parameters of the N and O atoms of the nitrosyl group were allowed to vary, the resulting values for oxygen became at least four times those for the nitrogen atom (Table I). For $[Ru(NO)(NO_2)_4(OH)]^{2-}$ this is illustrated in Fig. 2. It indicates that the scattering power of the proximal atom of the nitrosyl group was underestimated, while that of the terminal atom was overestimated.

Simultaneously we were investigating the crystal structure of MS_2 of SNP [16]. Least-squares refinement based on the X-ray diffraction data of the SNP crystal with 9.5(2)% MS_2 population led to the geometry with a side-on bound NO group shown in Fig. 3 [16]. The nitrosyl is in an eclipsed, rather than the sterically less demanding staggered confor-

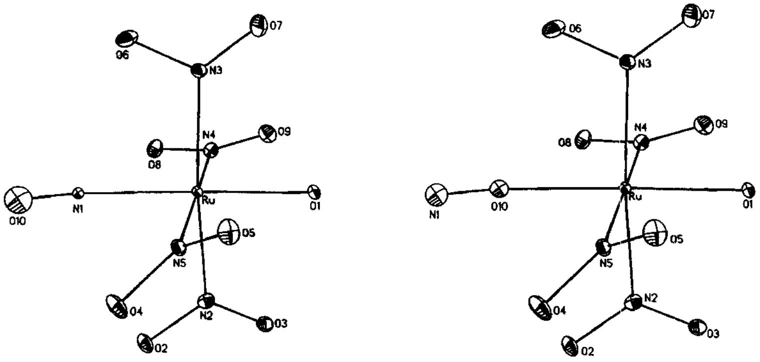


FIGURE 2 ORTEP of the Ru-NO (left) and Ru-ON (right) models of the MS_1, showing the differences in the nitrosyl thermal parameters. 50% probability ellipsoids are shown

mation with respect to the equatorial ligands. Since in the metastable state the N and O atoms are displaced from the mirror plane that in the ground state contains the NO ligand, the MS_2 nitrosyl group exists in the two orientations shown in Fig. 3. The remainder of the anion shows little change from the tetragonal symmetry of the ground state. Thus, the photo-induced species do not correspond to electronically excited states, but to linkage isomers. This suggested that MS_1 could correspond to the O-bound, isonitrosyl isomer. Support of this hypothesis was obtained by simple permutation of the N and O scattering factors in the least-squares refinement of the structure in MS_1. This produced very reasonable mean-square displacements, the values for the terminal NO being comparable to those for the oxygen atom in the ground state structure. This was repeated in two other studies of MS_1 on $K_2[Ru(NO_2)_4(NO)(OH)]$ and *trans*-$[RuCl(NO)(py)_4][PF_6]_2 \cdot 1/2H_2O$, the results of which are included in Table I.

Independent confirmation was obtained from the 80 K neutron data analysis of MS_1 of SNP by Rüdlinger *et al.*, who refined the average positions of the ground- and excited-state atoms (~ 37% MS_1), assuming the nitrosyl geometry [18, 19]. The excited-state equivalent isotropic thermal parameters of Rüdlinger *et al.* are *higher* for the proximal than for the distal atom, while, as in the X-ray study, in the ground state they are lower for the proximal atom. An important difference between X-ray

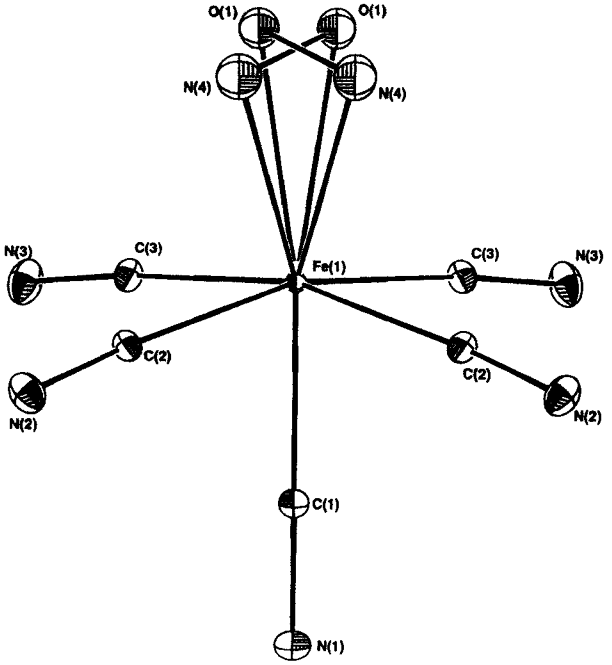


FIGURE 3 ORTEP of MS_2 of the SNP anion. Both mirror related NO orientations are shown with 50% probability thermal ellipsoids

and neutron scattering is that for X-rays the oxygen is the more strongly scattering atom. The situation is reversed for neutron scattering, the neutron scattering amplitudes being b = 9.36 fm and 5.80 fm for nitrogen and oxygen, respectively. Thus, in the neutron case the scattering power of the proximal atom is *over-* rather than *under*estimated when the incorrect nitrosyl geometry is used for MS_1, leading to the observed anomaly. The neutron thermal parameters thus support the conclusion based on the X-ray results.

As was pointed out by Güdel [20], long lifetimes impose unusually severe restrictions on the nature of the metastable species. These restrictions can be met only in case of very large changes in atomic configuration, or a multi-electron promotion. Our results provide a logical explanation for the long lifetimes that are observed.

TABLE I Isotropic "thermal" mean-square displacements (Å^2) for nitrosyl atoms in the ground state and for MS_1 according to the M-NO and M-ON models

	$Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ ref. [16]		
	ground state	MS_1, Fe(NO)	MS_1, Fe(ON)
proximal	0.0056(1)	0.0040(4)	0.088(5)
distal	0.0116(1)	0.0163(5)	0.0102(4)
	$K_2[Ru(NO_2)_4(NO)(OH)]$ ref. [15]		
	ground state	MS_1, Ru(NO)	MS_1, Ru(ON)
proximal	0.0072(5)	0.0037(13)	0.008(1)
distal	0.0141(5)	0.022(2)	0.015(2)
	$[RuCl(NO)(py)_4][PF_6]_2\cdot 1/2H_2O$ ref. [21]		
	ground state	MS_1, Ru(NO)	MS_1, Ru(ON)
proximal	0.0081(4)	0.0042(5)	0.0108(6)
	0.0128(5)	0.0061(5)	0.0175(7)
distal	0.0135(4)	0.0232(7)	0.0117(6)
	0.0203(5)	0.0293(8)	0.0151(6)

SOLID-STATE PHOTOCHEMISTRY OF NITROSYL COMPLEXES OF Ru (II)

To elucidate the role of chemical substitution on the stability of the linkage isomers, we tested a number of complexes of Ru [21] by low-temperature irradiation followed by DSC. In these experiments a sample is cooled to 110 K, irradiated and subsequently heated at a constant rate, 4° /min in our case, while the enthalpy supplied is being monitored. A typical DSC curve, obtained from a polycrystalline sample of *trans*-$[RuCl(NO)(py)_4][PF_6]_2\cdot 1/2H_2O$, previously irradiated with 457 nm light, is shown in Fig. 4. The total enthalpy release is obtained by integration over the shaded area. The population of the metastable state can be estimated from the known mass of the sample and the approximate value of 1eV for the energy difference between MS_1 and the ground state [22]. Decay temperatures and conversion percentages for several Ru complexes are listed in Table II, while Table III shows the decay temperatures obtained by Morioka *et al.* using the IR spectroscopy as a probe for the presence of linkage isomers [23]. All compounds listed in these tables belong to the $\{MNO\}^6$ family. It is evident that the light-induced linkage isomers are not limited to a small group of complexes, but occur for a variety of compounds. We want to emphasize that many other complexes studied by us were inactive. However, our tests were restricted mostly to 457 nm light and to temperatures above the boiling point of liquid nitrogen. Our data are not sufficiently extensive to formulate a relation between chemical composition and the stability and population of the metastable states. But, in general, the higher frequency of the stretching vibration of the NO group in the ground state, the higher the decay temperature of MS_1. This is illustrated in Fig. 5 and further discussed in the following paragraphs.

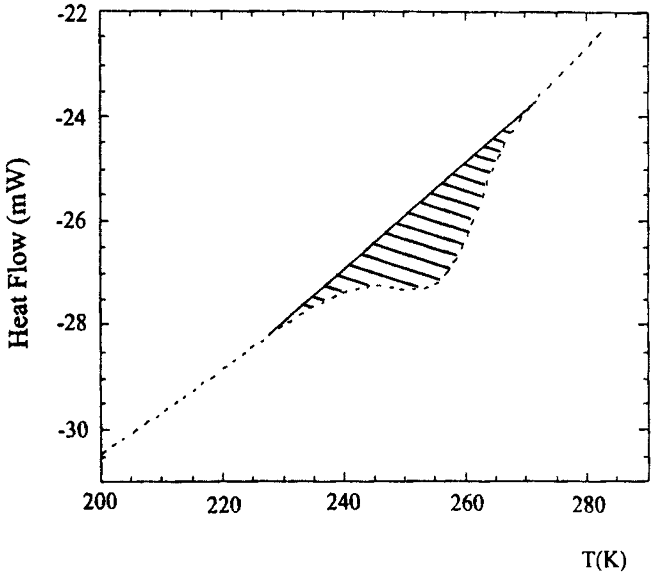


FIGURE 4 Heat flow vs. temperature, for a constant temperature increase of 4 K/min, of a previously laser-irradiated polycrystalline sample of *trans*-$[RuCl(NO)(py)_4][PF_6]_2 \cdot 1/2H_2O$. Shaded area corresponds to the total enthalpy release during the transformation from MS_1 to the ground-state

TABLE II Decay temperatures, frequencies of the NO stretching vibrations in the ground state and conversion percentages for several ruthenium (II) nitrosyl complexes [21]

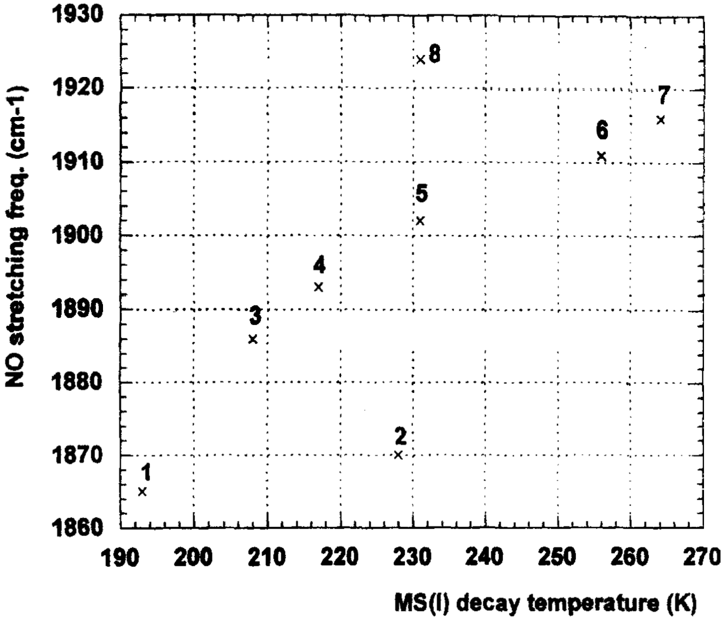
compound	*MS_1, Tc (K)*	*MS_2, Tc (K)*	*ν (NO), cm^{-1}*	*conversion % (may not be maximal)*
$[Ru(bpy)(NO)(NO_2)(OH)(H_2O)]$ $[NO_2]^a$	193	no	1865	5
trans-$[Ru(NO)(OH)(py)_4][PF_6]_2$	223	171	1870	16/1
$K_2[Ru(NO_2)_4(NO)(OH)]$	208	173	1886	16/1
$K_2[RuCl_5(NO)]$	216	no	1895	5
trans-$[Ru(Br)(NO)(py)_4][PF_6]_2$	208	150	1902	9/2
trans-$[RuCl(NO)(py)_4][PF_6]_2 \cdot 1/2H_2O$	256	171	1911	50/1
$[Ru(NH_3)_5(NO)][NO_3]_3$	265	no	1917	15
$[Ru(bpy)_2(NO)(H_2O)]$ $[ClO_4]_3^a$	231	188	1924	4/2

[a] compounds received from T.J. Meyer group.

TABLE III Decay temperatures and frequencies of the stretching vibrations of NO in the ground state [23]

compound	*MS_1, Tc (K)*	*ν (NO), cm^{-1}*
trans-$[RuBr(NO)(en)_2]Br_2$	229	1877
trans-$[RuCl(NO)(en)_2]Cl_2$	246	1878
trans-$[Ru(H_2O)(NO)(en)_2]Cl_3$	267	1904

The *trans* influence was observed and intensively studied in the octahedral complexes of Ru and Os [24–26]. It seems logical to link the stability of the L-Ru-ON fragment (MS_1) with the nature the *trans* ligand. To test this dependence we prepared a series of compounds with the general formula *trans*-$[Ru(NO)L(py)_4]^{2+}$ ($L=I^-, Br^-, SCN^-, Cl^-, OH^-$), as well as $[Ru(NH_3)_5(NO)]^{3+}$. The latter can be considered an analog of *trans*-$[Ru(NO)(NH_3)(py)_4]^{3+}$. The stretching frequencies of NO in the ground state are 1832, 1870, 1902, 1906, 1911 and 1917 cm^{-1} for the I^-, OH^-, Br^-, SCN^-, Cl^- and NH_3 *trans* ligands, respectively. Except for OH^-, there is an agreement with the suggested order of increasing π-donor ability $OH^- < NH_3 < Cl^- < SCN^- < Br^- < I^-$ [27]; the NO bond getting weaker, the larger the π-donor ability of the trans ligand. OH^- appears to be an exception, which may be explained on the basis of a σ-,



1	[Ru(NO)(bpy)(NO2)(OH)(H2O)][NO2]
2	[Ru(NO)(OH)(py)4][PF6]2
3	K2[Ru(NO)(NO2)4(OH)]
4	K2[Ru(NO)Cl5]
5	[Ru(NO)Br(py)4][PF6]2
6	[Ru(NO)Cl(py)4][PF6]2
7	[Ru(NO)(NH3)5][NO3]3
8	[Ru(NO)(bpy)2(H2O)][ClO4]3

FIGURE 5 Plot of the decay temperature of MS_I vs. the ground-state NO stretching frequency

rather than a π-interaction [25]. The decay temperatures of MS_1, which corresponds to the L-Ru-ON geometry, are 208K, 256K and 265K for the L=Br^-, Cl^- and NH_3 *trans* ligands, respectively. No metastable state was found for L=I^-, which may have a decay temperature below that of liquid nitrogen. Thus, the decay temperatures occur in the same sequence as the π-donor ability of the trans ligand and the stretching frequencies of NO. Photochemical decomposition was observed in the case of L=SCN^-.

These observations suggest that, in a series of compounds with the same *cis* ligands, the weak π-donor in the *trans* position with respect to NO stabilizes the L-Ru-ON fragment, (MS_1). Data obtained by Morioka and co-workers on Ru nitrosyls with ethylenediamine as the *cis*-ligand (Table III) provide further support for this hypothesis, as the same trend is found for the Br^-, Cl^- and H_2O *trans* ligands.

The effect of *cis*-ligands can also be pronounced. This is illustrated in Table IV, which compares stretching vibrations of the NO group in *trans*-hydroxylnitrosylruthenium complexes having different *cis* ligands. The influence of the nature of the cis-ligand on the decay temperatures requires further study.

TABLE IV Influence of the *cis* ligands on the stretching vibration of the NO

compound	*ν (NO), cm^{-1}*
$[Ru(NH_3)_4(NO)(OH)]Cl_2$	1834[a]
trans-$[Ru(NO)(OH)(py)_4][PF_6]_2$	1870
$K_2[Ru(NO_2)_4(NO)(OH)]$	1886
trans-$[Ru(NO)(OH)(bpy)_2]$ $[PF_6]_2$	1890[b]

[a] reference [25]. [b]reference [33].

Other factors, such as the size and nature of the cavity surrounding the NO group, may affect the relative stability of the linkage isomers. Additional experimental and theoretical work is needed to obtain a more comprehensive understanding of the photochemisrty of the nitrosyl complexes.

X-RAY DIFFRACTION AND DENSITY FUNCTIONAL STUDY OF [Ni(NO)(η^5-Cp*)] IN THE GROUND AND LIGHT-INDUCED METASTABLE STATES

As noted above, Rest and co-workers [11–13] discovered photochemical reactions for the nitrosyl complexes of Ni, Mn and Cr, which lead to

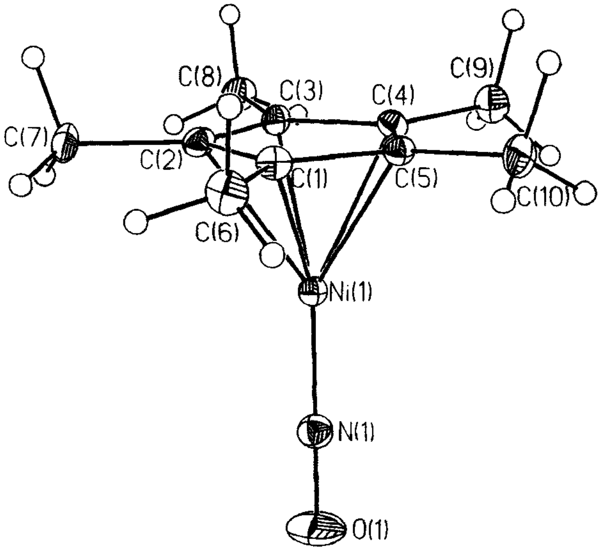


FIGURE 6 ORTEP of [Ni(NO)(η^5-Cp*)] in the ground state. 50% probability ellipsoids are shown, except for the H atoms (25K)

products with very low stretching vibrations of the nitrosyl ligand. To investigate if the photochemistry of Rest's complexes is related to that of compounds with the $\{MNO\}^6$ configuration, we studied the structure of [Ni(NO)(η^5-Cp*)] ($\{MNO\}^{10}$) in the ground and light-induced state [28]. [Ni(NO)(η^5-Cp*)] was selected as it is a solid at room temperature, unlike [Ni(NO)(η^5-Cp)], which is a liquid, thus avoiding experimental complications. An ORTEP plot of the [Ni(NO)(η^5-Cp*)] molecule in the ground state is shown in Fig. 6. The least-squares refinement of the light-induced metastable state revealed a structure with a side-bound nitrosyl (Fig. 7). The most important changes in the bond lengths and angles are summarized in Table V. A population of the metastable state species of 46(1)% was obtained in the course of the refinement. A diene-like distortion of the pentamethylcyclopentadienyl ring was evident. There are similarities between the metal nitrosyl geometries found in [Ni(η^2-NO)(η^5-Cp*)] and SNP (MS_2) regarding the (Ni, Fe)-O distances, which are 2.09 and 2.07 Å for Ni and Fe, respectively, and the elongation of the (Ni, Fe)-N bonds. As in MS_1, we were not able to detect a significant lengthening of the N-O bond in the metastable state, even though it would be expected based on the 447 cm^{-1} decrease in the NO stretching frequency.

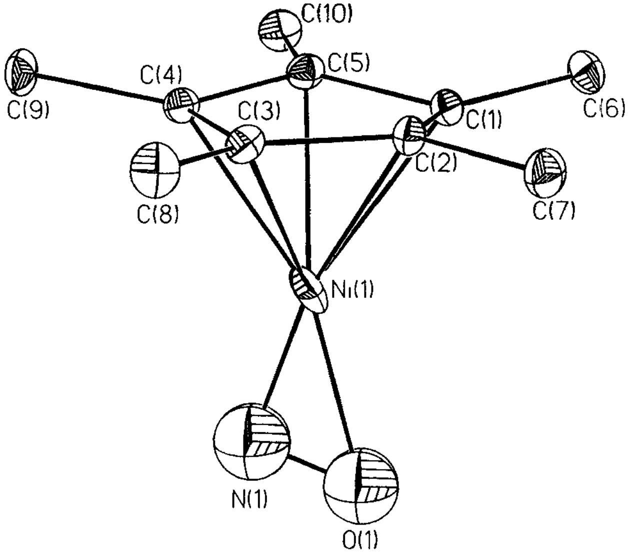


FIGURE 7 ORTEP of $[\mathrm{Ni(NO)}(\eta^5\text{-}\mathrm{Cp}^*)]$ in the light-induced state. 50% probability ellipsoids are shown, except for the H atoms (25K)

TABLE V Selected bond lengths (Å) and angles (deg.) for ground-state and metastable-state structures of $[\mathrm{Ni(NO)}(\eta^5\text{-}\mathrm{Cp}^*)]$ at 25K [28]

bond, angle	*ground state*		*metastable state*	
	molecule A	*molecule B*	*molecule A*	*molecule B*
Ni-N	1.620(3)	1.614(3)	1.697(18)	1.724(10)/1.716(10)[†]
Ni-O			2.096(18)	2.077(10)/2.079(10)
Ni-plane[††]	1.719(1)	1.718(1)	1.732(6)	1.750(6)
N-O	1.177(3)	1.181(4)	1.134(18)	1.126(30)/1.128((32)
Ni-N-O	179.2(3)	179.1(3)	93(1)	91(1)/92(1)

[†] two positions of the NO group were found in the metastable state for the B molecule.
[††] the mean plane through the C(1), C(2), C(3), C(4), C(5) atoms of the Cp ring.

TABLE VI Calculated (B3LYP functional and LANL2DZ basis set) and experimental[a] structural parameters (Å, deg.) for the ground state, $[\mathrm{Ni(NO)}(\eta^5\text{-Cp}^*)]$, metastable state, $[\mathrm{Ni}(\eta^2\text{-NO})(\eta^5\text{-Cp}^*)]$ and hypothetical $[\mathrm{Ni(ON)}(\eta^5\text{-Cp}^*)]$ structures [28]

bond, angle	*$[\mathrm{Ni(NO)}(\eta^5\text{-Cp}^*)]$*		*$[\mathrm{Ni}(\eta^2\text{-NO})(\eta^5\text{-Cp}^*)]$*		*$[\mathrm{Ni(ON)}(\eta^5\text{-Cp}^*)]$*
	experimental	*theoretical*	*experimental*	*theoretical*	*theoretical*
Ni-C(1)	2.107(3)	2.188	2.092(12)	2.117	2.191
Ni-C(2)	2.106(3)	2.188	2.132(12)	2.117	2.191
Ni-C(5)	2.105(3)	2.188	2.106(12)	2.200	2.191
Ni-C(3)	2.109(3)	2.188	2.142(11)	2.200	2.191
Ni-C(4)	2.106(3)	2.188	2.142(12)	2.236	2.191
Ni-N	1.620(3)	1.628	1.697(18)	1.740	
Ni-O			2.096(18)	2.121	1.697
N-O	1.177(3)	1.214	1.134(18)	1.278	1.224
C(1)-C(2)	1.437(4)	1.448	1.456(14)	1.460	1.448
C(1)-C(5)	1.434(4)	1.448	1.412(13)	1.460	1.448
C(2)-C(3)	1.436(5)	1.448	1.454(13)	1.436	1.448
C(4)-C(5)	1.425(4)	1.448	1.434(13)	1.436	1.448
C(3)-C(4)	1.433(5)	1.448	1.473(14)	1.455	1.448
C-C(CH3)	1.504(4)	1.507	1.515(14)	1.507	1.507
Ni-N-O (deg)	179.2(3)	180.	93(1)	87.9	180.
total energy (a.u.)		-689.2808		-689.2443	-689.2128

[a] Values given for the A molecule of the asymmetric unit. Two independent molecules, A and B are present in the asymmetric unit.

We performed full geometry optimizations at the DFT level for the ground state of $[\mathrm{Ni(NO)}(\eta^5\text{-Cp}^*)]$, the experimentally observed metastable state, and a hypothetical isonitrosyl structure. Details of the calculations which were carried out with an effective core potential LANL2DZ basis set, can be found elsewhere [26]. The most significant result is that the species $[\mathrm{Ni}(\eta^2\text{-NO})(\eta^5\text{-Cp}^*)]$ and $[\mathrm{Ni(ON)}(\eta^5\text{-Cp}^*)]$

correspond to local minima at 0.99 and 1.85 eV above the ground state on the potential energy surface and, thus, according to theory, can be stable at low temperature. The experimental geometries of [Ni(NO)(η^5-Cp*)] and [Ni(η^2-NO)(η^5-Cp*)] were reasonably well reproduced, as shown in Table VI.

Results of similar calculations recently became available for SNP in the ground state and in both metastable states [29]. The authors concluded that local minima exist on the ground state Born-Oppenheimer surface for both side-on and inverted NO. Calculated barriers were found sufficiently large to explain the long lifetime at low temperature. A remarkable result of these calculations is that shortening of the N-O bond by 0.01 Å in the isonitrosyl complex (MS_1) is accompanied by softening of the N-O stretching frequency. It explains why we did not observe elongation of the NO bond in MS_1 in either one of the X-ray diffraction experiments. For MS_2, the DFT calculations by Delley *et al.* of SNP [29], and our calculations of the Ni complex show a modest elongation of the N-O bond by 0.03 and 0.06 Å, respectively. The trend for elongation of the N-O bond in a side-bound configuration is thus consistently reproduced, even though the theoretical values may not be accurate. Further studies are needed to resolve discrepancy with the crystallographic data on MS_2

POTENTIAL APPLICATIONS

Recently it was shown that SNP, and other transition metal nitrosyls of which light-induced metastable states can be generated, may be suitable for high-capacity information storage elements [30, 31]. The pronounced change in color, especially in the violet and red spectral ranges, can be utilized for serial (bit-by-bit) and holographic information storage in single crystals and powder specimens. The photochromism scales with the number of anions transferred into the metastable states. This, in turn, is a function of time, since the population of the metastable states depends on the light intensity and length of irradiation. The extent of the change in absorption can by itself be used as information. Furthermore, the population of the metastable state results not only in changes of the absorption, but also of the refractive index (photorefractive effect). Refractive index and absorption gratings were recently prepared in two-wave mixing experiments on a single crystal of SNP [31].

CONCLUDING REMARKS

We have identified two new binding modes of nitric oxide. In two respects the side-bound nitrosyls are geometrically distinct from the "bent nitrosyls" previously observed. First, the observed Ni-N-O and Fe-N-O angles of 93(1)° and 82(1)° are far from the ranges of corresponding angles reported in the Cambridge Structural Data Base, which are 130–180° and 135–180° for Ni and Fe nitrosyls respectively. Secondly, the experimental values for the Ni-O and Fe-O distances (2.09 and 2.07 Å respectively) are typical for covalent bonds between these atoms, and much shorter than those observed for the bent nitrosyls.

The new species can be considered as possible intermediates in certain chemical transformations. For instance, side-on bound nitrosyl has already been proposed as a transition state in the hydrolysis of a terminal nitrosyl, which results first in the formation of a η^2-hydroxylamide group, and then in the liberation of the hydroxylammonium cation [32].

The linkage isomerism provides an explanation for the long lifetimes of the light-induced states, which can not easily be understood on the basis of an electronically excited state interpretation.

This work is preliminary to crystallographic studies of transient species on a time-resolved scale. The experiments, to be carried out in the next few years, should give new insight into photo-induced chemical processes [21].

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