Inorg. Chem. **1995,** *34,* 4113−4116 **4113**

Infrared Absorption Spectra of Sodium Pentacyanonitrosylosmate(II) Dihydrate in Two Excited Electronic Metastable States

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Received December 1, 1994[⊗]

Pentacyanonitrosylosmate(2−) ion ($[Os(CN)_5NO]^{2-}$), as the sodium salt, can be excited selectively to two long-lived electronic metastable states (MSI and MSII) by irradiation at low temperature with light in the blue−near-UV region. The MSI and MSII states are similar to those found in nitroprusside salts, including isomorphous $Na_2[Fe(CN)_5NO]{\cdot}2H_2O$, and in RuNO complexes. IR bands due to CN, NO, and OsN stretching and OsNO bending modes show frequency downshifts upon excitation of $[Os(CN)_5NO]^{2-}$ to MSI and MSII states. This implies softening of the corresponding bonds. Frequency shifts of vibrational modes of the OsNO group are much larger than the corresponding shifts of CN modes. This further supports the conclusion that metastable states are reached through an electronic transition involving mainly the metal(*n*d)−NO grouping (n = 3, 4, 5). Upon heating, the MSI and MSII states of the osmium compound decay at two different onset temperatures, $T_I < T_{II}$, in inverse order to that reported for the other complexes. Furthermore, we report a thermally driven MSI → MSII excitation transfer process taking place at temperatures in the range $T_{II} > T \geq T_I$. This proves that, at the equilibrium molecular conformation, the MSII energy level lies below the MSI level and that there must be a crossing of the corresponding electronic energy curves at thermal energies above the MSI vibrational ground level.

Introduction

Excited electronic states are central to the understanding of chemical and photochemical reactions. Often, however, the lifetimes of such states are much too short to allow a detailed study. The production of metastable electronically excited states is therefore of particular interest for basic physical chemistry and also because of the potential application of these states as optical information storage elements.

The generation of two such long-living metastable states by light irradiation at low temperatures has been demonstrated by a variety of techniques in several transition metal−nitrosyl compounds, including salts of the nitroprusside $[Fe(CN)_5NO]^{2-}$ ion[1−4] and the potassium salts of $[RuCl_5NO]^{2-}$ and $[Ru(NO_2)_4(OH)(NO)]^{2-}$ complexes.[5,6] It has also been suggested that a metastable state exists in NiCpNO (Cp: η^5-cyclopentadienyl).[7] These findings strongly suggest that the metal(*n*d)−NO group is the main reason for the phenomenon. This is further substantiated by vibrational spectroscopic[8] and neutron[9,10] and X-ray[11] diffraction studies in sodium nitroprusside and EXAFS structural studies in NiCpNO[12] showing that the major perturbation in mode frequencies and bond lengths upon population of metastable states occurs in the metal−NO group. In what follows, we shall use the labels MSI and MSII to refer to the metastable states of the Fe and Ru complexes which exhibit, respectively, the smallest and largest downshifts in NO stretching frequency.

Previously, we reported two independent sets of IR absorption bands corresponding to light-induced MSI and MSII states of nitroprusside ion in $Na_2[Fe(CN)_5NO]{\cdot}2H_2O$ (SNP)[2] and

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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$Ba[Fe(CN)_5NO]\cdot 3H_2O$.[3] On heating, the two sets of bands vanish following decay processes with an onset temperature T_I for MSI *higher* than the corresponding temperature for the MSII state (T_{II}). This temperature ordering has since been confirmed by employing differential scanning calorimetry (DSC) in several nitroprusside salts[4] and also in $K_2[RuCl_5NO]$[5] and $K_2[Ru(NO_2)_4(OH)(NO)]$.[6]

We report here IR spectroscopic evidence for the existence of MSI and MSII metastable states in $[Os(CN)_5NO]^{2-}$ ion similar to those found in nitroprusside and RuNO complexes. By choosing the irradiation wavelength in the proximity of each one of the absorption bands exhibited by the complex in the blue–near-UV spectral region, it is possible to populate *selectively* MSI or MSII states. The MSI/MSII system of energy levels exhibits striking behavior. At variance with those of previous systems, the MSII state has an onset decay temperature T_{II} which is *higher* than T_I for MSI. Furthermore, $Na_2[Os(CN)_5NO]\cdot 2H_2O$ is the first compound in the series of related species where it has been found that *MSII can be populated by thermally induced decay of the MSI state.*

Crystal and Spectroscopic Data

Sodium pentacyanonitrosylosmate(II) dihydrate, $Na_2[Os(CN)_5NO]\cdot 2H_2O$, is isomorphous with other $Na_2[M(CN)_5NO]\cdot 2H_2O$ (M = Fe, Ru) salts. It crystallizes in the orthorhombic space group $Pnnm(D_{2h}^{12})$ with $a = 6.312(1)$ Å, $b = 12.090(2)$ Å, $c = 15.828(3)$ Å, and $Z = 4$.[13] The complex anion exhibits a distorted octahedral configuration of ligands around osmium with approximate C_{4v} symmetry. There is one complex ion per asymmetric unit. The nearly linear $(NC)_{ax}OsNO$ axis lays on a crystallographic mirror (*ab*) plane making an angle of about 30° with the *a* axis. The mirror plane bisects opposite $(CN)_{eq}Os(CN)_{eq}$ angles between adjacent CN ligands. The comparison of bond distances and angles with the iron and ruthenium analogues shows appreciable differences with nitroprusside ion only in metal–ligand bond lengths [$d(Os-N) = 1.7774(8)$ Å, average $d(Os-C) = 2.06(1)$ Å; $d(Fe-N) = 1.653(5)$ Å, average $d(Fe-C) = 1.928(9)$ Å] and practically no differences, within experimental accuracy, with the $[Ru(CN)_5NO]^{2-}$ ion.

The electronic spectrum of $Na_2[Os(CN)_5NO]\cdot 2H_2O$ (in aqueous solution) in the blue–near-UV region shows two broad absorption bands with maxima of 89 and 97 M^{-1} cm^{-1} at 23 420 cm^{-1} (427 nm) and 31 850 cm^{-1} (314 nm), respectively.[13]

The 33 vibrational modes of the $[Os(CN)_5NO]^{2-}$ ion and their corresponding IR and Raman (R) activities are distributed among the symmetry species of the ideal C_{4v} molecular point group according to $\Gamma = 8A_1(IR,R) + A_2(silent) + 4B_1(R) + 2B_2(R) + 9E(IR,R)$. Under the symmetry C_s of the site occupied by the anion in the $Na_2[Os(CN)_5NO]\cdot 2H_2O$ crystal, the representation of the vibrational modes changes into $\Gamma = 19A' + 14A''$. All modes should be in this case IR and Raman active.

Experimental Section

Synthesis of the $[Os(CN)_5NO]^{2-}$ ion is reported by Baraldo *et al.*[13] and Baran and Müller[14] and of the sodium salt by Baraldo *et al.*[13] Low-temperature IR spectra of $Na_2[Os(CN)_5NO]\cdot 2H_2O$ were measured with an FT-IR Bruker 113v spectrometer equipped with a mid-IR DTGS detector and working at 2 cm^{-1} resolution. Powder samples as Nujol mulls sandwiched between CsI disks were positioned at the cold tip of an Oxford OX8 ITL cryostat (kept at 80 K). The samples were then irradiated with the 457.9 nm Ar^+ laser (no. 166, Spectra Physics) line at 30 mW cm^{-2} and also with light from a mercury lamp filtered with 10 mm of a 1 M $NiSO_4$ solution and a Schott BG3 2 mm thickness filter to isolate the 280–340 nm spectral region. Irradiation time was about 4 h.

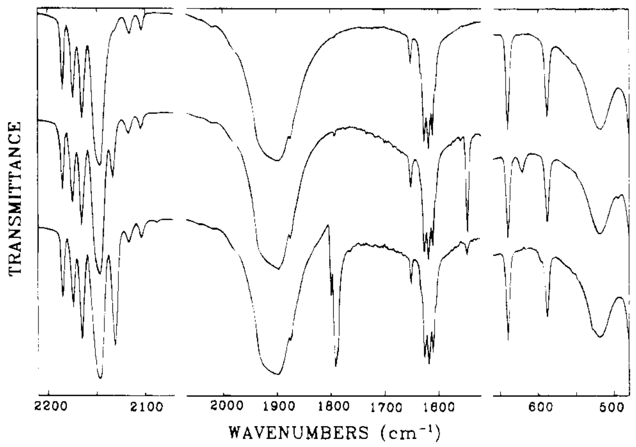

Figure 1. Low-temperature (80 K) IR absorption spectra of ground state (GS) and metastable (MS) anions in $Na_2[Os(CN)_5NO]\cdot 2H_2O$. For the sake of clarity, the curves have been displaced vertically. Upper curve, before irradiation; middle curve, after irradiation with light from a mercury arc limited to the 280–340 nm spectral region; lower curve, after irradiation with the $\lambda = 457.9$ nm line of an Ar^+ laser.

Table 1. Wavenumbers (cm^{-1}) and Assignments of Bands Due to Electronic Ground State (GS) and Excited MSI and MSII Metastable States of $[Os(CN)_5NO]^{2-}$ Ion in the Low-Temperature IR Spectra of $Na_2[Os(CN)_5NO]\cdot 2H_2O$

GS	MSI	MSII	assignment[a,d]
2185	2166[b]		$\nu(CN)_{ax}(A_1)$
2175	2156[b]		$\nu(CN)_{eq}(A_1)$
2165	2145[b]		$\nu(CN)_{eq}(B_1)$[c]
2147	2131	2133	$\nu(CN)_{eq}(E)$
2132			$\nu(^{13}CN)_{eq}(B_1)$
2116			$\nu(^{13}CN)_{eq}(E)$
2104	2088		
		1782	?
	1799		$\nu(NO)$
1897	1790	1546	
	1788 sh[d]		
1875	1764		$\nu(^{15}NO)$
640	596 sh[d]	621	$\delta(OsNO)E$
588	528 sh[d]	495	$\nu(OsN)A_1$

[a] Under C_{4v} ideal symmetry. [b] Obtained from difference spectra. [c] As in SNP, the B_1 mode is activated by crystal field effects on the anion at the site of C_s symmetry and also through coupling with the strongly polar $\nu(CN)_{eq}(E)$ mode.[19] [d] sh, shoulder; ax, axial; eq, equatorial.

Results and Discussion

Vibrational Modes of Electronically Excited $[Os(CN)_5NO]^{2-}$. In Figure 1 are compared the low-temperature IR absorption spectrum of ground state (GS) $Na_2[Os(CN)_5NO]\cdot 2H_2O$ and vibrational spectra of the electronically excited compound with part of the anions in the MSI and MSII metastable states. Wavenumbers and assignments of internal modes are presented in Table 1.

Assuming negligible changes in the transition dipole moment of the $(CN)_{eq}(E)$ stretching mode upon excitation to MSI and MSII states, we can estimate the population attained for these states by comparing IR band intensities. Irradiation with the 457.9 nm laser line, close to the optical absorption maximum at 427 nm, preferentially populates the MSI state (yield about 28%). In contrast, irradiation with filtered light from a mercury arc, centered on the near-UV absorption maximum at 314 nm, selectively populates the MSII state (yield about 8%).

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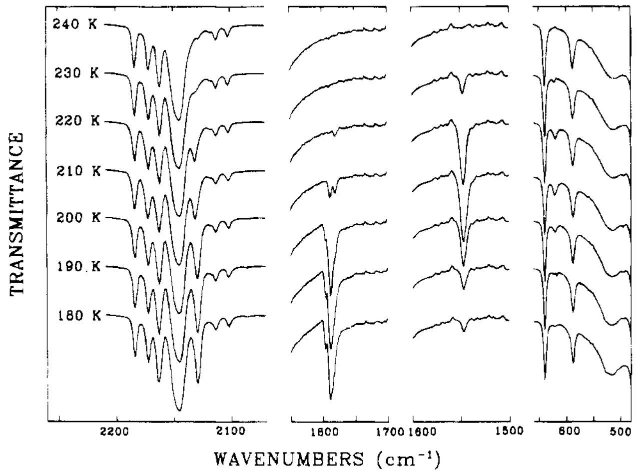

Figure 2. IR spectral behavior upon heating of $Na_2[Os(CN)_5NO]\cdot 2H_2O$ electronically excited with the λ = 457.9 nm laser line at 80 K.

All detected vibrational modes exhibit frequency downshifts upon excitation to MSI and MSII states. This points to a softening of the involved bonds.

The new set of MSI CN stretching bands at 2166, 2156, 2145, and 2131 cm^{-1} are shifted 19, 19, 20, and 16 cm^{-1}, respectively, with respect to the corresponding GS ν(CN) values. These values are about twice the corresponding values reported for sodium nitroprusside (SNP).[8]

Because of the relatively low population obtained for the MSII state, in the ν(CN) region only the strong degenerate $\nu(CN)_{eq}$(E) mode could be detected at 2133 cm^{-1}, shifted 14 cm^{-1} from GS $\nu(CN)_{eq}$(E).

The MSI NO stretching band at 1790 cm^{-1} is shifted 107 cm^{-1} with respect to the GS ν(NO) mode, a value slightly smaller than corresponding values reported for the related compounds. The ratio between integrated band intensities of MSI and GS ν(NO) modes is about one-half of the corresponding ratio between MSI and GS $\nu(CN)_{eq}$(E) intensities. This suggests a reduction in approximately a factor of 2 in the squared transition dipole moment of the NO mode upon excitation to the MSI state. The MSI NO band shows a sharp feature at 1799 cm^{-1} on its high-frequency side. A similar feature is also present in the NO band of the SNP MSI state.[8] In the MSI NO spectral region, a MSII peak appears at 1782 cm^{-1}. This feature is similar to one detected in SNP[8] and could not be assigned.

The MSII ν(NO) peak at 1546 cm^{-1} is shifted by 349 cm^{-1}. This shift is the largest thus far reported for the series of nitroprusside- and RuNO-containing salts. It is surpassed only by the corresponding value (447 cm^{-1}) reported for NiCp(NO).[7] The squared transition dipole moment for the MSII ν(NO) mode seems to be about 60% of the corresponding GS ν(NO) value.

The MSI counterpart of GS peaks at 640 and 588 cm^{-1}, assigned to the δ(OsNO) and ν(OsN) modes, are observed as shoulders at 596 and 528 cm^{-1}, respectively. The corresponding MSII δ(OsNO) and ν(OsN) vibrations are detected as peaks at 621 and 495 cm^{-1}.

Thermal MSI → MSII Excitation Transfer. Figure 2 shows the IR spectral behavior upon heating of $Na_2[Os(CN)_5NO]\cdot 2H_2O$ electronically excited with the λ = 457.9 nm laser line at 80 K. Two major conclusions can be drawn from these data. First, the onset decay temperature T_{II} of the MSII state (of about 220 K) is *higher* than the corresponding T_I temperature (about 190 K) for the MSI state. In fact, it is the *highest* thus far reported for nitroprusside and RuNO complexes, where $T_I > T_{II}$. Second, and more interesting, at the decay temperature T_I, the MSII state starts increasing its population at the expense of MSI. Not all MSI molecules convert into the MSII state, and part of them seem to decay into the ground state. This is suggested by the variation with temperature of the sum of the MSI and MSII $\nu(CN)_{eq}$(E) band intensities shown in Figure 3. The MSI state almost vanishes at about 210 K when the thermally filled MSII state reaches it maximum population. On further heating, the MSII state disappears above 230 K. In summary, the MSII state can be populated by thermally induced decay of the MSI state. This proves that, at the equilibrium molecular conformation, the MSII energy level is *below* the MSI level, in agreement with the energy ordering reported for MSI and MSII states in SNP[15] and $K_2[Ru(NO_2)_4(OH)(NO)]$.[6] Also, the thermally driven MSI → MSII excitation transfer indicates that there must be a *crossing* of MSI and MSII electronic energy curves with a barrier which can be easily overcome at thermal energies above the MSI vibrational ground level. The situation is depicted schematically in Figure 4.

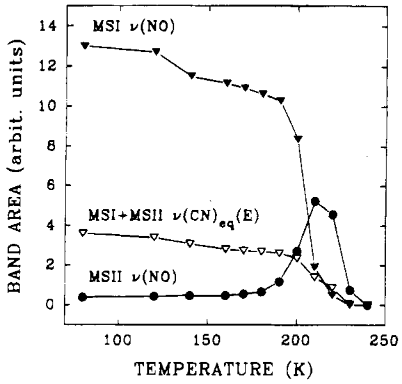

Figure 3. Thermal behavior of IR band intensities of MSI and MSII $\nu(CN)_{eq}$(E), MSI ν(NO), and MSII ν(NO) modes.

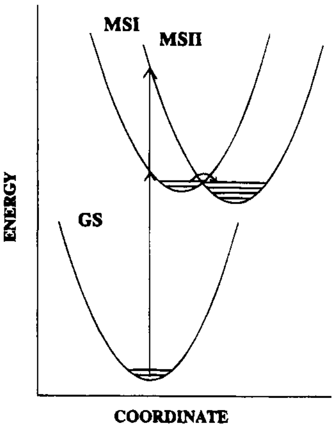

Figure 4. Schematic representation of electronic energy curves and vibrational levels for ground state (GS) and excited MSI and MSII states of $[Os(CN)_5NO]^{2-}$ ion.

On the Electronic Structure of MSI and MSII States. The subject is far from being solved, and the detailed electronic characterization of MSI and MSII states is at present a matter of controversy. Usually, following an early proposal for the electronic structure of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$,[16] the MSI and MSII states are assigned to relaxed derivatives arising from a metal-to-ligand charge transfer transition $...6e(d_{xz},d_{yz})^4 2b_2(d_{xy})^2$: $^1A_1(GS) \rightarrow 6e(d_{xz},d_{yz})^4 2b_2(d_{xy}) 7e(\pi^*NO)$: ^1E.[17] However, for the best studied MSI state in nitroprusside salts, this assignment

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conflicts with several spectroscopic and structural data and a parent electronic configuration $...6e(d_{xz},d_{yz})^4 2b_2(d_{xy})5a_1(d_{z^2}){:}^1B_2$ for this state has been proposed.[18] In addition to the reported weakening of the strong metal−NO bond and of the N−O bond upon excitation to the MSI state, population of the empty σ^*-(d_{z^2}) orbital could also be responsible for the mode softening exhibited by the less strong trans to metal−NO bond ($\Delta\nu(RuCl_{ax}) = -17$ cm^{-1} in $K_2[RuCl_5NO]$[5]) and of the trans to NO ligand ($\Delta\nu(CN)_{ax} = -19$ cm^{-1} for $Na_2[Os(CN)_5NO]\cdot 2H_2O$, $\Delta\nu(CN)_{ax} = -8$ cm^{-1} for SNP[8], $\Delta\nu(OH) = -29$ cm^{-1} in $K_2[Ru(NO_2)_4(OH)(NO)]$[6]). Population of a $\sigma^*(d_{z^2})$ orbital is also supported by a recent electron density study of the MSI state in $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ by X-ray diffraction methods.[11] For the other, the MSII state, we can consider three possible assignments. (i) It could be a relaxed derivative arising from the population of the $7e(\pi^*NO)$ orbital reached either from the GS HOMO $2b_2(d_{xy})$ level as described above or from the 6e-(d_{xz},d_{yz}) level through the transition $...6e(d_{xz},d_{yz})^4 2b_2(d_{xy})^2{:}^1A_1 \rightarrow 6e(d_{xz},d_{yz})^3 2b_2(d_{xy})^2 7e(\pi^*NO){:}^1A_1$. (ii) As is the MSI state, it could be also a relaxed derivative arising from the population of the antibonding $5a_1(d_{z^2})$ orbital but now reached from the $6e(d_{xz},d_{yz})$ level through the transition $...6e(d_{xz},d_{yz})^4 2b_2(d_{xy})^2{:}^1A_1 \rightarrow 6e(d_{xz},d_{yz})^3 2b_2(d_{xy})^2 5a_1(d_{z^2}){:}^1E$. For the latter two possibilities to be compatible with the observed selective generation of the MSII state, it has to be admitted that relaxation beyond the crossing point with the MSI state following the Franck−Condon GS → MSII transition (see Figure 1) proceeds faster than a MSII → MSI excitation transfer for energies $E(\mathrm{MSII}) > E(\mathrm{MSI})$. This transfer would occur through the filling of the hole in the 6e orbital with an electron from the filled $2b_2$ level.

Summary and Concluding Remarks

The existence of two electronically excited metastable states (MSI and MSII) of $[Os(CN)_5NO]^{2-}$ ion as its sodium salt at low temperatures is reported. These states are similar to those found in $[Fe(CN)_5NO]^{2-}$ and RuNO complexes. Therefore, the phenomenon thus far known to originate in the metal(*n*d)−NO group with $n = 3,4$ also takes place in systems with metal(5d)-NO grouping.

Either the MSI or MSII state of $[Os(CN)_5NO]^{2-}$ can be *selectively* populated by irradiation with light in the blue or near-UV region, respectively. Corresponding wavelengths are close to the location of the two lowest-energy electronic absorption maxima.

Several IR-active vibrational modes of $[Os(CN)_5NO]^{2-}$ ion in both MSI and MSII states have been detected and assigned (*cf.* Figure 1 and Table 1). Frequency downshifts affecting the ν(NO), δ(OsNO), and ν(OsN) modes are much larger than corresponding shifts observed for the ν(CN) modes. This further supports the conclusion that MSI and MSII states are reached through an electronic excitation mainly involving the metal-(*n*d)−NO group.

The existence of a thermally driven MSI → MSII excitation transfer process in $Na_2[Os(CN)_5NO]\cdot 2H_2O$ which has not been detected to occur in the nitroprusside and RuNO complexes has now been put into evidence. This occurred because the MSII state, lying energetically *below* the MSI state, has a decay temperature T_{II} *higher* than the corresponding T_I temperature for the MSI state in the osmium compound. This temperature ordering is just the *reverse* of that observed for other compounds, where $T_I > T_{II}$. Furthermore, the thermal MSI → MSII process suggests that there must be an *internal conversion* or *intersystem crossing* between the MSI and MSII electronic energy curves. The latter possibility is favored by the strong spin−orbit coupling acting in the heavy osmium atom.

Acknowledgment. The authors acknowledge Dr. J. A. Olabe (Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina) for providing us with $Na_2[Os(CN)_5NO]\cdot 2H_2O$ and to P. Schaiquevich (Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina) for technical assistance. We also acknowledge Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina for financial support to the QUINOR and PROFIMO programs and PID 3601/92 and LANAIS EFO, CONICET-UNLP for performing the FTIR spectroscopy.

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