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Light-induced metastable states in nitrosyl–ruthenium complexes containing ethylenediamine and oxalate ion ligands

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The metastable state which is produced by irradiation with the green-blue region of light was studied by IR and other spectroscopic techniques for solid states of newly synthesized nitrosyl–ruthenium complexes; *cis*-[Ru(Hox)(en)$_2$NO]Cl$_2$·EtOH, *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$, *cis*-K[Ru(ox)$_2$(en)NO]·3H$_2$O, *cis*-[Ru(Hox)(ox)(en)NO], and *cis*-K[Ru(ox)$_2$(en)NO] [ox = (CO$_2$)$_2$$^{2-}$]. Continued irradiation at 77 K results in development of a photostationary state in the same way as for sodium nitroprusside. The population of the metastable state molecule in the photostationary state of each sample depends on the irradiation wavelength and reaches a maximum at 441.6 nm which is the shortest wavelength in the present study. A broad absorption band with an absorbance maximum at ≈600 nm is observed for the metastable state of a *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ single crystal. The short wavelength tail of the band is considered to be involved in the photostationary equilibrium under blue light radiation. The metastable state molecules decay to the ground state at temperatures considerably higher than the two metastable molecules (MS$_1$ and MS$_2$) of sodium nitroprusside. The decay temperature of *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$, which is defined as the temperature at which the rate constants of the thermal decay becomes 10^{-3} s^{-1}, is 277 K, which is the highest value reached among the metastable states of nitrosyl complexes reported so far. In the Raman spectra of *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$, the Ru-(NO) stretching vibrations are observed at 604 cm^{-1} and 476 cm^{-1} for the ground and metastable state molecules, respectively.

Introduction

The light-induced metastable states, MS$_1$ and MS$_2$, of sodium nitroprusside, Na$_2$[Fe(CN)$_5$NO]·2H$_2$O, which are produced by blue light irradiation and annihilated by red light irradiation, are attracting the interest of many researchers. They are types of excited molecular state and are distinguished from the ground state by their thermal and spectroscopic properties.[1–5] The metastable states are believed to be caused by the charge-transfer from the iron d orbital to the nitrosyl π* orbital, and characterized by the notably downshifted ν(NO) frequencies.[4,6] Similar metastable states have been found in several nitrosyl–ruthenium and nitrosyl–osmium complexes.[7–10]

At 77 K, the metastable states are extremely long lived and do not show any indications of spontaneous decay. When the temperature is raised, thermal decay becomes evident and the temperature at which the thermal decay becomes significant varies between substances. Under the definition of the decay temperature T_d as the temperature at which the decay rate constant is 0.001 s^{-1}, T_d of MS$_1$ of sodium nitroprusside is 182 K and that of *trans*-[RuCl(en)$_2$NO]Cl$_2$, which has been investigated in our previous paper, is 246 K.[10,11]

The light-induced metastable state in nitrosyl complexes is a subject which contains several problems worthy of further study; for example: the capability for information storage,[12] molecular structures,[13] optical properties,[11,14] excited state dynamics,[4,15] and the dynamics of thermal decay.[5,9–11,15,16] In the present paper, we studied the metastable state formation and the properties of the metastable states in newly synthesized nitrosyl–ruthenium complexes which have ethylenediamine and oxalato ion ligands. Ethylenediamine and the oxalato ion are ligands with a poor π bonding ability and they are expected to give a metastable state with a high thermal stability.[10]

Experimental

The starting material [Ru(ox)(en)$_2$][Ru(ox)$_2$(en)] was prepared according to the procedure of Broomhead and Kane-Maguire.[17] A mixture of *cis*-[Ru(Hox)(en)$_2$NO]Cl$_2$·EtOH (abbreviated to **1a**, hereafter), *cis*-K[Ru(ox)$_2$(en)NO]·3H$_2$O (**2**), *cis*-[Ru(Hox)(ox)(en)NO] (**3**), and *cis*-K[Ru(ox)$_2$(en)NO] (**4**) was obtained from [Ru(ox)(en)$_2$][Ru(ox)$_2$(en)] treated with NO gas in an acidic solution, and the complexes were separated and purified by ion exchange column chromatography (SP-Sephadex C-25 and QAE-Sephadex A-25).

Yield for **1a**: 40%. Anal. Found: C, 20.57; H, 4.61; N, 15.08%. Calc. for C$_8$H$_{23}$N$_5$O$_6$Cl$_2$Ru ([Ru(Hox)(en)$_2$NO]Cl$_2$·CH$_3$CH$_2$OH): C, 21.01; H, 5.07; N, 15.43%. IR(Nujol): ν(NO) at 1915 cm^{-1}, ν(CO) at 1615 and 1670 cm^{-1}. ^{13}C NMR (DMSO-d_6–TMS): δ 44.32, 44.55, 47.53, 55.92 (-CH$_2$-), 161.46, 164.28 (COO$^-$).

Yield for **2**: 15%. Anal. Found: C, 15.40; H, 3.12; N, 9.04%. Calc. for C$_6$H$_{14}$N$_3$O$_{12}$KRu (K[Ru(ox)$_2$(en)NO]·3H$_2$O): C, 15.65; H, 3.07; N, 9.13%. IR(Nujol): ν(NO) at 1875 cm^{-1}, ν(CO) at 1615, 1670 and 1720 cm^{-1}. ^{13}C NMR (DMSO-d_6–TMS): δ 48.06, 48.29 (-CH$_2$-), 167.59, 169.79, 171.19, 175.14 (COO$^-$).

Yield for **3**: 22%. Anal. Found: C, 19.85; H, 2.55; N, 10.73%. Calc. for C$_6$H$_9$N$_3$O$_9$Ru ([Ru(Hox)(ox)(en)NO]): C, 19.23; H, 2.42; N, 11.21%. IR(Nujol): ν(NO) at 1890 cm^{-1}, ν(CO) at 1630, 1675, 1700 and 1720 cm^{-1}. ^{13}C NMR (D$_2$O–TSP-d_4): δ 45.23, 46.16 (-CH$_2$-), 162.28, 162.92, 164.91, 165.18 (COO$^-$).

Yield for **4**: 16%. Anal. Found: C, 17.50; H, 2.07; N, 10.27%. Calc. for C$_6$H$_8$N$_3$O$_9$KRu (K[Ru(ox)$_2$(en)NO]): C, 17.74; H, 1.98; N, 10.34%. IR(Nujol): ν(NO) at 1880 cm^{-1}, ν(CO) at 1615, 1640 and 1710 cm^{-1}. ^{13}C NMR (D$_2$O–TSP-d_4): δ 43.47, 45.54 (-CH$_2$-), 165.25, 165.98, 166.31, 171.96 (COO$^-$). The *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**) was obtained from the reaction of

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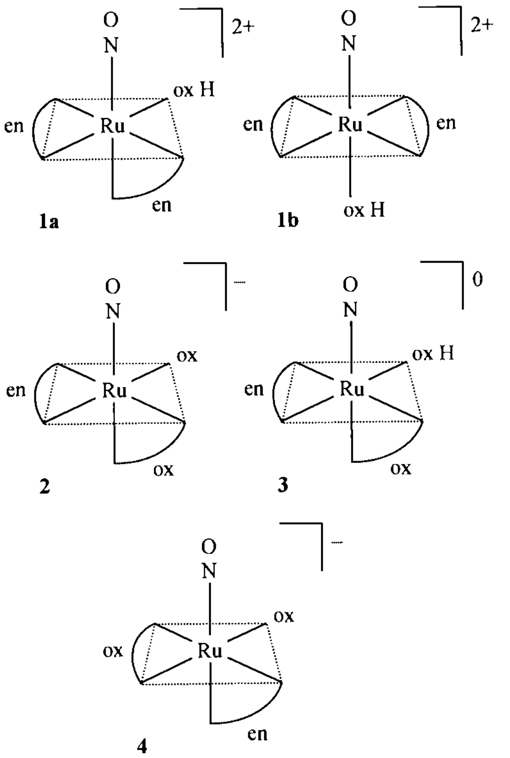

Fig. 1 Molecular structures of *cis*-[Ru(Hox)(en)$_2$NO]Cl$_2$·EtOH (**1a**), *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**), *cis*-K[Ru(ox)$_2$(en)NO]·3H$_2$O (**2**), *cis*-[Ru(Hox)(ox)(en)NO] (**3**), and *cis*-K[Ru(ox)$_2$(en)NO] (**4**).

trans-[Ru(OH)(en)$_2$NO]Cl$_2$ with oxalic acid in aqueous solution. Yield: 50%. Anal. Found: C, 17.70; H, 4.44; N, 16.43%. Calc. for $C_6H_{17}N_5O_5Cl_2Ru$ ([Ru(Hox)(en)$_2$NO]Cl$_2$): C, 17.53; H, 4.17; N, 17.03%. IR(Nujol): ν(NO) at 1876 cm^{-1}, ν(CO) at 1643 cm^{-1}. ^{13}C NMR (D$_2$O–TSP-d_4): δ 48.20 (-CH$_2$-), 169.02, 173.80 (COO$^-$). The simplified structures of these are shown in Fig. 1. Details of the preparation, characterization, and X-ray structural determinations will be published separately.

The formation of the metastable state was monitored by infrared spectroscopy. The ν(NO) band of the metastable state molecule is observed in the region from 1750 to 1800 cm^{-1}, while that of the ground state molecule is observed at *ca.* 1900 cm^{-1}. From the intensity of the metastable state band, the relative population change can be estimated. To evaluate absolute values of the population of the metastable state molecule, the intensity decrease of the ground state ν(NO) band was measured.

The samples were dispersed in a KBr pellet and attached to the cold finger of a liquid N$_2$ cryostat (Oxford Instruments, DN1754) which has CaF$_2$ windows. The temperature was controlled within 0.1 K by a hand-made circuit. Several lines from a He–Cd laser, a He–Ne laser or an Ar ion laser were irradiated.

Visible absorption spectra of a single crystal of **1b** were measured at 77 K for both the ground and metastable states. For the measurements, a columnar crystal was thinned to 175 µm and attached to a holder with an aperture of 300 µm diameter. A Xe-lamp light source and a spectrometer equipped with an ICCD detector (Princeton Instruments, ICCD-576G/1) were used.

Absorption spectra of aqueous solutions of **1a**, **1b**, **2** and **4** were measured in the wavelength range from 350 to 650 nm by using a UV/VIS spectrophotometer (JASCO, V-560).

Raman measurements were carried out on single crystals of **1b** at 77 K. The 441.6 nm light from a He–Cd laser was used for the excitation. The 441.6 nm light plays dual roles: one is a light source for the Raman scattering, and the other is the production of the metastable state. To obtain spectra of the ground state at the same temperature, the 632.8 nm light from a He–Ne laser which annihilates the metastable state molecule was additionally irradiated. Raman spectra were recorded by a triple polychromator (JASCO, TRS-501) equipped with a liquid N$_2$-cooled CCD detector (Princeton Instruments, LN/CCD-1100PB).

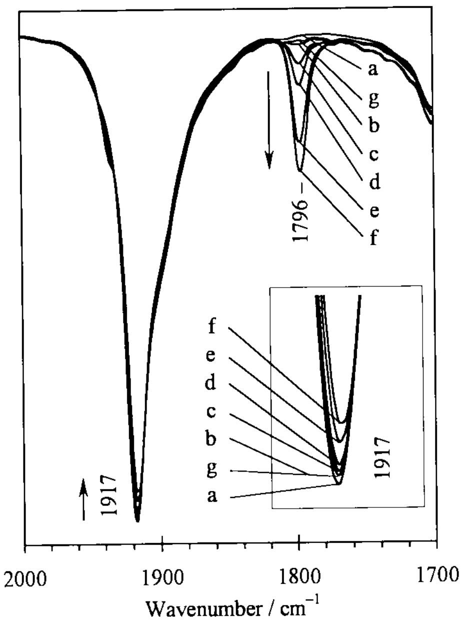

Fig. 2 Infrared spectra of an irradiated sample of *cis*-[Ru(Hox)-(en)$_2$NO]Cl$_2$·EtOH (**1a**) at 77 K: before (a) and after irradiation at 514.5 nm (b), 488.0 nm (c), 476.5 nm (d), 457.9 nm (e), 441.6 nm (f), and 632.8 nm (g).

Results and discussion

Population of the metastable state

Fig. 2 shows infrared spectra of **1a** before (trace a) and after irradiation with various wavelengths (b–g) at 77 K. The alphabetical order in this figure corresponds to the sequence of the measurements; *i.e.*, the spectrum before irradiation (trace a) was measured at first, then the spectra after irradiation with various wavelengths were taken in alphabetical order (from trace b to g). Upon irradiation of blue light, a new band at 1796 cm^{-1} that can be assigned to ν(NO) of the metastable state appears. Correspondingly, the ν(NO) band of the ground state molecule at 1917 cm^{-1} becomes weaker, indicating the depletion of the ground state molecule. In each measurement from b to g, irradiation for an hour under *ca.* 50 mW cm^{-2} power density was applied to ensure that a steady state had been achieved; *i.e.* further irradiation did not affect the spectrum. The intensity of the 1796 cm^{-1} band increases as the irradiated wavelength becomes shorter. This fact is independent of the sequence of irradiation and, therefore, it is clear that the photostationary state is reached by the continued irradiation. Upon 632.8 nm irradiation, the spectrum returns to nearly the original shape, which shows the ground state molecule becomes dominant in the photostationary equilibrium under the 632.8 nm irradiation conditions.

Spectral changes caused by the 441.6 nm irradiation in **1b**, **2**, **3** and **4** are shown in Fig. 3. Only one ν(NO) band of the metastable state is observed in the 1760–1800 cm^{-1} region in each of these complexes and **1a** (Fig. 2). In the case of sodium nitroprusside, the ν(NO) bands of MS$_1$ and MS$_2$ are observed at 1836 and 1665 cm^{-1}, respectively.[11,18] We were unable to find bands attributable to the metastable state in the 1500–1700 cm^{-1} region. It is supposed that only one type of metastable state is formed in the present complexes in the same way as [RuX(en)$_2$NO]$^{n+}$ (n = 2 for X = Cl, Br; n = 3 for X = H$_2$O) salts.[10]

The percentage population of the metastable state P as a function of the irradiated wavelength λ, evaluated from the decrease in intensity of the ground state ν(NO) band, is shown in Fig. 4 compared with UV-VIS absorption spectra of aqueous solutions of complexes **1**, **2** and **4**. Because of its low solubility, the absorption spectrum of **3** could not be obtained. In each compound, the population increases as the wavelength of irradiated light becomes shorter, and reaches a maximum at 441.6 nm, which is the shortest wavelength utilized in the present study.

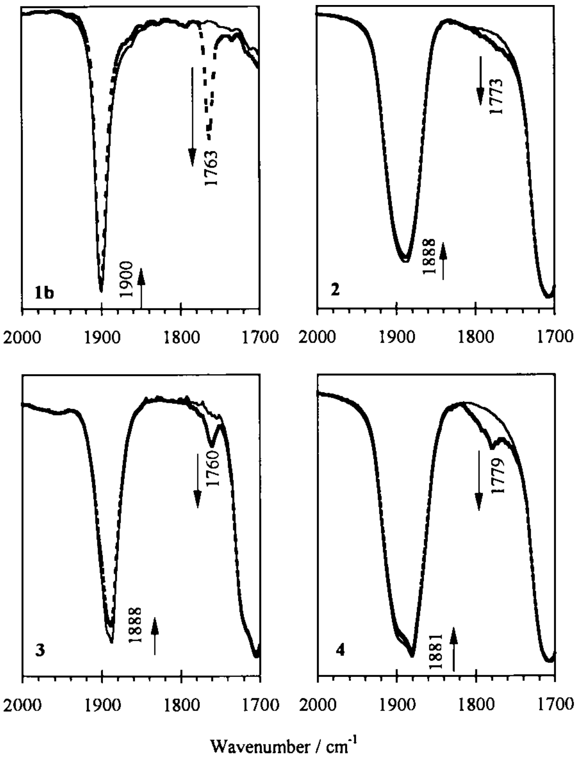

Fig. 3 Infrared spectra of *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**), *cis*-K[Ru(ox)$_2$(en)NO]·3H$_2$O (**2**), *cis*-[Ru(Hox)(ox)(en)NO] (**3**), and *cis*-K[Ru(ox)$_2$(en)NO] (**4**) at 77 K before (solid line) and after (dotted line) 441.6 nm irradiation.

The metastable state is thought to be populated as a result of the structural relaxation of the ruthenium-to-nitrosyl charge-transfer state that is produced by the photo-excitation.[4,7] According to the previous studies on visible absorption spectra of nitrosyl–ruthenium complexes, bands at around 450–500 nm with molar extinction coefficients of *ca.* 50 dm^3 mol^{-1} cm^{-1}, which is the lowest region in excitation energy, are assigned to the MLCT bands.[19–21] Therefore, absorption bands in the visible region of **1a**, **1b**, **2**, and **4** shown in Fig. 4 are assigned to the MLCT bands. It is clear that irradiation in the MLCT band region produces the metastable state, which is consistent with the charge-transfer scheme for metastable state formation.[4,7]

In spite of the correlation between the $P(\lambda)$ curve and the MLCT band, the wavelength that leads to the highest population, 441.6 nm, is shorter than the peaks of the MLCT bands in **1a**, **2** and **4**. The reason for this is attributable to the kinetics in the photostationary state. The transition rate $C_{\mathrm{fwd}}(\lambda)$ from the ground state to the metastable state under irradiation with wavelength λ is expressed by:

$$C_{\mathrm{fwd}}(\lambda) = \alpha_{\mathrm{fwd}}\, \varepsilon_{\mathrm{GS}}(\lambda)\, N_{\mathrm{GS}}\, I(\lambda),$$

and the rate of the backward transition is expressed by:

$$C_{\mathrm{bwd}}(\lambda) = \alpha_{\mathrm{bwd}}\, \varepsilon_{\mathrm{MS}}(\lambda)\, N_{\mathrm{MS}}\, I(\lambda),$$

where $I(\lambda)$ is the intensity of the radiation, $\varepsilon_{\mathrm{GS}}(\lambda)$ and $\varepsilon_{\mathrm{MS}}(\lambda)$ are the molar extinction coefficients of the ground state and the metastable state molecules at wavelength λ, N_{GS} and N_{MS} are the numbers of the ground state and the metastable state molecules, a_{fwd} and a_{bwd} are constants which are independent of λ. Because the transition rates in both directions are equal in the photostationary state, that is $C_{\mathrm{fwd}}(\lambda) = C_{\mathrm{bwd}}(\lambda)$,

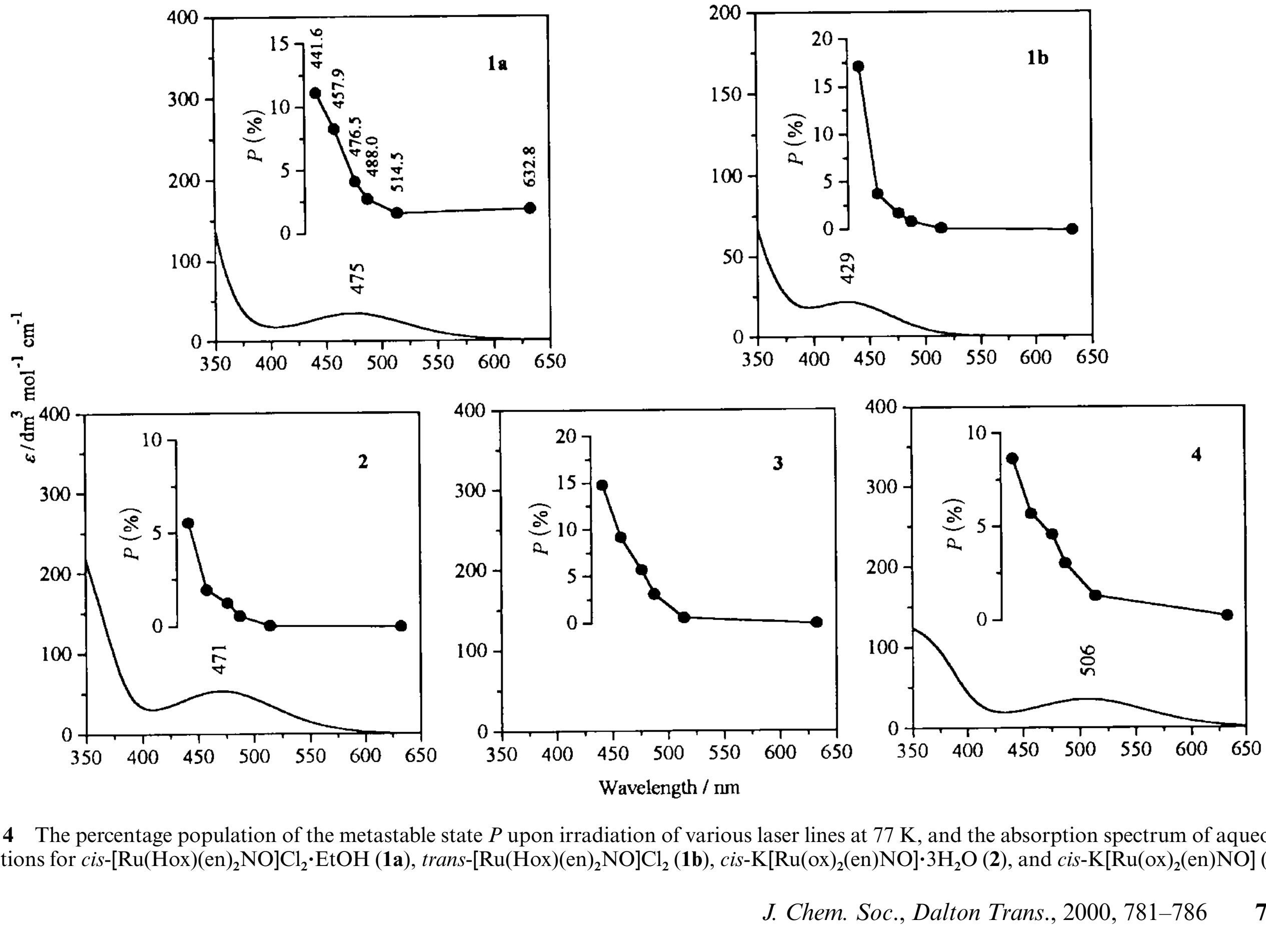

Fig. 4 The percentage population of the metastable state P upon irradiation of various laser lines at 77 K, and the absorption spectrum of aqueous solutions for *cis*-[Ru(Hox)(en)$_2$NO]Cl$_2$·EtOH (**1a**), *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**), *cis*-K[Ru(ox)$_2$(en)NO]·3H$_2$O (**2**), and *cis*-K[Ru(ox)$_2$(en)NO] (**4**).

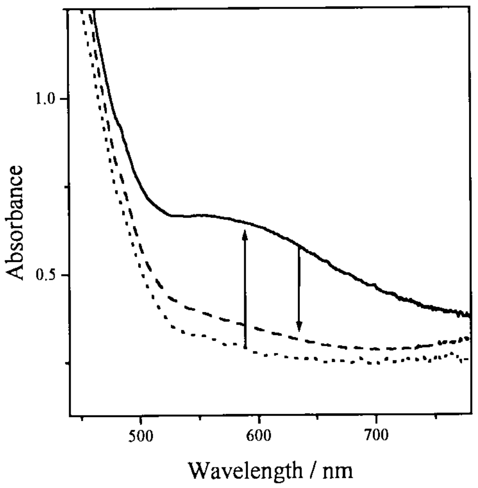

Fig. 5 Visible absorption spectra of *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**) at 77 K: before irradiation (dotted line), after 441.6 nm irradiation (solid line), and after 632.8 nm irradiation (dashed line).

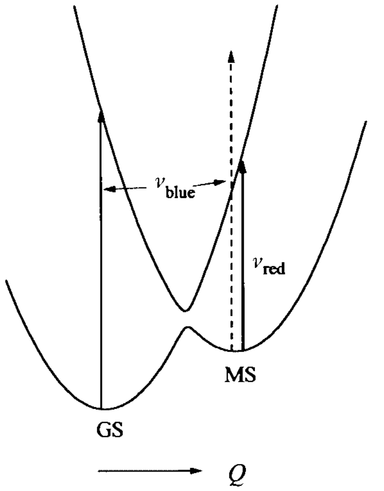

Fig. 6 Proposed energy surfaces for the ground (GS) and the metastable states (MS).

$$\frac{N_{GS}}{N_{MS}} = \frac{a_{bwd}}{a_{fwd}} \cdot \frac{\varepsilon_{MS}(\lambda)}{\varepsilon_{GS}(\lambda)} \equiv \eta(\lambda)$$

The population of the metastable state $P(\lambda)$ is given by

$$P(\lambda) = \frac{N_{MS}}{N_{GS} + N_{MS}} = \frac{1}{1 + \eta(\lambda)}$$

Thus, the increase of $P(\lambda)$ in the 450 nm region, the shorter-wavelength wing of the MLCT band, indicates the rapid decrease of $\varepsilon_{MS}(\lambda)/\varepsilon_{GS}(\lambda)$ in this region.

In order to obtain information on $\varepsilon_{MS}(\lambda)$, visible absorption spectra of single crystals of **1b** were measured. As shown in Fig. 5, a broad band the center of which is at about 600 nm appears upon irradiation at 441.6 nm and disappears by the irradiation at 632.8 nm and, therefore, the band is assigned to the metastable state and dominates $\varepsilon_{MS}(\lambda)$. The $\varepsilon_{MS}(\lambda)/\varepsilon_{GS}(\lambda)$ value is high for λ in the region 500–800 nm and gives $P(\lambda) \approx 0$ under the red light irradiation, but it decreases for $\lambda < 500$ nm and results in the increase of $P(\lambda)$(see Fig. 4, **1b**). A similar band has been observed in the metastable state of sodium nitroprusside, where the absorption peak is located at 680 nm.[22,23]

Next, a brief discussion on the photostationary equilibrium is given on the basis of the charge-transfer model. Based on the assumption that the metastable state is formed by the MLCT excitation followed by structural relaxation, a simplified scheme is drawn in Fig. 6. GS and MS represent the ground state and the metastable state, and the coordinate Q expresses some structure change. According to the X-ray crystallographic studies on sodium nitroprusside (MS$_1$) and $K_2[Ru(NO_2)_4(OH)NO]$, the metastable state molecule is a linkage isomer in which the NO group is bound to the metal atom through the oxygen atom.[13,24] Our recent Raman spectroscopic study of ^{15}NO-substituted sodium nitroprusside supports the linkage isomer model.[25] Therefore, the coordinate Q will represent a rotation of the nitrosyl group.† Thus, blue light (ν_{blue}) causes the MLCT excitation of the GS and the structural relaxation to the MS, with flipping of the NO group. Because the MS absorbs ν_{blue} to some extent and the backward transition to the GS takes place, the population of the MS is limited in spite of the extremely long lifetime of the MS at 77 K. The efficient excitation of the MS (LMCT excitation) is caused by red light (ν_{red}) and, therefore, the MS is depleted by irradiation of red light.

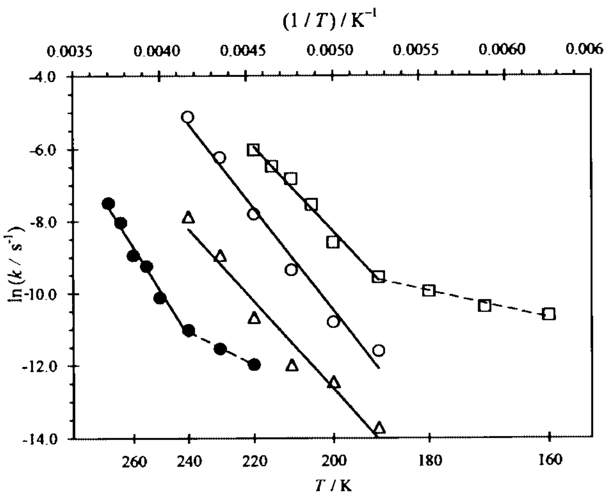

Fig. 7 Arrhenius plots for the rate constants of thermal decay of MS: *cis*-[Ru(Hox)(en)$_2$NO]Cl$_2$·EtOH (**1a**)(△), *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**)(●), *cis*-K[Ru(ox)$_2$(en)NO]·3H$_2$O (**2**)(○), and *cis*-K[Ru(ox)$_2$(en)-NO] (**4**)(□). Activation energies and frequency factors, E_a and Z, are $E_a = 4300$ cm^{-1} and $Z = 7.6 \times 10^8$ s^{-1} for **1a**; $E_a = 5400$ cm^{-1} and $Z = 1.3 \times 10^9$ s^{-1} for the high-temperature region of **1b**; $E_a = 1800$ cm^{-1} and $Z = 5.8 \times 10^{-1}$ s^{-1} for the low-temperature region of **1b**; $E_a = 3700$ cm^{-1} and $Z = 1.1 \times 10^6$ s^{-1} for **3**; $E_a = 3600$ cm^{-1} and $Z = 4.1 \times 10^7$ s^{-1} for the high-temperature region of **4**; and $E_a = 760$ cm^{-1} and $Z = 2.1 \times 10^{-2}$ s^{-1} for the low-temperature region of **4**.

Thermal decay

Thermal decay of the metastable state becomes significant above *ca.* 180 K. On the basis of an assumption that the integrated absorbance of the $\nu(NO)_{MS}$ band is proportional to the density of the metastable state molecule, the time-dependent population changes of the metastable state molecule were measured for **1a**, **1b**, **3** and **4**.‡ Linear relationships were observed between ln $A(t)$ and t, indicating the first-order kinetics of the thermal decay, ($A(t)$ denotes the integrated absorbance at a time t). Rate constants obtained at various temperatures are summarized in Arrhenius plots shown in Fig. 7. Possibly, the deviation from the Arrhenius law in **1b** and **4** may be ascribed to the structural phase transition. The activation energy E_a and the frequency factor Z in the Arrhenius law were calculated from straight lines fitted to the ln k *vs.* ($1/T$) plots. In **1b** and **4**, two sets of E_a and Z were assumed for the higher and lower temperature regions.

The Arrhenius formula can be utilized to obtain rate

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† In the case of sodium nitroprusside, another metastable state MS$_2$ is formed in the intermediate position between GS and MS (here, MS is tentatively assigned to the species corresponding to MS$_1$ in sodium nitroptrusside).[13]

‡ The measurements for **2** were not carried out because of the low intensity of its $\nu(NO)_{MS}$ bond.

Table 1 N–O stretching frequencies, decay temperatures, and wavelengths of MLCT bands[a]

	ν(NO)/cm^{-1}			
Compounds	GS	MS	T_d/K	MLCT[b] λ/nm
trans-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**)	1900	1763	277	429
trans-[Ru(H$_2$O)(en)$_2$NO]Cl$_3$[10]	1904	1786	267	426
cis-[Ru(Hox)(ox)(en)NO] (**3**)	1888	1760	255	
trans-[RuCl(en)$_2$NO]Cl$_2$[10]	1878	1744	246	441
Na$_2$[Ru(CN)$_5$NO]·2H$_2$O(MS$_2$)[16]	1932	1648	240[c]	436
trans-[RuBr(en)$_2$NO]Br$_2$[10]	1877	1738	229	451
cis-[Ru(Hox)(en)$_2$NO]Cl$_2$·EtOH (**1a**)	1917	1796	226	475
Na$_2$[Os(CN)$_5$NO]·2H$_2$O (MS$_2$)[9]	1897	1546	220[c]	427
cis-K[Ru(ox)$_2$(en)NO] (**4**)	1881	1779	211	506
cis-[RuBr(en)$_2$NO]Br$_2$[10]	1881, 1902	1759, 1777	211	490
cis-[RuCl(en)$_2$NO]Cl$_2$[10]	1879, 1901	1759, 1775	206	485
[RuCl$_3$(en)NO] (mixture of *fac*- and *mer*-)[10]	1865	1728, 1744	205	
K$_2$[RuCl$_5$NO][7]	1893	1768	194[d]	510
K$_2$[Ru(NO$_2$)$_4$(OH)NO][8]	1886	1772	187[d]	
Na$_2$[Fe(CN)$_5$NO]·2H$_2$O(MS$_1$)[11]	1949	1838	182	498[21]

[a] The species that have higher decay temperatures are listed for the compounds in which MS$_1$ and MS$_2$ are produced. [b] Absorption maxima in aqueous solutions. [c] Estimated by inspection of the IR band intensity upon heating samples irradiated at 77 K. Not that this definition of T_d is different from that for the other compounds. [d] Calculated from data of activation energies and frequency factors obtained by DSC measurements.

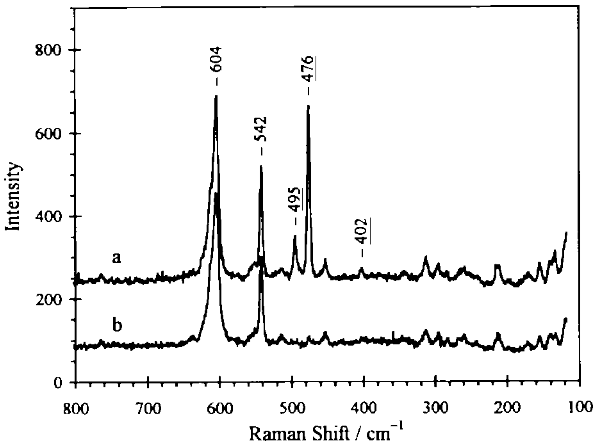

Fig. 8 Raman spectra of *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**) irradiated at 441.6 nm at 77 K (trace a) and at 441.6 and 632.8 nm simultaneously (trace b). Underlined frequencies are those of the metastable state (see text).

constants at arbitrary temperatures on the basis of E_a and Z values determined experimentally. A "decay temperature" is a convenient measure to compare the thermal stability of the metastable states among substances. We defined a decay temperature T_d as the temperature at which the rate constant becomes 0.001 s^{-1}.[10,11] Roughly speaking, T_d is the temperature above which the thermal decay is significant and the temperature at which the exothermal peak is observed in the DSC measurement.[5] The decay temperatures calculated from E_a and Z values, the ν(NO) frequencies, and the peak wavelengths of the MLCT bands are summarized in Table 1 together with those of the other nitrosyl complexes in which the light-induced metastable states have been studied. The compounds are arranged in order of decreasing decay temperature. On the whole, nitrosyl–ruthenium complexes having ethylenediamine and/or oxalate ion ligands exhibit high T_d values. The decay temperature of **1b**, 277 K, is the highest among those reported so far. Thus, the supposition that the coordination of ligands possessing only a σ-bonding ability might lead to the high decay temperature, which was suggested in our previous paper, seems to be valid in the present case.[10] It should be noted that ligands other than the nitrosyl group in *trans*-[Ru(Hox)(en)$_2$NO]Cl$_2$ (**1b**), *trans*-[Ru(H$_2$O)(en)$_2$NO]Cl$_3$ and *cis*-[Ru(Hox)(ox)(en)NO] (**3**) which show particularly high decay temperatures have poor π-bonding abilities. Steric effects may also influence the decay temperature. Taking account of the rotation of the nitrosyl group which is involved in metastable state formation, it is supposed that the steric hindrance around *cis*-ligands would affect the thermal decay. Studies along this line are necessary to clarify what properties of the substance the decay temperature depends on.

Raman spectra of the metastable state

Fig. 8 shows Raman spectra of the ground and the metastable states of a single crystal of **1b**. These spectra were taken with the 441.6 nm line from a He–Cd laser. The laser power was maintained at less than 1 mW to prevent damage due to local heating. Bands at 604 cm^{-1} and 542 cm^{-1} are due to the ground state molecule and were assigned to ν(Ru–NO) and ν(Ru–N)(ethylenediamine), respectively.[26] Since bands at 495, 476 and 402 cm^{-1} disappear under the simultaneous irradiation of 632.8 nm light, these three bands are assigned to the vibrational modes of the metastable state molecule. In the case of sodium nitroprusside, a weak δ(Fe–ON) band is observed at 582 cm^{-1} and a strong ν(Fe–ON) band is observed at 565 cm^{-1} in the Raman spectra of MS$_1$, whereas δ(Fe–NO) and ν(Fe–NO) Raman bands of the ground state are observed at 669 cm^{-1} and 662 cm^{-1}, respectively.[25] The 495 cm^{-1} and 476 cm^{-1} bands of **1b** are similar to the 582 cm^{-1} and 565 cm^{-1} bands of MS$_1$ of sodium nitroprusside in relative intensities and band positions relative to the metal–NO stretching band of the ground state. Therefore, they could be assigned to δ(Ru–ON) and ν(Ru–ON) modes of the metastable state molecule, respectively. It should be noted that the 476 cm^{-1} band is close in frequency to the 473 cm^{-1} band of the metastable state in *trans*-[RuCl(en)$_2$NO]Cl$_2$.[10]

We have assumed the Ru–O–N linkage for the metastable state of **1b**, the same structure as MS$_1$ of sodium nitroprusside.[13,24,25] The similarities of the Raman frequencies of the metal–nitrosyl moiety in both the compounds support this assumption. For confirmation of the Ru–O–N linkage, we plan vibrational spectroscopic studies using ^{15}NO and N^{18}O species in the metastable states, because it has been shown that the isomer shifts of δ(Ru–NO) are quite different between the Ru–N–O and Ru–O–N linkages.[25]

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