Inorg. Chem. **2004**, *43*, 3500–3506

Inorganic Chemistry
Article

# Light-Induced Metastable States in Oxalatenitrosylruthenium(II) and Terpyridinenitrosylruthenium(II) Complexes

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Received August 29, 2003

Two extremely long lived metastable states (SI and SII) can be accessed by irradiation with light in the blue-green spectral range at temperatures below 200 K in $Cs_2[Ru(ox)(NO)Cl_3]$, $[Ni(cyclam)][Ru(ox)(NO)Cl_3]\cdot 3H_2O$, and $[Ru(terpy)(NO)(OH)Cl][PF_6]$. The crystal structures of the ground states of the oxalate-containing compounds are presented, and the influence of the atomic distances of the cations/anions is discussed with respect to the decay temperatures. The radiationless thermal decay of the metastable states is detected by differential scanning calorimetry (DSC) for the three compounds. Both metastable states decay exponentially in time under isothermal conditions. The excited states are energetically separated from the ground state by potential barriers given by the activation energy of the Arrhenius law. In $[Ni(cyclam)][Ru(ox)(NO)Cl_3]\cdot 3H_2O$ the enthalpy maximum of the thermal decay of SII appears at 182 K, which is a relatively high decay temperature for SII. The reason for this strong temperature shift compared to those of the other compounds could be due to the polarization effect of $Ni^{2+}$ on the electron density at the Ru site via the Cl atom.

## Introduction

Since the discovery of extremely long lived light-induced metastable states in sodium nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ [NaNP], by Hauser et al.,[1] many complexes containing ruthenium(II),[2-4] osmium(II),[5] and nickel(II)[6] have been found with similar photophysical behavior. Characteristic for all compounds is the nitrosyl ligand (NO), so the existence of the metastable states does not depend on the presence of the 3d, 4d, or 5d electrons of the central metal atoms, but mainly on the optical and electronic properties of the NO ligand. The empty antibonding $\pi^*$(NO) orbital lies energetically between the empty and filled d states of the metal atom. Two metastable states (SI and SII) can be accessed by irradiation with light of the corresponding energy difference between the HOMO d orbital ($2b_2$, $d_{xy}$) and the LUMO $\pi^*$(NO) orbital (7e): $\Delta E = E(d_{xy}) - E(\pi^*(NO))$.[7] The metastablestates are separated by potential barriers from the

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10.1021/ic0350178 CCC: $27.50

ground state (GS) and from each other. The barrier height is responsible for the lifetimes of these states. A lifetime of $\tau > 10^8$ s can be realized at room temperature, if the activation energy $E_A$ exceeds 1.0 eV. These excited states can be detected with differential scanning calorimetry (DSC),[8] infrared/Raman spectroscopy,[9] Mössbauer spectroscopy,[10] extended X-ray absorption fine structure (EXAFS) spectroscopy,[6] and neutron[11] and X-ray diffraction.[12] The transfer of both states into the ground state is possible by irradiation with light corresponding to the energy difference between the HOMO of SI or SII and the LUMO ($\pi^*$(NO)), $\Delta E = E(\mathrm{SI,SII}) - E(\pi^*(\mathrm{NO}))$, or by heating the system. The radiationless thermal decay is a first-order reaction and can be described by the Arrhenius law. Otherwise, by irradiation with light in the spectral range of the absorption band of SI, the metal nitrosyl compounds can be partially transferred from SI into SII. It is also possible to go from SII to SI.[7a] This points to the reversibility of the population cycles for these metal nitrosyl compounds and suggests that, on the basis of strong differences in the refractive indices of about $\Delta n \approx 10^{-2}$ among SI, SII, and GS, these materials could be used for information storage with high capacity by employing volume holographic methods.[13] For this application it is necessary to get substances in which the new states are stable above room temperature with sufficient population of at least 2%.

Different strategies can be used for obtaining such materials. The first approach involves the modification of the well-known compound $Na_2[Fe(CN)_5NO]{\cdot}2H_2O$ by variation of the cation. It was found in an earlier study that exchange of the cation (by alkali or p-block metals) leads to an increase of the decay temperature of SI from 186 to 223 K, while the population of the metastable states decreases.[14] The maximum population for SI of 50% is reached in $Na_2[Fe(CN)_5NO]{\cdot}2H_2O$ and $Li_2[Fe(CN)_5NO]{\cdot}4H_2O$. A second approach is based on changing the metal center (i.e., Ru or Os instead of Fe) and its environment (Cl, $NH_3$, etc. as ligands instead of CN). In recent years, Morioka et al.[4] and Coppens et al.[15] presented new ruthenium nitrosyl compounds, in which SI is stable at about 270 K, but with a very low population (~2%).

We have prepared and investigated new ruthenium nitrosyl compounds $Cs_2[Ru(ox)(NO)Cl_3]$, $[Ni(cyclam)][Ru(ox)(NO)Cl_3]{\cdot}3H_2O$, and $[Ru(terpy)(NO)(OH)Cl][PF_6]$,[16] to analyze the influence of the *cis*- and *trans*-ligands and the metal–organic Ni complex on the decay temperature and the degree of population. We present the crystallographic structures for the compounds containing the oxalate ligand and, for the three compounds, the dynamics of the thermal decay of SI and SII, measured by differential scanning calorimetry. The photophysical results will be discussed with respect to the structural details.

## Experimental Section

**A. Synthesis**. All chemicals were of reagent grade and were used as commercially obtained. Terpy (2,2′6′,2″-terpyridine) was purchased from Aldrich Chemicals, $[Ni(cyclam)]Cl_2{\cdot}2H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) was prepared as already described,[17] and $K_2[Ru(NO)Cl_5]$ was prepared according to the method described in the literature.[18] Generally, electrochemistry[19] or a chemical oxidizing agent[20] is employed to prepare ruthenium nitrosyl compounds, but we preferred addition reactions,[21] which allow the control of the obtained products. All the described compounds are stable in air.

**$Cs_2[Ru(ox)(NO)Cl_3]$ (1)**. A 10 mL aqueous solution of $H_2C_2O_4$ (6 mmol) was added to a 10 mL solution containing 3 mmol of $K_2[Ru(NO)Cl_5]$. We adjusted the pH of this suspension to 3, with a concentrated KOH solution. Then the solution was stirred for 3 h under reflux. During this operation, we adjusted the pH three times to 3. At the end, no change of the pH was observed. After this clear red solution was cooled, it was added to 5 mL of a saturated solution of aqueous CsCl, and then the resulting solution was allowed to stand at room temperature to evaporate. After several days dark red crystals of the formula $Cs_2[Ru(C_2O_4)(NO)Cl_3]$, suitable for X-ray diffraction, appeared. They were collected by filtration, washed with cold water, and dried under vacuum. Anal. Calcd for $C_2NO_5Cl_3Cs_2Ru$ : C, 40.59; Cl, 18.01; N, 2.36. Found: C, 41.30; Cl, 18.55; N, 2.30.

**$[Ni(cyclam)][Ru(ox)(NO)Cl_3]{\cdot}3H_2O$ (2)**. **2** was obtained using the same procedure as for **1**. After the solution was cooled, a saturated aqueous solution of $[Ni(cyclam)]Cl_2{\cdot}2H_2O$ was added. After several days, red-brown crystals of the formula $[Ni(N_4C_{10}H_{24})][Ru(C_2O_4)(NO)Cl_3]{\cdot}3H_2O$, suitable for X-ray diffraction, appeared. Anal. Calcd for $C_{12}H_{30}Cl_3N_5NiO_8Ru$ : C, 22.55; H, 4.70; Cl, 16.68; N, 10.96. Found: C, 23.40; H, 4.30; Cl, 16.50; N, 11.15.

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**Table 1.** Crystallographic Data for Compounds **1**−**3** (New Measurement)

| | **1** | **2** | **3** |
|---|---|---|---|
| empirical formula | $C_2Cl_3Cs_2NO_5Ru$ | $C_{12}H_{30}Cl_3N_5Ni$-$O_8Ru$ | $C_{15}H_{12}ClN_4O_2$-$PF_6Ru$ |
| fw | 591.27 | 638.54 | 561.78 |
| cryst syst | triclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) |
| $a$ (Å) | 6.8497(7) | 9.111(2) | 9.688(2) |
| $b$ (Å) | 7.2981(8) | 10.005(2) | 13.936(3) |
| $c$ (Å) | 12.7495(14) | 15.443(3) | 14.544(3) |
| α (deg) | 87.540(13) | 89.69(3) | |
| $\beta$ (deg) | 80.048(13) | 73.22(3) | 105.86(3) |
| $\gamma$ (deg) | 67.762(12) | 64.27(3) | |
| $V$ (Å$^3$) | 580.89(11) | 1202.4(4) | 1888.9(7) |
| Z | 2 | 2 | 4 |
| temp (K) | 223(2) | 295(2) | 296(2) |
| calcd density (g cm$^3$) | 3.380 | 1.764 | 1.97 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 8.208 | 1.790 | 1.135 |
| final R1,[a] wR2[b] indices ($I > 2\sigma(I)$, obsd) | 0.0258, 0.0543 | 0.0404, 0.0891 | 0.0448, 0.1156 |
| R1, wR2 indices (all data) | 0.0273, 0.0549 | 0.0903, 0.1057 | 0.0687, 0.1240 |

[a] R1 factor definition: $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] SHELXL-97 wR2 factor definition: $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. Weighting scheme: $w = 1/[\sigma^2(F_o)^2 + (np)^2 + p]$, $p = (\max(F_o^2) + 2F_c^2)/3$.

**[Ru(terpy)(NO)(OH)Cl]PF$_6$ (3)**. A new preparation of this compound is presented here. A 10 mL alcoholic solution of terpyridine (3 mmol in methanol) was added to a 10 mL aqueous solution containing 3 mmol of $K_2[Ru(NO)Cl_5]$. We adjusted the pH of this suspension to 6, with a concentrated KOH solution. Then the solution was stirred for 3 h under reflux. During this operation, we adjusted the pH three times to 6. At the end, no change of the pH was observed. After this clear red solution was cooled, it was added to 5 mL of a saturated methanolic solution of $KPF_6$, and then the resulting solution was allowed to stand at room temperature to evaporate. After a couple of days, red crystals of the formula $[Ru(C_{15}N_3H_{11})(NO)(OH)Cl]PF_6$ appeared. They were collected by filtration, washed with cold water, and dried under vacuum. Anal. Calcd for $C_{15}H_{12}ClF_6N_4O_2PRu$ : C, 32.04; H, 2.14; Cl, 6.32; N, 9.97. Found: C, 33.5; H, 2.2; Cl, 6.5; N, 10.2. We performed X-ray diffraction on single crystals, and obtained a comparable resolution of the structure as proposed in the literature.[16]

**B. Determination of the Structure**. Selected crystallographic data and structure determination parameters for compounds **1** and **2** are given in Table 1, together with those of **3**, for comparison. For all the compounds, the data were collected in the GS of the molecules. Intensity data were collected at 223 K on a Stoe image plate diffraction system equipped with a $\phi$ circle, using Mo Kα graphite-monochromated radiation ($\lambda = 0.71073$ Å) for **1** and at room temperature using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for **2** and **3**.

A dark red square-pyramidal crystal of **1** with approximate dimensions 0.40 × 0.30 × 0.10 mm$^3$ was chosen for the X-ray structure determination. A triclinic unit cell was determined from 25 indexed reflections in the range $3.0° < 2\theta < 52.0°$, with an image plate distance of 70 mm, a $\phi$ range of 0−185°, and an increment of 1°. The number of intensity data measured was 3955 ($hkl$ range ±8, ±8, −14 to +15). The space group was $P\bar{1}$, using the Patterson interpretation routine of SHELXS-97.[22] Refinement was carried out by full-matrix least-squares techniques, with SHELXL-97[23] (see Table 1). An empirical absorption correction was applied using the DIFABS routine in the program PLATON,[24] transmission factors min/max = 0.0.403/0.797. The largest difference peak and hole were 0.848 and −0.662 e Å$^{-3}$.

A brown red square-pyramidal crystal of **2** with approximate dimensions of 0.36 × 0.20 × 0.06 mm$^3$ was chosen for the X-ray structure determination. A triclinic unit cell was determined from 25 indexed reflections in the range $14.12° < 2\theta < 25.9°$. The number of intensity data measured was 7240 ($hkl$ range ±12, ±14, 0−21). Intensities were corrected for Lorentz, polarization, and absorption effects with the MolEN program package.[25] The space group was $P\bar{1}$, using the Patterson interpretation routine of SHELXS-97. Refinement was carried out by full-matrix least-squares techniques, with SHELXL-97 (see Table 1). Due to the relatively weak diffracting crystal, hydrogen atomic positions were calculated at distances of 0.93 Å from carbon atoms and were fixed by using a rigid model in the refinement. The largest difference peak and hole were 1.009 and −0.836 e Å$^{-3}$.

The fractional coordinates as well as the atomic coordinates for all atoms and bond distances and angles for compounds **1**−**3** are given in the Supporting Information.

**C. Differential Scanning Calorimetry**. The samples (single crystals) for DSC measurements were ground to thin plates with a thickness of about 0.3 mm and were irradiated with unpolarized light. The irradiation was performed with a metal vapor lamp (HMI 575), filtered to the spectral range of 410−500 nm using an intensity of 200 mW/cm$^2$. The total exposure was $Q = 2800$ (W s)/cm$^2$. The temperature was kept constant at $T = 100$ K. The radiationless decay of SI and SII is detected by a modified DSC apparatus (Mettler DSC 30, TA 2000), which is equipped with two quartz windows inside and outside the furnace for the irradiation of the samples with light. The irradiated sample is heated with constant velocity $q$ (K/min) during detection of the exothermal heat flow $\dot{H}$ (mW), $\dot{H} = dH/dt$, which is the time derivative of the enthalpy $H$. $\dot{H} = q(dH/dT)$ is the temperature derivation.

In all spectra we have subtracted the heat flow of the unirradiated sample, measured before and after the irradiation, to get only the exothermal heat flow of SI and SII. From the peak integration we get the enthalpy $H$, which is proportional to the population of the metastable states:

$$H = \int_{T_0}^{T_E} \dot{H}\, dt' = 1/q \int_{T_0}^{T_E} \dot{H}\, dT'$$

$T_0$ and $T_E$ indicate the boundaries for the integration. The isothermal decay can be fitted by an exponential function, so we can evaluate all spectra using the Arrhenius law.[7a] Due to the monoexponential decay, the reaction order is $n = 1$ (first-order reaction) and we can fit the spectra using a modification of our earlier fit function:[8]

$$\dot{H}(T) = HZ \exp\left[-\frac{E_A}{k_B T} - \frac{Z}{q}\int_{T_0}^{T} \exp\left(-\frac{E_A}{k_B T}\right) dT'\right]$$

where the activation energy $E_A$ and the frequency factor $Z$ are the adjustable parameters. $H$ is the integrated enthalpy of the whole peak, and $k_B$ is the Boltzmann constant. In all spectra the dots correspond to the experimental data and the solid lines to the fits.

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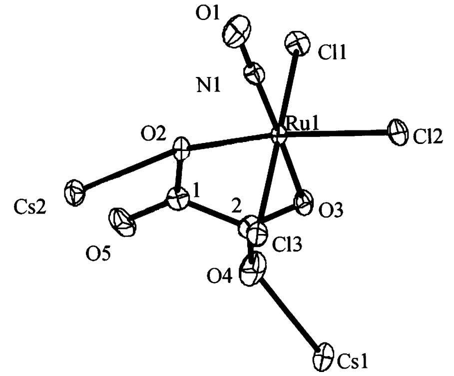

**Figure 1.** Asymmetric unit with atomic numbering scheme of **1**.

In this case the decay temperature is defined as the peak maximum in the heat flow vs temperature at a certain heating rate. The existence of the maximum is a result of the dynamic measurement with a heating rate $q \neq 0$.

## Results

**A. Description of the Structures**. Compounds **1** and **2** have the same anion in the unit cell, $[Ru(ox)(NO)Cl_3]^{2-}$, with analogous distances and geometry. Thus, we only present structural details of compound **1**, and compound **2** will only be briefly described in a further paragraph. The nature of the countercation induces changes in the orientation of the molecules in the unit cell, and consequently in the photophysical properties of the compounds.

**$Cs_2[Ru(ox)(NO)Cl_3]$ (1)**. The structure of **1** consists of $[Ru(NO)(C_2O_4)Cl_3]^{2-}$ anions, which are well separated from the $Cs^+$ cations. The asymmetric unit, along with the atomic numbering schemes, is shown in Figure 1. The $[Ru(ox)(NO)Cl_3]^{2-}$ units are also arranged antiparallel along the [111] direction. All the distances and angles as well as a view of the packing are given in the Supporting Information.

The ruthenium centers are in a distorted octahedral environment with one oxygen, from the oxalate ligand, and the nitrogen of the nitrosyl ligand in axial positions, the equatorial plane being filled with three chlorine atoms and the other oxygen atom from the oxalate. The Ru−O distances are 2.021(3) and 2.044(3) Å for Ru−O(3) and Ru−O(2), respectively, which is in accordance with the distances found in the corresponding trisoxalato complexes.[26] The bridging oxalate ligands are virtually planar and have bond distances and angles within normal limits. The Ru−N(1) distance is equal to 1.746(4) Å, in accordance with the Ru−N distance found in other ruthenium nitrosyl compounds.[27] The Ru−Cl average distance is equal to 2.3615(3) Å, which is typical, as well as N(1)−O(1) at 1.131(5) Å. The linearity of the Ru−N−O linkages is strongly indicative of the nitrosyl ligand bonding as $NO^+$, and thus, the oxidation state of the ruthenium centers is +2.

The environment of both cesium cations consists of 10 atoms: chlorine atoms and oxygen atoms from the oxalate ligand. These Cs−O and Cs−Cl average distances are particularly long (about 3.3 and 3.6 Å), and cannot reveal a strong interaction between the cesium and the oxygen or chlorine atom. This is different from what was observed in other oxalate compounds, which contain alkali-metal cations such as $Na^+$, for example, where the Na−O distance is 2.320(6) Å.[28]

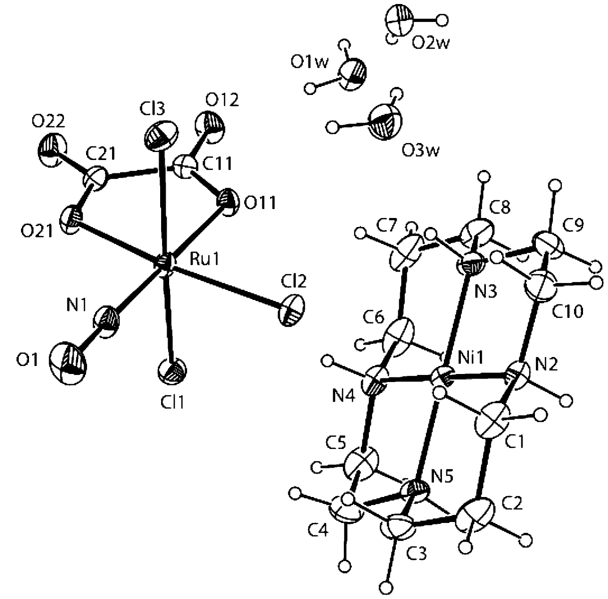

**Figure 2.** Asymmetric unit with atomic numbering scheme of **2**.

**$[Ni(cyclam)][Ru(ox)(NO)Cl_3]\cdot 3H_2O$ (2)**. Only the packing cell and the geometry of the cation are discussed here. The $[Ru(ox)(NO)Cl_3]^{2-}$ units are arranged in an antiparallel manner along the *b* axis (figure in the Supporting Information). The asymmetric unit, along with the atomic numbering schemes, is shown in Figure 2. Three molecules of the crystal water are present in the lattice.

The $[Ni^{II}(cyclam)]^{2+}$ counterion is quasi-planar. The distances in the $[Ni^{II}(cyclam)]^{2+}$ cations are comparable to the ones found in the free cation.[29] The environment of the nickel ions is a strongly distorted octahedron as is evident from the elongated distances to the axial positions: Ni−O(22) and Ni−O(21) distances are 3.125(2) and 3.528(2) Å, respectively. The Ni−Cl(2) distance is 3.026(2) Å, the Ru−Cl(2) distance is 2.3547(12) Å, and the Ru−Ni distance is 4.89 Å. Hydrogen bonding between the water molecules and the oxalate ligands occurs since the H(11)−O(12) distance is 1.908(8) Å.

**$[Ru(terpy)(NO)(OH)Cl]PF_6$ (3)**. The structure of **3** is in accordance with the one already published.[16] The asymmetric unit, along with the atomic numbering schemes, is shown in Figure 3.

**B. Photophysical Properties**. The light-induced metastable states SI and SII are found in all three Ru compounds. However, in comparison with $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (NaNP) the population is very low. In Figure 4, the heat flow of the thermal decay of **1**−**3** is shown in the range of 120−220 K.

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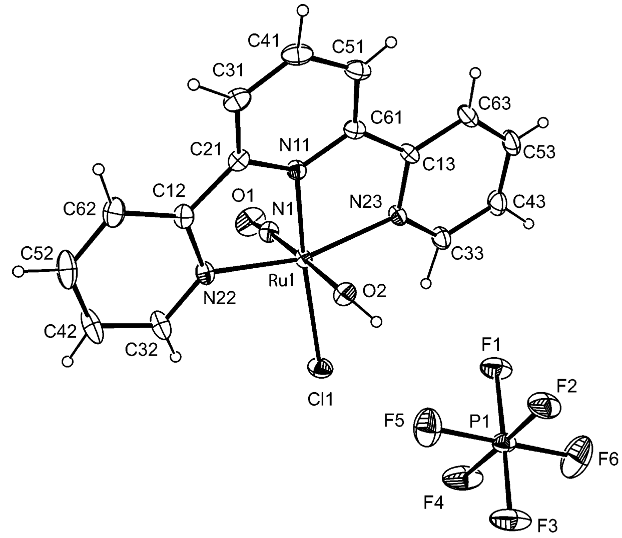

**Figure 3.** Asymmetric unit with atomic numbering scheme of **3**.

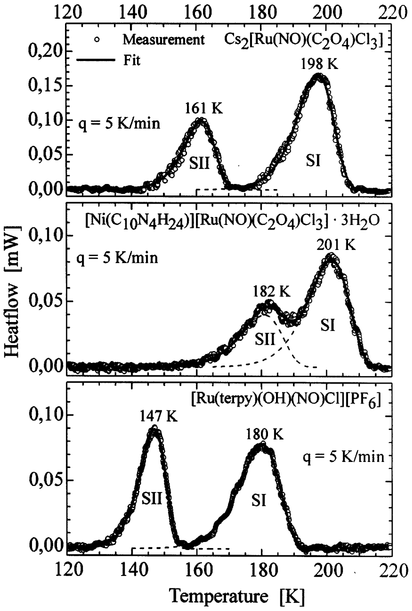

**Figure 4.** Exothermal heat flow $\dot{H}$ versus temperature of the metastable states SI and SII upon irradiation with unpolarized light for the three compounds (a) **1**, (b) **2**, and (c) **3**. The exposure has an amount of $Q = 2800$ (W s)/cm$^2$.

For **1** the maxima of the decay temperatures, detected with a heating velocity of $q = 5$ K/min, are found at $T$(SI) = 198 ± 1 K and $T$(SII) = 161 ± 1 K. Assuming the same behavior between enthalpy $H$ and population as found in NaNP[7a] (i.e., an enthalpy of 1 kJ/mol corresponds to a 1% population), we find a population of 1.3% for SI and 0.6% for SII, given by the enthalpies of $H$(SI) = 1.3 ± 0.2 kJ/mol and $H$(SII) = 0.6 ± 0.3 kJ/mol, respectively. The isothermal decay can be fitted by a pure exponential function so the reaction order is $n = 1$ and the Arrhenius law is valid. From the evaluation of the temperature dependence of the dynamical measurements of $\dot{H}$ by the Arrhenius law, the activation energies $E$(SI) = 0.60 ± 0.05 eV and $E$(SII) = 0.46 ± 0.05 eV and the frequency factors $Z$(SI) = (2.5 ± 1.0) × $10^{13}$ s$^{-1}$ and $Z$(SII) = (5 ± 1) × $10^{12}$ s$^{-1}$ are obtained. From the pure exponential decay under isothermal conditions we can clearly deduce that the excited $[Ru(NO)(ox)Cl_3]^{2-}$ anions are completely independent from each other and have no interaction with those in the ground state. By population of the metastable states we have only changed the number density in GS, SI, or SII.

Substituting the cation Cs$^+$ for $[Ni^{II}(cyclam)]^{2+}$ in **2**, the decay temperature of SI increases a little to $T$(SI) = 201 ± 1 K. But, as shown in Figure 4b, the decay temperature of SII is significantly increased to $T$(SII) = 182 ± 1 K, which is a high decay temperature for SII. The enthalpies or populations are very low: $H$(SI) = 0.8 ± 0.2 kJ/mol, $H$(SII) = 0.4 ± 0.2 kJ/mol. The activation energies and frequency factors are $E$(SI) = 0.55 ± 0.05 eV, $E$(SII) = 0.44 ± 0.05 eV, $Z$(SI) = (6 ± 1) × $10^{11}$ s$^{-1}$, and $Z$(SII) = (2 ± 1) × $10^{10}$ s$^{-1}$.

The terpyridine compound **3** was prepared for comparison with $K_2[Ru(NO_2)_4(OH)(NO)]$. In the latter we have found[2a] a significant shift of SII to higher temperatures compared to that of NaNP, but we could not decide whether it is a result of the OH ligand trans to the NO or of the equatorial $NO_2$ ligands. As shown in Figure 4c the decay temperatures of SI and SII of **3** decrease to $T$(SI) = 180 ± 1 K and $T$(SII) = 147 ± 1 K, compared with $T$(SI) = 199 ± 1 K and $T$(SII) = 166 ± 1 K for $K_2[Ru(NO_2)_4(OH)(NO)]$. Therefore, the OH ligand seems not to be responsible for the shift of the decay temperatures. The increase is produced by the equatorial $NO_2$ ligands.

The activation energies of **3** are $E$(SI) = 0.44 ± 0.05 eV and $E$(SII) = 0.46 ± 0.05 eV. The frequency factors differ by about 4 orders of magnitude, which results in a much smaller line width of SII: $Z$(SI) = (3 ± 1) × $10^{10}$ s$^{-1}$, $Z$(SII) = (1.5 ± 1.0) × $10^{14}$ s$^{-1}$.

Again the enthalpy or population is very low: $H$(SI) = 1.2 ± 0.2 kJ/mol, $H$(SII) = 0.9 ± 0.2 kJ/mol. A significant overlap of the decays is only found in complex **3**. For the integration of the peaks a linear baseline at $\dot{H} = 0$ is used, since the subtraction of the irradiated and unirradiated samples gives zero heat flow before, during, and after the decay regions. There is no detectable structural phase transition in the ground state or induced by the irradiation.

## Discussion

All iron and ruthenium nitrosyl compounds, in which SI and SII can be accessed, show the same behavior of excitation and thermal decay: the irradiation wavelength is determined by the energetic difference between the empty $\pi^*$(NO) orbital and the occupied mainly d orbitals of the metallic atom. At every population value, the new states are stable below the decay temperatures, so the transferred compounds in the ground state, SI, and SII are independent from each other. This is also confirmed by the pure exponential isothermal decay with the reaction order $n = 1$. The stored energy of both states is released to the lattice. The potential barriers can be calculated using Arrhenius' law. Therefore, the physical backgrounds of the metastable states in the iron and ruthenium nitrosyl compounds are identical. It is possible to shift the decay temperatures of SI and SII toward room temperature by variation of the ligands,[4,15]

**Table 2.** Activation Energy and Frequency Factor for States I and II for Some Ruthenium Nitrosyl Compounds

| | | SI | | SII | |
|---|---|---|---|---|---|
| compd | ref | activation energy (eV) | frequency factor ($s^{-1}$) | activation energy (eV) | frequency factor ($s^{-1}$) |
| **1** | | 0.60 | $2.5 \times 10^{13}$ | 0.46 | $5 \times 10^{12}$ |
| **2** | | 0.55 | $6 \times 10^{11}$ | 0.44 | $2 \times 10^{10}$ |
| **3** | | 0.44 | $3 \times 10^{10}$ | 0.46 | $1.5 \times 10^{14}$ |
| *cis*-K[Ru(ox)$_2$(en)(NO)] | 4c | 0.45 | $4.1 \times 10^{7}$ | | |
| *cis*-K[Ru(ox)$_2$(en)(NO)]3H$_2$O | 4c | 0.46 | $1.1 \times 10^{6}$ | | |
| *cis*-[Ru(Hox)(en)$_2$(NO)]Cl$_2$·EtOH | 4c | 0.53 | $7.6 \times 10^{8}$ | | |
| *cis*-[Ru(Hox)(ox)(en)(NO)] | 4c | 0.46 | $1.1 \times 10^{6}$ | | |
| *trans*-[Ru(Hox)(en)$_2$(NO)]Cl$_2$ | 4c | 0.67 | $1.3 \times 10^{9}$ | | |
| *trans*-[RuCl(en)$_2$NO]Cl$_2$ | 4b | 0.69 | $1.7 \times 10^{11}$ | | |
| *cis*-[RuCl(en)$_2$NO]Cl$_2$ | 4b | 0.46 | $1.7 \times 10^{8}$ | | |
| *trans*-[RuBr(en)$_2$NO]Br$_2$ | 4b | 0.53 | $5.2 \times 10^{8}$ | | |
| *cis*-[RuBr(en)$_2$NO]Br$_2$ | 4b | 0.36 | $3.7 \times 10^{5}$ | | |
| [RuCl$_3$(en)NO] (*fac*- and *mer*-) | 4b | 0.27 | $5.2 \times 10^{3}$ | | |
| *trans*-[Ru(H$_2$O)(en)$_2$NO]Cl$_3$ | 4b | 0.67 | $4.4 \times 10^{9}$ | | |
| K$_2$[Ru(NO$_2$)$_4$(NO)(OH)] | 2b | 0.65 | $3.6 \times 10^{14}$ | 0.47 | $3.8 \times 10^{12}$ |
| K$_2$[RuCl$_5$NO] | 2a | 0.71 | $3 \times 10^{15}$ | 0.47 | $5 \times 10^{15}$ |
| Na$_2$[Fe(CN)$_5$(NO)]·2H$_2$O | 8 | 0.70 | $5 \times 10^{15}$ | 0.50 | $8 \times 10^{14}$ |

whereby the underlying physical details of this potentiality remain unknown, but we see general trends.

(1) As shown in this paper the existence of SI and SII seems to be independent of whether the ruthenium complex is an anion or a cation, so the formal total charge can be negative or positive, i.e., $[Ru(NO)(C_2O_4)Cl_3]^{2-}$ **(1** and **2)** or $[Ru(terpy)(NO)(OH)Cl]^{+}$ **(3)**. The main point is that formally $Ru^{2+}$ and $(NO)^{+}$ are present, which guarantee an efficient charge-transfer transition from the d orbitals of the central atom to the $\pi^*$(NO) orbital.

(2) We assume that the temperature where a significant decay of the metastable states (decay temperature) can be detected depends on the amount of electron density in the $\pi^*$(NO) orbital, and on the nature of the chelating ligand. Therefore, we have prepared and investigated compounds **1**−**3** to introduce the ligand $C_2O_4$ with its closed-ring-like structure. However, we found that this ligand has no significant influence on the lifetime of the metastable states. As already reported, it seems that ligands such as O and N donor ligands (oxalate, ethylenediamine, terpyridine, ...) are less $\pi$-bonding and more $\sigma$-bonding, and they present the ability to give metastable states with high thermal stability,[4c] as summarized in Table 2, where the activation energy $E_A$ and frequency factor $Z$ for the states SI and SII of some metal nitrosyl compounds are presented. Since the lifetime $\tau$ is given by $\tau = Z^{-1} \exp(E_A/k_BT)$ at a certain temperature $T$, the high thermal stability is determined by a high activation energy $E_A$ and a low frequency factor $Z$. Figure 5 shows the temperature dependence of the lifetimes of SI/SII exemplarily for **2**. In the temperature range 90−330 K the lifetimes drop from thousands of years down to milli- and microseconds. In Table 2 we compare our results with literature results for various Ru compounds. One finds that the frequency factor $Z$ varies by over 10 orders of magnitude for SI, whereas $E_A$ varies by only a factor of about 2.5 (from 0.27 to 0.7 eV), so the variation of $Z$ is the more important contribution to the shift of the thermal stability. Therefore, compounds **1**−**3** have no significant higher thermal decay temperatures compared with the other compounds listed in Table 2. The values for $E_A$ and $Z$ were obtained from a fit using Arrhenius' law for the decay of the metastable states. To interpret the physical origin of the parameters, we also inspected the Eyring equation, which allows a more detailed analysis of the decay processes. In the Eyring equation the intermediate states are taken into account for the description of the decay process: SI/SII → intermediate states → GS. One obtains for the frequency factor $Z = (k_BT/h) \exp(\Delta S/R)$, where $h$ is Planck's constant, $R$ is the molar gas constant, and $\Delta S$ is the change in entropy during the decay process. The activation energy $E_A$ corresponds mainly to the activation enthalpy $E_A = \Delta H$. The frequency factor $Z$ is linearly dependent on the temperature and is determined by the change in entropy, which describes the order of the system. Unfortunately, because of the low population obtained for the presented compounds, we are not able to determine the values of $\Delta S$. Following the model of Carducci et al.,[30] which claims an isonitrosyl configuration (Fe−ON) for SI and a side-on configuration of NO for SII ($\eta^2$), the activation energy is composed mainly of two parts, on one side, the breaking of the Ru−NO bond and on the other side the rotation of the NO. Rotational energies are on the order of $10^{-3}$ eV, so they can be neglected compared to the binding

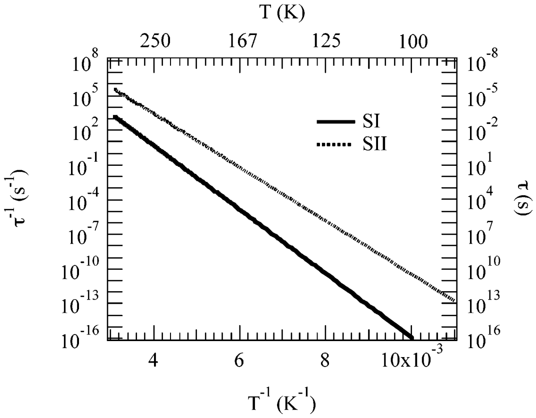

**Figure 5.** Temperature dependence of the lifetimes $\tau$ of SI/SII in **2**, calculated from the determined activation energy $E_A$ and the frequency factor $Z$ ($\tau^{-1} = Z \exp(-E_A/k_BT)$).

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[30] Carducci, M. D.; Pressprich, M. R.; Coppens, P. *J. Am. Chem. Soc.* **1997**, *119*, 2669−2678.

energies. In the Eyring description the large variation of the frequency factor *Z* for the different Ru compounds is due to the change in entropy $\Delta S$, which describes the change in the order of the system. Therefore, there must be a large range of variation with respect to the structural or electronic ordering among SI, SII, and GS.

(3) The decay temperatures of SI and SII depend on the environment in which the complex is embedded. The highest decay temperature of SII (182 K) has been found in **2**. The influence of the cation on the lifetime of SI/SII has been investigated systematically by Zöllner et al.[14] for a large variety of cations in $[Fe(CN)_5NO]$ compounds. The longest lifetime (highest decay temperature with a heating rate of 5 K/min) was found for the cation $Cu^{2+}$. In $Cu_2[Fe(CN)_5NO]\cdot 2H_2O$ the shortest Cu−Fe distances are 3.458 and 3.269 Å bridged over the axial and equatorial cyano ligands $N_{ax}$ ($Cu-N_{ax} = 2.160$ Å) and $N_{eq}$ ($Cu-N_{eq} = 1.976$ Å).[31] Here the polarization effect on the Fe electron density induced by $Cu^{2+}$ is produced over the diatomic cyano ligands (CN). In **2** the $Ni^{2+}$ is acting over the monatomic chlorine ligand Cl(2) (Ni−Cl(2) = 3.02 Å) directly on the electron density of the Ru (Ru−Ni = 4.89 Å). We assume that this is the reason for the strong shift to higher decay temperatures (of SII) in this compound. In the Cs compound **1**, on the other hand, the shortest distance between Cs(1) and Cl is 3.5 Å and the decay temperatures are found at lower values. An interesting result is the short distance of 2.872 Å between the fluorine atom F(6) of $PF_6$ and the oxygen O(1) of the nitrosyl ligand in **3**, which is only 0.487 Å longer than the Ru−Cl bond inside the cation. If the metastable states are explained by a structural change in the Ru−N−O region, as proposed by Carducci et al.,[30] this interaction has to be broken, which should be detectable using vibrational spectroscopy by a frequency shift of the breathing and deformation modes of the $[PF_6]^-$ anion. The small shift of the decay temperature maxima to lower values with respect to those of compounds **1** and **2** is not a significant hint for this interaction. The local environment of the Ru atom can also be responsible for the decrease. As found in a lot of other nitrosyl compounds[15] the crystal water has no influence on the decay temperatures, so only the cation can produce this shift, probably by hydrogen−bridge bonds of the cyclam to the oxalate or by polarization effects from the cation in the range of the Ru−N−O bonds.

At present, we have no explanation concerning the effect of the nature of the ligand on the intensity of the populations of the states.

In summary we have found two extremely long lived metastable states (SI and SII) in Ru compounds, using DSC. Their population and decay behavior are the same as those found in Fe complexes, so they are based on the same physical principle. Consequently, we can generally propose that these metastable states can be accessed in nitrosyl compounds, in which a charge-transfer transition (d → $\pi^*$(NO)) exists, whereby the $\pi^*$(NO) orbital lies energetically between the d orbitals of the central atom. To get a long lifetime at room temperature, a high activation energy and a low frequency factor are needed. Since we have not measured the structure of the presented compounds in the excited states, we follow the proposal of Carducci et al.[30] that the products formed upon light irradiation are linkage isomers of the normally N-coordinated nitrosyl ligands.

**Acknowledgment.** Gratitude is expressed to Pr. S. Decurtins, to the Swiss National Science Foundation (Project No. 20-45750.95), to INTAS (Grant No. 2000-0651), and to the Deutsche Forschungsgemeinschaft (Grant Wo618/5-1) for financial support.

**Supporting Information Available:** Crystallographic data for compounds **1**−**3** in CIF and PDF formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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