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Synthesis, crystal structure, spectroscopic, and photoreactive properties of a ruthenium(II)-mononitrosyl complex

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ABSTRACT

A compound of formula $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$, in which Cl-py is the 4-chloropyridine, has been synthesized in four steps and fully characterized. It crystallizes in the $P\bar{1}$ triclinic space group as $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2{\cdot}1.25H_2O$. Upon irradiation at $\lambda = 473$ nm in the solid state, the N-bounded nitrosyl ligand (ground state GS: $[Ru^{II}(NO)]$) turns into O-bounded nitrosyl metastable state 1 (MS1: $[Ru^{II}(ON)]$). The population of the long-lived metastable $Ru^{II}(ON)$ isomer is equal to 27% on powder samples, therefore 3 times less than that of the parent $[Ru^{II}Cl(NO)(py)_4](PF_6)_2$ derivative. Spectroscopy and TD-DFT studies are proposed to find a rational for this difference at the molecular level, which is tentatively related to different UV–visible spectra in the metastable $Ru^{II}(ON)$ isomer. Surprisingly, and while the switching efficiency of $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$ appears relatively modest, its capability for releasing the biologically active nitric oxide ($NO^{\cdot}$) radical under irradiation in solution is find to be about 100 times that of the $[Ru^{II}Cl(NO)(py)_4](PF_6)_2$ derivative.

1. Introduction

Photochromism, in which a molecule is reversibly photo-transformed between two isomers having different absorption spectra, has been a promising research topic in modern molecular science [1], in relation to the intriguing concepts of molecular switches and memories [2], and molecular machines [3]. Various classes of molecules have been reported to possess photo-switching capabilities, such as diarylethenes [4], spiropyrans [5], or azobenzenes [6]. A particular interest is devoted to solid state photo-isomerization which could lead to applications for data storage, and ultrafast photonic devices [7–10]. Although it may occasionally be observed in few classes of photochromic species like spiropyrans [11,12], it is usually hampered by the effect of the crystal rigidity which prevents any significant intramolecular motion involved in the isomerization process. Therefore, solid state isomerization is mainly observed in systems in which the atomic rearrangements are restricted to the minimum. This requirement is fulfilled in N-salicylidene anilines derivatives which undergo a tautomeric (proton transfer supported by the solid state environment) equilibrium between ketonic and enolic forms, if we [13,14], with typical population of metastable states limited to a few percent [15], and in metal-(nitrosyl) complexes (N-bounded nitrosyl, ground state GS), which are reversibly isomerized to a metal-(*iso*-nitrosyl) (O-bounded nitrosyl, metastable state MS1), as follows:

$$\underset{\text{GS}}{[\text{M}-(\text{NO})]} \rightleftharpoons \underset{\text{MS1}}{[\text{M}-(\text{ON})]}$$

Indeed, since the discovery of long-lived metastable states in sodium nitroprusside ($Na_2[Fe(CN)_5(NO)]{\cdot}2H_2O$) [16], the NO/ON isomerization has been observed in various metal-nitrosyl derivatives (*e.g.* iron, ruthenium, osmium, manganese, iron, nickel and platinum) in solid state [17–21]. Few years ago, we have observed a remarkably large population ($\geqslant$92%) of the metastable state MS1, in $[Ru^{II}Cl(NO)(py)_4]^{2+}$ ($\mathbf{1}^{2+}$, in Scheme 1) after irradiation of a crystal of $[Ru^{II}Cl(NO)(py)_4](PF_6)_2 \cdot 0.5H_2O$ at $\lambda = 473$ nm [22], while the previous highest populations reported was that of Hauser, in 1977, with only 50% of MS1 in a single crystal of sodium nitroprusside [16]. In a previous investigation [23], we have targeted the role devoted to the solid state environment to account for this effect. Indeed, we have observed that the population of the metastable $[Ru^{II}Cl(ON)(py)_4]^{2+}$ units strongly depends on the nature of the counterions, present in the vicinity of the nitrosyl ligand. In this second investigation, we wish to target the influence of the intramolecular electronic properties to the rate of isomerization. $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$, an alternative system closely related to

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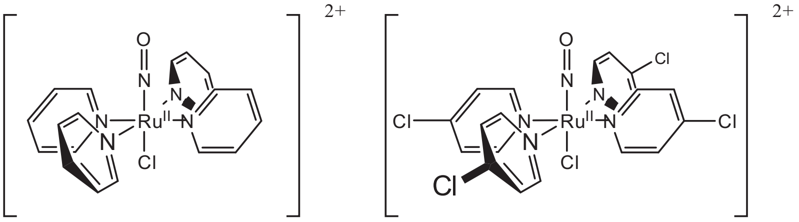

1^{2+} 2^{2+}

Scheme 1. Ruthenium(II)-nitrosyl based cations.

$[Ru^{II}Cl(NO)(py)_4](PF_6)_2$ will be described and fully characterized. Then, the solid-state photochromic properties of both $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$, and $[Ru^{II}Cl(NO)(py)_4](PF_6)_2$ will be compared. The observed differences will be tentatively rationalized from a computational investigation of the spectroscopic properties of the switchable cations conducted within the framework of the time-dependent density functional theory (TD-DFT) method [24]. The molecular structure of the two cations involved in this study is shown in Scheme 1 ($\mathbf{2}^{2+}$ for $[Ru^{II}Cl(NO)(Cl\text{-}py)_4]^{2+}$).

2. Experimental

2.1. General procedures

$[Ru^{II}Cl(NO)(py)_4](PF_6)_2$ was synthesized following the previously reported procedure [22]. 4-Chloropyridine hydrochloric, 4-aminopyridine and the Griess reagent used for the NO detection were obtained from Sigma. Ruthenium trichloride hydrate $Ru^{III}Cl_3{\cdot}xH_2O$ was obtained from Strem Chemicals. The solvents were analytical grade and used without further purification. Elemental analyses were performed at LCC with a Perkin Elmer 2400 serie II Instrument. ^1H NMR spectra were obtained at 298 K in D_2O, or $(CD_3)_2SO$ as internal reference and were recorded on a Bruker Avance 400. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer, using a diamond ATR. Ultraviolet–visible spectra were recorded on Jasco V-670 spectrophotometer.

2.2. Synthesis of $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$

"Ruthenium (II) blue" solution. $RuCl_3{\cdot}xH_2O$ (500 mg, 2.4 mmol) was dissolved in 25 mL of hydrochloric acid (3 mol L^{-1}) and stirred for 20 min. The solution was then heated to 100 °C under vacuum until dryness (black product). The dry $RuCl_3$ residue was dissolved in a mixture of ethanol (30 mL) and distilled water (25 mL) and was heated to 100 °C for 4 h to give "Ruthenium (II) blue" (intermediate). CAUTION: the solution of "ruthenium blue" is unstable and has to be readily used for the synthesis of the desired complexes.

$[Ru^{II}Cl_2(4\text{-}NH_2py)_4]$. 4-Aminopyridine (1.534 g, 16.32 mmol) was dissolved in 15 mL (1/3 H_2O–2/3 ethanol) and was added to "Ruthenium (II) blue" (500 mg, 2.4 mmol $RuCl_3{\cdot}xH_2O$). The solution was refluxed for 1.5 h, and then concentrated to the half of its initial volume. 50 mL of acetone was added to precipitate the complex. Yield (325 mg, 25%), black powder. Elemental analysis found: C, 43.89; H, 4.48; N, 20.50%. $C_{20}H_{24}Cl_2N_8Ru$ requires C, 43.80; H, 4.41; N, 20.43%. ^1H NMR, (D_2O, 400 MHz, 298 K): δ 7.90 (8Hα, d, J 7.17), 6.76 (8Hβ, d, J 7.12). IR (KBr) ν_{max} (cm^{-1}): 3304 (NH_2), 3180 (NH_2), 1611 (NH_2), 1508 (C=N).

$[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$. $[Ru^{II}Cl_2(4\text{-}NH_2py)_4]$ (271 mg, 0.494 mmol) was dissolved in a mixture of 20 mL of ethanol and 5 mL of distillated water. Sodium nitrite (204 mg, 2.96 mmol) in solution in water (5 mL) was added to the complex. The resulting solution was refluxed for 4 h. 4 mL of hydrochloric acid (37%) was then added and the solution was refluxed for additional 45 min. The solution was left to cool down to room temperature, then NH_4PF_6 (260 mg, 1.6 mmol in 3 mL of water) was added to precipitate the complex as an orange powder. The solution was filtered, washed with water and dried under vacuum. Yield (204 mg, 45%. Elemental analysis found: C, 25.95; H, 1.78; N, 8.01%. $C_{20}H_{16}Cl_5F_{12}N_5OP_2Ru$ requires C, 26.38; H, 1,77; N, 7.69%. ^1H NMR($(CD_3)_2SO$, 300 MHz, 298 K): δ 8.54 (8Hα, d, ^3J 5.2), 7.92 (8Hβ, d, ^3J 5.4). IR (KBr) ν_{max} cm^{-1}: 3044 ($C\text{–}H_{aromatic}$), 1910 (N—O), 1614 (C=N), 1424 (C=C), 825 (P-F).

2.3. X-ray crystallography

Single crystals suitable for X-ray diffraction were obtained as yellow plates by slow evaporation of a solution of $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$ in an acetonitrile/water mixture. Data were collected at low temperature (100(2) K) on a Bruker Kappa Apex II diffractometer equipped with a 30 W air-cooled microfocus, using MoKα radiation ($\lambda = 0.71073$ Å), and an Oxford Cryosystems Cryostream cooler device. Phi- and omega- scans were used for data collection. The structure was solved by direct methods with SHELXS-97 [25]. All non-hydrogen atoms were refined anisotropically by means of least-squares procedures on F2 with the aid of the program SHELXL-97 [25]. All the hydrogen atoms were refined isotropically at calculated positions using a riding model except those of water molecules which were not found in difference Fourier maps and therefore they were not included into the model. The oxygen atom of one water molecule is disordered over two positions (O2 and O2′) in a 43:57 ratio and the water molecule O3 has an occupancy of 0,25. In the solvent region some residual electron density were difficult to model, therefore the SQUEEZE function of PLATON [26] was used to eliminate the contribution of this electron density from the intensity data for the final refinement. The crystal structure of $[Ru^{II}Cl(NO)(Cl\text{-}py)_4](PF_6)_2$ has been deposited with the Cambridge Crystallographic Data Center.

2.4. Computational methods

The molecular geometries of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ were computed using the GAUSSIAN-09 program package [27] within the framework of the DFT at the B3LYP/6-31G* level [28–30], the LANL2DZ pseudopotential being used to account for relativistic effects on the ruthenium atom [31]. The widely applied B3LYP functional was selected for a better consistency with our previous investigation of $\mathbf{1}^{2+}$ [23]. The computations were performed in the presence of acetonitrile with the SCRF method implemented in Gaussian, using the