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Note

A convenient preparation of pentaaquanitrosylchromium(2+) sulfate: The crystal structure revisited

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Abstract

The complex pentaaquanitrolsylchromium(2+) sulfate, $[Cr(OH_2)_5(NO)]SO_4$ has been prepared in a high yield by the hydrolysis of $[Cr(NCCH_3)_5(NO)](BF_4)_2$ in dilute sulfuric acid. Crystals of $[Cr(OH_2)_5(NO)]SO_4 \cdot H_2O$ have been grown and characterized by X-ray crystallography. Continuous photolysis of $[Cr(NCCH_3)_5(NO)]^{2+}$ in acetonitrile solution with 404 nm light results in a release of NO with the quantum yield $\Phi = 0.55$ mol einstein^{-1} at 298 K with the resulting solvated Cr^{2+} ion being trapped by molecular dioxygen present in the solution.

Keywords: Nitrosyl complexes; X-ray crystal structure; Chromium–nitrosyl; Photolysis; Acetonitrile complex

1. Introduction

Acetonitrile (MeCN) molecules coordinated to a metal centre are easily displaced by other ligands and MeCN complexes have accordingly found extensive use as synthetic precursors. With this in mind, we have studied the use of the compound $[Cr(NCCH_3)_5(NO)](BF_4)_2$ (**1**), first isolated by Taylor in 1980 [1], as a possible entry into chromium–nitrosyl chemistry and we have found that hydrolysis of **1** in dilute sulfuric acid leads to a quantitative formation of the cation $[Cr(OH_2)_5(NO)]^{2+}$ as judged from the optical absorption spectra. From such a solution it is possible to isolate $[Cr(OH_2)_5(NO)]SO_4$ (**2**) in a high yield, and single crystals were grown and examined by X-ray diffraction. Furthermore, we report here the photophysical properties of the cation in **1** in solution.

2. Results and discussion

2.1. Preparation of $[Cr(OH_2)_5(NO)]SO_4$ (2)

The compound **2** was first prepared by Ardon in 1962 [2] by the reaction between $[Cr(OH_2)_6]^{2+}$ and NO and isolated as a sulfate salt after a column chromatography purification. Later, complexes including the $[Cr(NO)]^{2+}$ core have been prepared by the reduction of CrO_3 with NH_3OH^+, and in 1992 Ardon [3], following that procedure, prepared after a column chromatography purification a solution of $[Cr(OH_2)_5(NO)]^{2+}$ from which crystals of **2** suitable for X-ray crystallography were grown. The isolation of solid **2** from such an eluate is, however, not easy, and a detailed recipe for the isolation of **2** in the solid state does not appear in the literature. A product contaminated with solid Na_2SO_4 has been reported [4], and studies [5,6] of the properties of $[Cr(OH_2)_5(NO)]^{2+}$ have therefore been done directly on the eluate from the column chromatography purification.

We have found that hydrolysis of **1** in sulfuric acid (Eq. (1))

$$\begin{aligned}&[Cr(NCCH_3)_5(NO)](BF_4)_2 + 5H_2O + H_2SO_4\\&\quad\rightarrow [Cr(OH_2)_5(NO)]SO_4 + 5CH_3CN + 2HBF_4 \qquad (1)\end{aligned}$$

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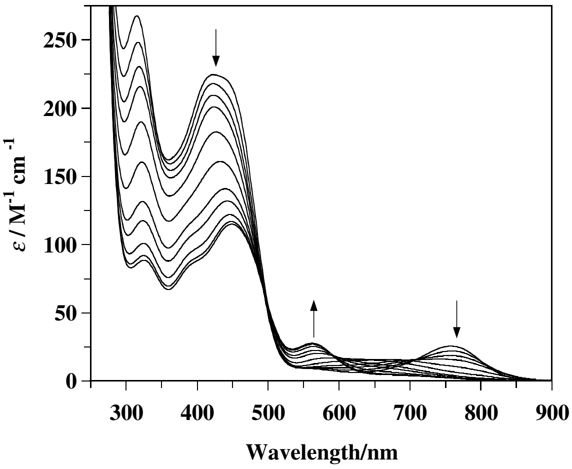


Fig. 1. Optical absorption spectra recorded during the hydrolysis of $[Cr(NCCH_3)_5(NO)]^{2+}$ in 0.50 M H_2SO_4 yielding $[Cr(OH_2)_5(NO)]^{2+}$. The spectra were recorded at 1, 5, 11, 16, 30, 47, 68, 82, 109, 141 and 175 min after dissolution of $[Cr(NCCH_3)_5(NO)](BF_4)_2$.

yields $[Cr(OH_2)_5(NO)]^{2+}$ quantitatively within 3 h (Fig. 1). The solubility of **2** in acetone is very low, in contrast to **1**, and by performing the hydrolysis in a mixture of sulphuric acid and acetone solid **2** separates out during the reaction.

2.2. Crystal structure

Large single crystals were grown from the mother liquor and the X-ray crystallography revealed that the crystals include one crystal water molecule per cation and should accordingly be formulated as $[Cr(OH_2)_5(NO)]SO_4 \cdot H_2O$ (**2 · H₂O**). Furthermore, the crystals are orthorhombic (space group *Pnma*, $T = 122$ K) and notably not isomorphous with the crystals obtained by Ardon [3] (monoclinic, space group $P2_1/n$, $T = 293$ K). A molecular structure of the cation in **2 · H₂O** is shown in Fig. 2. The bond distances in the cation are within 0.01 Å identical to those reported by Ardon except the Cr–O1 distance which Ardon reports to be 2.057(2) Å, 0.039 Å longer than in **2 · H₂O**, probably due to a difference in hydrogen bonding. The packing of the crystal is determined by hydrogen bonds between the coordinated water ligands and the sulfate anion and crystal water, respectively. Furthermore, an O2–H···O4 hydrogen bond is present.

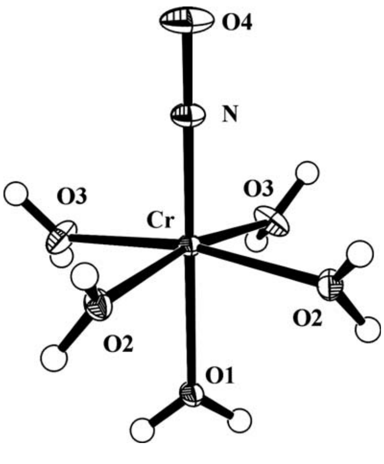


Fig. 2. ORTEP plot of the cation in $[Cr(OH_2)_5(NO)]SO_4 \cdot H_2O$. Important distances (Å) and angles (°): Cr–O1 2.0177(9); Cr–O2 2.0300(6); Cr–O3 1.9944(7); Cr–N 1.6969(10); N–O4 1.1841(15); Cr–N–O4 179.80(12); O1–Cr–N 178.70(5).

2.3. Optical absorption spectra

The absorption spectra of [Cr(L)$_5$(NO)] type complexes consist of three absorption maxima assigned as $d_{xy} \leftarrow \{d_{xz}, d_{yz}, \pi^*(NO)\}, \{\pi^*(NO), d_{xz}, d_{yz}\}^* \leftarrow \{d_{xz}, d_{yz}, \pi^*(NO)\}$ and $d_{x^2-y^2} \leftarrow d_{xy}$ transitions [7,8]. The absorption spectrum of **1** is seen in Fig. 3 with the absorption maxima located at 749, 436 and 313 nm and with the molar absorption coefficients being 33.0, 242 and 306 M^{-1} cm^{-1}, respectively. It is noteworthy, that the absorption spectrum of **1** in Fig. 3 is different from that of spectrum of **1** in Fig. 1 taken 1 min after dissolution in 0.5 M H_2SO_4. The NO ligand apparently labilizes the MeCN ligand situated *trans* to an extent that this MeCN ligand is substituted by a water ligand within the time of the dissolution of **1**. The process followed spectrophotometrically in Fig. 1 is accordingly the substitution of the residual four equatorial MeCN ligands. The absorption spectrum of **2** is identical to the final spectrum in Fig. 1 and to the spectra reported by Lay [4].

2.4. Photolytic behaviour

Bakac has shown [6] that photolysis of **2** in aqueous solution leads to a release of NO as shown in Scheme 1.

In a deoxygenated solution the back-reaction is, however, so fast that no net photochemistry was observed on continuous photolysis. This contrasted the behaviour in

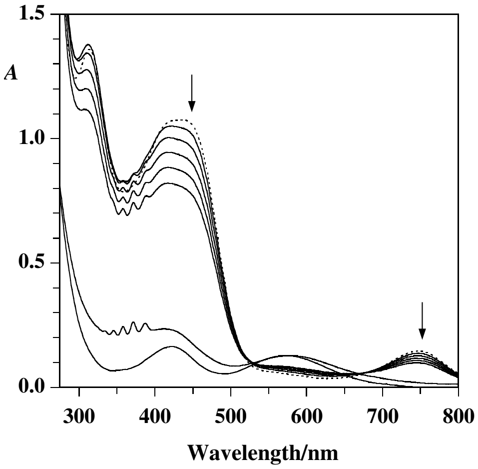
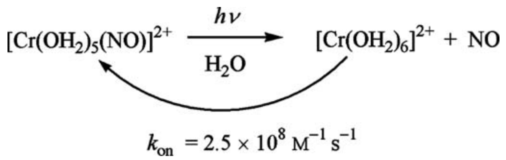


Fig. 3. Continuous photolysis ($\lambda_{irr} = 404$ nm) of an aerated ($p(O_2) = 0.20$ bar) 4.45×10^{-3} M MeCN solution of $[Cr(NCCH_3)_5(NO)](BF_4)_2$ at 298 K with the intensity (I_0) of the continuous light flux being 5.07×10^{-6} einstein s^{-1} dm^{-3}. The spectra were recorded after 0(···), 2, 4, 6, 8, 10, 150 and 1200 min photolysis.



Scheme 1.

oxygenated solution where oxidative trapping of $[Cr(OH_2)_6]^{2+}$ takes place through a formation of a superoxo complex as shown in the following equation:

$$[Cr(OH_2)_6]^{2+} + O_2 \rightarrow [Cr(OH_2)_5(O_2)]^{2+} + H_2O \qquad (2)$$

Other Cr(III) species eventually formed through a series of further reactions. Kept in the dark, H_2O solutions of **2** was found to be stable and unreactive toward molecular oxygen.

We have found that the photolytic behaviour of **1** is similar. Kept in the dark oxygenated MeCN solutions of **1** are stable, and no net photochemistry has been observed on irradiation of **1** in deoxygenated MeCN solutions with UV or Vis light. In oxygenated MeCN a photodecomposition of **1** takes place as shown in Fig. 3. The sharp peaks between 330 and 400 nm are characteristic of HNO_2 [9] which most likely is formed by the reaction of NO with O_2 [10] and traces of water in the solution (Eq. (2)).

$$4NO + O_2 + 2H_2O \rightarrow 4HNO_2 \qquad (3)$$

On a longer time scale (1 d) those peaks disappear as a result of further oxidation to NO_3^-. The final spectrum is typical for a Cr(III) species. The nature of final Cr(III) species was not investigated.

From the experiment shown in Fig. 3, the quantum yield, defined as the amount of decomposed **1** relative to the amount of absorbed photons, can be calculated to be $\Phi = 0.55$ mol einstein^{-1} at the irradiation wavelength $\lambda_{irr} = 404$ nm. On irradiation in this band an electron is promoted from a Cr–N(O) π orbital to a Cr–N(O) π^* orbital. This should weaken the Cr–nitrosyl bond in agreement with the observed high quantum yield.

3. Experimental

3.1. Preparation of $[Cr(OH_2)_5(NO)]SO_4$ (2)

The reactions were carried out in standard Schlenk equipment under a nitrogen atmosphere and exposure to light was minimized owing to the photolability of the nitrosyl complexes. All solvents were purged with nitrogen prior to use.

To a mixture of $NOBF_4$ (1.22 g, 10.4 mmol) and acetonitrile (20 cm^3) was added $[Cr(CO)_6]$ (0.55 g, 2.50 mmol) and the reaction mixture was stirred for 2 h. The reaction mixture was filtered in order to remove a small amount of unreacted $[Cr(CO)_6]$. Diethyl ether (100 cm^3) was then added to the brown filtrate with stirring and a yellow-brown precipitate of $[Cr(NCCH_3)_5(NO)](BF_4)_2$ formed. The mother liquor was decanted away and the precipitate was redissolved in a mixture of 2 M H_2SO_4 (2 cm^3, 4.0 mmol) and acetone (20 cm^3). The solution was stirred for 3 h during which the colour changed from yellow-brown through green to red-brown and a red-brown precipitate eventually formed. Filtration followed by several washings with acetone and drying in a nitrogen flow yielded 0.42 g of $[Cr(OH_2)_5(NO)]SO_4$ (63% based on chromium). Storage of the filtrate at 5 °C over-night yields a small crop of X-ray quality crystals of $[Cr(OH_2)_5(NO)]SO_4 \cdot H_2O$. *Anal.* Calc. for $H_{10}CrNO_{10}S$: H, 3.76; Cr, 19.39; N, 5.03. Found: H, 3.73; Cr, 19.31; N, 5.22%. Electronic spectrum in 10^{-3} M $HClO_4$ (λ/nm, ε/M^{-1} cm^{-1}) at 25 °C: (561, 27.7), (449, 115), (325, 88.6). IR (KBr) 1733 cm^{-1} (ν_{NO}).

3.2. X-ray crystallography

Crystal data for $\boldsymbol{2 \cdot H_2O}$: $H_{12}CrNO_{11}S$, $M = 286.17$, red-brown block, $0.38 \times 0.23 \times 0.15$ mm^3, orthorhombic, space group *Pnma* (No. 62), $a = 21.9990(4)$, $b = 6.6690(5)$, $c = 6.8960(16)$ Å, $V = 1011.7(2)$ Å^3, $Z = 4$, $D_c = 1.879$ g/cm^3, $F(000) = 588$, Nonius KappaCCD diffractometer, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 122(2)$ K, $1.85° < 2\theta < 50.01°$. 5570 reflections collected. The structure was solved and refined by the use of SHELXS-97 and SHELXL-97 [11], respectively. The H-atoms were located experimentally. Final goodness-of-fit (on F^2) = 1.245, $R(F) = 0.0377$, $wR(F^2) = 0.093$, R indices based on all 5570 reflections with $I > 2\sigma(I)$ (refinement on F^2, 76 parameters). Absorption correction was applied with $\mu = 1.382$ mm^{-1}.

3.3. Other physical measurements

Absorption spectra were recorded on a Cary 5E UV–Vis–NIR or Shimadzu UV-2401 PC spectrophotometer. Infrared spectra were recorded on a a FT-IR 1760X instrument using a KBr disc. Continuous photolysis was carried out on stirred solutions ($V = 3.00$ cm^3) in a thermostatted ($T = 298$ K), square quartz cuvette with a 1.000 cm pathlength on an optical train using collimated light from a Hg lamp and the appropriate interference filters for wavelength isolation. Chemical actinometry was performed by the use of $K_3[Fe(C_2O_4)_3]$ solutions [12].

Acknowledgements

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Appendix A. Supplementary data

Further details on the crystal structure may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldhafen, Germany; fax +49 7247 808

666, e-mail: Crysdata@fiz-karlsruhe.de on quoting the depository number CSD-415674. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.12.024.

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