

Synthesis, molecular structure, and redox behavior of an oxo-bridged dimer of a ruthenium-bpb nitrosyl

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A contribution to the special issue dedicated to the 70th birthday of Professor Brian James (University of British Columbia, Canada).

Abstract

We have prepared the oxo-bridged dimer $[\text{Ru}(\text{bpb})(\text{NO})_2(\mu\text{-O})]$ in 60% isolated yield from the reaction of the known $\text{Ru}(\text{bpb})(\text{NO})\text{Cl}$ with silver nitrite. The compound exhibits a ν_{NO} of 1758 cm^{-1} (KBr pellet). The crystal structure reveals a linear ON-Ru-O-Ru-NO fragment with the oxo atom serving as an inversion center in the molecule. The redox behavior in DMF is characterized by a reversible reduction followed by a second but irreversible reduction in this solvent.

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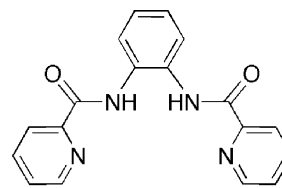
1. Introduction

Nitrosyl complexes of the group 8 metals have been studied for many decades [1,2]. This is due in large part to the fact that the interaction of nitric oxide (NO) with iron is biologically relevant both for heme and non-heme proteins [3]. The use of synthetic models in the study of the heme–NO interactions has provided a wealth of information concerning the electronic structure and the predicted geometries of the FeNO moiety in these systems. However, a common byproduct of iron porphyrin chemistry in aerobic environments is the μ -oxo dimer $[(\text{porphyrinato})\text{Fe}]_2(\mu\text{-O})$. Several of these iron porphyrin oxo-bridged dimers have been characterized by X-ray crystallography [4–7].

In 1998, we described an unexpected product formed during work with organoosmium nitrosyl porphyrins [4]. This product, namely $[(\text{OEP})\text{Os}(\text{NO})_2(\mu\text{-O})]$ (OEP = octaethylporphyrinato dianion) was characterized by spectroscopy and by X-ray crystallography, and displayed a linear oxo-bridged ON-Os-O-Os-NO linkage. We found this product

to be rather unreactive towards acid, and attributed this lack of reactivity of the oxo-bridge to the removal of electron-density in this bridge by the two *trans* NO ligands. We have not, to date, been successful at obtaining the corresponding ruthenium analogue $[(\text{porphyrinato})\text{Ru}(\text{NO})_2(\mu\text{-O})]$.

Mascharak and coworkers have utilized the bpb ligand (H_2bpb = 1,2-bis(pyridine-2-carboximido)benzene) for the design and construction of metal nitrosyl complexes that behave as NO-donors under mild photochemical conditions [8]. Importantly, they have investigated possible similarities between the bpb ligand and porphyrin ligands [9]. Ford [10,11], and Mascharak [8,12–15], have published extensively on the photochemical release of NO from group 8 metal–NO compounds with related polydentate ligands.



H_2bpb

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Based on the work of Mascharak, we explored the possibility of designing (bpb)Ru(NO)-containing compounds that will complement our work on ruthenium nitrosyl porphyrins. In this article, we describe: (i) the preparation and spectroscopic properties of an oxo-bridged dimer of a ruthenium nitrosyl compound containing the bpb ligand system, (ii) its crystal structure, and (iii) its electrochemical properties.

2. Experimental

2.1. General

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk glassware and/or in an Innovative Technology Labmaster 100 Dry Box. Solutions for spectral studies were also prepared under a nitrogen atmosphere. Solvents were distilled from appropriate drying agents under nitrogen just prior to use.

2.2. Chemicals

1,2-Bis(pyridine-2-carboxamido)benzene (H₂bpb) [16] and Ru(bpb)(NO)Cl [8] were prepared by the literature methods. Silver nitrite, tetra-*n*-butylammonium hexafluorophosphate (NBu₄PF₆), and anhydrous DMF were purchased from Aldrich Chemical Company and used as received. Chloroform-*d* (99.8%) was obtained from Cambridge Isotope Laboratories. Diethyl ether, CH₂Cl₂ and THF were distilled from calcium hydride under a nitrogen atmosphere just prior to use. Nitrogen of ultra high purity was purchased from Trigas (Houston, TX).

2.3. Instrumentation

Infrared spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer. Proton NMR spectra were obtained on Varian Mercury VX 300 MHz spectrometer and the signals referenced to the residual signal of the solvent employed (CHCl₃ at δ 7.24 ppm). ESI mass spectra were obtained on a Micromass Q-TOF mass spectrometer. UV–Vis spectra were recorded on a Hewlett–Packard model 8453 diode array instrument. Electrochemical measurements were performed with a BAS CV-50W instrument. A three-electrode cell was used (Pt working and auxiliary electrodes, Ag/AgCl reference electrode). The solutions used were 1.0 mM in analyte in 10 ml of 0.1 M NBu₄PF₆. Nitrogen gas was bubbled through the solution for about 8 min before each set of measurements and was passed continuously over the surface of the solution during the measurements.

2.4. Synthesis

A solution of AgNO₂ (0.06 g, 0.4 mmol) in DMF (10 ml) was added slowly, via cannula, to a solution of Ru(bpb)(NO)Cl (0.20 g, 0.4 mmol) in DMF (5 ml). The mixture was stirred under nitrogen gas overnight at room

temperature. Dichloromethane (30 ml) was added, whereby a white precipitate formed. The solution was filtered, and filtrate was heated at \sim 100 °C under vacuum to remove the solvent. The IR spectrum of the residue showed two bands in the ν_{NO} region at 1758 cm⁻¹ (major) and 1840 cm⁻¹ (minor). The residue was washed several times with CH₂Cl₂ to remove an as-yet uncharacterized byproduct. The remaining orange residue, after the wash with CH₂Cl₂, was dried under vacuum for several hours to give the orange-red compound [(bpb)Ru(NO)]₂(μ -O) (0.11 g, 60% yield based on Ru). IR (KBr, cm⁻¹): ν_{NO} = 1758 vs, $\nu_{\text{Ru-O-Ru}}$ = 816 s; also 3057 vw, 2984 vw, 1631 s, 1595 s, 1563 m, 1470 s, 1447 w, 1372 s, 1359 w, 1268 w, 1112 w, 1092 w, 1028 w, 970 w, 752 m, 725 w, 682 w, 571 w, 512 w. ¹H NMR (CDCl₃; δ ppm): 8.28 (m), 8.07 (m), 8.05 (m), 7.93–7.84 (overlapping m), 7.30 (m), 6.93 (m); also, 5.30 (s, trace CH₂Cl₂) and 1.58 (s, trace H₂O). ESI mass spectrum: *m/z* 913.0 [(Ru(bpb)-NO)₂O + H]⁺ (100%).

The complex is soluble only in DMF and insoluble or only sparingly soluble in most organic solvents.

2.5. X-ray crystallography

Suitable crystals for X-ray crystallography were grown by vapor diffusion of CH₂Cl₂ (25 ml) into a DMF solution of the compound at room temperature under inert atmosphere. A red prism-shaped crystal of dimensions 0.16 × 0.10 × 0.10 mm was selected for structural analysis. Intensity data for this compound were collected at 90(2) K using an instrument with a Bruker APEX CCD area detector [17,18] using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Cell parameters were determined from a non-linear least squares fit of 5577 peaks in the range 2.27° < θ < 28.18°. A total of 15194 data were measured in the range 2.09° < θ < 26.00° using ω oscillation frames. The data were corrected for absorption by the semi-empirical method [19] giving minimum and maximum transmission factors of 0.840 and 0.897. The data were merged to form a set of 3859 independent data with R_{int} = 0.0234 and a coverage of 100.0%. The monoclinic space group $P2_1/n$ was determined by systematic absences and statistical tests, and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 [20]. Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the displacement parameters of the bonded atoms. A total of 305 parameters were refined against seven restraints and 3859 data to give $wR(F^2)$ = 0.0541 and S = 1.001 for weights of $w = 1/[\sigma^2(F^2) + (0.0280P)^2 + 1.5000P]$, where $P = [F_o^2 + 2F_c^2]/3$. The final $R(F)$ was 0.0211 for the 3587 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.002 in the final refinement cycle. The final difference map had maxima and minima

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