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Structures and spectroscopic properties of three [Ru(OAc)(2mqn)$_2$NO] (H2mqn = 2-methyl-8-quinolinol) isomers: An experimental and density functional theoretical insight

Jianru Wang [a,c], Huifen Pan [b], Jiao Liu [b], Yan Zhao [d], Yanbo Wu [b], Hongfei Wang [a,b,*]

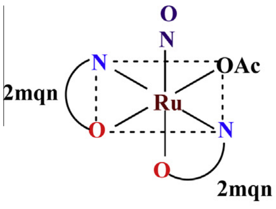
[a] State Key Lab of Quantum Optics and Quantum Optics Devices, Institute of Opto-Electronics, Shanxi University, Taiyuan 030006, China
[b] Key Laboratory of Chemical Biology and Molecular Engineering of Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China
[c] Institute of Basic Medicine, Shanxi Medicial University, Taiyuan 030012, China
[d] Beijing National Laboratory for Molecular Sciences, Beijing 100190, China

HIGHLIGHTS

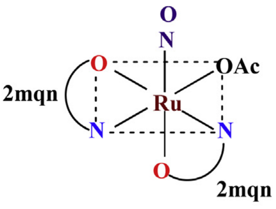
- Good agreement between the optimized geometries and crystal structures had been achieved.
- UV–vis and IR NMR spectra were successfully assigned with DFT calculations.
- NMR spectra were calculated with GIAO method and compared with experimental data.
- The frontier orbitals of complex isomers were analyzed for better understanding their reactivities.

GRAPHICAL ABSTRACT

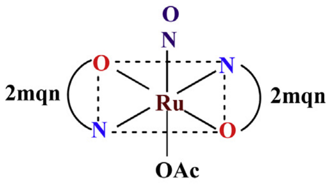
Molecular geometry, electronic spectra, infrared and NMR spectra of [Ru(OAc)(2mqn)$_2$NO] (H2mqn = 2-methyl-8-quinolinol) isomers were studied with density functional theory (DFT) at B3LYP level with 6-311++G(d,p) and Aug-cc-pVDZ-PP as basis set.



***cis*-1**



***cis*-2**



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ABSTRACT

Structures, electronic spectra, infrared and NMR spectra of three [Ru(OAc)(2mqn)$_2$NO] (H2mqn = 2-methyl-8-quinolinol) isomers were calculated at the B3LYP level with 6-311++G(d,p) and Aug-cc-pVDZ-PP as the basis set. Good agreement between the optimized geometries and structural parameters from crystal structures had been achieved. UV–vis absorption and vibration spectra were experimentally measured and theoretically assigned with DFT calculations. The calculated spectra reasonably correspond to the recorded spectra and the results indicated that DFT calculation is reliable and helpful to analyze the geometries and spectra of isomers. With the gauge independent atomic orbital (GIAO) method, chemical shifts in ^{1}H NMR of these isomers were also calculated, which could match with the experimental data. There was a large degree of mixing between NO orbitals and the metal *d* orbitals in the frontier orbitals, which suggested that the peculiarity of {Ru(II)-NO$^+$} group affect the structure and reactivity of nitrosylruthenium(II) complexes containing 8-quinolinolate and its derivatives.

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Introduction

Metal-nitrosyl complexes have attracted considerable attention not only in coordination chemistry but also in other fields, such as biochemistry and material science [1–4], because of their

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* Corresponding author at: Key Laboratory of Chemical Biology and Molecular Engineering of Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China. Tel./fax: +86 351 7018623.
E-mail address: wanghf@sxu.edu.cn (H. Wang).

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electron-transfer properties [5–10], light-induced linkage isomerism [11], and catalytic activities [12,13].

Among the different classes of metal nitrosyls, ruthenium complexes seem to be those of major importance [14,15]. Ruthenium complexes have attracted much attention because of their favorable optical and electronic properties for use in light energy conversion and molecular recognition. Nitrosylruthenium complexes are known to be ideal models for studying the photoinduced linkage isomerization [11,16,17]. Moreover, photo-triggered isomerism of a coordinated sulfoxide ligand, where the ground state is S-bonded and the meta-stable state is O-bonded, has been investigated recently [18–20]. Studies on these compounds revealed that the isomerization pathway and efficiency can be tuned through judicious choice of ligand structure.

Series of nitrosylruthenium complexes with 8-quinolinol or its derivatives as ligands were synthesized, and the photo-induced isomerization of $[Ru(OAc)(qn)_2NO]$ (qn = 8-quinolinol or its derivatives) were reported [21–23]. There are three geometrical isomers, *cis*-1, *cis*-2 and *trans* isomers for $[Ru(OAc)(2mqn)_2NO]$ (H2mqn = 2-methyl-8-quinolinol), and the schematic structures of three isomers and structure of H2mqn ligand were shown in Fig. 1. The crystal structures of *cis*-1, *cis*-2 and *trans* isomers for $[Ru(OAc)(2mqn)_2NO]$ (H2mqn = 2-methyl-8-quinolinol) were determined by X-ray diffraction [24]. Upon irradiation with light, reversible photoisomerization between *trans* isomer and *cis* isomer could be observed [25]. The photochemical and photophysical reactivities of these complex isomers are complicated; the study of these species faces more challenges, as it is not only NO, but also three other ligands involved in isomerization. Therefore, the theoretical calculations and analyses were necessary to investigate their electronic structures and spectroscopic properties.

In this paper, the geometries of three isomer of $[Ru(OAc)(2mqn)_2NO]$ were fully optimized and compared with their crystal structures. The recorded electronic, infrared and NMR spectra of three isomers were compared with the results of DFT calculation, and the spectroscopic characteristics of three isomers were analyzed by combination of experimental measurements and quantum chemical calculations. Furthermore, the electronic structures and molecular orbitals of *cis* and *trans* isomers were calculated to obtain a more clear understanding for the photo-induced reactivity for nitrosylruthenium(II) complexes.

Experimental

Cis-1 and *cis*-2 $[Ru(OAc)(2mqn)_2NO]$ was synthesized according to Ref. [24], and *trans* $[Ru(OAc)(2mqn)_2NO]$ complex was prepared by photoisomerization from *cis*-1 isomer. Both *cis* and *trans* isomers were confirmed by the ^1H NMR spectra. DMSO-d_6 (Cambridge Isotope Laboratories, Inc., 99.9 atom%D) was used as a solvent and the chemical shifts were referred to an internal TMS (0.03% V/V). The complex (3 mg) was dissolved in DMSO-d_6 (0.55 cm^3) and transferred into an NMR tube, and then ^1H NMR spectra were recorded on a BRUCKER 600 M spectrometer. The proton chemical shifts are reported in parts-per-million (d) with respect to tetramethylsilane (TMS) as internal reference (d = 0.0 ppm).

After *cis* and *trans* isomer complexes were dissolved in DMSO, UV–visible spectra were measured, respectively. Electronic absorption spectra were recorded on a Thermo 220 spectrophotometer in the region 200–800 nm. IR spectra were recorded on a Thermo 370 spectrophotometer, and the sample was prepared using standard KBr Pellet Method.

Theoretical calculations

All the calculations were carried out with the Gaussian09 package [26]. The original coordinates for atoms of the *cis* and *trans* $[Ru(OAc)(2mqn)_2NO]$ complexes in the calculations were obtained from the crystal structures determined by X-ray diffraction [24]. All the geometries were fully optimized without imposing any symmetry constraint, and no imaginary frequencies were found. The charge for the complex is 0, and the spin multiplicity is 1. The B3LYP functional [27–29] with mixed basis set (6-311++G(d,p) + Aug-cc-pVDZ-PP or Lanl2dz) was applied. The correlation-consistent basis set Aug-cc-pVDZ-PP or Lanl2dz was used to describe the core electrons of Ru atom [30], and the 6-311++G(d,p) basis set was employed for the ligand atoms [31].

Frequency calculations were performed at the DFT levels to establish whether stationary points from the geometry optimization calculations were in real minima and were compared with the experimental frequency. Visualization was performed using Gaussian view 5 [32]. The UV–vis spectroscopies were calculated with time-dependent (TD) approach at the B3LYP level. The TD calculations were performed both in gas phase and in DMSO solution (the solvent effect was simulated by the Polarization Continuum Model, PCM) [33,34]. ^1H NMR chemical shifts were calculated using the Gauge-independent atomic orbital (GIAO) method [35,36] in DMSO solution.

Results and discussion

Molecular geometry

To compare the calculated results with the experimental data, the selected key bond lengths and bond angles of the optimized geometries for three isomers, together with the X-ray diffraction determined structures, were tabulated in Table 1. As the table shows, the predicted bond lengths and angles were in good agreement with the values based upon the X-ray crystal structure data. Most of the predicted bond lengths and bond angles deviated from

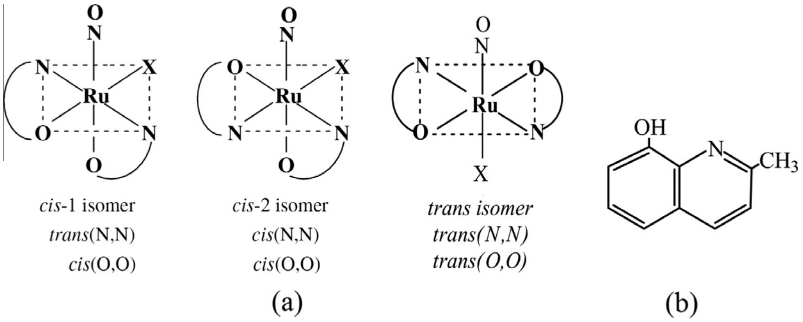

Fig. 1. Schematic structures of *cis*-1, *cis*-2 and *trans* isomers (a), and structure of ligand H2mqn (b).

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