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

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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.

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GRAPHICAL ABSTRACT

Molecular geometry, electronic spectra, infrared and NMR spectra of $[Ru(OAc)(2mqn)_2NO]$ (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.



ABSTRACT

Structures, electronic spectra, infrared and NMR spectra of three $[Ru(OAc)(2mqn)_2NO]$ (H2mqn = 2methyl-8-quinolinol) isomers were calculated at the B3LYP level with 6-311++G(d,p) and Aug-ccpVDZ-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 ¹H 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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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)(2mgn)₂NO] (H2mgn = 2-methyl-8-guinolinol), and the schematic structures of three isomers and structure of H2mgn 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-d₆ (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 cm³) 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).

Table 1

Optimized vs. experimental geometries (in Å and °).

	cis-1			cis-2			trans		
	exp.	cal.		exp.	cal.		exp.	cal.	
		Lanl2dz ^a	Aug-cc-pVDZ ^b		Lanl2dz	Aug-cc-pVDZ		Lanl2dz	Aug-cc-pVDZ
Ru-N0	1.721	1.774	1.744	1.740	1.774	1.743	1.721	1.765	1.735
Ru-N1	2.110	2.144	2.136	2.127	2.170	2.166	2.125	2.159	2.143
Ru-N2	2.113	2.143	2.131	2.116	2.165	2.157	2.102	2.148	2.136
Ru-O1	1.972	2.023	1.998	1.984	2.026	2.001	2.018	2.062	2.044
Ru-O2	1.993	2.058	2.035	2.003	2.046	2.019	2.039	2.066	2.042
Ru-OA1	2.053	2.103	2.080	2.024	2.078	2.053	1.984	2.056	2.031
N0-00	1.160	1.141	1.147	1.152	1.141	1.148	1.146	1.144	1.151
OA1-CA1	1.265	1.296	1.299	1.294	1.298	1.301	1.282	1.308	1.311
CA1-OA2	1.259	1.235	1.234	1.221	1.234	1.233	1.231	1.227	1.226
CA1-CA2	1.544	1.520	1.520	1.518	1.519	1.519	1.494	1.522	1.520
Ru-N0-00	175.2	174.2	174.9	171.3	172.8	173.2	173.2	177.5	177.5
O1-Ru-N1	81.8	80.2	80.5	80.6	79.5	79.6	80.1	79.2	79.7
O2-Ru-N2	81.4	80.5	81.0	81.7	80.3	80.8	80.9	79.2	79.9

^a With 6-311++G(d,p) and Lanl2dz as basis set.

^b With 6-311++G(d,p) and Aug-cc-pVDZ-PP as basis set.

Table 2
Total energies (Hartree) and orbital energies (eV) of HOMO and HOMO-LUMO gap for
[Ru(OAc)(2man) ₂ NO] complexes.

	cis-1	cis-2	trans	
Total energy	-1485.317	-1485.315	-1485.312	
LUMO	-2.770	-2.772	-2.847	
НОМО	-5.838	-5.866	-5.731	
LUMO-HOMO gap	3.068	3.094	2.884	

the experimental value by less than 0.03 Å and 2°, respectively. The best overall agreement with the experimental value was obtained with those of the 2mgn and –OAc ligands group (deviated less than 0.02 Å) and -NO, -CO group (deviated less than 0.01 Å), which is predominantly below the uncertainty caused by the experimental error range and solid-state effects [37,38]. For the examined cis-1 and cis-2 complexes, the calculated Ru-O1 bond distances trans to the NO were shorter than the Ru-O2 bonds cis to the NO. Ru-O (of -OAc group) bond for trans complexes is also shorter than those for cis-1 and cis-2 complexes, which are all consistent with the experimental data. The phenomenon can be explained by the well known trans-strengthening effect of the linear nitrosylruthenium(II) complexes because the NO acts as a strong π -acceptor and the phenolato oxygen as a π -donor [39]. The Ru–NO bond angles for both the cis-1, cis-2 and trans isomers, were proven to be linear consistent with the experimental data from which the calculated data deviated by 1–4° [21–24,40]. The differences between the calculated and X-ray determined coordination angles of O and N atoms from two ligands with Ru atom is less than 1.3°. The above results suggest that DFT calculation could provide reliable structural parameter for titled complex.

DFT calculation at B3LYP level with 6-311++G(d,p) for the atoms on the ligands and Lanl2dz for Ru atom were also performed. As shown in Table 1, the differences between the predicted and the experimental bond lengths for six coordination bonds range from 0.03 to 0.07 Å, which is obviously larger than that observed by using Aug-cc-pVDZ-PP basis set for Ru. The similar situation were met for calculation of $[Ru(OAc)(2cqn)_2NO]$ (H2cqn = 2-chloro-8-quinolinol) complexes at B3LYP level with 6-311++G(d,p) and Lanl2dz as basis set, in which chlorine atom at 2-position of 8-quinolinol has an electron attractive nature [41]. As the optimization with the Aug-cc-pVDZ-PP for Ru atom predicted more closer geometry parameters to the crystal structures than that with Lanl2dz for Ru atom, the Aug-cc-pVDZ-PP

basis set was selected for describing Ru atom in the following molecular orbital analyses and spectra simulations.

Molecular orbital analyses

The contour plots of the frontier orbitals for *cis*-1, *cis*-2 and *trans* [Ru(OAc)(2mqn)₂NO] complexes are shown in Fig. 2. For both *cis*-1, *cis*-2 and *trans* isomer, the highest occupied molecular orbital (HOMO) is described as a 2mqn ligand-based orbital which contains a very small amount of Ru (*d*) and NO (*p*) character, while the lowest unoccupied molecular orbital (LUMO) is best represented by an antibonding overlap of the Ru (*d*) and π^* NO (*p*) orbitals. There is a large degree of mixing between the orbitals of NO and the metal *d* orbitals in the frontier orbitals, explaining that the peculiarity of the {Ru(II)-NO⁺} group affects the structure and reactivity of nitrosylruthenium(II) complexes containing 8-quino-linolate and its derivatives.

The HOMO–LUMO interactions were calculated to recognize the reactivities of the various systems [42,43]. For *trans* isomer, the NO orbital contribute a little more to HOMO than those of *cis*-1 isomer and *cis*-2 isomer, and its HOMO/LUMO gap is smaller than those of the corresponding *cis* isomers (see Table 2). It suggests that the *trans* isomer complexes are more active and less stable than that of *cis* type complexes, which is consist with experimental results [21,23].

For both nitrosyl Fe or Ru species coordinated with other ligands, the HOMOs are ligand and metal located orbitals, while LUMOs are mainly metal-NO located orbitals [41,44-48]. Therefore, {Fe-NO} or {Ru-NO} group is important for photochemical behavior of Fe-NO and Ru-NO complexes. This, however, is not the case for those extensively studied ruthenium polypyridyl complexes (e.g. $[Ru(bpy)_{3-n}(L)_n]^{2+}$, L = diimine ligands). In such systems, it was found in previous study that the HOMO was typically centered on the ruthenium and represented the Ru (d) t_{2g} set, while the LUMO was bpy (π^*), and the MLCT transition played an important role in photochemical and photophysical process for these ruthenium-N-donor complexes [49–51]. The frontier orbitals type of these nitrosylruthenium complexes were obvious different with those of ruthenium polypyridyl complexes, which suggested that there are different excited state pathway in the photo reaction of these complexes and the electronic transition from the 8-quinolinolate ligands to the {Ru(II)-NO⁺} group plays an important role in the photophysical and photochemical process of [Ru(OAc)(2mqn)₂NO] complexes.



Fig. 2. Contour diagrams of the calculated LUMO (top) and HOMO (bottom) of [Ru(OAc)(2mqn)2NO] isomers. Positive values of the wave function are represented in green.



Fig. 3. Recorded and calculated electronic absorption spectra of *cis*-1 (a), *cis*-2 (b) and *trans* (c) isomers (blue: experimental; black: calculated). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Electronic absorption spectra

UV-vis absorption spectra of *cis*-1, *cis*-2 and *trans* [Ru(OAc) (2mqn)₂NO] in DMSO were shown in Fig. 3, there is one strong absorption peak near 270 nm in UV region and one weak absorption peak near 400 nm in visible region for *cis*-1, *cis*-2 and *trans* isomer. The three isomers exhibit similar absorption curve in visible region, there is 12 nm shift of absorption peak between *cis*-1 isomer and *cis*-2 isomer and just 5 nm shift of absorption peak between *cis*-1 isomer and *trans* isomer, for *cis*-1 isomer with maxima at 404 nm, *cis*-2 isomer with maxima at 399 nm, respectively.

The three isomers, *cis*-1, *cis*-2 and *trans* type, were calculated as having two prominent absorption bands in the region between 200 and 800 nm. The lowest-energy peak at about 400 nm is dominated by the HOMOs–LUMOs excitation (Table 3) in the visible region. The absorption peak calculated for *cis*-1, *cis*-2 and *trans*

isomers to be at 438 nm, 419 nm and 428 nm, which deviated from the experimental value about 30 nm. Analysis of the electronic structures and orbital components of the complexes indicates that these absorption bands mainly originate from $\pi(2mqn) \rightarrow [d(Ru) + \pi^*(NO)]$ charge transfer processes, labeled as LMCT and LL/CT processes (ligand-to-ligand' charge transfer, here L' stands for NO and L for 2mqn).

The stronger bands in UV region were calculated to be at 258, 257 and 259 nm, close to the experimental peaks at 266, 267 and 271 nm for *cis*-1, *cis*-2 and *trans* isomer, respectively. The calculated wavelengths have an error less than 12 nm in comparison with the experimental data by TDDFT method considering the solvent effect. This peak corresponds to the π - π * transition mainly localized on the 2mgn ligand (Intra-ligand charge transfer, ILCT).

The absorption spectra and orbital analyses indicate that the HOMO \rightarrow LUMO excitations of an electron from a bonding $\pi_{2mqn}^ d\pi$ orbital to an antibonding $\pi_{NO}^*-d\pi$ orbital allows relating the

Table 3

Experimental maximum absorption wavelength (nm) and the significant transitions band for *cis*-1, *cis*-2 and *trans* isomers, together with corresponding assignment and transition contributions.

Wavelength (1	nm)			Assignment	
exp	cal		f		
<i>cis</i> -1 [Ru(OAc) 404	(2mqn) ₂ NO] 438	466.87	f=0.0845	HOMO-2 → LUMO + 1(4.91%) HOMO-1 → LUMO + 1(91.99%)	$\begin{split} & d_{Ru} + \pi_{OAC} \rightarrow d_{Ru} + \pi^*_{NO} \\ & \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{NO} \end{split}$
		409.19	<i>f</i> = 0.0734	HOMO → LUMO + 1(3.09%) HOMO → LUMO + 2(93.22%) HOMO → LUMO + 3(6.78%)	$\begin{array}{l} d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^{*} \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \end{array}$
266	258	262.06	<i>f</i> = 0.0680	HOMO-5 → LUMO + 2(21.42%) HOMO-4 → LUMO + 2(35.89%) HOMO-4 → LUMO + 3(42.69%)	$\begin{aligned} \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \\ \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \\ \pi_{2mm} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \end{aligned}$
		259.48	<i>f</i> = 0.3577	HOMO 4 \rightarrow LUMO + 2(22.3%) HOMO-4 \rightarrow LUMO + 2(22.3%) HOMO-4 \rightarrow LUMO + 3(59.71%)	$\pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^{2} + \pi_{NO}^{NO}$ $\pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^{2} + \pi_{NO}^{NO}$ $d_{m} + \pi_{m}^{2} + \pi_{m}^{2} + \pi_{NO}^{2}$
		256.78	<i>f</i> = 0.3511	HOMO \rightarrow LUMO + 0(7.40%) HOMO-5 \rightarrow LUMO + 3(55.32%) HOMO-1 \rightarrow LUMO + 5(9.51%)	$\begin{array}{l} \mathbf{d}_{\mathrm{Ru}} + \pi_{2\mathrm{mqn}} + \pi_{\mathrm{NO}} \rightarrow \pi_{2\mathrm{mqn}} \\ \pi_{\mathrm{OAC}} + \pi_{2\mathrm{mqn}} \rightarrow \mathbf{d}_{\mathrm{Ru}} + \pi_{2\mathrm{mqn}}^{*} + \pi_{\mathrm{NO}}^{*} \\ \pi_{2\mathrm{mqn}} \rightarrow \mathbf{d}_{\mathrm{Ru}} + \pi_{2\mathrm{mqn}}^{*} \end{array}$
		245.88	<i>f</i> = 0.0569	HOMO-1 → LUMO + $6(12.36\%)$ HOMO-10 → LUMO + $1(70.28\%)$ HOMO-8 → LUMO + $1(6.26\%)$ HOMO-6 → LUMO + $4(9.37\%)$	$ \begin{split} &\pi_{2mqn} \rightarrow \pi_{2mqn}^{2} \\ &d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{NO}^{*} \\ &d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^{*} \\ &d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} \end{split} $
cis-2 [Ru(OAc)	$(2mqn)_2NO]$				
392	419	465.17	<i>f</i> = 0.0510	HOMO-2 → LUMO + 1(7.43%) HOMO-1 → LUMO + 1(81.1%) HOMO → LUMO(11.47%)	$\begin{array}{l} d_{Ru} + \pi_{OAC} \rightarrow d_{Ru} + \pi_{NO}^{*} \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^{*} \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^{*} \end{array}$
		407.44	<i>f</i> = 0.0707	HOMO-1 → LUMO + 3(4.46%) HOMO → LUMO + 2(85.11%) HOMO → LUMO + 3(10.43%)	$\begin{array}{l} d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow \pi_{2mqn}^{*} \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{2mqn}^{*} + \pi_{NO}^{*} \end{array}$
267	257	259.01	<i>f</i> = 0.2936	HOMO-4 → LUMO + 2(16.11%) HOMO-4 → LUMO + 3(45.22%) HOMO-3 → LUMO + 3(8.89%)	$\pi_{OAC} + \pi_{2mqn} \rightarrow \pi_{2mqn}^*$ $\pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^* + \pi_{NO}^*$ $\pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^* + \pi_{NO}^*$
		258.28	<i>f</i> = 0.0590	HOMO-11 → LUMO(19.77%) HOMO-10 → LUMO(47.12%) HOMO-5 → LUMO + 3(14.53%)	$ \begin{aligned} & d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{NO} \\ & d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi^*_{NO} \\ & \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Pu} + \pi^*_{2mqn} + \pi^*_{NO} \end{aligned} $
		255.08	<i>f</i> = 0.2802	HOMO-10 → LUMO(10.64%) HOMO-10 → LUMO + 1(14.17%) HOMO-1 → LUMO + 3(33.06%)	$\begin{aligned} d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^* \\ d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^* \\ d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{2mqn}^* + \pi_{NO}^* \end{aligned}$
		252.52	<i>f</i> = 0.0887	HOMO-11 → LUMO + 1(19.87%) HOMO-10 → LUMO + 1(21.58%) HOMO-6 → LUMO + 2(27.07%)	$ \begin{aligned} & d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{NO}^* \\ & d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^* \\ & d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow \pi_{2mqn}^* \end{aligned} $
trans [Ru(OAc)(2mqn) ₂ NO]				
399	428	513.55	f = 0.0260	$HOMO-1 \rightarrow LUMO + 1(100\%)^{b}$	$d_{Ru} + \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{NO}$
		426.1	f = 0.1302	HOMO-1 \rightarrow LUMO + 3(3.61%) HOMO \rightarrow LUMO + 2(96.39%)	$\begin{split} & d_{Ru} + \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{2mqn} + \pi^*_{NO} \\ & d_{Ru} + \pi_{2mqn} + \pi_{NO} \rightarrow \pi^*_{2mqn} \end{split}$
271	259	266.16	<i>f</i> = 0.2170	HOMO-7 → LUMO + 1(12.37%) HOMO-5 → LUMO + 5(9.25%) HOMO-4 → LUMO + 2(50.91%)	$\begin{aligned} & d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi_{NO}^{*} \\ & d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{OAC}^{*} + \pi_{NO}^{*} \\ & d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow \pi_{2mqn}^{*} \end{aligned}$
		256.82	<i>f</i> = 0.1187	HOMO-10 → LUMO(23.35%) HOMO-5 → LUMO + 3(12.44%) HOMO-3 → LUMO + 3(27.88%)	$\begin{array}{l} \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{NO} \\ d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{2mqn} + \pi^*_{NO} \\ d_{Ru} + \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{2mqn} + \pi^*_{NO} \end{array}$
		254.23	<i>f</i> = 0.0850	HOMO-11 → LUMO(11.71%) HOMO-10 → LUMO(49.62%) HOMO-3 → LUMO + 3(9.54%)	$ \begin{split} & d_{Ru} + \pi_{OAC} + \pi_{2mqn} + \pi_{NO} \rightarrow d_{Ru} + \pi^*_{NO} \\ & \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{NO} \\ & d_{Ru} + \pi_{2mqn} \rightarrow d_{Ru} + \pi^*_{2mqn} + \pi^*_{NO} \end{split} $
		252.05	<i>f</i> = 0.3002	$HOMO-5 \rightarrow LUMO + 3(12.77\%)$ $HOMO-4 \rightarrow LUMO + 3(14.05\%)$ $HOMO-3 \rightarrow LUMO + 3(15.91\%)$	$\begin{array}{l} d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^* + \pi_{NO}^* \\ d_{Ru} + \pi_{OAC} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^* + \pi_{NO}^* \\ d_{Ru} + \pi_{2mqn} \rightarrow d_{Ru} + \pi_{2mqn}^* + \pi_{NO}^* \end{array}$

^a Oscillator strength.

^b The contribution percentage to the wave functions of the excited states were given in parentheses.

weakening of the Ru—NO bond, and causes the photo-dissociation of NO from ruthenium–nitrosyls to form 5-coordinated transition state, possibly the 2mqn ligands rotate and then recombine with NO to form the isomer.

Infrared spectra

Fig. 4 shows the infrared spectra recorded on KBr Pellet and calculated vibrational frequencies for *cis*-1, *cis*-2 and *trans* isomers. The observed and calculated vibrational frequencies for *cis*-1, *cis*-2

and *trans* isomers in the 2000–1000 cm⁻¹ region were summarized in Table 4. As the hybrid B3LYP functional tends to overestimate the fundamental normal modes of vibration, the computed frequencies were scaled with appropriate values to bring harmonization between theoretical and experimental wavenumbers [52]. In present study, the scale factor is about 0.96 ~ 0.98 for this kind of complexes.

The vibrational modes and complete vibrational frequency assignments could be made with the help of DFT calculation. The four important vibration correspond to the four ligands



Fig. 4. Recorded and calculated IR spectra of *cis*-1 (a), *cis*-2 (b) and *trans* (c) isomer in the 2000–1000⁻¹ cm region (blue: experimental; black: calculated). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coordinated metal central Ru were picked in Table 4. The clear and strong vibration at ~1840 cm⁻¹ is the stretching vibration for NO in Ru–NO group, and that of ~1640 cm⁻¹ is the stretching vibration of CO in –OAc group, respectively. The vibration peak at ~1565 cm⁻¹ and ~1505 cm⁻¹ correspond to vibration of two 2mqn ligands. These spectral signals in IR are characteristic for the isomers, assignment and monitoring of these picks are valuable to investigate the mechanism of the photo-induced reaction [53–55].

NMR spectra

¹H NMR spectra of 2mqn ligands for *cis*-1, *cis*-2 and *trans* isomers in DMSO were shown in Fig. 5. The calculated ¹H NMR

chemical shifts of *cis*-1, *cis*-2 and *trans* isomers, ordered from largest to smallest in order, were summarized in Table 5. For *cis*-1 isomer, the recorded ten ¹H aromatic resonances of the 2mqn ligands range from 6.78 to 8.56 ppm, the calculated values range from 7.14 to 8.70 ppm. For *cis*-2 isomer, the recorded ten ¹H aromatic resonances of the 2mqn ligand range from 6.74 to 8.49 ppm, the calculated value range from 7.18 to 8.58 ppm. For *trans* isomer, the recorded ten ¹H aromatic resonances of the 2mqn ligand is from 7.01 to 8.49 ppm, the calculated value is from 7.32 to 8.58 ppm. The ¹H NMR chemical shifts of $-CH_3$ in -OAc group were also list in Table 5. The average value of recorded three ¹H aromatic resonances is at 1.66, 1.78 and 1.00 ppm for *cis*-1, *cis*-2 and *trans* isomers, and the calculated value for $-CH_3$ in -OAc group of *cis*-1, *cis*-2 and *trans* isomers is at 1.85, 1.99 and

Table 4

Observed and calculated vibrational frequencies (cm⁻¹) and intensities in the 2000–1000 cm⁻¹ region for *cis*-1, *cis*-2 and *trans* isomers.

cis-1		cis-2		trans		Assignment
exp.	cal.	exp.	cal.	exp.	cal.	
1843.53	1924.66	1839.45	1921.25	1821.10	1900.52	v N=O: vs
1621.25	1668.26	1625.33	1663.26	1657.95	1715.64	v C=O (of OAC): m
1566.19	1598.15	1564.15	1596.75	1564.15	1595.08	δ2mqn: m
1505.01	1540.06	1505.01	1540.31	1505.01	1540.83	δ2mqn: m
1429.55	1473.96	1425.47	1465.74	1427.51	1462.47	$\delta 2mqn + v CH3$ (of OAC): s
1370.41	1387.83	1370.41	1387.13	1354.10	1357.98	δ2mqn: m
1315.35	1329.74	1301.08	1354.88	1323.51	1311.77	$\delta 2mqn + v C-O (of OAC)$: s
1278.64	1311.71	1276.60	1328.68	1370.49	1281.63	δ2mqn: m
1107.34	1133.43	1109.38	1133.17	1111.42	1134.95	δ2mqn: m
1011.50 1029.27		1015.57	1030.38	1011.50	1026.44	δ2mqn: m



Fig. 5. Recorded and calculated ¹H NMR spectra of *cis*-1 (a), *cis*-2 (b) and *trans* (c) isomers (blue: experimental; black: calculated). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5

Experimental and calculated ¹H NMR chemical shifts of *cis*-1, *cis*-2 and *trans* isomers (ordered from largest to smallest in order).

	cis-1		cis-2		trans	
	exp.	cal.	exp.	cal.	exp	cal.
	8.56	8.70	8.49	8.58	8.49	8.58
	8.48	8.51	8.44	8.41	8.46	8.44
	7.68	7.78	7.70	7.87	7.63	7.84
	7.66	7.75	7.50	7.78	7.61	7.78
2mqn ligands	7.42	7.73	7.40	7.73	7.42	7.76
	7.39	7.64	7.37	7.50	7.42	7.64
	7.26	7.51	7.23	7.49	7.18	7.47
	7.21	7.47	7.21	7.48	7.16	7.41
	6.85	7.15	7.14	7.36	7.04	7.36
	6.78	7.14	6.74	7.18	7.01	7.32
CH ₃ of –OAc group	1.66	1.85	1.78	1.99	1.00	1.37
CH ₃ of ligand 1	3.17	3.34	3.29	3.30	3.24	3.41
CH_3 of ligand 2	2.84	2.90	2.74	2.83	3.24	3.34

1.37 ppm, respectively. In general, the calculated pattern of ${}^{1}\text{H}$ NMR agree with experimental values, through it is still need to improve the accuracy for calculation assignment.

Conclusions

DFT calculation at B3LYP level with mixed basis set 6-311++G(d,p) and Aug-cc-pVDZ-PP provided more closer optimized structural parameters to their crystal structures. The calculation could provide valuable geometrical information for these compounds. Good agreement between the calculated and recorded UV-vis spectra, FT-IR spectra and ¹H NMR spectra were achieved. Meanwhile, UV-vis, IR spectra were successfully assigned with DFT calculations. DFT calculations for the electronic structures and spectral characteristic of $[Ru(OAc)(2mqn)_2NO]$ complexes provided a rationale for the understanding of photophysical and photochemical properties of the isomers. Furthermore, a density functional theory analysis provides new pathway to investigate the dynamic process and mechanism of photo reaction.

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