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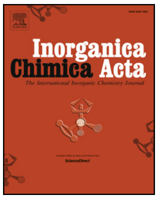

Research paper

Probing electronic structures of redox-active ruthenium-quinonoids appended with polycyclic aromatic hydrocarbon (PAH) backbone

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ABSTRACT

The newly designed electrically neutral complexes [Ru(acac)$_2$(Q)] (**1–3**) involving redox-active polycyclic aromatic hydrocarbon (PAH) derived quinonoids (Q): Q$_1^{(O,O)}$ (**1**) and Q$_2^{(O,NH)}$ (**2**), Q$_2^{(NH,NH)}$ (**3**) (acac = acetylacetonate) were prepared from the metal precursor [Ru^{II}(acac)$_2$(CH$_3$CN)$_2$] and preformed pyrene-4,5-dione (Q$_1$) and partially deprotonated pyrene-4,5-diamine (H$_4$Q$_2$), respectively. The structural characterization of **1–3** established their molecular identities including intermolecular π-π stacking interactions between the extended π-system of pyrene in the adjacent molecules and the hydrogen bonded 1D-polymeric form of **3**. The redox sensitive C-O and C-N bond distances of Q in **1**, **2** and **3** revealed the dominating ground state electronic forms of [(acac)$_2$Ru^{III}-Q$_1^{(O,O)\bullet-}$] (S = 0), [(acac)$_2$Ru^{III}-Q$_2^{(O,NH)\bullet-}$] (S = 0) and [(acac)$_2$Ru^{II}-Q$_2^{(NH,NH)o}$] (S = 0), respectively, where strong antiferromagnetic coupling between Ru^{III}(t$_{2g}^5$) and Q$^{\bullet-}$ resulted in S = 0 state in **1** or **2**. Complexes **1–3** exhibited reversible single oxidation and reduction within the potential window of ± 1.5 V versus SCE in CH$_3$CN, which progressively shifted to the negative potential on moving from **1** to **2** to **3**, primarily due to the difference in electronegativity between O and N donors of Q. The collective consideration of experimental (EPR, electronic spectra) and theoretical (DFT, TD-DFT) results of **1**^{n}-**3**^{n} (n = +1, 0, −1) revealed (i) extensive mixing of metal–ligand orbitals due to the inherent covalency factor and (ii) Q$^{\bullet-}$ and Ru^{II} based oxidations of **1**/**2** and **3**, respectively, led to the {Ru^{III}-Q^o} electronic form at the metal–ligand interface of the oxidized state (**1**$^+$-**3**$^+$), while the reduced state (**1**$^-$ −**3**$^-$) could best be described by the resonating form of {Ru^{II}-Q$^{\bullet-}$}↔{Ru^{III}-Q^{2-}}.

1. Introduction

Accessibility of varying redox states of biochemically relevant quinonoid moieties [1] (Q^0, Q$^{\bullet-}$, Q^{2-} [2]) and ruthenium ion (Ru^{II}, Ru^{III}, Ru^{IV}) as well as extensive delocalization of charge at the Ru-Q interface due to the closeness of their frontier orbitals [3] and the covalency factor [4] have led to unpredictable electronic structural forms (Scheme 1) [5].

Intensive studies using a wide variety of quinonoid frameworks in combination with ruthenium metal fragments having co-ligands of different electronic and steric features have revealed the following significant points. (i) Quite often intermediate description (i.e. the resonating form) fits rather better than any precise electronic form (Ru^{II}-Q^o or Ru^{II}-Q$^{\bullet-}$ or Ru^{II}-Q^{2-}) [6], (ii) emergence of complex phenomenon such as valence tautomerism [7] or redox induced electron transfer (RIET) [8] and (iii) difficulty in sketching a general narrative even out of the analogous systems [9]. Furthermore, potential application of ruthenium-quinonoid systems in catalysis has been addressed [10]. This indeed has prompted the continuing efforts in evaluating newer classes of ruthenium-quinonoid based molecular set up [11].

In this context, the present article deals for the first time with a group of ruthenium complexes (**1–3**) involving polycyclic aromatic hydrocarbon (PAH, pyrene) derived *cis*-quinonoids [12] comprising of O,O (quinone, **1**), O,NH (iminoquinone, **2**) and NH,NH (diminoquinone, **3**) donors.

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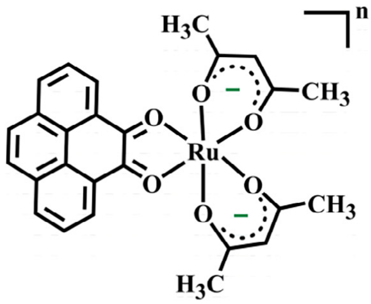

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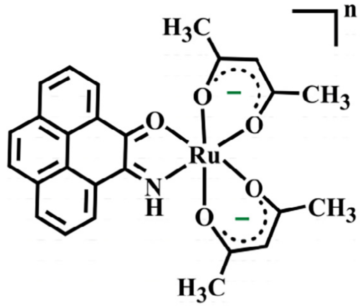

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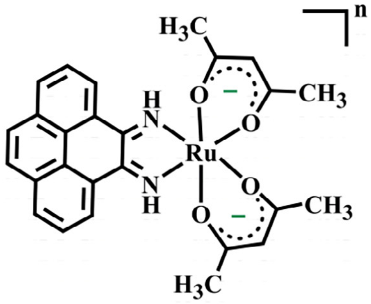

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Besides structural elucidation, electronic structural aspects of $\mathbf{1}^n$-$\mathbf{3}^n$ have been assessed by a combined experimental and theoretical approach. This establishes the intrinsic sensitivity of the valence and spin situations both at the native and accessible reversible redox states of $\mathbf{1}^n$-$\mathbf{3}^n$ ($n = +1, 0, -1$) as a function of the nature of the donor centers in the quinonoids.

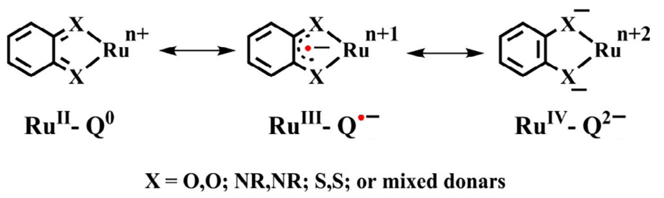
2. Experimental section

2.1. Materials

The precursor complex $Ru^{II}(acac)_2(CH_3CN)_2$ [13] and the ligands [14,15] were prepared according to reported procedures. Pyrene was purchased from Sigma-Aldrich. All other chemicals and reagents were reagent grade and were used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used.

2.2. Physical measurements

^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. The electrical conductivity was checked by using an autoranging conductivity meter (Toshcon Industries, India) in CH_3CN. The EPR measurements were carried out with an X-band (9.5 GHz) Bruker EMX Plus at 4 K. Cyclic voltammetric and differential pulse voltammetric measurements were done using a PAR model 273A electrochemistry system under dinitrogen atmosphere. Glassy carbon working electrode, platinum wire auxiliary electrode, and saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. A platinum wire-gauze working electrode was used for the constant potential coulometry experiment. Tetraethylammonium perchlorate (TEAP) used as the supporting electrolyte and the solute concentration was $\sim 1 \times 10^{-3}$ M. The scan rate used was 100 mV s^{-1}. All electrochemical experiments were performed under dinitrogen atmosphere. Elemental analyses were recorded on a Perkin Elmer 240C elemental analyzer. Spectroelectrochemical studies were performed in CH_3CN/0.1 M Et_4NClO_4 at 298 K using BAS SEC2000. Electrospray mass spectra (ESI-MS) were recorded on a Bruker Maxis Impact instrument (282001.00081).



Scheme 1. Alternate electronic forms of ruthenium-quinonoids.

2.3. Preparation of complexes

2.3.1. Synthesis of $[Ru(acac)_2(Q_1)]$ (**1**)

The metal precursor $[Ru(acac)_2(CH_3CN)_2]$ (100 mg, 0.26 mmol) and pyrene-4,5-dione (Q_1) (61 mg, 0.26 mmol) in 50 mL ethanol were heated to reflux for 5 h under dinitrogen atmosphere. The reaction mixture was then evaporated to dryness under reduced pressure and the solid thus obtained was purified on a neutral alumina column using 2:1 petroleum ether-dichloromethane as eluant. Evaporation of solvent under reduced pressure yielded pure **1**.

1: Yield: 83.47 mg (60%). Anal. Calc. for $C_{26}H_{22}O_6Ru$ (%): C, 58.75; H, 4.17. Found: C, 58.53; H, 4.19. Molar conductivity (Λ_M(CH_3CN, Ω^{-1} cm^2 M^{-1})): 4. ESI$^+$-MS, *m/z*: 532.06 $[\mathbf{1}+H]^+$ [532.04 calc for $C_{26}H_{22}O_6RuH^+$]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.70 (d, 1H, 8.0 Hz, Q_1), 8.25 (t, 1H, 8.0 Hz, Q_1), 8.10 (s, 1H, Q_1), 7.40 (d, 1H, 8.0 Hz, Q_1), 5.22 (s, 1H, acac), 2.69 (s, 3H, acac), 2.09 (s, 3H, acac).

2.3.2. Synthesis of $[Ru(acac)_2(Q_2)]$(**2** and **3**)

A mixture of $[Ru(acac)_2(CH_3CN)_2]$ (100 mg, 0.26 mmol) and pyrene-4,5-diamine (H_4Q_2) (61 mg, 0.26 mmol) in 50 mL ethanol was heated to reflux for 6 h in presence of excess NEt_3 base under dinitrogen atmosphere. The solvent was then removed under reduced pressure and purified by column chromatography on a neutral alumina column, which led to the initial elution of green product **2** by 1.5:1 petroleum ether-dichloromethane followed by the brown product **3** by 1:1 petroleum ether-dichloromethane. Evaporation of solvent under reduced pressure yielded pure complexes **2** and **3**.

2: Yield: 41.66 mg (30%). Anal. Calc. for $C_{26}H_{23}NO_5Ru$ (%): C, 58.86; H, 4.37; N, 2.64. Found: C, 58.63; H, 4.16; N, 2.87. Molar conductivity (Λ_M(CH_3CN, Ω^{-1} cm^2 M^{-1})): 3. ESI$^+$-MS, *m/z*: 531.08 $[\mathbf{2}+H]^+$ [531.06 calc for $C_{26}H_{23}NO_5RuH^+$]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 14.58 (s, 1H, NH(Q_2)), 9.37 (d, 1H, 8.0 Hz, Q_2), 8.82 (d, 1H, 8.0 Hz, Q_2), 8.39 (d, 1H, 8.0 Hz, Q_2), 7.92 (m, 3H, Q_2), 7.85 (d, 1H, 8 Hz, Q_2), 7.72 (t, 1H, 8 Hz, Q_2), 5.50 (s, 1H, acac), 5.27 (s, 1H, acac), 2.56 (s, 3H, acac), 2.30 (s, 3H, acac), 1.90 (s, 6H, acac).

3: Yield: 48.50 mg (35%). Anal. Calc. for $C_{26}H_{24}N_2O_4Ru$ (%): C, 58.97; H, 4.57; N, 5.29. Found: C, 58.75; H, 4.29; N, 5.54. Molar conductivity (Λ_M(CH_3CN, Ω^{-1} cm^2 M^{-1})): 4. ESI$^+$-MS, *m/z*: 530.08 $[\mathbf{3}+H]^+$ [530.06 calc for $C_{26}H_{24}N_2O_4RuH^+$]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 12.06 (s, 1H, NH(Q_2)), 8.72 (d, 1H, 8.0 Hz, Q_2), 7.95 (d, 1H, 8.0 Hz, Q_2), 7.82 (m, 2H, Q_2), 5.26 (s, 1H, acac), 2.35 (s, 3H, acac), 1.67 (s, 3H, acac).

2.4. Crystal structure determination

Single crystals of **1**, **2** and **3** were grown by slow evaporation of their 1:1 CH_2Cl_2-petroleum ether, 1:1 CH_2Cl_2-hexane and 1:2 CH_2Cl_2-CH_3CN solutions, respectively. X-ray crystal data were collected on a RIGAKU SATURN-724 + CCD single crystal X-ray diffractometer using Mo-Kα radiation. Data collection was evaluated by using the CrystalClear-SM Expert software. The data were collected by the