The Preparation, Isolation and Properties of Tris(8-quinolinolato-N^1,O^8)-ruthenium(III)

GARY S. RODMAN and JEFFREY K. NAGLE*

Department of Chemistry, Bowdoin College, Brunswick, Maine 04011, U.S.A.

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Abstract

The synthesis, isolation, and electronic properties of tris(8-quinolinolato-N^1,O^8)ruthenium(III) are described. Elemental analysis, magnetic susceptibility, IR and optical spectroscopies were used to establish the identity of the complex, which was found to exist in the expected low spin arrangement. The significance of these results in relation to analytical procedures based on the reaction between ruthenium and 8-quinolinol is discussed.

Introduction

One of the most widely used complexing agents in analytical chemistry is the 8-quinolinolato anion, qol [1–4]. It forms stable complexes with virtually every metal ion, often of composition $M(qol)_n$, where n is the oxidation number of the metal [1, 3]. While many of these complexes have been thoroughly investigated using a variety of techniques, including X-ray crystallography [5], many second and third row transition metal complexes with qol have not. Recent reports of the isolation of luminescent complexes formulated as $Pt(qol)_2$ and $Ir(qol)_3$ [6–13] have drawn increased attention to such complexes due to their possible involvement in photocatalytic processes [6–8, 11, 12].

Although there have been reports of the use of qol as a complexing agent for ruthenium in analytical applications [14–28], the resultant complexes were apparently never isolated or satisfactorily characterized. An ESR study of a solution assumed to contain $Ru(qol)_3$ has also been described [29].

In contrast to the situation for qol, complexes of 8-quinolinethiolato (qtl) with platinum metals, including Ru(III), have been isolated and characterized [30–33]; the structures of $Pt(qtl)_2$ and $Pd(qtl)_2$ have been established by X-ray crystallography [34, 35].

Here the isolation and characterization of the stable complex $Ru(qol)_3$ is reported for the first time. In addition, some of its spectroscopic and electronic properties are reported and discussed.

Experimental

Tris(8-quinolinolato-N^1,O^8)ruthenium(III)

Powdered sodium hydroxide (0.5 g, 13 mmol) was dissolved in 50 cm^3 of water and Hqol (Aldrich Gold Label, 1.7 g, 12 mmol) was added to form a yellow solution of Naqol. The solution was filtered and 1.0 g, 3.8 mmol, of '$RuCl_3 \cdot 3H_2O$' (Alfa) was added. The mixture was refluxed for 90 min, and the resultant dark precipitate was separated by filtration.

The precipitate was dissolved in 600 cm^3 of trichloromethane and filtered to remove a fine, black, insoluble material. The green trichloromethane filtrate was evaporated to 50 cm^3 and cooled to −20 °C. No crystals formed, and so the solvent was completely evaporated, yielding 0.95 g of dark green powder, corresponding to a 47% yield of $Ru(qol)_3$. The product was recrystallized by dissolving in boiling methylbenzene followed by addition of a tenfold volume excess of 1,1′-oxybis[ethane]. Microcrystals formed upon cooling the mixture to −20 °C. The crystals were washed with 1,1′-oxybis[ethane]. *Anal.* Found: C, 60.51; H, 3.36; N, 7.95. $C_{27}H_{18}N_3O_3Ru$ requires C, 60.78; H, 3.40; N, 7.88%.

Infrared spectra of KBr discs of Hqol and $Ru(qol)_3$ samples dried at 110 °C were obtained using a Perkin-Elmer Model 621 spectrophotometer. Ultraviolet and visible spectra were recorded with a Shimadzu Model UV-240 spectrophotometer.

Magnetic susceptibility studies were carried out using a Gouy balance constructed from a Becker's Sons Type RO. 1 analytical balance, a Harvey Wells Model L-75A electromagnet, and a Harvey Wells Model HS-1050A precision magnet power supply. The applied magnetic flux density was monitored with a Bell Model 640 Incremental Gaussmeter and was maintained at 805 ± 1 mT. The pole face

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*Author to whom correspondence should be addressed.

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diameter was 114 mm and the pole gap 38 mm. A 130 mm length pyrex tube of 3 mm inner diameter was filled with sample to a height of 45 mm and suspended from the balance with nylon string or silver chain. The tube was calibrated with Hg[Co(NCS)$_4$] [36]. All weights were determined as the average of three values. Diamagnetic correction factors of -1.04 mm^3 mol^{-1} for qol and -0.29 mm^3 mol^{-1} for Ru^{3+} were used [36].

Results and Discussion

The elemental analysis and solubility properties both strongly suggest that, as expected, ruthenium(III) and qol react to form a neutral complex of formula Ru(qol)$_3$. This is supported by the shift of the C–O in-plane bend from 470 cm^{-1} in Hqol to 528 cm^{-1} in Ru(qol)$_3$, indicative of metal–ligand bonding [37]. A similar shift was found for Fe(qol)$_3$ [37]. A listing of the IR bands from 300 to 1600 cm^{-1} is given in Table I.

TABLE I. Infrared Stretching Frequencies of Ru(qol)$_3$ in a KBr Pellet.[a]

ν (cm^{-1})	Intensity	ν (cm^{-1})	Intensity
1595	vw	1285sh	vw
1588	w	1272	m
1570	m	1221	w
1561sh	vw	1175	vw
1498	s	1109	m
1459	s	1031	w
1450sh	vw	920	w
1442sh	vw	822	m
1421sh	vw	804	w
1386	vs	780	w
1374	s	755sh	w
1357sh	vw	744	m
1319	s	660sh	vw
		650	w
		595	vw
		528	w
		322	w

[a] Abbreviations: sh, shoulder; vw, very weak; w, weak; m, moderate; s, strong; vs, very strong.

The Bohr magneton number [38] was determined to be 2.00 ± 0.02, well within the 1.8 to 2.0 range of values recently reported for other low-spin Ru(III) complexes [39], including the room temperature values for Ru(H$_2$O)$_6$$^{3+}$ of 2.03 [40] and 1.92 [41]. These values are close to the theoretical spin-orbit value of 2.1 calculated for low spin Ru(III) using a gas phase spin-orbit coupling constant [39]. Only one example of a high spin Ru(III) complex has been reported, NH$_4$[RuCl$_5$(NO)]; its Bohr magneton number is 5.86 [42].

The room temperature UV-visible absorption spectrum of Ru(qol)$_3$ in trichloromethane is shown in Fig. 1. The absorbance at 429 nm was found to obey Beer's law over a concentration range of 1×10^{-6} mol dm^{-3} to 2×10^{-3} mol dm^{-3}, the molar absorptivity ϵ being $1.22 \pm 0.03 \times 10^4$ dm^3 mol^{-1} cm^{-1}. The close similarity between this spectrum and that reported earlier [21] (λ_{max} = 430 nm, $\epsilon = 1.20 \times 10^4$ dm^3 mol^{-1} cm^{-1}) using an extraction procedure to determine ruthenium concentrations suggests that the identity of the species extracted into trichloromethane was Ru(qol)$_3$. In another such study [26] an absorption maximum at 420 nm ($\epsilon = 1.09 \times 10^4$ dm^3 mol^{-1} cm^{-1}) was determined.

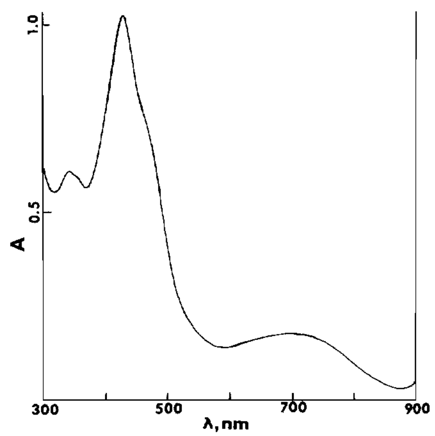

Fig. 1. Absorption spectrum of Ru(qol)$_3$ (8.4×10^{-5} mol dm^{-3}, 1.0 cm cell pathlength) in trichloromethane.

The 429 nm transition, as well as the broad one at 705 nm ($\epsilon = 1.9 \times 10^3$ dm^3 mol^{-1} cm^{-1}), can both be assigned as ligand to metal charge transfer (LMCT) in nature. Jørgensen's equation [43]:

$$\nu_{LMCT}\,(10^{-3}\ \mathrm{cm}^{-1}) = 30(\chi_L - \chi_M) + \Delta SP \qquad (1)$$

where χ_M and χ_L are the optical electronegativities for Ru(III) and qol, respectively and ΔSP is the change in spin-pairing energy accompanying the transition, may be applied to determine χ_L. Using values for $\chi_M = 2.1$ and $\Delta SP = 3.0 \times 10^{-3}$ cm^{-1} [44] and the energies of the two visible transitions determined here, eqn. 1 yields $\chi_L = 2.5$ (705 nm) and $\chi_L = 2.8$ (429 nm). For comparison, a value for bpy of 2.5 is found for the 667 nm band of Ru(bpy)$_3$$^{3+}$ (bpy is 2,2′-bipyridine) [45], previously assigned as LMCT with some intraligand admixture [46]. The value $\chi_L = 2.8$ calculated from the 429 nm transition energy is in good agreement with that calculated from the 578 nm LMCT band [47] of Fe(qol)$_3$, $\chi_L = 2.7$. However, the possibility of ligand field assignments for these transitions cannot be ruled out given the known energies of such transitions in other Ru(III) complexes [41, 44].

Assuming octahedral coordination, there are two geometrical isomers possible for Ru(qol)$_3$, *fac* (C$_3$) and *mer* (C$_1$) [37]. Although preparations of Fe(qol)$_3$ were found to yield principally the *fac* isomer [37, 48, 49], Fe(qol)$_3$ is high spin [49, 50] while Ru(qol)$_3$ is low spin, and the predominance of the *fac* isomer for Ru(qol) cannot be inferred. In fact, a recent chromatographic and NMR study of the complexes Co(qol)$_3$, Rh(qol)$_3$, and Ir(qol)$_3$ [51] revealed the *mer* isomers to be the major products isolated in unrecrystallized form. Far IR [37] or proton NMR [51] of Ru(qol)$_3$ would enable the identity of the principal geometric isomer isolated to be determined.

Even the *fac* and *mer* octahedral isomers are probably idealized geometries given the tendency of low-spin d^5 complexes to Jahn-Teller distort. Appreciable trigonal distortions for Ru(III) chelate complexes have been established by X-ray crystallography [52], and the ESR results reported for Ru(qol)$_3$ are consistent with this possibility [29].

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