

## Synthesis and characterization of Ru(II) complexes with polyfunctional quinazoline-(3H)-4-ones

B Prabhakar†, K Laxma Reddy‡ & P Lingaiah\*

Department of Chemistry,  
Kakatiya University, Warangal 506 009

Received 7 February 1991; revised 16 May 1991;  
accepted 16 August 1991

A few Ru(II) complexes of the type Ru(O-N-O)<sub>2</sub> with tridentate O-N-O donors and of the type RuCl<sub>2</sub>(O-N)<sub>2</sub> with bidentate O-O and O-N donors have been synthesized and characterized on the basis of analytical, conductivity, thermal, magnetic, IR, electronic and PMR spectral data. The IR and PMR spectral data of the metal complexes indicate that the ligands like 2-methyl/phenyl-3-(2'-hydroxybenzalamino) quinazoline-(3H)-4-one (MHBQ/PHBQ) act as uninegative tridentate, 2-methyl/phenyl-3-(carboxymethyl) quinazoline-(3H)-4-one (MCMQ/PCMQ) as uninegative bidentate and 2-methyl/phenyl-3-(furfuralamino) quinazoline-(3H)-4-one (MFQ/PFQ), 2-methyl/phenyl-3-(acetamino) quinazoline-(3H)-4-one (MAQ/PAQ), 2-methyl/phenyl-3-(uramino) quinazoline-(3H)-4-one (MUQ/PUQ) and 2-methyl/phenyl-3-(thiouramino)quinazoline-(3H)-4-one (MTUQ/PTUQ) as neutral bidentate ligands. The electronic spectral data of the complexes indicate that the arrangement around Ru(II) is octahedral.

Polyfunctional ligands like 2-methyl/phenyl-3-(2'-hydroxy-benzalamino) (MHBQ/PHBQ), 2-methyl/phenyl-3-(furfuralamino) (MFQ/PFQ), 2-methyl/phenyl-3-(acetamino) (MAQ/PAQ), 2-methyl/phenyl-3-(carboxymethyl) (MCMQ/PCMQ), 2-methyl/phenyl-3-(uramino) (MUQ/PUQ) and 2-methyl/phenyl-3-(thiouramino) (MTUQ/PTUQ) quinazoline (3H)-4-ones contain both an oxygen/nitrogen donor centre on the substituent at the 3-position to chelate with the metal ions. The ligands may form stable bidentate or tridentate chelates with Ru(II) metal ion. To further probe into the coordinating behaviour of such ligands and in continuation of earlier work<sup>1-5</sup>, we report here the synthesis and spectroscopic characterization of Ru(II) complexes.

### Experimental

All the chemicals used were of AR grade. The ligands were prepared by literature methods<sup>6,7</sup>. The pu-

rity of these compounds was checked by TLC and m.p. determinations. The complex RuCl<sub>2</sub>(DMSO)<sub>4</sub> was prepared by the published method<sup>8</sup>.

### Preparation of complexes

The complex, RuCl<sub>2</sub>(DMSO)<sub>4</sub> (0.2 g), was suspended in toluene (30 ml) and added to three molar excess of the ligand in acetone (40 ml). The contents were refluxed for 1 h to get a clear solution, which was then evaporated under reduced pressure to remove the excess solvent. The residue was treated with diethyl ether when a solid complex precipitated. This was filtered off, washed several times with diethyl ether and dried *in vacuo* over anhydrous calcium chloride.

The elemental analyses of the complexes were carried out at the Micro-Analytical Laboratory, Calcutta University. Molar conductivities of the complexes in DMF were measured using a Digisun digital conductivity meter, model DI-909. The thermal data of the complexes were obtained using a Stanton thermobalance at the Indian Institute of Chemical Technology, Hyderabad. The IR spectra of the ligands and their complexes (4000-200 cm<sup>-1</sup>) in nujol mulls and KBr pellets were obtained with a Perkin Elmer-283 spectrophotometer. The electronic spectra of the complexes in DMF were recorded on a Shimadzu MPS-5000 spectrometer. PMR spectra of the ligands and their complexes in *d*<sub>6</sub>DMSO were obtained using Jeol JNM-FX 100 NMR spectrometer.

### Results and discussion

All the complexes are stable at room temperature and are non-hygroscopic. They are soluble in DMF and DMSO but insoluble in water and common organic solvents.

The analytical data of the complexes are given in Table 1. The molar conductances in DMF at 10<sup>-3</sup>M are low to account for any dissociation (12-22 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) suggesting that they are non-electrolytes.

The decomposition temperatures, determined from their thermograms, are given in Table 1. The complexes are thermally stable upto 200°C and are not hydrated. This is confirmed by their DTA curves which do not exhibit any endothermic peak in the temperature range of 100-200°C and are not hydrated. The sharp decomposition associated with the loss of ligands starts above 250°C. The final decomposition products above 580°C in all the complexes correspond to their metallic oxides. The thermal stability of

† Present address: Chemical Engineering Division,  
National Chemical Laboratory, Pune 411 008.

‡ Department of Chemistry, Regional Engineering College,  
Warangal.

Table 1—Characterization data of ruthenium(II) complexes

Sl. No.	Complexes (colour)	m.p. (°C) <sup>a</sup>	Analyses (%) <sup>b</sup>				Molar conductance <sup>c</sup> (mho cm <sup>2</sup> mol <sup>-1</sup> )
			C	N	H	S	
1	[Ru(MHBQ) <sub>2</sub> ] Brown	270	58.40 (58.44)	12.72 (12.78)	3.62 (3.65)	—	12
2	[Ru(PHBQ) <sub>2</sub> ] Snuff	275	64.50 (64.53)	10.72 (10.75)	3.52 (3.58)	—	13
3	[Ru(MFQ) <sub>2</sub> Cl <sub>2</sub> ] Orange	293	48.22 (48.30)	10.42 (10.56)	3.50 (3.52)	—	18
4	[Ru(PFQ) <sub>2</sub> Cl <sub>2</sub> ] Yellow	315	54.73 (54.84)	9.08 (9.14)	3.33 (3.48)	—	12
5	[Ru(MAQ) <sub>2</sub> Cl <sub>2</sub> ] Brown	315	43.53 (43.56)	13.82 (13.86)	3.62 (3.69)	—	10
6	[Ru(PAQ) <sub>2</sub> Cl <sub>2</sub> ] Brown	305	53.58 (53.60)	11.48 (11.50)	3.52 (3.56)	—	11
7	[Ru(MCMQ) <sub>2</sub> (DMSO) <sub>2</sub> ] Pink	320	45.00 (45.01)	8.01 (8.07)	4.59 (4.61)	9.20 (9.23)	14
8	[Ru(PCMQ) <sub>2</sub> (DMSO) <sub>2</sub> ] Pink	318	52.82 (52.87)	6.82 (6.85)	4.38 (4.40)	7.80 (7.83)	19
9	[Ru(MUQ) <sub>2</sub> Cl <sub>2</sub> ] Reddish brown	293	39.68 (39.72)	15.40 (15.44)	3.54 (3.58)	—	20
10	[Ru(PUQ) <sub>2</sub> Cl <sub>2</sub> ] Yellow	285	48.00 (48.05)	13.12 (13.19)	3.50 (3.53)	—	14
11	[Ru(MTUQ) <sub>2</sub> Cl <sub>2</sub> ] Brown	300	38.00 (38.04)	14.62 (14.79)	3.40 (3.43)	8.42 (8.45)	15
12	[Ru(PTUQ) <sub>2</sub> Cl <sub>2</sub> ] Brown	280	46.28 (46.31)	12.63 (12.71)	3.32 (3.40)	7.24 (7.26)	16

<sup>a</sup> All the complexes decompose above the temperature cited; <sup>b</sup> Values in parentheses are the calculated ones <sup>c</sup> 10<sup>-3</sup>M solutions in DMF at room temperature.

Ru(II) complexes with various ligands is in the order: MCMQ < PCMQ < PFQ ≈ MAQ < PAQ < MTUQ < MFQ ≈ MUQ < PUQ < PTUQ < PHBQ < MHBQ. This order is commensurate with  $\pi$ -electron delocalization, the size of the molecule and the number of the rings formed<sup>9-11</sup>.

In the infrared spectra of all the ligands, a strong band corresponding to  $\nu(\text{C}=\text{O})$  of the quinazoline ring at 1700 cm<sup>-1</sup> is shifted to lower wavenumbers by 40-50 cm<sup>-1</sup> in the complexes, indicating that the carbonyl oxygen is invariably coordinated to Ru(II)<sup>12</sup>. The bands due to  $\nu(\text{OH})$  observed in the spectra of MHBQ, PHBQ<sup>13</sup>, MCMQ and PCMQ<sup>14</sup> disappeared completely in the spectra of their complexes confirming the coordination of these ligands by deprotonation. The band at 1640 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{N})$  of quinazoline remains unaltered in the spectra of complexes, whereas the band at 1600 cm<sup>-1</sup> due to the benzal-amino/furfuralamino group undergoes a red shift by 40-50 cm<sup>-1</sup>, suggesting coordination through the nitrogen<sup>15</sup>.

The  $\nu(\text{N}-\text{H})$  frequency observed in MAQ, PAQ, MUQ, PUQ, MTUQ and PTUQ at 3300 cm<sup>-1</sup> is shifted to a lower region ( $\Delta\nu = 50$  cm<sup>-1</sup>) in the complexes, indicating the involvement of the imino nitrogen in coordination<sup>16</sup>, whereas the bands due to  $\nu(\text{NH}_2)$ <sup>17</sup> (in MUQ, PUQ, MTUQ and PTUQ)  $\nu(\text{C}=\text{O})$  (in MAQ, PAQ, MUQ and PUQ)<sup>6</sup> and  $\nu(\text{C}=\text{S})$  (in MTUQ and PTUQ)<sup>18</sup> at 3400, 1660 and 860 cm<sup>-1</sup>, respectively, remain unchanged in the complexes, indicating the non-participation of nitrogen/oxygen/sulphur of these groups on coordination. The presence of DMSO groups in coordination sphere in Ru(II) complexes with MCMQ and PCMQ is also confirmed from their infrared data<sup>8</sup>. The mode of coordination is further supported by the appearance of  $\nu(\text{Ru}-\text{O})$ ,  $\nu(\text{Ru}-\text{N})$ ,  $\nu(\text{Ru}-\text{S})$  and  $\nu(\text{Ru}-\text{Cl})$  bands around 400, 500, 320 and 300 cm<sup>-1</sup> respectively<sup>19-21</sup>.

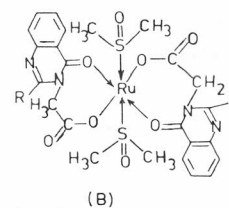
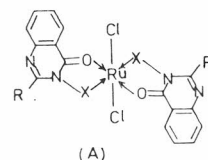
The PMR spectral data of the complexes is presented in Table 2. The PMR spectra of these complexes bear a general resemblance to those of the free ligands, nevertheless some differences are evident beca-

Table 2—PMR spectral data of ligands and their Ru(II) complexes

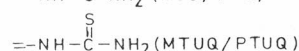
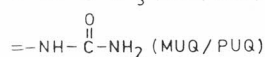
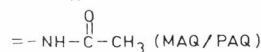
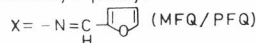
Complex	Chemical shifts [ $\delta$ ppm] <sup>a</sup>		
	—CH <sub>3</sub>	Aromatic protons (m)	—NH/ —NH <sub>2</sub> / —OH
1	2.4 (2.5)	7.2-8.6 (7.1-8.9)	— (10.5) <sup>b</sup>
2	—	7.12-8.92 (7.1-8.9)	— (10.5) <sup>b</sup>
3	2.6 (2.8)	7.25-8.92 (7.20-9.0)	—
4	—	7.15-9.15 (7.1-9.0)	—
5	2.65 (2.75)	7.20-8.7 (7.20-8.9)	8.2 <sup>c</sup> (6.9)
6	—	7.25-9.12 (7.20-8.9)	8.2 <sup>c</sup> (6.9)
7	2.55(2.60) 3.0-3.3 <sup>c</sup>	7.15-8.95 (7.1-8.9)	— (10.2) <sup>d</sup>
8 <sup>c</sup>	3.0-3.4 <sup>c</sup>	7.12-8.92 (7.1-8.9)	— (10.2) <sup>d</sup>
9	2.80(2.95)	7.25-9.10 (7.2-9.0)	8.1 <sup>c</sup> (6.9)
10	—	7.22-9.12 (7.1-8.9)	8.2 <sup>c</sup> (6.8)
11	2.55 (2.66)	7.2-9.1 (7.1-8.9)	8.1 <sup>c</sup> (6.9)
12	—	7.15-8.95 (7.1-8.9)	8.1 <sup>c</sup> (6.8)

<sup>a</sup> Free ligand values are in parentheses; <sup>b</sup> due to the OH of the carboxylic group in MHBQ and PHBQ; <sup>c</sup> due to NH/NH<sub>2</sub> of MAQ, PAQ, MUQ, PUQ, MTUQ and PTUQ; <sup>d</sup> due to the OH of the carboxylic group in MCMQ and PCMQ; <sup>e</sup> the peaks in the range 3.0-3.5 are broad and correspond to CH<sub>3</sub> protons of DMSO in complexes 7 and 8.

use of coordination. The signal due to the proton present on benzalimine carbon in MHBQ and PHBQ and furalimine carbon in MFQ and PFQ is overlapped by the bands of aromatic protons<sup>22</sup>. In complexes, this signal is shifted to  $\delta$  9.6 indicating a decrease in the electron density at benzalimine or furalimine carbon atom, which also supports the participation of nitrogen on coordination<sup>23</sup>. The PMR spectral bands observed for the free ligands due to the hydroxyl (in MHBQ and PHBQ) ( $\delta$ 10.5) and carboxylic (in MCMQ and PCMQ) ( $\delta$ 10.2) protons are absent in the spectra of the complexes confirming the coordination of oxygen by deprotonation<sup>20</sup>. A single intense band in the region  $\delta$ 3.0-3.5 in the complexes of MCMQ and PCMQ with a downfield shift of about 0.7-0.9 ppm from that of free DMSO, indicates the presence of



Where R = methyl / phenyl



(A) Ru(II) complexes of (O-N) donor ligands

(B) Ru(II) complexes of (O-O) donor ligands

S-bonded DMSO ligands in the complexes<sup>8</sup>. The broad signal recorded for NH ( $\delta$ 6.9) proton is shifted to downfield by 1.2 ppm indicating the participation of nitrogen of MAQ, PAQ, MUQ and PUQ in coordination<sup>22,23</sup>. However, the PMR signals due to NH<sub>2</sub> ( $\delta$ 6.4) protons in MUQ, PUQ, MTUQ and PTUQ remain unchanged in the complexes indicating the nonparticipation of nitrogen on coordination.

The electronic spectral bands observed at 2000 and 24000 cm<sup>-1</sup> in Ru(II) complexes may be due to  $^1T_{1g} \leftarrow ^1A_{1g}$  and  $^1T_{2g} \leftarrow ^1A_{1g}$  transitions, respectively characteristic of an octahedral geometry<sup>24</sup>. The absence of splitting of the lower energy band in the electronic spectra of Ru(II) complexes indicates that there is no tetragonal distortion<sup>25</sup>.

All the complexes are found to be diamagnetic in nature with a spin-paired  $^1A_{1g}$  ground term. The absence of a peak in the ESR spectra of these complexes, further confirms the diamagnetic nature of these complexes.

Based on the foregoing discussion, it is tentatively proposed to assign an octahedral geometry for all the Ru(II) complexes as shown in Figure I (A) and (B).

#### Acknowledgement

One of the authors (BP) is grateful to the CSIR, New Delhi, for the award of a senior research fellowship.

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