

## Synthesis and characterization of some ruthenium(II) and ruthenium(III) complexes using Allen's salt

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Received 31 January 1995; revised and accepted 28 April 1995

The Allen's salt,  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Br}_2$ , reacts with a series of neutral ligands viz, 2-(2-thienylpyridine)[TP], 2-(2-methylaminoethyl)-pyridine [MAEP], 2-acetylpyrrole [AP] and N,N'-ethylene-bis-(2'-aminobenzamide) [EBAB] and form Ru(II) complexes by substituting the dinitrogen and three ammonia molecules forming  $[\text{RuL}_n(\text{NH}_3)_2]\text{Br}_2$  ( $n = 1$  or  $2$ ). The reaction between the Allen's salt and the ligands possessing replaceable hydrogens results in the formation of complexes by substitution of ammonia and nitrogen, and also the oxidation of Ru(II) to Ru(III) takes place. The new complexes have been characterized by elemental analysis, conductance, magnetic, IR, ESR,  $^1\text{H}$  NMR and electronic spectral data.

The discovery of the first dinitrogen complex  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  (I)<sup>1</sup>, opened a new area in the coordination chemistry. Since then, a large number of dinitrogen complexes have been reported<sup>2,3</sup>. Reports of Allen *et al.*<sup>4</sup>, on the reduction of bound nitrogen in compound (I) to ammonia was however disproved later. Though this compound was not recognized as a model system of nitrogenase, it was found to be a better starting material for the preparation of Ru(II) and Ru(III) complexes<sup>5</sup>. The other synthetic precursor,  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ <sup>6</sup>, has been extensively used for the preparation of a large number of Ru(II) complexes<sup>7,8</sup>. We describe herein the synthetic application of Allen's salt and characterization of some new ruthenium complexes.

### Experimental

Ruthenium(III) chloride, 2-hydroxynaphthaldehyde [HNA], glyoxal-bis-(2'-hydroxyanil) [GBHA], 2-(2-thienyl)-pyridine [TP], 2-(2-methylaminoethyl)-pyridine [MAEP], 2-acetylpyrrole [AP], were purchased from Aldrich, USA and were used as such. The other ligands, N-(2-hydroxybenzamide) [HBA], 2-amino-N-(2'-carboxylphenyl)-benzamide [ACPB] and N,N'-ethylene-bis-(2-aminobenzamide)

[EBAB] were prepared by the procedure reported elsewhere<sup>9-11</sup>.  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Br}_2$  was prepared by the method developed by Allen and Senoff<sup>1</sup> and stored under  $\text{N}_2$  atmosphere. Hydrazine hydrate, solvents and other chemicals used in the study were of AR grade and were purified by standard methods.

Conductivity measurements were made using a Digisun digital conductivity meter Model DI-909. Vibrating sample magnetometer and Varian ESR spectrometer facilities available at RSIC, IIT Madras were used to obtain magnetic susceptibility data. IR spectra (KBr pellets) were recorded on Perkin-Elmer 283 spectrometer. Electronic spectra were recorded using Shimadzu MPS-5000 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on Bruker 80 SI instrument and elemental analysis were performed on a Perkin-Elmer CHN-analyser 2400 at Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Germany.

### Preparation of complexes

The following general method was used to prepare the complexes from compound (I). 0.5 g (1.337 mmol) of I was suspended in 10 ml distilled water and 2.67 mmol of a bidentate or a tridentate ligand-HNA, HBA, TP, MAEP, AP or ACPBH; or 1.34 mmol of tetradentate ligand GBHA or EBAB in methanol (20 ml) was added slowly with continuous stirring. After the addition of the ligand solution/suspension, the reaction mixture was heated at  $60^\circ$  for  $\sim 2$  h, and then concentrated to about 15 ml under reduced pressure. The solution containing some solid complex was cooled in a refrigerator overnight. The separated crystalline complexes were filtered and washed thoroughly with water and then the acetone and finally dried in a vacuum desiccator over  $\text{CaCl}_2$ , yield, 50-70%.

### Results and discussion

All the complexes are stable at room temperature and are non-hygroscopic. The elemental analysis data and other physical properties of the complexes are presented in Table 1.

The single concentration molar conductance of the complexes, 1-4, in DMF solution ( $10^{-3}$  M) is found to be in the range 29 to 37 mhos  $\text{cm}^2 \text{mol}^{-1}$  indicating them to be 1:1 electrolytes<sup>12</sup>. The

Table 1—Characterization data of the complexes

Sl. No.	Compound	Found (Calcd.), %				$\Omega_M$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{eff}$ (B.M.)
		C	H	N	Br		
1	[Ru(HNA) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br	48.23 (47.41)	3.78 (3.62)	5.52 (5.02)	13.92 (14.33)	30.7	1.82
2	[Ru(GBHA)(NH <sub>3</sub> ) <sub>2</sub> ]Br	35.61 (37.09)	2.92 (3.26)	13.02 (12.86)	15.98 (17.63)	35.5	1.65
3	[Ru(HBA) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br	50.86 (51.58)	3.85 (3.35)	3.89 (4.63)	14.32 (13.20)	29.2	1.94
4	[Ru(ACPB) <sub>2</sub> ]Br	47.89 (48.64)	2.92 (3.21)	8.46 (8.10)	10.02 (11.56)	36.8	1.71
5	[Ru(ACPB) <sub>2</sub> Cl] <sup>9</sup>	51.21 (51.97)	3.27 (3.40)	8.41 (8.66)	5.38* (5.49)	33.0	1.65
6	[Ru(TP)(NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>2</sub>	34.16 (34.84)	3.25 (3.73)	8.86 (9.03)	23.86 (25.75)	68.5	Diamag.
7	[Ru(AP) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>2</sub>	27.22 (28.19)	3.26 (3.55)	11.23 (10.96)	— (31.26)	54.9	Diamag.
8	[Ru(MAEP) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>2</sub>	32.61 (33.87)	4.93 (5.33)	14.56 (14.81)	29.63 (28.17)	65.3	Diamag.
9	[Ru(EBAB)(NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>2</sub>	30.98 (31.39)	3.75 (4.08)	13.82 (14.16)	25.03 (26.94)	56.2	Diamag.
10	[Ru(EBAB)(DMSO) <sub>2</sub> Cl] <sub>2</sub> (ref. 15)	44.65 (44.85)	7.36 (7.53)	10.42 (10.46)	12.98* (13.24)	54.8	Diamag.

\*% of Cl

magnetic susceptibility measurements and ESR spectra indicate that they are paramagnetic with one unpaired electron. This confirms that the diamagnetic Ru(II) has been oxidized to Ru(III). The magnetic moment values of complexes, **1-4**, are in the range 1.65 to 1.94 B.M. as expected for low spin Ru(III) complexes<sup>13</sup>.

The complexes **6-9**, were found to be diamagnetic with molar conductance values of 55-70 mhos cm<sup>2</sup> mol<sup>-1</sup> in solutions of 10<sup>-3</sup> M concentration. The molar conductance of electrolytes in DMF in this range indicates that they are 1:2 electrolytes<sup>12</sup>.

The metal ion precursor, [Ru(NH<sub>3</sub>)<sub>5</sub>(N<sub>2</sub>)]Br<sub>2</sub>, exhibits a characteristic absorption of  $\nu(\text{N}\equiv\text{N})$  at 2114 cm<sup>-1</sup> in IR spectrum. None of the complexes reported in this note show an absorption ~2000 cm<sup>-1</sup> in their IR spectra indicating the loss of N<sub>2</sub> from the coordination sphere. Except, complex **4**, all show absorptions ~1600-1630, 1250-1280 and 770-810 cm<sup>-1</sup> in the IR spectra. These are characteristic of the coordinated ammonia molecules.

The three ligands containing phenolic group, HNA, GBHA and HBA, exhibit characteristic absorptions,  $\nu(\text{O}-\text{H})$  at 3350, 3400 and 3500 cm<sup>-1</sup> respectively. In the spectra of the corresponding complexes, **1**, **2** and **3**, this absorption is absent indicating the deprotonation followed by the coordination to the metal ion. Further, coordination through phenolic oxygen is confirmed by the shift in  $\nu(\text{C}-\text{O})$  by 20-25 cm<sup>-1</sup> towards low frequency side. The  $\nu(\text{C}-\text{O})$  of HNA (1665 cm<sup>-1</sup>) gets shifted to 1640 cm<sup>-1</sup> in its Ru(III) complex indicating the complexation of HNA through phenolic and carbonyl oxygen atoms. In the case of HBA, the  $\nu(\text{C}=\text{O})$  shifted to a higher frequency side by 5 cm<sup>-1</sup> and the amide-II [ $\nu(\text{C}-\text{N}) + \delta(\text{N}-\text{H})$ ] absorption shifted to lower frequency side by 30 cm<sup>-1</sup> confirming that HBA coordinates through phenolic oxygen and the amide nitrogen atoms.

ACPB, a tridentate ligand<sup>7</sup>, coordinates through carboxylic oxygen, amine and amide nitrogen atoms, which is evident from the low frequency shifts of the absorptions at 3490, 3380 and 3160 cm<sup>-1</sup> assignable to  $\nu(\text{N}-\text{H})$  and  $\nu[\text{H}-\text{N}(\text{CO})]$  of

the ligands to 3400, 3240 and 3130  $\text{cm}^{-1}$  respectively in the IR spectrum of complex **4**. The characteristic absorption of  $-\text{COOH}$  group of ACPB at 1680  $\text{cm}^{-1}$  disappeared<sup>9,14</sup> and new absorptions corresponding to  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  of the coordinated carboxylic group were observed at 1550 and 1380  $\text{cm}^{-1}$  respectively. The magnetic and spectral properties of the complex are essentially same as compound obtained by the reaction between  $\text{RuCl}_3$  and  $\text{ACPBH}^7$ , but with a different counter-ion.

Three neutral bidentate ligands—TP, AP and MAEP and the tetradentate EBAB<sup>15,16</sup> have N, S; N, O and N, N as donor atoms. The following shifts in the IR spectra of complexes as compared to those of the ligands and new absorptions in the far-IR region confirm their coordination sites. The characteristic absorptions of TP at 1580  $\text{cm}^{-1}$   $\nu(\text{C}=\text{N})$ ; 740, 695  $\text{cm}^{-1}$   $\nu(\text{C}-\text{S})$  shifted to a lower frequency side to 1565 and 700, 665  $\text{cm}^{-1}$  indicating the coordination of TP through nitrogen and sulphur atoms of two heterocyclic rings. The ligand AP exhibits absorptions of  $\nu(\text{N}-\text{H})$  at 3200  $\text{cm}^{-1}$ ,  $\nu(\text{C}=\text{O})$  at 1690  $\text{cm}^{-1}$  and 1580, 1180  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$  which shifted to 3110, 1635, 1520 and 1130  $\text{cm}^{-1}$  on coordination, confirming the involvement of ring nitrogen and the carbonyl oxygen in chelation to the Ru(II) ion. MAEP having a ring nitrogen and a secondary amine nitrogen as electron pair donating atoms exhibit characteristic absorptions at 3400, 3380  $\text{cm}^{-1}$   $\nu(\text{N}-\text{H})$  and 1600  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$ . The shift of these absorptions in complex **8**, to a lower frequency side to 3300, 3210 and 1580  $\text{cm}^{-1}$  respectively is evident of the coordination through amine and ring nitrogen atoms. The IR spectrum of EBAB shows absorptions at 3460, 3360, 3275  $\text{cm}^{-1}$  assignable to  $\nu(\text{N}-\text{H})$ , 1625  $\text{cm}^{-1}$   $\nu(\text{C}=\text{O})$ -amide-I and at 1550  $\text{cm}^{-1}$  [ $\nu(\text{C}-\text{N}) + \delta(\text{N}-\text{H})$ ]-amide-II]. The characteristic  $\nu(\text{N}-\text{H})$  and amide-II absorptions shifted to 3350, 3270, 3200 and 1520  $\text{cm}^{-1}$  in the spectrum of the complex **9**, confirming the coordination of EBAB through amide and amine nitrogen atoms. The amide  $\text{C}=\text{O}$  stretching frequency shifted to a higher frequency side by 5  $\text{cm}^{-1}$ , indicating that the carbonyl oxygen is not coordinated to Ru(II). Further, it is interesting to compare the two complexes,  $[\text{Ru}(\text{ACPB})_2]\text{Br}$  with  $[\text{Ru}(\text{ACPB})_2]\text{Cl}^7$  and  $[\text{Ru}(\text{EBAB})(\text{NH}_3)_2]\text{Br}_2$  with  $[\text{Ru}(\text{EBAB})(\text{DMSO})_2]\text{Cl}_2^{15}$ . The first pair of compounds are identical in conductance, magnetic, IR, electronic and ESR spectral properties. They have different anions outside the coordination sphere. The latter pair of complexes are hexa-coordinated diamagnetic Ru(II) complexes having the tetra-

dentate ligand EBAB. Remaining two coordination sites are satisfied by the monodentate ligands  $\text{NH}_3$  and DMSO respectively, which are present in the starting compounds. An interesting difference in the reaction of  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$  with EBAB is the substitution of two DMSO molecules and two  $\text{Cl}^-$  ions from the coordination sphere of the metal ion by EBAB. The complex **9**, is formed by the substitution of the dinitrogen ligand and three ammonia molecules.

The trivalent low-spin Ru(III), a  $d^5$  ion, with  $^2T_{2g}$  as the ground term exhibits a complex electronic spectrum with eight transitions to high energy doublet states and two to quartet states<sup>17</sup>. Three of the transitions are of considerable intensity, while others are of low intensity and they are frequently obscured. The electronic spectra of Ru(III) complexes is often composed of well defined ligand to metal charge transfer bands<sup>17,18</sup>. The electronic spectra showed that all the complexes exhibit an absorption  $\sim 30,000 \text{ cm}^{-1}$ , which may be attributed to the  $\pi\text{Br} \rightarrow t_{2g}$  outer-sphere charge transfer in the ion-pair<sup>18</sup>. The complexes **1** and **3** show absorptions at 34500 and 36105  $\text{cm}^{-1}$  attributable to  $\pi\text{O} \rightarrow t_{2g}$ , while the complexes **2** and **4** exhibit absorptions at 27700 and 27879  $\text{cm}^{-1}$  respectively corresponding to  $\pi\text{N} \rightarrow t_{2g}$  transitions from the ligands. The two low energy spin-forbidden transitions corresponding to  $^4T_{1g} \leftarrow ^2T_{2g}$  and  $^4T_{2g} \leftarrow ^2T_{2g}$  and the high energy transition to doublet state  $^2A_{2g}$ ,  $^2T_{1g} \leftarrow ^2T_{2g}$  are observed in the electronic spectra of the four Ru(III) complexes investigated in the range 20184-23809, 18544-21126 and 16129-18691  $\text{cm}^{-1}$ . The parameters Dq, B and C have been evaluated using the electronic transitions<sup>15</sup> and are found to be 2688, 2432, 2508, 2127  $\text{cm}^{-1}$  (Dq); 512, 308, 304, 210 (B); 2047, 1231, 1217 and 840 (C) for complexes **1**, **2**, **3** and **4** respectively. The considerable decrease in the value of the Racah interelectronic repulsion parameter B and the  $\beta$  value (0.33-0.81) compared to those of free ion values suggest that the metal-ligand bonds are covalent.

The six coordinate low-spin Ru(II) species with  $d^6$  configuration has  $^1A_{1g}$  ground term which exhibits two spin-allowed transitions to  $^1T_{1g}$  and  $^1T_{2g}$  states in centro-symmetric complexes. Three of the four Ru(II) complexes (**6**, **7** and **8**) isolated have two bidentate ligands and two ammonia molecules, while the complex **9**, has a tetradentate nitrogen donor and two ammonia molecules. The low symmetry structures for these complexes can be excluded from the electronic spectral data. All the complexes exhibit only one charge transfer transition in high energy region and two

*d-d* transitions. The low symmetry complexes (the tetragonally distorted or *cis*-complexes), are expected to show more absorption since  ${}^1T_{1g}$  spans  ${}^1E_g + {}^1A_{2g}$  and  ${}^1T_{2g}$  level spans  ${}^1B_{2g} + {}^1E_g$ . Further, two MLCT transitions are expected. The electronic spectral absorptions of the complexes indicate the *trans*-disposition of the two ammonia molecules and that the complexes are essentially centro-symmetric. The spectral absorptions of complexes 6-9, assignable to  ${}^1T_{1g} \leftarrow {}^1A_{1g}$  and  ${}^1T_{2g} \leftarrow {}^1A_{1g}$  are found in the range 16130-18350 and 22220-23050  $\text{cm}^{-1}$  respectively. The ligand field parameters, Dq (1787-1935  $\text{cm}^{-1}$ ), B (250-435) and C (1000-1935) confirm the covalent nature of the metal-ligand bond.

The  ${}^1\text{H}$  NMR spectra of diamagnetic Ru(II) complexes and the corresponding ligands have been recorded in DMSO- $d_6$  and the data ( $\delta$ , ppm) are given below:

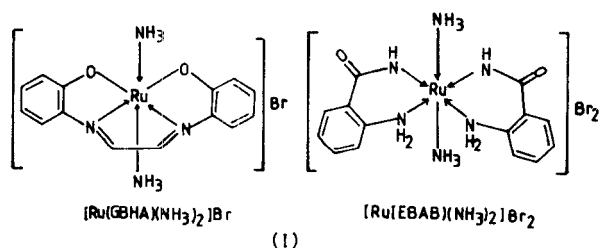
TP	7.1-8.0 <sub>(m)</sub>	Complex 6	6.8-8.0	aromatic H
MAEP	1.5-3.0	Complex 7	1.15-3.0	aliphatic H
	7.5		6.6	-NH
	7.0-7.3		7.0-7.3	aromatic H
AP	2.4	Complex 8	2.1	aliphatic H
	6.16		5.85	-NH
	6.7-7.1 <sub>(m)</sub>		6.7-7.1 <sub>(m)</sub>	aromatic H
EBAB	4.3-4.7 <sub>(m)</sub>	Complex 9	3.8-4.0 <sub>(m)</sub>	aliphatic H
	3.1		2.9	-NH <sub>2</sub>
	8.2		8.0	-C(O)-NH

All complexes exhibit a resonance signal between 4.0 and 4.6 ppm (6H's) corresponding to the coordinated ammonia molecules.

The aromatic proton resonance signals of TP at 7.1-8.0 ppm exhibits a shift of the lower end i.e., 6.8-8.0 ppm on coordination. The aliphatic or aromatic protons of MAEP show a similar trend, but the resonance signal corresponding to secondary amine proton changes from 7.5 ppm to 6.6 ppm, indicating the coordination of the amine nitrogen. The -CH<sub>3</sub> and -NH proton resonance signals of AP at 2.4 and 6.16 ppm got shifted to 2.1 and 5.85 ppm respectively, confirming the coordination of AP through carbonyl oxygen and ring nitrogen atoms. Similarly, the shifts in the resonance signals of aliphatic, aromatic, amine and amide protons of EBAB on coordination confirm the complexation of the ligand to  $[\text{Ru}(\text{NH}_3)_2]^{2+}$  group through amine and two amide nitrogen atoms.

The ESR spectra of the four complexes (1-4) have been recorded at room temperature and are

found to be simple three line spectra indicating that the complexes are of low spin Ru(III). The high spin Ru(III) complexes show many lines in the ESR spectra, because of splitting of each of the five transitions of Ru(III) ( $d^5$  ion) into six lines by the interaction with the nuclear spin ( $I = 5/2$ ) of  ${}^{99}\text{Ru}$  and  ${}^{101}\text{Ru}$  nuclei. Thus a total of thirty lines, i.e., a more complex spectra are expected for high spin Ru(III). The  $g$  values ( $g_1$ ,  $g_2$  and  $g_3$ ) calculated from the ESR spectra are in the range of 2.0-2.65. These are in the same order of the reported values of 1.5-3.7 (refs 19, 20). The ESR spectrum of complex 4,  $[\text{Ru}(\text{ACPB})_2]\text{Br}$  is similar to that of the complex  $[\text{Ru}(\text{ACPB})_2]\text{Cl}$  prepared by a different method using  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$  as the starting chemical<sup>7</sup>. The tentative structures proposed for the six coordinated ruthenium(II) and ruthenium(III) complexes are shown in Structure I.



### Acknowledgement

The authors are thankful to the UGC, New Delhi, for financial support. The spectral data recorded at RSIC, IIT, Madras, is also acknowledged.

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