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Study of binuclear ruthenium(II) complexes of amide ligands with two bidentate coordinating sites

Sujit Dutta and Pabitra K. Bhattacharya*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002, Gujarat, India

Binuclear ruthenium(II) complexes of binucleating amide ligands (L^1–L^5), obtained by the reaction of pyridine-2-carboxylic acid with aromatic and aliphatic diamines, have been prepared by the reaction of one equivalent amide ligand with two equivalents of [Ru(*dmso*)$_4$Cl$_2$]. The complexes are diamagnetic at room temperature. The metal to ligand ratio and the geometry around the ruthenium(II) centres in these complexes have been established with the help of ^{1}H NMR, ^{13}C NMR, IR and positive ion electrospray mass spectral studies.

The chemistry of the amide complexes of ruthenium receives ample attention in the context of metal peptide chemistry[1]. In this paper we are reporting the syntheses and characterisation of binuclear Ru(II) complexes of binucleating amide ligands.

Syntheses of the complexes of the type [Ru$_2$(L)(*dmso*)$_4$Cl$_4$] were achieved by refluxing two equivalent [Ru(*dmso*)$_4$Cl$_2$][5] with one equivalent of the amide ligands (L_1–L_5)[6]. The microcrystalline solid was isolated from the cold reaction mixture by filtration.

The IR, electronic spectral and cyclicvoltammetric data are given in Table 1 and elemental analytical and the ^{1}H NMR spectral data are given in the experimental section of the full text.

The microanalytical data (C, H, N) of these complexes are in good agreement with the calculated values, which conform to the gross composition of the binuclear complexes shown in Fig. 1.

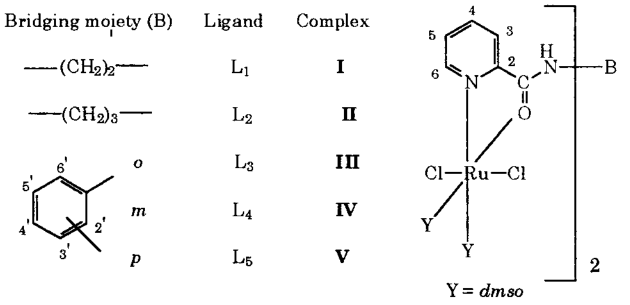


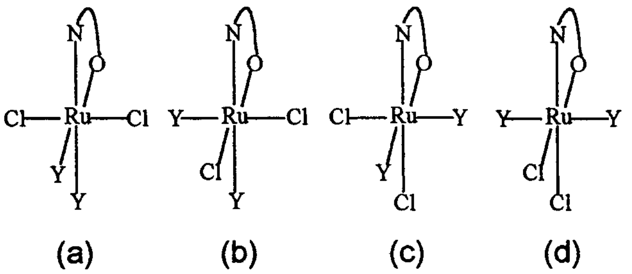
Fig. 1 The proposed structures of the complexes.

Solid state magnetic moment studies show that the binuclear complexes are diamagnetic as expected for the bivalent state (low spin, d^6, $S = 0$) of each ruthenium centre.

All the complexes exhibit two intense bands *ca* 410 nm and 325 nm with high extinction coefficient values in the electronic spectra, assigned to $t_2^6 \rightarrow \pi^*$ metal to ligand charge transfer transitions[8]. In the IR spectra of the complexes the negative shift of the νco of the amide linkage, compared to the free ligand indicates[9] that the oxygen atom of the amide linkage is coordinated to the ruthenium(II) centre. The positive shift in the νso compared to the same in the free *dmso* indicates[10] that the *dmso* molecules coordinate to the ruthenium(II) centre from the sulphur atom. The sharp band at 322 cm^{-1} (medium intensity) and at 283 cm^{-1} (high intensity) are assigned to $\nu_{Ru–Cl}$[11] and $\nu_{Ru–N(pyridine)}$[12] stretching modes, respectively.

The complexes **I** - **IV** display well resolved ^{1}H NMR spectra in *dmso*-d_6, while due to poor solubility the ^{1}H NMR spectrum of **V** could not be recorded. The presence of a sigma plane divides the complexes into two equivalent halves. Thus the signals appearing in the respective ^{1}H NMR spectra of the complexes can be assigned to the two equivalent sets of protons. The signal due to the NH protons of the amide linkage in the complexes appears at a down field region and integrates to two protons, this indicates that the deprotonation of the NH protons of the amide linkage does not take place, and this supports that the oxygen atom of the amide linkage co-ordinates to the ruthenium(II) centre. In the proton decoupled ^{13}C NMR spectrum of one representative complex, **I**, the signal at δ 170.5 has been assigned to the two equivalent carbon atoms of two amide linkages.

The Ru(II) centres in each of the five binuclear complexes may, in principle, exist in the following four geometrical isomeric forms:



In the IR spectra a single $\nu_{Ru–Cl}$ band is expected for a linear grouping of the *trans*-RuCl$_2$ moiety (as in a), whereas two $\nu_{Ru–Cl}$ bands of equal intensity are expected for a *cis*-RuCl$_2$ moiety (as in b, c and d)[13]. The appearance of a single $\nu_{Ru–Cl}$ band excludes the isomers b, c and d. Further in the ^{1}H NMR spectra, the appearance of two different signals for the methyl groups of the co-ordinated *dmso* molecules indicates that they are mutually *cis*- in orientation at each Ru(II) centre[14]. Thus the arrangements of the donor atoms around the Ru(II) centres is as depicted in (a) (Y = *dmso*).

The electrospray mass spectra of two representative complexes **II** and **V** were recorded. The peaks observed at *m/z* 941.8 for **II** and at *m/z* 974.4 for **V** correspond to the molecular ions of the corresponding complexes **II** and **V** respectively. (Calculated molecular weight : 940.1 for **II** and 974.1 for **V**).

The electrochemical properties of the complexes were studied in dimethylsulfoxide. The complexes **I, II** and **IV** show a quasi-reversible response, presumably due to two electrons, in the anodic side of the voltammogram (eqn 1) due to Ru(II)/ Ru(III) couple of both the ruthenium(II) centres simultaneously.

$$[(dmso)_2Cl_2Ru^{II}\text{–}Ru^{II}Cl_2(dmso)_2] \rightarrow$$
$$[(dmso)_2Cl_2Ru^{III}\text{–}Ru^{III}Cl_2(dmso)_2] + 2e- \qquad (1)$$

The complexes **III** and **V** show two reversible impulses, presumably each impulse is due to a single electron, in the anodic side of the cyclic voltammogram. Thus for **III** and **V** the oxidation of the ruthenium(II) centres is stepwise, where each oxidation process should be due to single electron, according to eqn 2.

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[*] To receive any correspondence.

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\begin{gathered}
[(dmso)_2\mathrm{Cl}_2\mathrm{Ru}^{\mathrm{II}}\text{–}\mathrm{Ru}^{\mathrm{II}}\mathrm{Cl}_2(dmso)_2] \rightarrow \\
[(dmso)_2\mathrm{Cl}_2\mathrm{Ru}^{\mathrm{III}}\text{–}\mathrm{Ru}^{\mathrm{II}}\mathrm{Cl}_2(dmso)_2] + 1e^{\cdot} \rightarrow \\
[(dmso)_2\mathrm{Cl}_2\mathrm{Ru}^{\mathrm{III}}\text{–}\mathrm{Ru}^{\mathrm{III}}\mathrm{Cl}_2(dmso)_2] + 1e^{\cdot} \qquad (2)
\end{gathered}
$$

The stepwise oxidation indicates interaction between the two ruthenium(II) centres through the bridging group. It is interesting to observe that no interaction between the ruthenium(II) centres is observed in case of the aliphatic diamide and *m*-phenylenediamide bridges. Whereas, interaction exists in the case of the *o*- and *p*-phenylenediamide bridges. This shows that the electronic interaction can take place through the π-delocalised aromatic rings and the effect is most felt in the case of complexes with *o*- and *p*- phenylenediamide bridges, where the electronic effects are maximum.

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Techniques used : C, H, N analysis; UV-VIS, IR, 1H NMR, 13C NMR, and electrospray mass spectral analysis; magnetic moment measurement and cyclic voltammetry.

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