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The Nature of Ru(bipy)$_2$Cl$_2$ in Dimethylsulphoxide Solutions

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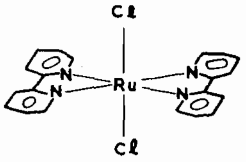
In recent years there has been an upsurge in interest in 2,2'-bipyridine (bipy) complexes of ruthenium(II) [1–5]. One reason for this has been the possible use of a derivative of Ru(bipy)$_3^{2+}$ as a catalyst in the photodecomposition of water [6, 7]. The route to one variety of these potential catalysts involves the reaction of a substituted bipyridyl with Ru(bipy)$_2$Cl$_2$. This bis bipyridyl complex can exist in two isomeric forms: the *trans* complex (1) where the two chloride ligands occupy axial sites, and the *cis* complex (2) where the chloride groups are in adjacent coordination sites. The published methods [6, 8, 9] for the preparation of Ru(bipy)$_2$Cl$_2$ do not contain any specific precautions against formation of either isomer and it is possible that mixtures of the isomers are produced.† It appears that the solubility, in 10% ethanol, of any *trans* isomer formed is less than that of the *cis* isomer, and hence recrystallisation enables mixtures to be resolved [10]. While both isomers, through rearrangements in a transition state, may be able to react with a bipyridyl derivative (bipy') to give Ru(bipy)$_2$(bipy')$^{2+}$, the *cis* isomer has the chloride groups in positions already suitable for this replacement and the reaction should be faster than with the *trans* isomer [11]. It is therefore of some interest to know the nature of the species present in solution.



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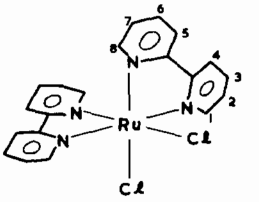

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Some evidence of relevance to this question has been obtained using i.r. and n.m.r. spectroscopy but the data is not wholly conclusive. Krause, by observation of the region in the i.r. around 700 cm^{-1}, concluded that the more soluble species is the *cis* isomer [10]. On the other hand the published ^{1}H n.m.r. spectrum, run in d$_6$-DMSO, could not be solved on the premise that just one isomer is present [12]. The authors concluded that either a mixture of isomers is present or there is a solvent interaction with one and/or other of the isomers. We have re-examined the ^{1}H n.m.r. spectrum and wish to report that it demonstrated that a single isomer was observed in solution.

Experimental

The compound Ru(bipy)$_2$Cl$_2$ was prepared by the method given by Whitten *et al.* [6]. ^{1}H n.m.r. spectra were run on Jeol FX-100 and Varian SC-300 spectrometers with d$_6$-DMSO as the solvent and the samples run at 30 °C. Ultra-violet/visible spectra were recorded on a Pye Unicam SP1750 over the range 320–700 mm. The solvent (DMSO) was dried by distillation, under reduced pressure, from CaH$_2$, and was stored over molecular sieves. In measuring the kinetic parameters 5 ml portions of solutions were removed from the reaction vessel at set intervals and quenched by addition to a further 5 ml aliquot of solvent that was at room temperature. The reaction was investigated at different temperatures in the range 78°–97 °C. Spectra were run on the diluted samples.

Results and Discussion

The n.m.r. spectra of the *cis* and *trans* isomers of diamagnetic Ru(bipy)$_2$Cl$_2$ should be sufficiently different to allow them to be distinguished by this technique. For the *trans* isomer (1) the four pyridine rings have equivalent environments whereas in the *cis* isomer (2) the pyridines of each ligand are inequivalent, but each is equivalent to one pyridine ring of the other bipyridyl. Thus the aromatic region in the spectrum of the *trans* isomer should contain four multiplets, while that of the *cis* isomers should consist of signals from eight distinguishable hydrogens. Figure 1 is part of the recorded spectrum of Ru(bipy)$_2$Cl$_2$ in d$_6$-DMSO, the solid having been completely taken into solution without any warming, This spectrum can be entirely assigned to the *cis* isomer, thereby demonstrating that it is the sole species present in solution. This result is at variance with the data published by Lytle *et al.*, but their sample was refluxed in solvent prior to running the

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†There is some debate over the existence of the *trans* isomer. Steric interactions between the 6,6' protons in the two ligands are thought to make this stereochemistry unattractive (W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, *12*, 135 (1969), and references therein) but Krause (ref. 10) reports the preparation of *trans*-[Ru(bipy)$_2$(ph)$_2$](ClO$_4$)$_2$. We have chosen not to discount the possibility that the *trans* isomer exists.

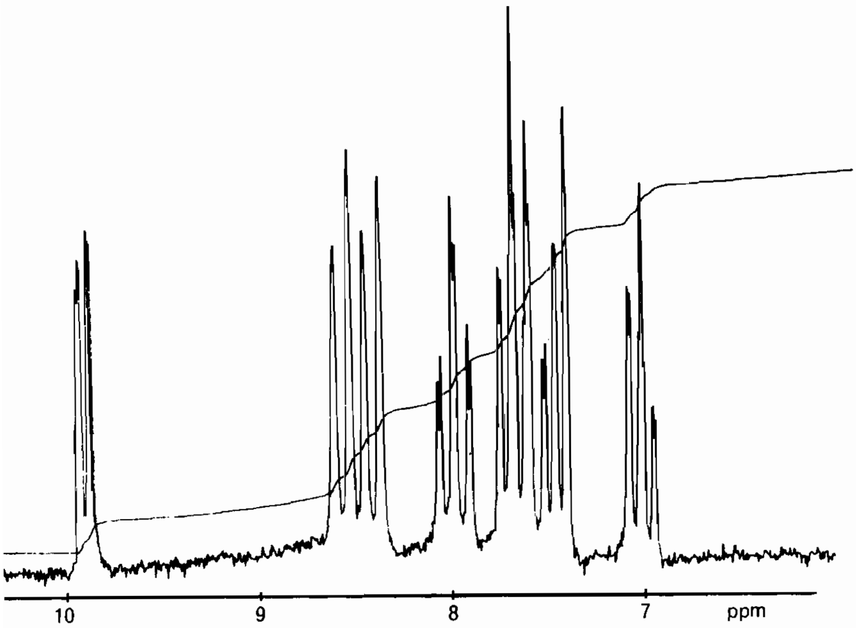

Fig. 1. The aromatic region of the 100 MHz ^1H nmr spectrum of $Ru(bipy)_2Cl_2$. Chemical shifts and their assignments, measured from the 300 MHz spectrum, are as follows: H_1 9.89, H_2 7.71, H_3 8.01, H_4/H_5 8.46/8.59, H_6 7.65, H_7 7.06, H_8 7.45.

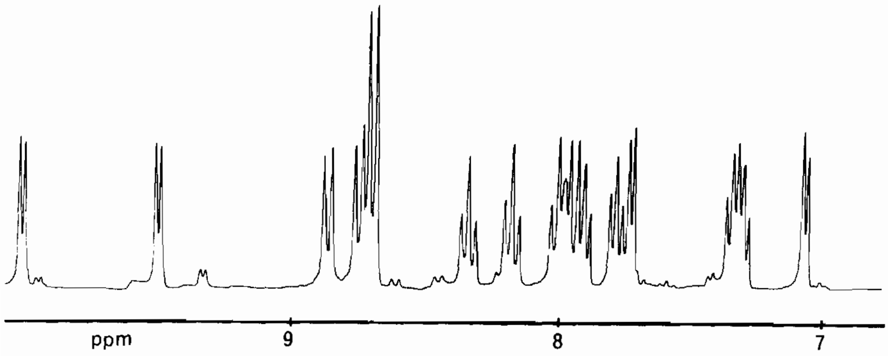

Fig. 2. The aromatic region of the 300 MHz ^1H nmr spectrum of the product that results from warming $Ru(bipy)_2Cl_2$ in d_6-DMSO to 120 °C, $[Ru(bipy)_2(Cl)(DMSO)]Cl$.

spectrum [12]. To investigate whether this heating might be the cause of the discrepancy, a sample of $Ru(bipy)_2Cl_2$ in d_6-DMSO was warmed to 120 °C for a few minutes and then cooled before the spectrum was recorded. The aromatic region, which is similar to that published previously but is better resolved, is more complicated than that in Fig. 1. To simplify the trace, the sample was run on a 300 MHz instrument and the spectrum, Fig. 2, indicates that there are sixteen distinguishable hydrogens present. This demonstrates that the four pyridine segments per molecule have different environments, which in turn provides a clue to the nature of the product present in solution. A configuration that fits this evidence is that of *cis*-$Ru(bipy)_2Cl_2$ only with one chloride ion replaced with a different monodentate ligand; in this case a molecule of solvent. Indeed, this is the only possible arrangement given the assumptions that the metal ion is six coordinate and that the bipyridyls still act as bidentate ligands.

The reaction, at elevated temperatures, between $Ru(bipy)_2Cl_2$ and DMSO was further investigated by obtaining the kinetic parameters of the process. Maxima occur in the u.v./visible spectrum of $Ru(bipy)_2Cl_2$ in DMSO at 384 nm and 560 nm, and at 430 nm for the product. Following the absorbance of the maximum at 560 nm provided information about the extent of reaction. The presence of isosbestic points in the kinetic runs indicates that only two species are involved in the reaction. This lends support to the idea that one chloride group is replaced in the solvolysis, and that the product is *cis*-[Ru(bipy)$_2$(Cl)(DMSO)] Cl. The reaction has a first order rate constant, and, from the n.m.r. evidence, the *cis* configuration is retained in the product. An Arrhenius plot gives the energy of activation as 19(1) kcal mol^{-1}. It is interesting to note that an additional point on this line comes from published data on the reaction of Ru(bipy)$_2$Cl$_2$ with pyridine (py) in DMSO [13]. These measurements were made at 56 °C and the product was [Ru(bipy)$_2$(Cl)(py)] Cl.

To summarise, ^{1}H n.m.r. spectroscopy in d$_6$-DMSO demonstrates that the synthesis of Ru(bipy)$_2$-Cl$_2$ by the method of Whitten *et al.* gives the *cis* isomer only. On heating the solution solvolysis occurs: one chloride ligand is replaced by a molecule of DMSO with retention of configuration about the Ru(II).

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