Inorganica Chimica Acta, 70 (1983) 251–253

NMR Studies on Ruthenium(II) α,α'-Diimine Complexes; Further Evidence for Unique Reactivity at $H_{3,3}'$ of Coordinated 2,2'-Bipyridines

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Received July 17, 1982

The ^1H NMR spectra of the complexes $[RuL_3](BF_4)_2$ are reported (L = 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 5,5'-dimethyl-2,2'-bipyridine or 1,10-phenanthroline). The relaxation behaviour of the protons attached to the ligands has been studied, and T_1 measurements are shown to be a valuable aid in the assignment of the spectra of such complexes. T_1 measurements confirm other chemical evidence for the unique nature of $H_{3,3}'$ of coordinated 2,2'-bipyridines, resulting from steric interactions.

Introduction

Tris(2,2'-bipyridine) complexes of transition metal ions have been known for many years [1–3], and have found applications in fields as diverse as colorimetric analysis [4] and solar energy conversion [5]. A number of recent observations have emphasised that the $H_{3,3}'$ protons of the ligand (Fig. 1) possess a unique reactivity in such octahedral complexes. Thus, Constable and Seddon have demonstrated that these protons are acidic, and undergo deuterium exchange on treatment with strong bases in the presence of a deuteron source [6], whilst Serpone has characterised *ortho*metallated iridium complexes in which the metal is directly bonded to C_3 of the ligand [7]. It is likely that some of the well-documented anomalies in the reactions of such complexes may be attributed to this hitherto undetected reactivity [8]. Many studies of α,α'-diimine complexes rely heavily on NMR techniques, and so it is very surprising that there have been few rigorous NMR studies of such complexes [9, 10]. This paper describes the use of T_1 relaxation time measurements in the assignment of the ^1H NMR spectra of ruthenium(II) α,α'-diimine complexes.

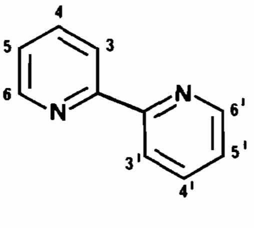

Fig. 1. The 2,2'-bipyridine ligand.

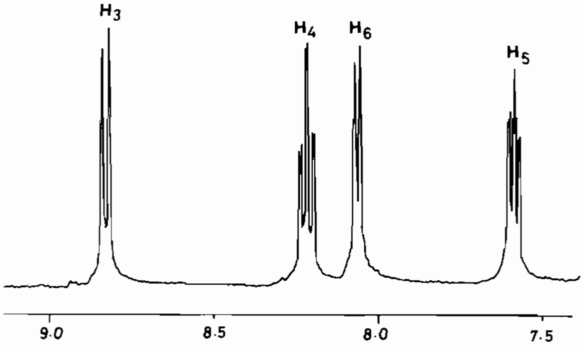

Fig. 2. The ^1H NMR spectrum (400 MHz) of $[Ru(bipy)_3](BF_4)_2$ in Me_2CO-d_6.

Results and Discussion

The 400 MHz ^1H NMR spectrum of $[Ru(bipy)_3](BF_4)_2$ is shown in Fig. 2. It is evident that on the ^1H NMR time scale the two rings are equivalent. Simple decoupling experiments established that the lowest field doublet at δ 8.827 was strongly coupled to the δ 8.225 multiplet, and that the δ 8.069 doublet was strongly coupled to the δ 7.585 multiplet, but it was not possible to determine whether the δ 8.827 doublet was due to H_3 or H_6. Experience with simple heterocycles suggests that the lowest field resonance should be assigned to H_6 [11] and, indeed, the lowest field doublet in the ^1H NMR spectrum of

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TABLE I. Chemical Shift and Coupling Constant Data for Ruthenium(II) α,α′-Diimine Complexes. 5 mmol solutions of the tetrafluoroborate salts in CD_3COCD_3. 400 MHz, 12 transients, 90° pulse, 30 °C.

Compound	Chemical Shift (δ)				Coupling Constants (Hz)		
	H_3	H_4	H_5	H_6			
$[Ru(bipy)_3]^{2+}$	8.827	8.225	7.585	8.069	$J_{5,6}$ 5.5	$J_{4,5}$ 7.5	$J_{3,4}$ 7.8
					$J_{3,5}$ 1.1	$J_{4,6}$ 1.4	
$[Ru(5,5'\text{-}Me_2bipy)_3]^{2+}$	8.680		7.380	7.823	$J_{5,6}$ 5.6		
$[Ru(5,5'\text{-}Me_2bipy)_3]^{2+}$	8.622	7.990		7.800	$J_{4,6}$ 1.8	$J_{3,4}$ 8.3	
bipy	8.491	7.920	7.410	8.680	$J_{5,6}$ 7.2	$J_{4,6}$ 1.6	$J_{3,4}$ 7.6
					$J_{3,5}$ 1.0	$J_{4,5}$ 7.3	
$[Ru(phen)_3]^{2+}$	8.418[a]	8.408[b]	7.811[c]	8.798[d]			

[a] H5 and H6. [b] H4 and H7. [c] H3 and H8. [d] H2 and H9.

TABLE II. T_1 Relaxation Data for Ruthenium(II) α,α′-Diimine Complexes. 5 mmol solutions of the tetrafluoroborate salts in CD_3COCD_3. 400 MHz, 12 transients, IRFT, 30 °C.

Compound	T_1 (sec)			
	H_3	H_4	H_5	H_6
$[Ru(bipy)_3]^{2+}$	1.12	1.84	1.45	2.17
$[Ru(4,4'\text{-}Me_2bipy)_3]^{2+}$	0.81		1.30	1.16
$[Ru(5,5'\text{-}Me_2bipy)_3]^{2+}$	0.97	1.11		2.22
bipy	6.37	5.72	6.22	6.67
$[Ru(phen)_3]^{2+}$	1.77[a]	1.96[b]	1.51[c]	1.71[d]

[a] H5 and H6. [b] H4 and H7. [c] H3 and H8. [d] H2 and H9.

the free ligand is so assigned [12]. However, previous workers have assigned the lowest field resonance in the ^{1}H NMR spectrum of $[Ru(bipy)_3]^{2+}$ to H_3, claiming that the Van der Waals interactions resulting from the adoption of a *cis* configuration of the ligand results in a considerable (~0.4 ppm) deshielding of these protons [13]. This steric effect is clearly observed in the X-ray single crystal structure of $[Ru(bipy)_3](PF_6)_2$ [14]. We therefore investigated the ^{1}H NMR spectra of the ruthenium(II) complexes of 4,4′-dimethyl and 5,5′-dimethyl-2,2′-bipyridine (Figs. 3 and 4) in which the resonances due to H_3 and H_6 respectively may be unambiguously assigned (Table I) [15]. In each case the resonance assigned to H_3 is seen to be at lowest field, and in order to confirm this assignment we have studied the T_1 relaxation behaviour of the protons in these complexes. These results are presented in Table II. It is evident that the resonance assigned to H_3 in each case shows a considerably more rapid T_1 relaxation time than the other protons in the molecule. This is precisely the behaviour which is expected if H_3 is sterically strained, since the Van der Waals interactions between H_3 and H_3' provide an efficient relaxation mechanism [16]. It is particularly gratifying to observe such a rapid relaxation in the 4,4′-dimethyl substituted compound, in which there is no strong coupling to provide a spin–spin relaxation mechanism. In the case of the 5,5′-dimethyl-2,2′-bipyridine complex, it is now immediately evident that the low field doublet at δ 8.622 may be assigned to H_3, and the high field doublet at δ 7.99 to H_4. This is the same assignment which simple chemical shift arguments suggest. It is now possible to return to the $[Ru(bipy)_3]^{2+}$ spectrum, and it is now obvious that the lowest field doublet must be

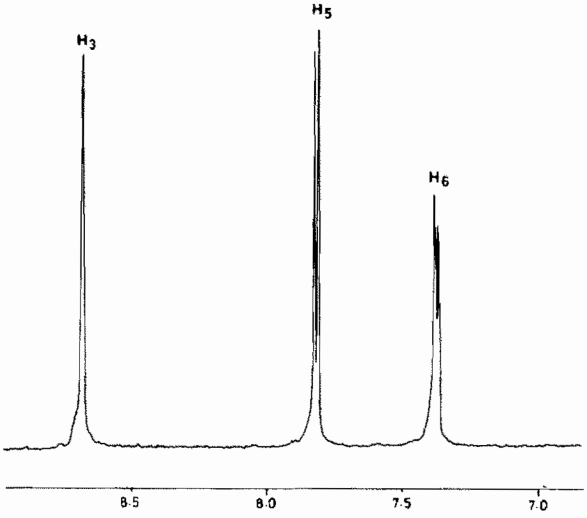

Fig. 3. The ^{1}H NMR spectrum (400 MHz) of $[Ru_{4,4'}\text{-}Me_2\text{-}bipy)_3](BF_4)_2$ in $Me_2CO\text{-}d_6$.

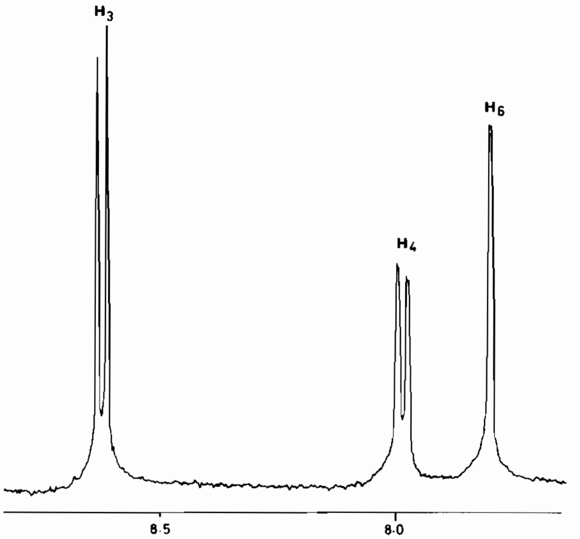

Fig. 4. The ^1H NMR spectrum (400 MHz) of $[Ru(5,5'\text{-}Me_2\text{-}bipy)_3](BF_4)_2$ in $Me_2CO\text{-}d_6$.

assigned to H_3, as suggested by previous authors. The final assignments for these complexes, and also for $[Ru(phen)_3]^{2+}$ and bipy are shown in Table I. The spectrum of the 1,10-phenanthroline complex does not show a strongly deshielded resonance, nor does it possess one proton environment relaxing considerably more rapidly than the others; this is entirely in accord with the absence of the 3,3' protons in this ligand. The relaxation times of all the protons of the 2,2'-bipyridine are increased on coordination to ruthenium, and this is exactly the effect expected, since interaction with the quadrupolar ruthenium nucleus will provide an efficient mechanism for relaxation.

Experimental

The complexes $RuL_3(BF_4)_2$ (L = 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 5,5'-dimethyl-2,2'-bipyridine, or 1,10-phenanthroline) were prepared by the method of Seddon and Anderson [17]. The ligands 4,4'-dimethyl-2,2'-bipyridine and 5,5'-dimethyl-2,2'-bipyridine were prepared by the dimerisation of the appropriate pyridine in the presence of palladium-charcoal and pyridine N-oxide [18].

All NMR spectra were recorded at 30 °C on a Bruker WH-400 spectrometer, using the solvent deuterium signal as an internal lock. T_1 measurements were made using an inversion-recovery Fourier Transform (IRFT) method, with a $(\pi - \tau - \pi/2 - A_t - D)_n$ (n = 12) sequence. All solutions were degassed by bubbling nitrogen through for five minutes prior to recording the spectra.

Conclusions

In conclusion, T_1 measurements provide a sensitive means for the assignment of ^1H NMR spectra of α,α'-diimine complexes, and provide an insight into important non-bonding interactions. In particular, we have demonstrated that the $H_{3,3'}$ protons of coordinated 2,2'-bipyridines show unique properties, and that the abnormal chemical properties associated with these protons are reflected in physical measurements.

Acknowledgements

We thank the S.E.R.C. for support, and Drs J. K. M. Saunders and J. D. Mersh for helpful advice.

References

1 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, *12*, 135 (1969).
2 W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.*, *54*, 959 (1954).
3 L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev.*, *2*, 173 (1967).
4 G. F. Smith and F. R. Richter, 'Phenanthroline and Substituted Phenanthroline Indicators', G. F. Smith Chemical Co., Columbus, 1944.
5 K. R. Seddon, *Coord. Chem. Rev.*, *41*, 79 (1982).
6 E. C. Constable and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 34 (1982).
7 W. A. Wickramasinghe, P. H. Bird and N. Serpone, *J. Chem. Soc., Chem. Commun.*, 1284 (1981).
8 R. D. Gillard, *Coord. Chem. Rev.*, *16*, 67 (1975).
9 F. E. Lytle, L. M. Petrowsky and L. R. Carlson, *Anal. Chim. Acta*, *57*, 239 (1971).
10 H. Elsbernd and J. K. Beattie, *J. Inorg. Nucl. Chem.*, *34*, 771 (1972).
11 T. J. Batterham, 'N.M.R. Spectra of Simple Heterocycles', Wiley–Interscience, New York, 1973.
12 S. Castellano, H. Gunther and S. Ebersole, *J. Phys. Chem.*, *69*, 4166 (1965).
13 K. R. Seddon and E. A. Seddon, *'The Chemistry of Ruthenium', Elsevier, Am*sterdam, to be published.
14 P. P. Rillema, D. S. Jones and H. A. Levy, *J. Chem. Soc., Chem. Commun.*, 849 (1979).
15 S. Anderson, E. C. Constable, J. E. Day and K. R. Seddon, manuscript in preparation.
16 See for example H. Gunther, 'N.M.R. Spectroscopy An introduction', Wiley, Chichester, 1980.
17 S. Anderson and K. R. Seddon, *J. Chem. Res., Synop.*, 74 (1979).
18 E. C. Constable and K. R. Seddon, unpublished results.