

The First Examples of 2,2':6',2''-Terpyridine as a Fluxional Bidentate Ligand

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2,2':6',2''-Terpyridine (terpy) forms octahedral complexes *fac*-[ReBr(CO)₃(terpy)], *cis*-[W(CO)₄(terpy)] and *fac*-[PtClMe₃(terpy)] in which the ligand oscillates between equivalent bidentate forms by a mechanism involving a 'tick-tock' twist of the metal moiety through an angle equal to the N–M–N angle of the octahedral centre and involving a seven-coordinate metal intermediate.

2,2':6',2''-Terpyridine (terpy) is a ligand with a very extensive coordination chemistry.¹ In principle, it can exhibit a variety of bonding modes to metals, *viz.* monodentate, bidentate, terdentate and bridging. However, in practice it almost invariably functions as a terdentate ligand, and although there have been reports^{2–5} of compounds in which bidentate bonding is suggested, X-ray crystallographic evidence has been obtained in only two instances,^{6,7} both involving compounds of ruthenium.

In this communication we report our preliminary results of a detailed NMR study of the complexes *fac*-[ReBr(CO)₃(terpy)] **1**, *cis*-[W(CO)₄(terpy)] **2** and *fac*-[PtClMe₃(terpy)] **3** in which it is conclusively demonstrated that the terpyridyl is acting as a bidentate ligand in solution. Furthermore, this ligand binding mode is shown to be fluxional, and from our studies on the platinum(IV) complex a precise mechanism for this fluxion can be proposed.

Our attention was drawn to this phenomenon by the room-temperature ¹H NMR spectrum of [ReBr(CO)₃(terpy)] **1** in which all signals (except one triplet) exhibited very slight line broadening. On cooling a solution of **1** to *ca.* –10 °C, the spectrum shown in Fig. 1(a) was observed. This consisted of multiplets due to eleven non-equivalent protons of the terpy ligand and clearly was associated with a bidentate chelate complex. These signals were unambiguously assigned to the protons labelled in Fig. 2. The pseudo-triplets due to the proton pairs D/K and H/L were in fact overlapping doublets and the lowest frequency multiplet was the result of two closely overlapping triplets of protons B/F. On raising the solution temperature dramatic changes occurred in the spectrum as indicated in Fig. 1(b) and (c), with exchange broadening occurring between analogous protons of the two outer rings according to the dynamic spin exchange problem ABCD ⇌ EFGH, and for the central ring according to JKL ⇌ JLK. At 140 °C this exchange had become rapid on the proton NMR timescale and a fast exchange spectrum was observed, Fig. 1(c). Throughout this temperature variation the triplet structure of the signal due to the central ring proton J remained totally unaffected. These observations offer conclusive evidence for an exchange between two equivalent chelate structures [structures (a) and (c) of Fig. 2], and represent a novel type of bidentate fluxionality, the first such example for

terpyridine and indeed for any oligopyridine. A bandshape analysis of the collapse of the A and E proton signals of the spectra yielded an activation energy, ΔG[‡] (298.15 K) of 71.6 ± 0.3 kJ mol^{–1} for the process.

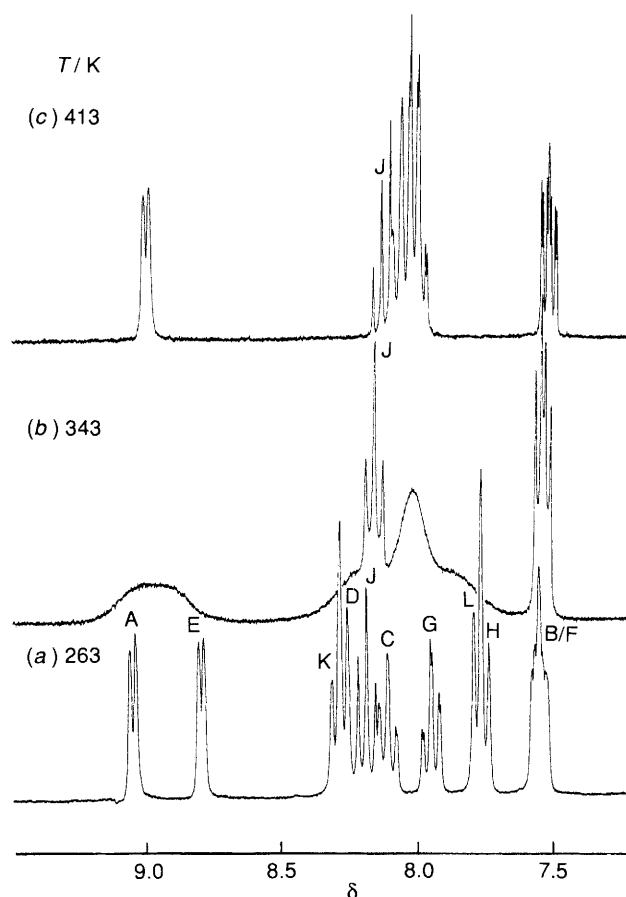


Fig. 1 Variable-temperature 250 MHz ¹H NMR spectra of [ReBr(CO)₃(terpy)] in Cl₂CDCDCl₂ showing the effects of the ligand fluxionality. Proton labelling refers to Fig. 2.

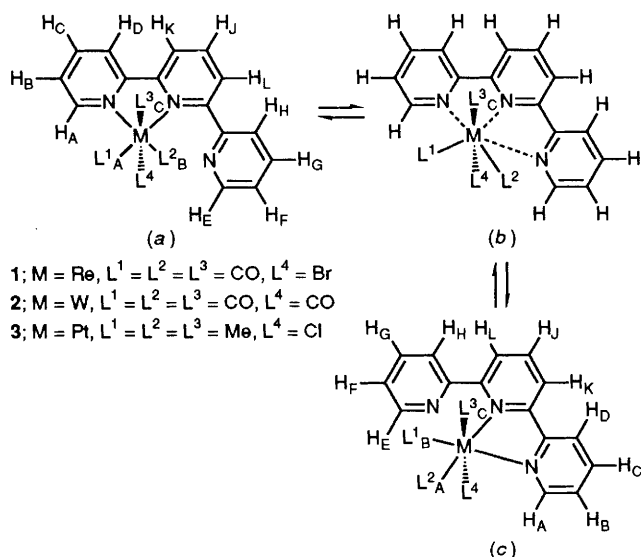


Fig. 2 The interconverting structures of the complexes $[ML_4(\text{terpy})]$ showing how the fluxion exchanges the proton environments

Table 1 Activation energies for terpyridine ligand fluxion

Complex	Exchanging signals	T_c/K	$\Delta G^\ddagger(T_c)/\text{kJ mol}^{-1}$
$[\text{ReBr}(\text{CO})_3(\text{terpy})]$ 1	H _A /H _E	343	71.6 ± 0.3^a
$[\text{W}(\text{CO})_4(\text{terpy})]$ 2	H _A /H _E	283	56.1
$[\text{PtClMe}_3(\text{terpy})]$ 3	H _B /H _F Me _A /Me _B	303 333	62.3 63.8

^a Value based on band-shape analysis over the temperature range 303–413 K and expressed as ΔG^\ddagger (298.15 K).

In order to investigate the generality of this novel fluxion the complexes *cis*- $[\text{W}(\text{CO})_4(\text{terpy})]$ 2 and *fac*- $[\text{PtClMe}_3(\text{terpy})]$ 3 were synthesised and similar NMR studies undertaken. The fluxionality was apparent in both complexes in a more facile form. Room-temperature spectra of complexes 2 and 3 showed very extensive line broadening, and cooling to -30 and -20 °C respectively was required to obtain their static spectra. Approximate activation energies were calculated from band coalescence temperatures, the values being substantially lower than that for the rhenium complex 1 (Table 1).

Variable-temperature NMR spectra of the platinum(IV) complex 3 provided insight into the mechanism of the fluxion, since the signals due to the equatorial Pt-methyls (*trans*-N) (labelled A and B) underwent dramatic exchange broadening during the fluxion (Fig. 3). However, the signal of the axial Pt-methyl (*trans*-Cl) (labelled C) remained sharp throughout, so that *total* Pt-methyl scrambling, a notable feature of PtXMe_3 complexes with chalcogen ligands,⁸ is clearly not occurring in the temperature range studied. Two likely mechanisms can be proposed for this bidentate N/N fluxion, namely, (i) a rotation mechanism involving loosening of the metal–N bonding with the outer pyridine ring, followed by a 180° rotation about the metal–N bond of the central pyridine ring, or (ii) a simultaneous loosening of both M–N bonds followed by an intramolecular twist of the metal moiety through an angle equal to the N–M–N angle at the octahedral centre. The first mechanism, however, would produce *no* exchange of the equatorial Pt-methyl environments A and B (Fig. 2), whereas the second mechanism *would* produce such exchange. We therefore propose that in these terpy complexes the metal moieties undergo a particularly novel oscillatory twist or ‘tick-tock’ mechanism as a result of the ligand trying, but failing, to adopt its more usual terdentate bonding.¹ This mechanism involves a seven-coordinate metal intermediate or

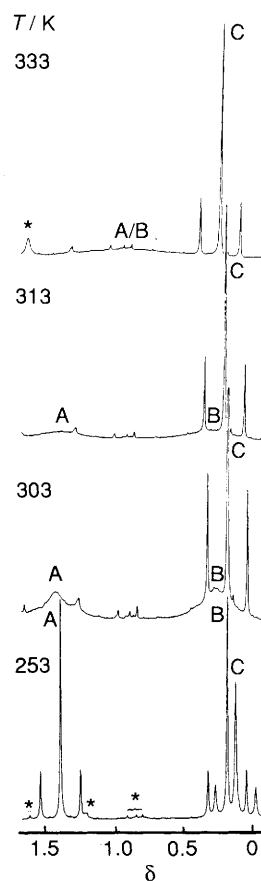


Fig. 3 Variable-temperature 250 MHz ^1H NMR spectra of the Pt-methyl signals of $[\text{PtClMe}_3(\text{terpy})]$ in CDCl_3 . The methyl labelling refers to the L¹, L² and L³ environments in Fig. 2. Impurity signals (*).

transition state structure [Fig. 2(b)] in which all three nitrogen donors contribute to the bonding.

In some very recent related work⁹ we have detected an analogous bidentate N/S fluxion in the complexes *fac*- $[\text{ReX}(\text{CO})_3\text{L}]$ [L = 2,6-bis(methylthiomethyl)pyridine, X = Cl, Br, I], but here the rotation mechanism (i) is more probable on account of the different Re–N and Re–S bond strengths.

We are currently pursuing more detailed NMR studies on the three series of complexes, *fac*- $[\text{ReX}(\text{CO})_3(\text{terpy})]$ (X = Cl, Br, I), *cis*- $[\text{M}(\text{CO})_4(\text{terpy})]$ (M = Cr, Mo, W) and *fac*- $[\text{PtXMe}_3(\text{terpy})]$ (X = Cl, Br, I) to examine the influences of different metals and halogens on this fluxional process. This new and novel bonding characteristic of terpyridine also has important implications to the structural chemistry of higher oligopyridines.

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References

- E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1987, **30**, 69.
- M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 5346.
- C. C. Addison, R. Davis and N. Logan, *J. Chem. Soc., Dalton Trans.*, 1974, 2070.
- R. D. Chapman, R. T. Loda, J. P. Riehl and R. W. Schwartz, *Inorg. Chem.*, 1984, **23**, 1652.
- A. J. Canty, N. Chaichit, B. M. Gatehouse, E. George and G. Hayhurst, *Inorg. Chem.*, 1981, **20**, 2414.
- G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas and A. H. White, *Aust. J. Chem.*, 1984, **37**, 929.
- N. C. Thomas and J. Fischer, *J. Coord. Chem.*, 1990, **21**, 119.
- K. G. Orrell, *Coord. Chem. Rev.*, 1989, **96**, 1.
- E. W. Abel, D. Ellis, K. G. Orrell and V. Šik, to be published.