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Detection of Isomeric Ruthenium(II) Tris-4-Substituted-2,2′-Bipyridyl and 4-Substituted-1,10-Phenanthroline Complexes

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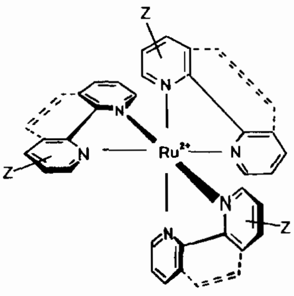
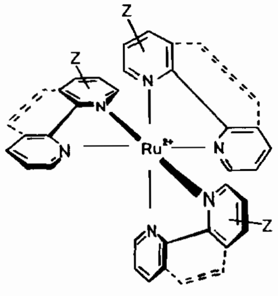
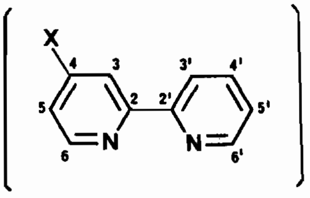
Ruthenium(II) tris complexes of unsymmetrically substituted 2,2′-bipyridyls and 1,10-phenanthrolines can exist as geometrical isomers (1) and (2). To our knowledge no efforts have been made to observe this type of isomerism within these series of complexes and indeed even mention of it appears scarce [1]. A recent assignment of the 220 MHz ^{1}H nmr spectrum of Ru(II) tris-5-nitro-1,10-phenanthroline complex contains no mention of signals arising from an isomer mixture, presumably because of accidental overlap of non-equivalent peaks [2]. In the present note we report selected ^{13}C and ^{1}H nmr data for some novel Ru(II) tris complexes of 4-substituted 2,2′-bipyridyls and 4-substituted 1,10-phenanthrolines, obtained as their chloride or iodide salts, [series (3) and (4)]. All but one of these compounds give rise to spectra having a degree of complexity over and above those for the corresponding free ligands, clearly demonstrating the presence of isomer pairs. From hereon we refer to the isomers (1) and (2) as facial and meridional respectively to signify the spatial arrangements of the 4-substituents.





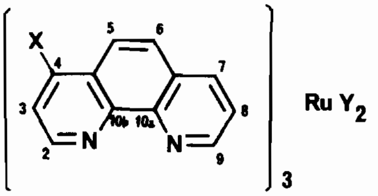


3a X = H

b X = NMe$_2$

c X = OMe

d X = Cl



4a X = H Y = I

b X = OPh Y = Cl

c X = Cl Y = I

d X = Me Y = Cl

The proton and noise decoupled ^{13}C nmr spectra of the series (3) and (4) were obtained of *ca.* 0.2 *M* solutions at 25.05 MHz (JEOL FX 100 spectrometer at 30 °C). Compounds were measured in DMSO-d$_6$ solution except (4b) which was measured in chloroform-d$_1$. Chemical shift data and assignments are given in Tables I and II. In the bipyridyl series the spectrum of the parent (3a) is simple but, in contrast, (3b) gives rise to extra lines which appear for each of the ten ring sites and this is particularly well illustrated by the signals assigned to the C-2 and C-2′ positions. Both carbon positions show four lines, centred at 157.7 and 155.4 ppm, with separations between the outermost lines of 0.46 and 0.56 ppm respectively, Fig. 1. Carbon atoms at other ring positions show less well resolved lines with narrower separation, (*cf.* C-4 in Fig. 1). The C-2 and C-2′ positions in the methoxy analogue (3c) appear as similar four line patterns centred at 157.5 and 156.7 ppm but the separation of the two outer lines *ca.* 0.3 ppm is smaller than in (3b). All other positions, except C-4, show evidence of non-equivalence but to a lesser degree. In contrast to (3b) and (3c) the C-2 and C-2′ signals for (3d) appear as sharp single lines. However, evidence for an isomer mixture is provided by extra lines (poorly resolved) for C-6 and C-6′ and broadened signals for the remaining sites, with the exception of C-4 which appears as a sharp line.

Among the complexes of the 4-substituted 1,10-phenanthrolines, (4b) shows extra lines which are resolved best at carbon sites alpha to the nitrogens, and at C-4 which appears as three lines (approximate intensities 1:2:1). In the spectrum of the 4-chloro analogue (4c), C-10a and C-10b are sharp singlets [*cf.* C-2 and C-2′ in (3d)] whereas C-2 and C-9 both give

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TABLE I. ^{13}C Nmr Chemical Shifts for Ru(II) Tris-chelates of 4-Substituted-2,2′-bipyridyls.

Compound No.	Substituent	C-2	C-3	C-4	C-5	C-6	C-2′	C-3′	C-4′	C-5′	C-6′
3a	H	156.77	124.36	137.36	127.67	151.01	156.77	124.36	137.36	127.67	151.01
3b	$N(CH_3)_2$	157.67[a]	106.67[b]	153.74[b]	109.89[b]	150.50[b]	155.38[a]	123.58[b]	136.30[b]	126.84[b]	147.50[b]
3c	OCH_3	157.55[a]	110.90[b]	166.23	114.22[c]	151.26[b]	156.67[a]	124.38[b]	137.20[c]	127.65[c]	151.10[b]
3d	Cl	157.79	125.00[c]	144.84	128.31[c]	151.98[b]	155.45	124.70[c]	137.95[c]	127.72[b]	151.65[b]

[a] Centre of four individual lines. [b] Two or three resolved lines apparent. [c] Broadened line apparent at 1000 Hz sweep.

TABLE II. ^{13}C Nmr Chemical Shifts for Ru(II) Tris-chelates of 4-Substituted-1,10-phenanthrolines.

Compound No.	Substituent	C-2	C-3	C-4	C-4a	C-5	C-6	C-6a	C-7	C-8	C-9	C-10[a]	C-10[b]
4a	H	152.57	126.16	136.64	130.65	127.87	127.87	130.65	136.64	126.16	152.57	147.02	147.02
4b	OPh	154.85[a]	109.80	162.03[a]	122.61	121.92	127.33[b]	ca. 130	136.34[b]	126.65	153.35[a]	147.42[a]	148.48[a]
4c	Cl	153.79[a]	126.75[a]	142.00[a]	129.43[b]	123.48[b]	128.31	130.60[b]	136.93[b]	126.21[a]	153.03[a]	146.78	147.99
4d	Me	151.56	126.75	147.30	129.02	124.80	127.53	129.02	136.34	126.02	152.52	146.53	146.53

[a] Two or more resolved lines. [b] Broadened line apparent at 1000 Hz sweep.

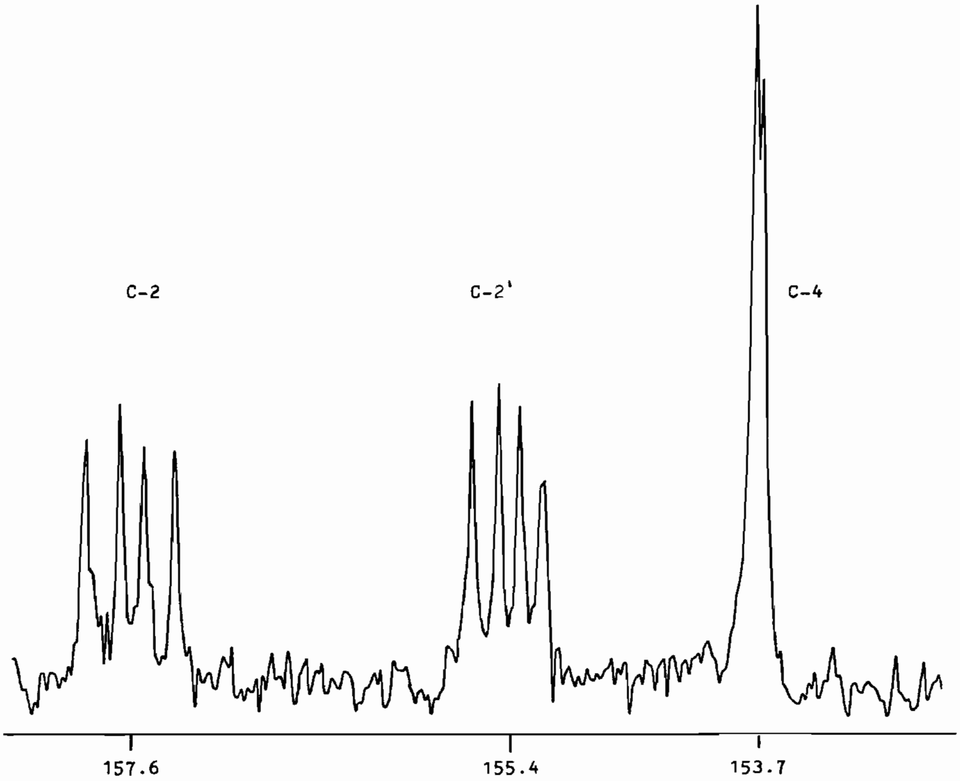

Fig. 1. Part of the ^{13}C nmr spectrum of (3b) showing signals for the C-2, C-2' and C-4 positions (200 Hz sweep width).

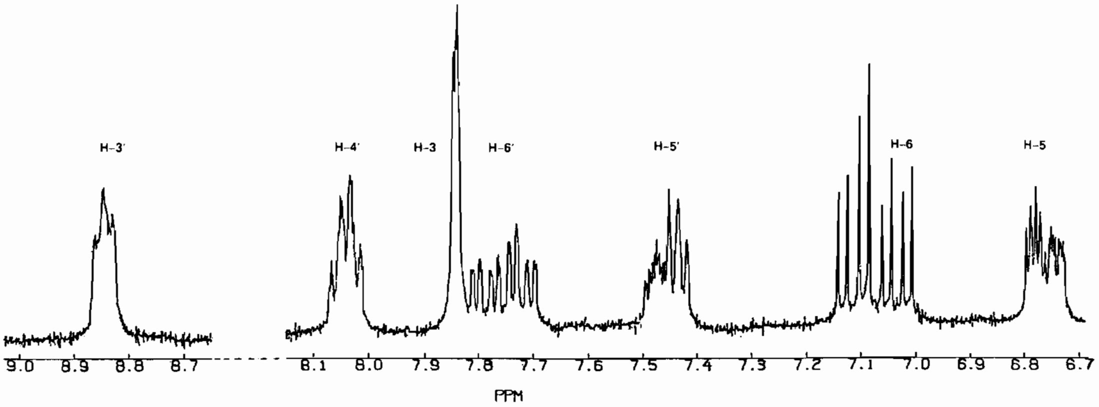

Fig. 2. The aromatic region of the ^1H nmr spectrum of (3b) in DMSO-d_6.

rise to extra lines. Other carbon positions also show broadening or line separation. However the spectrum of (4d) is simple showing only sharp lines (Table II), as indeed are the spectra of the ruthenium(II) tris complexes of 5-chloro and 5-methyl phenanthrolines which were also investigated.

The ^1H nmr spectrum of (3b) was obtained at 400 MHz in DMSO-d_6 and is reproduced in Fig. 2. It clearly reveals the presence of the two isomers, most notably by the appearance of four doublets for protons assigned to both the H-6 and H-6' positions.

The three ligands are magnetically equivalent in the facial isomer [type (1)] but are non-equivalent in the meridional [type (2)] isomer. In the latter, one of the substituted rings has the N-1, C-4 axis orthogonal to and coplanar with the corresponding axes of two substituted rings, a second is in a similar relationship to one substituted and one unsubstituted ring, and the third has the same arrangement with respect to two unsubstituted rings. The intensities of the four lines at the C-2 and C-2′ ring sites in the ^{13}C nmr spectra of (3b), Fig. 1, and (3c) are approximately equal implying the two isomers, facial and meridional, are present in the approximate ratio 25:75, in accord with the statistical probability for their formation.* However in the proton spectrum of (3b), Fig. 2, the protons at the H-6 positions give rise to three doublets of equal intensity (assignable to the meridional isomer) and a fourth doublet of somewhat higher intensity (arising from the facial isomer). By integration we find the sample contains the facial and meridional isomers in the ratio 35:65. The discrepancy between the results of the ^{13}C and ^{1}H nmr integrations (obtained for different samples) and the possibility of achieving separation of the isomers are under investigation.

Acknowledgements

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1 *E.g.* R. D. Gillard and R. E. E. Hill, *J. Chem. Soc. Dalton,* 1217 (1974).
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*As both are chiral they are, of course, formed as racemic mixtures.