Characterization of *mer* and *fac* isomers of $[Ru(2,3\text{-dpp})_3][PF_6]_2$ (2,3-dpp = 2,3-bis(2-pyridyl)pyrazine) by ^1H and ^{99}Ru NMR spectroscopy. Proton assignment by 2D techniques

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(Received July 27, 1992)

Abstract

A careful analysis of the proton 2D-COSY spectrum of the title compound permitted a complete assignment of the signals of the meridional and facial isomers, obtained in a 12:1 ratio. The observed chemical shifts of the pyrazine and pyridine protons are mainly due to ring current effects. The presence of the *mer* and *fac* isomers was confirmed by the appearance of two distinct resonances in the ^{99}Ru NMR spectrum.

Introduction

The title complex, first reported by Petersen and coworkers in 1986 [1], represents an important building block for the preparation of luminescent and redox-active supramolecules: it has been successfully employed as the core precursor in the synthesis of rather large systems such as the tetranuclear species $[Ru\{(\mu\text{-}2,3\text{-dpp})RuL_2\}_3]^{8+}$ (L = bpy [2, 3]; phen [2]; biq [3]) and the decanuclear species [4] $[Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})ML_2]_2\}_3]^{20+}$ (M = Ru, L = bpy or biq; M = Os, L = biq).

It has already been pointed out [3] that the cation $[Ru(2,3\text{-dpp})_3]^{2+}$ (I) (as every metal tris-chelate with unsymmetrical ligands) may have two different configurations, *fac* and *mer* (Fig. 1), depending on the arrangement of the two kinds of nitrogen (pyridinic and pyrazinic) around the metal.

^1H NMR spectroscopy is the most suitable tool to detect such isomeric species in solution and several authors have reported different resonances for protons of meridional and facial isomers [5–7]. Recently, for ruthenium(II) tris-chelates containing simple five- and six-membered heterocyclic moieties, full assignment of *mer* and *fac* isomers has been performed by use of 2D techniques [8]. Another powerful tool to detect geometrical isomers is ^{99}Ru NMR spectroscopy; it has been successfully employed in studying a number of ruthenium chelate complexes [6, 9, 10], being sufficiently sensitive to small variations around the metal core.

^1H and ^{99}Ru NMR investigations on the title compound have ascertained that in the preparation of **I** both isomeric species are produced, the *mer* isomer being by far the more abundant one. This paper deals with the details of this study, including the complete assignment of the proton signals by means of 2D homonuclear correlation spectroscopy (COSY).

Experimental

Synthesis and separations

Complex **I** was prepared following the literature method [1]. A partial separation of the two isomers was obtained by chromatography on a 2 × 20 cm neutral alumina column using a 2:1 (vol./vol.) toluene/acetonitrile mixture as eluant. After *c.* 200 ml of the eluant were passed, a first fraction (*c.* 25 ml) was collected that NMR analysis showed to contain the *fac* and *mer* isomers in a 1:6 ratio. A second fraction (*c.* 150 ml) contained the above products in a 1:15 ratio. The overall yield of the two isomers was 3 and 35% for *fac* and *mer*, respectively.

NMR spectroscopy

^1H and ^{99}Ru NMR spectra were taken on a Bruker AMX-400 spectrometer operating at 400.13 and 18.43 MHz, respectively.

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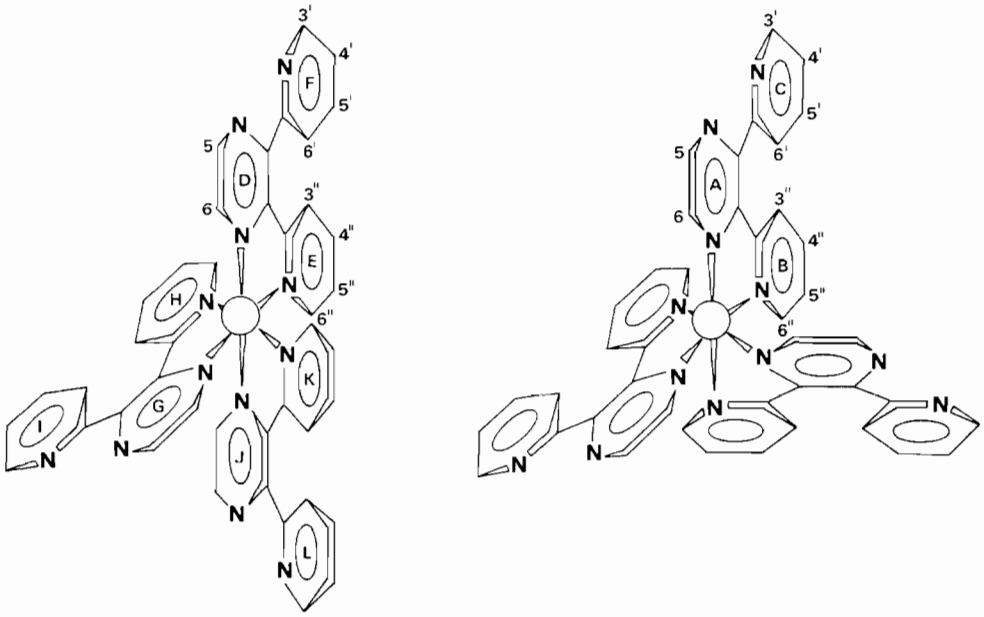

Fig. 1. *mer* (left) and *fac* (right) isomers of the cation $[Ru(2,3\text{-dpp})_3]^{2+}$ (**I**).

The ^1H NMR spectra were obtained at room temperature for approximately 0.01 M acetonitrile-d_3 solutions with TMS as internal reference. The experimental conditions were as follows: for standard 1D spectra: spectral width 8×10^3 Hz; data size 32 k; pulse width 6 μs (90° flip angle); number of scans 64; acquisition time 15 s; for 2D COSY experiments: time domain data matrices of 1024–1024 size covering 4×10^3 Hz spectral width; number of scans 16; recycle time 2.5 s; before Fourier transformation a sine-bell window function was applied in both dimensions. T_1 measurements were performed by the inversion recovery method.

The ^{99}Ru NMR spectra were obtained at 300 K for approximately 0.04 M acetonitrile-d_3 solutions, in 10-mm tubes. Spectral data were collected in locked mode and chemical shifts were externally referenced to $[Ru(CN)_6]^{4-}$ 0.5 M in water; positive chemical shifts indicate downfields shifts from the reference. Owing to the temperature dependence of the chemical shift (28 Hz/K, near room temperature) care was taken that the temperature of the sample was constant for long-term experiments. In order to reduce probe ringing effects, a $90x$–τ–$90y$–τ–(acq.) pulse sequence was used with two-step phase cycling. The 90° pulse was 40 μs and the delay time τ was 50 μs. The spectra were acquired with a spectral window of 10^4 Hz; a signal-to-noise value of 25 was obtained after 3×10^5 scans, with a recycle time of 0.15 s.

Results and discussion

In the experimental conditions adopted, the reaction between $RuCl_3\cdot3H_2O$ and 2,3-dpp in a refluxing 2:1 ethanol/water solution gives rise to a 1:12 mixture of *fac* and *mer* isomers of **I**, as deduced by NMR investigations (see below). Variable temperature experiments showed that these species do not interconvert even at 335 K.

There is a large predominance of the *mer* isomer (larger than those observed for other ruthenium tris-chelate complexes [8, 10]) that cannot be easily accounted for, considering that *trans* influence ought to favour the *fac* isomer (the pyridine group is a better σ-donor and a worse π-acceptor than the pyrazine group [7]) and also in view of the fact that the steric requirements should be very similar in both isomers. However, it is likely that the preferential formation of the *mer* isomer is the result of the kinetic control in one or more steps of the reaction that leads to **I**.

Owing to the complexity of the ^1H NMR spectrum of **I** (40 non-equivalent protons in less than 2 ppm), a complete assignment was achieved only by analysis of its homonuclear 2D-COSY spectrum. In Table 1 all proton chemical shifts are quoted along with the values of the so-called coordination-induced shifts [9] obtained by subtracting chemical shifts of each nucleus in the complexed and in the free ligand. Figure 2 shows the ^1H spectrum of **I**, in the region of pyrazine protons 5, for a sample containing the 'natural' *fac*/*mer* isomeric ratio.

Assignment strategy proceeded as follows: a careful analysis of the 2D spectrum clarified the connectivity patterns of the rings; furthermore, protons 6 and 6″ (α position to coordinating nitrogens) were easy identified owing to their noticeable upfield shift due to electron circulation of vicinal rings (e.g. ring G for

TABLE 1. ^{1}H NMR chemical shifts[a] in CH_3CN-d_3 for $[Ru(2,3\text{-dpp})_3][PF_6]_2$ and coordination induced shifts (in parentheses)[b]

Pyrazine protons 5,6				Pyridine protons (′)				Pyridine protons (″)			
	mer		*fac*		*mer*		*fac*		*mer*		*fac*
5D	8.59(−0.09)	5A	8.60(−0.08)	3′F	7.96(0.12)	3′C	7.97(0.13)	3″H	7.26(−0.58)	3″B	7.26(−0.58)
5G	8.63(−0.05)			3′I	7.98(0.14)			3″K	7.27(−0.57)		
5J	8.64(−0.04)			3′L	7.99(0.15)			3″E	7.28(−0.56)		
6D	8.07(−0.61)	6A	8.07(−0.61)	4′F	8.13(0.29)	4′C	8.13(0.29)	4″H	7.74(−0.10)	4″B	7.73(−0.11)
6G	7.88(−0.80)			4′I	8.12(0.28)			4″K	7.72(−0.12)		
6J	7.92(−0.76)			4′L	8.12(0.28)			4″E	7.72(−0.12)		
				5′F	7.65(0.38)	5′C	7.65(0.38)	5″H	7.43(0.16)	5″B	7.42(0.15)
				5′I	7.66(0.39)			5″K	7.37(0.10)		
				5′L	7.66(0.39)			5″E	7.38(0.11)		
				6′F	8.65(0.41)	6′C	8.66(0.42)	6″H	7.79(−0.45)	6″B	7.76(−0.48)
				6′I	8.67(0.43)			6″K	7.92(−0.32)		
				6′L	8.68(0.44)			6″E	7.93(−0.31)		

[a]In ppm from TMS; proton labels in Fig. 1; apparently isochronous signals differ for some thousandths of ppm; coupling constants (Hz): $J_{5,6}=3.0$, $J_{3',4'}=7.8$, $J_{3',5'}=1.2$, $J_{3',6'}=1.0$, $J_{4',5'}=7.6$, $J_{4',6'}=1.7$, $J_{5',6'}=4.8$, $J_{3'',4''}=8.2$, $J_{3'',5''}=1.3$, $J_{3'',6''}=0.8$, $J_{4'',5''}=7.4$, $J_{4'',6''}=1.5$, $J_{5'',6''}=5.7$. T_1 values range from 1.4 s (protons 4″ and 5″) to 2.5 s (protons 6′). [b]δ(complexed) − δ(free); 2,3-dpp in acetonitrile, δ (ppm): 8.68 (5 and 6), 8.24 (6′), 7.84(3′), 7.84(4′), 7.27(5′)

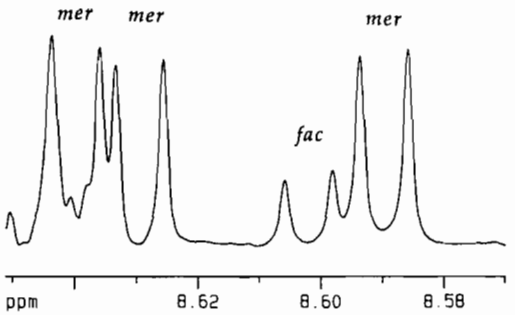

Fig. 2. ^{1}H NMR spectrum in acetonitrile of a 'natural' mixture of the *mer* and *fac* isomers of **I** in the proton-5 region.

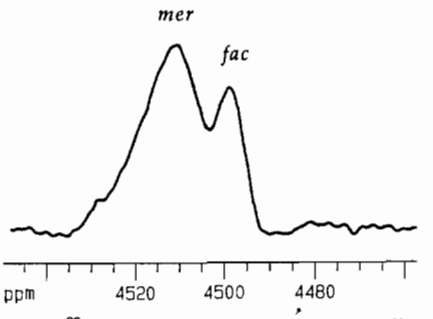

Fig. 3. ^{99}Ru NMR spectrum in acetonitrile of a mixture enriched in the *fac* isomer of **I** (first chromatographic fraction).

proton 6D). These protons are clearly grouped in two pairs (the *fac* proton and a *fac*-like proton distinct from the other two *mer* protons), as a result of their proximity to different heterocyclic rings. The *fac* proton 6A and the *fac*-like 6D are both close to pyrazine rings, whereas 6G and 6J are placed above pyridine rings. The latter protons are more shielded owing to the larger ring current effect of the pyridine ring compared to that of pyrazine ring. Furthermore, in order to assign the *mer* protons 6G and 6J, we had to take into account the secondary (different deshielding) effect of the rings D and E, that due to ring E being larger. The same considerations permitted us to identify each proton 6″ (and consequently 5″, 4″ and 3″). The four protons 6′ (and consequently 5′, 4′ and 3′) were unambiguously identified by inspecting the relevant coupling constants. Nevertheless the very subtle differences in chemical shift inside each group of four analogous protons of the peripheral rings (′), make proposed assignments not totally univocal.

Examining the coordination induced shifts for the pyridine protons (″), it is interesting to note the large anomalous upfield shifts exhibited by protons 3″ (and, to a lesser extent, by 4″), not observed previously [8]. As coordination forces the pyrazine and the pyridine rings (″) to be coplanar, protons 3″ and 4″ are exposed to the shielding magnetic anisotropy due to the ring currents of the pyridine rings (′), which are obliged to turn in order to minimize steric hindrance*.

On the contrary, the protons of the non-coordinating rings (′) are all deshielded to the extent that, being hard to attribute to the vicinal rings (″), is probably due to a significant increase in the electronic circulation on the same rings (′) induced by coordination.

The presence of the two isomers was confirmed by recording the ^{99}Ru NMR spectrum of a sample enriched in the *fac* species (Fig. 3). The different bandwidths

*In the crystal structure of $[Ru(2,3\text{-dpp})(bpy)_2]Cl_2$ the angle between the coordinated pyrazine ring and the pyridyl ring (′) is about 107°.

(260 and 120 Hz) are related to the symmetry of the species (owing to the quadrupolar nature of the ^{99}Ru nucleus), being narrower for the more symmetrical *fac* isomer. Furthermore the latter is more shielded than the other isomeric form, as previously found in an extensive study on a number of ruthenium(II) polypyridyl complexes [10]. Finally, the chemical shift values for both isomers (4510 and 4499 ppm) are slightly lower than that observed for $[Ru(bipy)_3]^{2+}$ (4575 ppm) in the same solvent [10], indicating a higher ligand field strength for 2,3-dpp (with respect to bipy) probably due to the better π-acceptor character of the pyrazine ring.

Acknowledgements

This work has been supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST); we thank Professor G. Fava-Gasparri and Professor M. Ferrari-Belicchi for providing unpublished results.

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