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Synthesis, Separation, and NMR Characterisation of the *fac*- and *mer*-Isomers of Tris(1-methyl-3-(pyridin-2-yl)-1,2,4-triazole)ruthenium(II) Hexafluorophosphate

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Abstract

The preparation of tris(1-methyl-3-(pyridin-2-yl)-1,2,4-triazole)ruthenium(II) hexafluorophosphate is described. The separation of facial and meridional isomers has been achieved through crystallisation methods. The isomers can be clearly distinguished by their ^{1}H NMR and ^{13}C NMR spectra. NMR evidence suggests that the triazole ring is bound to the central metal atom by the N4 donor atom. The title compound does not show any emission at room temperature or liquid nitrogen temperature. Electrochemical data suggest that the ligand (1-Mepytr) is a weaker π-acceptor than 2,2′-bipyridine, but has strong σ-donor properties.

Introduction

Ruthenium compounds with 2,2′-bipyridine (bpy) have been the subject of many studies, because of their potential applications as catalysts for the photochemical dissociation of water and as redox-catalysts on polymer modified electrodes [1–10]. The study of these compounds has also lead to a better understanding of electron transfer reactions both in the ground state and in the excited state [11]. Most of these investigations involved symmetric bipyridine type ligands, such as (substituted) bipyridines, phenanthrolines and biquinolines [12–18]. Only few compounds containing asymmetric bidentate ligands have been studied [19–22].

A number of compounds of the type $[Ru(bpy)_{n-3}L_n]^{3+}$ have been reported, where L = pyridylimidazole, pyridylpyrazole or pyridylthiazole. However, no systematic investigations have been carried out on their properties as a function of the nature of the five-membered ring. We decided to systematically investigate the properties of ruthenium complexes of a series of pyridyl-1,2,4-triazoles. It is expected that the difference in the bonding properties of the pyridyl nitrogen and the nitrogen of the triazole ring (the π-acceptor properties of five-membered rings such as imidazole, pyrazole and 1,2,4-triazole are weaker than those of pyridine [23–25]), will lead to compounds with interesting photochemical properties. It is hoped that such studies will result in a better understanding of the photophysical properties of $Ru(bpy)_3^{2+}$. The present work describes the synthesis and properties of the tris(1-methyl-3-(pyridin-2-yl)-1,2,4-triazole)ruthenium(II) ion. The bidentate ligand, hereafter abbreviated as 1-Mepytr, can chelate via the pyridyl N and N4 or N2 of the triazole ring (see Fig. 1 for atom numbering).

Compounds of the type $[Ru(LL')_3]^{2+}$ where LL′ is an asymmetric bidentate ligand, can exist in two geometrical isomers, facial and meridional (Fig. 2). The isomerism of such compounds can be investigated with proton-NMR and carbon-NMR spectroscopy. Until now only mixtures of facial and meridional $Ru(LL')_3X_2$ compounds have been reported [19, 20].

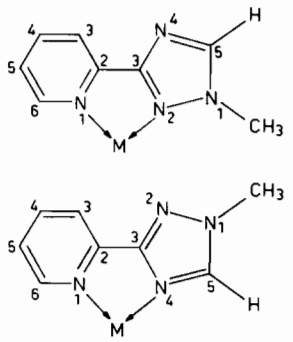

Fig. 1. 1-Methyl-3-(pyridin-2-yl)-1,2,4-triazole, showing atom numbering and coordination modes.

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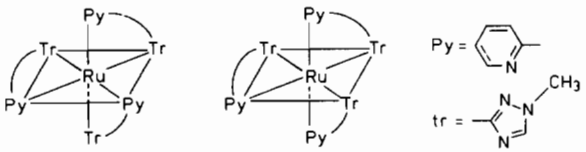

1A fac (cis) 1B mer (trans)

Fig. 2. Geometric isomers of $[Ru(1\text{-Mepytr})_3]^{2+}$, schematic representation.

Here we describe the isolation and characterisation of the pure (>99%) *facial* $Ru(1\text{-Mepytr})_3(PF_6)_2$ and almost pure (>95%) *meridional* $Ru(1\text{-Mepytr})_3(PF_6)_2$. The compounds have been characterised by NMR spectroscopy, electronic spectroscopy and electrochemical measurements.

Experimental

Materials

Reagent grade solvents were used without further purification. $RuCl_3 \cdot xH_2O$ was purchased from Janssen Chimica and was used without further purification. The ligand 1-Mepytr was prepared according to described methods from methylhydrazine, 2-cyanopyridine and formic acid [26]. Melting point (m.p.) 51–54 °C. (literature 47–48 °C.). Its purity was checked by NMR.

Preparation of $Ru(1\text{-Mepytr})_3(PF_6)_2$ Isomers

2 mmol of $RuCl_3 \cdot xH_2O$, 8 mmol of 1-Mepytr and 1 g L-ascorbic acid were refluxed in 100 ml of water/ethanol (1:1) for 6 h. After concentration to dryness, the solid was dissolved in 15 ml water and the product was precipitated with NH_4PF_6 (5 mmol in 10 ml water). After dissolving the precipitate in 5 ml of acetonitrile, it was passed down an Al_2O_3 column (grade 90 standardised for chromatographic absorption analyses; ethanol as eluent; column 40 X 2 cm). The resulting solution was concentrated to dryness and the solid obtained recrystallised from a water/acetonitrile mixture. Several fractions with light yellow crystals were collected separately. *Anal.* For the fraction containing >99% *fac*: Calc. for $[Ru(C_8H_8N_4)_3](PF_6)_2$: C, 33.07; H, 2.76; N, 19.28; Found: C, 32.71; H, 2.77; N, 19.23%. A fraction containing ~95% *mer* gave: Found C, 32.85; H, 2.76; N, 18.97%.

Equipment

Electronic spectra were recorded in ethanol on a Perkin-Elmer 330 spectrophotometer. The NMR spectra were obtained on a Jeol JNM-FX 200 NMR spectrometer. Samples were dissolved in deuterated DMSO. Electrochemical measurements were carried out using an E.G. and G. PAR model 174A Polarographic Analyser, an E.G. and G. PAR 175 Universal Programmer and a glassy-carbon electrode as work-electrode. The samples were measured in spectroscopic grade CH_3CN, dried over molecular sieves, with 0.1 M tetraethylammonium perchlorate as supporting electrolyte. The scan rate was 100 mV s^{-1}. A KCl-saturated calomel electrode was used as a reference electrode.

TABLE I. ^1H NMR Chemical Shifts, in ppm to TMS, of 1-Mepytr, Free Ligand and Coordinated to Ruthenium(II) (see Fig. 1 for atom numbering)[a]

Compound	Triazole ring		Pyridine ring			
	CH_3	H5	H3	H4	H5	H6
1-Mepytr	3.97	8.61	8.06	7.91	7.43	8.66
$Ru(1\text{-Mepytr})_3$						
fac	3.99	8.92	8.29	8.09	7.51	7.85
	(+2)	(+31)	(+23)	(+18)	(+8)	(−81)
mer	4.00	8.96	8.27	8.02	7.44	7.77
	(+3)	(+37)	(+21)	(+11)	(+1)	(−93)
	4.01	8.79	to	to	to	
	(+4)	(+18)	8.35	8.14	7.55	
		8.75	(+29)	(+23)	(+12)	
		(+14)				

[a]All compounds measured in perdeutero DMSO. Values between parentheses are differences of shifts to free ligand in 0.01 ppm.

Results and Discussion

Nuclear Magnetic Resonance Spectra

The proton chemical shifts of the compounds are listed in Table I. The signals have been assigned by comparison with the signals of the bipyridine complexes already described and by using the H-H coupling constants [19, 27–29].

In octahedral compounds with non-symmetric bidentate ligands, *facial* (*fac*) and *meridional* (*mer*) geometrical isomers are expected to occur. Additionally, optical isomerism is present in such compounds, but was not investigated in this work; *i.e.*, no attempts were undertaken to resolve enantiomers, e.g., by crystallisation with a chiral anion. In the *fac* isomer, the three ligands are magnetically equivalent because this isomer possesses a C_3-axis of symmetry (Fig. 2). The three ligands in the *mer* isomer are magnetically nonequivalent, and more complex signals are expected (and observed) in the NMR spectra.

The first fraction of yellow crystals appeared to contain more than 99% of *fac*-$Ru(1\text{-Mepytr})_3(PF_6)_2$ (Fig. 3a). The second fraction in the crystallisation procedure contained a mixture of 30% *fac* and 70% *mer* compound, whereas the third crop consisted of 95% *mer*-$Ru(1\text{-Mepytr})_3(PF_6)_2$ (Fig. 3b). Repeated

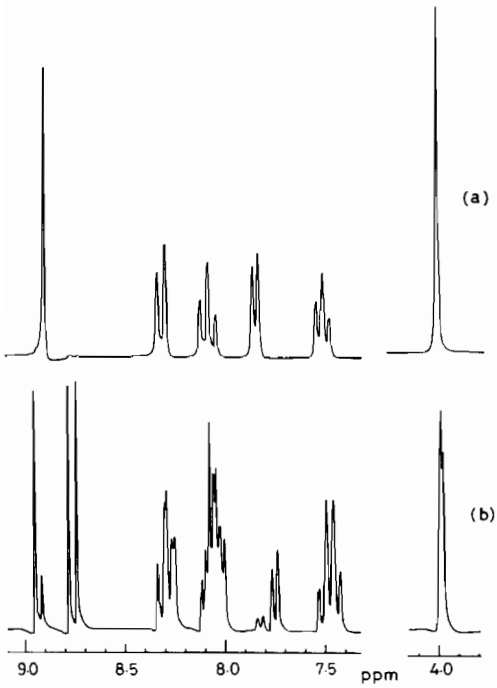

Fig. 3. ^{1}H NMR spectra of *fac* (a) and *mer* (b) [Ru(1-Mepytr)$_3$]$^{2+}$.

recrystallisation of this final fraction gave only little improvement in the purity of the isomer. The purification procedure was not continued, as the absolute yields became impracticably low. The overall isomeric ratio for the formation of *fac*:*mer* Ru(1-Mepytr)$_3$-(PF$_6$)$_2$ was approximately 1:2.

The X-ray structure analysis of the related compound Ru(1-Mepytr)(CH$_3$CN)Cl$_3$ [30] has shown that 1-Mepytr binds via N4 of the triazole ring to ruthenium. Examination of space-filling structural models of the compounds shows that for both the *fac* and the *mer* isomers no steric hindrance is to be expected when coordination takes place via this N4. Therefore it is likely that the same coordination mode will be present here. This is also consistent with the NMR spectra, because very little change is observed in the chemcial shift of the methyl group (Table I). Additional evidence about the coordination of the N4 atom of the triazole ring is provided by the resonance position of the H5 proton. For the *fac* isomer only one sharp resonance at 8.92 ppm is found. For the *mer* isomer three signals of equal intensities are observed at 8.96, 8.79 and 8.72 ppm. In the case of the *fac* isomer, the H5 proton is expected to lie in the shielding cone of one of the pyridine rings. In the *mer* isomer one of the three H5 protons in the molecule will be situated within the shielding cone of a pyridine ring while the other two will be close to a triazole ring. It is expected that the close proximity of a pyridine ring will cause a proton to be more shielded. These considerations lead us to believe that the triazole ring is coordinated through the N4 atom. In contrast for N2 coordination similar shifts in resonance position would be expected for the protons of the methyl group on the 2-position [19].

The carbon-13 NMR spectrum (Table II) of the *fac* compound appears very simple (Fig. 4) and looks like the spectrum of the free ligand. As expected from symmetry considerations all peaks are sharp singlets. The carbon-13 spectrum of the *mer* isomer is more complicated, because all signals are doublets or triplets, just as expected from the nonequivalence of the three ligands.

Electronic and Electrochemical Data

No differences were found in the electronic or electrochemical properties of the *fac* and *mer* isomers. In ethanol the electronic spectra show bands at 402 (log ϵ = 4.10), 271 (log ϵ = 4.61) and 239 (log ϵ = 4.53) nm. No emission was observed for the compounds either at room temperature or at liquid nitrogen temperature.

Cyclic voltammetry showed a quasi-reversible Ru$^{II/III}$ oxidation at 1.09 V *vs.* SCE, with a peak-to-

TABLE II. ^{13}C NMR Chemical Shifts, in ppm to TMS, of 1-Mepytr, Free ligand and Coordinated to Ruthenium(II) (see Fig. 1 for atom numbering)

Compound	Triazole ring			Pyridine ring				
	CH_3	C3	C5	C2	C3	C4	C5	C6
1-Mepytr	36.1	161.2	145.8	149.7	121.4	136.9	123.8	149.5
Ru(1-Mepytr)$_3$								
fac	37.9	161.6	147.9	149.8	122.3	137.8	127.6	153.0
	(+18)	(+4)	(+21)	(+1)	(+9)	(+9)	(+38)	(+35)
mer	38.0	161.7	147.8	149.8	122.0	137.9	127.0	153.3
	t[a]	d	s	t	d	d	t	t
	(+19)	(+5)	(+20)	(+1)	(+6)	(+10)	(+32)	(+38)

[a]s = singlet, d = doublet, t = triplet. All measurements in DMSO. Values in parentheses are differences of shifts to free ligand in 0.1 ppm.

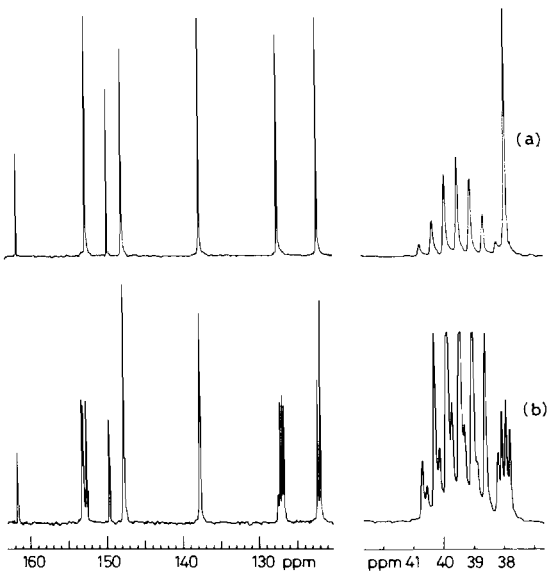

Fig. 4. ^{13}C NMR spectra of *fac* (a) and *mer* (b) $[Ru(1\text{-}Mepytr)_3]^{2+}$.

peak separation of 80 mV. No reductions of the type $Ru^{II/I}$ and $Ru^{I/0}$ were observed. In ruthenium polypyridyl complexes such reductions are believed to be bipyridyl based [31, 32]. It is well known that 1,2,4-triazole is a weak π-acceptor but a good σ-donor [33]. One would therefore expect pyridyltriazole to be a weaker π-acceptor than 2,2'-bipyridine. This will certainly influence the metal-to-ligand charge-transfer processes which are important for both the electronic and electrochemical processes. The less positive oxidation potential suggests a stabilisation of Ru(III) over Ru(II) compared to $[Ru(bpy)_3]^{2+}$ ($Ru^{II/III}$ for $[Ru(bpy)_3]^{2+}$ at +1.29 V). This points to an increased electron density on the central metal ion, and is in agreement with weak π-acceptor and strong σ-donor properties for the 1-Mepytr ligand. The absence of ligand-based reductions also points to weak π-acceptor properties. It is not possible to draw conclusions about the electronic properties of the ligand from the electronic spectra other than that 1-Mepytr is a strong σ-donor.

Conclusions

The separation of the two geometrical isomers of tris(1-Mepytr)ruthenium(II) hexafluorophosphate can easily be achieved through crystallisation methods.

The difference in symmetry between *fac* and *mer* isomers is evident from proton and carbon-13 NMR spectra.

^1H NMR spectra also indicate that the triazole ring is coordinated through its N4 atom.

The difference in geometry between the two isomers has no significant influence on the electronic properties of the compound: both isomers have identical electronic absorption spectra and oxidation/reduction potentials.

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