Ligand Reactivity in Polypyridine Complexes; $[Ru(bipy)_3]^{n+}$ Analogs Incorporating Pendant Polyamine Substituents

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Abstract

The complex cation $[Ru(bipy)_2L]^{2+}$ (bipy = 2,2′-bipyridine, L = 4,4′-dichloro-2,2′-bipyridine) is activated towards nucleophilic substitution of chloride. Reactions of $[Ru(bipy)_2L]^{2+}$ with potentially polydentate amines give rise to novel derivatives $[Ru(bipy)_2L']^{2+}$ which possess a central redox and photochemically active 'Ru(bipy)$_3$' core, and a potentially multidentate periphery for coordination to other metal centres.

Introduction

Ruthenium complexes of polypyridine ligands have stimulated considerable interest as primary photocatalysts for solar energy photoconversion [1]. The redox and photophysical properties of the ground and photoexcited states are particularly suited to such applications. These properties have been demonstrated to be sensitively dependent upon the nature of the polypyridine ligands. One of the problems associated with such photoconversion systems relates to the slow transfer of electrons from the photoexcited $\{[Ru(bipy)_3]^{2+}\}^*$ state to water or some other acceptor. Numerous heterogeneous systems of varying complexity and sophistication have been proposed in attempts to overcome this problem. We were interested in the development of functionalised derivatives containing an 'Ru(bipy)$_3$' chromophore as a photoactive centre, and a linked redox-active centre as a site for electron transfer. Specifically, we considered the preparation of complexes in which a functionalised 2,2′-bipyridine bearing polyamine substituents acts as the link between the ruthenium(II) centre and another metal centre. We have previously demonstrated that the chloride in $[Ru(bipy)_2L]^{2+}$ complexes (L = 4,4′-dichloro-2,2′-bipyridine) is activated towards nucleophilic displacement by a wide range of nucleophiles [2]. In this paper we describe the synthesis of ruthenium(II) complexes incorporating pendant polyamines by the reaction of $[Ru(bipy)_2L]^{2+}$ salts with amines $H_2(CH_2)_nNR(CH_2)_mNR_2$.

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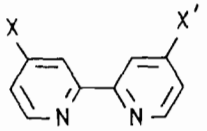
Experimental

'Ruthenium trichloride trihydrate' (Johnson-Matthey) and all diamines (Aldrich) were used as supplied. 4,4′-Dichloro-2,2′-bipyridine [3] and $[Ru(bipy)_2Cl_2]$ [4] were prepared by the literature methods. ^1H and ^{13}C NMR spectra were recorded on Bruker WM 250 or AM 400 spectrometers in acetone-d_6 or dmso-d_6 solution, using the solvent internal deuterium resonance as lock. Infrared spectra were recorded using Perkin-Elmer 983 or 1700 spectrophotometers in pressed KBr pellets. Electronic spectra were recorded on Uvikon or Pye-Unicam 8800 spectrophotometers.

Preparation of $[Ru(bipy)_2L][PF_6]_2$

4,4′-Dichloro-2,2′-bipyridine (0.225 g, 1 mmol) and $[Ru(bipy)_2Cl_2]$ (0.484 g, 1 mmol) were heated to reflux in $MeOCH_2CH_2OH$ (35 cm^3) for 4 h, after which period a clear orange solution had been obtained. This was treated with an excess of saturated aqueous ammonium hexafluorophosphate solution, and allowed to cool. The precipitate was collected by filtration, washed with water and diethyl ether, and dried *in vacuo* to yield $[Ru(bipy)_2L][PF_6]_2 \cdot H_2O$ as a red crystalline solid (0.81 g, 86%) (*Anal.* Found: C, 38.0; H, 2.3; N, 8.8. Calc. for $C_{30}H_{24}N_6Cl_2F_{12}OP_2Ru$: C, 38.05; H, 2.5; N, 8.9%).



L^1 X,X′ = $-NH(CH_2)_2NMe_2$
L^2 X,X′ = $-NH(CH_2)_2NH_2$
L^3 X,X′ = $-NH(CH_2)_3NH_2$
L^4 X,X′ = $-NH(CH_2)_4NH_2$
L^5 X,X′ = $-NH(CH_2)_3NH(CH_2)_3NH_2$
L^6 X,X′ = $-NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$

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TABLE I.

Complex	Yield (%)	Calculated (%)			Found (%)		
		C	H	N	C	H	N
$[Ru(bipy)_2L][PF_6]_2 \cdot H_2O$	86	38.1	2.5	8.9	38.0	2.3	8.8
$[Ru(bipy)_2(HL^1)][PF_6]_3$	82	39.8	3.9	12.2	39.9	4.1	12.1
$[Ru(bipy)_2L^2][PF_6]_2 \cdot 2H_2O$	67	40.35	4.0	13.9	40.3	3.6	13.8
$[Ru(bipy)_2L^3][PF_6]_2 \cdot 2H_2O$	94	41.6	4.2	13.5	41.6	3.8	13.3
$[Ru(bipy)_2(H_2L^4)][PF_6]_4 \cdot H_2O$	83	34.0	3.6	10.4	33.8	3.2	10.0
$[Ru(bipy)_2L^5][PF_6]_2 \cdot 6H_2O$	39	41.2	5.4	13.7	41.3	5.7	13.6
$[Ru(bipy)_2(HL^6)][PF_6]_3 \cdot H_2O$	58	38.4	4.5	14.9	38.4	4.1	14.8

Preparation of $[Ru(bipy)_2L^1][PF_6]_2$

$[Ru(bipy)_2Cl_2][PF_6]_2$ (0.093 g, 0.1 mmol) and $Me_2NCH_2CH_2NH_2$ (2.0 cm^3) were heated to reflux in $MeOCH_2CH_2OH$ (5 cm^3) for 6 h, after which period the deep red solution was concentrated *in vacuo*, to give a red oil. This was treated with saturated aqueous ammonium hexafluorophosphate solution, and the red precipitate so obtained collected by filtration, washed well with water, and dried *in vacuo* (over P_4O_{10}), to give dark red microcrystals of the compound $[Ru(bipy)_2(HL^1)][PF_6]_3$ (0.096 g, 82%) (*Anal.* Found: C, 39.9; H, 4.1; N, 12.05. Calc. for $C_{38}H_{45}N_{10}F_{18}P_3Ru$: C, 39.8; H, 3.9; N, 12.2%).

Preparation of $[Ru(bipy)_2X]^{2+}$ Complexes ($X = L^2$, L^3, L^4, L^5 or L^6)

These complexes were prepared in an exactly analogous manner to that described above for $[Ru(bipy)_2L^1]^{2+}$. Yields and microanalytical data are presented in Table I.

Results and Discussion

The complex cation $[Ru(bipy)_2L]^{2+}$ is readily prepared by the reaction of $[Ru(bipy)_2Cl_2]$ with L in $MeOCH_2CH_2OH$. The reaction is essentially complete after 4 h, and the cation is conveniently isolated as its hexafluorophosphate salt. Attempts to prepare the complex in ethanol were less successful, and considerable amounts of $[Ru(bipy)_2Cl(EtOH)]^+$ and $[Ru(bipy)_2(EtOH)_2]^{2+}$ derivatives were obtained, even after prolonged reaction times and in the presence of excess 4,4′-dichloro-2,2′-bipyridine. The ^1H NMR spectrum of $[Ru(bipy)_2L]^{2+}$ salts in acetone-d_6 or dmso-d_6 solution exhibited signals due to 11 unique protons, as expected for a complex in which the A and B rings of the 2,2′-bipyridine ligands are non-equivalent. The resonances due to the protons of the substituted 2,2′-bipyridine are particularly diagnostic, and may be used to monitor the displacement of chloride. Specifically, acetone-d_6 solutions of $[Ru(bipy)_2L]^{2+}$ salts exhibit resonances at δ 8.08 (d, J = 6.0 Hz), δ 7.68 (dd, J = 6.0, 2.1 Hz), and δ 9.04 (d, J = 2.1 Hz) which may be assigned to H_6, H_5 and H_3 of the substituted 2,2′-bipyridine ring respectively. These signals exhibit a marked solvent dependence, which is indicative of a considerable solvent-coordinated ligand interaction [5], and in dmso-d_6 the resonances ascribed to H_6, H_5 and H_3 of the 4,4′-dichloro-2,2′-bipyridine are observed at δ 7.68, δ 7.69 and δ 9.18 respectively. The complex was further characterised by its FAB mass spectrum which exhibited peaks centred at m/z 638, 783 and 928, all exhibiting the expected isotopomers for an $RuCl_2$ species, which may be attributed to $\{[Ru(bipy)_2L]\}^+$, $\{[Ru(bipy)_2L][PF_6]\}^+$ and $\{[Ru(bipy)_2L][PF_6]_2\}^+$ respectively.

The coordination of 4,4′-dichloro-2,2′-bipyridine to a positively charged metal centre results in an activation towards nucleophilic attack via a metal assisted addition–elimination pathway (Fig. 1) [2, 6]. Upon the addition of amines to the bright red solutions of $[Ru(bipy)_2L]^{2+}$ salts in $MeOCH_2CH_2OH$, an immediate colour change to brick red occurred. However, quenching of the reaction and work-up at this stage only led to the quantitative recovery of $[Ru(bipy)_2L][PF_6]_2$. We believe this colour change to be associated with the outer-sphere coordination of amine, as it displaces intimately associated solvent molecules. This is remarkably reminiscent of the marked solvent dependence observed in complexes of related polypyridines [5]. After the solution of $[Ru(bipy)_2L]^{2+}$ and amine had been heated to reflux for 4 h, no further colour changes had occurred, but work-up yielded only complexes of the substituted 4,4′-bis(amino)-2,2′-bipyridines. Reaction occurred smoothly and in high yield with $Me_2N(CH_2)_2NH_2$, $H_2N(CH_2)_2NH_2$, $H_2N(CH_2)_3NH_2$, $H_2N(CH_2)_4NH_2$,

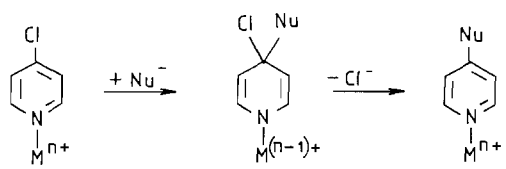

Fig. 1. The metal-assisted addition elimination mechanism.

$H_2N(CH_2)_3NH(CH_2)_3NH_2$ and $H_2N(CH_2)_2NH(CH_2)_2NH_2$ to give complexes of the substituted 4,4′-bis(amino)-2,2′-bipyridines.

The complexes with the 4,4′-bis(amino)-2,2′-bipyridines L^1–L^6 were isolated as their red hexafluorophosphate salts by the addition of an excess of aqueous ammonium hexafluorophosphate. The analytical data for these complexes is reported in Table I. The complexes also exhibited FAB mass spectra in accord with the proposed structures. The presence of the non-coordinated amino groups results in an enhanced hydrophilic character, and the complexes were commonly obtained as hydrates. The pendant amine groups also resulted in enhanced basic properties, and some of the complexes were protonated upon the side-chains.

The electronic spectra of the complexes exhibit characteristic changes associated with the formation of the amino complexes. Methanolic solutions of $[Ru(bipy)_2L][PF_6]_2$ exhibit absorption maxima at 446 nm (ϵ = 12, 620), 292 nm (ϵ = 76, 370), 254 nm (sh, ϵ = 23, 950) and 246 nm (ϵ = 24, 400). In the case of $[Ru(bipy)_2L^1][PF_6]_2$, maxima are observed at 469 nm (ϵ = 16, 460), 446 nm (ϵ = 16, 180), 292 nm (ϵ = 101, 810), 254 nm (ϵ = 67, 180) and 246 nm (sh, ϵ = 61, 690). Both complexes exhibit maxima in the 209–211 nm region. Similar spectra are observed for the other amino complexes. Treatment of the complexes with acid did not markedly alter the positions or intensities of any of the maxima above 220 nm, but resulted in intensity changes in the 209–211 nm bands.

The ^1H NMR spectra of the complexes with the amino substituted ligands are of some interest, and exhibit a very marked solvent dependence suggesting strong interactions between solvent molecules and the amino side-chains. The ^1H NMR spectrum of an acetone-d_6 solution of $[Ru(bipy)_2L^1][PF_6]_2$ at various temperatures is shown in Fig. 2. In the temperature range 264–308 K, the signals may be seen to split into two distinct sets of resonances, assignable to the 2,2′-bipyridine and the substituted rings respectively. The room temperature spectrum (290 K) exhibits a very broad resonance at δ 8.27, a broad doublet at δ 7.67 and a broad doublet of doublets at δ 7.15. These are assigned to H_3, H_6 and H_5 of the substituted rings on the basis of homonuclear decoupling experiments. Upon raising the temperature, these signals sharpen, and a high-temperature limiting spectrum, in which all of the resonances are sharp is observed at 308 K. This spectrum is exactly that expected from a $[Ru(bipy)_2L']^{2+}$ species with a 4,4′-disubstituted-2,2′-bipyridine [2]. Upon cooling to 264 K, these three resonances broaden, coalesce and begin to sharpen again. The apparent coalescent temperatures for H_3 and H_6 are 266 K and 255 K respectively. Over the temperature range 308–264 K the remaining signals in the spectrum, assigned to the unsubstituted 2,2′-bipyridine ligands, exhibit little if any changes. These observations are consistent with a process involving only the side-chains of the substituted 2,2′-bipyridine ligands. Associated changes in the aliphatic region of the spectrum are consistent with this interpretation, but are not conclusive. At room temperature, the methyl groups of the NMe_2 group are observed as a broad singlet at δ 2.90, but upon cooling collapses, with an apparent coalescence temperature of 220 K. Whether this is associated with the same fluxional process, or a separate one is not clear. It is tempting to propose that the processes are associated with rotation about the C_{ring}–NH bond. In the high temperature limiting spectrum there is free rotation about this bond; upon cooling rotation is restricted and various rotamers are present. We are currently undertaking further experiments to resolve these ambiguities. It is also apparent that upon cooling below 264 K, some further process is being frozen out, and this may be observed in both sets of resonances. Similar behaviour was observed with all of the other 4,4′-bis(amino)-2,2′-bipyridine complexes.

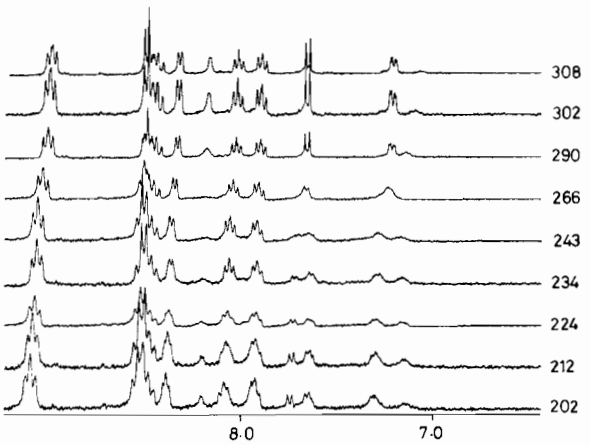

Fig. 2. 250 MHz ^1H variable temperature NMR spectra of $[Ru(bipy)_2L^1]^{2+}$ in acetone-d_6.

These fluxional processes are likely to be minimised by coordination of the terminal amines to a second metal centre, and we are currently investigating the coordination chemistry of these novel ligands.

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