Synthesis and Characterization of *cis*-(2,2'-Bipyridine)(2,2'-biquinoline)dichlororuthenium(II) and its Co-ordination Chemistry with Imidazole Derivatives

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The reactions of *cis*-[Ru(bipy)(bquin)Cl_2] (bipy = 2,2'-bipyridine, bquin = 2,2'-biquinoline) with several imidazole derivatives have been studied. Substitution of only one chloride ligand takes place exclusively *trans* to bquin, resulting in the synthesis of *cis*-[Ru(bipy)(bquin)(L)Cl]PF_6 (L = Him, 1-mim or 5-mim; Him = imidazole, 1-mim = 1-methylimidazole, 5-mim = 5-methylimidazole). This substitution preference for imidazoles indicates that bquin has a stronger electronic *trans* influence than bipy, and that the steric effects of bquin do not appear to obstruct the approach of a substituting ligand. By substitution of the second chloride the compounds *cis*-[Ru(bipy)(bquin)L_2][PF_6]$_2$ and *cis*-[Ru(bipy)(bquin)(1-mim)(Him)][PF_6]$_2$ were isolated. The properties of the compounds have been studied by ^{1}H NMR spectroscopy and electrochemistry. The studies show that *cis*-[Ru(bipy)(bquin)Cl_2] incorporates potential covalent binding properties for biomolecules like histidine and DNA.

Recently the antitumour activity of several ruthenium compounds has been reported.[1-4] Of these complexes the two most interesting compounds (in terms of tumour cure and drug development) are *trans*-[Ru(dmso)$_4$$Cl_2$] (dmso = dimethyl sulfoxide) and [H_2im][*trans*-Ru(Him)$_2$$Cl_4$] (Him = imidazole). For both complexes it is most likely that interaction takes place at the level of DNA,[5,6] and that intermediates formed in aqueous solutions are the active species.[7-11] The aim of our research is to understand better the tumour-inhibiting capacities due to covalent binding of ruthenium compounds to DNA bases, in general. Therefore, the reactions of ruthenium compounds containing pyridyl and labile chloride ligands with nucleic bases and imidazole derivatives are being studied. These classes of compounds became of special interest when the chiral selectivity in covalent binding to DNA of *cis*-[Ru(phen)$_2$$Cl_2$] (phen = 1,10-phenanthroline) was published[12] and more recently when the electrocatalytic cleavage of DNA by [Ru(terpy)(bipy)(H_2O)]$^{2+}$ (bipy = 2,2'-bipyridine, terpy = 2,2':6',2''-terpyridine) was reported.[13] It was decided to study first the co-ordination chemistry of *cis*-[Ru(bipy)$_2$$Cl_2$] with the nucleobases 9-methylhypoxanthine and 9-ethylguanine.[14,15] The binding of 1-methylimidazole (1-mim) to *cis*-[Ru(bipy)$_2$$Cl_2$] has been reported previously.[16] Imidazole derivatives are interesting ligands for ruthenium, because these compounds are present as fragments in biomolecules, like histidine and the nucleobases guanine and adenine. Since *cis*-[Ru(bipy)$_2$$Cl_2$] contains two chemically equivalent chloride ligands it was considered useful to extend this study to a ruthenium complex of formula *cis*-[Ru(bipy)LCl_2] in which the two Cl^- ligands are non-equivalent. The compound *cis*-[Ru(bipy)(bquin)Cl_2] (bquin = 2,2'-biquinoline) was chosen for a first study, of which the results are presented here. Due to its better π-accepting properties,[17] the bquin ligand is expected to have a larger *trans* effect than bipy and accordingly the position *trans* to bquin would be electronically favoured for substitution by a σ-donating ligand. In *cis*-[Ru(bipy)(bquin)Cl_2] the bipy and bquin ligands differ also substantially in steric properties with regard to the substitution sites (see Fig. 1), so it is *a priori* not clear which of these two effects will dominate. Imidazoles are very suitable ligands to study this competition with a powerful tool like ^{1}H NMR spectroscopy. Electrochemistry is an excellent method for characterizing the co-ordination sphere of the metal by comparison of metal-centred oxidation and ligand-reduction potentials.

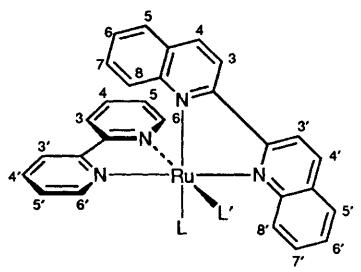

Fig. 1 The structure of *cis*-[Ru(bipy)(bquin)L(L')]$^{n+}$ (n = 0, 1 or 2) and the numbering of the protons of the bipy and bquin ligands (L,L' = Cl, Him, 1-mim or 5-mim) used

Although the syntheses of some [Ru(bipy)(bquin)L]$^{2+}$ (L is a bidentate ligand other than bipy or bquin) compounds have been described from *cis*-[Ru(bipy)(bquin)Cl_2] formed *in situ*,[18-22] the isolation of this latter complex has not been published as yet. In this paper the isolation and characterization of the complex *cis*-[Ru(bipy)(bquin)Cl_2] **1** is reported as well as the syntheses and characterization of the compounds *cis*-[Ru(bipy)(bquin)(L)Cl]PF_6, *cis*-[Ru(bipy)(bquin)L_2][PF_6]$_2$ [L = Him **2a**, **2b**, 1-mim **3a**, **3b** and 5-methylimidazole (5-mim) **4a**, **4b**] and *cis*-[Ru(bipy)(bquin)(1-mim)(Him)][PF_6]$_2$ **5** are described. The results of the ^{1}H NMR experiments are compared with the ^{1}H NMR data of *cis*-[Ru(bipy)$_2$(Him)Cl]PF_6 and *cis*-[Ru(bipy)$_2$(Him)$_2$][PF_6]$_2$.

Experimental

Physical Measurements.—Proton NMR spectra were recorded on a Bruker WM 300 MHz spectrometer. All spectra were recorded with the compounds dissolved in $(CD_3)_2CO$, except for the spectrum of *cis*-[Ru(bipy)(bquin)Cl_2] **1**, which was obtained from a solution in $(CD_3)_2SO$, after washing the compound with CD_3CN to remove some paramagnetic impurities. All signals were assigned by the use of homonuclear correlation (COSY) two-dimensional experiments. For the

COSY experiments 129 f.i.d.s of eight scans each, consisting of 1k data points were accumulated. All peak positions are relative to $SiMe_4$. Electrochemical experiments were performed with the use of an EG & G PAR C 303 potentiostat combined with an EG & G 384 B polarographic analyser. Differential pulse polarographic measurements between −2.0 and +2.0 V were carried out with a scan rate of 4 mV s^{-1} and a pulse height of 20 mV. For the cyclic voltammograms a scan rate of 40 mV s^{-1} was used. A three-electrode configuration was used with a saturated calomel electrode (SCE) as reference electrode, in combination with a glassy carbon working electrode and a platinum wire as auxiliary electrode. All experiments were carried out in a solution of 0.1 mol dm^{-3} tetrabutylammonium perchlorate in HPLC-grade MeCN. Elemental analyses for C, H, N and P were performed by the Microanalytical Laboratory, University College, Dublin, Ireland. Chlorine was analysed by titration with $AgNO_3$ after sample exclusion by Schöningen's method.

Materials.—Hydrated ruthenium trichloride, $RuCl_3 \cdot 3H_2O$, was obtained from Johnson Matthey. Intermediates $[\{Ru(bipy)Cl_3\}_n] \cdot H_2O$[23] and *cis*-$[Ru(bipy)_2(Him)Cl]PF_6$[16] were prepared according to literature procedures. The compound *cis*-$[Ru(bipy)_2(Him)_2][PF_6]_2$ was a kind gift from Dr. J. G. Vos (Dublin City University, Ireland). All ligands were obtained from Sigma, except for bipy and bquin which were obtained from Janssen Chimica. All ligands were used as commercially obtained without further purification. Elemental analyses of a few representative compounds were used to correlate the ^1H NMR spectra of the prepared ruthenium complexes.

Preparations.—*cis*-$[Ru(bipy)(bquin)Cl_2]$ **1**. A solution of $[\{Ru(bipy)Cl_3\}_n] \cdot H_2O$ (4.35 g, 11.4 mmol), bquin (3.07 g, 12 mmol) and ascorbic acid (3 g) in ethanol (250 cm^3) was heated at reflux for 5 d. After cooling the dark brown solution was kept for 3 d at −20 °C. A black powder was filtered off and washed with diethyl ether. The black product was dried in air. Yield 4.7 g (67%) (Found: C, 57.3; H, 3.5; Cl, 11.9; N, 9.4. $C_{28}H_{20}Cl_2N_4Ru$ requires C, 57.5; H, 3.4; Cl, 12.1; N, 9.6%).

cis-$[Ru(bipy)(bquin)(Him)Cl]PF_6 \cdot H_2O$ **2a**. Complex **1** (130 mg, 0.22 mmol) and imidazole (25 mg, 0.37 mmol) were heated at reflux for 5 min in ethanol–water (1:1 v/v, 40 cm^3). After addition of NH_4PF_6 (300 mg) to the blue solution, the ethanol was removed by rotary evaporation until a black solid appeared. The obtained black solid was recrystallized from acetone–water and dried *in vacuo* at 60 °C. Yield 98 mg (58%) (Found: C, 47.6; H, 3.2; Cl, 4.2; N, 10.1; P, 4.5. $C_{31}H_{26}ClF_6N_6OPRu$ requires C, 47.7; H, 3.3; Cl, 4.5; N, 10.8; P, 4.0%).

cis-$[Ru(bipy)(bquin)(Him)_2][PF_6]_2$ **2b**. Complex **1** (150 mg, 0.26 mmol) and imidazole (60 mg, 0.88 mmol) were heated at reflux for 7 h in ethanol–water (1:1 v/v, 40 cm^3). During the reaction the solution turned purple. Further preparation was carried out as described for complex **2a**. Yield 116 mg (49%) of a black solid (Found: C, 44.0; H, 3.1; N, 11.0; P, 6.5. $C_{34}H_{28}F_{12}N_8P_2Ru$ requires C, 43.5; H, 3.0; N, 11.9; P, 6.6%).

cis-$[Ru(bipy)(bquin)(1\text{-}mim)Cl]PF_6$ **3a**. Complex **1** (155 mg, 0.27 mmol) and 1-methylimidazole (90 mg, 1.1 mmol) were heated at reflux in ethanol (40 cm^3) for 8 h. After addition of an excess of a concentrated solution of aqueous NH_4PF_6 (30 cm^3) to the dark blue solution, the ethanol was removed by rotary evaporation. The black solid was filtered off, recrystallized from acetone–water and dried *in vacuo* at 60 °C. Yield 190 mg (92%).

cis-$[Ru(bipy)(bquin)(1\text{-}mim)_2][PF_6]_2$ **3b**. Complex **1** (150 mg, 0.26 mmol) and 1-methylimidazole (100 mg, 1.2 mmol) were heated at reflux in ethanol–water (1:1 v/v, 50 cm^3) for 3 d. Further preparation was carried out as described for complex **2a**. Yield 120 mg (47%) of black crystals.

cis-$[Ru(bipy)(bquin)(5\text{-}mim)Cl]PF_6$ **4a**. Complex **1** (250 mg, 0.43 mmol) and 4(5)-methylimidazole (50 mg, 0.61 mmol) were heated at reflux in ethanol (50 cm^3) for 24 h. Further preparation was carried out as described for complex **3a**. Yield 234 mg (70%) pf black powder.

cis-$[Ru(bipy)(bquin)(5\text{-}mim)_2][PF_6]_2$ **4b**. Complex **1** (200 mg, 0.34 mmol) and 4(5)-methylimidazole (200 mg, 2.4 mmol) were heated at reflux in ethanol–water (1:1 v/v, 40 cm^3) for 3 d. Further preparation was carried out as described for complex **2a**. Yield 282 mg (85%) of black crystals.

cis-$[Ru(bipy)(bquin)(1\text{-}mim)(Him)][PF_6]_2$ **5**. Complex **2a** (30 mg, 0.04 mmol) and 1-methylimidazole (15 mg, 0.22 mmol) were heated at reflux in ethanol–water (1:1 v/v, 40 cm^3) for 24 h. During the reaction the colour changed from dark blue to purple. Further preparation was carried out as described for complex **2a**. Yield 25 mg (65%) of black powder.

Results and Discussion

General.—The complex *cis*-$[Ru(bipy)(bquin)Cl_2]$ **1** was prepared by reaction of equimolar amounts of $[\{Ru(bipy)Cl_3\}_n] \cdot H_2O$ and bquin and an excess of ascorbic acid in absolute ethanol under refluxing conditions. This synthesis is identical to a literature procedure,[18] except for the addition of an excess of ascorbic acid. Without using the excess of ascorbic acid no pure compound could be isolated. It is proposed that ascorbic acid facilitates the reduction of Ru^{III} to Ru^{II} during the co-ordination of bquin. The compounds **2a**, **3a** and **4a** were prepared by reaction of compound **1** with a slight excess of ligand in a refluxing ethanol–water mixture for about 15 min. Their formation is likely to occur *via* equations (1) and (2) where

$$cis\text{-}[Ru(bipy)(bquin)Cl_2] + solv \longrightarrow cis\text{-}[Ru(bipy)(bquin)(solv)Cl]^+ + Cl^- \quad (1)$$

$$cis\text{-}[Ru(bipy)(bquin)(solv)Cl]^+ + L \longrightarrow cis\text{-}[Ru(bipy)(bquin)(L)Cl]^+ + solv \quad (2)$$

solv can be either ethanol or water. Upon heating **1** dissolves and reaction (1) takes place. Reaction (2) is relatively fast, as can be seen from the rapid colour change to blue upon the addition of L to the purple solution of *cis*-$[Ru(bipy)(bquin)(H_2O)Cl]^+$ in ethanol–water. The methyl substituent in compound **4a** is located at the 5- rather than the 4-position (see Fig. 2 for labelling of co-ordinated imidazoles). This agrees with the observation that 2-methylimidazole does not react with **1**. Complexes with bquin are light sensitive, leading often to loss of the bquin ligand. Despite carrying out the reactions in subdued light, the yield of **2a** is low due to decomposition. Compounds **2a**, **3a** and **4a** can also be synthesized by reaction of **1** and an excess of L in absolute ethanol at reflux during 8 h for L = Him or 24 h for L = 1-mim or 5-mim. The compounds **2b**, **3b** and **4b** were prepared by reaction of the compounds **2a**, **3a** and **4a** with an excess of ligand in refluxing ethanol–water for several hours. The formation of these compounds probably occurs as shown in equations (3) and (4).

$$cis\text{-}[Ru(bipy)(bquin)(L)Cl]^+ + H_2O \longrightarrow cis\text{-}[Ru(bipy)(bquin)L(H_2O)]^{2+} + Cl^- \quad (3)$$

$$cis\text{-}[Ru(bipy)(bquin)(L)(H_2O)]^{2+} + L \longrightarrow cis\text{-}[Ru(bipy)(bquin)L_2]^{2+} + H_2O \quad (4)$$

It is highly likely that these reactions occur *via* the intermediate complex *cis*-$[Ru(bipy)(bquin)L(H_2O)]^{2+}$ because

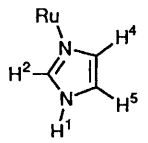

Fig. 2 Numbering of the protons of the imidazole derivatives

Table 1 Proton NMR chemical shifts of the ruthenium complexes in $(CD_3)_2CO$

Complex	1[a]	2a	3a	4a	2b	3b	4b	5
bipy								
H^3	8.44	8.35	8.30	8.30	8.08	8.05	8.05	8.05
H^4	7.71	7.82	7.80	7.79	7.77	7.78	7.78	7.78
H^5	7.03	7.27	7.26	7.25	7.37	7.34	7.34	7.35
H^6	7.50	7.68	7.60	7.63	7.83	7.72	7.75	7.72
$H^{3'}$	8.59	8.44	8.42	8.43	8.29	8.26	8.26	8.27
$H^{4'}$	8.09	8.15	8.12	8.12	8.20	8.18	8.18	8.19
$H^{5'}$	7.75	7.92	7.92	7.93	8.08	8.07	8.07	8.05
$H^{6'}$	9.72	10.29	10.27	10.27	9.90	9.84	9.88	9.84
bquin								
H^3	8.55	8.63	8.61	8.59	8.79	8.76	8.76	8.76
H^4	8.24	8.35	8.31	8.31	8.47	8.45	8.44	8.45
H^5	7.88	7.91	7.90	7.88	7.98	7.97	7.97	7.97
H^6	7.42	7.52	7.50	7.51	7.58	7.56	7.56	7.57
H^7	7.06	7.29	7.28	7.30	7.38	7.33	7.36	7.32
H^8	6.93	7.88	7.88	7.87	7.80	7.73	7.74	7.74
$H^{3'}$	8.74	8.83	8.81	8.78	9.01	8.99	8.98	8.98
$H^{4'}$	8.67	8.74	8.71	8.68	8.94	8.92	8.92	8.92
$H^{5'}$	8.16	8.18	8.17	8.15	8.29	8.27	8.27	8.27
$H^{6'}$	7.77	7.68	7.68	7.70	7.71	7.74	7.75	7.78
$H^{7'}$	7.67	7.35	7.39	7.39	7.44	7.48	7.48	7.50
$H^{8'}$	9.70	8.00	7.96	8.02	7.63	7.64	7.68	7.66
L								
H^1		11.8	3.64[b]	12.0	12.0	3.63[b]	11.7	11.7
H^2		7.92	7.87	7.90	8.07	8.09	7.83	8.24
H^4		6.92	6.86	6.64	7.24	7.05	7.01	7.14
H^5		7.20	7.11	2.12[b]	7.26	7.15	2.10[b]	7.25
L'								
H^1					12.0	3.67[b]	11.7	3.64[b]
H^2					8.09	8.13	7.95	8.13
H^4					7.42	7.29	7.26	7.40
H^5					7.52	7.31	2.19[b]	7.49

[a] In $(CD_3)_2SO$. [b] 3 H of methyl.

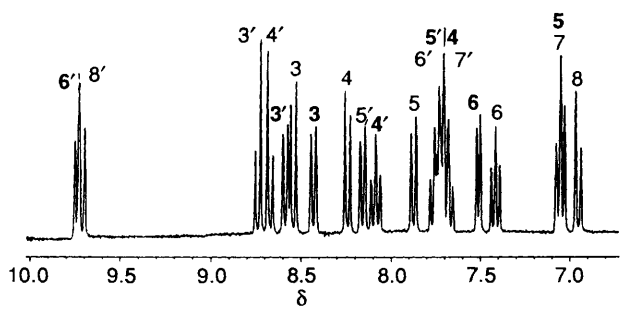

Fig. 3 300 MHz Proton NMR spectrum of *cis*-[Ru(bipy)(bquin)Cl_2] recorded in $(CD_3)_2SO$. Assignments are given in Table 1 (see also Fig. 1), bipy signals are in boldface

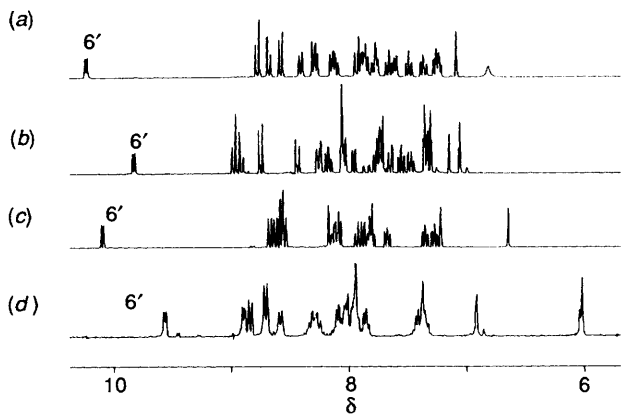

Fig. 4 Low-field region of the 300 MHz ^1H NMR spectra of compounds **2a** (*a*), **2b** (*b*), *cis*-[Ru(bipy)$_2$(Him)Cl]PF_6 (*c*) and *cis*-[Ru(bipy)$_2$(Him)$_2$][PF_6]$_2$ (*d*), all recorded in $(CD_3)_2CO$

the formation of **2b**, **3b** and **4b** does not take place in absolute ethanol. All these findings are identical with the reactivity of *cis*-[Ru(bipy)$_2$$Cl_2$] with 1-mim.[16] Compound **5** is the only compound of the mixed-ligand class *cis*-[Ru(bipy)(bquin)L(L')]$^{2+}$ that could be isolated. All other attempts to prepare more compounds of this class of complexes failed and mixtures of **2b**, **3b** and **4b** were isolated.

Proton NMR Spectroscopy.—All 300 MHz ^1H NMR spectra were assigned on the basis of COSY two-dimensional experiments (Table 1). The NMR spectrum of **1** (Fig. 3) was measured in $(CD_3)_2SO$ after washing the compound with CD_3CN. This extra purification step was needed to remove some ruthenium(III) impurities. The NMR spectrum of **1** contains 20 non-equivalent signals, in agreement with the lack of symmetry in the complex. The two doublets isolated in the low-field area of the NMR spectrum are remarkable. These doublets are assigned as the $H^{6'}$ of bipy and the $H^{8'}$ of bquin because of their orientation near the chloride ligands. The two doublets could be distinguished by the difference in their coupling constants ($H^{6'}$ of bipy *ca.* 6 Hz; $H^{8'}$ of bquin *ca.* 9 Hz[22]). From the NMR spectra of **2a**, **3a** and **4a** it is concluded that the mono-co-ordination of the imidazole derivatives takes place exclusively on the position *trans* to bquin, because the spectra contain an isolated doublet at *ca.* δ 10.3 [Fig. 4(*a*)] with a coupling constant of *ca.* 6 Hz. This doublet is assigned as the

Table 2 Electrochemical data for the complexes[a]

Complex	$E_{\frac{1}{2}}$/V (ΔE_p/mV)		
		Ligand reductions	
	$Ru^{2+/3+}$ oxidation	bquin	bipy
1	0.38 (90)	−1.25 (90)	−1.52 (110)
2a	0.71 (120)	−1.16 (120)	−1.59 (180)
3a	0.71 (110)	−1.16 (110)	−1.57 (200)
4a	0.69 (120)	−1.16 (120)	−1.59 (190)
2b	1.02 (110)	−1.03 (110)	−1.54 (150)
3b	0.99 (100)	−1.03 (110)	−1.50 (120)
4b	0.97 (100)	−1.04 (110)	−1.51 (110)
5	0.99 (100)	−1.03 (110)	−1.50 (120)
$[Ru(bipy)_3][PF_6]_2$[b]	1.27 (90)		−1.34 (100), −1.53 (110), −1.79 (100)
cis-$[Ru(bipy)_2Cl_2]$[b]	0.30 (110)		−1.67 (130), −1.85 (110)
cis-$[Ru(bquin)_2Cl_2]$[b]	0.43 (90)	−1.06 (110), −1.22 (140)	

[a] Measured in acetonitrile containing 0.1 mol dm^{-3} NBu_4ClO_4, by using differential pulse polarography with a scan rate of 4 mV s^{-1}; values in parentheses are peak-to-peak separations measured by cyclic voltammetry with a scan rate of 40 mV s^{-1}. Potentials quoted *vs.* SCE. [b] Recorded under identical conditions for comparison.

$H^{6'}$ of bipy which is still orientated near a chloride ligand. The signal of the $H^{8'}$ proton of bquin is found at *ca.* δ 8.0. This shift to higher field is due to the ring-current effect of the imidazole derivatives. From this we conclude that the electronic effects of the bquin ligand dominate over the steric effects at the $H^{8'}$ end of this ligand and the hypothesis is confirmed by the fact that in **1** bquin has a stronger *trans* effect than bipy. The NMR spectra of **2b**, **3b**, **4b** and **5** contain only non-equivalent signals. This implies that even the two imidazole ligands co-ordinated to the ruthenium are chemically non-equivalent. Important is the chemical shift of the $H^{6'}$ proton of bipy at *ca.* δ 9.9 [Fig. 4(*b*)] which was expected at much higher field, because of the ring-current effect of the imidazole ligands. The deshielding of the chemical shift of $H^{6'}$ of bipy is in agreement with the low-field region of the NMR spectra of *cis*-$[Ru(bipy)_2(Him)Cl]PF_6$ and *cis*-$[Ru(bipy)_2(Him)_2][PF_6]_2$ [Fig. 4(*c*) and 4(*d*)].

Electrochemistry.—The redox potentials of all the compounds are summarized in Table 2, with the potentials of $[Ru(bipy)_3][PF_6]_2$, *cis*-$[Ru(bipy)_2Cl_2]$ and *cis*-$[Ru(bquin)_2Cl_2]$ measured under identical conditions for comparison and are in good agreement with the values published in the literature.[24] All values of $E_{\frac{1}{2}}$ were determined using differential-pulse polarography. The cyclic voltammograms were measured to check whether the potentials are reversible or not. All of the waves with ΔE_p which are close to the values of ΔE_p for $[Ru(bipy)_3][PF_6]_2$ ($i_{pa} = i_{pc}$, ΔE_p = 90–120 mV at a scan rate of 40 mV s^{-1}) are reversible. All other waves can be regarded as quasi-reversible. The oxidation potential of compound **1** lies as expected between the potentials of *cis*-$[Ru(bipy)_2Cl_2]$ and *cis*-$[Ru(bquin)_2Cl_2]$. Substitution of a chloride ligand by an imidazole derivative increases the oxidation potential by 200–300 mV, but the absolute values still clearly show co-ordination of one Cl ligand. All oxidations are metal centred,[24] which implies an oxidation from Ru^{II} to Ru^{III}. The reduction potentials of all Ru(bipy)(bquin) compounds involve first the reduction of bquin, followed by the reduction of bipy. This is a known fact and is in agreement with the first reduction potentials of *cis*-$[Ru(bipy)_2Cl_2]$ and *cis*-$[Ru(bquin)_2Cl_2]$.[18,22–24] The substitution of a chloride ligand by an imidazole derivative lowers the first reduction potential (reduction of bquin) by *ca.* 100 mV but has practically no influence on the second reduction potential (reduction of bipy).

Conclusion

The preparation of *cis*-[Ru(bipy)(bquin)Cl_2] by the reaction of $[\{Ru(bipy)Cl_3\}_n]\cdot H_2O$ and bipy in ethanol proceeds in good yields, when ascorbic acid is present in the solvent. The ascorbic acid likely facilitates the reduction from Ru^{III} to Ru^{II} during the reaction.

The substitution of only one chloride ligand in **1** by an imidazole derivative only takes place at the co-ordination site *trans* with regard to bquin; this is ascribed to the fact that bquin has a stronger electronic *trans* influence than bipy. The steric effects of the bquin ligand on the substitution site are not that large to obstruct the approach of a substituting ligand.

The second chloride ligand can also be substituted by an imidazole derivative albeit slowly. Our study has shown that *cis*-[Ru(bipy)(bquin)Cl_2] incorporates potential covalent binding properties towards biomolecules like histidine and DNA.

Acknowledgements

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