Anion selectivity properties of ruthenium(II) tris(5,5′-diamide-2,2′-bipyridine) receptors dictated by solvent and amide substituent†

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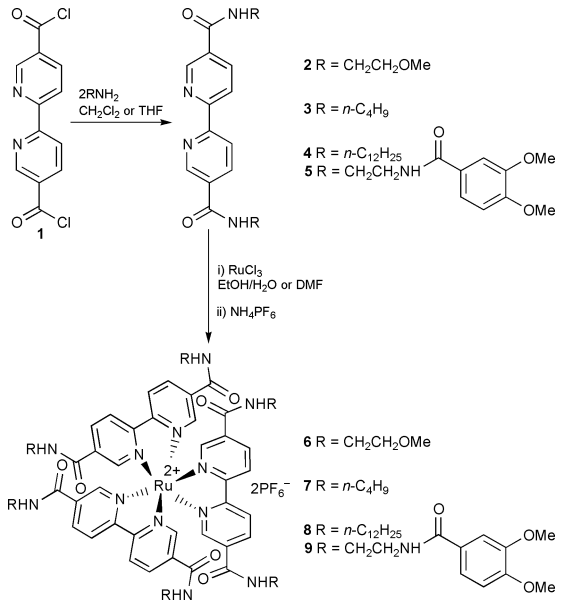
The ratio of the dichloromethane–methanol solvent mixture medium and nature of the receptor amide substituent critically dictates chloride *vs.* nitrate selectivity properties of new ruthenium(II) tris(5,5′-diamide-2,2′-bipyridine) receptors.

The selective recognition and sensing of anionic guests is a fundamental objective in supramolecular chemistry.[1,2] This is a consequence of the important role played by anions in a range of biological, chemical, medical and environmental processes.[3] Despite the fact that a wide range of solvents and solvent mixtures has been used in anion binding investigations, relatively little attention has been paid as to how the nature of the solvent medium and receptor structure can influence both the strength of anion–receptor complexation and importantly the anion binding selectivity trend the receptor displays. Previous research has shown that bis(heteroleptic) ruthenium(II) bipyridine cations $Ru(bpy)_2(bpy')^{2+}$ can bind and optically sense anions when bpy′ is a 4,4′- or 5,5′-diamide-2,2′-bipyridine ligand.[4,5] These receptors employ a combination of electrostatic and hydrogen bonding interactions to bind anionic guests. We report here the synthesis of new homoleptic receptors based on the ruthenium(II) tris(5,5′-diamide-2,2′-bipyridine) motif and demonstrate the anion binding strength, stoichiometry and chloride *vs.* nitrate anion selectivity critically depend on the nature of the receptor amide substituent and CH_2Cl_2:MeOH solvent mixture ratio.

The condensation of 5,5′-bis(chlorocarbonyl)-2,2′-bipyridine **1** with 2-methoxyethylamine, *n*-butylamine, *n*-dodecylamine 4′-carbonyl-1′,2′-dimethoxyphenyl-1,2-diaminoethane[6] gave the 5,5′-diamide-2,2′-bipyridine ligands **2**–**5** respectively in yields of 61–85% (Scheme 1).[5] The four host molecules **6**–**9** were prepared by reacting ligands **2**–**5** with ruthenium(III) trichloride in EtOH–H_2O (*via* 'ruthenium blue'[7]) or DMF. The receptors were purified by column chromatography on silica gel or Sephadex SP C25 and were isolated as their hexafluorophosphate salts in yields of 17–85%.‡

The Λ- and Δ-enantiomers of host **6** were resolved by cation exchange chromatography (Sephadex SP C25)[8] using sodium (−)-O,O′-dibenzoyl-L-tartrate. Figs. 1 and 2 show the crystal structure of the dichloride salt of Δ-**6**.§ The metal has a six-coordinate distorted octahedral environment being bonded to six nitrogen atoms [2.039(13)–2.095(13) Å] of the three bidentate ligands. The most interesting feature of the structure is that both chloride anions are encapsulated within the cavities formed around two triangular faces in the metal coordination sphere. As shown in Fig. 1, Cl2 forms hydrogen bonds to the three –NH groups at distances of 3.19, 3.29, 3.36 Å for N302, N202 and N602, respectively. However Cl1 forms only two hydrogen bonds to N102 at 3.21 and N502 at 3.27 Å. The third amide N–H group is directed away from the chloride, outwards from the cavity, and forms an intermolecular hydrogen bond N(402)···O(501) (1 − *x*, 0.5 + *y*, 2 − *z*) at 2.99 Å.

† Electronic supplementary information (ESI) available: crystal structure determination of receptor Δ-**6**. See http://www.rsc.org/suppdata/cc/b0/b008822f/



Scheme 1

There is a good geometric complementarity between the chloride anions and the interligand binding clefts, as illustrated in Fig. 2.

UV–VIS spectroscopic anion titrations were performed by adding tetrabutylammonium chloride, acetate and nitrate salts to receptors **6**–**9** in CH_2Cl_2 and CH_2Cl_2–MeOH solutions. Binding was generally signified by decreases in the absorbance and hypsochromic shifts for the MLCT and LC bands at *ca.* 260 and 300 nm, respectively. Values for the stability constants log β_1 and log β_2 were calculated using the Specfit program[9] and the data are summarised in Table 1. The results demonstrate how anion binding strength, stoichiometry and selectivity are

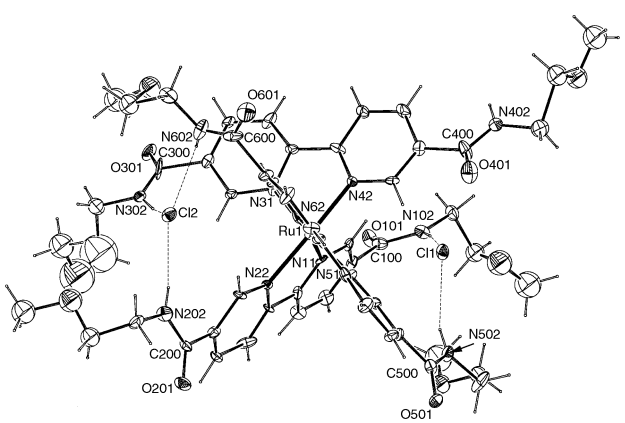


Fig. 1 The structure of Δ-**6** with ellipsoids at 20% probability. Hydrogen bonds to the chloride ions are shown as dotted lines.

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strongly dependent on the type of anion, the solvent system and the receptor amide substituent. For example, Table 1 shows the stability constants for all three anions decrease significantly as the methanol content increases from 1:0 to 9:1, 7:3 and then 1:1 CH_2Cl_2:MeOH. This can be rationalised by considering the high polarity of methanol and its ability to hydrogen bond with the receptor and the anionic guest. The complex stoichiometry is dependent on the binding strength and can be either 1:1 or 1:2 (host:guest). In 1:0 and 9:1 CH_2Cl_2:MeOH the host:guest ratio is 1:2. This correlates with the binding stoichiometry exhibited by **Δ-6** in the solid state (Fig. 1). In contrast, the observed host:guest ratio can be 1:2 or 1:1 in 7:3 CH_2Cl_2:MeOH, and is 1:1 in 1:1 CH_2Cl_2:MeOH. Table 1 also reveals how the anion selectivity depends on the solvent system. In 9:1 and 7:3 CH_2Cl_2:MeOH, all receptors display the selectivity sequence $Cl^- > NO_3^- > AcO^-$. The preference for chloride suggests this guest presents a superior match for the shape and/or dimensions of the binding site, while the unfavourable desolvation energy and non-complementary shape of acetate may explain why the weakest complexes are formed with this anion. It is noteworthy that receptors **6** and **7** remain chloride selective in 1:1 CH_2Cl_2:MeOH, while hosts **8** and **9** become selective for the nitrate anion. As the percentage of methanol is raised from 10 to 30 to 50%, the energy required to desolvate the anions prior to complexation increases and this can switch selectivity towards the anion with the lowest desolvation energy.[10] The hydration enthalpies ($-\Delta H_{hyd}$) of NO_3^-, Cl^- and AcO^- are calculated to be 293, 335 and 402 kJ mol^{-1}, respectively,[11] and these provide a good guide to the relative anion solvation energies in 1:1 CH_2Cl_2:MeOH. Hosts **8** and **9** possess large, lipophilic substituents which can partially shield the amide binding site from the surrounding solvent; the anion must therefore undergo significant desolvation prior to binding with these receptors. Consequently, the selectivity trend $NO_3^- > Cl^- > AcO^-$ for hosts **8** and **9** in 1:1 CH_2Cl_2:MeOH reflects the sequence of hydration energies $AcO^- > Cl^- > NO_3^-$ in the Hofmeister series.[12] In contrast, receptors **6** and **7** contain smaller amide substituents than their congeners **8** and **9**, and the anion desolvation energy does not dictate the selectivity sequence. The geometric complementarity between the chloride anion and hosts **6** and **7** is dominant (as exemplified by the crystal structure of **Δ-6** in Fig. 2) and overrides the unfavourable desolvation energy for this guest.

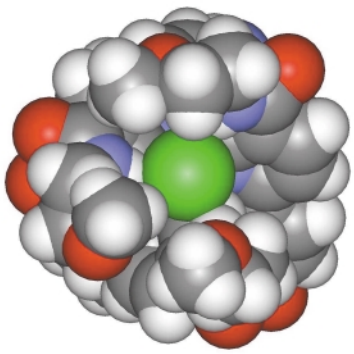

Fig. 2 CPK representation of **Δ-6** based on the crystal structure coordinates, illustrating the geometric complementarity between the chloride guest Cl2 (green) and the interligand binding pocket. (The methoxyethyl chain at the far side of the molecule has been removed to aid clarity.)

Table 1 Stability constants for receptors **6–9** and anions in CH_2Cl_2–MeOH solvent mixtures[a]

		Cl^-		NO_3^-		AcO^-	
Host	Solvent CH_2Cl_2:MeOH (v/v)	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2
8	1:0	[b]		[b]		[b]	
6	9:1	7.47	12.9	6.33	11.3	5.90	10.1
7	9:1	7.69	14.1	6.70	12.3	6.02	10.9
9	9:1	[b]		7.88	13.8	7.06	12.3
6	7:3	5.43		5.27		[c]	
7	7:3	6.44	10.8	5.64		[c]	
8	7:3	6.48	10.5	5.76		[c]	
9	7:3	5.94	10.2	5.42		[c]	
6	1:1	4.31		[c]		[c]	
7	1:1	4.45		[c]		[c]	
8	1:1	4.82		5.39		[c]	
9	1:1	4.51		5.03		[c]	

[a] Errors estimated to be ⩽7%; T = 293 K. [b] Binding too strong for calculation (host:guest complex stoichiometry is 1:2). [c] Binding too weak for calculation.

In summary, the chloride *vs.* nitrate selectivity of new ruthenium(II) tris(5,5′-diamide-2,2′-bipyridine) receptors depends on both solvation factors and the amide substituent on the host. This interrelation between solvation effects and receptor structure is also used to achieve anion binding selectivity in Nature.[11]

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Notes and references

‡ Receptors **6–9** were fully characterised by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry.

§ Receptor **Δ-6** was recrystallised from acetonitrile. *Crystal data*: $[RuL_3]Cl_2 \cdot 0.5\ MeCN \cdot 0.5\ EtOH \cdot 0.5\ H_2O$, $C_{56}H_{70.5}Cl_2N_{12.5}O_{13}Ru$, M = 1298.72, monoclinic, $P2_1$, a = 13.759(14), b = 16.711(17), c = 15.811(16) Å, β = 114.53(10)°, U = 3307 Å^3, Z = 2, D_c = 1.304 g cm^{-3}, 10237 independent reflections were collected with Mo-Kα radiation using the MARresearch Image Plate System at room temperature. The structures were refined on F^2 using SHELXL[13] to $R1$ = 0.1163, $wR2$ = 0.2983 for 5411 data with $I > 2\sigma(I)$ and $R1$ 0.2264, $wR2$ 0.3532 for all data. CCDC 182/1873. See http://www.rsc.org/suppdata/cc/b0/b008822f/ for crystallographic files in .cif format.

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