Ruthenium biimidazole complexes as anion receptors†

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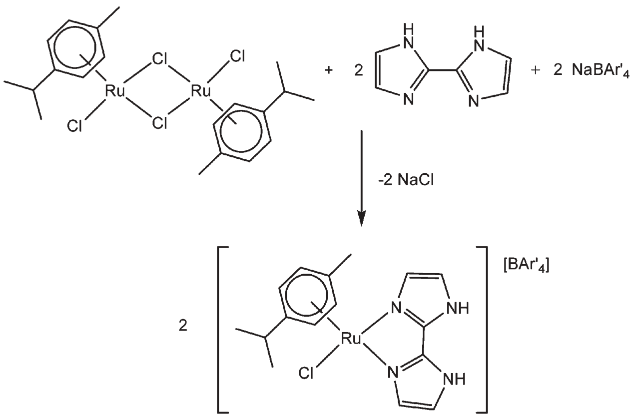
The behavior of the compound [RuCl(cym)(H_2biim)][BAr′$_4$] (cym = η^6-*para*-isopropylmethylbenzene, Ar′ = 3,5-bis-(trifluoromethyl)phenyl), synthesized from [{RuCl(cym)}$_2$-(μ-Cl)$_2$], H_2biim and NaBAr′$_4$, has been studied as a receptor of anions both in solution and in the solid state.

The occurrence of two N–H bonds able to simultaneously bind a hydrogen bond acceptor in molecules as simple as ureas[1] has prompted the study of their behavior as receptors of anions.[2] The same feature occurs in the *syn* conformation of 2,2′-biimidazole (H_2biim). However, the strong self-association of H_2biim molecules results in a low solubility and competes against anion binding. Thus, we have found that the low solubility of H_2biim in CD_3CN makes it NMR-invisible in this solvent, whereas in DMSO-*d*$_6$, in which H_2biim is sparingly soluble, δ (N–H) does not change appreciably upon addition of, for instance, an equimolar amount of tetrabutylammonium chloride. This behavior can be modified in two ways. The first one is the functionalization of biimidazole with appropriate organic substituents. This strategy has been recently used by Sessler *et al.*[3a] to change the solid state structural pattern, and by Causey and Allen to study the behavior towards anions in solution.[3b] The second way would be to coordinate H_2biim to a metal fragment, which would: (a) enforce the *syn* conformation and therefore preorganize H_2biim optimally for anion binding, (b) suppress self-association, (c) enhance the polarization of the biimidazole N–H bonds, making them better hydrogen bond donors, and, for cationic metal fragments, (d) add coulombic attraction to the hydrogen bond interaction. Biimidazole has been extensively used as a ligand and, in several instances, X-ray diffraction studies have showed the presence of hydrogen bonding between its N–H groups and an external anion.[4] Extended structures based on this motif have been exploited for crystal engineering.[3a,4d] However, the solution behavior of H_2biim complexes as receptors of anions has never been quantitatively studied.[5] Our first results in this area are the subject of the present paper.

Carmona *et al.* reported the high yield preparation of the compound [RuCl(cym)(H_2biim)][BF_4] (cym = η^6-*para*-isopropylmethylbenzene) by means of the reaction of [{RuCl(cym)}$_2$(μ-Cl)$_2$] with H_2biim followed by anion metathesis with $NaBF_4$.[6] The [RuCl(cym)(H_2biim)]$^+$ cation seemed a good candidate for our studies because of the ease of preparation, stability towards air and moisture, and the relative substitutional inertness usually attributed to [RuCl(η^6-arene)(L–L)]$^+$ complexes. In order to minimize the competition with external anions we preferred the BAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) counteranion.[7] Thus, the [RuCl(cym)(H_2biim)][BAr′$_4$] salt (**1**) was prepared in virtually quantitative yield by the reaction of [{RuCl(cym)}$_2$(μ-Cl)$_2$], H_2biim[8] and NaBAr′$_4$[9] (see Scheme 1), and spectroscopically characterized.[10]‡ A band at 3207 cm^{-1} in the IR spectrum of **1** (KBr pellet) was assigned to *ν*(N–H). In the 1 : 1 adducts obtained, on addition of tetrabutylammonium chloride or nitrate (see below), these bands shifted to 3099 and 3113 cm^{-1}, respectively, suggesting N–H···X interactions. Compound **1** was found to be very soluble, even in moderately polar dichloromethane, a feature common to most BAr′$_4$ salts.

The two N–H groups of coordinated H_2biim appeared as a singlet at δ 11.43 in the ^{1}H NMR of **1** in CD_3CN. The addition of tetrabutylammonium bromide, nitrate, hydrogensulfate, iodide or perrhenate shifted this signal to higher frequencies. Fast anion exchange was found in each case (titration curves are shown in Fig. 1 and in the Electronic Supplementary Information†), and binding constants were determined using the WinEQNMR program (see Table 1).[11]

The N–H ^{1}H NMR signal broadened and finally vanished when less than an equimolar amount of Bu_4NCl was added to the CD_3CN solution of **1**, indicating a strong **1**···Cl^- interaction in this solvent. The same was found for the more basic fluoride, dihydrogenphosphate and cyanide anions. In the more competitive DMSO-*d*$_6$ solvent, the N–H ^{1}H NMR signal remained visible when **1** was titrated with Cl^-, but not with F^-, $H_2PO_4^-$ or CN^-.



Scheme 1 Synthesis of [RuCl(cym)(H_2biim)][BAr′$_4$] (**1**).

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† Electronic Supplementary Information (ESI) available: General X-ray information and ^{1}H NMR titration plots of **1** in DMSO-*d*$_6$ and CD_3CN. See DOI: 10.1039/b510016j

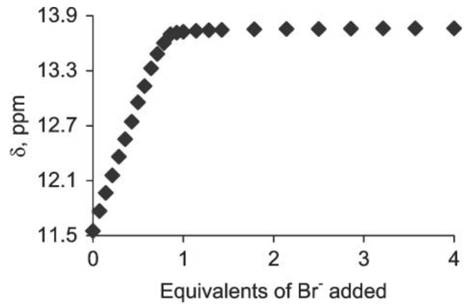

Fig. 1 ^1H NMR titration plot of receptor $[RuCl(cym)(H_2biim)][BAr'_4]$ (**1**) in CD_3CN with Br^-.

Table 1 Binding constants values for **1** in CD_3CN and DMSO-d_6[a]

Anion	K in CD_3CN/M^{-1}	K in DMSO-d_6/M^{-1}
Br^-	4527 (±841)	579 (±92)
NO_3^-	4828 (±587)	451 (±20)
HSO_4^-	5920 (±370)	651 (±88)
I^-	1114 (±207)	—
ReO_4^-	145 (±28)	—
Cl^-	—	970.3 (±21)

[a] Errors are given in parentheses

To obtain values of the binding constants, for a comparison to be made between the different anions, the titrations of **1** with Br^-, NO_3^- and HSO_4^- were repeated in DMSO-d_6, the results of which are showed in Table 1. In this solvent, the interaction between **1** and the anions I^- and ReO_4^- was found to be too weak, resulting in no observable change in the chemical shift of the N–H signals of **1**.

The supramolecular adducts $[RuCl(cym)(H_2biim)][Cl]$ and $[RuCl(cym)(H_2biim)][NO_3]$ were structurally characterized by means of single crystal X-ray diffraction, and graphical representations of the results are displayed in Fig. 2.§ Interestingly, these adducts crystallized separately from $[Bu_4N][BAr'_4]$, which remained in solution.¶ In the structure of the chloride adduct there are two molecules per asymmetric unit. In one of them (shown in Fig. 2a), the chloride anion interacts with the two N–H groups of only one of the Ru complexes. In the second, the chloride anion is disordered and is located over two sites in a 1 : 1 ratio. Each of these 50% occupancy chlorides interacts with the two N–H groups from one metal complex and with one N–H group from a neighbouring metal complex.

In the structure of the nitrate adduct, shown in Fig. 2b, each N–H group interacts with one nitrate oxygen, there being no additional contacts. Strong hydrogen bond interactions are indicated by the N···Cl (3.097(9) and 3.107(8) Å) and N···O (2.719(6) and 2.867(6) Å) distances.

The results shown in Table 1 indicate that **1** is a non-selective receptor. It is attractive to speculate that the complementarity in shape between host and guest found for $[RuCl(cym)(H_2biim)][NO_3]$ could partly compensate for the higher basicity of chloride and bromide with respect to nitrate, resulting in binding constants of the same order.

To conclude, we have investigated for the first time the solution behavior of metal biimidazole complexes as anion receptors. The compound $[RuCl(cym)(H_2biim)][BAr'_4]$ has been found to establish strong, non-selective interactions with several simple inorganic anions. The lack of selectivity can, at least in part, be attributed to ion pairing. In this context, the behavior of neutral metal biimidazole complexes is currently being investigated in our lab, and will be reported in a future publication.

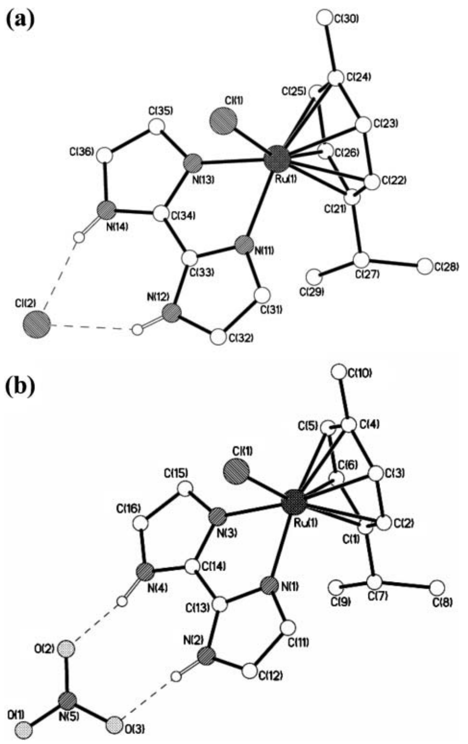

Fig. 2 (a) View of the crystalline structure of the adduct $[RuCl(cym)(H_2biim)][Cl]$. (b) View of the crystalline structure of the $[RuCl(cym)(H_2biim)][NO_3]$ adduct.

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Notes and references

‡ Synthesis of $[RuCl(cym)(H_2biim)][BAr'_4]$ (**1**): To a solution of $[\{RuCl(cym)\}_2(\mu\text{-}Cl)_2]$ (0.100 g, 0.163 mmol) in CH_2Cl_2 (20 mL) and MeCN (0.25 mL), $NaBAr'_4$ (0.290 g, 0.326 mmol) and H_2-biim (0.048 g, 0.359 mmol) were added. After stirring for 24 h, filtration and evaporation of the filtrate gave an orange solid that was washed with hexane (2 × 20 mL) and dried *in vacuo*. Yield: 0.380 g, 87%. ^1H NMR (CD_3CN): δ 11.43 (s br, 2 H, NH of H_2biim), 7.69 (m, 14 H, BAr'_4 and H_2biim), 7.38 (d, $^3J_{HH}$ = 1.56 Hz, 2 H, H_2biim), 5.86, 5.65 (AA′BB′ system, $J_{AB} = J_{A'B'}$ = 6.2 Hz, 4 H, cym), 2.71 (m, 1 H, CH of ^{i}Pr), 2.16 (s, 3 H, CH_3) and 1.11 (d, $^4J_{HH}$ = 7.2 Hz, 6H, CH_3 of ^{i}Pr). ^{13}C $\{^1H\}$NMR (CD_3CN): δ 161.6 (q, $^1J_{CB}$ = 49.9 Hz, C^i of BAr'_4), 138.2 (s, H_2biim), 134.7 (s, C^o of BAr'_4), 131.0 (s, H_2biim), 129.0 (q, $^2J_{CF}$ = 31.7 Hz, C^m of BAr'_4), 124.5 (q, $^1J_{CF}$ = 271.2 Hz, CF_3 of BAr'_4), 121.0 (s, C-^{i}Pr, cym), 120.3 (s, H_2biim), 117.7 (s, C^p of BAr'_4), 103.2 (s, C-Me, cym), 83.1 (s, C_A of cym), 81.5 (s, C_B of cym), 30.9 (s, CH of ^{i}Pr), 21.2 (s, CH_3 of ^{i}Pr) and 18.0 (s, CH_3 of cym). Anal. calc. for $C_{48}H_{32}BClF_{24}RuN_4$: C, 45.46; H, 2.54; N, 4.42. Found: C, 45.81; H, 2.39; N, 4.12%.

§ Crystal data for adduct $[RuCl(cym)(H_2biim)][Cl]$ (dichloromethane and water co-crystallized, see ESI†): $C_{16.50}H_{23}Cl_3N_4ORu$, crystal dimensions

0.23 × 0.18 × 0.10 mm, triclinic, space group *P*-1, a = 11.094(2), b = 12.523(3), c = 17.560(4) Å, α = 104.49(3), β = 92.84(3), γ = 110.07(3)°, V = 2193.9(8) Å^3, Z = 4, T = 293(2) K, D_c = 1.516 g cm^{-3}, Mo-K$_\alpha$ radiation (λ = 0.71073 Å), 13548 reflections collected, 4506 independent reflections ($3.61 \leqslant \theta \leqslant 21.00°$), R_1 = 0.0610, $wR2$ = 0.1430, GOF on F^2 = 1.107, CCDC 279201. Crystal data for adduct [RuCl(cym)(H$_2$biim)][NO$_3$]: $C_{16}H_{20}ClN_5O_3Ru$, crystal dimensions 0.21 × 0.12 × 0.05 mm, orthorhombic, space group *Pbca*, a = 16.048(3), b = 13.798(3), c = 16.470(4) Å V = 3646.9(13) Å^3, Z = 8, T = 180(2) K, D_c = 1.701 g cm^{-3}, Mo-K$_\alpha$ radiation (λ = 0.71073 Å), 23164 reflections collected, 4170 independent reflections ($3.55 \leqslant \theta \leqslant 27.48°$), R_1 = 0.0503, $wR2$ = 0.1040, GOF on F^2 = 1.014, CCDC 279202. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510016j

¶ Typically, the four ions are present in the crystals obtained from mixtures of a cationic receptor (added as its salt with a given counteranion) and tetrabutylammonium salt of the target anionic guest.

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