Molecular Recognition of Anions by a Novel Organocobalt Receptor: Oxyanion versus Halide Selectivity in Water

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The dissolution of $[Co\{2,6-(Me_2NCH_2)_2C_6H_3\}(\eta^5-C_5H_5)(H_2O)]PF_6$ (**1a**) in dry methanol or dry acetonitrile affords compounds **1b** and **1c**, respectively, in which the water ligand of **1a** has been substituted by MeOH or by CH_3CN. The crystal structure analysis of **1b** established that a strong intramolecular interaction exists between the methanolic proton and the NMe_2 group that was interacting with H_2O in **1a**. For **1c** no interaction could be found between the Co-bound acetonitrile ligand and this NMe_2 as it has changed its position in order to be as far away from the cobalt atom as possible. Whereas no reaction takes place between **1a** and an excess of sodium iodide in water or in methanol, in acetone I^- easily substitutes the water ligand of **1a** to afford high yields of the neutral compound **3**. Here also ^1H NMR spectroscopic data are in favour of a structure with no interaction between the NMe_2 and the iodide ligand as in **1c**. Protonation of the free NMe_2 unit of **1a** by adding increasing amounts of HPF_6 in water leads to the synthesis of **4a**. The p*Ka* of **1a** in D_2O was found to be 6.1. Treating **1a** with acidic buffered water solutions (pH = 5.5) leads to the in situ formation of **4a**. From these solutions, association constants were determined for Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ and NO_3^-. Significant selectivity in water for AcO^- and $H_2PO_4^-$ vs. halide anions has been established.

Introduction

The molecular recognition of anions[1−3] emerged with the discovery of a multiprotonated hollow, called katapinate,[4] which was the first host for a chloride ion. Crystal structure determinations established that the anion is indeed encapsulated within the macrobicyclic cavity of the host molecule.[5] Important results were reported when chloride and azide were selectively complexed in water by tetraprotonated macrotricyclic[6,7] and hexaprotonated macrobicyclic[8] molecules, respectively. In all these examples the anions were found to have formed hydrogen-bonding interactions with the protonated ammonium derivatives. It was therefore thought that complexation of anions should also be feasible with metallic cations located in related cavities.[9,10] A macrobicyclic biscopper cryptate complex was thus synthesised which was shown by potentiometric studies to display the expected interactions between the bis-metallic centres and a chloride anion. Another related compound containing one copper atom only displayed a chloride anion interacting with the Cu centre and the ammonium moieties of the ligand.[11] Until then only very rare examples derived from organometallic compounds had been reported to exhibit a related behaviour.[12−14]

We have recently described the synthesis and the preliminary behaviour of a simple organocobalt compound[15] which was built with the well-known mono-anionic pincer ligand extensively studied by van Koten et al.[16,17] In our compound, however, the N,C,N ligand is only coordinated to the cobalt centre in a bidentate fashion as one N atom does not interact directly with the metal. In fact we found that these organometallic species are interesting Brønsted acid receptors as a series of such acids were indeed coordinated to the (N,C,N)metal moiety without any hydrolysis of the Co−C bond being observed. It thus appeared that in these species the anions associated with the acids were interacting both with a metal cation *and* an ammonium unit as in the anion hosts mentioned above. We thus embarked on a project aimed at defining both the mechanism of the acid complexation by our cobalt complex and the thermodynamic data associated with the protonation of the amine unit that is not directly bound to Co in **1a**. This study allowed us to determine the association constants between the organocobalt host and various anions and to compare their selectivity with related known systems.

Results and Discussion

The key compound of this study is the aquo derivative **1a** in which an intramolecular hydrogen bond between one

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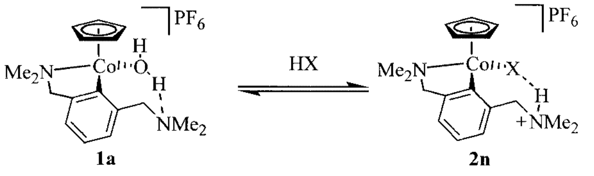
of the aquo protons and the noncoordinated nitrogen atom of the pincer ligand was established. The reaction of **1a** with acids affords the complexes **2a−e**, which display a related intramolecular H-bond between the dimethylammonium unit and the X atoms (see Scheme 1). These intramolecular H-bonds in both **1a** and **2a−e** contribute to the stability of the complexes by forming pseudo seven-membered organometallic rings.



Scheme 1. Complexation of HX by **1a** affords **2a−e** [**a** (X = F), **b** (X = Cl), **c** (X = Br), **d** (X = I), **e** (X = OAc)]

This stabilisation seems to play a key role for the coordination of the anion to the cobalt centre as, when treating **1a** *in water* with excess (up to 10^3 equivalents) of NaI, for instance, no complexation of the iodide was observed. Changing water for methanol in order to increase the solubility of **1a**, with the same excess of sodium iodide, did not lead to the coordination of I^- to cobalt. However, following this reaction by UV/Vis spectroscopy, we noticed the presence of new absorption bands at λ = 459, 560 and 675 nm vs. one band only for **1a** in water at λ_{max} = 465 nm. The ^1H NMR spectrum of **1a** in CD_3OD displays only slight modifications of the chemical shifts of the various signals of **1a** as compared to the same spectrum in [D$_6$]acetone. Single crystals of **1b** were obtained from a methanol/hexane solution of **1a**. The molecular structure of **1b** was determined by means of an X-ray diffraction study on one of these crystals (Figure 1 and Table 1). It was at once apparent that, in **1b**, a molecule of methanol has substituted the water molecule in **1a**. Importantly, a strong intramolecular OH···N bond is also found between the coordinated methanol and the free NMe_2 unit. The ^1H NMR spectrum of **1b** in [D$_6$]acetone containing traces of water showed the spectrum of **1a**, confirming that the coordination of methanol is easily reversed even by small amounts of water.

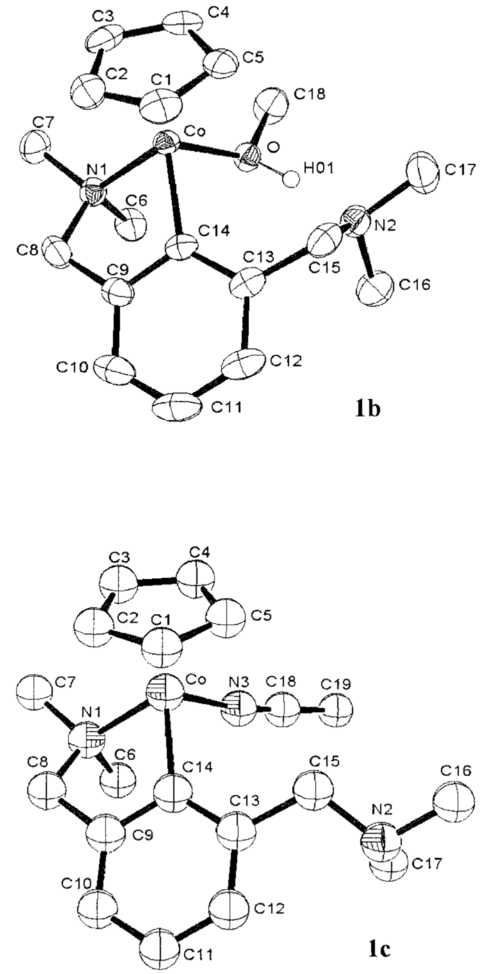


Figure 1. ORTEP representation of the cationic parts of **1b** and **1c**

In dry CD_3CN, **1a** displays a ^1H NMR spectrum which allows the identification of both unmodified **1a** and a new species **1c** in ratios depending on the concentration of **1a**. The ^1H NMR spectrum of **1c** shows the presence of one singlet for the NMe_2 group not interacting with the cobalt centre at δ = 2.30 ppm, together with the expected two singlets for the diastereotopic Co-bound NMe_2 unit. These features suggest that **1c** is a derivative of **1a** in which the water molecule has been substituted by a MeCN ligand. The X-ray diffraction study of a single crystal of **1c** (Figure 1 and Table 1) confirmed that **1c** is a MeCN adduct of **1a**. The conformation of the five-membered cyclometallated ring of the pincer ligand is very similar to that found for this ligand in **1a**. The only difference between **1a** and **1c** is a different orientation of the second NMe_2 group with respect to Co: it is now as far away from the acetonitrile ligand as possible, this being achieved by a rotation of ca. 90° around the $C_{13}-C_{15}$ vector.

As NaI is not soluble in CD_3CN we added one equivalent of NBu_4I to a solution of **1a** in order to check whether I^- can substitute the MeCN ligand in **1c**. We noticed no such complexation unless we increased the concentration of I^-: when adding more than 10 equivalents of NBu_4I a new species **3** was observed together with **1a** and **1c** (**3**:**1a**:**1c** = 0.07:0.16:0.77 with 12 equiv. of NBu_4I). The ^1H NMR spectroscopic data of **3** show significant high-field shifts for all the protons of the pincer ligand. Moreover the $\Delta\delta$ of the NMe_2 group bound to Co drops to 0.5 ppm as compared to its value in **1a**, **1b**, and **1c** (2.15, 2.11 and 1.47 ppm respectively). In the latter three compounds displaying these rather important $\Delta\delta$ values, the molecular structure shows a similar ring puckering of the five-membered cobaltacyclic ring, whereby one of the N−Me bonds eclipses either the Co−O or the Co···NCMe bond. The $\Delta\delta$ value found for **3** militates in favour of a staggered conformation in which the NMe_2 has now rotated around the C_8-N_1 vector by ca. 60° as shown in Figure 2. This latter feature is probably due to steric interactions between the bulky I^- ligand and the N−Me bond.

Table 1. Selected bond lengths and angles in complexes **1b** and **1c**

Bond lengths [Å]		Angles [°]	
1b			
Co−Cp$^{\#}$ [a]	1.713(2)	N_1−Co−C_{14}	82.7(9)
Co−C(Cp)$_{av}$	2.091(2)	N_1−Co−O	93.5(7)
Co−O	1.950(2)	O−Co−C_{14}	88.9(8)
Co−N_1	2.050(2)	Cp$^{\#}$−Co−N_1	128.0(4)
Co−C_{14}	1.952(2)	Cp$^{\#}$−Co−C_{14}	124.0(1)
N_1−C_8	1.489(3)	Cp$^{\#}$−Co−O	126.6(3)
C_8−C_9	1.497(4)	Co−N_1−C_8	103.8(1)
C_9−C_{14}	1.402(3)	N_1−C_8−C_9	107.9(2)
N_2−H_{01}	1.600(2)	C_8−C_9−C_{14}	115.4(2)
N_2−O	2.582(2)	C_9−C_{14}−Co	111.8(2)
		N_2−H_{01}−O	170.2(2)
		C_6−N_1−Co−O	−8.9(2)
		C_{14}−C_{13}−C_{15}−N_2	67.2(2)
1c			
Co−Cp$^{\#}$[a]	1.712(2)	N_1−Co−C_{14}	82.4(8)
Co−C(Cp)$_{av}$	2.089(2)	N_1−Co−N_3	95.3(8)
Co−N_1	2.051(2)	N_3−Co−C_{14}	93.9(9)
Co−N_3	1.902(2)	Cp$^{\#}$−Co−N_1	128.4(3)
Co−C_{14}	1.960(2)	Cp$^{\#}$−Co−C_{14}	123.9(3)
N_1−C_8	1.493(3)	Cp$^{\#}$−Co−N_3	122.1(3)
C_8−C_9	1.502(4)	Co−N_1−C_8	103.1(1)
C_9−C_{14}	1.409(3)	N_1−C_8−C_9	107.3(2)
N_2−N_3	4.403(3)	C_8−C_9−C_{14}	114.7(2)
		C_9−C_{14}−Co	111.6(2)
		C_6−N_1−Co−N_3	−15.1(2)
		C_{14}−C_{13}−C_{15}−N_2	153.5(2)

[a] Cp$^{\#}$: centroid of the cyclopentadienyl ring.

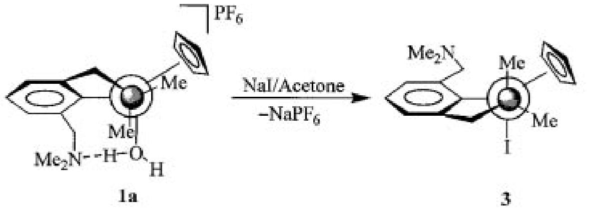


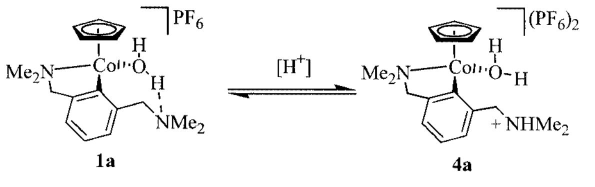
Figure 2. Newman representation of **3** around the Co−N_1 bond

This latter experiment showed unambiguously that iodide can indeed be coordinated to cobalt by displacement of the water *provided that the reaction is run in a non-protic solvent*. Indeed, the synthesis of **3** can be better achieved in acetone as, in this poorly coordinating solvent, **3** is obtained in almost quantitative yields. It is most likely that coordination of I^- takes place from an acetone solvate derivative **1d** akin to **1c** in which MeCN is substituted by acetone, knowing that cobalt has a much higher affinity for I^- than for acetone. We assume that in this solvent, **1a** might well be in equilibrium with the hypothetical acetone adduct **1d**, although the concentration of this latter species is far too low to be detected by ^{1}H NMR spectroscopy.

We have seen that the "CpCo(pincer)" moiety could be a host for HX, as HF, HCl, HBr, HI or HOAc could substitute the water ligand when an excess of one of these Brønsted acids is added to solutions of **1a** in methanol.[15]

From the results discussed above, it appears that the coordination of the X^- anions to Co is probably only possible once the NMe_2 unit of the pincer ligand not coordinated to cobalt in **1a** has been protonated by HX. We have indeed checked that a solution of **1a** and 10^3 equiv. of NaCl in water leads to the formation of **2b** only when decreasing the pH of the solution by addition of HPF_6.

We have also studied the protonation of **1a** in D_2O as a function of [H^+]. In this respect we have run the ^{1}H NMR spectra of several solutions of **1a** in D_2O to which various amounts of HPF_6 had been added. The correlation between the chemical shifts of certain protons of **1a** and the pH of the solutions allowed the determination of the pK_a of the species **4a**. The equilibrium between **1a** and **4a** (Scheme 2) must be fast on the ^{1}H NMR time scale, as only one signal is observed for the two species. Most of the signals of **1a** experience a decrease of chemical shifts upon lowering the pH of the D_2O solutions. However, the signal of one proton of a CH_2 group (at $\delta = 3.89$ ppm) displays a behaviour that is worthy of further discussion. At pH 8.0 the intensity of this doublet starts to decrease, it then gradually becomes broader as the pH drops and finally disappears when the pH is in the range 6.5 to 7.0. Surprisingly, at pH 4.05 it reappears as a doublet but at a very different chemical shift ($\delta = 5.02$ ppm). During this process the chemical shift of the second CH associated to the previous one does not change ($\delta = 4.59$ vs. 4.57 ppm). One explanation for this dynamic behaviour could be that the reversible protonation of the NMe_2 unit induces the cleavage of the OH···NMe_2 bond in **1a** and rotation around the C_{13}−C_{15} vector as in **1c**. Since the chemical shifts of the two protons of the CH_2 group resonate at very different chemical shifts in the two exchanging position it is reasonable to observe a broadening of the high-field shifted proton as it is known that the broadness of any given signal that is exchanging with another one is proportional to the square of the difference of the chemical shifts of both signals.[18] At pH < 4.5 the protonation of the NMe_2 close to this CH_2 is complete and thus exchange of the CH_2 group is no longer possible.



Scheme 2. Equilibrium between **1a** and **4a**

At pH ≥ 8.5 the NMe_2 interacting with H_2O is a broad singlet because this species is rapidly exchanging the two diastereotopic methyl groups by a fast coordination-decoordination of the N atom to the O−H group. We found good evidence for this while studying the behaviour of **1a** in [D$_6$]acetone. At room temperature the signal of the "free" NMe_2 group is a broad singlet at $\delta = 2.20$ ppm, but when the temperature is lowered (< −20 °C) the diastereotopic nature of this NMe_2 group is recovered, the difference in chemical shift between the two methyls being more than 0.6 ppm. At lower pH (4.05) the NMe_2, which until then is a broad singlet, appears as two broad signals, showing that the NMe_2 group is indeed completely protonated: the N atom can no longer invert its configuration and hence the exchange process is not detectable anymore. The pK_a value of **4a** in D_2O follows from the results reported in Figure 3, leading to a value of 6.1 ± 0.1.

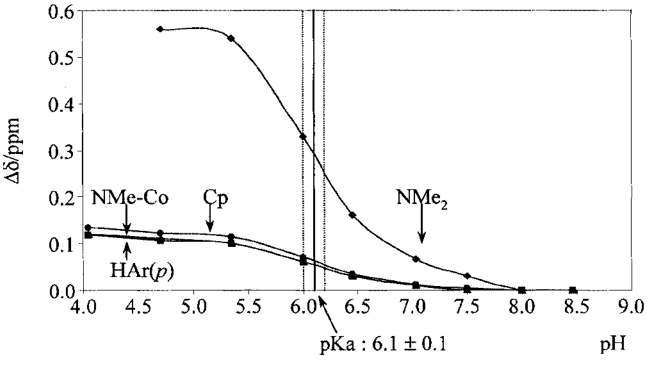


Figure 3. Variation of Δδ for significant signals as a function of pH

Association Constant Determinations

As we have seen that **1a** becomes a good host for anions at slightly acidic pH, we looked for the best buffer solutions to determine the thermodynamic data for the various complexations of anions by our system. We have thus chosen MES (2-[*N*-morpholino]ethanesulfonic acid) which leads to a pH of 5.5 in water. The K_{ass} values were obtained by following the addition of various amounts of anions (as their NH_4^+ or NEt_3H^+ derivatives)[19] to a buffered solution of **1a** by standard UV/Vis spectroscopy; the spectra of **4a** and **2b−d** are shown in Figure 4.

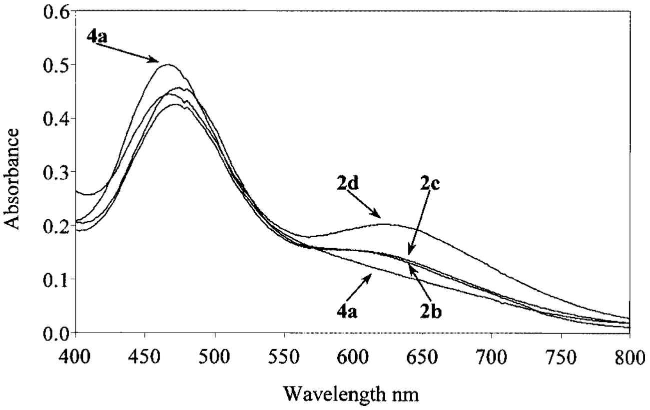


Figure 4. Superposition of UV/Vis of **4a** and **2b−d**

As the concentrations of the species **2b−d** are proportional to the absorption around 620−650 nm we used this modification to determine the association constants according to Equation (1). These constants are given in Table 2. The constant for the fluoride anion could not be measured by any of these techniques because this anion reacts with the buffer leading to the formation of an uncharacterised insoluble material.

Table 2. log K_{ass} for compounds **2b−g** in various solvents

Entry	Anion	Complexes	log K_{ass} in water pH = 5.5[b]	log K_{ass} in M/W[a] pH = 5.4[b]	log K_{ass} in methanol pH = 6.4[c]
1	Cl^-	**2b**	1.8[d] [e]	3.9[e]	3.4[e]
2	Br^-	**2c**	1.5[d,e]	3.1[e]	2.7[e]
3	I^-	**2d**	1.7[d,e]	3.2[e]	2.9[e]
4	CH_3COO^-	**2e**	3.0[e]	1.7[e]	1.9[e]
5	$H_2PO_4^-$	**2f**	3.1[e]	ns[f]	ns[f]
6	NO_3^-	**2g**	1.0[e]	1.4[e]	1.5[e]

[a] M/W = methanol/water (95:5). [b] MES. [c] MOPS. [d] UV/Vis. [e] ^1H NMR spectroscopy. [f] Not soluble.

$$\mathbf{4a} + NR_3HX \underset{\text{MES, } D_2O}{\overset{K_{ass}}{\rightleftharpoons}} \mathbf{2b\text{-}g} + D_2O + NR_3 \qquad (1)$$

$$K_{ass} = \frac{[\mathbf{2b\text{-}g}]}{[\mathbf{4a}][X^-]} \qquad \begin{array}{l} R = Et \quad X = Cl, Br \\ R = H \quad X = I, OAc, H_2PO_4, NO_3 \end{array}$$

This technique could not be applied to oxygen-containing anions such as acetate, nitrate or dihydrogenophosphate because the UV/Vis spectra of the complexes obtained by trapping of these latter ions do not display significant differences with the aquo derivative **4a**.

We checked that the K_{ass} obtained by analysis of the ^1H NMR spectra for the halide anions afforded results in line with those obtained by the UV/Vis technique. An example of the spectra obtained for different concentrations of iodide is shown in Figure 5 and 6, in which the chemical shift of the Cp ring in both **4a** and **2d** is represented. A related study was then performed for the $CH_3CO_2^-$, NO_3^- and $H_2PO_4^-$ anions, which led to the results reported in Table 2.

In order to be able to compare these data with related values for different anion hosts reported in the literature, we also determined these K_{ass} values in pure CD_3OD and

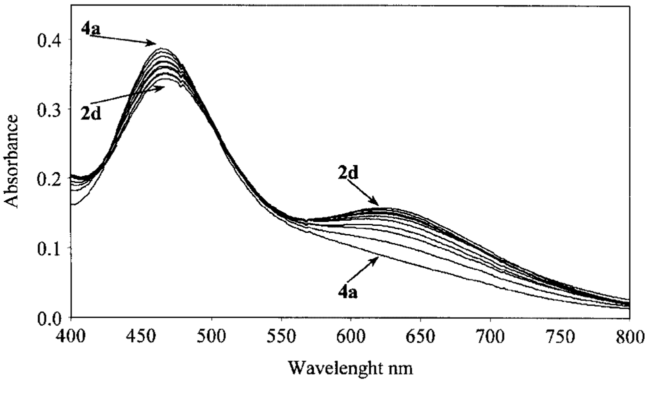


Figure 5. Evolution of the UV/Vis spectra of **4a** with increasing amounts of NH_4I (10, 20, 30, 40, 50, 60, 80 and 100 equiv.)

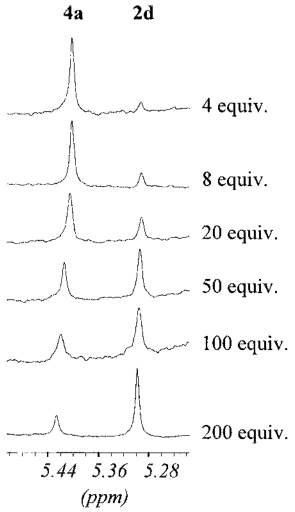


Figure 6. Evolution of the ^{1}H NMR spectra of **4a** with increasing amounts of NH_4I

in a 95:5 mixture of CD_3OD and D_2O. The relative concentration of **1a** and **1b**, as anticipated, is dependent on the amount of water present. In dry CD_3OD ($HDO/D_2O < 0.03\%$) the ratio of **1a** to **1b** is 5:95, whereas in CD_3OD/D_2O (95:5) this ratio is 40:60. These data are another illustration of a much stronger complexation of water to cobalt as opposed to methanol. In order to determine the pK_a of **1b** in pure CD_3OD and in CD_3OD/D_2O (95:5), we used the same procedure as described above for **1a** in D_2O. Addition of DPF_6 in CD_3OD resulted in a duplication of most of the signals of **1a** and **1b** in the ^{1}H NMR spectrum. We believe that the explanation for this phenomenon is due to the occurrence of four species, namely **1a**, **1b**, **4a** and **4b** (**4b** is the N-protonated derivative of **1b**). Particularly diagnostic of the existence of **4a** and **4b** are the presence of two pairs of CH_2 signals at chemical shifts analogous to those observed for **4a** in D_2O (see above).

As MES is poorly soluble in pure methanol, we decided to use MOPS (3-[*N*-morpholino]propanesulfonic acid) whose pH is slightly higher than that of MES (6.4 vs. 5.5). Solutions of **1a** in both solvents display the same ^{1}H NMR spectra, i.e. the Cp ring appears as three resonances. We believe that three different species should exist in these solutions, i.e. **1a**, **1b** and a compound in which the sulfonic group of the buffers has been trapped by the cobalt receptor. This compound is found in very low yield (< 5%) and it is always present in methanol solution whatever the concentration of the anions. A likely explanation for the occurrence of this species in methanol is based upon a different solvation of the sulfonic group, which is more solvated in water than in methanol. The occurrence of **1a** and **1b** in these solutions must be due to a very small degree of protonation of the nitrogen atom of either **1a** or **1b** by the buffer protons. However, despite the fact that it is not visible in the ^{1}H NMR spectrum, a small amount of the protonated form must exist to enable the trapping of the anions to take place. The presence of large quantities of buffer must be therefore be a strong enough driving force for the anion complexation to occur. The K_{ass} in this case was determined using a slightly different equation [Equation (2)] than above:

$$\mathbf{1a} + \mathbf{1b} + NR_3HX \underset{\text{i or ii}}{\overset{K_{ass}}{\rightleftharpoons}} \mathbf{2b\text{-}g} + D_2O + CD_3OD + NR_3$$

$$K_{ass} = \frac{[\mathbf{2b\text{-}g}]}{([\mathbf{1a}]+[\mathbf{1b}])[X^-]}$$

R = Et X = Cl, Br
R = H X = I, OAc, H_2PO_4, NO_3
i : MES, MeOD:D_2O (95:5)
ii : MOPS, MeOD

(2)

Several interesting comments can be made with respect to the K_{ass} values obtained in water or in methanol. There is an obvious important difference between the K_{ass} values measured for the halides and those obtained for the oxyanions. Whereas these values are much higher on going from water to methanol for the halides, the opposite is found for the oxyanions (see below). Schmidtchen has found a similar trend for the halide series when changing water for methanol.[20] However, in marked contrast to our results the complexation of the halide was somehow parallel to their sizes, iodide being by far the best complexed species. In our case K_{ass} for chloride is ca. five times higher than that for iodide. Our receptor is a competitive Cl^- host in methanol as compared to those reported elsewhere.[6,20] It is, however, important to note that the previously reported receptors were usually built from several ammonium units, whereas in our case this result was obtained by interaction of the Cl^- with Co^+ and one NH^+ moiety only. Our organocobalt receptor displays an interesting behaviour with respect to the oxyanions such as acetate and dihydrogenophosphate, since the stability of **2e−f** is higher than that of **2b−d** by at least one order of magnitude. The only previous data in water concerning these two anions are those of Schmidtchen who reported values of 1.86 and 2.1, respectively.[20] Upon comparing the selectivity of our receptor for oxyanions vs. chloride with that of other hosts (cf. Table 3) it appeared that the organocobalt complex is 10 times more selective than the better such hosts in water.

Table 3. Selectivity of hosts for oxyanions vs chloride

Entry	NO_3^-	CH_3COO^-	$H_2PO_4^-$	Receptors
1	0.2	15	20	**4a**
2	0.6	0.2[a]	–	Bis-Tren[8]
3	–	1.5	2.5	Macrotricyclic quaternary ammonium salt[20]

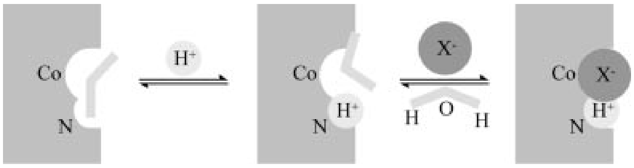
$HCOO^-$ value.

Our result is without precedent in the literature. The only known examples of a better complexation of the oxyanions have been found for non-protic solvents such as CH_3CN, DMSO and $CHCl_3$.[21−24]

As the respective hydration free energies of the chloride and the acetate anions are similar [$\Delta G_H(Cl^-) = -365\ kJ\cdot mol^{-1}$, $\Delta G_H(AcO^-) = -340\ kJ\cdot mol^{-1}$][3] the better acetate vs. chloride complexation can be rationalized by means of both a stronger coordination of an oxygen-containing anion to a cobalt(III) center and a stronger hydrogen bond between an NH^+ and an oxygen atom. In the case of the dihydrogenophosphate, a rather strong hydration energy has been reported [$\Delta G_H(H_2PO_4^-)$ = -465 kJ·mol^{-1}].[3] Thus the arguments given above cannot be sufficient to explain the stronger complexation of this anion vs. halides. We suggest that in this case the H_2PO_4 anion coordinated to the outer surface of the organocobalt receptor is partially solvated by several water molecules, thus contributing to the somehow surprising selectivity disclosed for this substrate.

Conclusion

Our organocobalt compound can be a genuine host for anion in water or in methanol provided that a source of protons is present in the solution. We have observed that a too-acidic medium can cause decomposition of the complex. This anion host is therefore most efficient in solutions whose pH is slightly acidic through the presence of a buffer. When no source of protons is present the aquo ligand cannot be displaced by any anions. This behaviour is reminiscent of an allosteric behaviour[25–27] of our molecule, as the bonding of the anion to the cobalt receptor is somehow modulated by prior protonation at another part of the molecule. This behaviour is represented schematically in Scheme 3.



Scheme 3. Representation of the allosteric phenomenon

Further work in line with this property, as well as modification of the cobalt complexes, is being actively pursued.

Experimental Section

General Remarks: All chemicals used [$NEt_3·(HF)_3$, $NEt_3·HCl$, $NEt_3·HBr$, NH_4I, NH_4OAc, NH_4NO_3 and $NH_4H_2PO_4$] were of analytical grade and dried under vacuum before use. Buffer solutions were prepared from 3-[*N*-morpholino]propanesulfonic acid (MOPS, hemisodium salt) or 2-[*N*-morpholino]ethanesulfonic acid (MES, 2 equivalents of hemisodium salt and 3 equivalents of acid). In water the pH of the thus obtained solutions is 7.1 and 5.5, respectively, whereas in methanol the pH is 6.4 and 5.4, respectively.

UV/Vis experiments were carried out in distilled water or in spectrophotometer UV-fluo methyl alcohol quality (Carlo Erba). Absorption spectra were recorded on a Uvikon XL spectrometer. pH was determined using a PHN78 (Tacussel electronique) with an ECS electrode.^{1}H NMR spectra were recorded at 300.13 MHz and $^{13}C\{^1H\}$ NMR spectra at 75.47 MHz on a Bruker FT instrument (AV-300). Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively, and referenced to external TMS. The starting materiel $[CpCo(NCN)H_2O]^+·PF_6^-$ (**1a**) was prepared according to a published method.[15] Elemental analyses were performed by the Service Central d′Analyse de l′Institut de Chimie (Strasbourg). Association constants were determined from a Scatchard plot [2n/X = f(2n)]. The respective concentrations of **4a** and **2n** in water or **1a**, **1b** and **2n** in methanol or methanol/water were determined by ^{1}H NMR integrations or UV/Vis Δabs variations. Reproducibility of multiple experiments afforded in general the same values for a determined anion within a 10% variation. All the selected values have an R^2 value greater than 0.90 and errors were estimated to be between 5 and 10%.

[Co{2,6-($Me_2NCH_2)_2C_6H_3$}(η^5-C_5H_5)(H_2O)]PF_6 (1a): ^{1}H NMR spectra of **1a** (5×10^{-4} M) in D_2O at pH 8.5: δ = 7.30 (d, $^3J_{H-H}$ = 7.1, 1 H, Ar), 7.21 (t, $^3J_{H-H}$ = 7.1, 1 H, Ar), 7.14 (d, $^3J_{H-H}$ = 7.1, 1 H, Ar), 5.26 (s, 5 H, C_5H_5), 4.59 and 3.87 (AB spin system, $^2J_{H-H}$ = 12.4, 2 H, CH_2N), 4.23 and 3.63 (AB spin system, $^2J_{H-H}$ = 14.0, 2 H, CH_2N-Co), 3.33 and 1.26 (2s, 6 H, Co-NMe_2), 2.31 (br. s, 6 H, NMe_2).

[Co{2,6-($Me_2NCH_2)_2C_6H_3$}(η^5-C_5H_5)(MeOH)]PF_6 (1b): *n*-Hexane (80 mL) was slowly added to a solution of **1a** (0.240 g, 0.5 mmol) in CH_3OH (20 mL) and the solution was cooled to 0 °C for two days. This afforded **1b** as brown crystals, which were collected by filtration, washed with hexane and dried in vacuo (quantitative yield). ^{1}H NMR (CD_3OD): δ = 7.24 (d, $^3J_{H-H}$ = 7.2, 1 H, Ar), 7.16 (t, $^3J_{H-H}$ = 7.2, 1 H, Ar), 7.07 (d, $^3J_{H-H}$ = 7.2, 1 H, Ar), 5.37 (s, 5 H, C_5H_5), 4.50 and 3.63 (AB spin system, $^2J_{H-H}$ = 12.4, 2 H, CH_2N), 4.29 and 3.57 (AB spin system, $^2J_{H-H}$ = 14.0, 2 H, H_2N-Co), 3.40 and 1.29 (2s, 6 H, Co-NMe_2), 2.26 (br. s, 6 H, NMe_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 152.8, 148.0, 131.2, 126.2 and 12.7 (C_6H_3), 85.9 (C_5H_5), 77.7 (CH_2N-Co), 68.2 (CH_2N), 59.1 and 49.2 (Co-NMe_2), 30.7 (NMe_2). $C_{18}H_{28}CoF_6N_2OP$ (492.33): calcd. C 43.91, H 5.73, N 5.69; found C 44.03, H 5.73, N 5.62.

[Co{2,6-($Me_2NCH_2)_2C_6H_3$}(η^5-C_5H_5)($NCCH_3$)]PF_6 (1c): Et_2O (80 mL) was slowly added to a solution of **1a** (0.240 g, 0.5 mmol) in CH_3CN (20 mL) and this solution was cooled to 0 °C for two days. This afforded **1c** as red crystals, which were washed with hexane and dried in vacuo (quantitative yield). ^{1}H NMR (CD_3CN): δ = 7.33 (m, 1 H, Ar), 7.09 (t, $^3J_{H-H}$ = 7.3, 1 H, Ar), 6.96 (m, 1 H, Ar), 5.38 (s, 5 H, C_5H_5), 4.12 and 3.47 (AB spin system, $^2J_{H-H}$ = 14.0, 2 H, CH_2N), 3.81 and 3.33 (AB spin system, $^2J_{H-H}$ = 13.0, 2 H, CH_2N-Co), 3.14 and 1.67 (2s, 6 H, Co-NMe_2), 2.30 (br. s, 6 H, NMe_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 153.2, 150.5, 150.2, 129.5, 125.7, 122.7 (C_6H_3), 135.4 ($N\mathit{C}CH_3$), 88.3 (C_5H_5), 76.7 (CH_2N-Co), 65.9 (CH_2N), 59.0 and 52.7 (Co-NMe_2), 45.7 (NMe_2), 1.1 ($NC\mathit{C}H3$) ppm. $C_{19}H_{27}CoF_6N_3P$ (501.34): calcd. C 45.52, H 5.43, N 8.38; found C 45.54, H 5.41, N 8.30.

[CoI{2,6-($Me_2NCH_2)_2C_6H_3$}(η^5-C_5H_5)] (3): NaI (0.750 g, 5.0 mmol) was added to a solution of **1a** (0.240 g, 0.5 mmol) in acetone (10 mL). The colour of the solution turned from purple to green in 5 minutes. After removal of insoluble material by filtration, the product was precipitated by addition of *n*-hexane. Yield: 2.21 g (75%). ^{1}H NMR ([D_6]acetone): δ = 7.13 (d, $^3J_{H-H}$ = 7.1, 1 H, Ar), 6.71 (t, $^3J_{H-H}$ = 7.1, 1 H, Ar), 6.66 (d, $^3J_{H-H}$ = 7.1, 1 H, Ar), 5.22 (s, 5 H, C_5H_5), 4.18 and 3.42 (AB spin system, $^2J_{H-H}$ = 12.2, 2 H, CH_2N), 3.74 and 3.18 (AB spin system, $^2J_{H-H}$ = 13.0, 2 H, H_2N-Co), 3.00 and 2.53 (2s, 6 H, Co-NMe_2), 2.22 (s, 6 H, NMe_2).

[Co{2-(Me_2NCH_2)-6-($Me_2ND^+CH_2)C_6H_3$}(η^5-C_5H_5)(D_2O)]$(PF_6)_2$ (4a): HPF_6 (pH 2.2 in D_2O) was added to a solution of **1a** (5×10^{-4} M) in D_2O, leading to a pH of ca. 4.0. ^{1}H NMR (D_2O): δ = 7.39 (d, $^3J_{H-H}$ = 7.2, 1 H, Ar), 7.32 (t, $^3J_{H-H}$ = 7.2, 1 H, Ar), 7.18

Table 4. X-ray diffraction data

	1b	**1c**
Formula	$C_{18}H_{28}CoN_2O.PF_6$	$C_{19}H_{27}CoN_3.PF_6$
Molecular weight	492.33	501.34
Crystal system	monoclinic	triclinic
Space group	$P2_{1/c1}$	$P\bar{1}$
a [Å]	14.229(1)	7.942(1)
b [Å]	10.291(1)	9.728(1)
c [Å]	15.290(1)	14.770(1)
α [°]		95.02(1)
β [°]	105.92(1)	102.46(1)
γ [°]		94.03(1)
V [Å^3]	2153.2(2)	1105.3(1)
Z	4	2
Color	brown	red
Crystal dim [mm]	0.20 × 0.20 × 0.05	0.12 × 0.10 × 0.08
$\rho_{calcd.}$ [g cm^{-3}]	1.52	1.51
F_{000}	1016	516
μ [mm^{-1}]	0.934	0.909
T [K]	173	173
λ [Å]	0.71073	0.71073
Radiation	Mo-K_α	Mo-K_α
Diffractometer	KappaCCD	KappaCCD
Scan mode	φ scans	φ scans
hkl limits	−19/20, −13/14, −21/21	−10/10, −11/12, −18/19
θ limits [°]	2.5/30.04	2.5/27.47
Data measured	10827	7449
Data with $I > 3\sigma(I)$	3956	3556
Number of variables	298	271
R	0.038	0.035
R_w	0.060	0.050
GOF	1.052	1.016
Largest peak in final difference [e Å^{-3}]	0.612	0.357

(d, $^3J_{H-H}$ = 7.2, 1 H, Ar), 5.40 (s, 5 H, C_5H_5), 5.01 and 4.57 (AB spin system, $^2J_{H-H}$ = 13.6, 2 H, CH_2ND$^+$), 4.24 and 3.70 (AB spin system, $^2J_{H-H}$ = 14.5, 2 H, CH_2N-Co), 3.45 and 1.47 (2s, 6 H, Co-NMe_2), 3.09 and 2.81 (2 br. s, 6 H, $^+$NDMe_2).

[Co{2-(Me_2NCH_2)-6-($Me_2ND^+CH_2$)C_6H_3}(η^5-C_5H_5)(CD_3OD)]-(PF_6)$_2$ (4b): HPF_6 (pH 0.7 in CD_3OD/D_2O 95:5) was added to a solution of **1a** (1 × 10^{-2} M) in CD_3OD/D_2O, leading to a pH of ca. 3.9. ^{1}H NMR (CD_3OD/D_2O 95:5): δ = 7.35−7.05 (m, 3 H, Ar), 5.36 (s, 5 H, C_5H_5), 5.10 and 4.50 (AB spin system, $^2J_{H-H}$ = 12.8, 2 H, CH_2ND$^+$), 4.34 and 3.72 (AB spin system, $^2J_{H-H}$ = 14.0, 2 H, CH_2N-Co), 3.58 and 1.21 (2s, 6 H, Co-NMe_2), 2.98 and 2.23 (2 s, 6 H, $^+$NDMe_2).

X-ray Crystallographic Study: Single crystals suitable for X-ray diffraction analysis were obtained as described above. Data were collected on a Nonius KappaCCD diffractometer, using Mo-K_α graphite-monochromated radiation (λ = 0.7107 Å), and ω scans. Absorption corrections were partially included in the data reduction procedure. The structures were solved by direct methods and refined against |F|. Hydrogen atoms were introduced in structure factor calculations as fixed contributors by their computed coordinates [d(C-H) = 0.95 Å, B(H) = 1.3*Beqv Å^2 of the attached carbon atom] except for the OH protons of **1a**, which were located in difference Fourier maps. The absolute structures were determined by refinement of Flack's x parameter. For all computations, the Nonius OpenMoLeN package[28] was used. Further experimental details are given in Table 4.

CCDC-181527 (**1b**) and -181526 (**1c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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