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Preparation and the covalent hydration of a hexafluoro-2,4-pentanedionatotetraaminecobalt(III) complex

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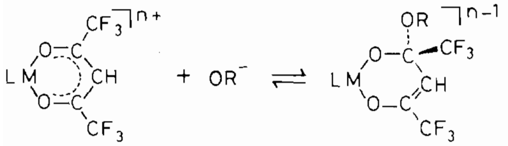
Abstract

Twelve title complexes are prepared as perchlorate salts. These are $Co(hfac)L^{2+}$ with $L=(MeNH_2)_4$, $(n\text{-}AmNH_2)_4$, *cis*-$(NH_3)_2$(en), (*R*-pn)(*S*-pn), cyclen, cyclam, *cis*-$(NH_3)_2$(bpy), (en)(bpy), (en)(phen), (tn)(bpy), (tn)(phen) and (bpy)(phen) where Hhfac = hexafluoro-2,4-pentanedione, $MeNH_2$ = methylamine, n-$AmNH_2$ = n-amylamine, en = ethylenediamine, pn = propylenediamine, cyclen = 1,4,7,10-tetraazacyclododecane cyclam = 1,4,8,11-tetraazacyclotetradecane, bpy = 2,2′-dipyridyl, phen = 1,10-phenanthroline and tn = 1,3-propanediamine. The thermodynamic covalent hydration equilibrium constants K_{OH} in water and K_{OMe} in methanol are estimated for these complexes and for previously obtained $Co(hfac)L^{2+}$ by UV spectrophotometry. The values critically depend on the involvement as L ligand of a bpy or a phen ligand. $pK_{OH} \approx -6.6$ and $pK_{OMe} \approx -8.7$ when L involves neither bpy nor phen ligand. $pK_{OH} \approx -8.7$ and $pK_{OMe} \approx -11.0$ when L involves either a bpy or a phen ligand. $pK_{OH} \approx -11.5$ and $pK_{OMe} \approx -14.6$ when L involves two bpy or phen ligands. The isomeric structure of the complex is also discussed on the basis of the fluorine NMR spectra.

Introduction

It has been shown recently that a cobalt(III) or a chromium(III) complex with a bidentate hfac ligand shows a unique hydrolysis phenomenon called covalent hydration in water and in methanol [1]. The lyate anion OR^- forms rapidly and reversibly a covalent bond to one of the carbonyl carbon atoms of the hfac ligand coordinating to the metal.



(1)

where M = Co(III) or Cr(III) and L is a ligand occupying the residual four coordination sites. We denote the thermodynamic equilibrium constant of eqn. (1) in water (R = H) and in methanol ($R=CH_3$) as K_{OH} and K_{OMe}, respectively. In a previous report, it has been shown that in the case of a tetraamine L ligand the K_{OH} is $2\text{–}12\times10^6$ M^{-1} for $Co(hfac)L^{2+}$ and $1\text{–}6\times10^{10}$ M^{-1} for $Cr(hfac)L^{2+}$ ($M = mol\ dm^{-3}$) [1]. It was pointed out that the magnitude depended significantly on the kind of metal, whereas it was rather independent of the kind of tetraamine L ligand. Later, we studied by UV spectrophotometry the K_{OH} for $Co(hfac)(bpy)_2^{2+}$ and $Co(hfac)(phen)_2^{2+}$ and found that their K_{OH} are extraordinarily large (3×10^{11} M^{-1}). This finding has stimulated us to study the magnitude of K_{OH} and K_{OMe} for additional $Co(hfac)L^{2+}$.

In the present work, we have prepared twelve such complex perchlorates and estimated the pK_{OH} and pK_{OMe} values. We have also estimated pK_{OH} and pK_{OMe} for $Co(hfac)L^{2+}$ prepared previously [1]. The isomeric structure of the complex is also discussed on the basis of the fluorine NMR spectra.

Experimental

A Shimadzu UV-2200 UV–Vis spectrophotometer was used. The other experimental procedures were similar to those described in previous reports [1, 2]. In the fluorine NMR measurements, trifluoroacetic acid was used as internal standard ($\delta = -76.5$ ppm). **Caution**: Although we have experienced no difficulty with the perchlorate salts of the complex mentioned herein, these compounds should be treated as potentially explosive and should be handled with care.

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$K[Co(CO_3)_2(en)]$ (1)

$KHCO_3$ (10 g) was added to a tricarbonatocobaltate solution prepared from $CoCl_2 \cdot 6H_2O$ (12 g) [3]. This solution was combined with an aqueous solution (6 ml) of en (3 g) and was stirred for 30 min at 60 °C. The resultant blue solution was treated with $KHCO_3$ (10 g) and ice-cooled. Inorganic salts were removed. The product (8 g) separated on addition of ethanol to the filtrate. It was twice recrystallized from water by addition of ethanol and was washed with ethanol and ether.

$K[Co(CO_3)_2(tn)]$ (2)

This substance was prepared analogously to **1** using tn. Yield 50%.

$K[Co(CO_3)_2(bpy)]$ (3)

Bpy (7.8 g) was added to a tricarbonatocobaltate solution prepared from $CoCl_2 \cdot 6H_2O$ (12 g) [3]. It was stirred for 2 h at 60 °C and was ice-cooled. The resultant precipitate of $[Co(CO_3)(bpy)_2]Cl$ was removed by filtration. The violet filtrate was evaporated to near dryness. The residue was extracted with hot methanol (200 ml). After filtration, it was left at room temperature. The product (4 g) separated after a while.

$[Co(CO_3)(MeNH_2)_4]ClO_4$ (4)

A 40% aqueous solution (40 ml) of $MeNH_2$ was added to a tricarbonatocobaltate solution freshly prepared from $Co(NO_3)_2 \cdot 6H_2O$ (14.6 g). It was stirred for 20 min at room temperature, treated with $MeNH_3Cl$ (15 g) and was further stirred for 2 h at 50 °C. Salts were removed and the red–violet filtrate was rotoevaporated to 40 ml. Salts were removed again. The filtrate was treated by saturated aqueous $NaClO_4$ (5 ml) and the resultant precipitates of $KClO_4$ were removed. The filtrate was rotoevaporated further to 20 ml, treated by saturated aqueous $NaClO_4$ (11 ml) and was cooled. The resultant red–violet crystals were recrystallized from hot water and washed with methanol. This substance is soluble in water but is insoluble in methanol. Yield 10 g.

$[Co(CO_3)(n\text{-}AmNH_2)_4]ClO_4$ (5)

n-$AmNH_2$ (40 ml) was added to a tricarbonatocobaltate solution prepared from $CoCl_2 \cdot 6H_2O$ (12 g). It was stirred for 2 h at 50 °C. The resultant pink–brown crystals were extracted with methanol. The extract was combined with a slight excess of methanolic $NaClO_4$ and was concentrated. The resultant pink crystals were recrystallized from methanol. This substance is insoluble in water. Yield 15 g.

$[Co(CO_3)(NH_3)_2(en)]ClO_4$ (6)

1 (3 g) and NH_4ClO_4 (1.2 g) were dissolved in 1 M NH_3 solution (20 ml) [4]. The solution was stirred at 50 °C until the color turned to red–violet. $KClO_4$ was removed by filtration. The product separated on evaporation of the filtrate.

$[Co(CO_3)(R\text{-}pn)(S\text{-}pn)]ClO_4$ (7)

An aqueous suspension (30 ml) of *trans*-$[CoCl_2(R\text{-}pn)(S\text{-}pn)]ClO_4$ (7.6 g) and Li_2CO_3 (2 g) was stirred for 1 h at 60 °C [5]. After filtration, the filtrate was evaporated to half volume. A red–violet product separated on addition of ethanol to the solution.

$[Co(CO_3)(cyclen)]ClO_4$ (8)

A tricarbonatocobaltate solution was treated with an equivalent amount of cyclen·4HCl [6]. This solution was concentrated and salts were removed. Red–violet crystals separated from the filtrate on addition of aqueous $NaClO_4$ and ethanol. Yield 60%.

$[CoCO_3(cyclam)]ClO_4$ (9)

A tricarbonatocobaltate solution was treated with an equivalent amount of cyclam·4HCl [7]*. The resultant red–violet crystals were recrystallized from methanol by addition of aqueous $NaClO_4$. Yield 30%.

$[CoCO_3(bpy)(phen)]ClO_4$ (10)

A solution of phen·H_2O (2 g) in 1 M $HClO_4$ (20 ml) was added drop by drop to an ice-cooled aqueous solution (10 ml) of **3** (4.1 g). It was stirred for 2 h at 50 °C and the product (3 g) separated.

$[Co(hfac)(MeNH_2)_4](ClO_4)_2$

4 (4 g) was decarbonized in 4 M $HClO_4$ (5 ml) at 40 °C. To this solution, a mixture of Hhfac (2.1 g) and 4 M NaOH (2.5 ml) was added slowly. It was stirred for 40 min at 50 °C. The resultant red–orange crystals were recrystallized from methanol with a trace of $HClO_4$ and were washed with ethanol and ether (2:8). They were kept in a refrigerator. Yield 4 g. *Anal.* Found: C, 18.2; H, 3.7; N, 9.5. Calc.: C, 18.4; H, 3.6; N, 9.5%.

$[Co(hfac)(n\text{-}AmNH_2)_4](ClO_4)_2$

5 (5.7 g) was decarbonized in 2 M $HClO_4$ (10 ml) and methanol (20 ml) at 40 °C. To this solution, a mixture of Hhfac (2.1 g) and 4 M NaOH (2.5 ml) was added slowly. It was stirred for 2 h at 50 °C and then evaporated. The resultant red oily product was extracted with a mixture of 6 M $HClO_4$ (3 ml) and methanol (20 ml). Red crystals separated on evaporation at room temperature and were recrystallized from methanol containing $HClO_4$. They were washed with dilute $HClO_4$, ethanol and ether (1:19) and kept in a refrigerator.

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*$[Ni(cyclam)](ClO_4)_2$ (50 g) was dissolved in 6 M HCl (200 ml) and warmed on a water bath for 5 h. Cyclam·4HCl separated on cooling the solution (yield 90%).

Yield 1 g. *Anal.* Found: C, 37.2; H, 6.6; N, 6.7. Calc.: C, 36.9; H, 6.6; N, 6.9%.

cis-[Co(hfac)(NH$_3$)$_2$(en)](ClO$_4$)$_2$·2H$_2$O

6 (2.5 g) was decarbonized in 1 M $HClO_4$ (20 ml). The resultant solution was treated with Hhfac (2.1 g) and 1 M NaOH (10 ml) at 50 °C. The resultant orange crystals (4 g) were recrystallized from methanol and washed with ethanol and ether (2:8). *Anal.* Found: C, 13.9; H, 2.8; N, 10.2. Calc.: C, 14.1; H, 3.2; N, 9.4%.

[Co(hfac)(R-pn)(S-pn)](ClO$_4$)$_2$

7 (3.9 g) was decarbonized in 1 M $HClO_4$ (20 ml). The resultant solution was combined with a mixture of Hhfac (2.1 g) and 1 M NaOH (10 ml) and was stirred for 1 h at 50 °C. Orange crystals separated and were recrystallized from methanol and water (9:1) with a trace of $HClO_4$. Yield 3.5 g. *Anal.* Found: C, 21.3; H, 3.4; N, 9.2. Calc.: C, 21.6; H, 3.5; N, 9.1%.

[Co(hfac)(cyclen)](ClO$_4$)$_2$·H$_2$O

8 (4.1 g) was decarbonized in 2 M $HClO_4$ (10 ml) at 40 °C. To this solution, a mixture of Hhfac (2.1 g) and 2 M NaOH (5.0 ml) was added drop by drop. It was stirred for 40 min at 50 °C. The resultant red crystals were recrystallized from dilute aqueous $HClO_4$ and washed with ethanol and ether (2:8). Yield 5 g. *Anal.* Found: C, 23.8; H, 3.5; N, 8.4. Calc.: C, 23.8; H, 3.5; N, 8.6%.

[Co(hfac)(cyclam)](ClO$_4$)$_2$

9 (4.2 g) was decarbonized in 2 M $HClO_4$ (10 ml) at 40 °C. To this solution, a mixture of Hhfac (2.1 g) and 2 M NaOH (5 ml) was added slowly. It was stirred for 40 min at 50 °C. The resultant red–orange crystals were recrystallized from methanol containing $HClO_4$ and washed with ethanol and ether (2:8). Yield 2.5 g. *Anal.* Found: C, 27.0; H, 3.8; N, 8.5. Calc.: C, 27.1; H, 3.8; N, 8.4%.

cis-[Co(hfac)(NH$_3$)$_2$(bpy)](ClO$_4$)$_2$·2H$_2$O (11)

cis-K[Co(CO$_3$)$_2$(NH$_3$)$_2$] (2.7 g) and bpy (1.56 g) were mixed in water (10 ml) and methanol (5 ml) [3]. 4 M $HClO_4$ (5 ml) was added drop by drop to this suspension, while the latter was ice-cooled and stirred. It was stirred further for 10 h at room temperature. The resultant red solution was decarbonized by 4 M $HClO_4$ (5 ml) at 40 °C and was combined with a mixture of Hhfac (1.0 g) and 2 M NaOH (3.5 ml). It was stirred for 20 min at 50 °C and was acidified by drops of 6 M $HClO_4$. The resultant orange crystals were recrystallized from methanol with a trace of $HClO_4$ and washed with ethanol and ether (2:8). Yield 1 g. *Anal.* Found: C, 26.2; H, 2.2; N, 8.2. Calc.: C, 26.1; H, 2.2; N, 8.1%.

[Co(hfac)(en)(bpy)](ClO$_4$)$_2$·H$_2$O (12)

This substance (1 g) was prepared from **1** (3 g) and bpy (1.56 g) by a treatment similar to that described for **11**, while the red solution of Co(CO$_3$)(en)(bpy)$^+$ resulted by stirring for 50 min at 40 °C. *Anal.* Found: C, 29.0; H, 2.7; N, 8.0. Calc.: C, 29.2; H, 2.7; N, 8.0%.

[Co(hfac)(en)(phen)](ClO$_4$)$_2$·H$_2$O

This substance (0.2 g) was prepared analogously to **12** using phen·H$_2$O (2.0 g). *Anal.* Found: C, 31.2; H, 2.4; N, 7.9. Calc.: C, 31.6; H, 2.4; N, 8.0%. [Co(CO$_3$)(en)(phen)]ClO$_4$ (2.3 g) separated during the process.

[Co(hfac)(tn)(bpy)](ClO$_4$)$_2$ (13)

This substance (2.0 g) was prepared from **2** (3.14 g) and bpy (1.56 g) analogously to **12**. *Anal.* Found: C, 30.9; H, 2.8; N, 7.9. Calc.: C, 31.1.; H, 2.8; N, 8.1%.

[Co(hfac)(tn)(phen)](ClO$_4$)$_2$·2.5H$_2$O

This substance (0.2 g) was prepared analogously to **13** using phen·H$_2$O (2.0 g). *Anal.* Found: C, 31.5; H, 2.7; N, 7.3. Calc.: C, 31.4; H, 3.2; N, 7.3%.

[Co(hfac)(bpy)(phen)](ClO$_4$)$_2$·1.5H$_2$O

10 (3 g) was decarbonized at 50 °C in 2 M $HClO_4$ (10 ml). It was filtered and the filtrate was neutralized by 2 M NaOH (5 ml). This solution was treated with a solution of Hhfac (1 g) and 2 M NaOH (5 ml) and was stirred for 1 h at 60 °C. The resultant pink precipitate changed to orange on addition of 6 M $HClO_4$. The orange precipitate was recrystallized from 2 M $HClO_4$ and acetone (1:1) and was washed with 0.5 M $HClO_4$, ethanol and ether (1:9). Yield 1.5 g. *Anal.* Found: C, 39.1; H, 2.2; N, 6.6. Calc.: C, 39.2; H, 2.4; N, 6.8%.

Results and discussion

Preparations

Our preparative method for **1** and **2** is more convenient than that given in a previous report [3]. Addition of excess $KHCO_3$ prevents the production of the monocarbonato species as a by-product. The general preparative course for Co(hfac)L^{2+} is that the hfac ligand reacts with the corresponding diaqua complex, which is derived from the carbonato complex. An alkaline condition is favoured when L involves bpy or phen. This is related to the fact that K_{OH} is large for such products.

UV–Vis spectra

These complexes are orange colored in an acidic medium and violet colored in a basic medium. The

TABLE 1. Absorption maxima of $Co(hfac)L^{2+}$

L	λ (nm) (ε)	
	In acidic water	In basic water
$(MeNH_2)_4$	508(106), 349(2390)	542(105)
$(n\text{-}AmNH_2)_4$	512(142), 332(2420)[a]	[b]
cis-$(NH_3)_2$(en)	488(122), 346(2806)	523(117)
(*R*-pn)(*S*-pn)	485(138), 348(2630)	518(132)
cyclen	515(387), 355(1910)	551(268)
cyclam	505(200), 356(1810)	538(198)
cis-$(NH_3)_2$(bpy)	490(115), 340(3420)sh[c]	534(129
(en)(bpy)	488(160), 340(3410)sh	519(156)
(en)(phen)	488(186), 348(3340)sh	521(168)
(tn)(bpy)	492(116), 342(3320)sh	522(128)
(tn)(phen)	492(63), 346(2160)sh	531(80)
(bpy)(phen)	502(147), 347(3840)sh	530(207)

[a]4% Ethanol. [b]Decomposition. [c]sh = shoulder.

absorption maxima are summarized in Table 1. In acidic water, the first band and the charge transfer band are observed at around 500 and 350 nm, respectively. In basic water the first band shifts by 30 nm to lower energy and the charge transfer band disappears. The spectra in methanol are essentially similar to the corresponding one in water, where the absorption coefficients are more or less the same. They are not shown in this report. These spectral features are quite similar to those already described for analogous $Co(hfac)L^{2+}$ with a tetraamine L ligand and can be explained by the shift of eqn. (1) [1, 2].

Fluorine NMR spectra in D_2O

The results are summarized in Table 2. One can explain these results by considering the symmetry aspect of the complex [8]. The two CF_3 groups are equivalent in $Co(hfac)L^{2+}$ of a C_{2v} or C_2 symmetry. They are inequivalent in $Co(hfac)L^{2+}$ of other symmetries or in $Co(hfacOH)L^+$. When a $Co(hfac)L^{2+}$ is of a C_2 or C_s symmetry, two diastereoisomeric $Co(hfacOH)L^+$ are possible. When $Co(hfac)L^{2+}$ is of a C_1 symmetry, four diastereoisomeric $Co(hfacOH)L^+$ are possible [8]. In the case of $Co(hfac)(MeNH_2)_4{}^{2+}$, one signal is observed in acidic water and one pair of signals in basic water. This is the case when the complex is of a C_{2v} symmetry. In the case of $Co(hfac)(en)(bpy)^{2+}$, one pair of signals is observed in acidic water and four pairs of signals in basic water. This is the case when the complex is of a C_1 symmetry. The mole ratio of the four diastereoisomeric $Co(hfacOH)(en)(bpy)^+$ is estimated as 4:22:29:45. In the case of $Co(hfac)(NH_3)_2(en)^{2+}$ and $Co(hfac)(NH_3)_2(bpy)^{2+}$, the *cis* configuration can be assigned on the basis of the fluorine NMR spectra. Their *trans* isomers are of a C_{2v} symmetry. In the case of $Co(hfac)(R\text{-pn})(S\text{-pn})^{2+}$, one can deduce from the spectra that four geometric isomers coexist in acidic water. In these isomers, the relative position of the two asymmetric carbon atoms differs. In the case of

TABLE 2. Fluorine NMR spectra of $Co(hfac)L^{2+}$ in D_2O

L	Point group of $Co(hfac)L^{2+}$	−δ (ppm) (intensity)		Isomer ratio
		1 mM CF_3CO_2H	5 mM Na_2CO_3	
$(MeNH_2)_4$	C_{2v}	76.09	73.78, 86.11	
cis-$(NH_3)_2$(en)	C_1	75.98, 76.07	73.68(29), 73.70(30), 73.76(15) 73.81(26), 85.51(29), 85.73(30) 85.78(26), 86.20(15)	15:26:29:30
(*R*-pn)(*S*-pn)	C_1	76.10, 76.12 76.14, 76.15 76.19, 76.21 76.22, 76.25	many signals	
cyclen	C_s, C_{2v}	76.15(3) 76.18(97) 76.42(97)	73.79(14), 73.85(30), 74.06(56) 85.39(30), 85.76(14), 85.95(56)	14:30:56
cyclam	C_2	76.16	73.60(39), 73.66(61), 85.60(61), 86.62(39)	39:61
cis-$(NH_3)_2$(bpy)	C_1	75.50, 76.10	73.28(18), 73.36(25), 74.16(8) 74.23(49), 85.17(8), 85.28(49) 85.66(25), 85.79(18)	8:18:25:49
(en)(bpy)	C_1	75.64, 76.18	73.52(22), 73.56(29), 74.11(4) 74.33(45), 85.27(45), 85.31(22) 85.52(29), 85.78(4)	4:22:29:45

TABLE 3. Fluorine NMR spectra of $Co(hfac)L^{2+}$ in CH_3OD

L	Point group of $Co(hfac)L^{2+}$	$-\delta$ (ppm) (intensity)		Isomer ratio
		1 mM CF_3CO_2H	5 mM $NaOCH_3$	
$(MeNH_2)_4$	C_{2v}	75.95	74.05, 81.28	
$(n\text{-}AmNH_2)_4$	C_{2v}	75.91	74.00, 81.11	
(*R*-pn)(*S*-pn)	C_1	75.86, 75.90 75.94, 75.97 76.00, 76.05 76.09		
cyclen	C_s, C_{2v}	76.02(2) 76.04(98) 76.39(98)	73.78(6), 73.89(19), 74.15(75) 83.25(6), 83.31(94)	6:19:75
cyclam	C_2	76.15	73.18(7), 73.68(93), 81.56(93), 82.97(7)	7:93
cis-$(NH_3)_2$(bpy)	C_1	75.43, 76.27	73.29(23), 73.31(15), 74.71(4), 74.74(58) 79.91(4), 81.91(58), 83.11(15), 83.20(23)	4:15:23:58
(en)(bpy)	C_1	75.74, 76.28	73.34(32), 74.49(28), 74.68(2), 75.18(38) 80.56(2), 82.68(38), 83.54(28), 83.81(32)	2:28:32:38

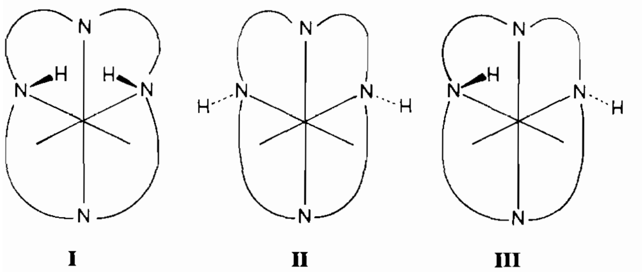

Fig. 1. Three possible *cis* coordination modes of cyclen and cyclam ligand.

$Co(hfac)(cyclen)^{2+}$, one can deduce that two isomers coexist in acidic water; one of coordination mode III (C_s) with mole ratio 97 and the other of coordination mode I (C_{2v}) or II (C_{2v}) with mole ratio 3 (Fig. 1). Correspondingly, three isomers of Co(hfacOH)-(cyclen)$^+$ coexist in basic water with mole ratio 14:30:56; two of coordination mode III and one of coordination mode I or II. On reacidification, the mole ratio of the two isomers was the same as the original 97:3. Thus, one may consider that the configurational change between III and I or II is rapid. This is interesting being in contrast with the slow configurational change between the Δ-*β*-*SS* and Δ-*β*-*SR* isomers in $Co(hfac)L^{n+}$ with a linear tetradentate L ligand such as 1,8-diamino-3,6-diazaoctane (trien), 1,9-diamino-3,7-diazanonane (2,3,2-tet), 4,7-diaza-1,10-decanediamine (3,2,3-tet) or ethylenediamine-*N*,*N'*-diacetato [9]. In the case of $Co(hfac)(cyclam)^{2+}$, it is deduced from the spectra that only one coordination mode I (C_2) or II (C_2) is favored in acidic and basic water.

Fluorine NMR spectra in CH_3OD

The results are summarized in Table 3. The spectra are essentially similar to the corresponding ones in water and can be analogously interpreted with isomer ratios differing more or less the same.

Equilibrium constant

Generally, absorption intensity was measured at 350 nm for four solutions of the complex (<0.1 mM); acidic, basic and two buffer solutions. In some cases, absorption intensity was measured for a simple solution of the complex. The composition of each solution is indicated in the footnote of Table 4. The K_{OH} was estimated from the absorption intensity and the pH value of the buffer solution [8]. The K_{OMe} was estimated from the absorption intensity and the pK_b value of the buffering agent in methanol [2]. The pK_b value in methanol of triethanolamine and of betaine was estimated as 8.0 and 11.3, respectively, by comparing the absorption intensity of an appropriate $Co(hfac)L^{n+}$ in different buffers ($pK_b = 6.30$ for triethylamine) [2]. Activity coefficient f_i of an ion of charge Z_i was estimated by

$$\log f_i = \frac{-0.51 Z_i^2 \sqrt{\mu}}{1+\sqrt{\mu}} \quad \text{in water}$$

TABLE 4. Covalent hydration equilibrium constant of Co(hfac)L^{2+} at *c.* 25 °C

L	$-pK_{OH}$	$-pK_{OMe}$
$(NH_3)_4$[a]	6.85	8.59
$(MeNH_2)_4$	6.34[b]	8.78[f]
$(EtNH_2)_4$	6.30[b]	8.76[f]
$(n\text{-}PrNH_2)_4$	6.74[b]	8.97[f]
$(n\text{-}BuNH_2)_4$	6.75[b]	8.93[f]
$(n\text{-}AmNH_2)_4$		8.91[f]
cis-$(NH_3)_2$(en)	6.63[b]	8.30[f]
$(en)_2$[a]	6.62	8.57
$(tn)_2$	6.49[b]	8.90[f]
(*R*-pn)(*S*-pn)	6.43[b]	8.26[f]
α-trien[a]	6.81	8.82
β-trien[a]	6.51	9.10
β-2,3,2-tet	6.36[b]	8.51[f]
β-3,2,3-tet	6.43[b]	9.04[f]
tren	7.10[b]	9.15[f]
cyclen	6.71[b]	9.11[f]
cyclam	6.51[b]	9.00[f]
cis-$(NH_3)_2$(bpy)	8.69[c]	10.82[g]
(en)(bpy)	8.76[c]	11.08[g]
(en)(phen)	8.73[c]	11.20[g]
(tn)(bpy)	8.65[c]	11.08[g]
(tn)(phen)	8.74[c]	11.20[g]
$(bpy)_2$	11.48[d]	14.54[h]
$(phen)_2$	11.51[d]	14.64[h]
(bpy)(phen)	11.41[e]	14.79[i]

[a]Ref. 2. [b]1 mM $HClO_4$, tris + HCl buffers (pH = 7.4 and 8.1), 2 mM or 5 mM Na_2CO_3. [c]3 mM $HClO_4$, MES + NaOH buffers (pH = 5.5 and 6.2), 3 mM Na_2CO_3. [d]0.6 M $HClO_4$, phthalic acid + KOH buffers (pH = 2.7 and 3.0), 0.2 mM NaOH. [e]0.3 M $HClO_4$, 1 mM and 3 mM $HClO_4$, 3mM Na_2CO_3. [f]1 mM H_2SO_4 or $HClO_4$, triethanolamine + HCl buffers, 5 mM $NaOCH_3$. [g]1 mM H_2SO_4, betaine + HCl buffers, 5 mM $NaOCH_3$. [h]0.1 M $HClO_4$, simple solutions of the complex (2 mM and 0.4 mM), 5 mM $NaOCH_3$. [i]0.3 M H_2SO_4, 1 mM and 5 mM *p*-phenolsulfonic acid, 1 mM $NaOCH_3$. $EtNH_2$ = ethylamine. $n\text{-}PrNH_2$ = n-propylamine. $n\text{-}BuNH_2$ = n-butylamine. tren = tris(2-aminoethyl)amine.

and by

$$\log f_i = \frac{-1.9Z_i^2\sqrt{\mu}}{1+2\sqrt{\mu}} \quad \text{in methanol}$$

The ionic strength μ was below 0.01. The results are summarized in Table 4. When L involves neither bpy nor phen ligands, the pK_{OH} and pK_{OMe} were -6.6 ± 0.3 and -8.7 ± 0.4, respectively. Those for L = tren slightly exceed these values. When L involves either one bpy or one phen ligand, the pK_{OH} and pK_{OMe} values are lower: -8.7 ± 0.1 and -11.0 ± 0.2, respectively. When L involves two bpy or phen ligands, the pK_{OH} and pK_{OMe} values are still low and are approximately -11.5 and -14.6. Thus, values of pK_{OH} and pK_{OMe} critically depend on the involvement as L ligand of a bpy or a phen ligand. One possible explanation for this enhanced covalent hydration may be that the backdonation of the d electrons of the Co(III) center to a bpy or a phen ligand makes the carbonyl carbon atoms of the hfac ligand electron-deficient. This electron-deficiency could be the driving force for the bond formation between one of the carbonyl carbon atoms and the lyate anion.

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