Bromo-complexes of Cobalt(II) in Acetone

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Equilibria of cobalt(II) perchlorate with lithium bromide in 0.1 mol dm^{-3} $LiClO_4$ acetone solution have been investigated by the combination of potentiometry and spectrophotometry at 25.0 °C. An Ag–AgBr electrode gave rise to a Nernstian response in the acetone solution saturated by AgBr. Potentiometry revealed equilibria (i) and (ii), where L refers to the solvent acetone molecule. The formation constants

$$[CoL_6][ClO_4]_2 + 2LiBr \xrightleftharpoons{\beta_2} [CoBr_2L_2] + 2LiClO_4 + 4L \qquad \text{(i)}$$

$$[CoBr_2L_2] + LiBr \xrightleftharpoons{K_3} Li[CoBr_3L] + L \qquad \text{(ii)}$$

of the dibromo- and tribromo-complexes were determined as $\log \beta_2 = 9.2 \pm 0.4$ and $\log K_3 = 5.30 \pm 0.03$. By spectrophotometric measurements, equilibrium (iii) occurred at higher LiBr concentration. The

$$Li[CoBr_3L] + LiBr \xrightleftharpoons{K_4} Li_2[CoBr_4] + L \qquad \text{(iii)}$$

formation constant of the tetrabromo-complex was determined as $\log K_4 = 1.89 \pm 0.05$. The spectral data of these complexes are presented and are compared with those of other systems.

Equilibria of cobalt(II) with halide ions have been investigated in many non-aqueous solvents.[1–10] These studies suggested the equilibria shown below, where X^- is a halide and L is a

$$[CoL_6]^{2+} + X^- \rightleftharpoons [CoXL_5]^+ + L$$

$$[CoXL_5]^+ + X^- \rightleftharpoons [CoX_2L_4] + L$$

$$[CoX_2L_4] \rightleftharpoons [CoX_2L_2] + 2L$$

$$[CoX_2L_2] + X^- \rightleftharpoons [CoX_3L]^- + L$$

$$[CoX_3L]^- + X^- \rightleftharpoons [CoX_4]^{2-} + L$$

solvent or neutral ligand.

The effects of halide ion concentration,[3–5] temperature,[6] and pressure [7,8] on the equilibria of cobalt(II) with halide in acetone have been studied. Fine [4] determined the formation constant and spectrum of each halogeno-complex by means of spectrophotometry. The formation constant of lower halogeno-complexes, however, is too large to obtain a reliable value by spectrophotometry in a poorly solvating solvent such as acetone.

We have reported the formation of the chloro-complexes of cobalt(II) in acetone [5] by the combination of spectrophotometry and potentiometry. In the present paper, the formation of the bromo-complexes of cobalt(II) in acetone is investigated, and the results are compared with those in acetic acid [1,2] and of halogeno-complexes with pyridine bases.[9,10]

Experimental

Reagents.—G.R. grade acetone was shaken with molecular sieves (Union Carbide Co., 3A; pore size = 3 Å) for 30 min. After decantation, the dehydrated acetone was distilled. The water content was determined by the Karl–Fischer method to be less than 5×10^{-3} mol dm^{-3}. Cobalt(II) perchlorate recrystallized from water was dried over phosphorus pentoxide *in vacuo* and recrystallized from dehydrated acetone. Lithium bromide and lithium perchlorate were dried at 120 and 170 °C, respectively.

Potentiometric Measurements.—Potentiometric measurements were performed with an Orion research digital pH/mV meter (model 801A) using the chemical cell, shown below, at

Ag–AgBr| sample solution
(0.1 mol dm^{-3} $LiClO_4$ acetone)||
||0.1 mol dm^{-3} $LiClO_4$ acetone solution||
salt bridge
0.1 mol dm^{-3} LiCl|Hg_2Cl_2–Hg
acetone solution

25.0 °C. The Ag–AgBr electrode was prepared by electrolyzing a silver electrode (Beckman silver electrode 39 261) in lithium bromide aqueous solution. After washing with water, the electrode was washed with acetone and stored in an $AgClO_4$–acetone solution.

Spectrophotometric Measurements.—Absorption spectra were measured with a Shimadzu double-beam spectrophotometer UV-200 with a stoppered quartz cell (volume 50 cm^3, light path 10 mm).

Results

Electromotive Force of Ag–AgBr *Electrode.*—From solubility measurements,[5] the equilibrium constant, K_s, of equation (1) in 0.1 mol dm^{-3} $LiClO_4$ acetone solution was obtained as K_s $(=[LiAgBr_2]/[LiBr]) = 4.19$. The concentration of free lithium bromide, [LiBr], in the solution saturated with AgBr is given by equation (2), where T_{LiBr} is the

$$AgBr(s) + LiBr \xrightleftharpoons{K_s} Li[AgBr_2] \qquad (1)$$

$$T_{LiBr} = [LiBr] + [LiAgBr_2] = (1 + K_s)[LiBr] \qquad (2)$$

total concentration of LiBr added.

Although the degree of the ion-pair dissociation of electrolytes is relatively high in acetone (dielectric constant = 20.7),

Table 1. Electromotive force of cobalt(II) perchlorate–lithium bromide acetone solutions containing 0.1 mol dm^{-3} lithium perchlorate

c_{Co} = 3.08 × 10^{-3} mol dm^{-3}		c_{Co} = 1.054 × 10^{-3} mol dm^{-3}		c_{Co} = 0.308 × 10^{-3} mol dm^{-3}	
$10^3 T_{LiBr}$/ mol dm^{-3}	E^a/mV	$10^3 T_{LiBr}$/ mol dm^{-3}	E^b/mV	$10^3 T_{LiBr}$/ mol dm^{-3}	E^c/mV
0.078	160.7	0.092	135.8	0.026	144.5
0.238	141.3	0.268	122.0	0.092	122.8
0.926	121.9	0.532	112.4	0.172	112.4
1.432	114.9	0.878	103.8	0.257	105.3
1.910	109.8	1.624	91.7	0.342	99.7
2.700	104.6	2.028	85.3	0.427	96.4
3.31	101.1	2.417	77.3	0.513	91.9
3.88	97.8	2.803	65.0	0.607	85.0
4.44	95.0	3.18	36.7	0.689	79.2
4.99	91.6	3.54	6.3	0.802	69.1
5.50	87.7	4.05	−13.6	0.926	50.8
6.03	84.0	4.74	−27.7	1.240	10.6
6.61	79.4	5.46	−37.2	1.395	0.6
7.26	74.0				
7.87	66.5				
8.29	58.6				
8.71	45.9				
9.11	25.6				
9.51	4.5				
9.88	−10.1				
10.38	−22.3				
10.95	−31.9				
11.62	−40.5				

[a] $E'_0 = -237.0$ mV. [b] $E'_0 = -235.6$ mV. [c] $E'_0 = -238.0$ mV.

that of LiBr is suppressed by the addition of a large excess of LiClO$_4$ (refs. 5 and 11). As in the present experiments the concentration of LiClO$_4$ is much higher than that of LiBr and is kept constant (0.1 mol dm^{-3}), the activity of the bromide ion, a_{Br}, is directly proportional to the concentration of free lithium bromide, [LiBr]. Thus, the e.m.f. at 25.0 °C is expressed by equation (3).

$$E = E_0 - 59.1 \log a_{Br} = E'_0 - 59.1 \log [\mathrm{LiBr}] \quad (3)$$

The e.m.f. of the chemical cell described in the Experimental section was measured at various concentrations of LiBr. A plot of e.m.f. as a function of log [LiBr] shows a straight line with a slope of 59.1. Thus, the chemical cell gives rise to a reversible potential.

Potentiometric Titration.—Various concentrations of cobalt(II) perchlorate were titrated with lithium bromide potentiometrically (Table 1). The equilibrium concentration of LiBr not bound to Co^{II}, [LiBr], was calculated from the e.m.f. by using equation (3). The formation function of the bromo-complex, $\bar{n}$, calculated using equation (4) was plotted

$$\bar{n} = (c_{LiBr} - [\mathrm{LiBr}])/c_{Co} \quad (4)$$

as a function of log [LiBr] (Figure 1), where $c_{LiBr} = T_{LiBr} - [\mathrm{LiAgBr_2}]$.

The plot falls on the same curve irrespective of the cobalt(II) concentration, c_{Co}, and shows a plateau at $\bar{n} = 3$. These facts indicate the formation of monomeric complexes up to the tribromo-complex in the region of log [LiBr] < −4 [equations (5)—(7)], where L refers to the solvent acetone

$$[\mathrm{CoL_6}][\mathrm{ClO_4}]_2 + \mathrm{LiBr} \overset{K_1}{\rightleftharpoons} [\mathrm{CoBrL_5}][\mathrm{ClO_4}] + \mathrm{LiClO_4} + \mathrm{L} \quad (5)$$

$$[\mathrm{CoBrL_5}][\mathrm{ClO_4}] + \mathrm{LiBr} \overset{K_2}{\rightleftharpoons} [\mathrm{CoBr_2L_2}] + \mathrm{LiClO_4} + 3\mathrm{L} \quad (6)$$

$$[\mathrm{CoBr_2L_2}] + \mathrm{LiBr} \overset{K_3}{\rightleftharpoons} \mathrm{Li}[\mathrm{CoBr_3L}] + \mathrm{L} \quad (7)$$

molecule. As will be mentioned below, the dibromo-complex is predominantly tetrahedral. With the successive formation constants, K'_1, K'_2, and K_3, defined by equations (8)—(10) respectively, the formation function is given by equation (11).

$$K'_1 = \frac{[\mathrm{CoBrL_5(ClO_4)}]}{[\mathrm{CoL_6(ClO_4)_2}][\mathrm{LiBr}]} = \frac{K_1}{[\mathrm{LiClO_4}]} \quad (8)$$

$$K'_2 = \frac{[\mathrm{CoBr_2L_2}]}{[\mathrm{CoBrL_5(ClO_4)}][\mathrm{LiBr}]} = \frac{K_2}{[\mathrm{LiClO_4}]} \quad (9)$$

$$K_3 = \frac{[\mathrm{Li(CoBr_3L)}]}{[\mathrm{CoBr_2L_2}][\mathrm{LiBr}]} \quad (10)$$

$$\bar{n} = \{[\mathrm{CoBrL_5(ClO_4)}] + 2[\mathrm{CoBr_2L_2}] + 3[\mathrm{Li(CoBr_3L)}]\}/c_{Co} = \frac{K'_1[\mathrm{LiBr}] + 2K'_1K'_2[\mathrm{LiBr}]^2 + 3K'_1K'_2K_3[\mathrm{LiBr}]^3}{1 + K'_1[\mathrm{LiBr}] + K'_1K'_2[\mathrm{LiBr}]^2 + K'_1K'_2K_3[\mathrm{LiBr}]^3} \quad (11)$$

By comparison of the plot of Figure 1 in the region of $\bar{n} < 3$ with the normalized curve, $(X, Y) = [\log x, (px + 2x^2 + 3qx^3)/(1 + px + x^2 + qx^3)]$, the formation constants are obtained as log β_2 (=log K_1K_2) = 9.2 ± 0.4 and log K_3 = 5.30 ± 0.03; K_1 was too small for reliable value to be obtained.

Spectrophotometric Measurements.—Some typical spectra of cobalt(II) perchlorate–lithium bromide (0.1 mol dm^{-3} LiClO$_4$) solutions are shown in Figure 2. At higher LiBr concentrations, these spectra show isosbestic points at 640, 672, and 687 nm. The spectrum at highest c_{LiBr} shows the

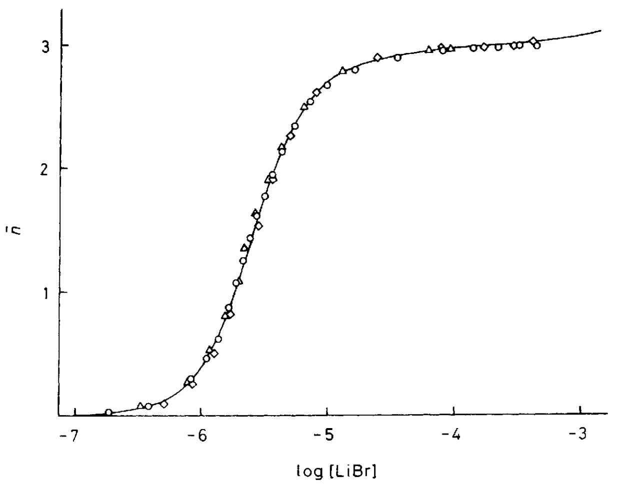

Figure 1. Plot of the formation function of the bromo-complexes of cobalt(II), $\bar{n}$, as a function of log [LiBr]. $c_{\mathrm{LiClO_4}} = 0.1$ mol dm^{-3}; $c_{\mathrm{Co}} = 3.08 \times 10^{-3}$ (○), 1.054×10^{-3} (◇), and 0.308×10^{-3} mol dm^{-3} (△). Solid line is the calculated curve, see text

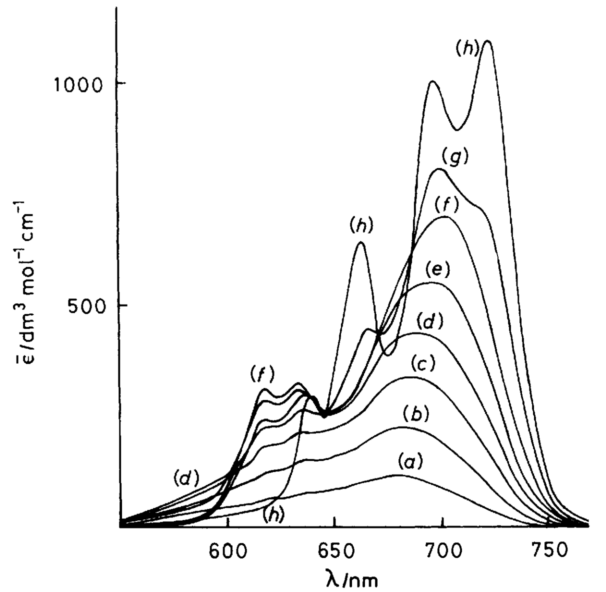

Figure 2. Absorption spectra of cobalt(II) perchlorate–lithium bromide acetone solution. $c_{\mathrm{LiClO_4}} = 0.1$ mol dm^{-3}; $c_{\mathrm{LiBr}} =$ (*a*) 0.467×10^{-3}, (*b*) 0.904×10^{-3}, (*c*) 1.336×10^{-3}, (*d*) 1.720×10^{-3}, (*e*) 2.101×10^{-3}, (*f*) 2.462×10^{-3}, (*g*) 10.48×10^{-3}, and (*h*) 238×10^{-3} mol dm^{-3}; $c_{\mathrm{Co}} = 0.889 \times 10^{-3}$ mol dm^{-3}

characteristics of the tetrabromo-complex.[2,10] These facts predict equilibrium (12). The apparent molar absorption coefficient of the solution in this region of c_{LiBr} is given by equation (13), where ε_3 and ε_4 refer to the molar absorption coefficient of the tribromo- and tetrabromo-complexes, respectively; this reduces to equation (14). A plot of the left-hand side of equation (14) as a function of log[LiBr] falls on the same straight line with a slope of unity irrespective of c_{Co}, where ε_3 was estimated by the interpolation of the mol ratio plot ($\bar{\varepsilon}$ *versus* $c_{\mathrm{LiBr}}/c_{\mathrm{Co}}$) to $c_{\mathrm{LiBr}} : c_{\mathrm{Co}} = 3$, and ε_4 from the spectrum at the highest c_{LiBr}. The concentration of free lithium bromide, [LiBr], was calculated by subtraction of the concentration of bromide co-ordinated to the complexes from the total concentration, c_{LiBr}. The concentrations of the complexes were calculated by the assumption that $[\mathrm{Li(CoBr_3L)}]/[\mathrm{Li_2(CoBr_4)}] = (\varepsilon_4 - \bar{\varepsilon})/(\bar{\varepsilon} - \varepsilon_3)$. The values of ε_3 and ε_4 were refined to give the best linear plot with a slope of unity at various wavelengths. The spectra of the tri- and tetra-bromo-complexes thus obtained are shown in Figure 3.

$$\mathrm{Li[CoBr_3L]} + \mathrm{LiBr} \overset{K_4}{\rightleftharpoons} \mathrm{Li_2[CoBr_4]} + \mathrm{L} \qquad (12)$$

$$\bar{\varepsilon} = \{\varepsilon_3[\mathrm{Li(CoBr_3L)}] + \varepsilon_4[\mathrm{Li_2(CoBr_4)}]\}/c_{\mathrm{Co}} = \frac{\varepsilon_3 + \varepsilon_4 K_4[\mathrm{LiBr}]}{1 + K_4[\mathrm{LiBr}]} \qquad (13)$$

$$\log\,(\bar{\varepsilon} - \varepsilon_3)/(\varepsilon_4 - \bar{\varepsilon}) = \log K_4 + \log\,[\mathrm{LiBr}] \qquad (14)$$

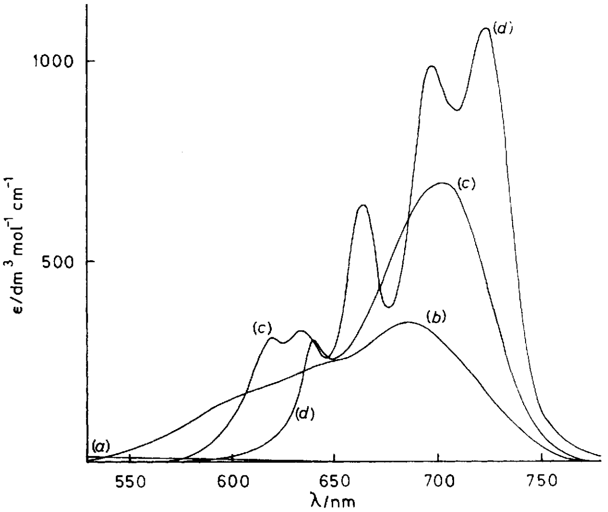

Figure 3. Absorption spectra of bromo-complexes of cobalt(II): (*a*) $[\mathrm{CoL_6}][\mathrm{ClO_4}]_2$, (*b*) $[\mathrm{CoBr_2L_2}]$, (*c*) $\mathrm{Li[CoBr_3L]}$, and (*d*) $\mathrm{Li_2[CoBr_4]}$ (L = acetone)

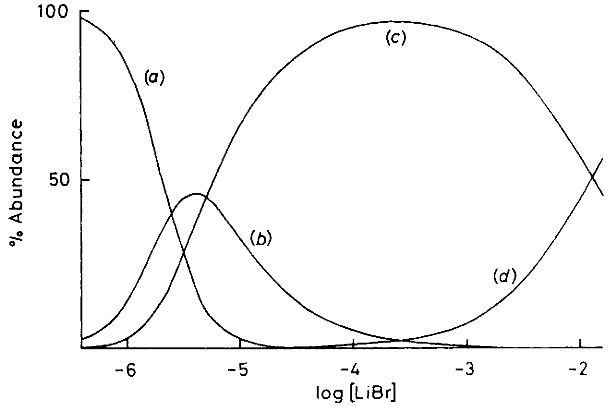

Figure 4. Distribution diagram of bromo-complexes of cobalt(II) in 0.1 mol dm^{-3} $\mathrm{LiClO_4}$ acetone solution: (*a*) $[\mathrm{CoL_6}][\mathrm{ClO_4}]_2$, (*b*) $[\mathrm{CoBr_2L_2}]$, (*c*) $\mathrm{Li[CoBr_3L]}$, (*d*) $\mathrm{Li_2[CoBr_4]}$ (L = acetone)

The formation functions and the distribution diagram of the bromo-complexes in 0.1 mol dm^{-3} $\mathrm{LiClO_4}$ acetone solution calculated using the formation constants, K'_1 to K_4, are shown in Figure 1 by a solid curve and in Figure 4, respectively.

The spectrum of the dibromo-complex was estimated from the spectra at low c_{LiBr} ($c_{\mathrm{LiBr}} : c_{\mathrm{Co}} < 3$). That is, the apparent

Table 2. Formation constants of halogeno-complexes of cobalt(II)

L	X	log β_2	log K_3	log K_4	log (K_3/K_4)
Acetone	Cl [a]	11.2	5.97	2.64	3.33
		±0.3	±0.03	±0.05	
	Br [b]	9.2	5.30	1.89	3.41
		±0.4	±0.03	±0.05	
Acetic acid	Cl [c]	6.35	2.9	0.8	2.1
		±0.08	±0.2	±0.1	
	Br [d]	5.44	2.81	0.4	2.4
		±0.03	±0.1	±0.2	
Pyridine	Cl [e]		4.10	0.48	3.62
			±0.03	±0.01	
	Br [f]		2.89	−0.74	3.63
			±0.03	±0.01	

[a] Ref. 5. [b] This work. [c] Ref. 1. [d] Ref. 2. [e] Ref. 9. Solvent = 1,2-dichloroethane. [f] Ref. 10. Solvent = 1,2-dibromoethane.

molar absorption coefficient, $\bar{\varepsilon}$, is given by equation (15) in this region. Thus, ε_2 is given by equation (16). The spectrum of

$$\bar{\varepsilon}c_{Co} = \varepsilon_0[CoL_6(ClO_4)_2] + \varepsilon_2[CoBr_2L_2] + \varepsilon_3[Li(CoBr_3L)]$$

$$= [CoL_6(ClO_4)_2]\{\varepsilon_0 + \varepsilon_2K'_1K'_2[LiBr]^2 + \varepsilon_3K'_1K'_2K_3[LiBr]^3\} \quad (15)$$

$$\varepsilon_2 = (\bar{\varepsilon}c_{Co}[CoL_6(ClO_4)_2]^{-1} - \varepsilon_0)K'_1K'_2{}^{-1}[LiBr]^{-2} - \varepsilon_3K_3[LiBr] \quad (16)$$

the dibromo-complex obtained from the values of ε_2 at various wavelengths is shown in Figure 3.

Discussion

Formation Constants.—The formation constants of the chloro- (ref. 5) and bromo-complexes are listed in Table 2 along with the results of other solvent systems. In the case of pyridine complexes the solvents are 1,2-dichloroethane for the chloro-complexes[9] and 1,2-dibromoethane for the bromo-complexes.[10] The dihalogeno-complexes of acetone and pyridine are predominantly tetrahedral, $[CoX_2L_2]$. Thus, the constants correspond to the equilibria shown below.

$$[CoL_6]^{2+} + 2X^- \overset{\beta_2}{\rightleftharpoons} [CoX_2L_2] + 4L$$

$$[CoX_2L_2] + X^- \overset{K_3}{\rightleftharpoons} [CoX_3L]^- + L$$

$$[CoX_3L]^- + X^- \overset{K_4}{\rightleftharpoons} [CoX_4]^{2-} + L$$

As in the case of the acetic acid system, the dihalogeno-complex is in equilibrium between octahedral, $[CoX_2L_4]$, and tetrahedral $[CoX_2L_2]$, configurations; the constant is corrected for the configurational equilibrium.[1,2] In all systems the ionic species form the uncharged ion pair with the counter ion, ClO_4^-, Li^+, or $N(C_4H_9)_4^+$.

The reference state of the constants of the acetone and acetic acid complexes is the pure solvent, *i.e.* the activity of the pure ligand or solvent is unity, whereas the constants of the pyridine complexes are based on the molar concentration of pyridine in the 1,2-dihalogenoethane. Consequently, if we compare the constants based on the same reference state, the formation constant of the halogeno-complexes of pyridine is much smaller than that of acetone and acetic acid. This fact is quite reasonable since the co-ordination power of pyridine (donor number = 33.1, ref. 12) is much higher than that of acetone (donor number = 17.0). As can be seen from Table 2, the co-ordination power of acetone is lower than that of acetic acid.

Table 3. Gravity centre ($10^{-3}\nu_c$/cm^{-1}) and oscillator strength (10^3f, in parentheses) of the absorption band of the tetrahedral halogeno-complexes of cobalt(II)

L	X [a]	$[CoX_2L_2]$	$[CoX_3L]^-$	$[CoX_4]^{2-}$	$[CoL_4]^{2+}$ [b]
Acetone	Cl	15.92	15.39	15.11	
		(3.92)	(4.05)	(5.34)	
	Br	15.41	14.86	14.44	16.58
		(4.05)	(5.82)	(6.89)	
Acetic acid	Cl	15.93	15.57	15.19	
		(0.53 [c])	(4.15)	(6.00)	
	Br	15.53	14.93	14.42	16.64
		(4.16 [c])	(4.99)	(8.91)	
Pyridine	Cl	16.39	15.74	15.03	
		(7.04)	(6.05)	(5.88)	
	Br	15.92	15.13	14.38	17.64
		(7.21)	(6.91)	(6.97)	

[a] References: see Table 2. [b] Estimated value of the tetrahedral complexes. See text. [c] Value for the mixture of the tetrahedral, $[CoX_2L_2]$, and octahedral, $[CoX_2L_4]$, configurations.

The ratio of K_3 to K_4 is shown in the last column of Table 2. The ratio is much larger than that calculated statistically for all systems and is almost the same between the chloro- and bromo-complexes for each ligand. This fact indicates that the electronic and steric effects of the Co–X bond on the Co–L bond are not significantly different between the chloride and bromide ions.

Spectra.—The wavenumber of the gravity centre (10^{-3} ν_c/cm^{-1}) and the oscillator strength (10^3f) of the absorption band of the tetrahedral halogeno-complexes are listed in Table 3. As the first co-ordination sphere of the tetrahalogeno-complexes is filled with the halide ion, these complexes show no significant change in ν_c by a change in solvent. The ν_c of the bromo-complexes is smaller than that of the chloro-complexes. The value of ν_c increases by decreasing the number of halide ions (n) co-ordinating to cobalt(II), and gives rise to a good linear correlation with the number n. This may indicate that the rule of average environment can be applied to both the ligand-field strength and the electron-repulsion parameter. The value of ν_c for the tetrahedral complex $[CoL_4]^{2+}$ estimated by the extrapolation of ν_c to $n = 0$ is listed in the last column of Table 3.

The value of the oscillator strength of the bromo-complex is larger than that of the corresponding chloro-complex. Except for the pyridine complex, the value increases by increasing the number of halide ions, n, co-ordinating to cobalt(II). The difference in the f value of $[CoX_4]^{2-}$ by a change in solvent is larger than that in the value of ν_c. This difference may indicate that the symmetry of the tetrahedral complex is slightly affected by the solvent structure.

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