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Formation of Mixed-ligand Complexes of Cobalt(II) with Bromide and Substituted Pyridines in 1,2-Dibromoethane

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The equilibria of a series of complexes of the $CoBr_2(R\text{-}py)_2$ type (where R-py=2-methyl-(2Me-py), 3-methyl-(3Me-py), 4-methyl-(4Me-py), 4-acetyl-(4Ac-py), and 4-cyanopyridine (4CN-py), and pyridine(py)) with TBA·Br (tetrabutylammonium bromide) in 1,2-dibromoethane have been investigated spectrophotometrically. In the presence of an excess of R-py, the dibromocomplex gives rise to the following configurational equilibrium:

$$\underset{\text{(tetrahedral)}}{CoBr_2(R\text{-}py)_2} + 2R\text{-}py \overset{K_c}{\rightleftharpoons} \underset{\text{(octahedral)}}{CoBr_2(R\text{-}py)_4}$$

with log K_C=0.67, 0.11, and 0.53±0.03 for the 4Me-py, 3Me-py, and py complexes respectively. The substitution equilibria of the tetrahedral complexes are written as:

$$CoBr_2(R\text{-}py)_2 + TBA\cdot Br \overset{K_3}{\rightleftharpoons} (TBA)CoBr_3(R\text{-}py) + R\text{-}py,$$

$$(TBA)CoBr_3(R\text{-}py) + TBA\cdot Br \overset{K_4}{\rightleftharpoons} (TBA)_2CoBr_4 + R\text{-}py.$$

The successive formation constants, log K_3, were determined as 2.23, 2.44, and 2.89±0.03 for the 4Me-py, 3Me-py, and py complexes respectively. The constants log K_4 for the 4Me-py, 3Me-py, 2Me-py, py, 4Ac-py and 4CN-py complexes are −1.07, −0.94, 0.09, −0.74, −0.09, and 0.47±0.01 respectively. The values of log K_3 and log K_4 show a linear correlation with the basicity of R-py, pK_b, except for the 2Me-py complex.

In nonaqueous solvents containing an excess of pyridine bases, R-py, the dihalogenocomplex of cobalt(II) is in a configurational equilibrium between tetrahedral [$CoX_2(R\text{-}py)_2$] and octahedral [$CoX_2(R\text{-}py)_4$] structures (where X=halogenide ion). Libuś and his co-workers[1,2] have studied the configurational equilibria for a series of complexes of cobalt(II) and other first-row transition metals by means of solubility and spectrophotometric measurements. The thermodynamic data of the equilibria with a series of substituted pyridines have been reported by Nelson *et al.*,[3–5] and the kinetic parameters have been measured by means of nitrogen-14 NMR[6] and T-jump method.[7,8] The addition of the halogenide ion to the dihalogenocomplex solution results in the formation of the tetrahedral trihalogeno [$CoX_3(R\text{-}py)^-$] and tetrahalogeno [$CoX_4{}^{2-}$] complexes.[9] Besides the visible spectra, UV,[10] near-IR,[9,11,12] and far-IR[13–15] spectra of the di- and trihalogenocomplexes in solution and in crystals have been measured.

Nelson *et al.*[5] have interpreted the solution behavior and spectra of the $CoX_2(R\text{-}py)_2$ complexes in terms of Co–N π bonding, which depends mainly on X^- and, to a lesser extent, on R-py and its pK_b. Wayland and Drago[16,17] have explained the effect of the Co–X bond strength on the Co–N bond in terms of the molecular orbital theory, whereas Graddon and Watton[18] and La Mar[19] have attributed the effects to the ligand-ligand repulsion.

The effect of the basicity of pyridine bases on the metal-nitrogen bond strength has been systematically investigated for the zinc complexes, $ZnX_2(R\text{-}py)_2$, by means of the heat of complex formation,[20,21] the far-IR spectra,[20,22–24] and the crystal structure:[24] and the role of the π bonding has been discussed. Almost no such systematic study has been attempted for the cobalt(II) complexes, however.

In a previous paper[9] we have investigated the equilibria of $CoCl_2(R\text{-}py)_2$ with tetrabutylammonium chloride (TBA·Cl) in 1,2-dichloroethane, and reported the linear correlation between the cobalt(II)-pyridine bond strength and pK_b of R-py. In the present paper, the equilibria of $CoBr_2(R\text{-}py)_2$ with TBA·Br in 1,2-dibromoethane are investigated spectrophotometrically, and the results are compared with those for the chlorocomplexes.

Experimental

Reagents. 1,2-Dibromoethane dehydrated by means of the molecular sieve was distilled. Tetrabutylammonium bromide (TBA·Br) was dried at 140 °C, and its purity was determined by argentometry. The substituted pyridines, R-py, and dibromobis(substituted pyridine)cobalt(II) were prepared by a method similar to that described in a previous paper.[9]

Measurements. The $CoBr_2(R\text{-}py)_2$ solution was prepared by dissolving $CoBr_2(R\text{-}py)_2$ crystals in 1,2-dibromoethane containing 10^{-3} mol dm^{-3} of R-py. This solution was titrated with a TBA·Br solution in a stoppered quartz cell (volume: 50 cm^3, light path: 10 mm), and the change in the visible spectra of the solution was measured by a Shimadzu double-beam spectrophotometer UV-200 at 25.0± 0.2 °C.

Results

Configurational Equilibria of Dibromocomplexes. The visible spectra of $CoBr_2(R\text{-}py)_2$ are shown in Fig. 1 (A). By the addition of 10^{-3} mol dm^{-3} of R-py, the formation of a lower pyridine complex such as $CoBr_2(R\text{-}py)$ is suppressed. The fact that the spectra have no peaks of such higher bromocomplexes as the tribromocomplex indicates that they are the spectra of the pure dibromocomplex. The solubilities of the 4Ac-py and 4CN-py complexes are too low for the spectra to be measured.

Upon the addition of a large excess of R-py, the absorbance decreases monotonously, while the ratios of the peak heights do not change. This spectral change can be interpreted in terms of the formation of an octahedral complex,[1-5,9] which has quite a small molar extinction coefficient compared with that of the tetrahedral complex; *i.e.*, the molar extinction coefficient of the tetrahedral complex of cobalt(II) is about 10^3, as is shown in Fig. 1, whereas that of the octahedral complex is less than 10 in the region of 600—700 nm.[2,25] We thus obtain the following equilibrium:

$$CoBr_2(R\text{-}py)_2 + 2R\text{-}py \overset{K_c}{\rightleftharpoons} CoBr_2(R\text{-}py)_4. \tag{1}$$

As the concentration of R-py, $C_{R\text{-}py}$, is much larger than that of the complex, C_{Co}, and as the absorption of the octahedral complex is negligible, the apparent molar extinction coefficient, $\bar{\varepsilon}$, is written as:

$$\bar{\varepsilon} = \frac{\varepsilon_2}{1+K_cC_{R\text{-}py}{}^2}. \tag{2}$$

We thus obtain Eq. 3 immediately:

$$\log\left(\frac{\varepsilon_2}{\bar{\varepsilon}}-1\right) = \log K_c + 2\log C_{R\text{-}py}. \tag{3}$$

Plot of the log ($\varepsilon_2/\bar{\varepsilon}$-1) values of the peaks of the dibromocomplex as a function of log $C_{R\text{-}py}$ gives rise to a straight line with a slope of 2. The equilibrium constants of configurational change, K_c, obtained from the intercept are listed in Table 1.

Formation of Tribromocomplexes. The change in the spectra of the $CoBr_2py_2$ solution (containing 0.05 mol dm^{-3} pyridine) upon the addition of TBA·Br is shown in Fig. 2. These spectra show an isosbestic point at 658 nm. In Fig. 3 the apparent molar extinction coefficient of the pyridine complex at 596 nm is plotted as a function of the mole ratio, $C_{TBA\cdot Br}/C_{Co}$, where $C_{TBA\cdot Br}$ refers to the total concentration of TBA·Br added. These results indicate a reaction of one molecule of bromide with a cobalt(II) complex, *i.e.*, the formation of a tribromocomplex:

$$CoBr_2py_2 + TBA\cdot Br \overset{K_3}{\rightleftharpoons} (TBA)CoBr_3py + py. \tag{4}$$

As will be shown in the next section, the successive formation constant of the tetrabromocomplex, K_4, is much smaller than that of the tribromocomplex, K_3; the formation of the tetrabromocomplex in this region of $C_{TBA\cdot Br}/C_{Co}$ is negligible. Thus, the total concentration of cobalt(II) is given by:

$$C_{Co} = [CoBr_2py_4] + [CoBr_2py_2] + [(TBA)CoBr_3py], \tag{5}$$

where [ ] denotes the equilibrium concentration. As the molar extinction coefficient of the octahedral com-

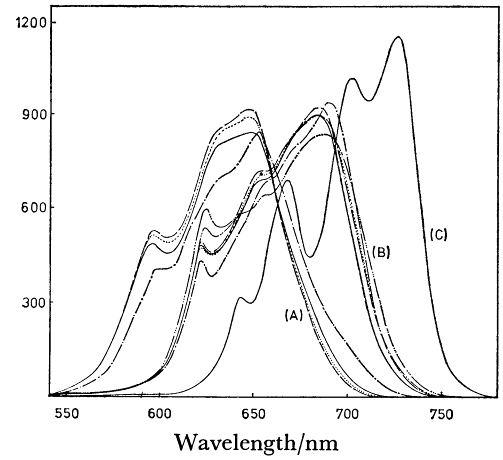

Fig. 1. Absorption spectra of $CoBr_2(R\text{-}py)_2$ (A), (TBA)-$CoBr_3(R\text{-}py)$ (B), and $(TBA)_2CoBr_4$ (C) in dibromoethane.
R-py: ——, 4Me-py; ······, 3Me-py; —·—, 2Me-py; ——, py; —··—, 4Ac-py; —···—, 4CN-py.

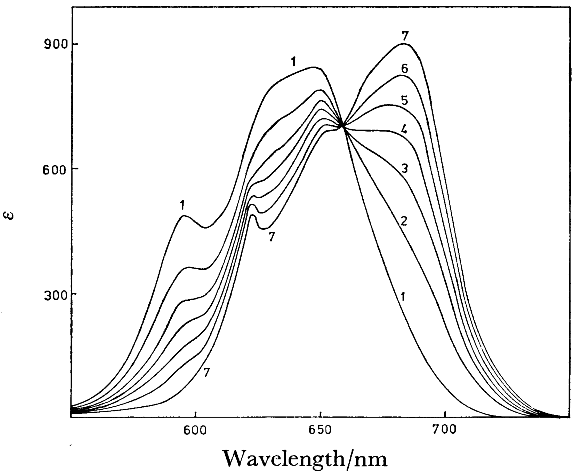

Fig. 2. Absorption spectra of pyridine complex at low TBA·Br concentrations.
$C_{TBA\cdot Br}$: 1, 0; 2, 2.72; 3, 4.50; 4, 6.04; 5, 7.77; 6, 9.89; 7, 25.5×10^{-4} mol dm^{-3}. $C_{Co}=9.84\times10^{-4}$ mol dm^{-3}. $C_{py}=5.00\times10^{-2}$ mol dm^{-3}.

Table 1. Equilibrium constants of configuratioanl change, K_c, and successive formation constants of trichlorocomplexes, K_3, and tetrachlorocomplexes, K_4

R-py	pK_b[a]	log K_c		log K_3		log K_4	
		Chloride[b]	Bromide	Chloride[b]	Bromide	Chloride[b]	Bromide
4Me-py	7.97	0.03±0.03	0.67±0.03	3.48±0.03	2.23±0.03	0.08±0.01	−1.07±0.01
3Me-py	8.32	−0.70	0.11	3.70	2.44	0.27	−0.94
2Me-py	8.04					1.18	0.09
py	8.80	0.27	0.53	4.10	2.89	0.48	−0.74
4Ac-py	10.49					1.06	−0.09
4CN-py	12.12					1.59	0.47

a) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous solution, Supplement," Butterworths, London (1972). b) Ref. 9.

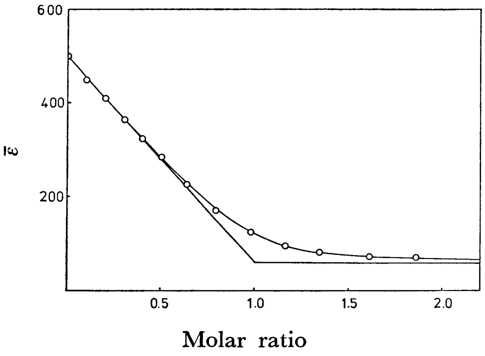

Fig. 3. Plot of apparent molar extinction coefficient at 596 nm as a function of mole ratio, $C_{\mathrm{TBA\cdot Br}}/C_{\mathrm{Co}}$. $C_{\mathrm{Co}}=1.01\times10^{-3}\,\mathrm{mol\,dm^{-3}}$. $C_{\mathrm{py}}=1.60\times10^{-2}\,\mathrm{mol\,dm^{-3}}$. Solid line is the plot of $\bar{\varepsilon}$ calculated by using the values of ε_3, ε_2, and K_3 shown in Fig. 1 and Table 1.

plex is negligibly small at this wavelength, we obtain:

$$\bar{\varepsilon} = \{\varepsilon_2[\mathrm{CoBr_2py_2}] + \varepsilon_3[\mathrm{(TBA)CoBr_3py}]\}C_{\mathrm{Co}}^{-1}, \qquad (6)$$

where the molar extinction coefficient of (TBA)-$\mathrm{CoBr_3py}$, ε_3, was evaluated by the extrapolation of the plot of $\bar{\varepsilon}$ to $C_{\mathrm{TBA\cdot Br}}/C_{\mathrm{Co}}=1$. The formation constant of the tribromocomplex:

$$K_3 = \frac{[\mathrm{(TBA)CoBr_3py}][\mathrm{py}]}{[\mathrm{CoBr_2py_2}][\mathrm{TBA\cdot Br}]}$$

is calculated by using Eqs. 5 and 6. The spectrum of the tribromocomplex obtained from the ε_3 values at various wavelengths, as evaluated by the extrapolation of the plot of $\bar{\varepsilon}$ to $C_{\mathrm{TBA\cdot Br}}/C_{\mathrm{Co}}=1$, is shown in Fig. 1. (B).

The value of the apparent molar extinction coefficient calculated by using the ε_2, ε_3, and K_3 values thus obtained is shown in Fig. 3 by a solid line; it is in good agreement with the experimental results. The K_3 of the pyridine complex is listed in Table 1, along with those of the 4Me-py and 3Me-py complexes obtained in the same manner as the pyridine complex.

Formation of Tetrabromocomplexes. 10^{-4} mol of $\mathrm{CoBr_2}$ were dissolved in 100 cm^3 of 2×10^{-3}—10^{-1} mol dm^{-3} TBA·Br 1,2-dibromoethane solutions ($C_{\text{R-py}}=0$). The spectra of the solutions (Fig. 1 (C)) show the characteristics of the tetrabromocomplex.[25] The spectra have no peaks of other complexes and do not change upon a change in the concentration of TBA·Br. Concequently, the spectrum of Fig. 1 (C) is that of pure $\mathrm{(TBA)_2CoBr_4}$.

The addition of a large excess of bromide to the $\mathrm{CoBr_2(R\text{-}py)_2}$ solution causes further spectral change, as is shown in Fig. 4. These spectra show an isosbestic point at 694 nm, and the spectrum at the highest $C_{\mathrm{TBA\cdot Br}}$ value shows the characteristics of the tetrabromocomplex. Thus, the reaction in this region of $C_{\mathrm{TBA\cdot Br}}$ may be written as:

$$\mathrm{(TBA)CoBr_3(R\text{-}py)} + \mathrm{TBA\cdot Br} \overset{K_4}{\rightleftharpoons} \mathrm{(TBA)_2CoBr_4} + \mathrm{R\text{-}py}. \qquad (7)$$

The total concentration of cobalt(II) and the apparent molar extinction coefficient are written as follows:

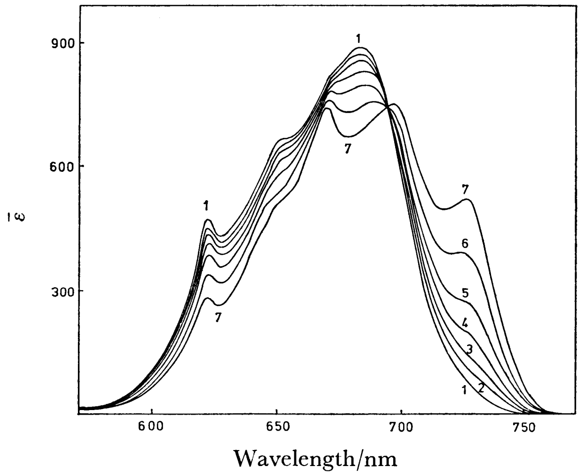

Fig. 4. Absorption spectra of pyridine complex at high TBA·Br concentrations.
$C_{\mathrm{TBA\cdot Br}}$: 1, 2.53; 2, 4.51; 3, 6.59; 4, 9.86; 5, 15.5; 6, 25.5; 7, 41.1×10^{-3} mol dm^{-3}. $C_{\mathrm{Co}}=1.33\times10^{-3}$ mol dm^{-3}. $C_{\mathrm{py}}=0.996\times10^{-2}$ mol dm^{-3}.

$$C_{\mathrm{Co}} = [\mathrm{(TBA)CoBr_3(R\text{-}py)}] + [\mathrm{(TBA)_2CoBr_4}], \qquad (8)$$

$$\bar{\varepsilon} = \{\varepsilon_3[\mathrm{(TBA)CoBr_3(R\text{-}py)}] + \varepsilon_4[\mathrm{(TBA)_2CoBr_4}]\}C_{\mathrm{Co}}^{-1}, \qquad (9)$$

where ε_4 refers to the molar extinction coefficient of $\mathrm{(TBA)_2CoBr_4}$. From Eqs. 8 and 9, we obtain the following equation:

$$\frac{[\mathrm{(TBA)_2CoBr_4}]}{[\mathrm{(TBA)CoBr_3(R\text{-}py)}]} = \frac{\bar{\varepsilon}-\varepsilon_3}{\varepsilon_4-\bar{\varepsilon}}. \qquad (10)$$

By using the equilibrium constant of Eq. 7, K_4, and Eq. 10, we obtain:

$$\log\frac{\bar{\varepsilon}-\varepsilon_3}{\varepsilon_4-\bar{\varepsilon}} = \log K_4 + \log\frac{[\mathrm{TBA\cdot Br}]}{[\mathrm{R\text{-}py}]}. \qquad (11)$$

The plot of the left-hand side of Eq. 11 as a function of log [TBA·Br]/[R-py] falls on a straight line with a slope of unity. This indicates the validity of the assumption of the equilibria (7).

In the cases of the 4Ac-py and 4CN-py complexes, the solution of the tribromocomplex, $\mathrm{(TBA)CoBr_3(R\text{-}py)}$, was prepared by saturating the 10^{-2} mol dm^{-3} TBA·Br solution with the $\mathrm{CoBr_2(R\text{-}py)_2}$ complex. The mole ratio of the TBA·Br and $\mathrm{CoBr_2(R\text{-}py)_2}$ of the saturated solution was determined as $C_{\mathrm{TBA\cdot Br}}/C_{\mathrm{Co}}=1$. Thus, the formation of only the tribromocomplex was ascertained. The spectra of the tribromocomplexes are shown in Fig. 1 (B).

Discussion

As can be seen from Fig. 5, there is no systematic correlation between the K_c and pK_b of R-py. Generally, the configurational change from tetrahedral to octahedral structures is enthalpy-driven, and the enthalpy is largely compensated by the entropy term.[3-5,26] Thus, the effect of the entropy change on the configurational equilibrium is so appreciable that the difference in the basicity of the pyridines may be overwhelmed by the change in the entropy. The K_c of the 3Me-py complex is considerably smaller than those of the py and 4Me-py complexes. This may indicate steric hindrance in the octahedral complex caused by the substitution at the 3-position of the pyridine.[16–19)]

As is revealed in Fig. 5, the plot of log K_3 and log K_4 *vs.* pK_b of R-py shows a linear correlation; *i.e.*, the Co–R-py bond strength decreases upon a decrease in the basicity of R-py. The fact that the constants, K_3 and K_4, of the 3Me-py complexes show normal values indicates that the steric effect of 3Me-py is not important in the tetrahedral complexes. La Mar[19)] has suggested the presence of steric hindrance of 3Me-py in the tetrahedral complexes, whereas Wayland and Drago[17)] have denied this argument on the basis of the rasults of the molecular model and the contact shift of proton NMR. Our results support the latter conclusion. The K_4 value of the 2Me-py complex is much larger than those of the complexes of the other pyridines having comparable pK_b value. Thus, the steric effect of 2Me-py is significant even in the tetrahedral configuration.

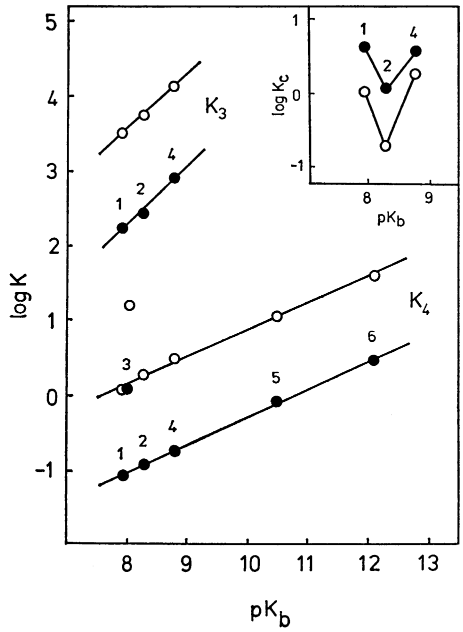

Fig. 5. Plot of log K_c, log K_3, and log K_4 as a function of pK_b of R-py.
R-py: 1, 4Me-py; 2, 3Me-py; 3, 2Me-py; 4, py; 5, 4Ac-py; 6, 4CN-py. Filled circle: bromocomplexes, open circle: chlorocomplexes (Ref. 9).

The ratio of the successive formation constants, K_3/K_4, is much larger than the statistical one, $(K_3/K_4)_{stat}=8/3$. As has been shown in the previous paper,[9)] this fact can be interpreted in terms of the steric hindrance increasing in the order of: $CoX_2(R\text{-}py)_2 < CoX_3(R\text{-}py)^- < CoX_4^{2-}$.

The formation constants, K_3 and K_4, of the bromocomplexes are smaller than those of the corresponding chlorocomplexes: this trend agrees with the results of other systems.[25)] The difference in log K_4 between the chloro- and bromocomplexes (Δ log $K_4=1.16$) is almost the same as that of log K_3 (Δ log $K_3=1.24$). This may indicate that the steric effect of the bromocomplex is of the same magnitude of that of the chlorocomplex. This is consistent with the fact that the magnitude of the steric effects of the octahedral 3Me-py chlorocomplex and the tetrahedral 2Me-py chlorocomplex is almost the same as those of the bromocomplexes respectively.

The effect of the basicity of substituted pyridine on the metal-pyridine bond strength has also been discussed. Wong and Brewer[22)] have suggested that, when the substituent on pyridine is more electron-attractive than hydrogen, the metal-nitrogen σ bond is weakened by the decrease in electron density on the nitrogen atom of pyridine, but that the π bond is strengthened by the back-donation of the π electron from metal to nitrogen. Thus, the decrease in metal-pyridine bond strength upon the decrease in σ bonding is partially compensated by the increase in π bonding. Steffen and Palenik[24)] have concluded that the linear correlation of the Zn–N bond length in $ZnCl_2(R\text{-}py)_2$ with the pK_b of R-py suggests a minimum contribution of π bonding. As can be seen from Fig. 5 a linear correlation of the Co–N bond strength with pK_b is observed even for the cobalt(II) complex. This can be interpreted in terms of the linear correlation between the π bond and the σ bond, or a minimum contribution of the π bond to the Co–N bond. Wayland and Drago[16)] have suggested that the contribution of the π bond is not so significant

TABLE 2. FREQUENCY OF THE GRAVITY CENTER AND OSCILLATOR STRENGTH OF THE ABSORPTION BAND OF THE TETRAHEDRAL HALOGENO COMPLEXES OF COBALT(II) IN 1,2-DIHALOETHANE, ACETIC ACID, AND ACETONE[a)]

		1,2-Dihaloethane		Acetic acid[d)]		Acetone[e)]
		Chloride[b)]	Bromide[c)]	Chloride	Bromide	Chloride
CoX_2S_2	$\nu_c/10^3$ cm^{-1}	16.39	15.92	15.93	15.53	15.92
	$f/10^{-3}$	(7.04)	(7.21)	(0.53)[f)]	(4.16)[f)]	(3.92)
CoX_3S^-	$\nu_c/10^3$ cm^{-1}	15.74	15.13	15.57	14.93	15.39
	$f/10^{-3}$	(6.05)	(6.91)	(4.15)	(4.99)	(4·50)
CoX_4^{2-}	$\nu_c/10^3$ cm^{-1}	15.03	14.38	15.19	14.42	15.11
	$f/10^{-3}$	(5.88)	(6.97)	(6.00)	(8.91)	(5.34)

a) Anionic species form ion-pairs with the tetrabutylammonium ion or the lithium ion. b) Ref. 9. S is pyridine. c) This work. S is pyridine. d) Ref. 25. S is acetic acid. e) Ref. 28. S is acetone. f) Mixture of tetrahedral and octahedral dihalocobalt(II) complexes.

for the ligand with no low-lying empty π orbital such as pyridine.

Much as with the chlorocomplexes, the dibromocomplexes and the tribromocomplexes have virtually the same visible spectra irrespective of the change in the pyridine bases, although those of the 2Me-py complexes are slightly shifted to a higher wavelength (Figs. 1 (A) and (B)). The frequency of the gravity center, ν_c, and the oscillator strength, f, of the absorption band are listed in Table 2, along with the data on chlorocomplexes in 1,2-dichloroethane,⁽⁹⁾ bromo- and chlorocomplexes in acetic acid,⁽²⁵⁾ and chlorocomplexes in acetone.⁽²⁸⁾

The plot of ν_c *vs.* the number of the halogenide ion coordinated to cobalt(II) gives rise to a good linear relationship. The ν_c of cobalt(II) coordinated by four pyridine molecules tetrahedrally, $Co(py)_4^{2+}$, is estimated as $\nu_c = 17.64 \times 10^3\ cm^{-1}$. This may indicate that the rule of average environment can be applied to both the ligand-field strength and the electron-repulsion parameter. The trend of change in f with the number of the halogenide ion in the complex depends on the neutral ligand. This may indicate that the structures of the dihalogeno- and trihalogenocomplexes are seriously affected by the structure of the solvent or neutral ligand. On the other hand, as can be seen from Fig. 1, the effect of the basicity of the neutral ligand on the spectra is very small.

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References

1) W. Libuś and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).

2) W. Libuś, K. Chachulska, and M. Mesik, *Inorg. Chem.*, **19**, 2259 (1980).

3) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, **1963**, 5449.

4) S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, **1965**, 3284.

5) J. de O. Cabral, H. C. A. King, S. M. Nelson, T. M. Shepherd, and E. Körös, *J. Chem. Soc.*, *A*, **1966**, 1348.

6) G. D. Howald and R. S. Marianelli, *Inorg. Chem.*, **9**, 1738 (1970).

7) R. D. Farina and J. H. Swinehart, *J. Am. Chem. Soc.*, **91**, 568 (1969).

8) R. D. Farina and J. H. Swinehart, *Inorg. Chem.*, **11**, 645 (1972).

9) K. Sawada and T. Suzuki, *J. Inorg. Nucl. Chem.*, **43**, 2301 (1981).

10) Y. Bando and S. Nagakura, *Inorg. Chem.*, **7**, 893 (1968).

11) D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, **4**, 139 (1965).

12) A. B. P. Lever and S. M. Nelson, *J. Chem. Soc.*, **1966**, 859.

13) C. Postmus, J. R. Ferraro, A. Quattrochi, K. Shobatake, and K. Nakamoto, *Inorg. Chem.*, **8**, 1851 (1969).

14) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

15) N. H. Agnew, R. J. Collin, and L. F. Larkworthy, *J. Chem. Soc.*, *Dalton Trans.*, **1974**, 272.

16) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 4697 (1966).

17) R. S. Drago and B. B. Wayland, *Inorg. Chem.*, **7**, 528 (1968).

18) D. P. Graddon and E. C. Watton, *Aust. J. Chem.*, **18**, 507 (1965).

19) G. N. La Mar, *Inorg. Chem.*, **6**, 1939 (1961).

20) P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, **46**, 131 (1968).

21) L-T. Ang and D. P. Graddon, *J. Inorg. Nucl. Chem.*, **38**, 2279 (1976).

22) P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, **47**, 4589 (1969).

23) P. T. T. Wong, *Inorg. Chem.*, **14**, 2271 (1975).

24) W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, **16**, 1119 (1977).

25) K. Sawada and M. Tanaka, *J. Inorg. Nucl. Chem.*, **39**, 339 (1977).

26) K. Sawada, T. Nakamura, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **42**, 1471 (1980).

27) U. Carunchio, U. B. Ceipidor, and A. Messina, *Inorg. Chim. Acta*, **6**, 613 (1972).

28) K. Sawada, T. Onoda, and T. Suzuki, *J. Inorg. Nucl. Chem.*, in press.