52. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part VI.* The Cobalt*(II)*–Phenanthroline System.*

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The rate constants for dissociation of [Co $phen_3$]$^{2+}$ and [Co phen]$^{2+}$ have been determined from exchange experiments involving [^{14}C]phenanthroline and $^{60}Co^{2+}$. The values obtained are, respectively, $1{\cdot}4 \times 10^{16}$ exp $(-20{,}600/\boldsymbol{R}T)$ and $1{\cdot}6 \times 10^{14}$ exp $(-19{,}400/\boldsymbol{R}T)$ min.$^{-1}$. The kinetic parameters are compared with those of analogous systems and, in particular, the energies of activation are explained in terms of the crystal field theory of co-ordinate bonding.

THE rates of dissociation of complexes of cobalt(II), unlike those of cobalt(III), are rapid at ordinary temperatures.[1] This is strikingly shown by the behaviour towards exchange of such complexes with " labelled " metal or ligand species.[2] Apart from certain quadridentate complexes of cobalt(II) in pyridine,[3] all exchange reactions of cobalt(II) complexes which have so far been examined are fast.

* Part V, *J.*, 1957, 4521.

[1] Taube, *Chem. Rev.*, 1952, **50**, 69.

[2] Stranks and Wilkins, *ibid.*, 1957, **57**, 743.

[3] West, *J.*, 1954, 395.

The lability of cobalt(II)–phenanthroline complexes has been demonstrated in at least three different ways: (*a*) the ready development of a red colour (due to ferroin) when mono-, bis-, or tris-phenanthrolinecobalt(II) ions are added to ferrous ions in aqueous solution,[4] (*b*) the rapid exchange of $[\mathrm{Co\ phen_3}]^{2+}$ with $^{60}\mathrm{Co}^{2+}$ at 15° in aqueous solution [5] (two points we shall return to later), and (*c*) the ability of $[\mathrm{Co\ phen_3}]^{2+}$ to catalyse the exchange of $[\mathrm{Co\ phen_3}]^{3+}$ with [^{14}C]phenanthroline.[6] The processes involved in (*a*) and (*b*), although fast, can, however, be measured and in the present study the kinetics of dissociation of $[\mathrm{Co\ phen_3}]^{2+}$ and $[\mathrm{Co\ phen}]^{2+}$ * have been determined from measurement of exchange rates at 0—15°.

EXPERIMENTAL

Materials.—[^{14}C]Phenanthroline hydrate was prepared as described previously.[7] Radiochemically pure cobalt(II) nitrate solution was prepared from neutron-irradiated metallic cobalt. In the kinetic studies, " AnalaR " chemicals were used. The following complex compounds were prepared:

$[\mathrm{Co\ phen_2Cl_2}],\mathrm{H_2O}$.—Phenanthroline hydrate (0·36 g.), 0·2M-cobalt nitrate (3 c.c.), and 2M-hydrochloric acid (4 c.c.) were mixed and left in ice overnight; pink crystals separated. These were washed with a small amount of ice-cold water and dried over silica gel (Found: C, 56·3; H, 3·5; N, 11·2; Co, 11·8. $\mathrm{C_{24}H_{16}N_4Cl_2Co,H_2O}$ requires C, 56·6; H, 3·6; N, 11·0; Co, 11·6%). The *complex* labelled with ^{60}Co was prepared with one-tenth of the above quantities.

$[\mathrm{Co\ phenCl_2}]$ was prepared as described by Pfeiffer and Werdelmann [4] (Found: C, 46·7; H, 3·0; N, 9·1. Calc. for $\mathrm{C_{12}H_8N_2Cl_2Co}$: C, 46·5; H, 2·6; N, 9·0%).

$[\mathrm{Co\ phen(H_2O)_4}][\mathrm{C_{10}H_6(SO_3)_2}],\mathrm{H_2O}$ was precipitated when a saturated solution of disodium naphthalene-1 : 5-disulphonate was added to a solution containing the $[\mathrm{Co\ phen}]^{2+}$ ion (Found: Co, 9·5. $\mathrm{C_{22}H_{14}O_6N_2S_2Co,5H_2O}$ requires Co, 9·6%). The pinkish *hydrate* on drying ($\mathrm{P_2O_5}$) at 80° *in vacuo*, was dehydrated to a purple *salt* which rapidly regained the pink colour in air (Found: Co, 11·35. $\mathrm{C_{22}H_{14}O_6N_2S_2Co}$ requires Co, 11·2%).

Cobalt analysis of phenanthroline-containing complexes was conveniently carried out by adding an excess of EDTA in buffer to the complex in solution, extraction with benzene of the phenanthroline liberated, and estimation of the excess of EDTA by back-titration with standard zinc solution.[8]

Exchange Runs.—(a) $[\mathrm{Co\ phen_3}]^{2+}$–phen *exchanges.* A mixture was usually prepared from 0·8 mmolar cobalt(II) nitrate and 5·2 mmolar phenanthroline, forming the tris-complex and free phenanthroline *in situ*. Boiled-out conductivity water was used and nitrogen passed through the solution during the whole of the experiment. Later work indicated that omission of these precautions did not markedly alter the exchange rate, although the pale yellow solution became brown within several hours in the presence of oxygen. Because of the rapidity of the exchange, each point on the exchange curve was obtained from a separate experiment and each exchange run consisted of at least six points. Exchange was initiated by adding a stock solution of [^{14}C]phenanthroline (2·0 c.c.) to the inactive mixture described above (12·5 c.c.) which had settled to the desired temperature, and was terminated by the rapid addition of concentrated sodium perchlorate solution, which precipitated $[\mathrm{Co\ phen_3}](\mathrm{ClO_4})_2$ together with some phenanthroline perchlorate. The latter was removed by washing the mixture with absolute alcohol, and the residual complex was washed with ether and dried. This procedure reproducibly gave 10—15% zero-time exchange. In one run (No. 2), separation was effected by extracting the free phenanthroline by vigorous shaking with ice-cold chloroform and assaying it as $[\mathrm{Fe\ phen_3}](\mathrm{ClO_4})_2$ and the unextracted $[\mathrm{Co\ phen_3}]^{2+}$ as the insoluble perchlorate in a similar manner to that in the $[\mathrm{Ni\ phen_3}]^{2+}$–phen exchanges.[9] The two procedures gave similar values for k_{exch}, based on the expected relationship $R = k_{\mathrm{exch}}[\mathrm{Co\ phen_3}^{2+}]$. The results of the short

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* Probable co-ordinated water molecules are not considered in this and subsequent formulæ.

[4] Pfeiffer and Werdelmann, *Z. anorg. Chem.*, 1950, **261**, 197.

[5] West, *J.*, 1954, 578.

[6] Ellis, Wilkins, and Williams, *J.*, 1957, 4456.

[7] *Idem*, *J.*, 1956, 3975.

[8] Schwarzenbach, " Complexometric Titrations," transl. by Irving, Methuen, London, 1957.

[9] Wilkins and Williams, *J.*, 1957, 1763.

kinetic study are shown in Table 1. Separate experiments obviated possible photochemical catalysis. The estimated energy of activation was 20·6 ± 0·5 kcal. mole^{-1}.

TABLE 1. *Exchange of* [Co phen$_3$]$^{2+}$ *with phenanthroline.*

Run no.	Temp.	[Complex] (mmole l.$^{-1}$)	[phen] (mmole l.$^{-1}$)	$t_{\frac{1}{2}(\text{exch})}$ (sec.)	10^6R (sec.$^{-1}$ mole l.$^{-1}$)	10^3k (sec.$^{-1}$)
1	0·0°	1·63	2·81	93	13·3	8·2
2	0·0	0·80	2·76	140	6·4	8·0
3	6·6	0·80	2·80	55	16·2	20·2
4	11·4	0·80	2·80	31	28·8	35·8

(b) [Co phen$_3$]$^{2+}$–[Co phen$_2$]$^{2+}$ *exchange.* A solution for exchange was prepared by adding solid phenanthroline hydrate (516 mg.) to 0·198M-cobalt nitrate (5·0 c.c.), warming the whole to effect dissolution, and allowing the mixture to equilibrate at 0°. Such a solution contains approximately equal amounts of the tris- and the bis-species. [^{60}Co phen$_2$Cl$_2$],H$_2$O (6 mg.), well-powdered to facilitate dissolution, was added with vigorous shaking to initiate reaction. The exchange was stopped at various times by adding the solution to concentrated ammonium oxalate solution which immediately precipitated the bis-species as the ochre-yellow complex oxalate. This was rapidly centrifuged off and the clear supernatant liquid added to sodium perchlorate solution to precipitate the pale yellow perchlorate of the tris-complex. Both materials were washed with water, alcohol, and ether and radio-assayed. Thus the rates of fall in activity of the bis- and the increase in the tris-complex could be followed as the exchange [Co phen$_3$]$^{2+}$ + [^{60}Co phen$_2$]$^{2+}$ $\rightleftharpoons$ [Co phen$_2$]$^{2+}$ + [^{60}Co phen$_3$]$^{2+}$ proceeded. From the observations of a very small zero-time exchange for the tris-complex, the fall in activity of the bis-complex from the commencement to the completion of exchange (570 to 306 counts/min.) and the amounts of precipitates obtained from both exchange reactants, it was concluded that in these conditions about 54% of the phenanthroline-containing complex was in the bis-form and that separation was effective. The $t_{\frac{1}{2}}$ exchange values were 35 sec. (bis-end) and 42 sec. (tris-end), the latter being used as the more reliable result, so that

$$R_3 = k_3[\text{tris}] = \frac{0{\cdot}693}{t_{\frac{1}{2}}} \cdot \frac{[\text{bis}][\text{tris}]}{[\text{bis}] + [\text{tris}]}$$

and since [bis]([bis] + [tris]) = 306/570 (from the counts above), $k_3 = 8{\cdot}9 \times 10^{-3}$ sec.$^{-3}$ at 0·0°. A similar result was obtained in a second experiment.

(c) [Co phen]$^{2+}$–Co^{2+} *exchanges.* The mono-complex ion could be separated as an insoluble precipitate from cobalt(II) by adding either thiocyanate or disodium naphthalene-1 : 5-disulphonate. The latter was preferred because the precipitate of the complex salt was finer and could be easily " matted " on the aluminium planchettes. In all the runs, an excess (usually 5—10 times) of cobalt nitrate was added as a standard solution to phenanthroline hydrate and after warming to effect dissolution the exchange solution was equilibrated at the reaction temperature. Precautions to exclude oxygen were taken. ^{60}Cobalt nitrate solution was added and samples were removed at various times and plunged into an ice-cold solution of the precipitating agent. A pink precipitate of the complex was formed immediately and its appearance represented the exchange time. It was washed thrice with water, then alcohol and ether before being dried at 90° to the pentahydrate. It was radio-assayed in this form as a 14·0 ± 0·1 mg. mat on small planchettes. The efficiency of the separation was indicated by very small zero-time exchanges. Usually five separation points were taken to construct the normal exchange curve, which, in general, was an excellent first-order straight line. The results are shown in Table 2. Runs nos. 1—4 indicate that $R = k_1$[Co phen^{2+}] and is pH-independent between 4·6 and 5·8, both results expected in view of the more extensive investigation of the nickel analogue.[10] Since the cobalt complexes would be expected to have a lower stability than those of nickel, one run was performed with nearly 100-fold ratio of [Co^{2+}] to phenanthroline (no. 5) which ensures the formation of only the mono-species,[11] and although the rate was *decreased* this was shown to be almost completely as a result of the greatly increased ionic

[10] Wilkins and Williams, *J.*, 1957, 4514.

[11] Sone, Krumholz, and Stammreich, *J. Amer. Chem. Soc.*, 1955, **77**, 777.

strength (run no. 6). Finally runs 7—9 at different temperatures (with runs **1**, **3**, and **4**) provided the data for a determination of the energy of activation as 19·4 ± 0·5 kcal. mole^{-1}.

(d) [Cu phen$_3$]$^{2+}$–phen *exchange*. There appears to be ample evidence both from spectral [12] and from potentiometric [13] data that in the presence of excess of phenanthroline, copper(II) ion forms the species [Cu phen$_3$]$^{2+}$. Copper chloride (0·08 mmole) and phenanthroline hydrate (0·5 mmole) were mixed in water (10 c.c.) and allowed to settle at 0°. An aqueous solution of [^{14}C]phenanthroline (3·6 mg. in 2 c.c.) at 0° was added. Addition of sodium perchlorate within 10 sec. precipitated [Cu phen$_3$](ClO$_4$)$_2$ [4] which showed equilibrium activity. This was checked in another run when the excess of ligand was extracted with chloroform and treated as in (a).

TABLE 2. *Exchange of* [Co phen]$^{2+}$ *with* Co^{2+}.

Run no.	pH	Temp.	[Co phen^{2+}] (mmole l.$^{-1}$)	[Co^{2+}] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (sec.)	10^5R (sec.$^{-1}$ mole l.$^{-1}$)	10^3k (sec.$^{-1}$)
1	5·8	0·0°	15·2	135·6	540	1·75	1·15
2 [a]	4·6	0·0	15·3	143·2	570	1·68	1·09
3	5·3	0·0	15·3	253·6	590	1·69	1·11
4	5·5	0·0	30·6	238·8	500	3·76	1·23
5	5·5	0·0	15·2	1341·0	790	1·32	0·87
6 [b]	5·5	0·0	15·3	143·2	680	1·40	0·92
7	5·6	10·8	15·3	143·2	145	6·61	4·32
8	5·6	10·8	15·3	143·2	130	7·37	4·82
9	5·6	15·2	15·3	143·2	86	11·14	7·29

[a] Adjusted with HCl. [b] NaNO$_3$ added to adjust ionic strength to that of 5.

In exchanges (a) and (c), temperatures below that of the room were obtained by using an ordinary thermostat in a refrigerated room.

In all experiments (a)—(d) an end-window counter with ancillary electronic equipment was used for radioassay.

Acid Dissociation.—When the yellow [Co phen$_3$]$^{2+}$ ion is treated with acid, the colour diminishes rapidly as the ion dissociates to lower complexes. There are no distinct bands in the visible spectra of the tris-, bis-, or mono-species but the interpretation of the dissociation experiments is greatly assisted by the fact that between about 3700 and 4000 Å the molar extinction coefficient of the tris- is about three times that of the bis-complex, and almost ten times that of the mono-complex. At these wave-lengths, the absorption of phenH$^+$ and Co^{2+}, the other products of the dissociation, is negligible. In addition, the bis- and the mono-species dissociate more rapidly than the tris-species. Because of these facts, the time variation of the optical density of the complex solution is a direct measure of $-d[\text{tris}]/dt$, Beer's law having been shown to be obeyed for the tris-complex. An allowance is made for a small residual absorption at the end of the experiment by plotting $\log(d_t - d_\infty)/(d_0 - d_\infty)$ against time, where d_0, d_t, and d_∞ represent the optical density at the time of the first observation, at time t and at the conclusion of the experiment; straight lines were obtained over several half-lives and from these k_3 was calculated. The concentrations of [Co phen$_3$]$^{2+}$ used varied from 2 to 5 × 10^{-3}M, the acid used was 0·25—0·5M-hydrochloric acid, and the wave-lengths of observation were 3750 and 4000 Å (ε_M for the tris-species at these wave-lengths is 470 and 200 respectively). Despite the rapidity of the dissociation, after some practice surprisingly consistent results were obtained. Runs were carried out by using a Unicam S.P. 600 spectrophotometer at room temperature and at approx. 2°, in the latter case two of the four compartments of the cell holder being filled with ice and water. Temperatures were recorded for about 15 min. before, at the beginning of, and at the end of, the experiments which continued only for about 1 min. (room temperature) or 5 min. (2°). The spectra at the end indicated a large amount of mono-complex in the equilibrium mixture with these conditions. For three separate experiments at 16·5° ± 0·3°, $t_{\frac{1}{2}}$(diss) was determined as 11, 14, and 12 sec. from the 3750 Å observation, and 12 sec. from that at 4000 Å. From these a mean value for $k_3 = 5{\cdot}9 \times 10^{-2}$ sec.$^{-1}$ was calculated, compared with an exchange rate constant of 6·7 × 10^{-2} sec.$^{-1}$ estimated for that temperature. At 2·0° ± 0·5°, $t_{\frac{1}{2}}$(diss) = 78 sec., and $k_3 = 8{\cdot}9 \times 10^{-3}$ sec.$^{-1}$ ($k_{\text{exch}} = 10{\cdot}2 \times 10^{-3}$ sec.$^{-1}$). From these results an estimated energy of activation of 19·5 ± 1·0 kcal./mole was obtained. By adding fresh solutions of the complex [Co phen$_2$Cl$_2$],H$_2$O or solid [Co phenCl$_2$] to 0·5M-hydrochloric acid,

[12] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.
[13] Pflaum and Brandt, *J. Amer. Chem. Soc.*, 1954, **76**, 6215.

$t_{\frac{1}{2}}$(diss) was observed to be <4 sec. and <2 sec. for the bis- and the mono-species respectively at 20°.

DISCUSSION

The equilibria involved in this study can be represented as follows:

$$[\mathrm{Co\ phen_3}]^{2+} \overset{R_3}{\rightleftharpoons} [\mathrm{Co\ phen_2}]^{2+} + \mathrm{phen} \quad . \ . \ . \ . \ . \ . \ . \ . \quad k_3, k_{-3}$$

$$[\mathrm{Co\ phen_2}]^{2+} \overset{R_2}{\rightleftharpoons} [\mathrm{Co\ phen}]^{2+} + \mathrm{phen} \quad . \ . \ . \ . \ . \ . \ . \ . \quad k_2, k_{-2}$$

$$[\mathrm{Co\ phen}]^{2+} \overset{R_1}{\rightleftharpoons} \mathrm{Co}^{2+} + \mathrm{phen} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad k_1, k_{-1}$$

The exchange rate constant (k_{exch}) for the [Co phen$_3$]$^{2+}$–phen system can be directly equated to k_3, the dissociation rate constant for the tris-species. This follows since R_2 and R_1 will have relatively low values (bearing in mind the values of k_2 and k_1 from the acid dissociation work) with the conditions of ligand exchange.[10, 14] In addition, the value for k_{exch} is similar to that of the [Co phen$_3$]$^{2+}$–[Co phen$_2$]$^{2+}$ exchange rate constant. From this study, $k_3 = 1{\cdot}4 \times 10^{16} \exp(-20{,}600/\boldsymbol{R}T)$ min.$^{-1}$. The similar value for k_3 in 0·5M-hydrochloric acid indicates that, as with the Fe(II) and Ni(II) analogues, dissociation is pH-independent in this range. The exchange results are not in conflict with those of West[5] who reported that the [Co phen$_3$]$^{2+}$–Co^{2+} exchange half-time was <28 sec. at 15°: his results are complicated however by the formation of chemical species, the mono- and bis-complexes, during the exchange process.

The rate of exchange of ^{60}Co between [Co phen]$^{2+}$ and Co^{2+} gives directly $k_1 = 1{\cdot}6 \times 10^{14} \exp(-19{,}400/\boldsymbol{R}T)$ min.$^{-1}$. It is apparent that, as for [Ni phen]$^{2+}$, the rate of dissociation is markedly pH-dependent.[10, 15] Pfeiffer and Werdelmann[4] reported that [Co phenCl$_2$] develops a red colour with ferrous sulphate only after several minutes at room temperature (we have observed that half-formation of the final red colour requires at least 5 min. at 17°). Such a result appears at variance with our exchange data [$t_{\frac{1}{2}}$(exch) ~ 1 min. at 17°] until it is considered that there will be competition for released phenanthroline (see equilibrium R_1) between cobalt(II) and iron(II) and that the rate of formation of [Fe phen$_3$]$^{2+}$ will depend on the relative values of k_{-1} and the rate constant for the slowest step in the formation of ferroin.

TABLE 3. *Kinetic data and C.F.S.E. changes for the dissociation of* [M(phen)$_3$]$^{2+}$ *and* [M(phen)]$^{2+}$ *complexes.*

Electronic system	Complex ion	$\Delta S^{\ddagger}$ (e.u.)	E_{act} (kcal. mole^{-1})	ΔE (Dq)[16b]
d^3	V phen$_3$$^{2+}$	—	—	2
d^5	Mn phen$_3$$^{2+}$	—	—	0
d^6	Fe phen$_3$$^{2+}$ [a]	+28	32·1	4
d^7	Co phen$_3$$^{2+}$	+5	20·6	0
	Co phen^{2+}	−4	19·4	—
d^8	Ni phen$_3$$^{2+}$ [b]	+1	25·2	2
	Ni phen^{2+} [c]	+5	26·2	—
d^9	Cu phen$_3$$^{2+}$		Fast	0
d^{10}	Zn phen$_3$$^{2+}$	—	—	0

[a] Basolo, Hayes, and Newmann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807. [b] See ref. 9. [c] See ref. 10.

We shall now consider the entropies and energies of activation compared with analogous systems (see Table 3). The values for $\Delta S^{\ddagger}$ differ markedly from the high positive value for the [Fe phen$_3$]$^{2+}$ dissociation. The latter has been explained[16a] in terms of greater ligand freedom in an expanded state intermediate between diamagnetic [Fe phen$_3$]$^{2+}$ and the paramagnetic [Fe phen$_2$]$^{2+}$ dissociated fragment. Such a spin change does not occur

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[14] Wilkins and Williams, *J. Inorg. Nuclear Chem.*, 1958, **6**, 52.

[15] Margerum, Bystroff, and Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211.

[16] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, (*a*) p. 269, (*b*) p. 96 *et seq.*

for the nickel(II) and cobalt(II) complexes and these have similar, more normal, values for $\Delta S^{\ddagger}$.

Basolo and Pearson have discussed,[16b] with particular reference to cobalt(III), the energies of activation which might be expected for different mechanisms (and transition states) for substitution. They proceed then to relate the rates of reactions of complex ions with the crystal field stabilisation energy (C.F.S.E.) for various *d*-electron systems and stereochemical configurations. We apply the reasoning developed by them to an understanding of the energies of activation of dissociation of Fe(II)–, Co(II)–, Ni(II)–, and Cu(II)–phenanthroline complexes. We assume that the dissociation of the complex involves a rate-determining " one-ended " detachment of one ligand and that for this process the transition state approximates to a combined square pyramid of nitrogen around the central metal plus two additional groups at a further distance, namely, one nitrogen of the leaving phenanthroline and one incoming water molecule. There will undoubtedly be some energy interaction with the entering water molecule and it would be impossible for us to calculate absolute energies of activation for such a scheme. However, it seems reasonable to suppose that, if this interaction with water and the other factors which influence the activation energy remains approximately constant for all these complexes which are extremely similar to one another in shape, etc., then the variations observed in the energy of activation from one complex to another will arise mainly from different changes in C.F.S.E. accompanying the octahedral to square-pyramid change (ΔE in Table 3), the latter approximating to the transition state for this purpose. A loss of C.F.S.E. would be expected to result in a slower reaction (higher energy of activation) than that of similar complex ion for which there was no loss of C.F.S.E. during the octahedral-square pyramid change. The C.F.S.E. change is indicated in Table **3** for the various ions, in terms of the Dq energy unit which from spectral data is about 3 kcal. mole^{-1} for bivalent transitional cations [17] and for [Ni phen$_3$]$^{2+}$ is 3·5 kcal. mole^{-1}.[12] A strong crystal field is assumed for the iron(II) case and a weak one for the manganese(II) and cobalt(II) complexes. It is considered that there is a retention of spin during the activation. An examination of Table **3** shows that the *differences* in activation energies for iron(II)–, cobalt(II)–, and nickel(II)–phenanthroline complexes do indeed fit very well with the ΔE values, and that it does appear that the other factors which influence the activation energy are similar for these complexes. A trigonal bipyramid or a pentagonal bipyramid as intermediate does not give the required relationship.[16b] Provided that the $\Delta S^{\ddagger}$ term is positive or only slightly negative, the exchanges of [Mn phen$_3$]$^{2+}$, [Cu phen$_3$]$^{2+}$, and [Zn phen$_3$]$^{2+}$ with [^{14}C]phenanthroline would be expected to be of the same order as with cobalt(II). Indeed, for the copper(II) case, $k \geqslant 0{\cdot}25$ sec.$^{-1}$ at 0° and this can be easily understood with an energy of activation only slightly less than 19 kcal. mole^{-1}. On the other hand, the positive value of ΔE for [V phen$_3$]$^{2+}$ indicates that, with this ion, slower rates might be expected, although its easy oxidation [18] might present experimental difficulties in any kinetic study.

Since optical forms of [Co phen$_3$]$^{2+}$ would be expected to racemise by a dissociative mechanism,[16a] much like [Ni phen$_3$]$^{2+}$, it may prove possible to resolve this ion despite its lability. The problem might be eased by using a ligand such as 4 : 7-dimethylphenanthroline since it is known that methyl ring-substitution in phenanthroline decreases the rate of dissociation of its metal complexes.[19]

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[17] For a review of ligand-field theory see Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 381.
[18] Brandt, Dwyer, and Gyarfas, *Chem. Rev.*, 1954, **54**, 959.
[19] Ellis and Wilkins, unpublished observations.