898. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part III.* Exchange and Electron-transfer Reactions involving Phenanthroline and Dipyridyl Complexes of Cobalt*(III).

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The tris-(1 : 10-phenanthroline)- and tris-(2 : 2'-dipyridyl)-cobalt(III) ions are inert to exchange with the corresponding free ligands in acid solution. They undergo exchange in neutral solution however owing, almost certainly, to catalysis by cobalt(II) impurity, present in small amounts in different samples of the cobalt(III) complexes. The addition of a small amount of cerium(IV) to the $[Co \ dipy_3]^{3+}$ ion suppresses exchange in neutral solution. By studying the effect of added cobalt(II) on the exchange rate the amounts of impurity in each complex can be assessed. The values obtained agree well with those from magnetic measurements. It is also possible to assign approximate (assumed) second-order rate constants to the two fast electron-transfer processes, involving cobalt(II) and cobalt(III) complexes with these ligands, and the results are briefly discussed. The importance of·traces of impurities in exchange studies, already emphasised by previous investigators, is reiterated.

It has been reported that, although tris-(1 : 10-phenanthroline)cobalt(III) chloride, $[Co \ phen_3]Cl_3$, gives a red colour with ferrous sulphate solution only on long boiling, one phenanthroline molecule can be easily removed by refluxing a suspension of the chloride in chloroform to form $[Co \ phen_2Cl_2]Cl$.[1] It is surprising that change of solvent should have such a drastic effect on the ease of dissociation of the complex and some doubt exists as to the " lability " of the complex, so that a statement such as " one molecule of the base is easily disengaged and replaced by aquo-groups," reasonable in view of the known facts about the compound, appears in the literature.[2]

The rates of substitution of cobalt(III) complexes are usually slow,[3] as, for example, in the slow exchanges that have been observed with such complexes.[4] About the only exception to this generalisation is the rapid $H_2^{18}O$ exchange with the $Co_{aq.}^{3+}$ ion. Since with the conditions of this experiment the $Co_{aq.}^{3+}$ ion contained substantial amounts of the $Co_{aq.}^{2+}$ ion, the known rapid Co(II)–Co(III) electron transfer plus the lability of the $Co_{aq.}^{2+}$ species forms an effective path for the apparent rapid exchange [5] of $Co_{aq.}^{3+}$. In continuation of our exchange studies [6] with [^{14}C]phenanthroline and [^{14}C]dipyridyl we have investigated the behaviour of the phenanthroline- and the dipyridyl-cobalt(III) complex in an attempt to resolve the problem of the lability of these ions.

* Part II, *J.*, 1957, 1763.

[1] Pfeiffer and Werdelmann, *Z. anorg. Chem.*, 1950, **263**, 31.
[2] Brandt, Dwyer, and Gyarfas, *Chem. Rev.*, 1954, **54**, 959.
[3] Taube, *Chem. Rev.*, 1952, **50**, 69.
[4] Stranks and Wilkins, *Chem. Rev.*, in the press.
[5] Hunt and Taube, *J. Chem. Phys.*, 1951, **19**, 602.
[6] Wilkins and Williams, *J.*, 1957, 1763.

<div align="center">EXPERIMENTAL</div>

Materials.—[^{14}C]Phenanthroline hydrate and [^{14}C]dipyridyl were prepared as described previously.[7] Various samples of the cobalt(III) complexes, [CoA$_3$](ClO$_4$)$_3$,xH$_2$O, were prepared as described below. " A " signifies either dipyridyl ($x = 3$; prefaced D) or phenanthroline ($x = 2$; prefaced P). Each sample was recrystallised at least twice from hot water.

Samples D1, D2, D4, and P4 were prepared by oxidation of the cobaltous complex with hydrogen peroxide.[8] The visible spectra of a 3·9 mmolar solution of D1 had $\varepsilon_{max.}$ 75·1 at 4460 Å (Yamasaki[9] reports a maximum at 4500 Å).

Several samples were prepared by refluxing the *purpureo*-chloride, [Co(NH$_3$)$_5$Cl]Cl$_2$ (0·4 g.), with dipyridyl or phenanthroline (0·6 g.) in 30% methanol (30 c.c.) until ammonia was no longer evolved.[1] Sample P1 separated (as the chloride) on concentration of the final solution;[1] samples D3 and P2 were precipitated by addition of sodium perchlorate to the refluxed solution.

Specimen P3 was prepared and isolated like P2 except that aquopenta-amminocobalt(III) nitrate was the starting material. The reaction was much slower than with the *purpureo*-chloride and was left for 40 hr. for completion. Sample D5 was obtained by recrystal-lising D4 from solutions containing cerium(IV). P5 was one of the products from the reaction between [Co en$_2$(Cl)(H$_2$O)]SO$_4$ and phenanthroline.[10] [Co phen$_3$]$^{3+}$ ion remains in the mother-liquor after removal of [Co en$_2$ phen]Cl(SO$_4$) and may be precipitated from it as the perchlorate.

These samples were analytically pure. Representative analyses follow: D1 (Found: C, 40·3; H, 3·4; N, 9·6. Calc. for C$_{30}$H$_{24}$O$_{12}$N$_6$Cl$_3$Co,3H$_2$O: C, 41·1; H, 3·5; N, 9·5%); P2 (Found: C, 45·3; H, 3·2; N, 8·9. Calc. for C$_{36}$H$_{24}$O$_{12}$N$_6$Cl$_3$Co,2H$_2$O: C, 45·3; H, 3·15; N, 8·9%).

Tris-(o-phenanthroline)cobalt(II) perchlorate monohydrate was prepared for magnetic measurements[11] (Found: C, 53·0; H, 3·3; N, 10·3. Calc. for C$_{36}$H$_{24}$O$_8$N$_6$Cl$_2$Co,H$_2$O: C, 52·9; H, 3·2; N, 10·3%).

Exchange Experiments.—Most of the runs described were performed at about neutral pH. The complex perchlorate was mixed with inactive base (phenanthroline or dipyridyl) and equilibrated at the required temperature. A small amount of radioactive base dissolved in water was added (zero time) and separation effected, at various times, by extracting the base with benzene, and, after concentration, precipitating the complex as perchlorate. The complex was counted as the perchlorate by methods already described.[12] In the experiments in acid solution a different method was required since perchlorate does not precipitate the complex or the base; as the latter is present as protonated species it is not extracted appreciably from aqueous solution. The exchange mixture after being cooled to 0° was treated with chloro-palladite in 2N-hydrochloric acid (after adding inactive base as carrier if necessary to give sufficient material for radioassay). The brown precipitate was left for a few minutes, centrifuged, and washed with water. It was then heated in boiling water, whereupon the cream-coloured [Pd phenCl$_2$][13] was obtained and was washed with ethanol, then ether, and dried at 105° (Found: C, 40·0; H, 2·2; N, 8·0. Calc. for C$_{12}$H$_8$N$_2$Cl$_2$Pd: C, 40·5; H, 2·2; N, 7·85%). The specific activity of the base before being mixed with cobalt(III) complex, directly after being mixed, and after being refluxed for some hours was measured (in the form of the palladium complex) and the similar values for each condition indicated that (*a*) no phenanthroline was removed from the complex by acid, and (*b*) no exchange occurred under these conditions.

Cobalt(II) *Catalysed Experiments.**—By observing the variation of the rate of exchange, which always followed a first-order law, with the concentration of added cobalt(II) salt, the concentration of cobalt(III) complex and of added base being kept constant, it was possible to estimate the amount of cobalt(II) impurity (x) in the original cobalt(III) sample, and the approximate second-order rate constant (k_2) for the electron-transfer process. The assumption was made that the electron-transfer process was of second order (reasonable in

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* In this section brackets are not used to enclose the formula of a complex ion; they are here used for the customary designation of molar concentration.

[7] Ellis, Wilkins, and Williams, *J.*, 1956, 3975.
[8] Nyholm and Burstall, *J.*, 1952, 3570.
[9] Yumasaki, *Bull. Chem. Soc. (Japan)*, 1937, **12**, 390.
[10] Jaeger, *Z. anorg. Chem.*, 1928, **170**, 384.
[11] Pfeiffer and Werdelmann, *ibid.*, 1950, **261**, 197.
[12] Popplewell and Wilkins, *J.*, 1955, 4098.
[13] Ryan, *Canad. J. Res.*, 1949, **27B**, 938.

view of the number of known electron transfers which obey this rate dependence [14] and also that the direct exchange of CoA_3^{3+} was extremely slow (k_1 very small) in neutral solution. With the cobalt(III) complex alone

$$R = \frac{0.693}{t_{\frac{1}{2}}} \cdot \frac{3[CoA_3^{3+}][A]}{3[CoA_3^{3+}] + [A]} = k_1[CoA_3^{3+}] + k_2[CoA_3^{3+}]x$$

$$\simeq k_2[CoA_3^{3+}]x$$

and with added y-molar Co^{2+} ion

$$R' = \frac{0.693}{t_{\frac{1}{2}}} \cdot \frac{3[CoA_3^{3+}][A]}{3[CoA_3^{3+}] + [A]} \simeq k_2[CoA_3^{3+}](x + y)$$

so that $k_2 \{= (R' - R)/[CoA_3^{3+}]y\}$ and x were easily obtained.

In these experiments it was considered that there was a sufficient concentration of ligand A to form a complex CoA_3^{2+} with all the cobalt(II) ion present so that it was not necessary to consider electron-transfer processes involving CoA_2^{2+}, etc. A solution of the cobalt(III) complex was prepared and similar amounts were used in all the catalysed experiments in order to duplicate as far as possible the amounts of impurity in each run. A small zero-time exchange occurred in the experiments catalysed by cobalt(II); this arose since the small amount of cobalt(II) complex, which attains an appreciable activity rapidly, follows the cobalt(III) complex in the separation procedure. The results of the exchange work are given in Table 1. The run numbers are given for designation purposes only. Work not recorded in the Table ruled out the possibility of photocatalysed exchange.

TABLE 1. *Exchange of* [Co phen$_3$]$^{3+}$ *with phenanthroline and* [Co dipy$_3$]$^{3+}$ *with dipyridyl under various conditions.*

Run No.	Sample	Species present	Temp.	[Complex] (mmole l.$^{-1}$)	[Base] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (exch.) (min.)	$10^5 R$ (min.$^{-1}$ mole l.$^{-1}$)
1	D1	—	45.2°	4.0	21.6	210	2.6
2	D1	—	45.2	3.9	12.4	150	2.8
3	D2	—	45.0	3.9	12.5	150	2.8
4	D3	—	45.0	3.9	12.4	206	2.0
5	D4	—	45.0	3.9	12.3	174	2.40
6	D4	15μM-Co(II)	45.0	3.9	12.3	47	8.84
7	D4	31μM-Co(II)	45.0	3.9	12.2	26	15.9
8	D4	2.1mM-S$_2$O$_8^{2-}$	45.0	4.2	10.3	complete exch. in 24 hr.	
9	D4	1.8mM-Ce(IV)	45.0	4.2	10.3	no exch. in 24 hr.	
10	D5	—	45.0	4.2	10.3	complete exch. in 20 hr.	
11	D4	2M-HCl	reflux	4.0	0.08	no exch. in 15 hr.	
12	P1	—	0.0	1.0	10.0	complete exch. in 5 min.	
13	P2	—	34.9	1.6	9.1	298	0.7
14	P3	—	45.0	1.3	9.4	26	7.3
15	P3	—	20.0	1.2	5.65	76	2.0
16	P3	31μM-Co(II)	20.0	1.2	5.77	50	3.06
17	P3	45μM-Co(II)	20.0	1.2	5.66	44	3.46
18	P3	O$_2$ through soln. 12 hr.	45.0	1.15	3.5	415	0.3
19	P4	—	17.0	1.6	10.0	45	5.0
20	P3	2M-HCl	reflux	4.0	0.08	no exch. in 17 hr.	

Attempted Resolutions.—Several attempts were made to resolve [Co phen$_3$](ClO$_4$)$_3$, tartrate, antimonyl tartrate, and α-bromocamphor π-sulphonic acid being used as resolving agents. Because of the very high solubility of most [Co phen$_3$]$^{3+}$ salts, extensive evaporation was necessary to isolate solids, none of which showed any optical rotation (sodium light). The ion should be resolvable, but working in acid solution may be a distinct advantage in view of its exchange (and possible racemisation) behaviour in neutral solution. It is perhaps significant that no direct resolution of a tervalent metal complex of phenanthroline or dipyridyl has been reported; rather the desired optical isomers have been obtained by oxidation of the corresponding optically-active bivalent metal complex.[2]

[14] (a) Amphlett, *Quart. Rev.*, 1954, **8**, 219; (b) Zwolinski, Marcus, and Eyring, *Chem. Rev.*, 1955, **55**, 157.

Acid Dissociations.—These experiments were carried out by dissolving the complex per-chlorate (40 mg.) in 5N-sulphuric acid (20 ml.). One portion was refluxed for 3 hr. and the other kept in ice-water. Within experimental error no difference in optical density between the two solutions was observed, indicating that no slow dissociation of the complex occurred.

Magnetic Measurements.—We are grateful to Dr. J. Lewis and Mr. A. Earnshaw for assistance with these measurements. The Gouy method, involving the normal arrangements, was used and measurements on the cobalt-(II) and -(III) compounds were carried out at room temp. (19°) and at liquid-nitrogen temperature. The absence of ferromagnetic impurities was indicated by the lack of variation of susceptibility with field strengths from about 6000 to 10,000 gauss.

If the mole-fractions of cobalt-(III) and -(II) complexes present in the impure samples of the cobalt(III) complexes are represented by x_3 and x_2, and their molar magnetic susceptibilities by ψ_3 (which should be independent of temperature) and ψ_2 at 292° and ψ_2' at 78° K, and the observed molar susceptibilities of the impure cobalt(III) sample are signified by ψ_{292} and ψ_{78} then

$$\psi_{292} = \psi_3 x_3 + \psi_2 x_2$$
$$\psi_{78} = \psi_3 x_3 + \psi_2' x_2$$

and

$$x_2 = (\psi_{78} + \psi_{292})/(\psi_2' - \psi_2)$$

The results are given in Table 2. The values of ψ_2 for [Co dipy$_3$](ClO$_4$)$_2$ at 292° and 78° K were assumed to be the same as for the analogous phenanthroline compound. The value of 96·6 was reported [8] for the former at room temperature so that the assumption is reasonable. The

TABLE 2. *Magnetic measurements of cobalt(II) and cobalt(III) phenanthroline and dipyridyl complexes.*

Compound	Temp. (° K)	$10^4\psi$	x_2	Temp. (° K)	$10^4\psi$
[Co phen$_3$](ClO$_4$)$_3$ (P3)	292	1·16	0·033	78	9·20
[Co phen$_3$](ClO$_4$)$_2$	292	108		78	352
[Co dipy$_3$](ClO$_4$)$_3$ (D1)	292	−1·74	0·018	78	2·69

estimation of the purity of the cobalt(III) dipyridyl complex was carried out on sample D1 although sample D4 was used for the kinetic method [*i.e.*, by adding cobalt(II)]. There was very little difference between these samples. There appeared to be a definite relation between the value of ψ_{292} and the kinetic rate (the lower the value of ψ_{292} the lower the rate). A value of 5·2 B.M. was obtained for the magnetic moment of [Co phen$_3$](ClO$_4$)$_2$,H$_2$O from these measurements with a molecular field constant θ of 17°.

RESULTS and DISCUSSION

An apparently pure sample of [Co dipy$_3$](ClO$_4$)$_3$ (D1) underwent exchange at a measurable rate in neutral solution (runs 1 and 2 are typical of several runs carried out with this material) and further recrystallisations did not alter this rate (D2, run 3). Exchange experiments with [Co phen$_3$]$^{3+}$ indicated that this ion was extremely labile (P1, run 12). It became apparent that samples of [Co phen$_3$](ClO$_4$)$_3$,2H$_2$O further purified by recrystallis-ation or prepared by different methods gave slower and differing rates of exchange in neutral solution (P2, P3, and P4, runs 13—15 and 19). Also a sample aerated for 12 hours gave markedly lower exchange rates (P3, run 18). These results redirected our attention to the dipyridyl work and the exchange of a new sample of [Co dipy$_3$](ClO$_4$)$_3$,3H$_2$O, prepared from cobalt *purpureo*-chloride (D3, run 4) indicated that with this compound, too, erratic rates could be obtained although the effect was much less marked than with the phenan-throline compounds.

Experiments in acid solution proved helpful. Neither complex lost colour even after 3 hours at 80—100° and did not undergo exchange after 15 hours' refluxing in 2M-hydro-chloric acid (runs 11 and 20). These results were independent of the nature of the sample. Since the acid and base forms of the ligands attain equilibrium rapidly, this reduced rate can-not arise from the presence of very small amounts of the free base forms in these acid con-ditions. Exchange studies have shown that the rates of dissociation of nickel, cobalt(II),

and iron(II) phenanthroline complexes are independent of pH and those of nickel and iron(II) dipyridyl complexes faster in acid; [6,16] so the results in acid strongly indicated that dissociation of the cobalt(III) complexes in neutral solution also was extremely slow and that the observed exchange arose from the presence of a catalyst, probably small amounts of cobalt(II) present as the aquated or complexed ion. With the condition of ligand exchange, the cobalt impurity will exist mainly as $[CoA_3]^{2+}$ in neutral solution but will be completely dissociated in strongly acid solution. This explanation is reasonable since it was shown in other exchange experiments (runs 6, 7, 16, and 17) in which small amounts of cobalt(II) ion were deliberately added, that a marked enhancement of exchange rate occurred. The results of runs 5—7 and 15—17 being used, the percentage of cobalt(II) impurity in samples D4 and P3 was estimated to be 1·4 and 5·4%, respectively. These results agreed reasonably with values from magnetic measurements (1·8 and 3·3%, respectively). The electron-transfer rates obtained for the systems $[Co\ dipy_3]^{3+}$–$[Co\ dipy_3]^{2+}$ at 45° and $[Co\ phen]^{3+}$–$[Co\ phen_3]^{2+}$ at 20° were 1120 and 268 mole^{-1} l. min.$^{-1}$, respectively.* No absolute quantitative reliance can be placed on these results in view of the assumed order-dependence for the electron-transfer process and because of the difficulty of reproducing similar amounts of impurity in all the runs. It did not seem worth while to extend these experiments in view of these difficulties and since direct exchange studies were in progress.[15] The observed catalysis by cobalt(II) also requires that both cobalt(II) complexes are labile, a result which has been observed in separate studies.[16]

Electron transfers between cobalt-(II) and -(III) complexes are almost invariably slow.[14,17] This has been explained by supposing that after the rapid electron transfer cobalt(III) is in a markedly different cobalt(II) environment and further readjustment is improbable. With complexes of such ligands as phenanthroline or dipyridyl however [which " produce " or " almost produce " a spin-paired cobalt(II) complex] this readjustment of environment may be eased, leading to rapid electron transfer, as observed.[18] It appears that most single-electron transfers involving phenanthroline and dipyridyl complexes are fast; [14,19] in some fashion the process is made easier by the presence of the π-electron cloud of the aromatic ligands.

These results emphasise the possible importance of traces of impurities in exchange reactions. In other investigations, enhancement of exchange rates has been ascribed to the presence of small amounts of chemical species.[4] In the present work the addition of a small amount of cerium(IV) [but not persulphate which decomposed the cobalt(II) complex] completely inhibited the neutral exchange (run 9). However, a product obtained by recrystallisation from a solution containing cerium(IV) (D5, run 10) still underwent exchange but the exchange was inhibited by the addition of cerium(IV). There is no question of the cerium's oxidising dipyridyl or forming a complex with it and thus removing it from the exchange mixture since dipyridyl can be extracted from the solution at the end of the experiment. The attempt similarly to quench the exchange with the phenanthroline complexes was vitiated by extensive oxidation of the phenanthroline by cerium(IV). It appears that it is easier to prepare the dipyridyl complex purer than the phenanthroline complex and as might have been expected the product from cobalt(III) reactants is purer than that involving oxidation of cobalt(II) complexes.

No exchange of $[Co\ en_3]^{3+}$ with [^{14}C]ethylenediamine is observed in 55 hours' refluxing in neutral aqueous solution.[20] Obviously cobalt(II) impurities are absent from these

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* *Note Added, September 23rd*, 1957.—The rate of electron transfer between [Co phen$_3$]$^{3+}$ and [Co phen$_3$]$^{2+}$ is of first order in each reactant in nitrate media, and from measurements at 0° and 4·2° a rate constant of 215 mole^{-1} l. min.$^{-1}$ is estimated.[15] The agreement with our value is good, the difference in ionic strength being considered.

[15] Neumann and Baker, personal communication.
[16] Ellis and Wilkins, unpublished work.
[17] Adamson, *Rec. Trav. Chim.*, 1956, **75**, 291.
[18] Orgel, 10th Solvay Conference, Brussels, May, 1956.
[19] George and Irvine, *J.*, 1954, 587.
[20] Popplewell and Wilkins, unpublished work.

experiments since otherwise the slow (but measurable) $[\text{Co en}_3]^{2+}$–$[\text{Co en}_3]^{3+}$ electron-transfer process [21] combined with the known lability of $[\text{Co en}_3]^{2+}$ would have led to very slow exchange with this system in a similar way to that described above. Finally, the observed inertness of $[\text{Co phen}_3]^{3+}$ and $[\text{Co dipy}]^{3+}$ is easily understood on the basis that it is a diamagnetic " inner-orbital " complex.[3]

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[21] Lewis, Coryell, and Irvine, *J.*, 1949, S386.