Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part I. The Exchange of [^{14}C]*Ethylenediamine with Certain " Labile " Metal–Ethylenediamine Complexes.*

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The exchange, in aqueous solution, of [^{14}C]ethylenediamine between ethylenediamine (en) and the complex ions [Zn en$_3$]$^{2+}$, [Cu en$_2$]$^{2+}$, and [Hg en$_2$]$^{2+}$, was complete within five seconds at 0°. Under suitable concentration conditions, the exchange with the [Ni en$_3$]$^{2+}$ ion was discernible at 0°, with $t_{\frac{1}{2}}$ exchange ~5 seconds. The general features of the latter exchange were elucidated and an approximate rate constant was obtained. The dissociation of the first ethylenediamine from the [Ni en$_3$]$^{2+}$ ion was shown to be faster in acid than in alkaline solution.

MOST of the work on the isotopic exchange of metal ions and of ligands with complex ions in aqueous solution has been qualitative. The immeasurably fast or very slow exchanges observed could, in most cases, be understood from a consideration of the chemical properties of the complex ions or even from a knowledge of the detailed electronic structure of the ion, especially in the case of octahedral complexes (Taube, *Chem. Rev.*, 1950, **50**, 69). Although some of these results were important, there was a need to study systems which would give measurable rates; and, recently, detailed kinetic studies of both four- and six-co-ordinated complexes have been described. These have usually been carried out by using labelled ligands rather than metal ions. Exchange of the latter, M^{m+} with (say) $MA_6{}^{n\pm}$ will, unfortunately, be accompanied almost always by interaction between these exchanging species, with the formation of all the possible intermediate ions in amounts governed by the successive formation constants of the system. This interaction may lead to theoretical and practical difficulties. The limited number of complex systems not behaving in this way are of two types: (*a*) complex ions which can co-exist with a substantial amount of metal ion without the formation of appreciable amounts of intermediate complex ions, because of their relatively small stability, and (*b*) the case where A_6 is one hexadentate molecule. An example of the former class is the ion [Fe(*o*-phenanthroline)$_3$]$^{2+}$, exchange of which with ferrous ion has been examined by Whitney, Schweitzer, and Comar (*J. Amer. Chem. Soc.*, 1955, **77**, 1390); and for the latter type (*b*) Jones and Long (*J. Phys. Chem.*, 1952, **56**, 25), for example, studied the exchange of [FeY]$^-$ with ferric ion (Y = ethylenediaminetetra-acetate ion). The complication mentioned above does not arise with ligand exchange, and the only drawback to its use is the certain amount of difficulty accompanying the preparation of the ligand (especially if organic) suitably labelled.

Ethylenediamine ($NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ = en) forms a large number of metal complexes several of which might, considering their properties and stereochemistry, exchange at measurable rates with ethylenediamine. [^{14}C]Ethylenediamine was synthesised (Popplewell and Wilkins, *J.*, 1955, 2521) and this paper is concerned with its exchange with certain " labile " complexes, these being ones which undergo substitution reactions rapidly and are complete in about one minute under ordinary conditions (Taube, *loc. cit.*). The definite rate of exchange observed with the nickel complex ion, [Ni en$_3$]$^{2+}$, in alkaline solution at 0°, encouraged us to study the [Zn en$_3$]$^{2+}$, [Hg en$_2$]$^{2+}$, and [Cu en$_2$]$^{2+}$ ions, under similar conditions, but unfortunately these exchanged at immeasurably fast rates. From the exchange rates an approximate dissociative rate constant was determined for the [Ni en$_3$]$^{2+}$ ion and it was possible to compare this with dissociative rates of the same ion in acid medium (cf. Bjerrum and Poulsen, *Nature*, 1952, **169**, 463).

Work is continuing on the exchange behaviour of certain " inert " metal–ethylenediamine complex compounds (for a preliminary survey of results, see Popplewell and Wilkins, Report on International Conference on Co-ordination Compounds, Amsterdam, 1955, *Rec. Trav. chim.*, to be published) and of phenanthroline–metal complexes containing [^{14}C]phenanthroline.

EXPERIMENTAL

Preparation of [^{14}C]*Ethylenediamine and* [^{14}C]*Ethylenediamine Dinitrate.*—The dihydrochloride was prepared as already described (Popplewell and Wilkins, *J.*, *loc. cit.*). A solution of the free [^{14}C]base in water was obtained by passing an aqueous solution of the salt through the hydroxy-form of an anionic exchange resin (Amberlite IRA-400). [^{14}C]Ethylenediamine dinitrate was obtained in almost quantitative yield by dissolving the dihydrochloride in the least amount of hot saturated lithium nitrate solution, adding alcohol, and cooling. The product was well washed with alcohol and found to be lithium- and chloride-free. The dihydrochloride was used to afford active complexes as described below.

Preparation of the Complexes.—The perchlorates were used in all exchange studies to obviate the possibility of induced anionic exchange. The exchange of [Au en$_2$]$^{3+}$ ion, for example, is accelerated by the addition of chloride ion (Popplewell and Wilkins, *Rec. Trav. chim.*, *loc. cit.*). Trisethylenediaminenickel(II) perchlorate was prepared from the chloride (Werner, *Z. anorg. Chem.*, 1899, **21**, 201) by addition of excess of sodium perchlorate in concentrated aqueous solution. It was recrystallised several times from water (Found : Ni, 13·5; en, 41·1. Calc. for $C_6H_{24}O_8N_6Cl_2Ni$: Ni, 13·4; en, 41·1%).

Trisethylenediaminezinc(II) perchlorate was prepared from the corresponding chloride (*idem, loc. cit.*) in a similar way to the nickel analogue (Found : Zn, 14·8; en, 40·4. Calc. for $C_6H_{24}O_8N_6Cl_2Zn$: Zn, 14·7; en, 40·55%).

Bisethylenediaminecopper(II) perchlorate was prepared from the corresponding chloride and recrystallised several times from water. The substance was anhydrous (Found : Cu, 16·7, 16·8; en, 31·2. Calc. for $C_4H_{16}O_8N_4Cl_2Cu$: Cu, 16·6; en, 31·4%). Lange (*Ber.*, 1926, **59**, 2107) reports it as a hemihydrate.

Bisethylenediaminemercury(II) perchlorate was prepared as described by Pfeiffer, Schmitz, and Böhm (*Z. anorg. Chem.*, 1952, **270**, 287), and recrystallised several times from water (Found : en, 23·2. Calc. for $C_4H_{16}O_8N_4Cl_2Hg$: en, 23·15%).

In all cases samples of the complexes containing [^{14}C]ethylenediamine and of suitable activity for the exchange experiments were most conveniently prepared by heating the pure inactive complex perchlorate (10 parts) with [^{14}C]ethylenediamine dihydrochloride (1 part) for a short while in a hot almost saturated solution and allowing the complex perchlorate to crystallise on cooling. In most cases the active complex was recrystallised a further time. In the case of the bisethylenediaminemercury(II) compound the small amount of the insoluble chloride which separated on addition of the dihydrochloride was filtered off in the hot before the perchlorate crystallised out on cooling.

Ethylenediamine was purified by storage over sodium hydroxide and distillation twice from fresh potassium hydroxide, the fraction of b. p. 117·3—117·4° being collected. Methyl alcohol was dried by reaction with magnesium and subsequent distillation from magnesium perchlorate.

Analyses.—For the nickel, zinc, and mercury complexes, the bound ethylenediamine was estimated (in the same way as was the free base) by direct titration with standard acid using bromocresol-green as indicator. With the copper compound we observed, like Johnson and Bryant (*J.*, 1934, 1783), that direct titration in this way did not give a sharp end-point, even by potentiometric titration, and the estimation was best carried out by adding a known excess of standard perchloric acid to a dilute solution of the copper complex (destroying the colour) and back-titrating with standard alkali until the first appearance of a blue colour, owing to the re-formation of a small amount of the intensely coloured copper–ethylenediamine complex. Analyses for the metal were carried out by standard methods (usually gravimetric).

Counting Procedure.—Counting was carried out on almost " infinitely thick " samples; the measured activity (in counts/min.) is then proportional to the specific activity of the material. The samples, of reproducible composition in any particular run, were prepared essentially as described by Adamson and Wilkins (*J. Amer. Chem. Soc.*, 1954, **76**, 3379) except that the cylindrical depression machined out of a thick aluminium disc was 1·0 cm. in diameter. The amount of material in this area of " mat " corresponding to an " infinite thickness " is about 22 mg. (Libby, *Analyt. Chem.*, 1947, **19**, 2) and is almost independent of the composition of the ^{14}C-containing material. Mats of 15—20 mg. were usually prepared; the variation of count with these amounts of material was very small. A series of tests of a standard substance were carried out and gave reproducibility of counting of about 4%. Samples were counted for a total of about 2500 counts (2% statistical accuracy). Standard electronic equipment was used in conjunction with a G.E.C. mica end-window counter and a Panax Universal lead castle. The usual allowance was made for background (about 11 counts/min.).

Exchange Experiments.—In all cases the complex was separated from the ethylenediamine in aqueous solution by precipitation with a large anion, *e.g.*, HgI_4^{2-}, $PtCl_4^{2-}$, or $S_2O_3^{2-}$. Usually in each system studied, appearance of activity in the initially inactive complex and disappearance in the initially active complex were observed. The exchanges were carried out in a simple apparatus described by Rich and Taube (*J. Phys. Chem.*, **1954**, **58**, **1**). In one compartment of a flask was placed an aqueous solution of the complex and in the other compartment an aqueous solution of ethylenediamine (in boiled-out distilled water). The two solutions in the flask were then immersed in a large Dewar flask containing ice and water and left for 10—15 min. After this time, the two solutions were rapidly mixed by shaking the vessel vigorously from side to side (zero time). An ice-cold solution of the precipitant was added almost immediately afterwards (when very early exchange times were required) and the time of exchange taken at the point of copious precipitation which in most cases appeared instantaneously. The precipitated complex was quickly centrifuged, and washed once with cold water, twice with alcohol, and twice with ether. It was dried in the air for 20 min., and then at 60° for 5 min. The distribution of activity between the exchanging species was that expected, within experimental error, from the equivalents of ethylenediamine in the complex and in the added ethylenediamine. The molarities of ethylenediamine recorded represent the total amount of species [en], [enH^+], and [enH_2^{2+}], present at the pH of the experiment. All measurements were carried out at 0°. Because of the nature of the experiments no attempt was made to maintain a constant ionic strength. Some exchanges were carried out in the dark with no different results.

Acid Dissociation Experiments.—These were carried out in the same way as the exchange experiments with a solution of the complex in one compartment and an excess of aqueous perchloric acid in the other.

Exchange of $[Ni\,en_3]^{2+}$ *Ion.*—Typical results are given in Table 1. These are rather fully tabulated in order to give some idea of the accuracy and reproducibility of the experiments.

TABLE 1. *Exchange of* $[Ni\,en_3]^{2+}$ *with ethylenediamine at* 0°.

Run no.	1	2	3	4	5
10^3 × Molarity of complex	5·5	5·3	5·3	51·3	4·6
10^3 × Molarity of ethylenediamine	0·93	1·0	15·74	153·7	147·3
Approx. pH of mixture	10·0	11·4	10·9	11·4	11·4
Original activity of complex (counts/min.)	0	0	353	349	406
Activity of complex (counts/min.) after various times (sec.)	125(5·1) 127(5·2) 120(8·3) 127(14·8)	200(3) 203(300) — —	296(2·8) 266(3·4) 258(6·0) 159(60)	296(2·8) 248(3·6) 269(4·0) 248(6·3) 173(120)	197(5·7) 183(7·0) 151(10·3) 137(12·0) 26(120)
$t_{\frac{1}{2}}$ exch. (sec.)	<1	<1	~6	~5	~10
$10k_1$ (sec.$^{-1}$)	>1·1	>1·2	1·7	2·1	1·9
10^3k_2 (sec.$^{-1}$ mole^{-1} l.)	>2·0	>2·0	3·1	3·8	3·4
k_3 ,, ,,	>127	>127	13·1	1·43	1·37

Usually two or more runs were carried out for a particular condition of exchange (as was the case for the other systems studied) and reasonable agreement as to the order of half-life of exchange, $t_{\frac{1}{2}}$ exch., obtained, *i.e.*, <1, ~5, or ~10 sec. In some cases samples from different preparations were used, with similar exchange behaviour. The complex was precipitated and counted as the insoluble salt $[Ni\,en_3][PtCl_4]$. Sodium chloroplatinite solutions were used as the precipitant, freshly prepared because of the fairly rapid hydrolysis of the $PtCl_4^{2-}$ ion, which might lead to the precipitation of hydroxy-chloroplatinites of irreproducible composition. Similar results were obtained when precipitation of $[Ni\,en_3]S_2O_3$ was used as the separation procedure, and when the activity was in the ethylenediamine rather than in the complex at the commencement of the experiment.

Basolo and Murmann (*J. Amer. Chem. Soc.*, **1952**, **74**, **5243**) have measured the formation constants, $K_n = [ML_n]/[ML_{n-1}][L]$, for the nickel–ethylenediamine system at 0° and report $\log K_1 = 7·92$, $\log K_2 = 6·77$, and $\log K_3 = 5·36$. By using these values and the measured pH of the complex solution before mixing with the ethylenediamine, it can be shown that the tris-species $[Ni\,en_3]^{2+}$ was present before mixing to the extent of 90% or more in all exchange runs. After the mixing, the nickel was present almost entirely as the tris-species. This means that a small amount of bis-species $[Ni\,en_2(H_2O)_2]^{2+}$ will be *very* rapidly converted into the tris-species during the mixing (since the formation rates are much faster than the dissociative rates) which will lead to a small amount of induced exchange (Runs 3 and 5). In Runs 3, 4, and 5, extrapolation of the log (1 − fraction exchange)/time plot (Wahl and Bonner, "Radioactivity Applied to Chemistry," Chapman and Hall, Ltd., London, 1951, p. 16) gave zero-time induced exchanges of the order 15—25%.

For a dissociative mechanism, the rate of exchange, $R = k_1$[complex], or (more probably) $R = k_2$[complex][H_2O]. In addition, irrespective of the mechanism,

$$R = \frac{0{\cdot}693}{t_{\frac{1}{2}}\ \text{exch.}} \cdot \frac{3[\text{complex}][\text{en} + \text{enH}^+ + \text{enH}_2^{2+}]}{3[\text{complex}] + [\text{en} + \text{enH}^+ + \text{enH}_2^{2+}]}$$

(see Wahl and Bonner, *op. cit.*, pp. 7 *et seq.*). The factor 3 arises from the presence of three equally exchangeable ethylenediamine molecules in the nickel complex. Therefore k_1 (and k_2) can be determined from the values of the half-lives of the exchange under different conditions (see Table 1).

On the other hand, for an S_N2 associative mechanism involving ethylenediamine species,

$$R = k_3[\text{complex}][\text{en}] + k_4[\text{complex}][\text{enH}^+] + k_5[\text{complex}][\text{enH}_2^{2+}]$$

If it is assumed that the second and third paths for exchange are much less important than the first (both species involved are positively charged ions and the concentration of enH_2^{2+} at the pH of the experiments extremely small), then $R = k_3$[complex][en] and k_3 can be calculated in the same way as k_1 and k_2. The value $pK_{\text{enH}^+} = 10{\cdot}73$ at 0° (Basolo and Murmann, *loc. cit.*) was used in estimating the concentration of free base.

The reasonable constancy of k_1 (and k_2) but not of k_3 under the different conditions strongly suggests that the mechanism of exchange is a dissociative one (or an associative process involving a water molecule) as would be expected. The general variation of $t_{\frac{1}{2}}$ exch. with the relative concentration of exchanging species supports this idea even if the simplifying assumption made above is not strictly valid.

Exchange of Other Labile Ions.—In all cases examined here exchange was complete within the times of separation (which were in some cases as low as 3 sec.). The measurement of the exchange of the $[\text{Zn en}_3]^{2+}$ ion had to be approached in a different way from that of the analogous $[\text{Ni en}_3]^{2+}$ ion. A solution prepared from $6{\cdot}7 \times 10^{-3}$ mmol. of the solid $[\text{Zn en}_3](\text{ClO}_4)_2$ dissolved in 1 ml. of solution contains less than 20% of the tris-species, $[\text{Zn en}_3]^{2+}$, and even at much higher concentrations the tris-species will hardly be the dominant species in solution. This arises from the relatively low value of K_3 for the zinc–ethylenediamine system ($\log K_1 = 5{\cdot}92$, $\log K_2 = 5{\cdot}15$, and $\log K_3 = 1{\cdot}86$, at 25°; Bjerrum and Anderson, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, **1945**, **22**, 1773). Consequently free inactive ethylenediamine was added to a solution of the active solid sufficient to ensure predominance of the tris-species (>85%), and the exchange of this mixture with inactive ethylenediamine studied in the usual way. Basolo and Murmann (*loc. cit.*) report values for the copper–ethylenediamine system at 0° ($\log K_1 = 11{\cdot}34$ and $\log K_2 = 9{\cdot}95$). The successive formation constants of the mercury(II)–ethylenediamine complexes being assumed to be of a similar order (only $\log K_1K_2 = 23{\cdot}42$ has been measured; Bjerrum, *Chem. Rev.*, **1950**, **46**, 381), then under the conditions indicated in the Table $[\text{Hg en}_2]^{2+}$ and $[\text{Cu en}_2]^{2+}$ are the dominant species in solution.

In all cases the complex ions were separated from the ethylenediamine by precipitation as the $[\text{HgI}_4]^{2-}$ salt.

TABLE 2. *Exchange of* $[\text{Zn en}_3]^{2+}$, $[\text{Cu en}_2]^{2+}$, *and* $[\text{Hg en}_2]^{2+}$ *with ethylenediamine at* 0°.

Compound	Zn	Cu		Hg
$10^3 \times$ Molarity of complex	26·5	12·0	21·5	6·0
$10^3 \times$ Molarity of ethylenediamine	159·5	24·0	40·4	11·9
Original activity of complex (counts/min.)	500	271	0	162
Activity of complex (counts/min.) after various times (sec.)	166(6·0)	151(2·5)	205(5)	82(6·5)
	173(120)	147(4·0)	209(15)	82(39)
	—	151(120)	—	81(120)

DISCUSSION

The only two exchange studies that have previously been reported with the complex ions studied in this paper involve the trisethylenediaminenickel(II) ion. The exchange of nickel between this ion and the aquated nickel ion (Johnson and Hall, *J. Amer. Chem. Soc.*, **1948**, **70**, 2344), or the tetracyanonickelate ion at pH 9—11 (Long, *ibid.*, **1951**, **73**, 537), was shown to be extremely fast in water at room temperature. In agreement with these observations, the exchange of ethylenediamine with the $[\text{Ni en}_3]^{2+}$ ion in water is immeasurably fast at 20° even under the more favourable conditions (comparable rates of concentrations of exchanging species, see Table 1, Runs 3 and 4 at 0°). However a definite rate of exchange is observed if the temperature is reduced to 0°. The simple apparatus used to follow the exchange precluded the measurement of accurate rate constants, but the results almost certainly show that exchange takes place by a dissociative mechanism and that a bimolecular path involving the complex ion and an ethylenediamine species is not important. The dissociation of *one* ethylenediamine from the tris-complex leads to exchange when the ligand is labelled. This process is *very fast* in acid pH at 0°. This is easily shown by the fact that the lilac $[\text{Ni en}_3]^{2+}$ ion with excess of acid " instantly " becomes blue, forming the $[\text{Ni en}_2(\text{H}_2\text{O})_2]^{2+}$ ion, but then more slowly becomes green, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the latter process occupying some seconds. The rate of dissociation of the first ethylenediamine from the tris-complex is therefore much slower at alkaline than at acid pH.

Bjerrum, Poulsen, and Poulsen (" Proceedings of the Symposium on Co-ordination Chemistry," Danish Chemical Society, 1954, p. 51) have measured the successive formation and dissociation rate constants of the three nickel–ethylenediamine complex ions (among others) in methanol at low temperatures. Extrapolation of the values obtained to 0° by Bjerrum (using determined activation energies) gave $[\text{Ni en}_3]^{2+} \longrightarrow [\text{Ni en}_2]^{2+}$, $\log k_{-3} = +0{\cdot}9$ sec.$^{-1}$; $[\text{Ni en}_2]^{2+} \longrightarrow [\text{Ni en}]^{2+}$, $\log k_{-2} = -0{\cdot}2$ sec.$^{-1}$; $[\text{Ni en}]^{2+} \longrightarrow \text{Ni}^{2+}$, $\log k_{-1} = -1{\cdot}0$ sec.$^{-1}$. As in water, dissociation of the higher complexes in acid methanol proceeds faster than that of the lower complexes. Exchange studies in methanol proved unsatisfactory. At low temperatures the crystal growth of the precipitated complex, after separation, was slow, leading to a certain amount of heterogeneous exchange and a poor separation procedure. At all temperatures there was a large induced exchange (30—35%) and this was not very reproducible. Some results at 0° indicate a rate of exchange $R = 9{\cdot}2 \times 10^{-5}$ sec.$^{-1}$ mole^{-1} l. ($3{\cdot}34 \times 10^{-3}$M-complex, $11{\cdot}3 \times 10^{-3}$M-ethylenediamine, $t_{\frac{1}{2}} = 40$ sec.), showing that dissociation is slower in methanol than in water, at alkaline pH. It is interesting that Basolo, Hayes, and Neumann (*J. Amer. Chem. Soc.*, 1953, **75**, 5102) have shown that it is the *first* dissociation of the trisphenanthroline- and trisdipyridylnickel(II) ions in acid which is the *slow* step, and that the subsequent steps are the faster ones.

The exchange of the analogous zinc ion, $[\text{Zn en}_3]^{2+}$, with ethylenediamine is complete in water within five seconds, thus establishing the enhanced lability of this ion compared with the $[\text{Ni en}_3]^{2+}$ ion. The result, in addition, provides excellent support for the rapidity of mixing by the simple method used in the exchange experiments. In view of these results and of the chemical properties of the nickel- and zinc–ethylenediamine ions, it is difficult to understand that, whereas attempts to resolve the $[\text{Ni en}_3]^{2+}$ ion have proved unsuccessful (Bucknall and Wardlaw, *J.*, 1928, 2739), the resolution of the $[\text{Zn en}_3]^{2+}$ ion has been reported (Neogi and Mukherjee, *J. Indian Chem. Soc.*, 1934, **11**, 681).

Finally both bisethylenediamine complexes investigated also exchanged too rapidly to be studied. The " immediate " disappearance of the deep-blue colour of the $[\text{Cu en}_2]^{2+}$ ion on addition of excess of acid at 0° indicates that the dissociative path for exchange would probably be very rapid even in alkaline solution. Bjerrum, Poulsen, and Poulsen (*loc. cit.*) report that for this ion dissociation rates in methanol show a marked dependence on acidity. In addition it might be expected that a bimolecular path would be important for the planar $[\text{Cu en}_2]^{2+}$ ion since a fifth position is readily available for attachment of an ethylenediamine molecule in a transition state {although the thermodynamic tendency of a third molecule of ethylenediamine to attach itself to the $[\text{Cu en}_2]^{2+}$ ion is very small, (Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 297)}. Although there are indications of the existence of $[\text{Hg en}_3]^{2+}$ ions in solution, attempts to isolate the solid have been unsuccessful (see, for example, O'Brien, *J. Amer. Chem. Soc.*, 1948, **70**, 2771).

Nickel complexes with higher polydentate amines also dissociate rapidly. For example, Mann and Pope (*J.*, 1926, 482) report that the colour of $[\text{Ni tren}]^{2+}$ disappears immediately on addition of hydrochloric acid (tren = triaminotriethylamine, a quadridentate ligand). It appears that the only exception is the $[\text{Ni(tetrameen)}_2]^{2+}$ ion (tetrameen = tetra-*C*-methylethylenediamine) which dissociates in acid solution at a measurable rate ($t_{\frac{1}{2}} \sim 142$ sec.

at 25°; Basolo, Chen, and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 956). Since the monotetraminenickel(II) ion is unstable, the exchange of the bistetraminenickel(II) ion with nickel ion should not be complicated by mutual interaction (see p. 4098) and should proceed at a measurable rate.

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