398. *Racemisation of Optically Active Co-ordination Compounds. Application of the Arrhenius Equation.*

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Comparison has been made of the racemising properties, under various conditions and over a range of temperature, of optically active complex ions of chromium and cobalt, $[M(C_2O_4)_3]'''$, $[M\ en\ (C_2O_4)_2]'$, and $[M\ en_2(C_2O_4)]^{\cdot}$. The experimental evidence supports the view that inversion occurs by intramolecular rearrangement of the co-ordinated radicals, and on account of the simplicity of these reactions, conditions are favourable for probing the relationship between the quantities PZ and E in the modified Arrhenius rate equation, $k = PZe^{-E/RT}$. The rate of inversion of chromi-

oxalate is about twenty times faster than that of cobaltioxalate at 18°, the activation energies being approximately 15·8 and 26·0 kg.-cals. and the multiplying factors, *PZ*, 10^8 and $10^{14\cdot5}$ respectively. A direct proportionality between *E* and log *PZ* has been observed in various circumstances, but the results as a whole do not lend themselves to brief description. During the course of these investigations a resolution of $[\mathrm{Cr\ en\ (C_2O_4)_2}]'$ into its optical isomers was accomplished with the aid of brucine.

PRECISE measurements of the rates of racemisation of optically active co-ordination compounds have rarely been made, and data are lacking regarding their variation with temperature. The overall simplicity of these structural changes, the absence of side reactions, and the possibility of making systematic alterations in the composition of the molecular ions render them interesting subjects for quantitative investigation, which may be expected to throw light on the mechanism of inversion.* The family of complex ions, $[\mathrm{M\ en_3}]^{\cdot\cdot\cdot}$, $[\mathrm{M\ en_2(C_2O_4)}]^{\cdot}$, $[\mathrm{M\ en\ (C_2O_4)_2}]'$, and $[\mathrm{M(C_2O_4)_3}]'''$, where $\mathrm{M = Cr^{\cdot\cdot\cdot}}$ or $\mathrm{Co^{\cdot\cdot\cdot}}$ and en = ethylenediamine, appears to afford exceptional opportunities for study.

Hitherto, $[\mathrm{M\ en_3}]^{\cdot\cdot\cdot}$ had been found not to racemise, the cobalt compound retaining its optical activity even in hot acid solution (Werner, *Ber.*, 1912, **45**, 121), but the ions $[\mathrm{M\ en_2(C_2O_4)}]^{\cdot}$ racemised in aqueous solution, although the process when $\mathrm{M = Co}$ was extremely slow (*idem, Ber.*, 1914, **47**, 2171). Moreover, the complex ion $[\mathrm{Co\ en\ (C_2O_4)_2}]'$ had never been isolated, whereas the chromium analogue had been prepared but not resolved into optical isomers; and the trioxalato-complexes were known to undergo inversion in aqueous solution at conveniently measurable rates, the chromium racemising more rapidly than the cobalt complex at room temperature. The behaviour of these trioxalato-compounds has been reviewed by Johnson (*Trans. Faraday Soc.*, 1935, **31**, 1612).

The present investigation did not afford as full a comparison as was hoped of the racemising properties of these closely related types of complex ion, for it was found, contrary to Werner's observations (*loc. cit.*), that in all probability $[\mathrm{M\ en_2(C_2O_4)}]^{\cdot}$ did not racemise in solution, loss of rotatory power, when it occurred, being due to decomposition. A crystalline compound was prepared which may have contained the ion $[\mathrm{Co\ en\ (C_2O_4)_2}]'$ but was too sparingly soluble for purposes of resolution. The optically active forms of $[\mathrm{Cr\ en\ (C_2O_4)_2}]'$ were obtained for the first time. Thus the study of racemisation was necessarily restricted to $[\mathrm{Cr\ en\ (C_2O_4)_2}]'$, $[\mathrm{Cr(C_2O_4)_3}]'''$ and $[\mathrm{Co(C_2O_4)_3}]'''$.

A theory of inversion relating to the trioxalato-class of molecular ion based on the assumption of secondary ionisation was proposed by Thomas (J., 1921, **119**, 1140), *viz.*,

$$d\text{- or } l\text{-}[\mathrm{M(C_2O_4)_3}]''' \rightleftharpoons [\mathrm{M(C_2O_4)_2}]' + \mathrm{C_2O_4}''$$

The validity of the experimental evidence purporting to prove the presence in these solutions of appreciable amounts of oxalate ion has been questioned (Johnson, *loc. cit.*), although the equilibrium concentration of oxalate ion may, in fact, be so small as to escape detection. An alternative hypothesis is that inversion takes place by intramolecular rearrangement, without detachment of oxalate, though perhaps with the participation of the solvent. Support for this point of view is forthcoming. For instance, the rate of racemisation of chromioxalate is scarcely affected (slightly accelerated) by the presence in solution of a high concentration of oxalate ion (Beese and Johnson, *Trans. Faraday Soc.*, 1935, **31**, 1632); cobaltioxalate is similar in this respect (Table III) †; both chromioxalate and cobaltioxalate

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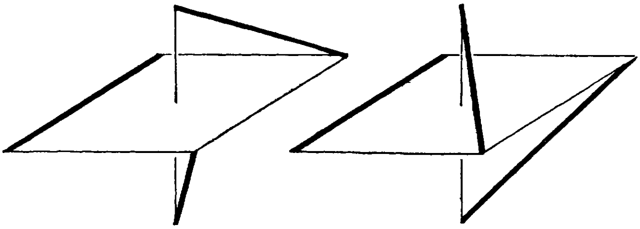
* The terms "racemisation" and "inversion" are used synonymously. The rate of loss of rotatory power is, of course, twice the rate of inversion.

† If, as is likely, two molecules of water take the place of an oxalate ion in the process of secondary ionisation (presumed), there is a finite probability that the *d*(or *l*)-configuration of the complex ion will be preserved and that, subsequently, an in-going oxalate radical will regenerate the original form of the trioxalato-complex. The presence in the solution of a soluble oxalate at high concentration will reduce the equilibrium concentration of $[\mathrm{Cr(H_2O)_2(C_2O_4)_2}]'$, and since this quantity determines the rate of production of $[\mathrm{Cr(H_2O)_4(C_2O_4)}]^{\cdot}$, which step necessarily involves loss of rotatory power, the rate of racemisation will be diminished; or, again, if racemisation occurs by "slow" intramolecular rearrangement of $[\mathrm{Cr(H_2O)_2(C_2O_4)_2}]'$, the addition of oxalate should retard the rate. Brief reference to these possibilities was made by Beese and Johnson (*loc. cit.*) but seems to have given rise to misunderstanding (Mathieu, *Bull. Soc. chim.*, 1938, **5**, 778).

racemise in the crystalline state (Johnson and Mead, *ibid.*, p. 1621; Johnson, *loc. cit.*, p. 1620); oxalate ions containing a radioactive isotope of carbon have been shown not to exchange with chromioxalate at 35° (Long, *J. Amer. Chem. Soc.*, 1939, **61**, 570).

An octahedral disposition of the six atoms (nitrogen or oxygen) linked to the metal being assumed in all cases, the net result of optical inversion is an interchange of two points of attachment in *cis*-positions (Fig. 1). Evidently this process happens more readily between co-ordinated oxalate than between ethylenediamine radicals. Whether racemisation invariably occurs by intramolecular rearrangement remains to be proved, but the fact that the complex ions $[\mathrm{M\ en_2(C_2O_4)}]^{\cdot}$ do not racemise is consistent with this view, since a given configuration will persist so long as the two molecules of ethylenediamine remain undisturbed; the detachment and subsequent recombination of the oxalate ion might be expected to provide opportunities for inversion. The decomposition of $[\mathrm{Cr\ en_2(C_2O_4)}]^{\cdot}$ in solution, which appears to involve the displacement of the oxalate ion, is also against the theory of racemisation by secondary ionisation. Gradual loss of rotatory power in crystalline *d*-$[\mathrm{Cr\ en\ (C_2O_4)_2}]\mathrm{K}$ has been observed, although to some extent this seems to be connected with the absorption of moisture by the crystals.

FIG. 1.



d(or *l*). *l* (or *d*).

Our investigations had as their main objectives the determination of activation energies of racemisation and of the influence upon these quantities of changes in the constitution of the complex ions and in the solvent medium. The interdependence of the terms *PZ* and *E* in the modified Arrhenius equation, $k = PZe^{-E/RT}$, has been the subject of theoretical and experimental studies in recent years with reference to a wide variety of organic reactions, notably by Fairclough and Hinshelwood (J., 1937, 538, and later papers). A rather striking apparent correlation between *E* and log *PZ* has been found in the case of chromi- and cobalti-oxalates, but the results as a whole are complicated.

RESULTS AND DISCUSSION.

Racemisation in Aqueous Solution.—At 18° the rate of inversion of chromioxalate is nearly 20 times faster than that of cobaltioxalate. A difference of 1700 cals. in the activation energies would account for it, but the actual values of *E*, calculated from the variation of the velocity constants with temperature, reveal an altogether unexpected state of affairs (Fig. 2; Tables I and V). The energies differ by 10^4 cals., and the values of *PZ* by a factor of 10^6, the effects being mutually compensating. The so-called " effective atomic number " (E.A.N.) of cobalt in cobaltioxalate is 36 (krypton-like), and of chromium in chromioxalate, 33; hence, the larger activation energy may arise, in part at least, from the larger oxalate–metal bond energy in the ground state, notwithstanding the instability of the complex ion in respect of the reaction $2[\mathrm{Co(C_2O_4)_3}]''' \longrightarrow 2\mathrm{CoC_2O_4} + 3\mathrm{C_2O_4}'' + 2\mathrm{CO_2}$, which takes place from an excited level. The chromioxalate ion is *apparently* the more robust because, in contrast to cobalt, tervalent chromium is more stable than the bivalent ion. The magnitude of *E* is practically identical for both the di- and the tri-oxalato-ions of chromium, suggesting a common mechanism of inversion. The introduction of a molecule of ethylenediamine seems hardly to affect the characteristics of the two remaining oxalate radicals. The greater speed of racemisation of $[\mathrm{Cr\ en\ (C_2O_4)_2}]'$ is occasioned by an almost ten-fold increase in *PZ*. Rideal and Thomas (J., 1922, **121**, 196) found 9650 cals.

as the activation energy of the racemisation of chromioxalate; recalculation of their data gives 9520 cals.

TABLE I.

Complex ion.	E (cals.).	$\log_{10}PZ$.	$E/100 \log_{10}PZ$.
[Cr en $(C_2O_4)_2$]′	15,800	8·9	17·8
[Cr$(C_2O_4)_3$]‴	15,750	8·05	19·6
[Co$(C_2O_4)_3$]‴	26,000	14·5	17·9

Racemisation in Aqueous Acetone.—The complex salts are insoluble in acetone, but dilute solutions can be obtained in aqueous acetone. Werner (*Ber.*, 1912, **45**, 3061) first directed attention to the marked retarding influence of acetone upon the rate of racemisation of chromioxalate. The results of quantitative investigation within the temperature range 19—38° are summarised in Table II. When the mol.-fraction of acetone is very small, the negative catalytic effect is mainly exerted on the factor PZ (presumably P); at higher concentrations, E and $\log_{10}PZ$ appear to increase proportionally. Acetone

FIG. 2.

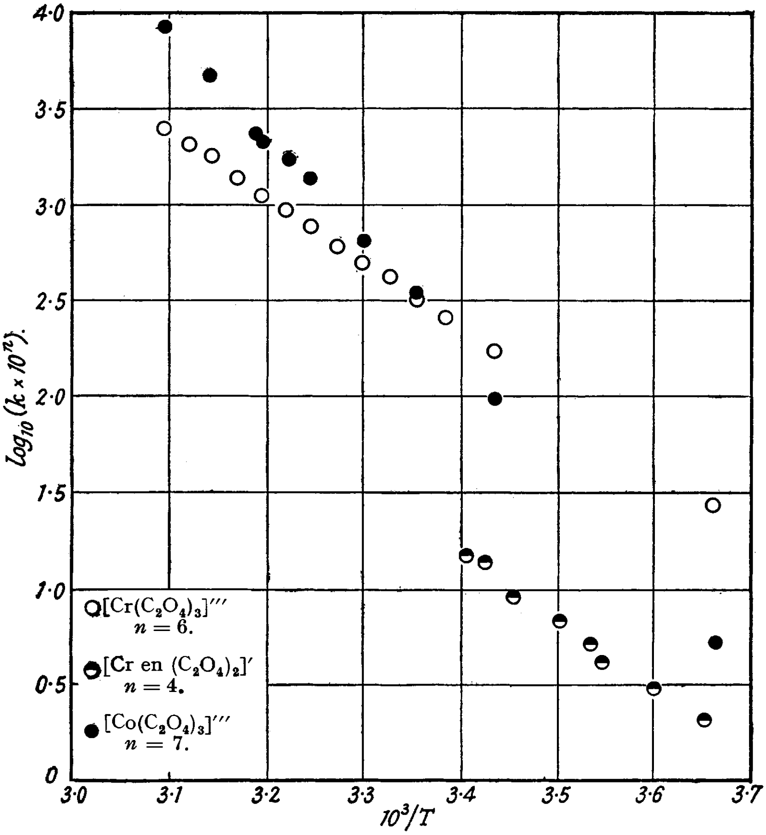


TABLE II.

Mol.-fraction of $COMe_2$.	$10^5 k_{30\cdot1°}$.	E, cals.	$\log_{10}PZ$.	$E/100 \log_{10}PZ$.
0	60·0	15,750	8·05	19·6
0·059	13·7	15,600	7·4	21·0
0·098	8·6	16,200	7·6	21·3
0·144	5·4	18,800	9·3	20·2

(mol.-fraction 0·144) depressed the rate of racemisation of [Cr en $(C_2O_4)_2$]′ rather less than that of chromioxalate, but the observation was necessarily made at a lower temperature

(9·8°, see below). The inversion of cobaltioxalate at 30° was slightly *accelerated* by the presence of acetone, but owing to the pronounced instability of cobaltioxalate in aqueous acetone, measurements of temperature coefficients of velocity were not attempted.

Urea, even at concentrations as high as 50% by weight, produced little or no effect upon the racemisation of chromioxalate.

Catalysed Racemisation.—Small concentrations of positively charged bi- and tervalent ions markedly accelerate the inversion of chromioxalate (Beese and Johnson, *loc. cit.*). The data in Table I suggest a possible connection between this phenomenon and the kinetically low value of P ($\log_{10}PZ \approx 8$). If this were so, similar though less pronounced catalytic effects would be anticipated for the dioxalatochromic complex ($\log_{10}PZ \approx 9$), whereas cobaltioxalate ($\log_{10}PZ \approx 14$) should be relatively immune from such influences. The dependence of PZ upon E somewhat obscures the argument, but the experimental observations given in Table III are in general agreement with these predictions. The concentrations of the complex salt solutions were about 10^{-2}M in all cases. With chromi- and cobalti-oxalates the working temperatures were so chosen, 18·2° and 37·5° respectively, that the uncatalysed rates of racemisation in pure water were nearly identical; the dioxalatochromic ion was conveniently studied at 9·8°. Slow decomposition of the complex ions, with precipitation of insoluble oxalates, took place in the presence of most multivalent cations, but, except where indicated by an asterisk, not appreciably during the time required for complete racemisation. In this respect cobaltioxalate was especially sensitive.

TABLE III.

Catalyst.	Concn. of catalyst (M).	Velocity constants (× 10^5). $[Cr(C_2O_4)_3]'''$.	$[Cr\,en(C_2O_4)_2]'$.	$[Co(C_2O_4)_3]'''$.
(None)	(H_2O)	17	52	17·5
$K_2C_2O_4$	1·5	39	54	43
$K_2C_2O_4$	0·5	26	—	27
K_2SO_4	0·5	24	—	29
KCl	0·5	21	52	—
$CaCl_2$	0·01	47	100 *	22 *
$MnCl_2$	0·01	42	76	21
$Ni(NO_3)_2$	0·01	158	—	21 *
$CuSO_4$	0·01	249	162	28 *
$ZnSO_4$	0·01	118	120	22
$HgCl_2$	0·01	18	47	—
$La(NO_3)_3$	0·001	72	88	19 *
$Ce(NO_3)_3$	0·001	81	106	22 *
$[Co(NH_3)_6]Cl_3$	0·01	†	62	†
$[Co\,en_3]Cl_3$	0·01	†	60	†
$[Cr\,en_3]Cl_3$	0·01	†	62	†

* See above. † See below.

The differences in respect of racemisation between the three complex ions towards (1) salts containing univalent positive ions at high concentrations, and (2) multivalent cations at low concentrations, are best presented as follows:

Ion.	$[Cr(C_2O_4)_3]'''$.	$[Cr\,en(C_2O_4)_2]'$.	$[Co(C_2O_4)_3]'''$.
Univalent	acceleration	no effect	acceleration
Multivalent	acceleration	acceleration	no effect

A satisfactory explanation of the behaviour towards (1) is not available. The diminution of the catalytic effect with increasing size of the positive ion is evident from Table III, col. 4, where the influence of large tervalent ions, *e.g.*, $[Co\,en_3]^{\cdot\cdot\cdot}$, is shown to be feeble even by comparison with representatives of the simple bivalent class. Chromi- and cobalti-oxalates were immediately precipitated by the complex cations and therefore could not be similarly investigated (cf. Beese and Johnson, *loc. cit.*, p. 1638). The influence of multivalent positive ions on the rate of inversion of chromioxalate is even more pronounced in aqueous acetone (mol.-fraction of acetone, 0·059) than in water, which is consistent, qualitatively at least, with the hypothesis that the effect is mainly exerted on the probability factor P. Some observations at 18° are recorded in Table IV.

TABLE IV.

Catalyst.	Concn., M.	$k \times 10^5$.	Catalyst.	Concn., M.	$k \times 10^5$.
None	—	5·5	$ZnSO_4$	0·01	76
$CaCl_2$	0·01	23	$La(NO_3)_3$	0·001	27
$MnCl_2$	0·01	21	$Ce(NO_3)_3$	0·001	33
$CuSO_4$	0·01	190			

Measurements of the temperature coefficients of catalysed racemisation are needed in order to supply a quantitative basis for discussion. Investigation of chromioxalate in the presence of 0·01M-manganese chloride over a limited temperature range in the neighbourhood of 20° gave $E = 15{,}700$ cals., $\log_{10}PZ = 8{\cdot}4$, indicating that the enhanced velocity of inversion is indeed linked with the probability factor, P. In some other cases, however, a large increase in P was accompanied by a substantial increment in the quantity E.

Unsuccessful attempts were made to induce racemisation of $[Cr\,en_2(C_2O_4)]^{\cdot}$, $[Co\,en_2(C_2O_4)]^{\cdot}$ and $[Co\,en_3]^{\cdot\cdot\cdot}$ by lanthanum ions in large concentration. Loss of rotatory power by the first complex ion was invariably attended by decomposition.

Conclusion.—The results being considered as a whole, variations in the magnitudes E and log PZ appear to be closely linked together; only when the change in one or other is small is a certain degree of independence manifest. Notwithstanding the large difference between the activation energies of racemisation of chromi- and cobalti-oxalates, the balance of available evidence points to a mechanism of intramolecular rearrangement in both cases. Caution must be exercised when considering values of PZ and E derived from the application of the simple Arrhenius equation (cf., Bell, *Trans. Faraday Soc.*, 1938, **34**, 229), for it is conceivable that the complementary relationship apparently existing between them is an indication of incorrect " weighting."

EXPERIMENTAL.

Preparation of Materials.—(1) Potassium chromioxalate, $K_3[Cr(C_2O_4)_3],3H_2O$, was prepared according to Croft's procedure (*Phil. Mag.*, 1842, **21**, 197), and purified by repeated precipitation with alcohol and recrystallisation from water. Sörensen's method (*Z. anorg. Chem.*, 1896, **11**, 1) was used for the cobaltioxalate $K_3[Co(C_2O_4)_3],3\frac{1}{2}H_2O$.

(2) Werner's method for dioxalatoethylenediaminochromic salts (*Annalen*, 1914, **406**, 286) gave very poor yields. The following method proved much more satisfactory: ethylenediamine hydrate (16 g.) was added to a solution of potassium chromioxalate (100 g.) in hot water (120 c.c.), and the mixture gently heated, with stirring, until a pink precipitate began to form; the heating was not prolonged unnecessarily, otherwise the pink $[Cr\,en_2(C_2O_4)][Cr\,en\,(C_2O_4)_2]$, which is useful for the preparation of oxalatobisethylenediaminochromic salts, became contaminated with a violet substance. After standing till cold, the precipitate (25 g.) was filtered off, the filtrate just neutralised with hydrochloric acid, and cooled in ice for 2 hours. The mauve-pink crystals which separated were recrystallised from warm water (50°); yield, 15 g. (Found: Cr, 14·55; C_2O_4, 48·4; N, 7·7; H_2O, 9·4. Calc. for $K[Cr\,en\,(C_2O_4)_2],2H_2O$: Cr, 14·3; C_2O_4, 48·5; N, 7·7; H_2O, 9·9%). The crystalline salt keeps indefinitely, but the absorption coefficients of an aqueous solution markedly diminish in the neighbourhood of the maximum at 5300 A. after several hours in the dark at room temperature, and a violet compound is precipitated. Alkalis accelerate the decomposition, but yellow light is without effect.

(3) Dioxalatoethylenediaminocobaltic salts have not hitherto been prepared, and the foregoing method fails for these because cobaltioxalates are unstable in hot alkaline solution. The oxidation with air or hydrogen peroxide of a suspension of cobaltous oxalate in a warm solution containing potassium oxalate and ethylenediamine oxalate proved fruitless. On addition of ethylenediamine hydrate to powdered potassium cobaltioxalate, yellow $[Co\,en_3]^{\cdot\cdot\cdot}$ was formed with evolution of heat; in concentrated aqueous solution the green compound $[Co\,en_3][Co(C_2O_4)_3]$ was precipitated. No reaction occurred when powdered potassium cobaltioxalate was heated in contact with an alcoholic solution of ethylenediamine hydrate. An attempt was made to carry through the following reactions:

$$[Co(NH_3)_2(NO_2)_4]' \xrightarrow{HCl} [Co(NH_3)_2(H_2O)_2Cl_2]^{\cdot} \xrightarrow{(NH_4)_2C_2O_4} [Co(NH_3)_2(C_2O_4)_2]' \xrightarrow{en} [Co\,en\,(C_2O_4)_2]$$

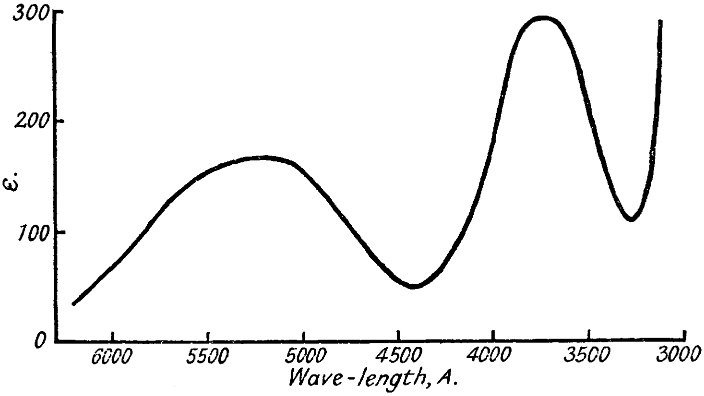
This sequence had been investigated by Riesenfeld and Klement (*Z. anorg. Chem.*, 1922, **124**, 1) who, however, thereby obtained the neutral binuclear complex $[(Co\,en\,NH_3)_2(C_2O_4)_3],\frac{1}{2}H_2O$.

We obtained the same compound (Found : H_2O, 1·1; N, 15·6; C, 22·0. Calc.: H_2O, 1·65; N, 15·7; C, 22·4%). This reddish-violet compound was very sparingly soluble in water and, unlike most un-ionised co-ordination compounds, was insoluble in organic reagents, *e.g.*, acetone. In the last step of the preparation an aqueous solution of the potassium or ammonium salt was warmed with ethylenediamine; ammonia was set free and the colour changed from bluish- to reddish-violet, pointing to the replacement of the oxalato- by the ethylenediamino-radical within the co-ordination sphere. The hot solution precipitated the reddish-violet compound; its colour, general properties, and empirical formula suggest that it has one of the two isomeric constitutions (I) or (II).

(I.) $[Co(NH_3)_2\,en\,(C_2O_4)][Co\,en\,(C_2O_4)_2]$ $[Co\,en_2(C_2O_4)][Co(NH_3)_2(C_2O_4)_2]$ (II.)

If $[Co(NH_3)_2(C_2O_4)_2]'$ has the *trans*-configuration inferred by Riesenfeld and Klement (*loc. cit.*), simultaneous replacement of both ammonia molecules by ethylenediamine is impossible, and neither compound can arise as a result of a process of simple substitution. Compound (II) was prepared by mixing concentrated solutions of $[Co\,en_2(C_2O_4)]Cl$ and $NH_4[Co(NH_3)_2(C_2O_4)_2]$ and was indistinguishable in appearance from the substance under investigation, but in any case the colours of (I) and (II) are certain to be very similar, since the replacement of ammonia by ethylenediamine produces little change in the absorption spectrum (Mathieu, *Bull. Soc. chim.*, 1936, **3**, 463). That of the compound of unknown constitution is shown in Fig. 3; the molecular extinction coefficients are large (cf. Mead, *Trans. Faraday Soc.*, 1934, **30**, 1052) because the substance contains 2 cobalt nuclei per mol. The band in the visible region is broad (possibly doubled), as would be expected from the superposition of the spectra of two closely related complex ions. Accurate absorption data exist for only one of the complex ions constituting (I) and (II), *viz.*, $[Co\,en_2(C_2O_4)]^{\cdot}$, and the question whether $[Co\,en\,(C_2O_4)_2]'$ has been prepared must remain open until a more refined spectrometric investigation has been made.

FIG. 3.



(4) Werner's preparation of oxalatobisethylenediaminochromic salts (*Annalen*, 1914, **405**, 212) from $[Cr\,en_2(C_2O_4)][Cr\,en\,(C_2O_4)_2]$ was simplified. A solution containing $K_3[Cr(C_2O_4)_3],3H_2O$ (100 g.) and ethylenediamine hydrate (32 g.) in water (240 c.c.) was gently heated until the deep pink complex salt began to form, and was then allowed to cool; yield, 35—45 g. The whole was ground into a thin paste with concentrated hydrochloric acid (40 c.c.) and mechanically stirred for 10 minutes, absolute alcohol (20 c.c.) then being gradually added, and a similar addition being made again after a further 5 hours' stirring. The residue was filtered off, washed with concentrated hydrochloric acid and then with absolute alcohol, and purified by recrystallisation from hot water (60°); yield 10 g. (Found : Cr, 14·9; N, 15·8; C_2O_4, 24·8; Cl, 10·1; H_2O, 15·2. Calc. for $[Cr\,en_2(C_2O_4)]Cl,3H_2O$; Cr, 14·9; N, 16·0; C_2O_4, 25·2; Cl, 10·2; H_2O, 15·45%).

(5) The yellowish-pink oxalatobisethylenediaminocobaltic chloride, prepared by Werner's method (*Ber.*, 1912, **45**, 3281) (Found: N, 17·1; Cl, 11·0; H_2O, 4·5. Calc. for $[Co\,en_2(C_2O_4)]Cl,H_2O$; N, 17·5; Cl, 11·1; H_2O, 5·6%), is far more stable than the corresponding chromium salt.

(6) Trisethylenediamino-compounds were prepared as described by Abegg (" Handbuch der anorgischen Chemie ").

Resolution of the Racemic Complex Ions.—(1) Chromioxalate was resolved by Werner (*Ber.*, 1912, **45**, 3061) and cobaltioxalate by Jaeger (*Rec. Trav. chim.*, 1919, **38**, 171), *l*-strychnine being employed in each instance; better resolution was achieved by Johnson and Mead (*Trans. Faraday Soc.*, 1933, **29**, 626; 1935, **31**, 1621). The optically active potassium salts are dihydrates.

(2) The dioxalatoethylenediaminochromic complex had not previously been resolved. Fractional precipitation of the strychnine and cinchonine salts was fruitless, but resolution was accomplished with brucine in the following manner: a solution of brucine sulphate (2·25 g.) in hot water (32 c.c.) was cooled to 30° and added gradually to a solution of *dl*-$K[Cr\ en\ (C_2O_4)_2],2H_2O$ (3 g.) in water (10 c.c.) also at 30°. The mixture was surrounded by ice and stirred continuously until precipitation of the dextrorotatory salt occurred (sometimes very slowly); yield 2 g. The brucine salt of the *l*-complex was obtained from the filtrate by addition of alcohol. Removal of the base as insoluble brucine iodide proved unsatisfactory on account of the coprecipitation of a double salt formed by $K[Cr\ en\ (C_2O_4)_2]$ with potassium iodide, and treatment of the brucine salt with aqueous potassium hydroxide caused decomposition of the complex ion, but the following method was successful. A mixture of finely powdered brucine salt (2 g.), 10% aqueous potassium hydroxide (2 c.c.), and absolute alcohol (60 c.c.) was stirred mechanically for 30 minutes; the brucine remained in solution but the *potassium* salt was filtered off, washed thoroughly with absolute alcohol and pure dry ether, and placed in a covered vessel out of contact with moist air (Found: C_2O_4, 48·4; H_2O, 9·9. *d*-$[Cr\ en\ (C_2O_4)_2]K,2H_2O$ requires C_2O_4, 48·5; H_2O, 9·9%); $\alpha_{5893} + 0{\cdot}65°$ ($c = 0{\cdot}6$; $l = 0{\cdot}19$), whence $[M]_D \approx + 2100°$.

(3) Attempts to resolve $K[Co(NH_3)_2(C_2O_4)_2]$ with strychnine and brucine were unsuccessful, thus supporting Riesenfeld and Klement's view (*loc. cit.*) that it has the *trans*-configuration.

(4) Werner (*Ber.*, 1914, **47**, 2171) was unable to resolve oxalatobisethylenediaminochromic salts by means of optically active acids, but, contrary to his observations, optically active forms were obtained by treatment of *d*- (or *l*-) $[Cr\ en_2Cl_2]Cl$ with a soluble oxalate, a result which has received independent confirmation by Mathieu (*Bull. Soc. chim.*, 1936, **3**, 476). Concentrated hydrochloric acid (15 c.c.) and $[Cr\ en_2(C_2O_4)]Cl,3H_2O$ (10 g.) were gently heated until the salt dissolved and the colour became dark red. Violet-red crystals (5 g.) separated on cooling. Resolution of $[Cr\ en_2Cl_2]Cl$ was carried out by fractional crystallisation of the bromo-*d*-camphorsulphonate (Werner, *Ber.*, 1911, **44**, 3132), and the *d*-chloride (2·5 g.) was added to an aqueous solution of ammonium oxalate (1·5 g. in 10 c.c.) at 65°; after being kept for 3 mins. at this temperature, during which its colour changed from violet-red to dark orange, the solution was cooled in ice, and addition of 0·5 c.c. each of dilute hydrochloric acid and absolute alcohol precipitated *d*-$[Cr\ en_2(C_2O_4)]Cl$. The optical activity was enhanced by extracting the apricot-pink crystals with ice-cold water, since the racemate is more soluble than either of the active forms; $\alpha_D + 0{\cdot}30°$ ($c = 0{\cdot}5$, $l = 0{\cdot}19$), whence $[M]_D \approx + 930°$.

The cobalt analogue was prepared from *d*-$[Co\ en_2Cl_2]Cl$ by an exactly parallel procedure. Werner (*Ber.*, 1912, **45**, 3281), who first used this method, recorded an inversion of the sign of rotation, which must have been due to the employment of light of wave-length other than 5893 A. The activity of the product was improved by recrystallisation from hot water; $\alpha_D + 0{\cdot}73°$ ($c = 0{\cdot}5$, $l = 0{\cdot}19$), whence $[M]_D \approx + 2300°$.

Measurement of Temperature Coefficients of Rates of Racemisation.—The apparatus used for the determination of the velocity of racemisation and its variation with temperature was essentially the same as that described by Beese and Johnson (*loc. cit.*). The solution under investigation was contained in a U-shaped glass cell (thickness 19 mm. or 8 mm.), the temperature of which was maintained constant within ±0·02°. The velocity constant of inversion, k, was calculated from $(2{\cdot}303/2t) \log_{10} \alpha_0/\alpha_t$. As a check on thermal or photochemical decomposition, the absorption coefficients at three wave-lengths near the absorption maximum in the visible spectrum were determined immediately after each experiment. In this connection a difficulty was encountered with cobaltioxalate. The interposition of a yellow Wratten filter between the sodium-vapour lamp and the deep green solution so reduced the field intensity as to make accurate observations of rotatory power impossible. In the absence of a filter the emission by the lamp of a weak band in the blue and a strong line at about 3300 A. caused decomposition of the complex ion. The difficulty was overcome with the aid of a glass cell (thickness 12 mm.) containing a concentrated solution of potassium nitrite, which eliminated the blue and ultra-violet radiations without materially reducing the intensity at 5893 A. The filter was incorporated permanently in the apparatus. With this precaution none of the racemising compounds suffered appreciable decomposition during the time of observation.

The data upon which Fig. 2 is based are given in Table V, but when examining them in relation to the activation energies (Table I) it should be noted that the rate measurements at some temperatures were more reliable than at others or were repeated a larger number of times. This fact, which cannot easily be indicated, was taken into account when calculating the values of *E*.

TABLE V.

d-[Cr$(C_2O_4)_3$]K_3,$2H_2O$		*d*-[Cr en $(C_2O_4)_2$]K,$2H_2O$		*d*-[Co$(C_2O_4)_3$]K_3,$2H_2O$	
(0·045 g. in 10 c.c.; 19 mm. cell).		(0·05 g. in 10 c.c.; 19 mm. cell).		(0·046 g. in 10 c.c.; 8·5 mm. cell).	
Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.	Temp.	$k \times 10^4$.
0·10°	0·28	0·70°	2·12	0·0°	0·005
18·20	1·75	4·70	3·08	18·08	0·0976
22·55	2·60	8·89	4·23	25·16	0·34
25·02	3·26	9·80	5·2	30·02	0·64
27·58	4·22	12·44	6·95	35·05	1·37
30·08	5·06	16·47	9·1	37·48	1·75
32·55	6·01	19·05	13·8	39·97	2·17
35·05	7·77	20·57	15·0	40·57	2·30
37·58	9·49			45·25	4·61
40·04	11·1			49·86	8·38
42·45	13·9				
45·05	17·8				
47·44	20·5				
50·08	24·9				

Some observations on aqueous solutions of *d*-[Cr $en_2(C_2O_4)$]Cl are shown below. The rotations, α_D, in the rows (1) and (2) refer to experiments at 18° and 30° respectively, and those in (3) to 18° with 0·1M-zinc sulphate as solvent. The letters *c* and *p* denote, respectively, colour change and formation of a precipitate.

TABLE VI.

t, mins.	0.	5.	10.	20.	30.	60.	90.	120.	180.	240.	360.	720.
(1) α_D	0·36°	0·36°	0·36°	0·36°	0·36°	0·36°	0·36°	0·36°	0·36°	0·36°	0·36°	0·22°(*p*)
(2) α_D	0·36	0·36	0·36	0·36	0·36	0·36	0·32(*c*)	0·29(*c*)	0·20(*p*)			
(3) α_D	0·36	0·36	0·36	0·36	0·36	0·36	0·36	0·36	0·30(*p*)			

The rotation of an aqueous solution of *d*-[Co $en_2(C_2O_4)$]Cl at 18° remained unchanged for 5 days. In order to investigate the effect of multivalent cations, solutions were made up in 0·1M-cerous nitrate and in M-calcium chloride. No change of rotation occurred in either case during 3 hours at room temperature, or even on boiling for a few minutes. Nevertheless, loss of rotatory power took place on prolonged boiling of an aqueous solution (see below), accompanied by a distinct change of colour:

t (hours)	0	3·3.	6·5	10	15	20	49
α_D	0·84°	0·65°	0·47°	0·32°	0·28°	0·20°	0·03°

A preliminary spectrometric examination suggests that a genuine racemisation may possibly occur independently of some decomposition. However, the fact of decomposition (which appears to have escaped the notice of previous observers) and ignorance of its nature render the system unsuitable for quantitative study.

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