STUDIES IN OPTICAL ACTIVITY. PART III. DEXTRO AND LAEVO COBALTIOXALATES.

By Christopher Hollis Johnson and Alfred Mead.

Received 22nd December, 1932.

A severe obstacle to the quantitative study of optical activity is the fact that no really simple molecule can be expected to exist in optically isomeric forms. The most elementary type of organic compound necessarily consists of four dissimilar atoms or radicles united to an atom of carbon. Furthermore, the rotatory power of a substance at any specific wave-length represents the sum of the separate contributions of its *active* absorption bands, the influence of the nearest band being predominant as a general rule. Measurements of optical rotation at a few selected wave-lengths are therefore not fundamental numerical quantities, and on account of their composite nature are frequently very sensitive to changes of environment. The amazing similarity between the curves of rotatory dispersion of a host of colourless organic compounds in the visible spectrum is due to the fact that in all cases the nearest absorption band is, so to speak, infinitely far away in the ultra-violet. The real centre of interest from a theoretical standpoint is the disposition of the curve of rotatory dispersion in the immediate neighbourhood of the absorption bands. In this direction the recent researches of Werner Kuhn and his collaborators have proved extremely fruitful, but at the same time have revealed the limitations to which such investigations are subject. In no case was it possible to explore more than one electronic band, and this usually appeared merely as a hump upon the curve of general absorption which ascended so steeply as the wave-length diminished that further penetration was impossible.

Complex ions of the type $[M(R_3)]^{---}$, consisting of a central atom (or ion) of a transitional element and three oxalate ions each attached at two points to the metal, as though to the six corners of a regular octahedron, sometimes exhibit optical isomerism.[1] The chromioxalate ion, $[Cr(C_2O_4)_3]^{---}$, is a well-known example. Relatively speaking, these ions are simple in constitution, and they usually possess two distinct absorption bands in the visible and near ultra-violet spectrum. In these respects they offer attractive opportunities for study, but some of them are photosensitive, and racemisation of the optical isomers generally occurs in aqueous solution.

Our choice of potassium cobaltioxalate for the initial investigation was determined chiefly by the comparatively slow rate of racemisation of the salt in water. The substance has previously been examined by Jaeger and Thomas,[2] but a number of important points were overlooked by these authors, and only a very moderate degree of accuracy was claimed for the measurements of rotatory dispersion. Their method of resolution was ill-adapted to the delicate nature of the compound. Thus,

---

[1] Werner, *Ber.*, **45**, 3061, 1912; Johnson, *Trans. Far. Soc.*, **28**, 845, 1932.

[2] *Proc. Kon. Akad. Wet. Amsterdam*, **21**, 693, 1919.

equivalent quantities of aqueous solutions of strychnine sulphate and potassium cobaltioxalate were mixed; the precipitated strychnine salt was dissolved by addition of sufficient cold water, and the solution left to evaporate in an open vessel in the dark for several weeks at a temperature of about 16° C. Successive fractions of the strychnine salt were removed at intervals and converted to the potassium salt by treatment with potassium iodide (strychnine iodide is very insoluble) and precipitation of the potassium cobaltioxalate with alcohol. Only the *d*-component was obtained in this way.

This method was soon abandoned, for, owing to the slight solubility of the strychnine salt and the slow rate at which it goes into solution, quite unmanageable volumes of water were required. Moreover, the crops obtained on evaporation were small, and often contaminated with products of decomposition. The obvious plan of hastening evaporation by placing the solutions in evacuated desiccators containing sticks of caustic soda proved rather clumsy, and the crystals obtained varied very much in respect of optical activity. But one interesting fact was established, namely that the majority of the fractions possessed much larger rotatory powers than those recorded by Jaeger and Thomas. The marked increase was surprising, because evidence was presented in their paper purporting to show that the compound had been completely resolved. Their argument was as follows. Potassium cobaltioxalate was found to crystallise from water at temperatures above 13·2° C. as mixture of the two optically isomeric forms, and single crystals selected at random gave sometimes a lævo- and sometimes a dextro-rotation. The first crystal examined gave a curve of rotatory dispersion almost identical in magnitude though in opposite sense to that of the salt obtained from the crops of strychnine cobaltioxalate. This concordance was advanced as proof of the efficiency of the latter method of resolution, but our results show that it must have been fortuitous, and indeed that both samples of their active potassium salt contained nearly 90 per cent. of the racemic substance. Clearly Jaeger and Thomas's claim of spontaneous fission by crystallisation of potassium cobaltioxalate needs further investigation. Molecular rotations have been calculated by means of their formula,[3] but whereas these authors credit potassium chromioxalate with larger rotatory power than potassium cobaltioxalate, our results show that the situation is reversed, even though the figures for the chromic compound have also been augmented.

No attention whatever seems to have been paid to the strychnine salt of cobaltioxalate, although it is obviously essential to concentrate upon it in order to find the best conditions for resolving the complex ion. This phase of the work has occupied us for a long time, progress being retarded by the difficulty of obtaining reproducible results and some very perplexing inconsistencies in behaviour. Reference is made in a subsequent paragraph to the discovery of an interesting property possessed by both the *d*- and *l*-strychnine salts which provides an explanation for many of the observed anomalies.*

[3] Jaeger, *Rec. Trav. Chim.*, **38**, 202, 1919.

* Throughout this paper constant reference is made to *d*- and *l*-cobaltioxalate. Since the rotation of the optically active salts changes direction at 6280 Å these terms are obviously arbitrary. *In accordance with custom, we define the d and l salts as those possessing right and left-handed rotation, respectively, on the long wavelength side of the position of zero rotation.*

Experimental.

Potassium cobaltioxalate was prepared by the method of Sörensen[4] from analytically pure reagents. Gradual addition of absolute alcohol in the final precipitation of the salt from water ensures a beautifully crystalline product. The dark green crystals and their aqueous solution are decomposed by blue light and are somewhat unstable thermally, so care has been taken to avoid these circumstances.

Analysis.—The analytical results establish the constitution $K_3[Co(C_2O_4)_3] \cdot 3\frac{1}{2}H_2O$ given by Jaeger and Thomas rather than $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ inferred by Sörensen. (Calculated ($3\frac{1}{2}H_2O$): oxalate 52·5 per cent., cobalt 11·5 per cent., water 12·5 per cent. Found: oxalate 52·2 ± 0·1 per cent., cobalt 11·6 ± 0·1 per cent., water 12·1 ± 0·2 per cent.).

Method of Resolution.

One gm. of potassium cobaltioxalate is dissolved in 10 to 20 c.c. of water and then about 110 c.c. of a saturated solution of neutral strychnine sulphate is added in approximately equivalent amount. The precipitated strychnine cobaltioxalate is filtered off and dried first by suction and subsequently upon a porous tile. This is strongly lævorotatory at the wave-lengths 5893, 5780, and 5461 Å., and the filtrate dextrorotatory. A number of lævorotatory residues can be prepared in this way and mixed together. The whole is then quickly extracted with successive quantities of warm water (30° to 40° C.), and the aqueous extracts placed in a bath of crushed ice. In an hour or so considerable quantities of glistening flaky crystals have deposited in all the beakers, and when separated and dried are found to be even more strongly lævorotatory than the original mixture. Repetition of the extraction and freezing process twice or thrice produces crystals having a lævo-rotation which is not increased by further treatment, and of which the rotatory power is approximately 50 per cent. higher than that of the original residue. Obviously, this procedure is extremely wasteful, and the ultimate yield of highly active salt is small; but, fortunately, small amounts suffice for measurements of rotatory dispersion and absorption. In point of fact, the complete curve of rotatory dispersion can be obtained with 0·2 gm. of the strychnine salt, but to secure a satisfactory yield of optically active potassium cobaltioxalate 3 or 4 gms. must be prepared.

The dextrorotatory filtrate is placed in the ice bath and being saturated, presumably, with respect to the strychnine salts of *d*- and *l*-cobaltioxalate it should deposit a mixture of these compounds in proportions depending on the relative trend of the solubility curves between room temperature and 0° C. Some irregularities might be anticipated on account of the extraordinary degree to which aqueous solutions of strychnine salts may remain supersaturated, and because of conceivable peculiarities in the rates of crystallisation. But our observations have confounded all expectations. The precipitates obtained in the initial experiments were optically inactive at 5461 Å., and therefore seemed to be mixtures of the two compounds in which a slight preponderance of the *l* salt neutralised the small rotation of strychnine ion. The lævorotation of the latter at the concentrations used in polarimetric measurements amounted to barely 0·05°, whereas lævorotatory strychnine cobalti-

---

[4] Sörensen, *Z. anorg. Chem.*, 11, 1, 1896.

oxalate gave readings of about 0·8°. Recently, in trying to repeat the experiments, we obtained not pseudo-racemic mixtures but strongly dextrorotatory crystals which were shown by calculation to be almost as pure as the best lævorotatory samples. Unfortunately, the result cannot be reproduced at will; only three attempts out of twenty have been successful. In the hope of eliminating this irregularity, we have investigated the effect of changing the concentrations of the reactants, the temperature of initial precipitation, hydrogen-ion concentration, and have employed more than one preparation of potassium cobaltioxalate and strychnine sulphate, but to no purpose. Inconsistencies of this sort have also been encountered during experiments on the crystallisation of the strychnine salts from water.

The important experimental fact is that strychnine *l*-cobaltioxalate has been isolated. This was not accomplished by Jaeger and Thomas. Attempts made to enhance the rotation along the lines indicated in the case of the other optical isomer were unsuccessful, and resulted in the diminution of the rotatory power.

The best means of preparing optically active potassium salts from the strychnine compounds is that recommended by Werner, in which strychnine salt is treated with potassium iodide solution, the insoluble strychnine iodide removed by filtration, and the potassium salt precipated with alcohol. In order to minimise racemisation, the solid strychnine salts were added to an excess of ice cold aqueous potassium iodide, triturated for five minutes, filtered, and precipitated with ice cold absolute alcohol. One reprecipitation was performed in a similar manner. The whole operation occupied about ten minutes, so the amount of racemisation cannot have been appreciable. Incidentally, the rate of racemisation was shown to be unaffected by the presence of potassium and iodide ions. But the method is not entirely satisfactory, and the yield of potassium salt is poor. Other means of converting strychnine compounds to the potassium salts were tried, but none proved successful.

A convenient method for preparing potassium *l*-cobaltioxalate is the following. Solutions of the racemic salt and of strychnine *nitrate* are mixed in equivalent proportions and the precipitate of strychnine cobaltioxalate removed by filtration. A small excess of solid potassium iodide is added to the filtrate, which precipitates all the strychnine as strychnine iodide. After filtration, just sufficient absolute alcohol is added to the clear solution to throw out the potassium salt. On account of the uncertainties attending the preparation of strychnine *l*-cobaltioxalate this method is of considerable value, for highly active specimens of potassium cobaltioxalate can be obtained, although there must necessarily be present some racemic compound. Strychnine nitrate is used instead of strychnine sulphate in the first step because potassium nitrate is considerably more soluble in aqueous alcohol than potassium sulphate, and thus contamination of the optically active salt is avoided.

Analytical.

The strychnine salts were analysed for strychnine, oxalate, and water of crystallisation, and shown to be *tri*-strychnine derivatives possessing the general formula $(Str)_3[Co(C_2O_4)_3] . xH_2O$. The only possible contaminants were potassium, sulphate, and hydrogen ions, and these were ruled out by qualitative tests.

Strychnine.—Unsuccessful attempts were made to estimate the strychnine gravimetrically, (*a*) as strychnine iodide, (*b*) as strychnine picrate,[5] and (*c*) as strychnine, by extracting the base with chloroform in the presence of concentrated ammonium hydroxide.[6] The first method failed on account of the pronounced tendency of the solutions to remain supersaturated, the second because of adsorption of picric acid by strychnine picrate, and the third owing to interaction between cobaltioxalate and chloroform which caused contamination of the strychnine. The results from (*c*) were about 3 per cent. too high, but at any rate proved that the compounds were *tri*-strychnine salts. Eventually the total nitrogen was estimated by means of a suitably modified Dumas combustion. Approximately 10 c.c. of nitrogen were collected in each analysis, so the method cannot be described as micro-analytical, but the micro-analytical technique formed the basis of our procedure. We are indebted to Dr. M. Nierenstein for providing a gas burette which could be read accurately to 0·05 c.c. and for much helpful advice. Excellent analytical results were obtained which confirmed our opinion that the high values hitherto recorded were spurious.

Water.—The water of crystallisation has been estimated in two ways; by dehydration over phosphorus pentoxide in highly evacuated desiccators in the dark, and by determining the loss of weight at 110° C. The second method is merely a check upon the first, since thermal decomposition involves a loss of carbon dioxide also, but the percentage loss of carbon dioxide varies so little with different degrees of hydration of the strychnine salt that the water content can be inferred to a close approximation. This method gives smaller and more variable figures than the other, which indicates that the expulsion of carbon dioxide from the solid is incomplete, a fact which may be connected with the mechanism of thermal decomposition within the crystal. Thus,

$$(1)\quad \underset{\text{(green)}}{[Co(C_2O_4)_3]^{---}} \rightarrow \underset{\text{(pink)}}{[Co(C_2O_4)_2]^{--}} + C_2O_4^{-}$$

$$(2)\quad 2C_2O_4^{-} \rightarrow C_2O_4^{--} + 2CO_2.$$

In the first step, an electron which has been shared between the cobalt and the oxalate instantaneously becomes the exclusive property of the former, the transfer being accompanied by a change of colour from green to pink. The second step is conceivably slow.* Crystals of strychnine cobaltioxalate decompose rapidly at temperatures above 80° C., but the potassium salt is more stable and even at 110° C. only slowly turns pink. In this case also, the hydration figure is lower than that obtained by desiccation over phosphorus pentoxide. The latter process occupies about ten days, and the fact that constant weight is eventually reached precludes the possibility that the disagreement between the results of the two methods is due to some decomposition accompanying dehydration.

Oxalate.—It is first essential to remove the strychnine, and this is best done with ammonium hydroxide and chloroform, as previously mentioned. Precipitation of calcium oxalate proved unsatisfactory, so

---

[5] A. W. Blyth, *Poisons: Their Effects and Detection*, 1890.

[6] *British Pharmacopœia*, p. 119, 1914.

* The photochemical decomposition seems to follow the same course. If a single orthorhombic crystal of strychnine cobaltioxalate is exposed to blue light, subsequent microscopic examination fails to reveal any change other than that of colour, but after the lapse of a day or two cracks appear on the surface, presumably caused by the escape of carbon dioxide.

the gravimetric method was abandoned in favour of direct titration against potassium permanganate. After extraction of the strychnine, the ammoniacal solution was boiled with excess of sulphuric acid in order to expel dissolved chloroform and decompose the complex ion, and titrated against 0·02 N permanganate. The thermal decomposition of cobaltioxalate in hot acid solution is accompanied by the oxidation of one-sixth of the oxalate, and in this connection an important observation has been made. If the ammoniacal solution (above) is decomposed by boiling prior to the addition of acid, appreciably more permanganate is used in the titration than if the solution is acidified before heating. The explanation is that cobaltic ion is partly precipitated as cobaltic hydroxide in hot alkaline solution, and therefore a portion of the oxalate escapes oxidation. The method of analysis of $K_3[Co(C_2O_4)_3]$ recommended by Sörensen[4] involves the precipitation of the cobalt with potassium hydroxide, and this, doubtless, is the cause of his high results. Further difficulties have been encountered in the analysis and consequently the figures given below are only approximate.

Results.

Strychnine *d*-cobaltioxalate ($13\frac{1}{2}H_2O$), Calculated: nitrogen 5·35 per cent., water 15·5 per cent., oxalate 16·8 per cent. Found: nitrogen 5·38 ± ·04 per cent., water 15·4 ± 0·3 per cent., oxalate 17·0 ± 0·5 per cent.

Strychnine *l*-cobaltioxalate ($9\frac{1}{2}H_2O$), calculated: nitrogen 5·60 per cent., water 11·4 per cent., oxalate 17·6 per cent. Found: nitrogen 5·58 ± 0·05 per cent., water 11·4 ± 0·4 per cent., oxalate 17·7 ± 0·5 per cent.

The analyses indicate that a molecule of the *d*-salt is associated with 13 or 14 molecules of water in the crystal, and the *l* compound with 9 or 10. Both are dull green in colour, are neither efflorescent nor deliquescent, and appear to crystallise in the orthorhombic system.

Only small quantities of optically active potassium salts have been obtained, because the yield of pure material from active strychnine salts is poor. The analytical figures for oxalate and water are fairly consistent and suggest the approximate formula $K_3[Co(C_2O_4)_3] . 2H_2O$ for both the *d*- and *l*-compound. The preparations were dried by treatment with alcohol and ether, which may account for the fluctuations (1·8 to 2·5 molecules of water per mol. of salt) actually observed.

Rotatory Dispersion.

Measurements of the variation of rotatory power with wave-length have been made by means of the polarimeter described in Part II, which appears concurrently with this paper. Equi-molecular solutions were prepared by dissolving 0·0156 gms. of the optically active potassium cobaltioxalates, and 0·0520 and 0·0494 gms. of the *d*- and *l*-strychnine salts, respectively, in 100 c.c. of aqueous solution. These were examined throughout the spectrum in a 30 cm. polarimeter tube. Determinations at two wave-lengths, 5461 Å and 5780 Å were also made in a Schmidt and Haensch polarimeter (crosses in Fig. 1), but to accomplish this, the length of tube had to be reduced to 20 cms. The strength of the solutions is only 3×10^{-4} molal, yet ten or fifteen minutes of vigorous shaking is required to dissolve the strychnine *d*-salt, which shows a remarkable reluctance to pass into solution. The curves of rotatory dispersion of the potassium and strychnine salts of *d*- and *l*-cobaltioxalate are shown graphically in Figs. 1 and 2. In Fig. 1 the measured values of rotation in the neighbourhood of the absorption band are plotted against wave-length in order to illustrate the degree of reproducibility of individual readings. In Fig. 2 the complete curves are drawn on a smaller scale, together with the corresponding absorption coefficients. The contribution of strychnine ion to the observed rotations of the strychnine salts is also indicated. The absorption of the coloured solutions was determined by means of a Hilger-Nutting spectrophotometer and the molecular absorption coefficients calculated from the relationship $I/I_0 = 10^{-\alpha tc}$, α being the molecular absorption coefficient, t the thickness in cms. of the coloured solution, and c the concentration in mols. per litre.

$K_3[Co(C_2O_4)_3]$.—When comparing the curves of rotatory dispersion of the optically active potassium salts, it is important to realise that the

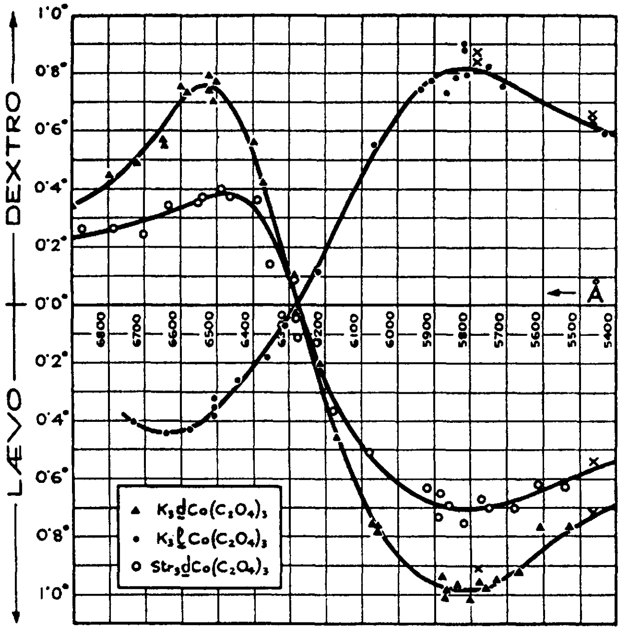

FIG. 1.—Observed Rotations.

d-salt was the purest yet obtained, whereas the *l* compound certainly contained a proportion of racemate, which accounts for its somewhat smaller rotatory power. The striking fact about the curves is that they are not exactly complementary. The axis of zero rotation is crossed at about the same wave-length, 6280 Å, but the relative magnitudes of the two maxima of rotation are not identical. Thus, for the *l*-cobaltioxalate the ratio of maximum rotation in the yellow to that in the red is approximately 1 : 0·5, whereas in the case of the *d*-salt it is 1 : 0·75. Another peculiar feature is that the general contour of the dispersion curves in the red is not the same. The *d*-salt gives a fairly sharp maximum of rotation around 6550 Å, whereas the *l*-salt has a much smoother curve with a maximum at about 6650 Å. In the latter case the rotation at 6700 Å is still almost equal to that at the maximum, but for the *d*-salt it is 30 per cent. lower than the maximum value. These results are contrary to the accepted principle that *d* and *l* forms of a compound are identical in rotatory power though opposite in sign.

The discrepancy could be caused by contamination of the active cobaltioxalates with an optically active impurity, or by errors inherent in the polarimetric method. The presence of an optically active impurity is extremely improbable. Strychnine is ruled out, since its contribution to the rotation of the tri-strychnine compounds is almost inappreciable (Fig. 2). An active form of cobaltioxalate can be imagined in which two cobalt atoms are linked by oxalate radicles, but there is no positive evidence of its existence. The absorption spectra of the cobaltioxalates are closely similar, and the *d*-and *l*-potassium salts racemise completely, and at the same rate, in aqueous solution. Polarimetric defects, if present, must be such as to produce too high dextrorotations and low lævorotations, but this is contrary to observation, as may be seen from Fig. 1 by comparing the points obtained with the new polarimeter and those recorded on the Schmidt and Haensch instrument. Now the sensitivity of the eye diminishes in passing from yellow to red, and it may be suspected that displacements of the dark band (Part II. gives instrumental details) towards the long wave-lengths by a dextrorotatory substance, are accompanied by unsymmetrical broadening of the band in the same direction, and hence give rise to spuriously large values of dextrorotation in the red. The supposition has been tested and shown to be false ; moreover, had this been the cause of the apparent anomaly, it must have affected the relative contours of the long wave-length maxima in a manner opposite to that actually observed.

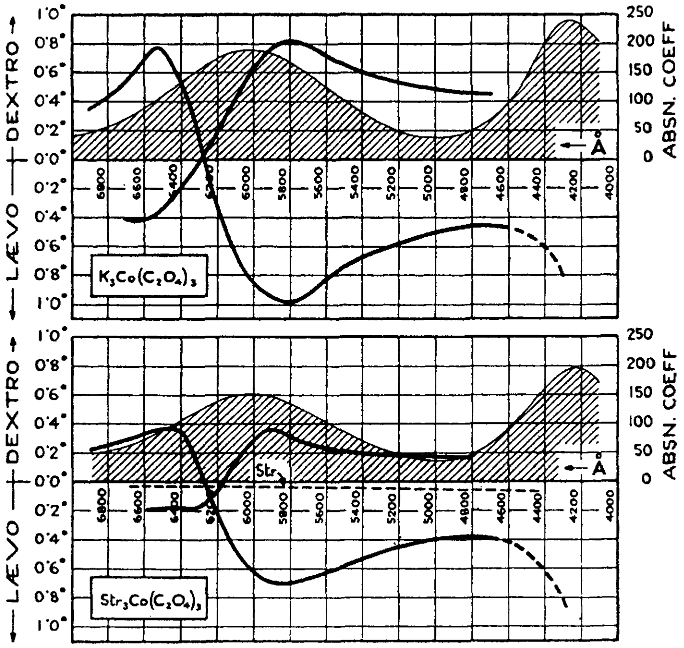

FIG. 2.

Nevertheless, it is a fact that racemic potassium cobaltioxalate is completely devoid of rotatory power at all wave-lengths, and this cannot be reconciled with the differences in the curves of rotatory dispersion of the two optically active components unless some kind of interaction (readjustment) takes place, when they are brought together in aqueous solution. A solution containing 0·0084 gm. of the *l*-salt, and 0·0072 gm. of the *d*-salt in 100 c.c. of water was found to be practically racemic (there was an apparent slight excess of the *l*-salt), whereas calculation based upon the dispersion curves predicted zero rotation in the yellow and marked dextrorotation in the red.

The curves of rotatory dispersion have been re-examined at points in the neighbourhood of the maxima, making use of new preparations of potassium *d*- and *l*-cobaltioxalate. The discrepancies remain. Much further work is contemplated, but progress is necessarily slow.

No significant differences have been detected in the absorption of aqueous solutions of the racemate and the optically active isomers, either as regards the location of maximum absorption or in the absolute values of the molecular absorption coefficients.

(Strychnine)$_3$ [Co(C$_2$O$_4$)$_3$].—It can be seen from Fig. 2 that the molecular rotatory power of the strychnine salt of *d*-cobaltioxalate is considerably less at all wave-lengths than that of the potassium salt which was prepared from it, and that the strychnine salt of the *l* compound is still less active.

It has recently been discovered that the solid strychnine salt of *d*-cobaltioxalate loses about one-quarter of its rotatory power in a week or so after preparation, and then remains without further change for an indefinite period. On the other hand, crystals of the strychnine salt of *l*-cobaltioxalate completely lose their dextrorotation at 5461 Å in the course of a couple of months at room temperatures, becoming slightly lævorotatory on account of the strychnine content. Conversion to the potassium salt results in the separation of racemic potassium cobaltioxalate.* In order to understand the differences between the curves in Fig. 2 it is necessary to consider these facts in relation to the history of the compounds. The strychnine salt of *d*-cobaltioxalate was prepared, and three days later a portion of it was converted to the potassium salt, and this and the remainder of the strychnine salt were used to determine the curves of rotatory dispersion. Measurements were commenced rather more than a week after the preparation of the strychnine compound. The potassium salt of *l*-cobaltioxalate was obtained from the corresponding strychnine derivative about a week after the preparation of the latter, but measurements of rotatory dispersion were not begun until a month from that date. Therefore the curve of rotatory dispersion of strychnine *d*-cobaltioxalate is that of the compound in its steady state, but the racemisation of the corresponding *l*-salt was already far advanced when the measurements were made. The apparent displacement of the position of zero rotation is partly due to the superposition of the lævorotation of strychnine, which is *relatively* large in this case, but

---

* These observations are at present being extended in a number of directions and, apart from their intrinsic interest, promise to throw light on many of the perplexing inconsistencies encountered during the research. As far as we know, this is the first example of racemisation of a complex ion occurring in the crystalline state. The difference in behaviour of the strychnine salts of *d*- and *l*-cobaltioxalate in regard to racemisation may conceivably bear upon the anomalies already discussed in connection with the rotatory dispersion of the corresponding potassium salts in solution, although at ordinary temperatures neither potassium salt shows any sign of undergoing racemisation in the solid state.

for obvious reasons no great reliance can be placed upon this particular curve.

It is noteworthy that the maxima of absorption of strychnine *d*-cobaltioxalate in aqueous solution occur at the same wave-lengths as for the corresponding potassium salt, but the molecular absorption coefficients are distinctly less. The photometric measurements were made soon after the preparation of the compound, but whether this is true in the case of absolutely fresh material has not yet been ascertained. Probably it is, because the curves obtained for strychnine *d*- and *l*-cobaltioxalates were identical within the limits of accuracy of the instrument (about 3 per cent.).

Discussion.

The molecular rotatory power of potassium *d*-cobaltioxalate is extraordinarily large; probably the largest yet recorded for a pure compound in the neighbourhood of an active absorption band.* Our measurements are shown graphically in Fig. 3 (curve 1) with those of Jaeger and Thomas (curve 3), and it is obvious that their compound was very far from being completely resolved. These authors state that their results are somewhat uncertain, so the differences in the character of the dispersion curves are not surprising. The molecular rotations were calculated according to the formula used by Kuhn and Braun,[7] that is, the product of the rotation per decimeter length and the molecular weight, divided by the percentage composition of the solution. The figures supplied by Jaeger and Thomas in their paper have been divided by ten in order to make them comparable.

An interesting feature of the curve of rotatory dispersion of $[Co(C_2O_4)_3]^{---}$ is the displacement of the position of zero rotation some 250 Å to the long wave-length side of the maximum of the absorption band. Werner Kuhn and Szabo[8] observed a displacement almost identical in amount but towards the short wave-lengths in the case of a complex aqueous solution of "potassium chromic tartrate," and from measurements of circular dichroism proved that the absorption band itself possessed a corresponding complexity, being compounded of more than one type of molecular vibration. We have recently found that the dispersion curve of potassium chromioxalate shows a shift of the position of zero rotation of about the same magnitude and in the same direction as that of the complex tartrate. This is especially interesting, because we are dealing here with a molecular ion of definite constitution. Thus the phenomenon may eventually prove to be a general one, connected with the peculiar nature of the broad absorption bands. An alternative explanation in the case of cobaltioxalate is to assume that an active absorption band in the ultra-violet, of opposite sign to that at 6020 Å, is making an appreciable contribution to the optical rotation in the visible spectrum. This would have the effect of shifting the zero point towards the long wave-lengths. There is some support for this idea from the trend of the dispersion curve in the blue in Fig. 2, but this part of the curve is dotted because the points are not yet sufficiently well established. The strong absorption in the band at 4250 Å and the high dispersion of the spectrometer permit the use of only 10 cm. length

---

* Our work on the corresponding salt of chromium is incomplete, but the figures appear to approach the same order of magnitude.

[7] *Z. physik. Chem.*, **8B**, 281, 1930.

[8] *Ibid.*, **15B**, 59, 1931.

of optically active cobaltioxalate solution, and consequently the readings are liable to large errors. On the supposition that the dotted curve is correct, it appears hardly likely that this absorption band is active, so the activity must arise from one lying in the ultra-violet. In order to test this point, we propose to explore the relatively transparent region between 3800 Å and 3300 Å.

The conspicuous symmetry of the sinuous curve of rotatory dispersion with respect to the zero axis of rotation justifies an attempt to analyse it by the method of Kuhn and Braun.[7] In the absence of measurements of circular dichroism, the analysis can only be performed in an approximate manner by selecting likely values of the important constants. However, this arbitrary procedure was used very successfully by Kuhn in his early work. The following constants were chosen (or derived):

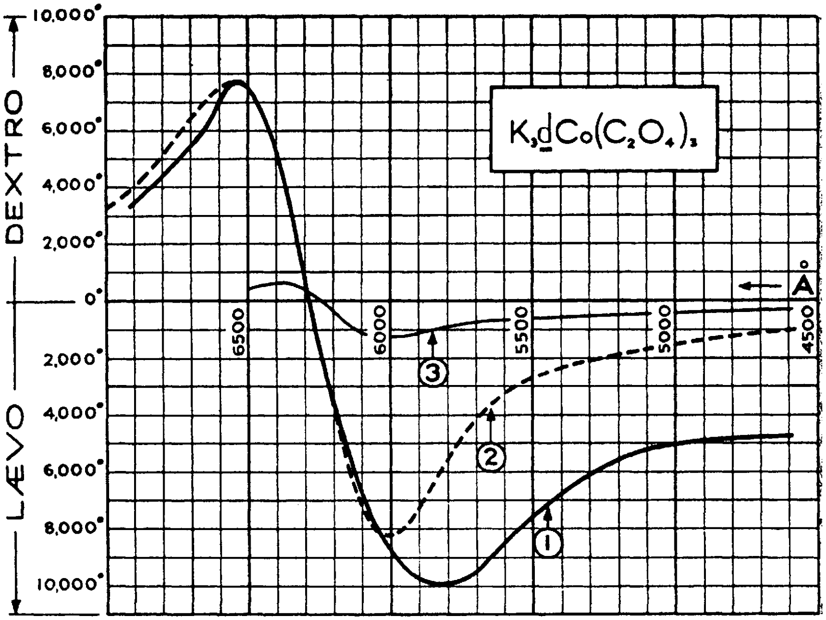

FIG. 3.—Molecular rotations.

$$[\Phi] = 134{\cdot}4, \quad \theta = 0{\cdot}22 \times 10^{14}, \quad \nu_0 = 4{\cdot}78 \times 10^{14}, \quad \nu_\phi = 4{\cdot}58 \times 10^{14}.$$

Their significance will be explained in a subsequent paragraph. The computed curve of molecular rotatory power is shown graphically in Fig. 3 (curve 2). Comparison of curves 1 and 2 reveals satisfactory concordance in the red, and very poor agreement in the region of shorter wave-lengths. But if the assumption is made that the experimental curve, 1, contains a significant contribution of lævorotation at all wave-lengths from an active band in the ultra-violet, the modified experimental and calculated curves can be brought into close correspondence, for the effect is to *increase* the values of $[\Phi]$, θ, and ν_0 and consequently eliminate the present discrepancy at the maximum of rotation in the yellow. This assumption has already been advanced, tentatively, on other grounds, but it is impossible to draw a definite conclusion until measurements of circular dichroism have been made.

According to Kuhn's theory of optical activity, coupled vibrators are responsible for the optical rotatory power of a molecule, and one of the most interesting results is that the distance separating the resonators can be calculated from relevant data. The following equations were derived.[7]

$$g_0 = \frac{2\sqrt{\pi}\,\nu_0[\Phi]}{2{\cdot}303 \times {\cdot}541 \times 100 \times \alpha_{\max} \times \nu_\phi} \simeq \frac{2{\cdot}85\,[\Phi]}{100\,\alpha_{\max}}, \quad . \quad (1)$$

$$d = \frac{g_0\lambda_0}{2\pi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

g_0 is the *anisotropy factor* (or coupling factor) which primarily controls the optical rotatory power, that is, the rotatory dispersion and circular dichroism, of an active absorption band. ν_0 and λ_0 are the frequency and wave-length, respectively, of zero rotation on the dispersion curve. ν_ϕ is the frequency corresponding to the maximum of rotation on the long wave-length side of the absorption band, and $[\Phi]$ *radians* is the molecular rotation at this point. $\alpha_{\max}$ is the molecular absorption coefficient at the position of maximum absorption ; d is the distance referred to above. Equation 2 is derived for the case of a vibrating electric moment possessing *two* components of the same magnitude, perpendicular to each other, and separated by the distance d. A departure from either or both of these conditions has the effect of making the calculated distance smaller than is actually the case. Incomplete resolution of the optical isomers affects the result in the same way, and another factor operating adversely is that the measured absorption coefficient (which occurs in the denominator) is likely to consist of inactive as well as active vibrational components. *The calculated value of d is therefore a minimum.* Yet the striking fact which emerges from Kuhn's researches is that in all cases the calculated distances are surprisingly large in relation to the probable molecular dimensions. Thus, for the active absorption band of the azide radicle (N_3) in the methyl ester of azidopropionic acid, and the dimethylamide of the same acid, $d_{\min}$ is approximately equal to 3 and 11 Ångstrom units respectively.[7] Kuhn has therefore concluded that the conditions stipulated in the derivation of equation 2 are complied with in all cases, a conclusion which seems highly improbable on general grounds. Further doubts as to the true significance of the calculated distances arise from Kuhn and Szabo's data [8] on aqueous solutions of "potassium chromic tartrate." For this substance, $d \geqq 80$ Å ! This extraordinary result is attributed to the formation of large "loose" compounds between the chromic and tartrate ions, their interaction being conceived as a kind of resonance rather than the formation of chemical bonds. But, according to an hypothesis recently developed by one of us,[1] an interaction of this sort is incapable of producing anisotropy in the absorption bands of chromic ion. Moreover, the chromic ion is particularly well suited to the formation of electron pair bonds [9] and a number of possible structures for chromitartrates can be imagined, some of which involve more than one chromic ion linked together by tartrate radicles. The rotatory power of such a complex solution might be expected to be sensitive to dilution which was what Kuhn and Szabo observed. But $d_{\min} \geqq 80$ Å is extremely difficult to accommodate on any theory.

In the light of these considerations, it is interesting to find that for

[9] Linus Pauling, *J.A.C.S.*, **53**, 1367, 1931.

cobaltioxalate, $[Co(C_2O_4)_3]^{---}$, $g_0 \simeq 2 \times 10^{-2}$, and $d_{min} \simeq 20$ Å, which is much larger than can be accounted for from the likely dimensions of the molecular ion. The polarimetric measurements were made on 0·0003 molal solutions of the potassium salt, at which concentration the average distance separating the optically active ions was fully 150 Å. The rotatory power was unaffected by dilution.

It is obvious from equations 1 and 2 that the large calculated values of d_{min} must be related to large values of the anisotropy factor, g_0, and therefore the measured quantity g_0 may actually represent a summation of these terms. It is desirable to find a physical basis for this conclusion. Werner Kuhn's model of the optically active molecule consists essentially of coupled resonators which are responsible for the absorption as well as the rotatory power. The resonators are sometimes described as vibrating electric moments and sometimes as vibrating electrons, although these terms are no longer used by spectroscopists. In what follows, an attempt is made to present the theory from the standpoint of molecular spectra.

One of the most striking contributions ever made to the study of optical activity is the beautiful work of Kuhn and Lehmann[10] on β-octyl nitrite. This compound possesses an absorption band in the near ultra-violet resolvable into five vibrational heads, each of which is shown to produce an anomalous (*i.e.* sinuous) curve of rotatory dispersion. It is therefore reasonable to postulate that an absorption band must possess vibrational components if it is to give rise to optical activity, the anisotropy being acquired by coupling of its vibrational levels with those of other vibrators in distant parts of the molecule. Each vibrational component of an active band will make a specific contribution to the optical activity.* So far, β-octyl nitrite is the only case in which an active absorption band has given spectroscopic evidence of structure. The broad active absorption band of potassium cobaltioxalate (Fig. 2) is a particularly clear example of the symmetrical but unresolvable type. Doubtless these bands consist of overlapping vibrational components. In Fig. 4 is illustrated the effect of summation of a number of closely spaced curves of anomalous rotatory dispersion. The summation curve (dotted) is seen to be quite smooth and apparently regular, just as observed in the case of cobaltioxalate. But the absorption coefficients of the corresponding band heads must also appear as a sum of these quantities in the measured curve of absorption, and since the anistropy factor is a ratio of rotatory power to absorption (equation 1), the two effects may neutralise one another, and therefore the existence

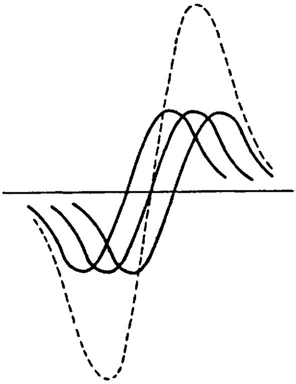

FIG. 4.

---

[10] *Z. physik. Chem.*, **18B**, 32, 1932.

* As a corollary it follows that an absorption " band " which is the result of a pure electron transition cannot promote optical rotatory power. The optically active complex salts of chromium are characterised by narrow lines in the red. There is no evidence from the work of Jaeger[3] or Kuhn and Szabo[8] that they make any appreciable contribution to the rotatory power, but we are studying various optically active compounds in order to be quite sure.

of overlapping vibrational bands is not in itself capable of accounting for the incredibly large calculated values of d_{min}. The explanation is perhaps the following. The theory [11] which led to the derivation of equations 1 and 2 is based upon the interaction of *two* characteristic frequencies of vibration, the essential condition being the coupling between them, although, apparently, weak coupling suffices to generate optical activity. Now weak coupling of the vibrational components of an electronic band with another characteristic frequency will cause scarcely appreciable changes in the energy levels involved in producing the absorption band, and hence affect the absorption to an insignificant degree. *But the coupling concerns several vibrational levels, and may actually extend to a number of different vibrators in the molecule*, and this will increase the anisotropy (and hence the rotatory power) much in the same way that an increase in the number of electrons in an atom or molecule enhances the ordinary refraction. For optical activity is but a very minute perturbation of ordinary refraction, being in fact a small circular double refraction as realised a hundred years ago by Fresnel, and thus there appears to be a distinct parallelism between the two effects. Here, then, is a phenomenon which can strongly influence the contribution of the vibrational components of an absorption band to optical activity without increasing its absorption, which is just what is required to explain the large calculated values of d_{min}. The conditions governing the coupling of resonators in a molecule are uncertain, but presumably the probability of interaction is greater the closer the approach of the energy levels, and the nearer the resonators are together. Optical activity is therefore likely to attain a high degree in dissymmetric molecules possessing a set of identical, or nearly identical, frequencies of vibration. Ions of the cobaltioxalate type are good examples, since the co-ordinated groups are all the same and the six electron pair bonds uniting them to the central atom are equivalent in strength and direction.[9] As may be seen from Fig. 5, the octahedral symmetry of compounds having co-ordination number six is particularly favourable to the development of optical activity. In the case of cobaltioxalate, the three oxalate radicles are doubly attached to the cobalt at positions (*1*, *2*), (*3*, *4*), and (*5*, *6*). Presumably the characteristic vibrations will be executed chiefly in the direction of the valence bonds which are at right angles to one another, and hence fulfil one of Kuhn's requirements [11] for optimum rotatory power, which are that the coupled vibrators be at right angles and separated by a finite distance in relation to the beam of polarised light. Considering, for example, vibrator *6*, it is evident that under no circumstances can its interaction with vibrator *3* promote activity since the vibrations are parallel, and that the nett result of coupling with *1*, *2*, *4*, and *5* will depend upon the path of the ray through the molecule. Thus, if the light is assumed to pass in a direction parallel to a line through *3* and *6*, the vibrator *6* may interact effectively with these four oscillators, but if the molecule be rotated through 90° about the *2*, *5* axis, vibrator *6* becomes coplanar with *2* and *5*, in relation

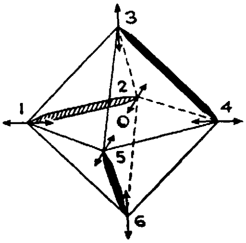

FIG. 5.

---

[11] Werner Kuhn, *Z. physik. Chem.*, **4B**, 14, 1929; *Trans. Far. Soc.*, **26**, 293, 1930.

to the beam of light, and their mutual influences cease to contribute to the optical activity. If an isotropic crystal could be obtained, the variation of rotatory power with direction might be studied from this standpoint, but unfortunately no suitable co-ordination compound appears to crystallise in the cubic system, and attempts made here to prepare alums from the sulphate of the *tri*-ethylene-diamine compound of chromic ion, $Cr(en_3)^{+++}$, have (as expected) proved futile.

Summary.

A satisfactory method of resolution of $[Co(C_2O_4)_3]^{---}$ into its optical isomers has been developed by taking advantage of the difference in solubility of the strychnine salts; and the isolation of strychnine *l*-cobaltioxalate has been accomplished for the first time. The analyses, absorption coefficients, and measurements of the variation of rotatory power with wave-length for the potassium and strychnine compounds of *d*- and *l*-cobaltioxalate are presented in detail. The molecular rotatory power of potassiun *d*-cobaltioxalate is probably the highest yet recorded in the case of a pure substance.

The curves of rotatory dispersion are not symmetrical with respect to the active absorption band, the position of zero rotation (6280 Å) being displaced some 250 Å towards the long wave-lengths from the maximum absorption at 6020 Å. The anisotropy factor, $g_0 \simeq 2 \times 10^{-2}$, and $d_{\text{min}} \simeq 20$ Å, the latter (according to Werner Kuhn) representing the minimum distance separating the components of the vibrating electric moment responsible for optical activity. This surprisingly large value of d_{min} and others obtained by Kuhn and his collaborators are discussed, and an hypothesis put forward to explain them.

The strychnine salts of *d*- and *l*-cobaltioxalate crystallise, respectively, with 14 and 10 molecules of water. The solid *l*-salt racemises completely if kept for a few weeks, whereas the *d*-salt quickly loses about 25 per cent. of its activity and then remains practically unchanged for as long as we have been able to observe it. This is the first example of a molecular ion undergoing racemisation in the crystalline state.

One of us (A. M.) wishes to express his gratitude to the Department of Scientific and Industrial Research for a maintenance-grant.

Department of Chemistry,
University of Bristol.