

phase. Differences may arise from the tendency of protons to be attracted toward or repelled from the charged surface, and indeed it was apparent in paper I<sup>15</sup> that undissociated PMA undergoes partial dissociation at a positively charged surface. Another way of looking at the matter is to say that conditions at the interface are so different from those in the interior of the solution that one could hardly expect to find the same values of  $K_a$  there if  $K_a$  is expressed in terms of the concentrations of the species concerned.

In order to be more sure about the extent of ionization at the interface, copolymers of methacrylic acid with methyl methacrylate were prepared and studied. At sufficiently high pH values there is no doubt that these copolymers are fully ionized and that the number of ionized groups for a given length of chain depends merely upon the methacrylic acid content of the polymer. Figure 7 shows the results obtained in this way with two copolymers. The peaks occur at the same potentials, and their heights are about what one would expect if the degree of ionization shown in Fig. 6 (computed from the pH) is correct. The striking similarity of the two figures indicates that the degree of ionization in the interior of the solution is close to the degree of ionization at the interface.

At sufficiently anodic potentials (below  $-0.23$  v.) the capacity values are almost independent of composition in the case of the two copolymers. The significance of this fact, and also of the sudden upturn at the left-hand end of the two curves, remains in doubt. The polymers of methacrylic acid (Fig. 6) do not show this behavior but exhibit the expected properties on anodic polarization. Thus the fully ionized material shows the lowest capacity and not much turning up, whereas the less fully ionized samples show a larger capacity and an upturn at the end corresponding to the phenomenon of induced ionization discussed in part I.<sup>15</sup>

Summing up, we find that it is usually possible to interpret the differential capacity curves of PMA, both ionized and un-ionized, obtained at a mercury-solution interface and that the results are in accord with previously held views concerning the structure of the double layer.

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## Anomalous Optical Rotations of Coördination Compounds<sup>1</sup>

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The previously reported change in sign of optical rotation of *d-cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl with a change in concentration is not observed if the light used is monochromatic. Results are compared using a sodium lamp, white light filtered through colored glass filters, and white light filtered through an interference filter plus colored glass filters. The effectiveness of the filter combinations in removing all but the NaD doublet from the spectrum produced by the sodium lamp are compared. A change in magnitude but not in sign of optical rotation was noted for K[Co(edta)] using different light sources.

It is well known that the specific rotations of highly colored coördination compounds can change with wave length of light from large negative values to large positive values. Differences in magnitude or even in sign of rotation also have been reported for solutions of the same complex at the same wave length for different concentrations. The specific rotation of a 0.4% solution of *d-cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl was reported to be  $-200^\circ$  and that of a 0.1% solution  $+215^\circ$ .<sup>2</sup> Such results have led to expressions of caution that concentrations should be reported in addition to the wave length of light used.<sup>3</sup>

The difficulties have arisen because of the need to increase the light intensity for densely colored solutions and this has been accomplished at the expense of spectral purity. The sodium lamp, with an orange cut-off filter to eliminate any light of shorter wave length, is commonly used as the source of the NaD doublet. For densely colored

coördination compounds a more intense source has been obtained by using various filter combinations which give very broad bands of transmitted light.

The purpose of this investigation was to study the change in sign of rotation with change in concentration and to determine the limits of usefulness of several light sources or filter combinations.

### Experimental

The *d-cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl was prepared and resolved by the method described by Bailar.<sup>2</sup> The directions refer to the compound as the *levo* form, but the rotation is actually positive at all concentrations for NaD light. The negative rotations are erroneous. The *d*-K[Co(edta)] (edta represents the ethylenediaminetetraacetate ion) was generously provided by Professor Francis P. Dwyer of the University of Sydney. The *d* prefix refers to the rotation of  $+1000^\circ$  at 5461 Å.

Optical rotations were obtained with a Rudolph Model 70 Polarimeter. The readings for 0.3 and 0.4% solutions of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl using the sodium lamp were obtained using a photoelectric attachment built by W. C. Erdman. All measurements were made at room temperature (25–30°) immediately after mixing the solutions.

The spectra of the sodium lamp with various filters were obtained with a Hilger constant deviation glass prism spectrograph. The transmission curves for the filters and solu-

(1) This work was supported by a grant from the Research Corporation. Presented at the 130th Meeting of the American Chemical Society in Atlantic City, New Jersey, September 19, 1956.

(2) J. C. Bailar, Jr., *Inorg. Syn.*, **II**, 224 (1946).

(3) W. C. Fernelius, *Advances in Chem.*, **8**, 9 (1953).

tions of the complexes were obtained with a Beckman Model DU spectrophotometer. The transmission curves for solutions of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl in methyl alcohol were found to be essentially identical with those obtained for freshly prepared aqueous solutions. However, the methyl alcohol solutions did not undergo color changes on standing for periods of an hour or two as was the case for aqueous solutions because of aqution reactions. For this reason methyl alcohol solutions of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl were used for the spectral studies of the sodium lamp. The exposures required for the spectrum of the sodium lamp filtered through the solution of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl were 30–60 minutes.

### Discussion

For densely colored solutions such as *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl the intensity of the sodium lamp is inadequate for measurements over a wide range of concentrations. In such situations workers<sup>4</sup> have used filter combinations such as a solution of 9.4 g. of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 8.9 g. of CuSO<sub>4</sub>·5H<sub>2</sub>O in 300 cc. of water, or for a more intense source a 3% solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> has been used. Frequently the authors have not given information concerning the light source used. Werner<sup>5</sup> reported a rotation of  $-200^\circ$  for a 0.25% solution of *d-cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl in a 2 dm. tube, but does not give details concerning the light source used. The optical density of such a solution is only slightly greater than for a 0.4% solution in a 1 dm. tube for which the reported value<sup>2,4</sup> is also  $-200^\circ$ . Presumably Werner used white light and a filter similar to the CuSO<sub>4</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution.

Figure 1 shows the transmission curves for the CuSO<sub>4</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution used by Bailar and Auten, for an interference filter (Baird Associates), and for

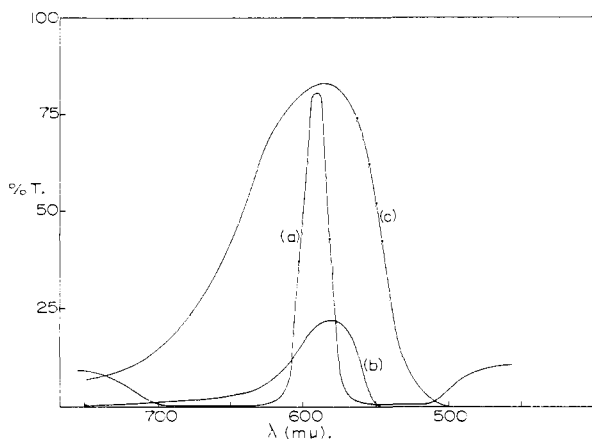


Fig. 1.—Transmission curves for a Baird interference filter, (a) a combination of Corning blue-green and orange cut-off filters, (b) and a CuSO<sub>4</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution in a 1 cm. cell (c).

the combination of an orange cut-off filter (Corning 3-66) and a blue-green filter (Corning 4-70). The CuSO<sub>4</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution gives a broad band which is not suitable for use with a solution which absorbs strongly in the vicinity of the NaD doublet. In fact the light transmitted through such a filter and a solution of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl is red, not yellow. The 3% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution would be much worse as an effective filter. The combination of

(4) J. C. Bailar and R. W. Auten, *THIS JOURNAL*, **56**, 774 (1934); R. W. Auten, B.S. Thesis, University of Illinois, 1933.

(5) A. Werner, *Ber.*, **44**, 3279 (1911).

colored glass filters gives lower intensity in the vicinity of the NaD doublet than the CuSO<sub>4</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution but the transmission in the red is also somewhat less which makes the glass filter slightly more effective. The interference filter gives a very narrow band with high transmission in the vicinity of the NaD doublet, but the transmission increases in the red and blue portions of the spectrum. The interference filter is provided with a yellow cut-off filter which is very effective in removing the blue light, but does not remove the red. It is the red light which is troublesome for the compounds investigated here.

The low transmission in the vicinity of the NaD doublet and high transmission in the red portion of the spectrum for [Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and K[Co(edta)] are shown in Fig. 2. If one uses a filter combina-

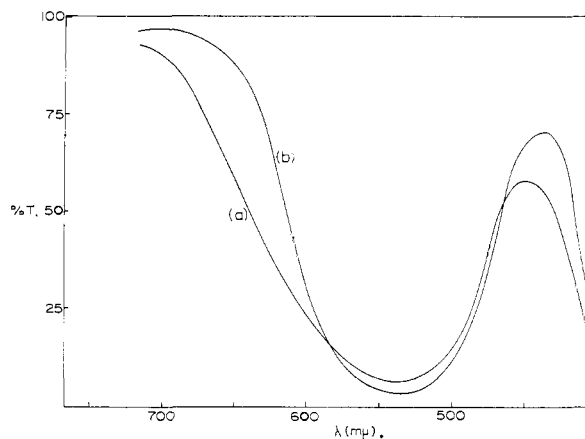


Fig. 2.—Transmission curves for a 0.4% solution of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl (a) and a 0.2% solution of K[Co(edta)] (b) in 1 cm. cells.

tion which gives a broad band of yellow light the wave length of the maximum of the transmitted band is shifted appreciably toward the red after passing through a solution of either complex. Any shift in the wave length of the band of transmitted light will vary with the concentration of the solution of the complex through which the light passes and a shift in optical rotation is to be expected.

The specific rotations for three different filter combinations and several concentrations of *d-cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl are given in Table I. The values obtained with the sodium lamp using the orange cut-off filter for 0.05, 0.1 and 0.3% solutions can be considered to be identical within experimental error. An increase of 0.01° in the observed rotation of a 0.05% solution in a 0.5 dm. tube would increase the specific rotation by 40°. The dry sample used for the preparation of the 0.3 and 0.4% solutions used for readings with the sodium light had stood for over a year and a 0.1% solution in a 1 dm. cell gave a specific rotation of  $+575^\circ$  indicating slight racemization. The readings for these solutions were obtained with a photoelectric attachment since the intensity of the transmitted light was too low for visual readings. The 0.3% solution in a 0.5 dm. tube represents the most dense solution (for concentration and tube length) for which reliable readings could be obtained. The specific rotation is slightly low for this solution unless an inter-

TABLE I  
SPECIFIC ROTATIONS OF SOLUTIONS OF *d-cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl

Concn., %	Tube length, dm.	Na lamp Orange filter	White light blue-green, orange and interference filters	White light blue-green and orange filters
0.05	0.5	+600°	+600°	....
	1	+640°	+580°	....
	2	+640°	+550°	....
	2 <sup>a</sup>	+600°	+540°	....
0.1	0.5	+620°	+640°	+520°
	1	+640°	+580°	+180°
	2	....	+410°	-75°
	2 <sup>a</sup>	....	+550°	+60°
0.25	0.5	+630°	+510°	+25°
	1	....	....	-160°
0.3	0.5	+515 <sup>oc</sup>	....	....
	0.5	+575 <sup>ob,c</sup>	....	....
0.4	0.1	+575 <sup>oc</sup>	....	....
	0.5	....	+350°	-150°
	1	....	....	-220°

<sup>a</sup> One decimeter tube of the active complex and one decimeter tube of the inactive complex. <sup>b</sup> The interference filter was used with the orange filter for this reading. <sup>c</sup> These readings were obtained for a different sample (sp. rot. +575° for 0.1% solution in 1 dm. tube) with a photoelectric attachment.

ference filter is added to eliminate the red light of low intensity from the sodium lamp. The results obtained with white light using the blue-green, orange cut-off and interference filters for dilute solutions and short tube-lengths are in good agreement with the results obtained with the sodium light. As the tube length or concentration increases, a decrease in the specific rotation is observed.

The specific rotations for 0.1 and 0.4% solutions in 1 dm. tubes are nearly the same as the reported values<sup>2,4</sup> if one uses white light and the combination of blue-green and orange cut-off filters. The change from positive to negative values can be accomplished by increasing the tube length instead of changing the concentration. The fact that the effect is due to the filtering action of the complex is clearly demonstrated by the decrease in the rotation of a 0.1% solution in a 1 dm. tube which is brought about by introducing another 1 dm. tube containing the racemic complex. If the tube length of a 0.1% solution is decreased to 0.5 dm., the specific rotation is raised to a value almost as large as that obtained with the sodium lamp.

The absorption spectrum of K[Co(edta)] (Fig. 2) is similar to that of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and one

might expect a similar change in specific rotation with change in concentration. The results in Table II indicate that a change in specific rotation with a change in concentration is observed using white light, but the negative rotation increases instead of changing sign.

TABLE II  
SPECIFIC ROTATIONS OF SOLUTIONS OF *d*-K[Co(edta)]

Concn. and tube length	Na lamp orange filter	White light orange and interference filters	White light blue-green and orange filters
0.05% 0.5 dm.	-200°	-200°	-280°
0.2% 1 dm.	....	-440°	-525°

The change in rotation with concentration using filtered white light is understandable when one considers the filtering effect of the complex. Even the interference filter transmits enough red light to give erroneous readings except at low concentrations. The sodium lamp with an orange cut-off filter has been considered as an ideal light source for any concentration for which readings could be obtained. However, a slight deviation was observed at high concentration.

The spectrum of the sodium lamp was recorded with a spectrograph, but no lines in the red were observed unless the exposure was long enough to give a considerable amount of fogging in the vicinity of the NaD doublet. However, when the light was filtered through a solution of *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl or K[Co(edta)], the intensity of the NaD doublet was reduced to something comparable to some of the lines in the red. The red lines were identified as argon lines. The interference filter reduced the intensity of the red lines greatly, but also reduced the intensity of the NaD lines. The blue-green filter reduced the intensity of the NaD lines too much for practical use.

If the specific rotation varies with the concentration of the solution being investigated, it is probably the light source which is the origin of the trouble. Truly monochromatic sources are not absolutely necessary in many cases, but care should be exercised particularly for measurements made in the vicinity of an absorption band. For colored solutions it is also important to check the zero setting of a Lippich polarimeter with an inactive sample of the same concentration as the active sample if the light is not truly monochromatic. The zero setting shifts with wave length and an error can be introduced for colored solutions.

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