size of the rubidium cation permits it to assume a covalency of six and add two molecules of water.

The infrared spectra of the 2,5-dioximinocyclopentanone compounds differ considerably from those of the 2,6-dioximinocyclohexanone compounds containing the same anion. This, together with the molecular weight data and the presence of a single molecule of water in the compounds, indicates that the structure of the 2,5-compounds is probably completely different from that of the 2,6- compounds. The 2,5- compounds are probably analogous to the known[5–7] coordination compounds of simple α-oximino ketones and contain coordinate bonds to the ketone, one oxime group, and water, and a valence bond to the sulfonate anion. Solution would then involve simply separation of the anion, resulting in the two fragments found.

These structural suggestions admittedly are tentative, and complete elucidation of the structures of these compounds must lie with X-ray diffraction studies. It is apparent, however, that the 2-6-dioximinocyclohexanone compounds represent an unusual class of materials, since they are almost certainly coordination compounds, yet they are not "complexes" in the classic sense because they exist only in the solid state.

(5) T. W. J. Taylor and E. K. Ewbank, *J. Chem. Soc.*, 2818 (1926).
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Circular Dichroism of Coordination Compounds. IV. Some Metal Complexes with Dithiooxalic Acid[1]

BY JINSAI HIDAKA AND BODIE E. DOUGLAS

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The circular dichroism (CD) and absorption data for the visible and ultraviolet regions are reported for the complex ions $[Co(C_2S_2O_2)_3]^{3-}$, $[Rh(C_2S_2O_2)_3]^{3-}$, and $[Cr(C_2S_2O_2)_3]^{3-}$, along with the preparation and absorption data of $[Co(en)_2(C_2S_2O_2)]Cl \cdot 2H_2O$. The CD data made it possible to relate the assignments of transitions for the tris(dithiooxalato) complexes and to assign their absolute configurations.

Introduction

There have been many papers[2] concerned with the absorption spectra of complexes formed by ligands containing sulfur, but few have dealt with complexes of dithiooxalate[3] and the interpretation of their spectra. The interpretation of the spectra of the dithiooxalate complexes has been made difficult by the presence of broad, intense bands in the visible region which overlap the intense near-ultraviolet absorption bands of the ligand itself. In an earlier paper in this series[4] it was demonstrated that circular dichroism (CD) data are very useful for locating the individual components in such situations. The present study is concerned with visible and near-ultraviolet absorption and CD spectra of $(+)_{546}$-$[Co(C_2S_2O_2)_3]^{3-}$, $(+)_{546}$-$[Cr(C_2S_2O_2)_3]^{3-}$, and $(+)_{546}$-$[Rh(C_2S_2O_2)_3]^{3-}$ and the absorption spectrum of the new compound $[Co(en)_2(C_2S_2O_2)]Cl$.

Experimental

Measurements.—Absorption measurements were made at room temperature using a Cary Model 14 spectrophotometer for 2×10^{-5}–2×10^{-2} M solutions in 1-cm. cells. Optical rotations were obtained with a Rudolph Model 80Q6 polarimeter at room temperature and CD spectra were recorded with a Roussel–Jouan dichrograph at 4–5°, maintained by circulating ice water through the cell compartment. Measurements of CD (2, 1, 0.2, and 0.1 cm. cells) and optical rotation (5 cm. cell) were made using 2×10^{-4}–1×10^{-3} M solutions. In the CD measurements, the slit widths were always kept under 0.1 cm.

Preparation of Bis(ethylenediamine)dithiooxalatecobalt(III) Chloride Dihydrate, $[Co(en)_2(C_2S_2O_2)]Cl \cdot 2H_2O$.—Potassium dithiooxalate (3.5 g.) was added to a solution (35 ml.) of *cis*-$[Co(en)_2Cl_2]Cl$ (5.4 g.) and the mixture was warmed at about 60° on a water bath. The color of the solution changed from violet to dark brown. After about 10 min. a reddish brown crystalline powder began to separate along with some black material. The mixture was filtered and the precipitate discarded. The filtrate was kept for a few hours in an ice bath and filtered to remove a crop of reddish brown crystals which were separated by filtration. The crude product was recrystallized from a small volume of hot water and washed with 50% ethanol and then with absolute ethanol. The fine crystals obtained were dried in a vacuum desiccator over H_2SO_4. *Anal.* Calcd. for $[Co(N_4C_4H_{16})(C_2S_2O_2)]Cl$: C, 12.53, H, 4.82; N, 16.74; S, 19.16. Found: C, 12.97; H, 5.08; N, 17.06; S, 19.43. The optical resolution of this complex using silver α-bromo-*d*-camphor-π-sulfonate and silver antimonyl-*d*-tartrate as resolving agents was attempted without success.

Other Preparations and Resolutions. The compounds $(+)_{546}$-$KBa[Co(C_2S_2O_2)_3] \cdot 5H_2O$, $(+)_{546}$-$KBa[Rh(C_2S_2O_2)_3] \cdot 6H_2O$, and $KCa[Cr(C_2S_2O_2)_3] \cdot 6H_2O$ were prepared and resolved using $(-)_{546}$-*cis*-$[Co(en)_2(NO_2)_2]Cl$ as the resolving agent following the directions of Dwyer and Sargeson.[5] The observed specific rotations (546 mμ) of the Co and Rh complexes were: +500° (lit.[5]

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(1) This work was supported by a research grant (GM 10829-06) from the Division of General Medical Studies, Public Health Service.

(2) (a) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962); (b) C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, 1963, p. 131.

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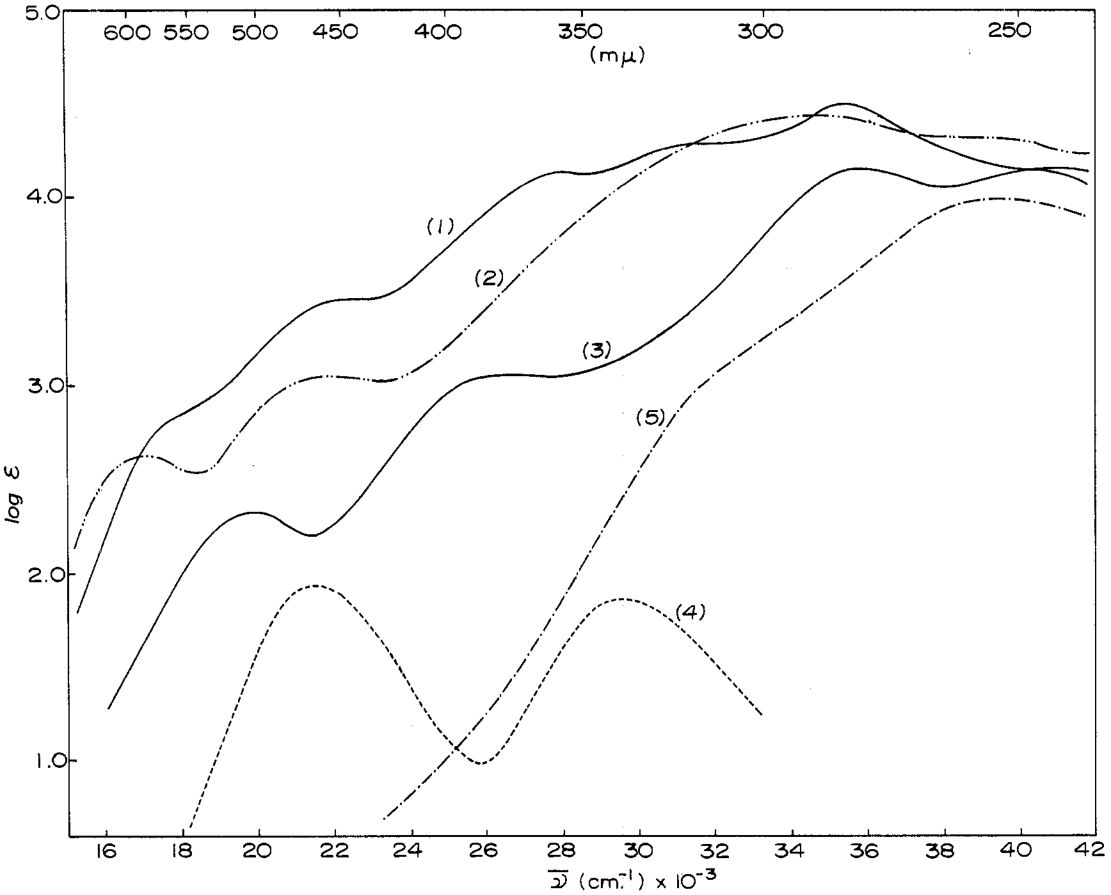

Fig. 1.—Absorption curves of (1) $KBa[Co(C_2S_2O_2)_3]\cdot 5H_2O$, (2) $KCa[Cr(C_2S_2O_2)_3]\cdot 6H_2O$, (3) $[Co(en)_2(C_2S_2O_2)]Cl\cdot 2H_2O$, (4) $[Co(en)_3]Cl_3$, and (5) $K_2C_2S_2O_2$.

+500°) and +520° (lit.[5] +530°), respectively. These solutions were sufficiently stable (optically) so that CD data could be recorded over limited wave length regions for fresh samples. It was not possible to isolate the resolved Cr(III) complex because of its high solubility and rapid racemization. The filtrate from the precipitation of the less soluble diastereoisomer, $(-)_{546}$-$[Cr(C_2S_2O_2)_3]Ca(-)_{546}$-$[Co(en)_2(NO_2)_2]$ was used directly for qualitative CD measurements. It contained the $(+)_{546}$ isomer.

Results and Discussion

Absorption Spectra.—Jørgensen[2a] has discussed sulfur-containing ligands with respect to the spectrochemical series. He found that these ligands are more widely distributed through the series than any others, presumably because of varied extents of π-bonding character between the central metal ion and sulfur. As is seen in Fig. 1 the two absorption bands of $[Co(en)_3]Cl_3$ are shifted toward lower frequencies and increased in intensity on replacement of ethylenediamine by $C_2S_2O_2^{2-}$ to give $[Co(en)_2(C_2S_2O_2)]^+$ and $[Co(C_2S_2O_2)_3]^{3-}$. Thus the low-frequency band at 19,800 cm.$^{-1}$ (log ε 2.3) of $[Co(en)_2(C_2S_2O_2)]Cl$ can be related to the first band of $[Co(en)_3]Cl_3$ and assigned to a d–d transition which gains intensity through Co–S π-bonding. Likewise the shoulder at about 25,500 cm.$^{-1}$ (log ε 2.97) can be related to the second band (d-d) of $[Co(en)_3]Cl_3$. The high intensity and broad character of this shoulder is caused partly by overlap with the nearby ligand band. The absorption curve of $KCa[Cr(C_2S_2O_2)_3]$ in the visible region shows two bands at 17,000 cm.$^{-1}$ (log ε 2.62) and 21,800 cm.$^{-1}$ (log ε 3.03), although the corresponding Co(III) complex shows only two shoulders in this region. It is well known that the absorption bands assigned to d-d transitions of Cr(III) (d^3) complexes are very similar to those of similar Co(III) (d^6) complexes.

The intense bands at 35,500 cm.$^{-1}$ (log ε 4.47) of $KBa[Co(C_2S_2O_2)_3]$, 34,700 cm.$^{-1}$ (log ε 4.43) of $KCa[Cr(C_2S_2O_2)_3]$, and 35,800 cm.$^{-1}$ (log ε 4.10) of $[Co(en)_2(C_2S_2O_3)]Cl$ are assigned as internal ligand transitions which are shifted by complex formation, as suggested by Jørgensen[2a] for $[Ni(C_2S_2O_2)_2]^{2-}$. The shoulders at about 27,000 and 31,000 cm.$^{-1}$ of $KBa[Co(C_2S_2O_2)_3]$ are assigned as ligand bands (*vide infra*). The absorption curve of $KBa[Rh(C_2S_2O_2)_3]$ (Fig. 3) is so featureless as to defy analysis without the aid of other information such as CD data.

Circular Dichroism.—In Fig. 2, the CD and absorption curves of $KBa[Co(C_2S_2O_2)_3]$ are shown; there is a CD peak which corresponds very closely to each of the five absorption peaks in the region 17,500-35,500 cm.$^{-1}$. The intense CD peak at 35,200 cm.$^{-1}$ corresponds to the coordinated ligand absorption band (35,500 cm.$^{-1}$) and the CD peaks (26,100 and 30,900 cm.$^{-1}$) correspond to the absorption shoulders (27,000 and 31,000 cm.$^{-1}$). These are also ligand bands related to the broad shoulder of the free ligand absorption curve at about 31,500 cm.$^{-1}$. In this same region the CD peaks for the Rh(III) complex (Fig. 3) are very similar,

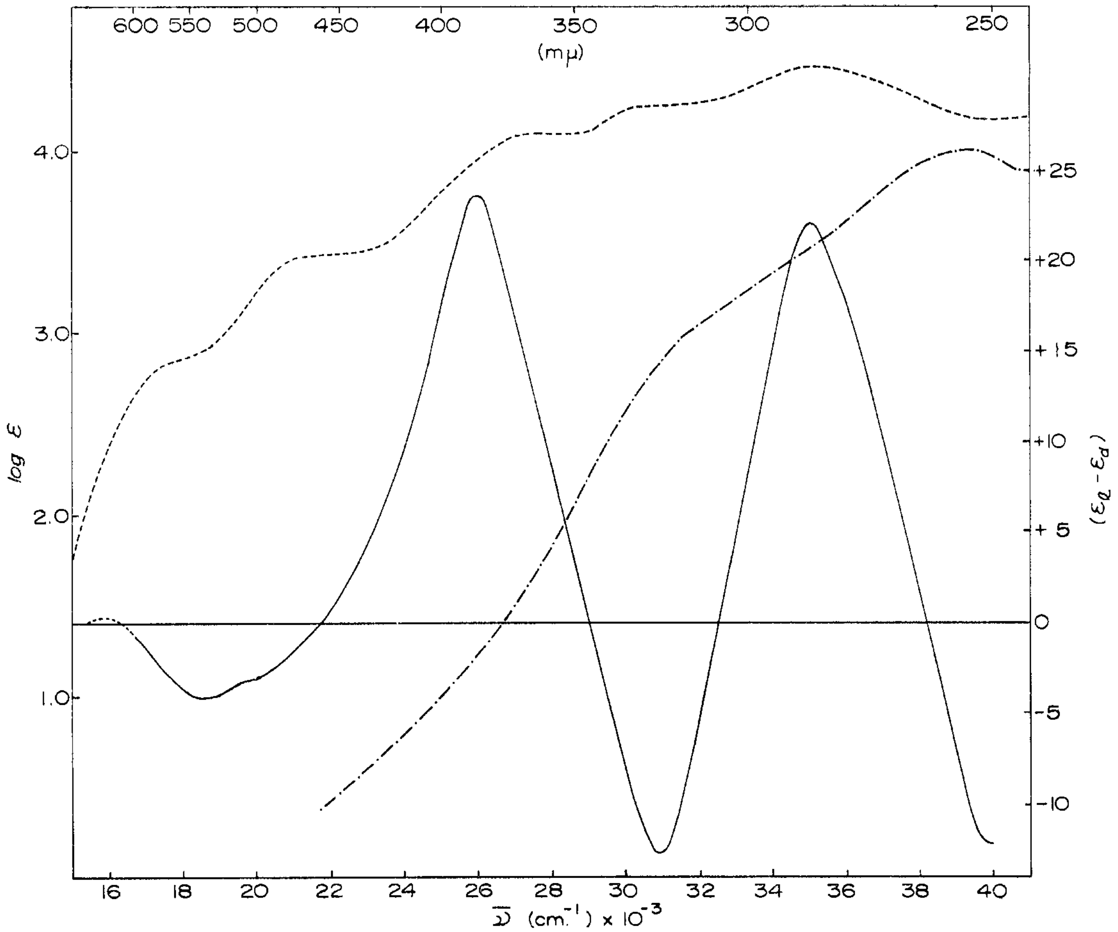

Fig. 2.—Circular dichroism curve of (+)$_{546}$-KBa[Co($C_2S_2O_2$)$_3$]·5H_2O (———), absorption curve of KBa[Co($C_2S_2O_2$)$_3$]·5H_2O (- - - -), absorption curve of $K_2C_2S_2O_2$ (–·–·–).

but shifted to higher frequencies. In general, for similar complexes, the absorption bands of Rh(III) complexes are shifted toward higher frequencies and have somewhat higher intensities as compared to Co(III) complexes. The qualitative curve of (+)$_{546}$-[Cr($C_2S_2O_2$)$_3$]$^{3-}$ also shows CD bands [(+) at *ca.* 24,000, (−) at *ca.* 28,000, and (+) at *ca.* 33,000 cm.$^{-1}$] similar to those of the Co(III) and Rh(III) complexes in this region. Although the completely resolved isomer was not isolated it seemed clear that the ($\epsilon_l - \epsilon_d$) values are appreciably lower for the Cr(III) complex than for those of Co(III) and Rh(III).

The CD peaks of KBa[Co($C_2S_2O_2$)$_3$] (Fig. 2) in the visible region are of much lower intensity than those in the ligand band region, as expected for d–d transitions. The negative band is split into two components (18,900 and 20,200 cm.$^{-1}$) which correspond reasonably well with the absorption bands at about 17,500 and 20,900 cm.$^{-1}$. A small positive CD peak is observed at about 15,800 cm.$^{-1}$.[6] Since this complex has D_3 symmetry, two components are expected for each of the two bands ($^1T_{1g}$ and $^1T_{2g}$) observed for a complex with O_h symmetry. These components[7] are $^1A_2$ and ^1E_a (CD of opposite sign) for the first band and $^1A_1$ and ^1E_b for the second band with only the $^1A_1$ component magnetic dipole forbidden. From the consideration of signs and in relation to the absorption curve, the small positive CD peak at 15,800 cm.$^{-1}$ and the negative peak at 18,900 cm.$^{-1}$ are considered to belong to the first band. Although the more intense ^1E_a component was found to occur at lower frequency than $^1A_2$ for [Co(en)$_3$]$^{3+}$,[8] the reverse was reported for tris(acetylacetonato)cobalt(III).[9] The latter pattern is also anticipated for the [Co($C_2S_2O_2$)$_3$]$^{3-}$ ion since some π-bonding is expected as for the acetylacetonato complex. Bürer[10] has examined the effect of π-bonding on the rotational strength of individual components for Co(III) and Cr(III) D_3 complexes. For Co(III) complexes containing six-membered chelate rings he found that π-bonding increased the rotational strengths of both E components so that each of them was much greater than the A_2 component. The present results are consistent with Bürer's data using the assignments: $^1A_2$ (15,800 cm.$^{-1}$), ^1E_a (18,900 cm.$^{-1}$), and ^1E_b (20,200 cm.$^{-1}$). The apparent position of the ^1E_b CD shoulder does not coincide closely with the corresponding absorption peak, but it is expected to be greatly affected by the adjacent intense positive CD

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(6) Data in this region were provided by A. M. Sargeson, Australian National University.

(7) S. Sugano, *J. Chem. Phys.*, **33**, 1883 (1960); N. K. Hamer, *Mol. Phys.*, **5**, 339 (1962); S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

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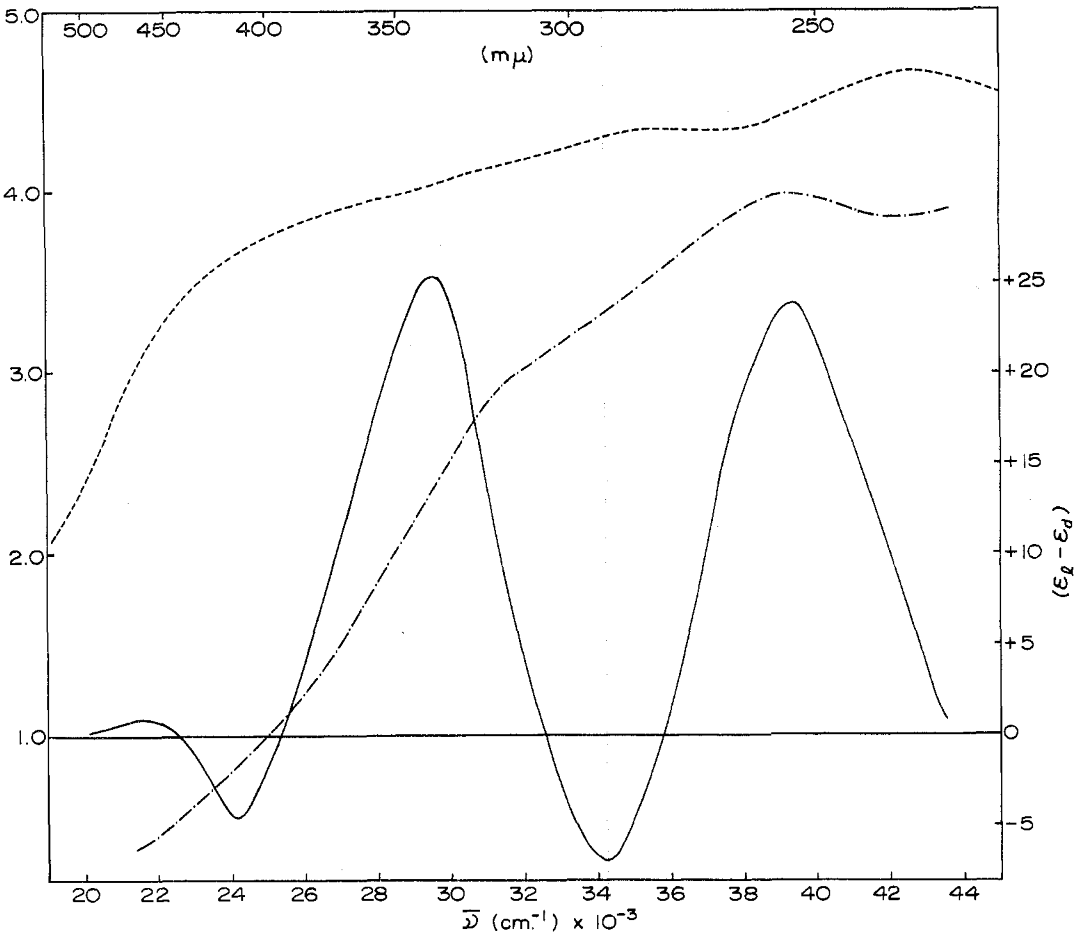

Fig. 3.—Circular dichroism curve of $(+)_{546}$-KBa[Rh($C_2S_2O_2$)$_3$] · $6H_2O$ (———), absorption curve of KBa[Rh($C_2S_2O_2$)$_3$] · $6H_2O$ (– – – –) absorption curve of $K_2C_2S_2O_2$ (–·–·–·).

peak. The overlap of these two components would have the effect of shifting the apparent maximum of the ^1E_b peak to lower frequency and decreasing its intensity.

No peaks or shoulders which can be assigned to metal transitions can be seen from the absorption spectrum of KBa[Rh($C_2S_2O_2$)$_3$] (Fig. 3). It is apparent the curve is shifted to higher frequencies relative to the Co(III) and Cr(III) complexes. However, as was seen for the ligand band region, the CD curves for the Co(III) and Rh(III) complexes are also similar in the low-frequency region. Earlier data for optically active Rh(III) complexes[11] also indicate similarity to the corresponding Co(III) complexes. The small positive peak (21,600 cm.$^{-1}$) (Fig. 3) corresponds to the 15,800 cm.$^{-1}$ peak ($^1A_2$) of the Co(III) complex (Fig. 2), and the negative peak (24,100 cm.$^{-1}$) corresponds to the 18,900 cm.$^{-1}$ (^1E_a) peak of the Co(III) complex. Another negative component (^1E_b) is expected at higher frequencies, but apparently this cannot be seen because it is covered by the much more intense positive peak centered at 29,600 cm.$^{-1}$.

The qualitative CD curve for $(+)_{546}$-KCa[Cr($C_2S_2O_2$)$_3$] shows a negative peak (17,600 cm.$^{-1}$) and a positive peak (21,000 cm.$^{-1}$) in the region of the two visible absorption bands. The positive peak is considered to be the ^1E_b component. From the position of the negative peak (probably ^1E_a) it seems likely that another component (presumably $^1A_2$) should be present at lower frequency. The limited range of the dichrograph (600 mμ) prevented the investigation of this region. The relative intensities of the peaks assigned as ^1E_a and ^1E_b are *ca.* 5:1.

Absolute Configurations.—The signs of the CD components of the first band have been used as the basis for the assignment of the absolute configurations of dihedral complexes.[8,10] Since the ^1E_a component is negative for the Co(III), Cr(III), and Rh(III) $(+)_{546}$-[M($C_2S_2O_2$)$_3$]$^{3-}$ complex ions, they are assigned the Δ configuration. The assignments of the ^1E_a components for the Cr(III) and Rh(III) complexes are less certain than those for the Co(III) complex because one component cannot be located in each of the former cases. However, the complexes with the same configuration are expected to show the same sign pattern for the CD peaks in the ligand band region as is observed for these three complexes. This fact supports the assignment of configurations and strengthens the assignments of the ^1E_a components.

Infrared Absorption Spectra.—The infrared absorption spectra of [Co(en)$_2$($C_2S_2O_2$)]Cl and the three tris-(dithiooxalato) complexes were recorded to confirm

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[11] F. M. Jaeger, *Rec. trav. chim. Pays-Bas.*, **38**, 171 (1919); J.-P. Mathieu, *Compt. rend.*, **198**, 1599 (1934); *J. Chem. Phys.*, **33**, 78 (1936); W. Kuhn and K. Bein, *Z. anorg. allgem. Chem.*, **216**, 321 (1934); M. M. Billardon, *Compt. rend.*, **251**, 2320 (1960).

the expected coordination through S. Metal complexes of dithiooxalate[12] were reported to show a strong band at 1600 cm.$^{-1}$ (C=O stretch) and two bands at about 1080 and 940 cm.$^{-1}$ assigned to a coupled C–C and C–S stretching vibration and a coupled C–S stretching and C–O bending mode, respectively. These bands appear for the three tris(dithiooxalato) complexes studied here. Corresponding bands at 1600 and 1070 cm.$^{-1}$ were observed for $[Co(en)_2(C_2S_2O_2)]Cl$, but no band appeared which clearly corresponded to the coupled C–S and C–C mode.

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Stoichiometry of the Reaction between Uranium(IV) and Chlorite

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The stoichiometry of the reaction between uranium(IV) and chlorite was studied at room temperature with rapid mixing techniques. Under some conditions, results consistent with the mechanism

$$U(IV) + Cl(III) = U(VI) + Cl(I) \quad \text{(slow)}$$
$$Cl(I) + Cl(III) = Cl(V) + Cl^- \quad \text{(fast)}$$

and the over-all reaction

$$U(IV) + 2Cl(III) = U(VI) + Cl(V) + Cl^-$$

were obtained. Analyses were performed on the amount of U(IV) consumed and Cl(V) [*i.e.*, ClO_3^-] produced in the reaction. The value of the $[Cl(III)]/[U(IV)]_{consumed}$ ratio in the absence of scavengers was found to vary from 1.5 to 2.5. With phenol present initially, the second (fast) step was not observed and the $[Cl(III)]/[U(IV)]_{consumed}$ ratio decreased to 1. This is used as evidence that Cl(I) is indeed an intermediate. Kinetic experiments between U(IV) and Cl(I), Cl(III), Cl(IV), and Cl(V) were carried out to obtain further evidence for the proposed mechanism. The results of these studies showed that the relative rates of the reaction between U(IV) and the various halogenates were Cl(III) > Cl(IV) > Cl(I) > Cl_2 > Cl(V).

The reaction between uranium(IV) and chlorite was studied previously by means of oxygen tracer experiments.[1] The results of these experiments were quite complex and indicated that the stoichiometry of the reaction must be better understood in order that a detailed mechanism could be proposed. This research was taken up with this purpose in mind.

For most of the reactions of uranium(IV) reported in the literature, the stoichiometry is not complicated. However, it was somewhat complex in the present case in that chlorate was produced under strongly reducing conditions. This is probably brought about by the fact that the oxidation of uranium(IV) involves an over-all loss of two electrons and the total reduction of the chlorite involves a gain of four electrons.

A study of the kinetics of the disproportionation of chlorite has been made by Barnett.[2] He reports the following rate law at 25°.

$$-d[HClO_2]/dt = 2.35 \times 10^{-2}\ M^{-1}\ \text{sec.}^{-1} \times [HClO_2]^2 \quad (1)$$

Chloride ion catalyzed the disproportionation of chlorite and changed the ratio of products formed. The fraction of the chlorite ion appearing as the product chlorate is much less in the chloride catalyzed reaction than in the uncatalyzed reaction. These observations may be better understood by means of the mechanism proposed by Taube and Dodgen.[3] In the uncatalyzed reaction, the primary step suggested is

$$2HClO_2 = HClO + H^+ + ClO_3^- \quad (2)$$

and in the catalyzed reaction

$$HClO_2 + Cl^- + H^+ = 2HClO \quad (3)$$

In concentrated solutions, the oxidation of chlorite by hypochlorite is reported to yield mainly chlorine dioxide,[3] which accounts for the change in the reaction products during the disproportionation of sodium chlorite.

Experimental

All of the chemicals that were used in this research were of reagent grade. Uranyl nitrate was used as the starting material in the preparation of uranyl perchlorate. The nitrate was dissolved in a solution of perchloric acid, which was in slight excess of the stoichiometric amount required to convert it to the perchlorate. The mixture was heated until it became an orange viscous mass and most of the nitrate was volatilized as nitric acid. After it was cooled, more perchloric acid was added and the above procedure was repeated until spot checks of the concentrated (>10 M) solution showed a nitrate concentration of $<10^{-4}$ M. The indicator used for this was diphenylbenzidine dissolved in concentrated sulfuric acid. The resulting uranium perchlorate pentahydrate was recrystallized twice from water.[4]

It was critical for this study that the uranium solutions be free

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[1] D. M. H. Kern and G. Gordon in "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, New York, N. Y., 1964, p. 655.

[2] J. Barnett, Thesis, University of California, 1935.

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