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Laser Induced Optical Activity of Acido Complexes of Cobalt(III) and Chromium(III)*

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Irradiation of racemic octahedral complexes of Cobalt(III) and Chromium(III) with a laser beam at wavelengths close to the maximum of circular dichroism bands resulted in induction of optical activity in the complexes. In the case of trisoxalato Co^{III}, Cr^{III} and di-μ-hydroxy tetraxalato dicobaltate(III) photostationary states were attained within an hour with respect to induced optical activity. The induction of optical activity has been interpreted as due to the dissymmetry factor. The extent of photoresolution amounts to a few per cent in these complexes.

Introduction

The chemistry of metal oxalato complexes has been investigated in detail by Harris and coworkers.[1-5] Photochemical and thermal racemization rates of d-$K_3Cr(ox)_3$ in dimethyl sulphoxide water mixtures have been determined and the importance of hydrogen bonding ability of the solvent has been pointed out.[6] During the course of racemization studies, some preliminary experiments on the laser irradiation of dl-$K_3[Cr(ox)_3]$ showed induction of optical activity into the complex. Following this experimental observation we extended the study to a few acido complexes of Co^{III} and Cr^{III} to see whether photoresolution is a general feature of these systems.

Experimental Section

The complexes $Co(en)_3^{3+}$, $Co(ox)_3^{3-}$, and $Cr(ox)_3^{3-}$ (en ≡ ethylenediamine, ox ≡ oxalate) were prepared according to the procedures in Inoganic Syntheses.[7] $Cr(Mand)_3^{3-}$ and $Cr(DTC)_3$ (Mand ≡ Mandelate, DTC ≡ diethyldithiocarbamate) complexes were prepared by heating a mixture of chromium nitrate and the ligand in stoichiometric proportions whent the corresponding complexes precipitated out of the solution. $Co(thox)_3^{3-}$ (thox ≡ thiooxalate) and ($[Co(OH)(ox)_2]_2^{4-}$) (Durrant's salt) were prepared following the procedures given in the literature.[8,9]

The optical activity was measured in a 10 cm. cell with the help of a Perkin-Elmer Spectropolarimeter model 141 at 589 nm. The readings were accurate to 0.001.

Irradiation was performed using an Argon ion laser for wavelengths 488.0 nm. and 514.5 nm. and a He-Ne laser for 632.8 nm. The general procedure consisted of irradiating a 0.01 *M* solution of the dl complex in a 10 cm. quartz cell at room temperature with the laser beam for a definite period of time. A one-ml. aliquot from the irradiated sample was diluted to 10 ml. with the solvent and the optical activity was determined. The thermal blank was similarly diluted and this was used for the determination of the optical activity of the dark solution. Chomium mandelate in DMSO, dithiocarbamato complex in chloroform, and chromium oxalate in 40 v/v DMSO were used and the other complexes were examined in aqueous solution.

Results and Discussion

Tsuchida[10] was the first to report the resolution of an inorganic complex compound, namely trisoxalato Cobalt(III) anion by irradiation with circularly polarized light. The circular dichroism values of diastereomers in a racemic complex are equal and opposite in sign, a condition which leads to unequal absorption of circuarly polarized light by the diastereomers. Thus on irradiating the dl complex at a wevelength where thc complexe has maximum value for circular dichroism and a low absorption, the reaction may proceed asymmetrically, inducing optical activity into the system.

The complexes investigated in this study do satisfy the conditions referred to above and as a result give rise to optical activity. The wavelengths of irradiation (table I) were as far as possible close to the wavelengths of maximum circular dichroism values, since it was dictated by the emission lines of Argon ion and

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(*) Some of the results reported in this paper were obtained in 1968.

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Table I. Data on induced optical activity of Co^{III} and Cr^{III} complexes.

Complex	t(Min)	(A°)	0.A [a]
$[Co(en)_3]^{3+}$	90	4880	0.002
$[Co(thox)_3]^{3-}$	30	5145	0.003
$[Co(ox)_3]^{3-}$	60	6328	0.005
$[Co(ox)_2(OH)_2Co(ox)_2]^{4-}$	90	6328	0.005
$[Cr(Mand)_3]^{3-}$	150	5145	0.003
$[Cr(DTC)_3]$	90	6328	0.004
$[Cr(ox)_3]^{3-}$	30	5145	0.005

[a] Precision is ± 0.001.

Helium-Neon lasers. The maximum amount of optical activity induced in these systems is given in table I. The systems studied clearly fall into two categories, namely a) those which attain photostationary states as a function of time and b) systems which are irregular in behaviour. The results show that $Cr(ox)_3^{3-}$, $Co(ox)_3^{3-}$ and $[Co(ox)_2(OH)]_2^{4-}$ attain photostationary states within 30,60 and 90 minutes respectively (Figure 1). Although the latter two complexes are known to undergo redox decomposition, it was found that the decomposition is only significant at shorter walengths so that the amount of Co^{II} produced in these systems at 632.8 nm. is quite small. The optical activity in these complexes attained an equilibrium value and retained this value so that thermal racemization could be studied with the photoresolved solutions unlike earlier reports.[10]

The maximum extent of photoresolution is governed by the dissymetry factor[11] (CD/ε) and this amounts to 4 and 2 percent in the case of $Cr(ox)_3^{3-}$ and $Co(ox)_3^{3-}$ respectively. The complex (+) $Cr(ox)_3^{3-}$ has a CD of 2.83 M^{-1} cm.$^{-1}$ [11] at 552 nm and E of 74 M^{-1} cm.$^{-1}$. Using these values the dissymmetry factor works out to be 0.04. The maximum possible resolution has been calculated using the equation $C_+E_+ = C_-E_-$ where C and E are concentrations and absorptivities of the enantiomers respectively. The limiting ratio of C_+/C_- $(5+0.04)/(5/0.04)$ predicts a value of 1.016 using 10 mM of $Cr(ox)_3^{3-}$ solution. Using a value of +1600° at 589 nm for the specific rotation, the maximum expected value of optical rotation is 0.0051 which is in very good agreement with the experimentally observed value of 0.005. A similar calculation was performed for a 10 mM solution of $Co(ox)_3^{3-}$ using a CD of 3.30[11] at 617 nm, E of 153 at 602 nm and a specific rotation of +3000° at 589 nm and the calculated value of 0.0054 is in reasonable agreement with the observed value of 0.005. Although the thermal racemization rate is quite fast in the case of $Cr(ox)_3^{3-}$, the rate is diminished due to the fact that the solvent system is 40 v/v DMSO solution. Hence the very good agreement between the calculated and experimentally observed rotations.

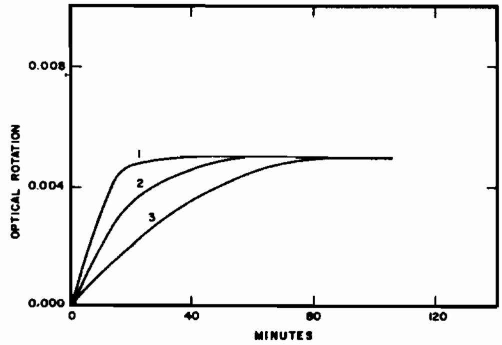

Figure 1. Optical rotation as a function of time. 1. $Cr(ox)_3^{3-}$ 2. $Co(ox)_3^{3-}$ 3. Durrant's Salt. $[Co(ox)_2Co(ox)_2]^{4-}$.

The other systems studied did not appear to reach photostationary states and this may partly be due to redox decomposiion in the case of Co^{III} systems. At present it is not clear why $Cr(DTC)_3$ and $Cr(mandalate)_3^{3-}$ fail to attain photostationary states since no side reaction such as decomposition occur in these systems. Thus it appears that photochemically one can induce optical activity in Cr^{III} and Co^{III} systems at wavelengths of high circular dichroism and low absorption.

If the photochemical reaction is one of inversion of an isomer to its enantiomer, one can achieve photoresolution of the complex provided the thermal racemization rate is slow, as in the case of $Cr(ox)_3^{3-}$ in water-DMSO mixtures.

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