

## The Circular Dichroism of the Outer-sphere Complex of the (+)-Co en<sub>3</sub><sup>3+</sup> Ion with Nitrosonaphtholate Ions in Chloroform Solution

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The extraction of (+)-Co en<sub>3</sub><sup>3+</sup> ions into chloroform from an aqueous solution containing nitrosonaphtholate ions has been followed by measuring the circular dichroism of the complex. It is shown that the extracted species is an outer-sphere complex [Co en<sub>3</sub>(nitrosonaphtholate)<sub>3</sub>].

The spectral properties of this complex is discussed in relation to the outer-sphere—inner-sphere substitution reaction that occurs on heating.

Although the Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and the Co en<sub>3</sub><sup>3+</sup> ions are usually extremely inert in regard to substitution in the inner coordination sphere, examples are recorded when the amine ligands of such ions are replaced by others. Apart from the well-known heterogeneous catalytic reactions involving, *e.g.*, active carbon,<sup>1-3</sup> there are also reactions in homogeneous solutions of this type. Ablov<sup>4</sup> reported that 8-hydroxyquinoline reacts with Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> when heated on the steam-bath producing Co(oxinate)<sub>3</sub>. Neville and Gorin<sup>5</sup> reported that tris-cysteinato cobalt(III) was formed from hexammine cobalt(III) chloride. Larsson and Norman<sup>6</sup> found that diethyldithiocarbamate ions (dte<sup>-</sup>) react with Co en<sub>3</sub><sup>3+</sup> to form the complexes Co(dte)<sub>3</sub>, easily extracted into organic solvents.

It can be argued that such reactions are homogeneously catalyzed by small amounts of Co(II) species, originally present or formed as intermediates. However, it was suggested by Larsson and Norman<sup>6</sup> that such reactions could also proceed through the labilization of the inert Co—N bonds by the action of one or more ligands bound in the outer-coordination sphere. If, *e.g.*, electron-filled orbitals of the latter ligands interact with the antibonding e<sub>g</sub><sup>\*</sup> orbitals of the central group, the Co—N bonds would tend to be less firm and, consequently, a dissociative process could take place. In order to decide between these two possible mechanisms, it is necessary to study an outer-sphere ligand that reacts with Co(II) species by oxidizing these to a Co(III)

complex. In such a case it seems unlikely that any Co(II) intermediates could ever be formed from the original Co(III)N<sub>6</sub> complexes.

It was found in this laboratory—as it certainly may have been found earlier elsewhere—that a solution of 1-nitroso-2-naphthol dissolved in an ammonium ion-ammonia buffer containing Co en<sub>3</sub><sup>3+</sup> ions produced a clear-red precipitate when heated on the steam bath. As this precipitate dissolved in chloroform and carbon tetrachloride, it can be rather safely assumed to be Co(nitroso-naphtholate)<sub>3</sub>. The reaction is thus analogous to that described by Ablov.<sup>4</sup> As the Co(nitrosonaphtholate)<sub>3</sub> complex, well-known from analytical chemistry, is known<sup>7</sup> to be formed from Co(II) species that are oxidized by an excess of nitrosonaphthol, it seems that one has here an example of the outer-sphere initiated type of reaction.

#### PLAN OF INVESTIGATION AND EXPERIMENTAL PROCEDURE

In order to verify the theory that an outer-sphere Co en<sub>3</sub><sup>3+</sup>—nitrosonaphtholate interaction actually existed, some extraction experiments were performed. Using the optically active ion (+)-Co en<sub>3</sub><sup>3+</sup> it was demonstrated that this ion could be extracted from an aqueous NH<sub>4</sub><sup>+</sup>—NH<sub>3</sub> buffer into a chloroform phase containing 1-nitroso-2-naphthol: It was proved that the organic phase exhibited a circular dichroism, after equilibration, in the same wavelength region as does the Co en<sub>3</sub><sup>3+</sup> ion. It was, therefore, probable that the extracted species was the neutral outer-sphere complex ((+)-Co en<sub>3</sub>)(nn)<sub>3</sub>; (nn will here denote the nitrosonaphtholate ion).

In order to prove that no decomposition or substitution reaction had occurred and that the products of such reactions were not responsible for the observed circular dichroism, the following procedure was adopted: After proper separation, a known volume of each phase was treated with aqueous hydrochloric acid (in the case of the aqueous phase, a certain volume of chloroform was added) and reequilibrated. After separation the circular dichroism of the organic phase was determined.

The absorption spectra were recorded by a Hitachi EPS-3 T spectrophotometer and the circular dichroism spectra by a Roussel Jouan Dichrographe, Model B. All measurements were performed at 25°C.

#### RESULTS

This procedure forces all the nitrosonaphthol into the chloroform phase, and all the Co en<sub>3</sub><sup>3+</sup> ions into the acidic aqueous phase. The concentration of re-extracted Co en<sub>3</sub><sup>3+</sup> could then be calculated from the observed circular dichroism and the known molar circular dichroism of (+)-Co en<sub>3</sub><sup>3+</sup> at the concentration of hydrochloric acid (about 0.1 M) that was used. The results of this procedure are given in Table 1. It is evident that all originally extracted Co en<sub>3</sub><sup>3+</sup> can be re-extracted and that, consequently no decomposition occurs.

As we now know the concentration of the Co en<sub>3</sub>(nn)<sub>3</sub> complex in the chloroform phase the molar circular dichroism of this complex could be determined. The resulting CD spectrum in the wavelength range, in which measurements could be performed unobstructed by the strong absorption of the nitrosonaphthol, is presented in Fig. 1. It is seen that the magnitude is about ten times that usually found for the Co en<sub>3</sub><sup>3+</sup> ion.

The absorption spectrum of the chloroform phase—diluted to 1/21 of its original equilibrium concentration—was also recorded. It was found that

Table 1. Checking of the conservation of the amount of (+)-Co en<sub>3</sub><sup>3+</sup> after extraction. ( $\epsilon_1 - \epsilon_r$  of (+)-Co en<sub>3</sub><sup>3+</sup> in a 0.1 M HCl solution = 1.95 M<sup>-1</sup>cm<sup>-1</sup>. A 2 cm cell was used in the CD measurements.) Solutions before the original extraction:

4 ml 4.80 mM (+)-Co en<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub> in 2 M NH<sub>3</sub>, 0.1 M NH<sub>4</sub>Cl.  
4 ml 33 mM nitrosonaphthol in CHCl<sub>3</sub>.

	Observed deflection of the equilibrated HCl-phase	Observed CD of the equilibrated HCl-phase	Concentration of (+)-Co en <sub>3</sub> <sup>3+</sup> in the equilibrated HCl-phase	Concentration of (+)-Co en <sub>3</sub> <sup>3+</sup> in the CHCl <sub>3</sub> phase	Concentration of (+)-Co en <sub>3</sub> <sup>3+</sup> in the aqueous phase
<i>Experiment 1.</i> 1 ml of the CHCl <sub>3</sub> phase + 5 ml 0.1 M HCl	5.6 ± 0.3 mm	5.6 × 1.5 × 10 <sup>-4</sup>	$\frac{5.6 \times 1.5 \times 10^{-1}}{2 \times 1.95}$ = 0.215 mM	5 × 0.215 = = 1.08 mM	
1 ml of the aqueous phase + 5 ml 0.1 M HCl + 2 ml CHCl <sub>3</sub>	15.8 ± 0.3 mm	15.8 × 1.5 × 10 <sup>-4</sup>	$\frac{15.8 \times 1.5 \times 10^{-1}}{2 \times 1.95}$ = 0.608 mM		6 × 0.608 = = 3.65 mM
<i>Experiment 2.</i> 3 ml of the CHCl <sub>3</sub> phase + 5 ml 0.1 M HCl	15.9 ± 0.3 mm	15.9 × 1.5 × 10 <sup>-4</sup>	$\frac{15.9 \times 1.5 \times 10^{-1}}{2 \times 1.95}$ = 0.612 mM	$\frac{1}{2} \times 0.612 =$ = 1.02 mM	
2 ml of the aqueous phase + 4 ml 0.1 M HCl + 2 ml CHCl <sub>3</sub>	33.7 ± 0.3 mm	33.7 × 1.5 × 10 <sup>-4</sup>	$\frac{33.7 \times 1.5 \times 10^{-1}}{2 \times 1.95}$ = 1.296 mM		3 × 1.296 = = 3.89 mM
Mean values				1.05 mM	3.77 mM
Amount of (+)-Co en <sub>3</sub> <sup>3+</sup> originally present (μmoles)				4 × 4.80	
» » (+)-Co en <sub>3</sub> <sup>3+</sup> present after extraction (μmoles)				4 × 1.05 + 4 × 3.77 = = 4 × 4.82	

the spectrum on a logarithmic scale could be superimposed on a plot of log  $\epsilon$  of a pure nitrosonaphthol solution in those parts of the spectrum, where nitrosonaphthol has its absorption maxima (275 nm and 380 nm). In the range 290–330 nm and 400–500 nm there was found an excess absorbancy compared to the nitrosonaphthol spectrum. This excess must correspond to the part of the absorption that is caused by the nitrosonaphtholate ions extracted together with the Co en<sub>3</sub><sup>3+</sup> ions, at least in the 400–500 nm range. The spectra of nn and Hnn measured by Dyrssen and Johansson<sup>8</sup> indicate a large difference of molar absorptivity of the two species in this range. The excess absorbancy in the 290–330 nm range may be caused, partly by the larger value of  $\epsilon_{nn}$

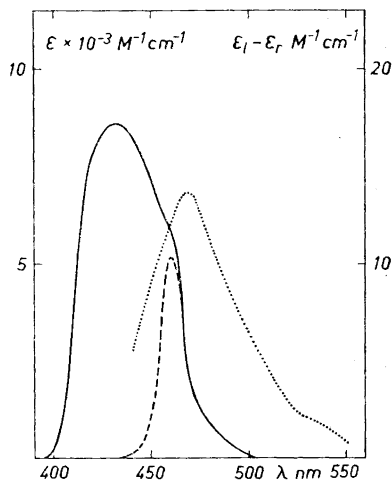


Fig. 1. Molar circular dichroism (·····) and molar absorptivity (—) of the complex (+)-Co en<sub>3</sub> (nitrosonaphtholate)<sub>3</sub> extracted into chloroform.

The curve (-----) represents the part of the absorption that originates from the *d*-*d* transition.

(especially in the 290–300 nm range), and partly by the absorption of the Co en<sub>3</sub><sup>3+</sup> ion, but also by a charge-transfer absorption band characteristic of outersphere complexes and usually found in this region. In Fig. 1 the excess absorbancy has been calculated as molar absorptivity in regard to the cobalt concentration of the chloroform phase (Table 1). Now, if our assumptions are correct, the maximum molar absorptivity should be three times the relative excess of the molar absorptivity of nn and Hnn at the same wavelength (430 nm). This excess was estimated to be  $2.84 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  from the data of Dyrssen and Johansson<sup>8</sup> by once more using the  $\log \epsilon_{\text{Hnn}}$  as a base line in relation to  $\log \epsilon_{\text{nn}}$ . Remembering that these authors measured their spectra on aqueous solutions, one can consider the agreement between the value of maximum absorptivity from Fig. 1 ( $8.60 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $3 \times 2.84 \times 10^3 = 8.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  as satisfactory. This agreement is then an independent indication that the extracted outer-sphere complex is the neutral species Co en<sub>3</sub>(nn)<sub>3</sub>.

#### DISCUSSION

Close examination of the molar absorptivity curve of Fig. 1 reveals a shoulder at about 480 nm. By resolution of the composite band, the band indicated in Fig. 1 by a dotted line was obtained. From the position of this band and the fact that the Hnn and nn spectra show<sup>8</sup> an isosbestic point here it seems most reasonable that it corresponds to the first *d*-*d* transition of the Co en<sub>3</sub><sup>3+</sup> ion. This transition is magnetically allowed and gives rise to the circular dichroism observed in this part of the spectrum. It is, therefore, interesting to note that the absorption intensity is about ten times that which is usually found. Now we recall that the molar circular dichroism has also been found to be about ten times as great as the normal value of the (+)-Co en<sub>3</sub><sup>3+</sup> ion. It then seems that the increase of circular dichroism reflects an increase of rotational strength of the transition in question and that this

increase in its turn is caused by the increase of the electric transition moment that is reflected by the observed increase of absorption intensity.

Furthermore the only possible reason for such a great increase of the intensity of the formally forbidden  $d-d$  transition of  $\text{Co en}_3^{3+}$  can be an unusually strong coupling between this transition and a charge-transfer transition from which the  $d-d$  transition "borrows" a considerable amount of intensity. This charge-transfer transition is probably the one indicated by the excess of absorbancy in the 300–330 nm range referred to above.

The usefulness of a scientific hypothesis is measured by its ability to predict previously not known facts. It has been suggested<sup>6</sup> that the power of outer-sphere ligands to labilize the bonds of an inert inner-sphere complex depends on the coupling of filled outer-sphere ligand orbitals and unfilled inner-sphere orbitals. From this hypothesis and the observed fact that nitrosonaphtholate ions produce such a labilizing effect in  $\text{Co en}_3^{3+}$ , one expects an effective coupling between charge transfer transitions and the  $d-d$  transitions of the  $\text{Co en}_3^{3+}$  ion. Such a coupling has now actually been found.

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