A Proof for Sterically Specific Outer Sphere Complex Formation with [Co(en)₃]³⁺

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Werners observation,[1] that the molecular rotation of a dissymmetric metal complex ion is more or less affected by the "gegenion" has been studied recently in a number of investigations [2-5] leading to the conclusion that the effect is almost certainly caused by ion-association. The effects are larger the greater the charge and polarizability of the anion.

Expressed in terms of the rotational strength, R, measured by the circular dichroism band area, the principal changes which occur on increasing the anion concentration consist, in the case of $(+)$-Co(en)$_3$$^{3+}$, of a decrease in $R(E_a)$ and an increase in $R(A_2)$. Additionally there is a small increase in $R(E_b)$ and a new charge transfer band appears at lower wavelengths. Qualitatively the same behaviour is found with the tris-diamine complexes of chromium(III) and rhodium(III).[6] The most important anions that have been reported to induce strong effects are: PO_4^{3-}, $S_2O_3^{2-}$, $Se_2O_3^{2-}$, and $Fe(CN)_6^{4-}$,[5,7,8] but other anions in high concentration also give effects. Bjerrum has pointed out [9] that optical activity measurements are unreliable when the optical medium (refractive index) is changed radically. Larsson has reported [3,4] an extremum in the dependence of the optical rotation of the Co(en)$_3$$^{3+}$ ion on the $S_2O_3^{2-}$ concentration, interpreted to be caused by the formation of at least two complexes. The effect is reversed as the asymmetric field is cancelled by a symmetric association of a second or third $S_2O_3^{2-}$ ion. Bjerrum proposes,[10] however, that the latter effect may be caused by the change in refractive index with higher thiosulphate concentration.

The present communication shows that anions of ethylenediaminetetraacetic acid (EDTA = H$_4$Y) also strongly affect the circular dichroism (CD) of $(+)$-Co(en)$_3$(ClO$_4$)$_3$
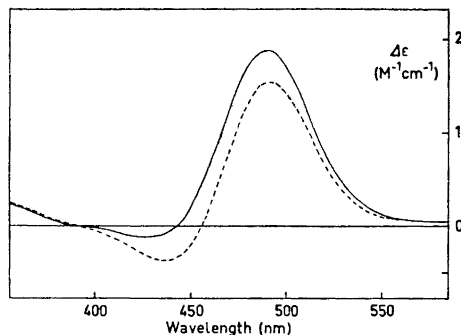
Fig. 1. Circular dichroism spectrum of $(+)$-Co(en)$_3$(ClO$_4$)$_3$; —— in water, — — — in 0.05 M EDTA^{2-}.

(Fig. 1). This effect depends in a complicated way on pH (Fig. 2) and is proved to be due exclusively to association of EDTA with $(+)$-Co(en)$_3$$^{3+}$.

CD was recorded with a Cary 6002 CD−ORD spectrometer on solutions of $(+)$-Co(en)$_3$(ClO$_4$)$_3$+EDTA (using cells with 20 mm path-length) with varied EDTA concentration or varied pH. It was checked that the CD of pure $(+)$-Co(en)$_3$$^{3+}$ was independent of pH.

Table 1.

$C_{Co(en)_3^{3+}}$ (mM)	$C_{EDTA} = C_{Th(NO_3)_4}$ (mM)	$\theta_{max(470)}$ (°)	$\theta_{max(490)}$ (°)	$\dfrac{\theta_{max(490)}}{\theta_{max(430)}}$
5.00	0	−0.040	0.610	15.3
5.00	25.0	−0.040	0.611	15.3
5.00	50.0	−0.045	0.603	13.4

24

Finally, solutions of $(+)$-Co(en)$_3{}^{3+}$ with and without EDTA and Th(NO$_3$)$_4$ (in equal concentrations) were compared (Table 1). The measured ellipticities at the peaks at 430 nm and 490 nm, respectively, and the ratio between them are given in the figures. The latter quantity should better account for those effects not due to the medium.[5]

The "Thorium experiment" (Table 1) shows that the CD-effect is in fact caused by the formation of a complex between Co(en)$_3{}^{3+}$ and EDTA, and not by a different refractive index of the EDTA-solution, as the effect is fully cancelled by the presence of the Th^{4+} ions, which complex with EDTA (the total EDTA concentration was not changed, and a test with only Th(NO$_3$)$_4$ added to the $(+)$-Co(en)$_3$(ClO$_4$)$_3$ solution showed that this salt did not affect the CD-spectrum).
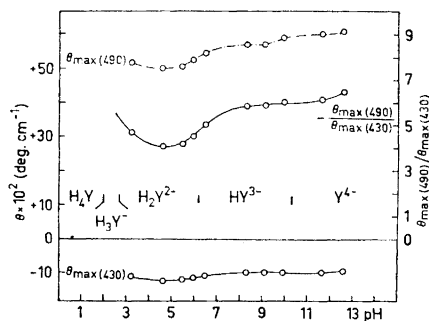

Fig. 2. Circular dichroism (ellipticity units) of 0.05 M $(+)$-Co(en)$_3{}^{3+}$ in 0.05 M EDTA as a function of pH.

$\theta_{\max(490)}$ = ellipticity at the 490 nm peak.
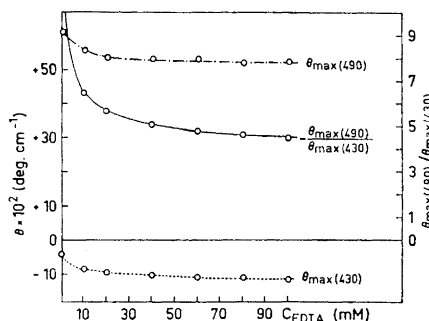$\theta_{\max(430)}$ = ellipticity at the 430 nm peak.

Fig. 3. Circular dichroism (ellipticity units) of 0.05 M $(+)$-Co(en)$_3{}^{3+}$ in EDTA of varying concentration; pH = 6.

Fig. 3 shows a very rapid saturation with increasing EDTA concentration which is explained by the formation of a strong outer-sphere complex [Co(en)$_3$] H$_{4-n}$Y^{3-n} ($n=1$, 2, 3, or 4). There is, however, no extremum in the concentration range studied, so no evidence for the formation of any complexes higher than the 1:1 complex was obtained.* Therefore the non-monotonous behaviour of the curves of Fig. 2 must be caused by rearrangements in [Co(en)$_3$] H$_{4-n}$Y^{3-n} with changing n. (It is obvious that with increasing pH and n the concentration of [Co(en)$_3$] H$_{4-n}$Y^{3-n} cannot decrease but rather must increase.)

If, as has been suggested by Mason,[6],[11] the oxy-anion approaches the $(+)$-Co(en)$_3{}^{3+}$ ion along the C$_3$-axis (hydrogen bonding to the amino hydrogen atoms), the strongest perturbation of the electronic spectrum should be expected with only *one* "C$_3$-plane" occupied. This could happen by association of a twisted dipolar form of H$_3$Y$^-$ or H$_2$Y^{2-} (I) while the more negatively charged species, HY^{3-} and Y^{4-} cancel the effect *via* a random orientation in a coaxial area around the C$_3$-axis (II).

I   II
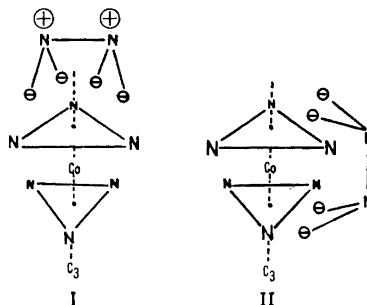
The effects reported here on the circular dichroism spectrum of $(+)$-Co(en)$_3{}^{3+}$ in the presence of EDTA are among the strongest such effects yet reported (*cf.* Smith and Douglas,[7] Mason and Norman[6]) in the region of very low concentration of the active anion and may be used to obtain further information about the bonding

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* If as appears from the curves in Fig. 3 the "half-CD-effect" takes place already at [H$_2$Y^{2-}] ≈ 6 mM, and if this is interpreted to indicate that [Co(en)$_3{}^{3+}$] $\approx$ [Co(en)$_3$(H$_2$Y)$^+$], then the stability constant, $K=$[Co(en)$_3$ H$_2$Y$^+$]/[Co(en)$_3{}^{3+}$][H$_2$Y^{2-}] has a value of roughly 3×10^2 M^{-1} (I ≈ 0.03).

between hexamine metal complex ions and polarizable anions.* It should also be of great value to correlate the spectroscopic effect with the geometry of the perturbing field.**

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* A synthesis of Co(en)₃ EDTA for the purpose of an X-ray structure determination is under way.

** It has been found in this laboratory that $Co(en)_3^{3+}$ is labilized by UV-irradiation so that EDTA, probably already co-ordinated in the outer sphere, can form Co(III)EDTA. In this reaction the absolute configuration of the chelate complex is not retained.[12]

Heteroaromatic Boron Compounds

V. On the Synthesis of a Dithienoborepin

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In connection with our work on heteroaromatic boron compounds, we are interested in studying the physical and chemical properties of borepin (I) derivatives, which are isoelectronic with the
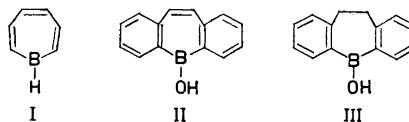
aromatic tropylium cations. A first attempt to reach the borepin system was made by van Tamelen *et al.*[1] in 1960, who prepared the dibenzoborepin (II) starting from *o,o′*-dilithiobibenzyl and butyl borate to obtain the anhydride of the borinic acid (III), which was dehydrogenated to II by side-chain bromination with N-bromosuccinimide followed by dehydrohalogenation with methanolic sodium methoxide. In their preliminary report van Tamelen *et al.* did not make clear the extent of aromatic stabilization in II. According to Dewar[2] great stabilization should not be expected, in view of the low stabilization of the dibenzotropylium ion.[3-5]

In another preliminary communication Leusink *et al.*[6] describe the synthesis of the 3-phenyl-3-benzoborepin IV, which was prepared by reacting the tin derivative V, obtained from *o*-diethynylbenzene (VI) and dimethyltinhydride, with phenyl boron dichloride.[6]

From the stability of IV towards air-oxidation and from its UV and NMR spectral data, Leusink *et al.* concluded that IV had aromatic properties.

Pettit and coworkers[7] on the other hand have shown that annelation of a thiophene ring to the tropylium ion increases its stability. Thus the thienotropylium ion VII has $pK_{R^+} = +6.0$, while that of the