SHORT COMMUNICATION

Splitting of the First Band of [Co^{III}(X)(edtaH)]-type Complexes

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Recently it was reported[1] that the absorption band of rare-earth cation split into several bands by interacting with EDTA in solution. The main purpose of the present communication is to report that somewhat similar splitting occurred with a cobaltic EDTA complex anion.

The visible and ultraviolet absorption spectra of [Co^{III}(edta)]Na·4H$_2$O, [Co^{III}(NO$_2$)(edtaH)] Na·H$_2$O and [Co^{III}(Br)(edtaH)]Na·3H$_2$O* were examined. The salts were prepared by the method of Schwarzenbach[2]. Measurements were made by a Beckman DU spectrophotometer. The spectra of the bromo complex was measured in 60% perchloric acid solutions to prevent its aquation, and the other two salts in aqueous solutions. The absorption curves obtained and their analyses are shown in Figs. 1 and 2. The curve analyses were made by use of the same method as described in a previous paper[3].

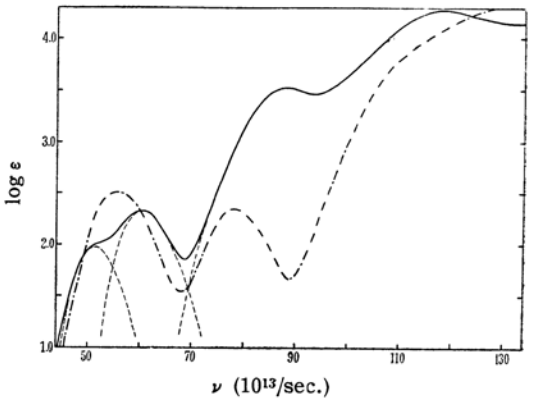

Fig. 1. Absorption curve of the nitro complex.
——— [Co^{III}(NO$_2$)(edtaH)]Na·H$_2$O: Ia band, ν_{max}=60.4 (log ε_{max}=2.32); Ib band, 51.4 (1.97); nitro specific band, 88.6 (3.52); third band, 118.5 (4.27).
-·-·-·- [Co^{III}(edta)]Na·4H$_2$O: first band, 55.9 (2.51); second band, 78.1 (2.36).

As is seen in Fig. 1, the first absorption band of [Co(NO$_2$)(edtaH)]$^-$ distinctly split

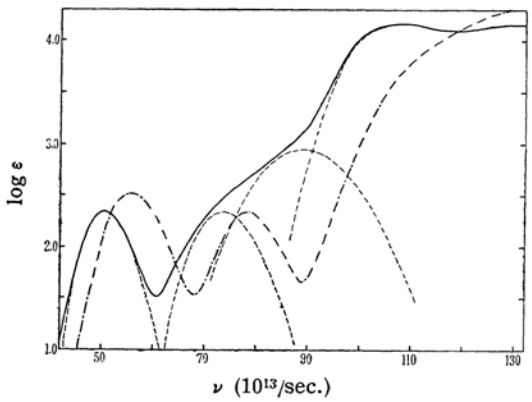

Fig. 2. Absorption curve of the bromo complex.
——— $[Co^{III}(Br)(edtaH)]Na\cdot 3H_2O$: first band, $\nu_{max}=50.6$ ($\log \varepsilon_{max}=2.34$); second band, ca. 73.5** (ca. 2.34); bromo specific band, 89.0 (2.95); third band, ca. 108 (4.16).
-·-·-·- $[Co^{III}(edta)]Na\cdot 4H_2O$.

into two components. This is the first example of such splitting in connection with the complexes containing one or more nitro ligands. The Ia-component is in the region of shorter wave lengths as compared with the first band of $[Co(edta)]^-$. This is in agreement with what is expected from the higher position of the nitro-group on the spectro-chemical series. The sub-component Ib is in the long wave length side of the first band of $[Co(edta)]^-$. Contrary to the nitro complex, no splitting is observed in $[Co(Br)(edtaH)]^-$ (Fig. 2). Since distinct splittings were reported[4,5] for $[Co(NH_3)_5(Br)]^{2+}$ and *trans*-$[Co(en)_2(Br)_2]^+$, the present result is rather unexpected. The reason for this is unknown. To solve the problem it will be necessary to collect more extensive data for the spectra of the complexes belonging to several different structural types.

The occurrence of a nitro or bromo specific band in these nitro or bromo complexes confirms the opinion that these complexes contain the EDTA anion as quinquedentate ligand. The third absorption bands due to co-ordination of the nitro and bromo anions are also observed. The specific and the third bands are equally shifted towards longer wave lengths than those of the corresponding nitro- or bromo-pentammine cobaltic complexes, as follows:

	Specific band	Third band
$[Co(NO_2)(edtaH)]^-$	88.6×10^{13}/sec.	118.5×10^{13}/sec.
$[Co(NO_2)(NH_3)_5]^{2+}$	92.4[6]	125.7[6]
$[Co(Br)(edtaH)]^-$	89.0	ca 108
$[Co(Br)(NH_3)_5]^{2+}$	95.4[4]	118.4[4]

Further work is in progress on the analogous EDTA complexs of Cr(III) and V(III).

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* edta represents a quadrivalent ethylenediaminetetraacetate anion $C_{10}H_{12}N_2O_8^{4-}$ and edtaH a tervalent anion $C_{10}H_{13}N_2O_8^{3-}$.

** This value was estimated by Sone's formula, $\nu_2=1.189\,\nu_1+13.31$ (see ref. (3)).

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3) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).
4) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **266**, 49 (1951).
5) M. Linhard and M. Weigel, ibid., **271**, 101 (1952).
6) M. Linhard and M. Weigel, ibid., **267**, 113 (1951).