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EFFECTS OF SOLVENT MOLECULES ON THE d-d TRANSITION SPECTRUM OF POTASSIUM ETHYLENEDIAMINETETRAACETATOCOBALTATE(III)

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The absorption spectra of the title compound were measured in a variety of solvents. It was found that the peak position (λ_{max}) of the first d-d absorption band is strikingly influenced by solvent molecules. The magnitude of this influence could be estimated by using the acceptor numbers of the solvents.

It was found in a previous work that potassium ethylenediaminetetraacetatocobaltate(III) dihydrate, $K[Co(edta)]\cdot 2H_2O$, is solubilized by macrocyclic polyethers, so called crown ethers, in a variety of organic solvents. In the course of this work, the author found that the color of this cobalt(III) complex changes from reddish violet in water to bluish violet in acetone. This complex is quite stable and inert against the ligand substitution or redox reaction in these solvents, and thus this color change seems to be due to the outersphere interaction of $[Co(edta)]^-$ anion with solvent molecules. In order to elucidate the origin of this color change clearly, the λ_{max} values of the first d-d absorption band of this complex were examined on the basis of the acceptor numbers (AN) which were proposed by Mayer and Gutmann[1] as a measure of estimating the electrophilic ability of solvents. Tentatively the result was compared with the solvent effects on the peak position for $[Co(en)_3](ClO_4)_3$ (en: ethylenediamine).

The complexes were prepared by usual methods. 18-crown-6 ether and solvents were of reagent grade and used without further purification. $K[Co(edta)]\cdot 2H_2O$ was dissolved by the addition of the crown ether in acetone, acetonitrile, ethanol, and methanol. The absorption spectra were measured at ambient temperature in solvents: acetone, dimethylsulfoxide (DMSO), acetonitrile, ethanol, methanol, and water. The λ_{max} values were determined on a Shimadzu UV-210 spectrophotometer. The values are not affected by the addition of various amounts of the crown ether and potassium chloride. Thus, the interaction with 18-crown-6 and potassium ion does not influence the λ_{max} values in these solvents.

In Fig. 1 are plotted the λ_{max} values of the first d-d absorption band of $K[Co(edta)]\cdot 2H_2O$ against the acceptor numbers of the solvents: acetone, DMSO, acetonitrile, ethanol, methanol, and water. The λ_{max} value is shifted to the longer wavelength region as the acceptor number becomes smaller. For example, the λ_{max} value is 536 nm in water (AN=54.8) and is shifted to 547 nm in acetone (AN=12.5). According to the literature,[2] protic solvents such as ethanol,

methanol, and water can strongly solvate the anion through hydrogen bonding, while dipolar aprotic solvents such as acetone, DMSO, and acetonitrile solvate the anion weakly. Therefore, the λ_{max} values in the longer wavelength region are corresponding to those of weakly solvated $[Co(edta)]^-$ anions and the values in protic solvents seem to be greatly contributed by solvating molecules as outersphere ligands

In contrast, this is not the case of $[Co(en)_3]^{3+}$, which is a cation and may be strongly solvated even in aprotic solvents. In this case, the λ_{max} value is not so influenced by solvent molecules: 468 nm in acetone, 468 nm in DMSO, 468 nm in acetonitrile, 468 nm in methanol, and 467 nm in water.

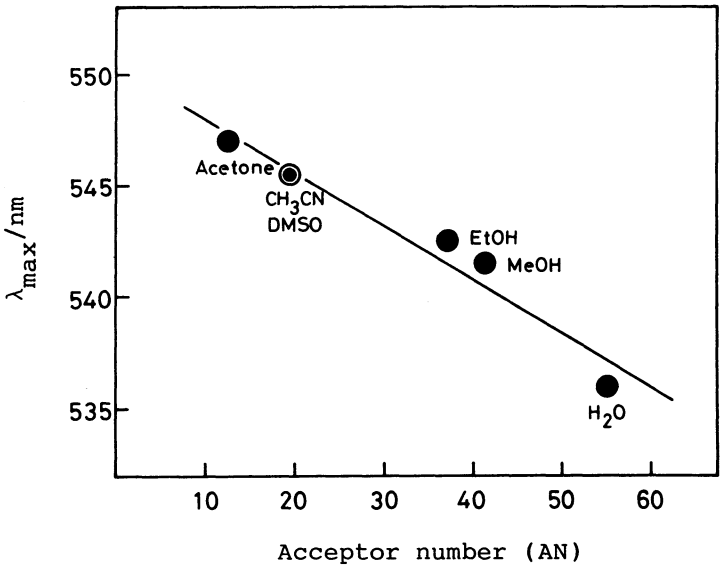

Fig. 1. The relationship between the λ_{max} values of the first d-d absorption band of $K[Co(edta)]\cdot 2H_2O$ and the acceptor numbers of solvents: acetone, DMSO, acetonitrile (CH_3CN), ethanol (EtOH), methanol (MeOH), and water.

Consequently, the colors (corresponding to λ_{max} values) of $[Co(edta)]^-$ anions are caused by the ligand, edta, and differently by solvating molecules. Figure 1 indicates that the plot of the λ_{max} values gives a straight line[3] and thus the λ_{max} value in a solvent can be quantitatively estimated by using the acceptor number of the solvent. The correlation coefficient $\Delta\lambda_{max}$ is 0.24 in this case. Therefore, the peak position λ_{max} in the solvent is calculated by the following equation.

$$\lambda_{max} = \overset{\circ}{\lambda}_{max} - 0.24 \times AN(solvent)$$

where $\overset{\circ}{\lambda}_{max}$ and AN(solvent) refer to the peak position (approximately 550 nm determined by extrapolation) in hexane as a standard solvent (AN=0) and the acceptor number of the solvent, respectively. The first term in this equation corresponds to the inherent peak position of the $[Co(edta)]^-$ anion which is not solvated and the second term to the outersphere ligand effect which is contributed by solvating molecules.

It is concluded that the color of this cobalt(III) complex is changed by the outersphere coordination of solvent molecules and the color change can be predicted by using the acceptor number of the solvent.

References

1) U. Mayer, V. Gutmann, and W. Gerger, Monatsh. Chem., 106, 1235(1975).
2) A. J. Parker, Quart. Revs., 16, 163(1962).
3) The plot of the corresponding wavenumbers (cm^{-1}) also gives a straight line.

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