August, 1988] © 1988 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn., 61, 2967—2968 (1988)* 2967

Solvatochromism of the Co(III) Complexes with Macrocyclic N_3O_3-Type Ligands

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(Received December 24,1987)

Synopsis. The color and visible spectrum of [Co(tacnta)] and [Co(tacntp)]·$3H_2O$ depend remarkably on the acceptor number of the solvent, as also do those of K[Co(edta)]·$2H_2O$ and related chelates. The changes are especially large in the case of [Co(tacntp)]·$3H_2O$, extending to solvents of high acidity. A plausible explanation is given for this solvatochromism.

Two types of solvatochromism are known to take place in solutions of metallic complexes.[1,2] They are: (i) the solvatochromism caused by structural changes in the first coordination sphere, for example, that of [Cu(acac)(tmen)]ClO_4 studied by Fukuda, Sone, and collaborators[1] which depends on the donor number (DN) of the solvent,[3] and (ii) the solvatochromism caused by the solute-solvent interactions in the second coordination sphere, for example, that of [Fe(bipy)$_2$-(CN)$_2$] studied by Schilt[4] which depends on the acceptor number (AN) of the solvent.[3]

Recently, we synthesized the Co(III) complexes of two macrocyclic N_3O_3-type ligands, 1,4,7-triazacyclononane-*N,N′,N″*-triacetate (tacnta) and 1,4,7-triazacyclononane-*N,N′,N″*-tripropionate (tacntp) (cf. Fig. 1). In the course of this work, we noticed that they show a characteristic solvatochromism in polar solvents, which seems to be related to that of K[Co(edta)]·$2H_2O$ and related complexes reported by Taura,[5] Ogino, and collaborators.[6] Since these are all inert 6-coordinated complexes, it seems that the observed solvatochromism is due to the solvent-solute interaction in the second coordination sphere. The outline of our spectral observations, and their plausible explanation, are given in this paper.

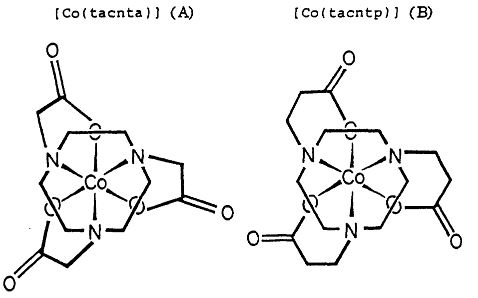

Fig. 1. Structures of the ligands and complexes.

Experimental

Preparation of Ligands. Tacnta was prepared according to the method described in the literature.[7] Tacntp was prepared similarly, but using 3-chloropropionic acid instead of chloroacetic acid. Because they were difficult to purify, the raw products obtained were directly converted to the Co(III) complexes.

Preparation of Complexes. [Co(tacnta)] was prepared according to the method described in the literature[7] (Found: C, 39.31; H, 5.12; N, 11.73%). To prepare [Co(tacntp)]·$3H_2O$, $CoCl_2\cdot 6H_2O$ was added to the aqueous solution of tacntp. After adjusting the pH to ca. 5.5 with NaOH(aq), the mixture was stirred vigorously for several hours, and then evaporated to a small volume, and purified by passing into a column of Sephadex G-15. The eluent was evaporated to a small volume, and methanol was added to it to yield the complex as a violet powder. After washing twice with methanol, the residue was recrystallized from formamide-ethanol. Found: C, 38.78; H, 6.76; N, 9.14%. Calcd for $CoC_{15}H_{30}N_3O_9$: C, 39.57; H, 6.64; N, 9.23%.

Solvents. Methanol was purified by distillation over magnesium. Other solvents (Guaranteed Grade) were used without further purification.

Measurements. The electronic absorption spectra of the complexes were measured on a Hitachi 340 Recording Spectrophotometer using a 10-mm cell at room temperature (ca. 25 °C).

Results and Discussion

Some of the visible absorption spectra of [Co(tacnta)] (A) and [Co(tacntp)]·$3H_2O$ (B) obtained are shown in Fig. 2. Each of them shows two bands: the band I at ca. (19—20)$\times 10^3$ cm^{-1} and the band II at ca. (26—27)$\times 10^3$ cm^{-1}, as expected from their *fac*-N_3O_3-type structure.[8] Both bands shift slightly according to the solvent polarity, so that a remarkable color change from bluish violet to reddish violet comes about.

If the $\tilde{\nu}_{max}$ value of the band I is plotted against the Acceptor Number (AN) of the solvent, it can be seen that there is a good parallelism between these values,

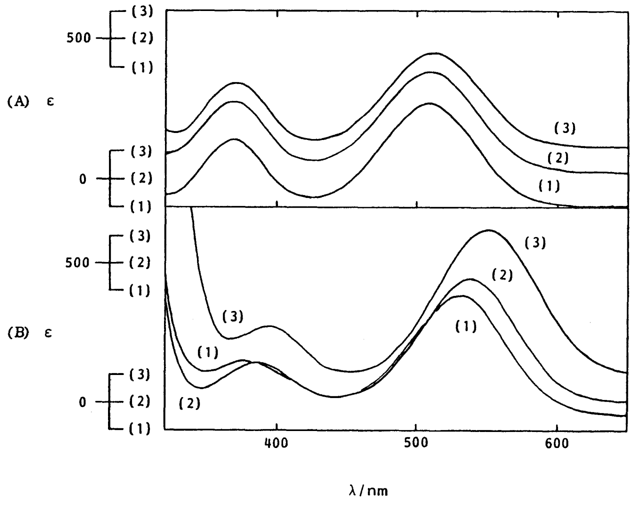

Fig. 2. Electronic spectra of the complexes. A: [Co(tacnta)]. Solvents: 1, HCOOH; 2, H_2O; 3, $HCONH_2$. B: [Co(tacntp)]·$3H_2O$. Solvents: 1, HCOOH; 2, H_2O; 3, $(CH_3)_2SO$.

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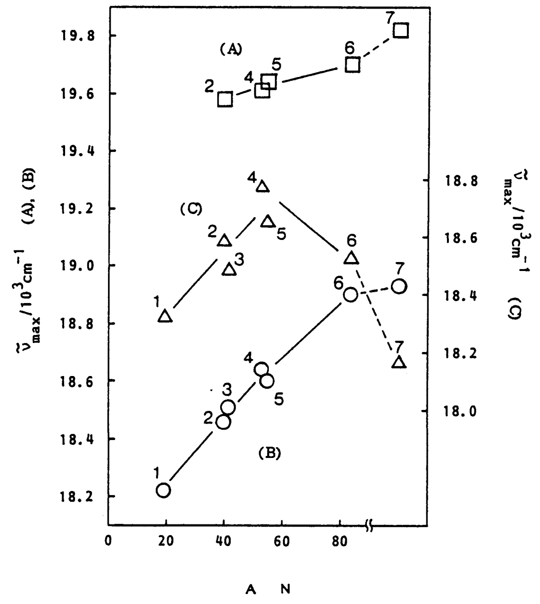
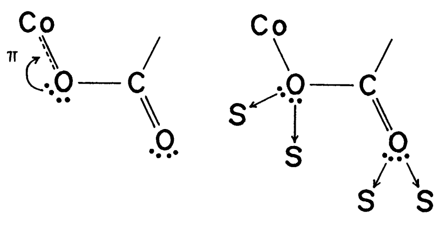


Fig. 3. Relation of $\tilde{\nu}_{max}$ with AN. A: [Co(tacnta)], B: [Co(tacntp)]·$3H_2O$, C: K[Co(edta)]·$2H_2O$.[a)] Solvents: 1, $(CH_3)_2SO$; 2, $HCONH_2$; 3, CH_3OH; 4, CH_3COOH; 5, H_2O; 6, HCOOH; 7, H_3PO_4 (85%).[b)] a) The AN of H_3PO_4 (85%) is expected to be higher than HCOOH, but is not exactly known. So the points 7 are given on a blank scale. b) The points 1, 2, and 3 on curve C were found to be slightly lower than those in the literature,[6)] but the differences ($\Delta\tilde{\nu}$: (0.03—0.06)$\times 10^3 cm^{-1}$) were mostly in the range of experimental error. The points 4, 6, and 7 on the same curve were newly obtained in the present study.



I II

Fig. 4. Effect of solvation by acceptor solvent molecules (S in II) on the structure of a coordinated COO^- group(I).

as that observed with K[Co(edta)]·$2H_2O$ and related complexes.[5,6)] Figure 3 shows such a plot. It can be seen that the rise in $\tilde{\nu}_{max}$ with increasing AN is small with [Co(tacnta)], but with [Co(tacntp)]·$3H_2O$ it is much larger than with K[Co(edta)]·$2H_2O$, the curve of which tends to drop when the AN becomes very large.[9,10)]

One can now explain the solvatochromism as follows. The COO^- groups of these complexes, which are most susceptible to outer influences, are solvated by the polar solvents which accept their lone-pair electrons. The strength of this solvation is governed by the AN of the solvent. This solvation weakens the $(Co \leftarrow O)\sigma$ and π bonds as shown in Fig. 4, by pulling out the lone-pair electrons on the O atoms toward the solvent molecules. The weakening of the σ bonds decreases the value of 10 Dq, but the weakening of the π bonds increases it.[11)] Since the weaker π bonds will be more strongly affected by this kind of solvation, the value of the apparent 10 Dq tends to increase, shifting $\tilde{\nu}_{max}$ to a higher value.

It is also plausible that the large solvatochromism of [Co(tacntp)]·$3H_2O$ is related to the relative weakness of the COO^--Co bonds in it which belong to the more deformable 6-membered chelate rings, as compared with those in the other complexes which belong to the rigid 5-membered chelate rings.

The authors are cordially grateful to Prof. Susumu Takamoto of Gakushuin University for his kind aid in the preparation of the macrocyclic ligands.

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9) This drop which was found in the present study is probably caused by the notable weakening of the $(Co \leftarrow O)\sigma$ bonds in very strong acceptor solvents, which eventually will lead to a decrease in 10 Dq; the fact that the tacnta and tacntp complexes do not show such a drop may be taken as proof of their robustness in such acceptor solvents.

10) A set of curves which are similar in shape, and in the magnitude of the shifts in $\tilde{\nu}_{max}$, to those in Fig. 3 can also be observed with the $\tilde{\nu}_{max}$ values of the band II. Here, however, the accuracy of the curves A and B is lower, since band II is weaker than band I and is more difficult to locate exactly in some cases.

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