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Carbon-13 Nuclear Magnetic Resonance Spectra of Potassium (Ethylenediaminetetraacetato)cobaltate(III) in Organic Solvents

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The carbon-13 NMR spectra of the $[Co(edta)]^-$ (edta = ethylenediaminetetraacetate) anion were observed in water and a variety of organic solvents: ethylene glycol, methanol, formamide, ethanol, 2-propanol, chloroform, dichloromethane, dimethyl sulfoxide, acetonitrile, dimethylformamide, benzonitrile, and dimethylacetamide. The spectra in organic solvents were obtained after 1–2-h accumulations for the concentrated solutions (0.5 M) of the complex anion that were prepared by the addition of a macrobicyclic polyether, cryptand 222, to the solvents. The ^{13}C NMR signals of the coordinated carboxylates are markedly shifted downfield in protic solvents in comparison with aprotic solvents (the greatest difference in chemical shift is 3.9 ppm), while the NMR chemical shifts of methylene carbons of ligands are not significantly influenced by solvent molecules. The magnitudes (δ values) of this downfield shift of the coordinated carboxylate ^{13}C signals are found to be correlated linearly with the electrophilic ability of the solvent molecules. This finding leads to the conclusion that the $[Co(edta)]^-$ anion interacts with solvent molecules through the hydrogen-bonding between solvent hydrogens and carboxyl oxygens of the complex anion.

Introduction

It has been found that potassium (ethylenediaminetetraacetato)cobaltate(III) dihydrate, $K[Co(edta)]\cdot 2H_2O$, is solubilized by macrocyclic polyethers, crown ethers, and cryptand 222, in a variety of organic solvents including chloroform of low polarity (the dielectric constant is 4.8).[1] By use of this phenomenon, in the previous work,[2] the absorption spectra of this cobalt(III) complex were obtained in acetone, acetonitrile, dimethyl sulfoxide, ethanol, methanol, and water, and the peak position of the first d–d absorption band was found to be considerably influenced by solvent molecules. Then, it was proposed that this influence should be due to the outer-sphere interaction between the $[Co(edta)]^-$ anion and solvent molecules because the cobalt(III) complex anion is quite stable and seems to be inert toward the ligand substitution in these solvents. In the present work, in order to obtain more detailed information about this outer-sphere interaction (solvation), the carbon-13 NMR spectra of this complex were measured in a variety of solvents and the values (δ) of chemical shifts for different carbons of the ligand (edta) were examined on the basis of the acceptor numbers (AN) of solvents, which were proposed by Mayer, Gutmann, and Gerger[3] as a measure of estimating the electrophilic ability of solvents.

Experimental Section

Materials. $K[Co(edta)]\cdot 2H_2O$ was prepared by the usual method.[4] Cryptand 222 (Merck), deuterium oxide, and protonated solvents[5] were of reagent grade and were used without further purification. The complex was dissolved by the addition of an excess amount of cryptand 222 in ethylene glycol, methanol, formamide, ethanol, 2-propanol, chloroform, dichloromethane, dimethyl sulfoxide, acetonitrile, dimethylformamide, benzonitrile, and dimethylacetamide.

Measurements. The carbon-13 NMR spectra were recorded at ambient temperature on the solutions of the complex anion (0.5 M) for water and for organic solvents containing cryptand 222 (0.75 M). A JEOL JNM-FX100 NMR spectrometer was operated in the Fourier transform mode at 25.047 MHz. Dioxane in D_2O, which was sealed inside the sample tube, was taken as an external reference (67.4 ppm from TMS). The accumulation of solvent signals was allowed to overflow to keep the memory for the spectrum. A pulse interval of 3.0 s was generally used, and each spectrum was obtained after 1000–1500 scans. The chemical shifts are not influenced by the addition of various amounts of cryptand 222 and by the change of concentration of the cobalt(III) complex.[6] Furthermore, the ^{13}C NMR spectra were measured for the solution of the anhydrous cobalt(III) complex to check the influence of hydrate waters (1.0 M) that dissolve with the dihydrate complex. The hydrate waters do not influence the chemical shifts of the cobalt(III) complex anion.[7] Therefore, it is clear that water molecules contained in the solvents used here are not a problem for the following discussion.

Results and Discussion

In Figure 1 is shown the carbon-13 NMR spectrum of $K[Co(edta)]\cdot 2H_2O$ (edta = $^{-}OOCCH_2(^{-}OOCCH_2)NCH_2CH_2N(CH_2COO^{-})CH_2COO^{-}$) in aqueous solution. The two signals that appear at the low magnetic field (~180 ppm) are assigned to the carbons of the coordinated carboxylates of the axial and equatorial acetates, as indicated in the expanded spectrum.[8] The signals in the region of about 60–70 ppm correspond to the carbons of the backbone ethylene (the part of ethylenediamine) and the methylene carbons of axial and equatorial acetates. The expanded spectrum in this region is also presented in Figure 1. The signals in the region 60–70 ppm are clearly separated into three signals except for the signal of dioxane as a reference. The two signals downfield of this region are assigned to the methylene carbons of axial and equatorial acetates, which are surrounded by slightly different environments.[8] The mode of this NMR spectrum supports the fact that the complex anion exists in aqueous solution as only one species that is completely coordinated in octahedral geometry by a hexadentate ligand, ethylenediaminetetraacetate (edta).

In contrast, the carbon-13 NMR spectrum in acetonitrile, which is presented in Figure 2, includes some signals from the added macrobicyclic polyether, cryptand 222 (C222). These signals could all be assigned as numbered in Figure 2 (expanded spectra) by reference to the assignment of cryptand 221 (C221).[9] Cryptand 222 has trapped the potassium cation for a time longer than the NMR time scale, so that the ^{13}C signals that correspond to

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[1] (a) Taura, T. *Inorg. Chim. Acta* **1985**, *98*, L15. (b) Taura, T. Presented at the 50th Annual Meeting of the Chemical Society of Japan, April 1985 (Abstract I, 1K18).

[2] Taura, T. *Chem. Lett.* **1984**, 2011.

[3] Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235.

[4] Dwyer, F. P.; Gyarfas, E. C.; Mellor, D. P. *J. Phys. Chem.* **1955**, *59*, 296.

[5] The same values of chemical shifts could be obtained in the deuteriated solvents D_2O, CD_3OD, $Me_2SO\text{-}d_6$, and $CDCl_3$.

[6] The ^{13}C NMR spectra for 0.1 M solutions of this complex were preliminarily recorded at 35 °C for H_2O, CH_3OH, C_2H_5OH, $CHCl_3$, Me_2SO, and CH_3CN on a JEOL JNM-FX60 NMR spectrometer operating in the Fourier transform mode at 15.04 MHz. The δ values are the same between 0.5 and 0.1 M solutions within experimental error (±0.1 ppm). It seems that there is no influence of ion association with K^+ or the $K^+\cdot C222$ complex on the ^{13}C NMR chemical shifts of the $[Co(edta)]^-$ anion.

[7] The ^{13}C NMR spectra of the anhydrous salt of this complex anion in CH_3OH and $CHCl_3$ were measured. There is no detectable difference (experimental error ±0.1 ppm) between the chemical shifts for the anhydrous salts and the dihydrate used in this work. The anhydrous salt of this complex was obtained by heating its dihydrate in an oven at 110 °C.

[8] Howarth, O. W.; Moore, P.; Winterton, N. *J. Chem. Soc., Dalton Trans.* **1974**, 2271.

[9] Schmidt, E.; Tremillon, J.-M.; Kintzinger, J.-P.; Popov, A. I. *J. Am. Chem. Soc.* **1983**, *105*, 7563.

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Table I. ^{13}C Chemical Shifts (ppm from TMS) for the Ligand Carbons of $K[Co(edta)]\cdot 2H_2O$ in Water and Organic Solvents

solvent	AN	$-COO^-$[a]		$-CH_2COO^-$[a]		$-CH_2N<$[a]
		ax[b]	eq[b]	ax[b]	eq[b]	en[b]
H_2O	54.8	183.3 (183.0)[c]	182.7 (182.4)[c]	66.3 (66.0)[c]	66.1 (65.8)[c]	64.3 (64.0)[c]
EG		182.4	181.6	66.6	66.2	d
CH_3OH	41.3	181.6	180.9	65.9	65.9	63.8
FA	39.8	181.7	181.0	66.0	66.0	63.9
C_2H_5OH	37.1	181.0	180.4	66.0	66.0	64.0
$2\text{-}C_3H_7OH$	33.5	180.7	180.1	66.5	66.3	64.1
$CHCl_3$	23.1	180.6	180.0	66.0	66.0	63.8
CH_2Cl_2	20.4	180.4	179.7	66.4	66.4	64.4
Me_2SO	19.3	180.0	179.2	66.2	66.2	64.0
CH_3CN	18.9	179.9	179.3	66.0	65.8	63.7
DMF	16.0	179.5	178.9	66.3	65.9	63.8
C_6H_5CN	15.5	179.9	179.3	66.4	66.4	64.1
DMA	13.6	179.5	178.8	66.4	66.0	64.0

[a] edta = $^-OOCCH_2(^-OOCCH_2)NCH_2CH_2N(CH_2COO^-)CH_2COO^-$. [b] ax, eq, and en refer to axial, equatorial, and ethylenic. [c] Reference 9. [d] Overlapped with the signal of solvent carbons.

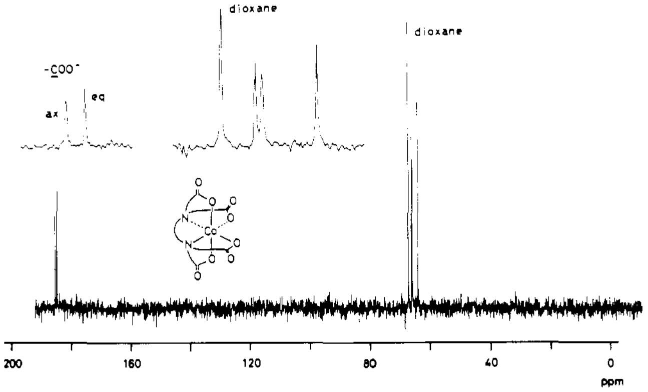

Figure 1. Carbon-13 NMR spectrum of $K[Co(edta)]\cdot 2H_2O$ (0.5 M) in aqueous solution. ax and eq refer to axial and equatorial, respectively.

cryptand 222 containing the K^+ ion ($K^+\cdot C222$) appear separately from those of the free one. The assignment of these signals was carried out by reference to the assignment for $K^+\cdot C221$[9] and by the comparison of the peak heights of the signals. The chemical shifts of these signals do not significantly change in all organic solvents used here; the δ values of C222 carbons in acetonitrile, for example, 70.9, 70.1, and 56.5 ppm for free C222 and 70.8, 68.0, and 54.2 ppm for C222 complexed with the K^+ ion. So, the chemical shifts of cryptand 222 are not significantly influenced by solvent molecules. The region for the $[Co(edta)]^-$ anion in the ^{13}C NMR spectrum shows the same mode of signals as that in aqueous solution. Thus, in all solvents only one species of this complex exists; no carboxylate dissociates from the cobalt(III) ion.

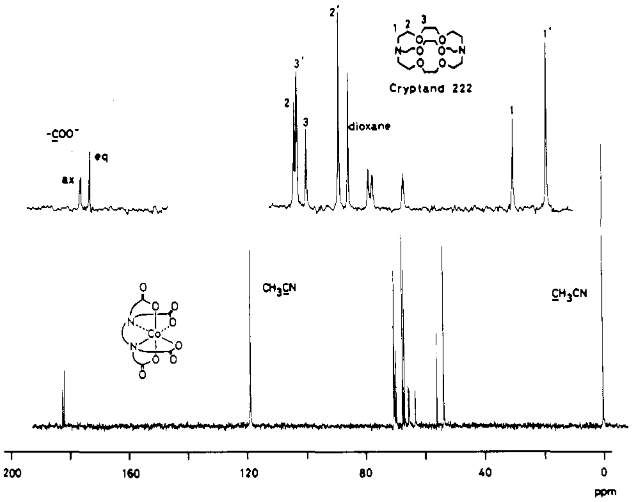

Figure 2. Carbon-13 NMR spectrum of $K[Co(edta)]\cdot 2H_2O$ (0.5 M) in acetonitrile containing cryptand 222 (0.75 M). The signals numbered in the ^{13}C NMR spectrum correspond to the carbon atoms numbered in the structure of cryptand 222 (expanded spectrum). The carbon atoms of the $K^+\cdot C222$ complex are also shown and differentiated by primes.

Solvent Influence on ^{13}C NMR Chemical Shifts. Now we can see the influence of solvent molecules on ^{13}C chemical shifts of the $[Co(edta)]^-$ anion, quantitatively. In Table I are presented the ^{13}C chemical shifts (δ values) for the ligand carbons of $K[Co(edta)]\cdot 2H_2O$ in water and in a variety of organic solvents: ethylene glycol (EG), methanol (CH_3OH), formamide (FA), ethanol (C_2H_5OH), 2-propanol ($2\text{-}C_3H_7OH$), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethyl sulfoxide (Me_2SO), acetonitrile (CH_3CN), dimethylformamide (DMF), benzonitrile (C_6H_5CN), and dimethylacetamide (DMA). It is clear that NMR chemical shifts of carboxyl carbons vary to a considerable extent in these solvents. For example, the values are 183.3 and 182.7 ppm in H_2O (protic solvent) and 179.9 and 179.3 ppm in CH_3CN (aprotic solvent). The differences in both solvents are more than 3 ppm. These differences are larger than those between $[Co(edta)X]$ type inner-sphere complexes,[8] which are coordinated by ligand X = H_2O, Cl, Br, OH, and NO_2 in place of one carboxylate, or $[Co(edda)X_2]$ type complexes,[10] which are coordinated by edda = ethylenediaminediacetate and ligand X_2 = $(NH_3)_2$, $(NO_2)_2$, and $(H_2O)_2$. The solvent influence should be due to the outer-sphere interaction between the complex anion and solvent molecules because the inner-sphere of $[Co(edta)]^-$ anion is completely occupied by the ligand edta as described before. Therefore, this influence is tentatively examined on the basis of the acceptor numbers (AN) of the solvents, which were proposed by Mayer, Gutmann, and Gerger as a measure of estimating the electrophilic ability of solvents.[3] In Table I, was obtained the correlation that the δ values for carboxyl carbons become greater (downfield shift) as the acceptor number of the solvent becomes greater. This means that protic solvents that have large AN values strongly interact in the outer sphere with the carboxylates of the $[Co(edta)]^-$ anion, and this interaction causes the downfield shifts in protic solvents.

Suppose that the downfield shift corresponds to the decrease of the shielding effect in a diamagnetic contribution due to the decrease of the electron density on the carboxyl carbons. This finding leads to the conclusion that carboxyl groups are most strongly electron-withdrawn by water molecules, which have the greatest electrophilic ability of these solvent molecules, and through the hydrogen bonding between water hydrogens and carboxyl oxygens of the $[Co(edta)]^-$ anion.

In contrast to the NMR signals of carboxyl carbons, those of methylene carbons are not so influenced by solvent molecules: 66.3, 66.1, and 64.3 ppm in H_2O and 66.0, 65.8, and 63.7 ppm in CH_3CN. In all other solvents these methylene signals appear in similar positions. Therefore, the solvent molecules could not interact strongly with the sites other than carboxyl groups.

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(10) Gailey, K. D.; Igi, K.; Douglas, B. E. *Inorg. Chem.* **1975**, *14*, 2956.

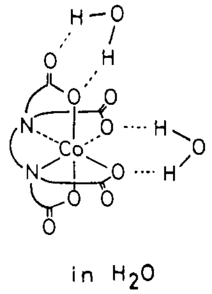

Figure 3. Proposed mechanism for the interactions between the [Co(edta)]$^-$ anion and water molecules.

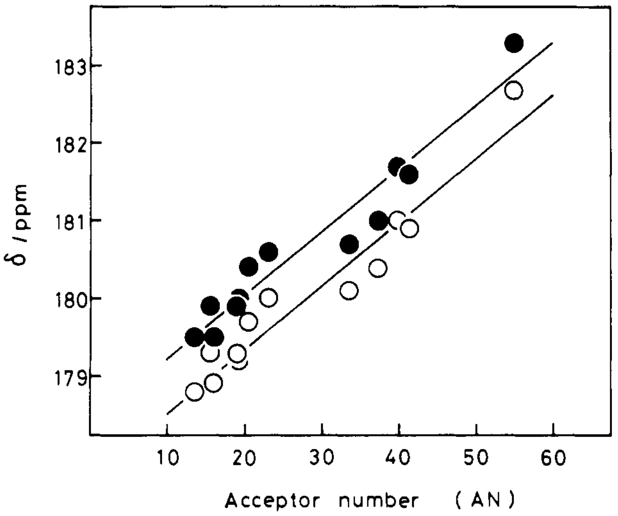

Figure 4. Relationship between the $\delta(^{13}C)$ values of the carboxyl carbons of K[Co(edta)]·2H_2O and the acceptor numbers of the solvents: ●, δ_1 of axial carboxyl carbons; ○, δ_2 of equatorial carboxyl carbons. The data are plotted for the solvents presented in Table I except for EG.

Therefore, the situation is proposed in Figure 3 for the interaction between the [Co(edta)]$^-$ anion and protic solvents such as water. This interaction is supposed to influence the carbon-13 NMR spectrum of K[Co(edta)]·2H_2O.

Correlation with the Acceptor Numbers of Solvents. The chemical shifts (δ values) of carboxyl carbons seem to be correlated linearly with the acceptor numbers of solvents. In Figure 4 are plotted the δ values (ppm) of the carboxyl carbons of K[Co(edta)]·2H_2O against the acceptor numbers of the solvents: H_2O, CH_3OH, FA, C_2H_5OH, 2-C_3H_7OH, $CHCl_3$, CH_2Cl_2, Me_2SO, CH_3CN, DMF, C_6H_5CN, and DMA. Figure 4 indicates that the plots of the δ_1 (filled circles) and δ_2 (open circles) values, which correspond to the chemical shifts of axial and equatorial acetate carboxyl carbons, respectively, give straight lines, and thus the δ values in a solvent can be approximately estimated by using the acceptor number of the solvent. The chemical shifts of the carboxyl carbons in the solvent are calculated by the following equations (error bars are for one standard deviation):

$$\delta_1 = \delta_1{}^\circ + (0.081 \pm 0.007) \times \mathrm{AN(solvent)} \qquad (1)$$

$$\delta_2 = \delta_2{}^\circ + (0.082 \pm 0.007) \times \mathrm{AN(solvent)} \qquad (2)$$

where $\delta_1{}^\circ$, $\delta_2{}^\circ$, and AN(solvent) refer to the chemical shifts ($\delta_1{}^\circ = 178.4 \pm 0.2$ and $\delta_2{}^\circ = 177.7 \pm 0.2$ determined by a linear least-squares analysis) in hexane as a standard solvent (AN = 0) and the acceptor number of the solvent, respectively. The first terms in these equations could correspond to the inherent chemical shifts of the carboxyl carbons of the [Co(edta)]$^-$ anion that is not solvated, and the second terms, to the electron-withdrawing effect that is attributed to solvating molecules.

The second terms in the above equations are quite similar between those for axial and equatorial carboxyl carbons (0.081 ± 0.007 for δ_1 and 0.082 ± 0.007 for δ_2). This indicates that solvent molecules equivalently interact with these carboxyl oxygens; namely, there exists no stereoselective solvation in this system though the environments around the two types of carboxylates are stereochemically different.

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Registry No. EG, 107-21-1; FA, 75-12-7; DMF, 68-12-2; DMA, 127-19-5; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; 2-C_3H_7OH, 67-63-0; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; Me_2SO, 67-68-5; CH_3CN, 75-05-8; C_6H_5CN, 100-47-0; K[Co(edta)], 14240-00-7.