The Effect of Quinolyl Endgroups on Podand Fluctuations – 1-DNMR and 2 D-EXCSY-NMR of Co(II)-Complexes

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Dedicated to Prof. Dr. V. Gutmann on the occasion of his 70th birthday

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Crown Ether, Complex Formation, Ligand Fluctuation, 2D EXCSY NMR

Ligand fluctuations in complexes $[Co(Kr5)]X_2$ (Kr5 = 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane) with X = ClO_4^-, $CF_3SO_3^-$ can be detected by NMR spectroscopy above room temperature in inert solvents such as nitromethane. This unusually slow ligand movement is due to the strong coordination of the quinolyl end groups to the Co(II) ion as demonstrated through measurements with oligo-ethylene-glycols. In contrast to the ^{13}C spectra, the ^1H 2D EXCSY NMR spectra reveal cross peaks which are due to a magnetisation exchange between the chemically non-equivalent protons in the $-CH_2-$ groups of the podand. This process is associated with a movement of the chain segments towards each other.

Introduction

The dynamic behaviour of metal complexes with crown ethers and non-cyclic polydentate ligands depends both on the cavity size of the ionophore and on the chemical nature of the donor atoms [1]. In most cases the ligand fluctuations in these complexes are much faster than solvent exchange reactions with the same donor atom [2]. Therefore, the numbers of chemically nonequivalent nuclei of the free and the coordinated ligands are usually identical in the NMR spectra due to averaging processes. This is true even for paramagnetic transition metal complexes which yield large chemical shifts by ligand coordination, more than 100 ppm can be observed under favourable conditions. This fact may be explained by a change of mechanism if solvent mobilities and crown ether fluctuations are compared. In complexes such as $[Co(CH_3OH)_6]^{2+}$ the solvent mobility shows a dissociative nature (I_d) [3]. In crown ether complexes the dissociation of a donor atom is assisted, however, by the incoming donor atom also connected to the carbon chain. Therefore, an associative mechanism (I_a) should be valid for crown ether fluctuation [2]. This process can be slowed down according to a donor acceptor model if there are alternating strong and weak donor atoms in the multidentate ligand. The introduction of nitrogen donor atoms may lead to an improved metal-ligand interaction, and ligand fluctuations should be slowed down if this dissociation cannot be effectively assisted by a neighbouring weak donor.

These ideas have been tested with the podand 1,13-bis-(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix-5) [4, 5]. This ligand Kr5 consists of two parts, namely two strongly coordinating quinolyl groups and a sterically flexible polyether chain (Fig. 1). This ligand should show weaker coordi-

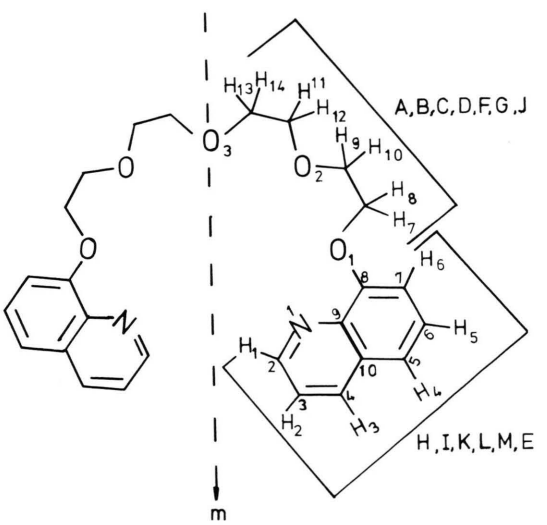

Fig. 1. Podand Kr5, mirror planes m (in-plane and out-of-plane), alkyl protons A, B, C, D, F, G, J, and quinolyl protons H, I, K, L, M, and E = H_1 (spectrum in Fig. 2).

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nating properties than crown ethers since in the former case no macrocyclic effect exists [6]. On the other hand, the open chain ligand leads to reduced steric hindrance as compared to a cyclic ligand. The nitrogen donor of the quinolyl rings, in combination with the chelate effect (Fig. 1), leads to a stronger complex formation than in complexes with oligoglycols [7, 8].

Experimental

Chemicals

Kryptofix-5 (Merck) was used without further purification. All solvents were dried with molecular sieves (3 Å) and stored under argon.

Synthesis of [Co(Kr5)]X_2, X = ClO_4^-, $CF_3SO_3^-$

1.78 mmol $[Co(CH_3OH)_6]X_2$ [2] is dissolved in 20 ml CH_3OH. At room temperature an equimolar amount of Kryptofix-5 is added, and in the case of the perchlorate anion the complex precipitates after several minutes. It is filtered and washed twice with methanol. The trifluoromethanesulfonate solution is evaporated under vacuum conditions.

NMR measurements

The NMR spectra (^1H, ^{13}C, ^{19}F and ^{35}Cl) were recorded with a JEOL JNM-GX-270 spectrometer. The power mode was used in the 2D ECXSY NMR spectra [9]. The fluctuation processes were shifted to a suitable temperature range so that mixing times of a few milliseconds could be used. For longer mixing times the signals would vanish due to a fast paramagnetic relaxation. For these spectra a data matrix of 512×256 points was appropriate.

Results and Discussion

NMR spectroscopy and structures

Kr5 forms 1:1 complexes with $Co(ClO_4)_2$ and $Co(CF_3SO_3)_2$. The ^1H NMR spectra are identical for both compounds (Fig. 2). If the coordinated ligand would be totally randomized on the NMR time scale [10], ten different chemical shifts could be expected. However, thirteen signals are found at room temperature, which are labelled from A to M as shown in Fig. 2. Some of these are broadened at higher temperatures. It can be shown by integration, that signal *J* is formed by two overlapping peaks. From the appearance of 14 signals it can be concluded that the movement of the ligand is slow at room temperature, which leads to an incomplete averaging of some ligand protons by a Kr5 fluctuation process.

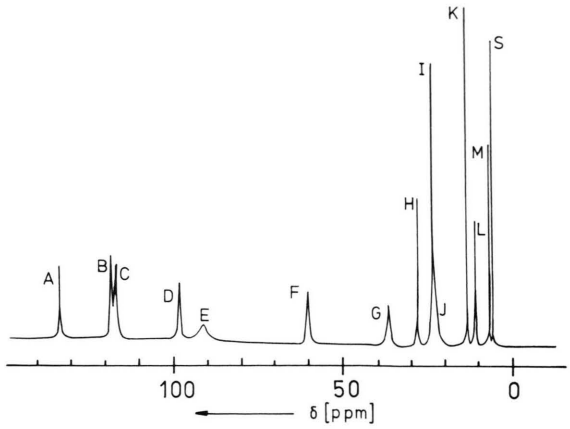

Fig. 2. 270 MHz ^1H NMR spectrum of 0.2 M $Co(Kr5)(CF_3SO_3)_2$ in CD_3NO_2 at 25 °C (S residual solvent protons).

Five sharp signals (H, I, K, L, and N) in the ^1H NMR spectrum (Fig. 2) and five relatively well resolved doublets (δ(30 °C) = 515, 252, 177, 152 and 28 ppm) in the ^{13}C NMR spectrum can be associated with the CH groups of the quinolyl rings. The relatively small line widths of these peaks indicate a large distance to the paramagnetic metal center. The two quinolyl groups are chemically equivalent in the complex, as confirmed by spectra integration. Consequently they do not reveal any kinetic broadening. According to this interpretation two mirror planes, in-plane and perpendicular to the plane, exist both for the coordinated and uncoordinated quinolyl groups (Fig. 1). The remaining ^1H NMR signals are due to the alkyl chain and to one missing CH-group of the quinolyl rings, respectively (Fig. 2: signals A, B, C, D, E, F, G, J). The missing quinolyl proton can be distinguished from the alkyl protons by the temperature dependence of its line width. In contrast to the kinetically broadened $-CH_2-$ groups, the line width of signal E in the ^1H spectrum (Fig. 2) is only influenced by the paramagnetism of the Co(II) ion and shows line narrowing at higher temperatures. This signal E can, therefore, be associated with H_1 (Fig. 1) which is close to the nitrogen donor atoms of the quinolyl rings. Due to its neighbourhood to the co-

balt ion the paramagnetic broadening of C_2 (Fig. 1) in the ^{13}C NMR spectrum suppresses the C–H coupling. The remaining ^{13}C signals of the quinolyl rings (C_9, C_{10}, C_2, C_8) have the chemical shifts $\delta(30\,^{\circ}C)$ = 372, 82, 32, −8 ppm, respectively (Fig. 1).

The ^1H NMR signals A, B, C, D, F, G, and J are associated with the protons of the polyether chain (Fig. 1, 2). The symmetry of the polyether chain protons is reduced by coordination, and only one mirror plane remains. The ^{13}C signals of these alkyl groups are shifted to high field by ligand coordination in analogy to most crown ether Co(II) complexes ($\delta(30\,^{\circ}C)$ = −33, −64, −138, −189 ppm) [2]. The ^{13}C NMR spectra give the same number of inequivalent nuclei for the coordinated and uncoordinated Kr5 carbon skeleton. Therefore, it can be deduced that the protons of the $-CH_2-$ groups become chemically non-equivalent, and that only the out-of-plane mirror plane is retained for Kr5 in $[Co(II)Kr5)]^{++}$ (Fig. 1). A schematic proposal for the structure of $[Co(II)Kr5)]^{++}$ is given in Fig. 3, and two types of alkyl protons of the chain are indicated (black and white protons).

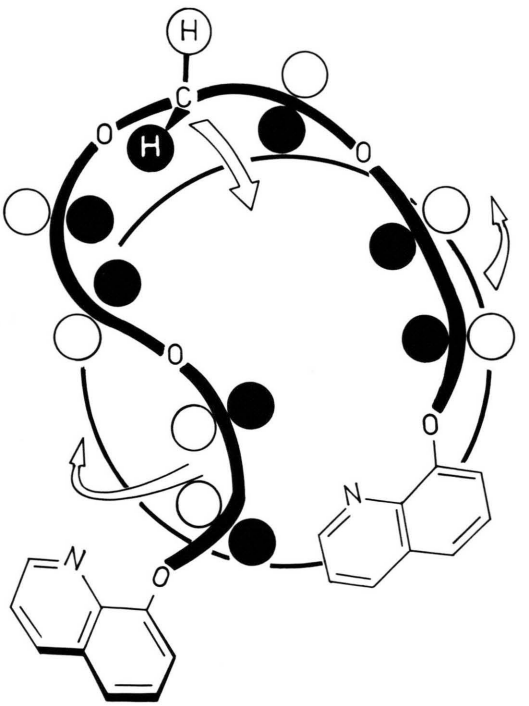

Fig. 3. Schematic structure proposal of $[Co(II)Kr5]^{++}$.

Especially in non-coordinating solvents such as nitromethane the anions ClO_4^- and $CF_3SO_3^-$ are able to bind at macrocyclic complexes despite a sufficient number of donor atoms in the ligand [11]. This anion coordination could cause a steric hindrance for the fluctuation of the Kr5 donor atoms. Appreciable coordination of ClO_4^- and $CF_3SO_3^-$ at $[Co(II)Kr5)]^{++}$ can be excluded on the basis of conductivity measurements. The specific conductivity $\varkappa(25\,^{\circ}C)$ of a 0.1 M solution of $[Co(Kr5)](ClO_4)_2$ in nitromethane is $8.6 \cdot 10^{-3}\,\Omega^{-1}cm^{-1}$, and $7.1 \cdot 10^{-3}\,\Omega^{-1}cm^{-1}$ for the respective triflate complex. These data are identical with those found for completely dissociated 2:1 electrolytes [12].

A more sensitive detection of anion coordination can be performed by NMR spectroscopy. The ^{35}Cl nucleus was chosen for the detection of ClO_4^- in the coordination shell of Co(II), and the same was done for $CF_3SO_3^-$ with ^{19}F. The ^{35}Cl NMR resonance is especially suitable for such an investigation since the quadrupole moment of the chlorine nucleus leads to a relaxation due to electrical field gradients. Therefore, coordinated ClO_4^- shows an extremely large line width, while the signal of the highly symmetrical free ClO_4^- is relatively sharp. The NMR line widths found for both types of nuclei are about 30 Hz at room temperature indicating no significant amount of anion coordination. Furthermore, in both cases the line widths decrease with increasing temperature, a behaviour typical for a pure paramagnetic line broadening mechanism. A chemical exchange process for the anions ClO_4^- and $CF_3SO_3^-$ can, therefore, again be excluded. This finding is confirmed by solid state investigations of [Rb(Kr5)]I [13].

Kinetics of ligand fluctuation

Above 35 °C the $-CH_2-$ ^1H NMR signals are broadened due to chemical exchange. A complete ^1H DNMR line shape analysis [10] for the exchange network is not possible in an unambiguous way since a very large number of pathways could be involved. The exchange reaction is more easily analysed, however, by means of 2D EXCSY NMR spectroscopy (Fig. 4). The existence of cross-peaks directly indicates the exchange between the appropriate chemical sites [9]. These peaks, however, can be caused not only by chemi-

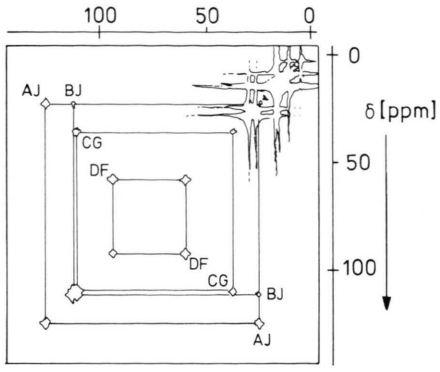

Fig. 4. ^{1}H 2D EXCSY NMR spectrum of $Co(Kr5)(CF_3SO_3)_2$ in CD_3NO_2 at 50 °C, peak notations according to Fig. 2, mixing time τ_m = 3 ms.

cal exchange or cross-relaxation but also by scalar couplings. This possibility can be ruled out by recording COSY spectra. Cross-relaxation plays no role because it is suppressed by the paramagnetism of $[Co(II)Kr5]^{++}$ [14]. The ^{1}H EXCSY spectra reveal that the general network of eight exchanging sites can be simplified to four pairs of two site reactions. The quantitative evaluation of the kinetic parameters then can be performed more easily by 1D NMR line shape analysis [10] (Table I). The values for single exchange reactions given in Table I show different accuracies. This fact results from peak overlappings, *e.g.* signal B with C, and J with a quinolyl signal.

The results of the DNMR measurements can be explained by the schematic structure proposal of $[Co(II)Kr5)]^{++}$, given in Fig. 3. The two $-CH_2-$ protons of the alkyl chain in $[Co(II)Kr5)]^{++}$ are chemically non-equivalent (Fig. 3: black and white

Table I. Rate constants of Kr5 fluctuation in $Co(Kr5)(CF_3SO_3)_2$, network of pathways according to the spectra in Figs. 2, 4.

Signals	k (60 °C) [s^{-1}]	$\Delta H^{\#}$ [kJ/mol]	$\Delta S^{\#}$ [J/K·mol]
A ⇌ J	1433 ± 143	38 ± 4	−70 ± 26
B ⇌ J	1465 ± 350	40 ± 9	−64 ± 35
C ⇌ G	1467 ± 350	35 ± 9	−79 ± 35
D ⇌ F	1350 ± 270	47 ± 7	−45 ± 30

protons), whereas the number of ^{1}H NMR chemical shifts for the triethylene glycol Co(II) complex is identical to that of the free ligand. Therefore, it can be concluded that the observed exchange process in $[Co(II)Kr5)]^{++}$ is initiated by breaking the bond between Co(II) and the quinolyl chelate ring. The aromatic rings are able to turn away from the metal ion. This enables the alkyl chain to alter its conformation in such a way that the two protons of the $-CH_2-$ groups interchange. Due to this reaction the neighbouring protons (Fig. 3: black protons) in equivalent $-CH_2-$ groups of the alkyl chain move away from each other, whereas those further away (Fig. 3: white protons) move closer together. The carbon atoms, however, show an exchange process between chemically equivalent sites as shown by the number of ^{13}C signals and the lack of exchange peaks in ^{13}C EXCSY spectra. The strong Co−N bond has to be broken as the rate determining step and therefore an unusually slow exchange results in comparison to podands and coronands with merely oxygen donor atoms.

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