¹H NMR Detection of $CoOH_2$ ⇌ CoOH Interconversions in High-Spin Cobalt(II) Complexes

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The $CoOH_2^{n+}$ ⇌ $CoOH^{(n-1)+}$ + H^+ (n = 0, 2) interconversion has been monitored through water ¹H NMR T_1^{-1} measurements for two square-pyramidal high-spin cobalt(II) complexes with water coordinated in the apical position. The protons of both the aqua and hydroxo species exchange rapidly on the NMR time scale, the upper limits being 1.1×10^{-4} and 4.0×10^{-5} s, respectively. The pH dependence of the absolute T_1^{-1} values is related to the pK_a of the coordinated water but does not reflect the number of exchangeable protons. The results are meaningfully compared with those relative to the cobalt carbonic anhydrase system.

Introduction

The detection of the H_2O ⇌ OH^- + H^+ equilibrium in water molecules coordinated to metal ions in metalloproteins is generally difficult since such equilibrium takes place together with many other acid–base equilibria involving histidines, amine nitrogens, tyrosines, etc. In principle, the water molecule that is coordinated to a paramagnetic ion and is in fast exchange with the bulk water can be monitored through NMR measurements of water nuclei.[1] Particularly important in this respect is the water ¹H longitudinal relaxation rate, which may experience large enhancements upon coupling of the nucleus with paramagnetic centers.[2,3] ²H and ¹⁷O nuclei are much less sensitive to the coupling to unpaired electrons since they possess efficient physical relaxation mechanisms due to their quadrupolar moment. Only in concentrated solutions of model complexes or in the presence of metalloproteins experiencing large electronic relaxation rates can they be used with some success.[4,5]

Owing to the relevance of the matter in inorganic biochemistry a controversy exists on whether a coordinated OH^- can be detected through water ¹H NMR techniques under fast-exchange conditions and, if so, how the results of such measurements would compare with those obtained on the corresponding systems containing undissociated water at low pH values. Data on simple model compounds would be quite desirable, especially on cobalt(II) complexes, since cobalt(II) has been widely used as a paramagnetic probe in zinc-containing proteins.[6] The limitation comes from the scarcity of suitable compounds; the complex aqua[tris((3,5-dimethyl-1-pyrazolyl)methyl)amine]cobalt(II) displays pK_a = 9.0 ± 0.1, but it is only slightly soluble and the hydroxo species is rather unstable.[7] The complex does not show any pH dependence of water ¹H T_1^{-1} values at 80 MHz.[7] For the more soluble aqua(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(II) complex[8] (I), which has a pK_a of 8.44,[9] an ¹⁷O NMR investigation is available[10] showing that H_2O is capable of exchanging on the NMR time scale whereas OH^- is not. We have investigated through ¹H NMR spectroscopy complex

I and the aqua(1,5-diazacyclooctane-1,5-diacetato)cobalt(II)[11] complex (II), which is reported to have pK_a = 9.27.[12]

I　　　　　　　II
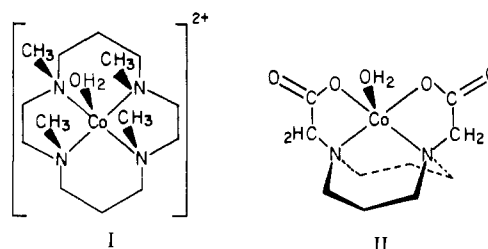
Experimental Section

The complexes I and II have been prepared according to the literature data.[8,11] Complex I was used as perchlorate salt. The electronic spectra have been recorded on a Cary 17D spectrophotometer. The ¹H NMR data have been obtained on a CXP 100 Bruker equipped with a variable-field electromagnet ranging from 0.094 to 1.7 T. The T_1 measurements have been performed through the inversion recovery method and the T_1 values have been obtained through a two-parameter best fitting. T_2^{-1} values have been determined through line width measurements by using the relation $T_2^{-1} = \pi(\Delta\nu)$.

Results and Discussion

Both of the complexes investigated are square pyramidal with an apical water molecule.[11,13] The steric requirements of the ligands prevent further donor atoms from approaching the sixth coordination position. The electronic spectra of water solutions of both complexes are pH dependent: while those of complex I are reported elsewhere,[9] those of complex II are shown in Figure 1. The pK_a value estimated from the latter data is 9.44 ± 0.10, which is consistent with the value of 9.27 obtained potentiometrically.[12] The electronic spectra indicate that also the high-pH form is five-coordinate. N_3^- is capable of binding the metal ion of the complexes:

$$CoLOH_2^{2+} + N_3^- ⇌ CoLN_3^+ + H_2O \qquad (1)$$

The electronic spectrum of the azide derivative of complex II (Figure 1) indicates that high-spin five-coordination is maintained and therefore a 1:1 adduct is formed by removal of the coordinated water molecule. The same behavior is shown by complex I.[9]

The water proton longitudinal relaxation rates (T_1^{-1}) of solutions containing the paramagnetic complexes I and II are sizably larger than the values of pure water. This is due to the coupling between the resonating protons and unpaired electrons on the metal ion. The difference between the measured relaxation rates for the paramagnetic solutions and the rates for pure water is indicated as T_{1p}^{-1}. Such relaxation

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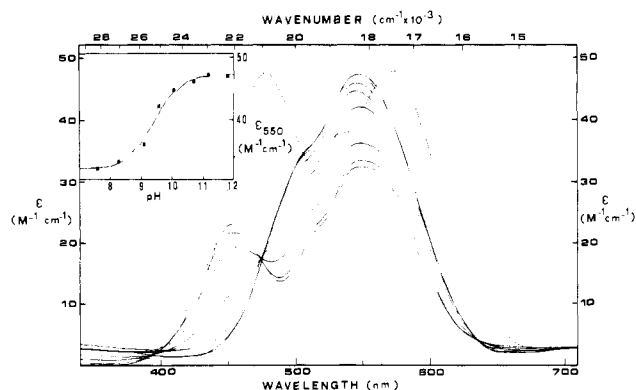
Figure 1. Electronic spectra of complex II in water solution as a function of pH (—), from 7.6 to 11.8 in order of increasing ϵ_{550}. The data are best-fitted to pK_a of 9.44 (inset). The spectrum of the azide adduct is also shown (- - -).

Table I. Temperature Dependence of the ^{1}H T_{1p}^{-1} Values (s^{-1}) Measured in Water Solutions of Complexes I and II

Complex I, 0.107 M, 50 MHz		
temp, °C	pH 7.24	pH 11.9
5	9.6	17.2
25	8.4	14.9

Complex II, 0.051 M, 60 MHz		
temp, °C	pH 7.4	pH 11.0	pH 8.4 + N$_3^-$
10	6.3	3.9	1.5
32	4.8	3.4	1.4
55	3.1	2.9	1.2

values are also pH dependent; in particular the T_1^{-1} values increase with pH in the case of complex I whereas they decrease in the case of complex II (Figure 2). The data are fitted to pK_a values of 8.6 ± 0.2 and 9.3 ± 0.1, respectively. Clearly in both cases there are two species in equilibrium whose population depends on the same pK_a values as found from other techniques.[9,12] The T_{2p}^{-1} values estimated through line width measurements are slightly larger than the corresponding T_{1p}^{-1} values. For example T_{1p}^{-1} is 11.2 and 4.6 s^{-1} at pH 7 whereas T_{2p}^{-1} is 15.6 and 8.8 s^{-1} at the same concentration of Figure 2 for complexes I and II, respectively.

Addition of NaN$_3$ at low pH values causes a marked decrease of the water ^{1}H T_1^{-1} values; since N$_3^-$ substitutes the coordinated water molecule as in other complexes of this kind,[7] the residual paramagnetic effect observed in the presence of the azide adducts is probably due to outer-sphere relaxation.

The temperature dependence of the water ^{1}H T_{1p}^{-1} values of solutions containing the aqua complexes is reported in Table I; with increase of the temperature the T_{1p}^{-1} values sensibly decrease in every case. The contrary would be expected if the relaxation rate were determined by the proton-exchange rate;[14] therefore, the proton exchange is a fast process all over the pH range investigated.

The decrease of T_{1p}^{-1} with increasing temperature may be accounted for if the correlation time for the nuclear relaxation, τ_c, decreases with increasing temperature; in the present case τ_c is determined by the electronic relaxation time T_{1e}. The temperature dependence of the latter may be rather complex, depending on the particular relaxation mechanism operative.[15]

The water ^{1}H T_1^{-1} measurements have been performed at various magnetic fields in the Larmor frequency range 4–60
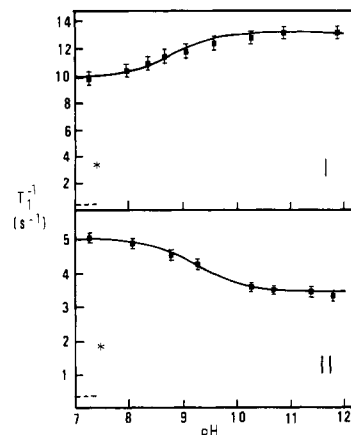

Figure 2. Water proton T_1^{-1} values measured at 25 °C in the presence of complexes I (0.15 M, 80 MHz) and II (0.05 M, 60 MHz) as a function of pH. The values obtained with the azide adducts (*) are also shown, together with the T_1^{-1} values of pure water (- - -).
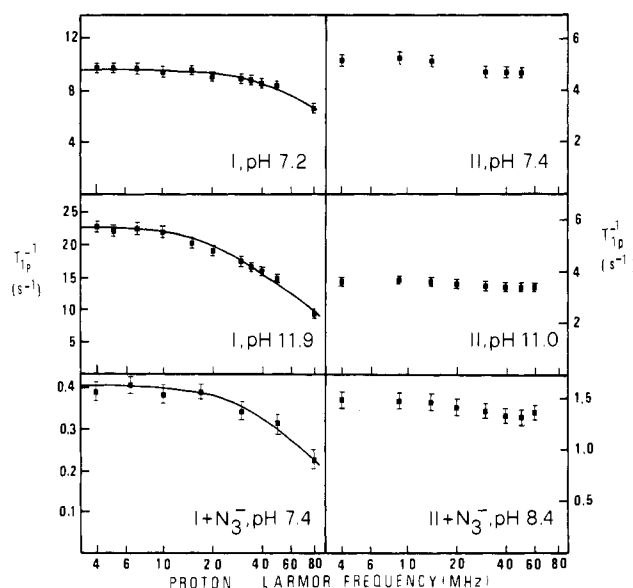

Figure 3. Field dependence of water proton T_{1p}^{-1} values at 25 °C for complexes I (0.107 M) and II (0.051 M) at low and high pH and for the corresponding azide adducts (9.7 × 10^{-3} and 0.051 M, respectively). The data for complex I are best-fitted to eq 2.

MHz. If the coupling between the protons and the paramagnetic center is assumed to be dipolar[16] and if every orbital contribution to the relaxation is neglected, the paramagnetic contribution T_{1p}^{-1} depends on magnetic field according to an equation of the type (2),[17] where ω_I and ω_S are the nuclear

$$T_{1p}^{-1} = T_1^{-1} - T_{1dia}^{-1} = KG\left(\frac{3\tau_c}{1 + \omega_I^2\tau_c^2} + \frac{7\tau_c}{1 + \omega_S^2\tau_c^2}\right)$$

$$(2)$$

$$K = \frac{[M]}{111}\left(\frac{2}{15}S(S + 1)\right)\gamma_I^2 g^2\beta^2 \qquad G = \sum_i \frac{n_i}{r_i^6}$$

and electronic Larmor frequencies and G is a constant including the number of protons and their distance from the paramagnetic center.[18]

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(16) When the correlation time is the electronic relaxation time, as in this case, contact contributions can be estimated to be about 2 orders of magnitude smaller than dipolar contributions for typical values of $A/\hbar$ (Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1964**, *40*, 2686).

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Table II. G (cm^{-6} $\times$ 10^{-45}) and τ_c (s $\times$ 10^{12}) Values Obtained from a Best-Fitting Procedure of the Data for Complex I

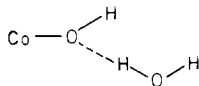|	pH 7.24		pH 11.9		pH 7.4 + N$_3^-$
	5 °C	25 °C	5 °C	25 °C	25 °C
G	3.0	3.1	3.6	3.5	1.0
τ_c	3.4	2.6	6.7	5.6	3.8

Reasonable G values for a regularly coordinate water molecule (Co–O distance 1.9–2.1 Å) are in the range (3–5) $\times$ 10^{45} cm^{-6}. The experimental T_1^{-1} values reported in Figure 2 are typical for τ_c of the order of 10^{-12} s as found for other five-coordinated cobalt(II) complexes.[18,19]

the field dependence of T_{1p}^{-1} for both complexes is reported in Figure 3. The constancy of the observed T_{1p}^{-1} at low field[20] is consistent with the above qualitative estimate of τ_c, arising from a situation in which $\omega_S \tau_c \ll 1$. The variation of T_{1p}^{-1} over the field range investigated is rather small, and too small for complex II in order to attempt an analysis of the data according to eq 2. A two-parameter (G and τ_c) fit of the data of complex I to eq 2 has been performed (Table II).

Although the absolute figures of Table II may be affected by the several assumptions implicit in eq 2, the values obtained for the same system under different experimental conditions may still be meaningfully compared. It is apparent that the observed pH dependence is largely accounted for by a sizable increase in τ_c of the high-pH species, while the G value is almost unchanged.

Furthermore, the same experiments performed at 5 °C confirm that the temperature dependence observed is due to a change in τ_c and not to a gross change in the overall hydration of the complex or in the exchange rate of the hydrated species. On the other hand, in the azide derivative the small value of T_1^{-1} is mainly due to a more than 3-fold decrease in G, as expected for the removal of the coordinated water.

The frequency independence observed for complex II does not allow discrimination between a decrease in τ_c or a decrease in the number of interacting protons with pH. However, the presence of a sizable proton-relaxation enhancement at high pH and the comparison with the azide data indicate that the interaction of the hydroxide proton with the paramagnetic metal is again detected. Beyond any experimental uncertainty or theoretical approximation a sizable metal–OH proton interaction is apparent in both of the hydroxo complexes investigated. However, the expected 2-fold decrease in G due to the water deprotonation may not be apparent, as shown by the analysis of the frequency dependence of the T_{1p}^{-1} values. The pH independence of G may be accounted for by a decrease in the metal–oxygen distance upon deprotonation[21] and/or by the proximity of a hydrogen-bonded proton from a solvent molecule.[22]

The Exchange of the OH Proton and a Comment on Cobalt(II) Carbonic Anhydrase.

The water ^{1}H T_1^{-1} values of solutions containing cobalt(II)-substituted carbonic anhydrase have been a matter of controversy of crucial importance.[23]

The enzyme displays an acid–base equilibrium whose pK_a for example is $\sim$6 for the bovine isoenzyme and 7.5 for human isoenzyme B. According to various authors the group responsible for the equilibrium could be a coordinated water molecule.[23,24] The bovine isoenzyme B shows water ^{1}H T_1^{-1} values at 80 MHz essentially pH independent in the pH range 6–10;[25] the human isoenzyme B shows higher T_1^{-1} values at high pH than at low pH.[26] Such findings are not inconsistent with the acid dissociation of the coordinated water, since T_{1p}^{-1} does not simply depend on the number of protons, as predicted by theory and here experimentally found.

Another controversial point regards the exchange mechanism of the proton of the possible CoOH form.[27]

This paper shows that fast-exchanging hydroxide protons coordinated to metal ions can be detected through ^{1}H relaxation measurements. On kinetic grounds, an upper limit for the exchange rate of a hydroxide group as such is set by its diffusion rate ($\simeq$10^{10} M^{-1} s^{-1}) times its concentration.[28]

In the present systems, because of the relatively high pK_a values and the small relaxing capability of the metal, the observed relaxation rate would be in principle within the diffusion limit. In fact, even in the worst case (complex I at pH 9 and 5 °C) the calculated paramagnetic relaxation rate for the bound hydroxide proton is 2.5 $\times$ 10^4 s^{-1}, while the upper limit for the dissociation rate constant of OH$^-$ is 10^{10} M^{-1} s^{-1} $\times$ 10^{-5} M = 10^5 s^{-1}.

However, from the detection limit of ^{17}O line broadening caused by I at pH 10.5[10] the actual upper limit for the exchange rate of the OH$^-$ moiety can be set around 2 $\times$ 10^3 s^{-1}, i.e., 1 order of magnitude less than required by the ^{1}H relaxation rate. Therefore, there has to be a mechanism that allows the independent fast exchange of the hydroxide proton from the complex and its incorporation into the bulk solvent. The simplest possible mechanisms are A and B. Scheme A

A

B
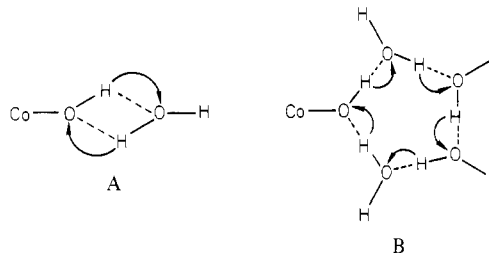
has already been proposed.[29,30] Scheme B, although similar to the previous one, involves more than one water molecule, analogous to that proposed for proton exchange in Cr(OH$_2$)$_5$(OH)$^{2+}$ [31] and Pt(NH$_2$)(NH$_3$)$_5$$^{3+}$ [32] and for intramolecular proton transfer in zwitterionic compounds.[28] This by no means implies that the same type of mechanism has to hold in carbonic anhydrase, although it would satisfactorily explain the ^{1}H NMR data. Indeed, in the case of cobalt carbonic anhydrase both the low pK_a value ($\sim$6) for the proposed H$_2$O $\rightleftharpoons$ OH$^-$ equilibrium and the higher relaxing capability of the pseudotetrahedral cobalt(II) ion in the high-pH form rule out

(19) Bertini, I.; Canti, G.; Luchinat, C., submitted for publication.

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the possibility of direct OH⁻ exchange.[33]

On the other hand the catalytic efficiency of the enzyme would require that, if the active species is in the hydroxo form, the oxygen atom is also in fast exchange with the bulk solution.[34] As a matter of fact, fast ^{17}O exchange has been detected through ^{17}O NMR on the copper derivative over the entire pH range of existence of the enzyme.[35] From the aforementioned observation[28,31,32] that intramolecular protonation can be a very fast process if the basic groups between which the proton is transferred are close enough in space and have close pK_a values, a pathway is going to be proposed for the fast exchange of the OH moiety as part of a water molecule.[36]

The proposed pathway stems from the availability of a fifth coordination position on the metal ion in the active site of carbonic anhydrase.[23] The exchange is allowed by the transient binding of a water molecule as a fifth ligand; a proton can be then transferred to the hydroxide group,[31,32] which can exchange as a water molecule leaving a coordinated hydroxide.

Registry No. I, 82110-97-2; I, azide adduct, 81899-99-2; II, 56627-65-7; II, azide adduct, 82080-84-0.
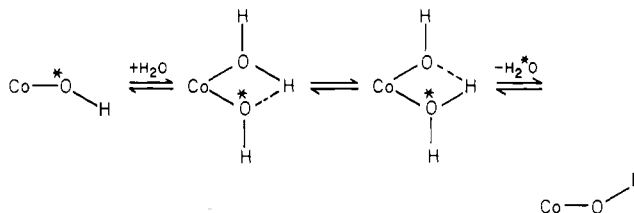
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Effect of Metal Dilution on the Spin-Crossover Behavior in [Fe_xM_{1-x}(phen)_2(NCS)_2] (M = Mn, Co, Ni, Zn)

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The effect of metal dilution on the spin-crossover behavior of [Fe(phen)_2(NCS)_2] has been studied in the mixed-crystal series [Fe_xM_{1-x}(phen)_2(NCS)_2] (M = Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺) by using the ^{57}Fe Mössbauer-effect technique. It has been found that, in the host lattice with ionic radius $r(M^{2+}) > r(Fe^{2+})$, the amount of rest paramagnetism in the region well below the transition temperature T_c increases with metal dilution, whereas in the host lattice with $r(M^{2+}) < r(Fe^{2+})$, the residual diamagnetism in the region well above T_c decreases with metal dilution. These observations are interpreted qualitatively in terms of "negative" and "positive" local pressure, respectively, changing the Fe–N bond length and thus influencing the ligand field potential accordingly.

Introduction

In the last few years, studies in the field of spin crossover in transition-metal complexes have established that the spin-transition characteristics depend very markedly on the ligand, nature of the noncoordinating anion, minor intraligand substitutions, solvent molecules trapped in the lattice, metal dilution, temperature, pressure, etc.[1-6] All these influences on the $^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$ spin-transition behavior of iron(II) systems have been discussed in a recent review article.[7]

On the basis of some metal dilution of [Fe(2-pic)_3]Cl_2·EtOH in the corresponding isomorphous [Zn(2-pic)_3]Cl_2·EtOH lattice, Renovitch and Baker[8] ruled out any antiferromagnetic interactions in [Fe_{0.15}Zn_{0.85}(2-pic)_3]Cl_2·EtOH. Recent detailed Mössbauer spectroscopic studies on [Fe_xZn_{1-x}(2-pic)_3]Cl_2·

EtOH ($x = 1-0.0009$)[9,10] have shown that the transition temperature T_c, defined as the temperature at which equal amounts of the high-spin (HS) state and the low-spin (LS) state coexist, decreases on dilution. However, the thermally induced HS $\rightleftharpoons$ LS crossover is still observable even at the lowest possible iron concentrations. These results have been interpreted on the basis of a "domain model",[9-12] which suggests that the spin transition takes place through a coupling between the electronic state and the vibrational modes and that the conversion of the electronic state occurs simultaneously in a group of molecules that form a so-called "cooperative domain". Heat capacity measurements on [Fe(phen)_2(NCS)_2] were earlier interpreted by Sorai and Seki[9] on the basis of this "domain model". They had proposed that the abrupt transition in [Fe(phen)_2(NCS)_2] was due to a "strong coupling" in domains consisting of about 100 molecules. The present investigation on [Fe_xM_{1-x}(phen)_2(NCS)_2] ($x = 0.001-1$ and M = Mn, Co, Ni, Zn) was undertaken to study how metal dilution of the "strongly coupled" system [Fe(phen)_2(NCS)_2]

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