A Proton Nuclear Magnetic Resonance Investigation of the Protonation of Bis(ethylenediamine)glycinatocobalt(III) in Strongly Acidic Media

By **Jacques Fastrez** * and **Viviane Daffe**, Laboratoire de Chimie Générale et Organique, Place L. Pasteur, 1, B 1348 Louvain la Neuve, Belgium

The protonation equilibrium $[Co(en)_2(glyO)]^{2+} + D^+ \rightleftharpoons [Co(en)_2(glyOD)]^{3+}$ in strongly acidic solution has been investigated by ^1H n.m.r. spectroscopy (en = ethylenediamine, glyO = glycinate). Similar pK_{BD^+} values (*ca.* −1.2) are observed in D_2SO_4 and DCl solutions. Plots of $\log_{10}([BD^+]/[B])$ *versus* D_0 are linear but with a slope between 0.4 and 0.5 indicating that the protonated complex has a much larger solvation requirement than its conjugate base.

ALTHOUGH the acid–base behaviour of weak organic bases in strongly acidic media has been investigated very thoroughly,[1] much less work has been done on this subject with organic complexes; reported examples are the protonation of isothiocyanato- and azido-complexes of rhodium(III) and cobalt(III).[2,3]

RESULTS AND DISCUSSION

We have measured the equilibrium (see below) of protonation of an ethylenediamine glycinato-complex of cobalt(III) in both D_2SO_4 and DCl solutions by proton

$$\underset{(B)}{[Co(en)_2(glyO)]^{2+}} + D^+ \rightleftharpoons \underset{(BD^+)}{[Co(en)_2(glyOD)]^{3+}}$$

magnetic resonance. The change in the position of the CH_2 signal as a function of the acid concentration was recorded. The protonation ratio $I = [BD^+]/[B]$ is obtained from formula (1) where ν_{BD^+} and ν_B are the

$$I = (\nu_{obs.} - \nu_B)/(\nu_{BD^+} - \nu_{obs.}) \qquad (1)$$

chemical shifts in Hz referred to the tetramethylammonium ion † for the completely protonated and unprotonated complexes respectively, and $\nu_{obs.}$ the chemical shift observed at intermediate acidities. These values are used to calculate the pK_{BD^+} value from equation (2),[4]

$$\log_{10}I = -mD_0 + pK_{BD^+} \qquad (2)$$

where D_0 is the acidity function in a deuteriated solvent. The D_0 values are interpolated from literature tables.[5,6] The following parameters were obtained by least-squares fitting of $\log_{10}I$ *versus* D_0 and used to recalculate the frequencies ($\nu_{calc.}$). In deuteriosulphuric acid, from 20 points for 0—77% D_2SO_4: $pK_{BD^+} = -(1.17 \pm 0.04)$, $m = 0.39 \pm 0.01$, $\nu_B = 25.4$, $\nu_{BD^+} = 67.4$ Hz, $r = 0.996$, $|\nu_{obs.} - \nu_{calc.}|_{mean} = 0.7$ Hz, and $|\nu_{obs.} - \nu_{calc.}|_{max.} = 2.1$ Hz. In deuterium chloride, from 21 points for 0—33% DCl: $pK_{BD^+} = -(1.14 \pm 0.02)$, $m = 0.48 \pm 0.01$, $\nu_B = 25.6$, $\nu_{BD^+} = 73.0$ Hz, $r = 0.996$, $|\nu_{obs.} - \nu_{calc.}|_{mean} = 0.7$ Hz, and $|\nu_{obs.} - \nu_{calc.}|_{max.} = 2.0$ Hz. For the DCl data, ν_{BD^+} cannot be determined experimentally. The value quoted is that which gave the best linear plot as judged from the correlation coefficient (r) and the standard error. The parameters m and pK_{BD^+} are not very sensitive to changes in the values of ν_B and ν_{BD^+} between reasonable limits (*e.g.* if ν_{BD^+} in DCl is changed from 70 to 75 Hz, the pK_{BD^+} changes from −1.16 to —1.13, and the slope m from 0.53 to 0.47).

The value of ($\nu_{BD^+} - \nu_B$) comes close to the difference in chemical shift between the corresponding chelated ester and its hydrolysis product (*ca.* 47 Hz),[7] a strong indication that the protonation occurs on the carbonyl group.

For technical reasons, the p*K* values had to be measured in deuteriated solvents. Had the measurements been done in protic acids, a pK_a more negative by 0.3—0.4 units would have been obtained.[5,6] Very similar pK_{BD^+} are obtained in hydrochloric and sulphuric acid solutions. This is not always the case as shown in the work of Staples [2] because at high acid concentration ion pairing is certainly important.

The pK_a values reported here are about halfway between the ranges of those corresponding to the protonation and the deprotonation of carboxylic acids [1,8,9,‡] (see below).

$$RCOO^- \xrightleftharpoons[-H^+]{pK_{a(1)}} RCOOH \xrightleftharpoons[-H^+]{pK_{a(2)}} RCOOH_2{}^+$$

The slopes of the plots of $\log_{10}I$ *versus* D_0 are quite small; the ionisation ratio increases more slowly than predicted from the D_0 scale. This behaviour reflects the much higher solvation requirement of the protonated form than of its conjugate base.[10] The glycine complex thus behaves differently from the transition-metal complexes studied so far [2,3] for which slopes close to 1 or higher were observed. In organic chemistry, values of m less than unity are frequently obtained with oxygen bases [10,11] whose conjugate acids have a localised positive charge. The tentative generalisation that protonation on oxygen leads to lower m values and large differences in solvation requirement between the basic and acidic

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[*] Chercheur Qualifié to the Fonds National Belge de la Recherche Scientifique.

[†] To correct, at least partially, for the possible solvent-effect shift on ν_B and ν_{BD^+}, the signal was referred to a positively charged ion. The position of the reference signal itself moves relative to sodium 4,4-dimethyl-4-silapentanesulphonate (dss) or dimethylsulphate by *ca.* 3—4 Hz between water and concentrated acid, upfield in D_2SO_4, downfield in DCl.

[‡] Rather large systematic differences between the observed and calculated chemical shifts are found in the work reported in ref. 9; the data are also consistent with more negative pK_a values and larger m values.

forms appears to be obeyed in the case of transition-metal complexes too. It might have been expected that since both forms of the complex are positive ions, the difference in solvation requirements would be quite low. Apparently, this is not the case and the *m* value is determined by the atom being protonated. More work would be needed to check the generality of this conclusion.

EXPERIMENTAL

Materials.—Sodium 4,4-dimethyl-4-silapentanesulphonate (dss) (Wilmad Glass Co.), tetramethylammonium bromide (Merck), dimethylsulphate (Fluka), [$^2H_2$]sulphuric acid, 98% in D_2O (Aldrich), [$^2H_1$]hydrogen chloride, 38% in D_2O (Baker), and ^2H_2O, 99.7 atom % D (Aldrich) were commercial products used without further purification.

[Co(en)$_2$(glyO)][SO$_4$]. The complex [Co(en)(glyO)]I$_2$ was prepared according to Liu and Douglas [12] and purified by passing through a Sephadex G10 column. The counter ion was then exchanged on an Amberlite IRA 401 column (SO_4^{2-} form). The complex was recrystallised from ethanol–water and characterised by i.r. and analysis (Found: C, 19.85; H, 6.00; N, 19.35. Calc. for $C_6H_{22}CoN_5O_7S$: C, 19.6; H, 6.05; N, 19.05%).

[Co(en)$_2$(glyO)]Br$_2$. This complex was obtained by hydrolysis of [Co(en)$_2$(glyOMe)Br]Br$_2$ prepared according to Alexander and Busch,[13] between pH 7.0 and 7.5 (10 h at 50 °C). The complex was precipitated with ethanol, washed with dichloromethane, ethanol, and diethyl ether, and recrystallised from ethanol–water. The product was characterised by i.r. and analysis (Found: Br, 36.95. Calc. for $C_6H_{22}Br_2N_5O_3$: Br, 37.1%).

Methods.—The samples contained dss (10 mg), tetramethylammonium bromide (10 mg), and complex (50 mg). The complex was first dissolved in a weighed quantity of D_2O and left for a few minutes to allow the protons attached to the nitrogens to exchange so that the CH_2 signal would become a singlet; a weighed quantity of acid was added and after 15 min for temperature equilibration the spectrum was recorded at 25 °C on a JEOL FX 60 spectrometer. For the measurements in DCl, the acid concentration was determined by titration of 0.05—0.1 cm^3 of solution with 2N Na[OH]. For the sulphuric acid solutions, the starting D_2SO_4 solution was titrated.

[0/517 *Received, 3rd April*, 1980]

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