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A COMPUTER PROGRAM FOR THE SIMULTANEOUS DETERMINATION OF THE FIRST- AND SECOND-ION-ASSOCIATION CONSTANTS. AN APPLICATION TO THE SYSTEM ACETYLACETONATOBIS(ETHYLENEDIAMINE)COBALT(III) AND CHLORIDE IONS IN DIMETHYLSULFOXIDE[1)]

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A computer program has been developed for the simultaneous determination of the first- and second-ion-association constants from spectroscopic(NMR, UV, or CD) or conductance measurements, and applied to the system, acetylacetonatobis(ethylenediamine)cobalt(III) and chloride ions in dimethylsulfoxide.

Recently, we have reported the assignment for the NMR spectra of the acetylacetonatobis(ethylenediamine)cobalt(III) cation, $[Co(en)_2(acac)]^{2+}$, in d_6-dimethylsulfoxide(d_6-DMSO).[2)] In the $[Co(en)_2(acac)]^{2+} \cdots\cdot Cl^-$ system in d_6-DMSO, the first-association takes place at the amine hydrogens(trans H_A), which are trans to the coordinated oxygen and pointing roughly parallel to the molecular two-fold axis, and the second-association at the cis N-H which is directed away from the C_2-axis, called hereafter as cis H_B. The respective ion-association constants were not determined at that time.

On the other hand, the first- and the second-ion-association constants for 2-1 electrolytes do not appear to have been determined simultaneously. The commonly adopted method is to determine the two association constants separately under different conditions, mainly based on the method of Fuoss and Edelson or Jenkins and Monk.[3)] Thus, we set up a general computer program to determine both association constants simultaneously. We first outline briefly the contents of this program.

Let us consider the ion-association equilibrium between cation M and anion X,

$$M + X \underset{}{\overset{K_1}{\rightleftharpoons}} MX \qquad (1)$$

$$MX + X \underset{}{\overset{K_2}{\rightleftharpoons}} MX_2 \qquad (2)$$

Electric charges are omitted for brevity. Let the initial concentrations of cationic and anionic species be denoted by c_M and c_A, respectively, and let the equilibrium concentrations of M, X, MX, and MX_2 be (c_M-x-y), (c_A-x-2y), x, and y. The association constants K_1 and K_2 are defined by

$$K_1 = x/(c_M-x-y)(c_A-x-2y) \quad (3a)$$

$$K_2 = y/x(c_A-x-2y) \quad (3b)$$

Let us consider the case where the NMR chemical shift of some nucleus of cationic species is measured for several combinations of c_M and c_A. Since we have a rapid dynamical equilibrium, the measured chemical shift, D_{obs}, is the weighted average of the chemical shifts of this nucleus in each species,

$$D_{obs} = D_f(c_M-x-y)/c_M + D_1x/c_M + D_2y/c_M \quad (4)$$

where D_f, D_1, and D_2 are the chemical shifts in free(not ion-associated), first-ion-associated, and second-ion-associated species. The quantities c_M, c_A, D_{obs}, and D_f are assumed to be known and the values of K_1, K_2, D_1, and D_2 are to be determined.

The x and y are expressed analytically from Eqs.(3a) and (3b) as functions of K_1, K_2, c_M, and c_A[4] and substituted into Eq.(4). D_{obs} is now a function of four unknowns, K_1, K_2, D_1, and D_2. In order to minimize the sum $\sum_i (D^i_{obs} - D^i_{calc})^2$, a general non-linear least-squares method[5] has been used. Initially we assign appropriate values to K_1, K_2, D_1, and D_2 and the Jacobian matrix was calculated, and the parameter corrected. This procedure was cycled iteratively until convergence is attained. When another method of measurement is used, Eq.(4) is modified to an appropriate form and the other part of the program needs no modification.[6]

We have studied the system, $[Co(en)_2(acac)](ClO_4)_2$ .... Me_4NCl in d_6-DMSO at 25°C, by measuring the amine proton chemical shifts at 100 MHz as a function of the chloride concentration. The ionic strength was adjusted by Me_4NClO_4 to μ=0.12 and c_M to 0.030 mol dm^{-3}. In Fig. 1, the observed chemical shifts(relative to internal TMS) of amine hydrogens are plotted against the concentration of Me_4NCl. Since the perchlorate anion is not a hydrogen bond acceptor and shown to be completely dissociated in dipolar aprotic solvents,[7] the value of D_f was obtained in the absence of Me_4NCl. Trans H_A is the site of first-association and its chemical shift is affected by the first-association. Cis H_B is the site of second-association but its chemical shift is influenced by the first-association, as well as the second-association. Thus, its chemical shift can be used to determine the association constants. The least-squares fitting to the data of cis H_B(D_f = 535.0 Hz) yielded D_1 =555.0 ± 3.6 Hz and D_2 = 609.1 ± 3.1 Hz and the association constants K_1 = 89.20

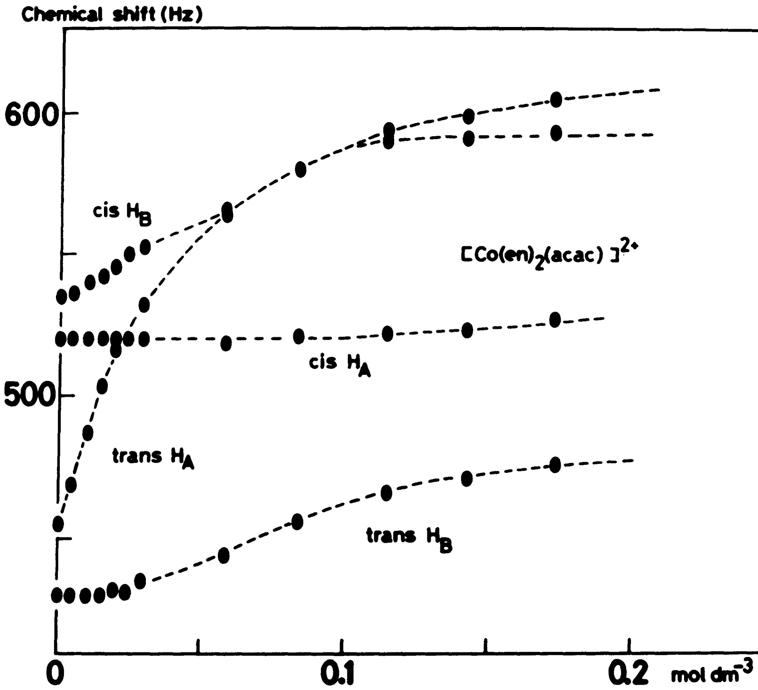

Figure 1. The observed amine proton chemical shifts of $[Co(en)_2(acac)]^{2+}$ vs. the concentration of Me_4NCl. The complex concentration is 0.030 mol dm^{-3} and μ=0.12 with Me_4NClO_4.

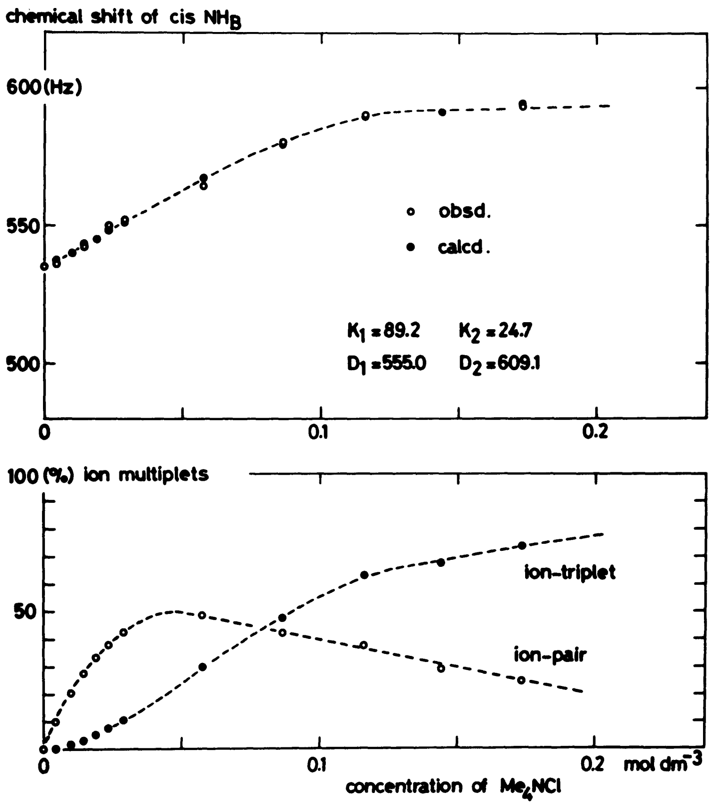

Figure 2. (a) (top) The observed and calculated chemical shift of cis H_B of $[Co(en)_2(acac)]^{2+}$ against the concentration of Me_4NCl.
(b) (bottom) The calculated percentages of the ion-pair and ion-triplet.

± 0.08 and K_2 = 24.71 ± 0.02 $dm^3\ mol^{-1}$. The estimated errors are based on the 99% confidence level. In Fig. 2(a) is plotted the observed and the calculated chemical shift of cis H_B against the chloride concentration. Figure 2(b) shows the plots of respective percentage of ion-pair and ion-triplet calculated from the association constants. The association constants obtained here appear to be substantially smaller than those obtained by the conductance method for, e.g., cis-$[Co(en)_2(Cl)_2]^+$ .... Cl^- in DMSO(K = 397 ± 10 at 25°C).[8] We have examined the ion-association equilibria between several cis-$[Co(en)_2(X)_2]^{n+}$ cations and chloride ions in DMSO by NMR and difference CD techniques, and found that the association constants obtained by the former technique are always smaller than those obtained by the latter technique.[9] These trends seem to reiterate the difference in informations available from different methods.[10] The NMR method sees only those ion-multiplets which are formed between chloride ions and the amine hydrogens of the complex cation via hydrogen bonding.

References and Notes

1) Part 18 of "Proton Magnetic Resonance Spectra of Metal Ammine Complexes."
2) H. Nakazawa, U. Sakaguchi, H. Yoneda, and Y. Morimoto, Inorg. Chem., in press(Part 17 of this series).
3) (a) R. M. Fuoss and D. Edelson, J. Am. Chem. Soc., 73, 269(1951); (b) I. L. Jenkins and C. B. Monk, J. Chem. Soc., 1951, 68.
4) By solving an algebraic equation of order three by the method of Cardan.
5) See, for example; C. Hirose, Kagaku-no-ryoiki, 28, 66(1974), and references cited therein.
6) A complete list of this program is available upon request to H.Y.
7) W. A. Millen and D. W. Watts, Aust. J. Chem., 19, 43 and 51(1966).
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10) See, for example; H. Schneider, in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker Inc., N.Y.(1969), Vol. 2, Chap. 11.

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