accord with speculations concerning the strong mixing of metal and porphyrin orbitals and the low stabilities of its axial ligand complexes.[19,20]

Registry No. ZnTMTPyP, 40603-58-5; Zn(etioporphyrin), 40148-68-3; Zn(mesoporphyrin DME), 15376-02-0; Zn(protoporphyrin DME), 15304-09-3; Zn(dibromodeuteroporphyrin DME), 40603-60-9; Zn(*ms*-tetraphenylporphine), 14074-80-7; Zn(*ms*-tetrapyridylporphine), 31183-11-6; zinc, 7440-66-6; copper, 7440-50-8.

Acknowledgments. We thank the U. S. Atomic Energy Commission (Contract No. AT-(40-1)-4047), the Gulf Educational Foundation, and the Howard University Biomedical Interdisciplinary Project for financial support.

(19) L. J. Boucher, *Coord. Chem. Rev.*, 7, 289 (1972).

(20) Note Added in Proof. We find that the Cu-ZnTPyP reaction is strongly catalyzed by NO_3^-, possibly indicating an activated complex containing all three species. This is reasonable since both metal ion incorporation[6] and acid-catalyzed solvolysis reactions[8] of zinc-TMTPyP involve a nitrate term.

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Cobalt-59 Nuclear Magnetic Resonance Shifts and the Acidity of Amine Protons in Tris(ethylenediamine)cobalt(III)

J. Wilinski[1] and R. J. Kurland*

Received February 5, 1973

The acidity of NH protons in metal-amine complexes is relevant to several proposed mechanisms for substitution reactions of these complexes, as, for example, in the SN1 conjugate base mechanism for substitution of cobalt(III) amines.[2] Since such NH protons are only very weakly acidic, nmr techniques are useful in supplementing other measures of the extent of neutralization in strongly basic solutions.[3,4] We report here a ^{59}Co nmr determination of K_n, the pseudothermodynamic constant for the neutralization reaction HA + $OH^- = H_2O + A^-$, where HA represents tris(ethylenediamine)cobalt(III)–$Co(en)_3{}^{3+}$–and A^- its conjugate base. In our work, the ratio of maximum observed shift to line width was about 20, which corresponds to a greater effective resolution than that reported in proton nmr determinations of the neutralization constant for $Co(en)_3{}^{3+}$ [3] and for platinum-amine complexes.[4]

Experimental Section

Cobalt-59 nmr measurements were taken as free induction decay spectra at 1.41 T (14.1 kG) and 30° on a Bruker BKR 321s variable-frequency pulsed spectrometer which had been modified for external lock, field-frequency control. Frequency shift measurements (taken with respect to the ^{59}Co resonant frequency of $Co(en)_3{}^{3+}$ in aqueous neutral solutions) were reproducible, for a given sample, to ±10 Hz over a 24-hr period. The relatively short relaxation times–3-10 msec–were the principal source of error in frequency measurements. Samples were run immediately on preparation (in tightly stoppered tubes to prevent CO_2 absorption) as 0.5 *M* aqueous solutions of $Co(en)_3Cl_3$ to which known volumes of *ca.* 19 *M* NaOH solutions were added. These NaOH solutions were standardized just before use by titration against primary standard KHP.

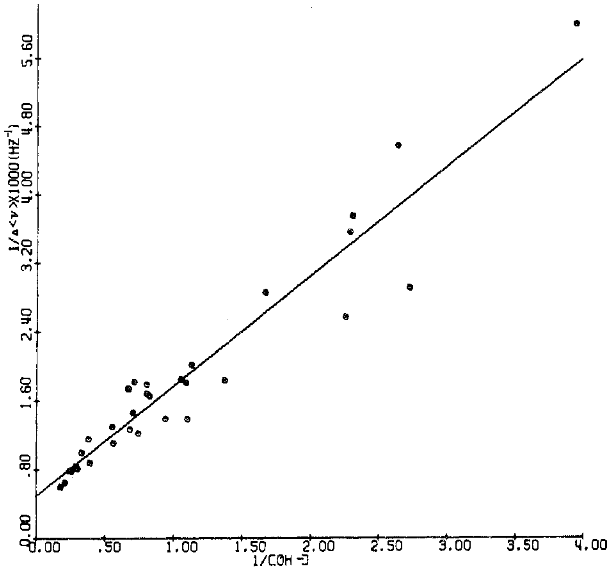

Figure 1. Least-squares fit to eq 1 of the inverse observed frequency shift as a function of inverse molar hydroxide ion concentration, corrected for the amount consumed by neutralization.

Results and Discussion

The variation of ^{59}Co frequency with OH^- concentration is most conveniently analyzed by the double-reciprocal plot[5] shown in Figure 1. This linear plot follows from eq 1, which

$$(\Delta\langle\nu\rangle)^{-1} = (\Delta\nu_0)^{-1} + (K_n\Delta\nu_0(OH^-))^{-1} \qquad (1)$$

is valid for fast exchange between $Co(en)_3{}^{3+}$ and its conjugate base and for ideal solution behavior. In eq 1, $\Delta\langle\nu\rangle$ and $\Delta\nu_0$ are, respectively, the observed frequency shift and the frequency shift of the conjugate base, both taken with respect to the frequency of $Co(en)_3{}^{3+}$ in neutral solution; K_n is the neutralization constant defined above. An iterative least-squares procedure, which corrected the nominal OH^- concentration for the amount consumed by the neutralization, was used to fit the data points to eq 1. This least-squares treatment gave $K_n = 0.39 \pm 0.05\ M^{-1}$ and $\Delta\nu_0 = -(2.0 \pm 0.3) \times 10^3$ Hz.[6] The value for K_n is in agreement with that determined by Navon, *et al.*,[3] from proton nmr and optical measurements.

Two other explanations for the large ^{59}Co nmr shifts produced by increased OH^- concentration could, in principle, be offered: (1) base-catalyzed substitution of a coordinated nitrogen by OH^- or by H_2O; (2) ion-pair formation between OH^- and $Co(en)_3{}^{3+}$. The first explanation is precluded on the following grounds. The ^{59}Co frequencies changed immediately to their equilibrium values on addition of appropriate amounts of strong acid; however, it is known that the hydrolysis of $Co(en)_3{}^{3+}$ is slow ($k_2 = 7 \times 10^{-4}\ M^{-1}$ at 70°).[7] Ion-pair formation as a source of the ^{59}Co frequency shifts is unlikely, since the frequencies of $Co(en)_3{}^{3+}$ in 1.7 *M* NaCl solution and in neutral solution without added salt differed by less than 10 Hz.

The value of $\Delta\nu_0$, the frequency shift for the $Co(en)_3{}^{3+}$

---

(1) NDEA Fellow.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 183.

(3) G. Navon, R. Panigel, and D. Meyerstein, *Inorg. Chim. Acta*, 6, 299 (1972).

(4) L. E. Erickson, *J. Amer. Chem. Soc.*, 91, 6284 (1969).

(5) K. E. Van Holde, "Physical Biochemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1971, p 61.

(6) This negative shift corresponds to the frequency for the conjugate base being less than that for $Co(en)_3{}^{3+}$ or to an *upfield* shift for the conjugate base.

(7) J. A. Friend and E. K. Nunn, *J. Chem. Soc.*, 1567 (1958).

conjugate base, can be used to estimate two other quantities of interest. For the lowest energy d-d transition of the conjugate base, one gets an estimated wavelength shift of 3 nm, based on the well-known correlation between ^{59}Co nmr frequencies and d-d transition wavelengths.[8,9] The fact that wavelength shifts have not been observed for $Co(en)_3^{3+}$ in strongly basic solutions[3,10] is consistent with this estimated value. An approximate upper limit for the mean lifetime for exchange (presumably due to proton transfer) between $Co(en)_3^{3+}$ and its conjugate base can be estimated from $\Delta\nu_0$: $\tau << 5 \times 10^{-4}$ sec for 0.39^{-1} *M* OH^- solutions of $Co(en)_3^{3+}$.

We found the ^{59}Co frequency of $Co(en)_3^{3+}$ to vary with DMSO concentration in mixed DMSO-water solutions. Although the behavior was qualitatively similar to that observed for basic solutions, the maximum observed shift with DMSO was about one-eighth as large as that at comparable OH^- concentrations and the reciprocal relation given in eq 1 was not obeyed. Since hydrogen bonding between DMSO and the amine protons probably occurs, one would expect a ^{59}Co frequency variation with increased DMSO concentration similar to that observed for the deprotonation reaction, although not as great in magnitude. The result that the ^{59}Co frequency change with DMSO concentration does not obey the reciprocal relation (eq 1) suggests that more than one amine group on a given complex may be hydrogen bonded to DMSO; accordingly, it would be necessary to invoke several equilibria in order to interpret quantitatively the variation of the ^{59}Co frequency change with DMSO concentration.

Registry No. Cobalt-59, 7440-48-4; $Co(en)_3^{3+}$, 14878-41-2.

Acknowledgments. We thank Dr. Tara Dasgupta for the $Co(en)_3Cl_3 \cdot 3H_2O$ sample used in this work and Drs. Gordon M. Harris and Ralph G. Wilkins for stimulating discussions.

[8] R. Freeman, G. R. Murray, and R. E. Richards, *Proc. Roy. Soc., Ser. A,* **242**, 4555 (1957).

[9] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, pp 374-377.

[10] R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 4878 (1956).

Contribution from the Chemistry Department,
University of Malaya, Kuala Lumpur, Malaysia

Proton Magnetic Resonance Study of $[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$

Tong-Chiew Tan[1] and Yau-Yan Lim*

Received February 6, 1973

Recently, proton magnetic resonance spectroscopy has been widely used in the study of ion association in solution.[2] The property that is being observed is the isotropic shift of the cationic protons in the presence of the paramagnetic anion. The interpretation of the isotropic nmr shift of the cation has stirred considerable interest for quite some time and it was only recently that it was established that the isotropic nmr shift, $\Delta\nu_p$, is the sum of two terms:[3,4] the Fermi contact shift, $\Delta\nu_c$, and the dipolar or "pseudocontact" shift, $\Delta\nu_{dip}$. Information such as ion-pair geometries and concentration association constants in various solvents can usually be determined from such a study.[5]

In this article, we report some additional findings obtained from the study of $[(C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$ in nitrobenzene, propylene carbonate, and chloroform. A special feature of this compound is that in contrast to the one studied earlier,[5] the cation is unsymmetrical and smaller in size. It would therefore be of interest to examine how these changes in the properties of the cation would affect the ion-pair geometry and association constant for the 1:1 electrolyte in nonaqueous solvents.

Experimental Section

The nmr spectra were obtained on a Hitachi Perkin-Elmer R-20B spectrometer at 34 (±0.5)°. Tetramethylsilane was used as the internal reference. The visible spectra were obtained with a Beckman DB-G spectrophotometer.

Preparation of Complexes. $[(n\text{-}C_4H_9)_3NCH_3]Br$ was prepared[6] by treating $(n\text{-}C_4H_9)_3N$ (Merck, for synthesis LAB) with CH_3Br (Fluka, Purum) using cyclohexane as solvent in the dark.

$[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PCoBr_3]$ was prepared by the method reported by Rettig and Drago.[7] The crude product was recrystallized from 2-butanol and dried over silica gel under vacuum. The melting point was 155-157° (uncorrected).

Anal. Calcd for $C_{31}H_{45}Br_3CoNP$: C, 48.91; H, 5.92; N, 1.84; Br, 31.51. Found: C, 48.69; H, 6.05; N, 1.70; Br, 31.7.

$[(n\text{-}C_4H_9)_3NCH_3][(C_6H_5)_3PZnBr_3]$ was prepared in the same way as the Co(II) analog. The melting point (uncorrected) was 139-141°.

Anal. Calcd for $C_{31}H_{45}Br_3ZnNP$: C, 48.5; H, 5.87. Found: C, 48.18, H, 5.93.

Analyses were performed by the Australian Microanalytical Service, Division of Applied Chemistry, CSIRO, and University of Melbourne.

Solvents. It was necessary to remove all traces of ethanol in the chloroform used (Merck; zur analyse) by column chromatography[7] because the complex was found to be decomposed by chloroform containing about 0.6-1.0% of ethanol as a preservative.[5] Nitrobenzene (H & W; Analar Standard) was fractionally distilled at reduced pressure and stored over molecular sieves 4Å. Propylene carbonate (Fluka; Purum) was dried over molecular sieves and distilled under reduced pressure. The distillate was stored over molecular sieves for at least 24 hr before use.

Treatment of Nmr Data. As shown previously,[5] for the equilibrium $C + A \rightleftharpoons CA$, where C represents the cation, A the anion, and CA the ion pair, the association constant K_{as} is defined as

$$K_{as} = [CA]/[C][A] \qquad (1)$$

where brackets denote concentration in terms of moles per liter of solution, and K_{as}^{-1} is given by

$$K_{as}^{-1} = \frac{[A_0]\Delta\nu_{pi}}{\Delta\nu_{oi}} - [A_0] - [C_0] + \frac{[C_0]\Delta\nu_{oi}}{\Delta\nu_{pi}} \qquad (2)$$

where $[A_0]$ and $[C_0]$ denote the initial concentration of anion and cation, respectively, $\Delta\nu_{pi} = \nu_{pi} - \nu_{di}$ is the isotropic shift of the *i*th set of protons, and $\Delta\nu_{oi} = \nu_{oi} - \nu_{di}$ is the observed isotropic shift of the *i*th set of protons.

In this article, for the solvent nitrobenzene the set of equivalent methylene protons next to the nitrogen atom as well as the methyl protons next to the nitrogen atom is used for calculation. It is found that the K_{as} values obtained by both methods agree within the limit of experimental error. The observed isotropic shifts for the *N*-methyl protons are used for the calculation of K_{as} in the solvent

---

[1] Abstracted in part from the M.Sc. thesis of T.-C. Tan, University of Malaya, Kuala Lumpur, Malaysia, 1973.

[2] L. Rosenthal and I. M. Walker, *Inorg. Chem.*, **11**, 2444 (1972), and references therein.

[3] P. K. Burkert, H. B. Fritz, W. Gretner, H. J. Keller, and K. E. Schwartzhans, *Inorg. Nucl. Chem. Lett.*, **4**, 237 (1968).

[4] D. G. Brown and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 1871 (1970).

[5] Y.-Y. Lim and R. S. Drago, *J. Amer. Chem. Soc.*, **94**, 84 (1972).

[6] J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968).

[7] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 2966 (1966).