ruthenium(II)[5] and permit a calculation of the self-exchange rate constant for this cobalt porphyrin. The electron-transfer mechanism for the reaction of $Co^{III}TMpyP$ with $Ru(NH_3)_6^{2+}$ is certainly of the outer-sphere type and the Marcus theory[11] can be applied to this system. According to this theory, for an outer-sphere electron-transfer reaction for which $\Delta G°$ is not too negative

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2}$$

where k_{12} and K_{12} are the rate and equilibrium constants, respectively, for the electron transfer reaction and k_{11} and k_{22} are the appropriate self-exchange rate constants.

The equilibrium constant K_{12} for the reaction

$$CoP(H_2O)_2{}^{5+} + Ru(NH_3)_6{}^{2+} \rightleftarrows CoP(H_2O)_2{}^{4+} + Ru(NH_3)_6{}^{3+}$$

is calculated from the present results and $E°' = -0.066$ V for $Ru(NH_3)_6^{2+} \rightleftarrows e^- + Ru(NH_3)_6^{3+}$ at $\mu = 0.5$ M.[12] This calculation leads to $K_{12} = 8.9 \times 10^5$. Since $k_{12} = 1.2 \times 10^5$ $M^{-1}\ s^{-1}$[5] and $k_{11} = 8.2 \times 10^2\ M^{-1}\ s^{-1}$ for $Ru(NH_3)_6^{2+/3+}$[13] we obtain that $k_{22} = 20\ M^{-1}\ s^{-1}$ for $CoTMpyP^{4+/5+}$.

Electron transfer to metalloporphyrins can occur through axial ligands or through the porphyrin ring system with the preferred pathway quite likely dependent upon the nature of the axial ligands as well as on the metalloporphyrin and reducing agent.[3] Sutin has suggested that for low-spin iron porphyrins in which electron transfer proceeds via the porphyrin π system, the self-exchange rate may be approximated by a value derived from the $Fe(phen)_3^{2+/3+}$ system.[14] It is thus implicitly assumed that three 1,10-phenanthroline molecules with their highly delocalized electron densities provide a ligand environment sufficiently similar to the porphyrin ligand that the self-exchange rates are comparable provided that the spin state of the metal is the same in both complexes. It has been shown, for example, that the $Fe(phen)_3^{2+/3+}$ estimate is not applicable to high-spin iron porphyrins.[15]

A direct comparison of the self-exchange rates of $CoTMpyP^{4+/5+}$ and $Co(phen)_3^{2+/3+}$ can be attempted with the knowledge that the oxidized form of both complexes involves low-spin cobalt[7,16] although the spin state of the aquo complex of $CoTMpyP^{4+}$ is less certain. The self-exchange rate constant for $Co(phen)_3^{2+/3+}$ is 21 $M^{-1}\ s^{-1}$[17,18] while the value for $CoTMpyP^{4+/5+}$ is 20 $M^{-1}\ s^{-1}$. The close agreement of the rates substantiates the Sutin hypothesis and suggests that, for the reduction of the diaquo form of $Co^{III}TMpyP$ by $Ru(NH_3)_6^{2+}$, electron transfer involves the π system of the porphyrin ligand.

Acknowledgment. We wish to acknowledge support of this research by the National Institutes of Health through Research Grant No. GM-17574 (R.F.P.) and by the National Science Foundation through Research Grant No. GP-41981X (W. R.H.)

Registry No. $(CoTMpyP)Cl_5$, 53149-77-2.

References and Notes

(1) University of Cincinnati.
(2) Ithaca College.
(3) R. F. Pasternack and N. Sutin, *Inorg. Chem.*, **13**, 1956 (1974).
(4) R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).
(5) R. F. Pasternack, *Inorg. Chem.*, **15**, 643 (1976).
(6) (a) R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967); (b) W. R. Heineman, B. J. Norris, and J. F. Goelz, *ibid.*, **47**, 79 (1975).
(7) (a) R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973); (b) *Biochem. Biophys. Res. Commun.*, **51**, 507 (1973).
(8) R. F. Pasternack, E. G. Spiro, and M. Teach, *J. Inorg. Nucl. Chem.*, **36**, 599 (1974).
(9) D. F. Rohrbach, E. Deutsch, and W. R. Heineman, "Characterization of Solutes in Non-Aqueous Solvents", G. Mamantov, Ed., Plenum Press, to be published.
(10) T. P. DeAngelis and W. R. Heineman, *J. Chem. Educ.*, **53**, 594 (1976).
(11) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964), and references cited therein.
(12) D. K. Lavallee, C. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **12**, 570 (1973).
(13) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).
(14) N. Sutin, *Chem. Br.*, **8**, 148 (1972).
(15) R. F. Pasternack and E. G. Spiro, in preparation.
(16) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).
(17) J. V. McArdle, H. B. Gray, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **96**, 5737 (1974).
(18) B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959).

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164

Water-Exchange Studies on Aqueous Manganese(II)- and Cobalt(II)-*o*-Phenylenediaminetetraacetate Complexes

Gordon Liu, Harold W. Dodgen, and John P. Hunt*

Received May 2, 1977 AIC70307W

Previous oxygen-17 NMR studies[1] on Mn^{II}–EDTA complexes have shown the presence of a seven-coordinate complex in aqueous solution. Lingafelter and Rose[2] and co-workers have recently done x-ray work on the Co(II) complexes of EDTA and *o*-phenylenediaminetetraacetate (PhDTA) finding a significant difference in structure, the EDTA complex being roughly octahedral, while PhDTA produces a more trigonal-prismatic structure. We thought it of interest to apply the oxygen-17 NMR techniques[3] to this ligand.

Experimental Section

The pure ligand was kindly prepared and supplied by Dr. E. F. K. McCandlish via Dr. Norman J. Rose. A cobalt(II) complex solution was prepared in 1% $^{17}OH_2$; [Co(II)] = 0.0595 *M*, [PhDTA] = 0.0655 *M*, pH 6. The solution did not appear to undergo oxidation in air (Rose et al. found none also). The Mn(II) complex did appear air sensitive and was therefore prepared under a nitrogen atmosphere, giving a light rosy pink color. The composition was [Mn(II)] = 0.0493 M, [PhDTA] = 0.0543 M, pH 6.3. For these studies 1% $^{17}OH_2$ was used as the blank or reference. The NMR techniques, equipment, and data treatment are discussed previously.[1]

Results

For the Co(II) solution at 30 and 80 °C only small line broadening and shift were seen (close to detection limit). For one H_2O/Co(II) we expected ca. 150 Hz shift (paramagnetic) and found ca. 18 Hz.

For Mn(II) large line broadenings and shifts were observed from 25 to 84 °C (see Table I). The shift data showed the water exchange to be in a fast-exchange limit. Treatment of the data in the usual way gave the following parameters: k_1(25 °C) (rate constant for a single H_2O exchange) = 3.5×10^8 s^{-1}, $\Delta H^{\ddagger} = 8.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 7.6$ cal mol^{-1} deg^{-1}, and A/h (scalar coupling constant) = 6.04×10^6 Hz.

Discussion

The results on the Co(II) complex are consistent with those of Rose et al.,[2] namely, that the complex is predominantly six-coordinate at pH 6–7, without bound water.

A comparison of the $Mn^{II}EDTA$ and $Mn^{II}PhDTA$ results is of interest. The analogous parameters for $Mn^{II}EDTA$ are k_1(25 °C) = 4.4×10^8 s^{-1}, $\Delta H^{\ddagger} = 7.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = 6.8$ cal mol^{-1} deg^{-1}, and $A/h = 6.04 \times 10^6$ Hz. These are remarkably similar to the PhDTA values and suggest to us that the present Mn(II) species is $Mn(PhDTA)(H_2O)^{2-}$ (seven-coordinate). We do not have direct evidence that the ligand is completely ligated in this case so that we can only be sure that there is one H_2O per Mn and the total coordination number is simply speculative. The "counting" of bound water is done assuming that A/h is constant (per H_2O) for Mn(II) complexes regardless of the presence of other ligands and here

Table I. Shift and Line Broadening Data for $Mn^{II}PhDTA^{a}$

Temp, °C	Shift, Hz	Q, K	Δ, Hz	$10^5 T_{2}{}'_{p}$, s
26.3	151 ± 36	4.42	2869 ± 37	0.55
39.2	138 ± 21	4.22	2118 ± 30	0.71
49.2	131 ± 2	4.13	1096 ± 8	1.43
59.2	125 ± 2	4.07	736 ± 24	2.13
69.0	122 ± 2	4.09	495 ± 7	3.17
83.8	118 ± 5	4.12	341 ± 29	4.60

[a] Here Q is defined as $TS[H_2O]/[Mn]$ and $T_{2}{}'_{p}$ as $[Mn]/\pi\Delta$ and T is the Kelvin temperature, S is the relative shift $(\Delta\nu/\nu_0)$, and Δ the line broadening in Hz. The errors are average deviations of five or six separate measurements at each temperature. The frequency was 11.495 MHz.

even a possible increase in coordination. The A/h per H_2O of $Mn(H_2O)_6{}^{2+}$ is, for example, $(5.8 \pm 0.2) \times 10^6$ Hz from our latest measurements. Seven-coordination is not unreasonable and thus the constancy of A/h seems to hold in this case, as well as in systems we have so far studied. A theoretical explanation for this observation is lacking. We can only suggest that the "S" state ion is largely ionically bound to the ligands.

Acknowledgment. This work was supported by NSF Grant GP-38771X.

Registry No. $Mn^{II}(PhDTA)(H_2O)^{2-}$, 63658-44-6; $Co^{II}(PhDTA)^{2-}$, 63625-64-9.

References and Notes

(1) M. S. Zetter, M. W. Grant, E. J. Wood, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **11**, 2701 (1972).

(2) Private communication from N. J. Rose; submitted for publication in *Inorg. Chem.*

(3) J. P. Hunt, *Coord. Chem. Rev.*, **7**, 1 (1971).

Contribution from the Department of Chemistry,
Revelle College, University of California, San Diego,
La Jolla, California 92093

Kinetics of Substitution in $Cr(en)_2LBr^{n+}$ Complexes

Laura Randolph and R. G. Linck*

Received February 16, 1977 AIC70123H

The mechanism of substitution on Cr(III) centers of the type $Cr(NH_3)_5X^{2+}$ or $Cr(H_2O)_5X^{2+}$ has recently been reviewed by Swaddle;[1] he has concluded on the basis of free energy correlations[2] and studies of the volume of activation[3] that the mechanism of such substitution is associative, I_a in the nomenclature of Langford and Gray.[4] This conclusion is to be contrasted with that of $Co(NH_3)_5X^{2+}$ complexes in which an I_d mechanism has been assigned.[4-6] We were interested in examining the consequences of this difference in the series of molecules of stoichiometry $M(en)_2ABr^{n+}$, in which Br^- is aquated, A is the "directing" group, and M is Co(III) or Cr(III). The data for the Co(III) complexes have long been available; the work that we report here allows the desired examination to be made.

Experimental Section

Materials. ***cis*-$[Cr(en)_2H_2OBr]Br_2 \cdot H_2O$.** Four and one-half grams of *cis*-$[Cr(en)_2Cl_2]ClO_4$[7] was dissolved in 40 mL of water and heated until the complex was in solution; the solution was cooled and a few drops of acetic acid added, followed by 7.5 g of $NaNO_2$ and 11.5 g of $NaClO_4$. The precipitate, which formed slowly, was removed, washed with ethanol, and dried; yield 2.9 g of *cis*-$[Cr(en)_2(ONO)_2]ClO_4$.[8] This material was treated with 15 mL of 2.0 N HBr, warmed to 60 °C, and then treated with 15 mL of concentrated HBr, heated for 5 min, and cooled. The precipitate was removed by filtration, washed with ethanol, and dried; yield 1.3 g (36%). Recrystallization was achieved by dissolving the material in 7 mL of 2.0 N $HClO_4$, filtering, and adding 5 mL of concentrated HBr to precipitate the product. Anal. Calcd for *cis*-$[Cr(en)_2H_2OBr]Br_2 \cdot H_2O$: Cr, 11.61. Found: Cr, 11.67. The spectroscopic parameters are λ_{max}, Å (ϵ, M^{-1} cm^{-1}): 5160 (72.9) and 3870 (59.4); lit.[9] values 5190 (72.2) and 3870 (60.5).

trans-$[Cr(en)_2H_2OBr]Br_2$ was prepared from *trans*-$[Cr(en)_2F_2]ClO_4$ as described by Fee, Harrowfield, and Jackson.[10] Anal. Calcd for *trans*-$[Cr(en)_2H_2OBr]Br_2$: Cr, 12.09. Found: Cr, 11.91. The spectroscopic parameters are λ_{max}, Å (ϵ, M^{-1} cm^{-1}): 5610 (22.4), 4550 (22.5), and 3830 (44.9); lit. values[9] 5610 (23.2), 4550 (24.9), and 3840 (44.8).

The 2-amino-2-(hydroxymethyl)-1,3-propanediol was from Eastman Kodak and was recrystallized from water prior to use. Pyridine was obtained from J. T. Baker. A solution of acidic ($HClO_4$) $LiClO_4$ was prepared from $LiCO_3$ and G. F. Smith perchloric acid with doubly distilled water.

Techniques. Kinetic runs were accomplished as follows: after separate thermostating of a dilute acidic solution of the Cr(III) complex and the base, 2-amino-2-(hydroxymethyl)-1,3-propanediol (whose concentration was chosen sufficiently high to act as a buffer), these two solutions were mixed, causing rapid deprotonation, followed by slower loss of Br^-. This latter step was monitored in the thermostated compartment of a Cary Model 14 recording spectrophotometer. The pH of the solutions was measured on a Radiometer Model 51 meter. Data points from kinetic runs were analyzed by a nonlinear least-squares computer program.

Results

Kinetics of *trans*-$Cr(en)_2OHBr^+$ Aquation. The rate of aquation of Br^- from *trans*-$Cr(en)_2OHBr^+$ was measured by the change in absorbance at 5800 Å. To confirm that this absorbance represents the desired reaction

$$trans\text{-}Cr(en)_2OHBr^+ \xrightarrow{k_b} Cr(en)_2(OH)(H_2O)^{2+} + Br^- \qquad (1)$$

we quenched a reacting solution after 5 half-lives by adding excess acid and examined the products spectrophotometrically. Using the spectral data of Woldbye,[11] we established that the resulting spectrum was that expected for *trans*-$Cr(en)_2(H_2O)_2{}^{3+}$ with small amounts of *trans*-$Cr(en)_2H_2OBr^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$. A quenching experiment at 10 half-lives confirmed that the source of the *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ was from the primary reaction and was not a result of isomerization of the products. The stoichiometry of the reaction is thus as indicated in eq 1 with the composition of the product species being 95% trans and 5% cis. (Of course, the state of protonation of the product depends on the pH of the solution.) Further confirmation of the stoichiometric assignment is achieved by comparison of the value of the absorbance observed after 10 half-lives, A_{00}, with that calculated on the basis of the extinction coefficients and K_a of the product species. For our experiment at pH 8.1, where the dominant product is *trans*-$Cr(en)_2(OH)_2{}^+$, we find $A_{00} = 0.485$ and calculate $A_{00} = 0.515$. At pH 7.13, where more *trans*-$Cr(en)_2OHH_2O^{2+}$ is present, we find $A_{00} = 0.535$ and calculate $A_{00} = 0.531$. The calculated and observed values agree within the errors generated by reading extinction coefficients off of Woldbye's graphs.[11]

The rate of loss of Br^- was studied at three temperatures over a range of [Cr(III)] from 7.4 to 13.0×10^{-3} M. There is no dependence on $[H^+]$ over the range pH 6.15–8.20, as can be seen from the data in Table I. Also to be found there are the calculated rate constants determined by nonlinear least-squares treatment of the k,T points.

To verify that the process was understood and to determine a kinetic value for the acidity of *trans*-$Cr(en)_2H_2OBr^{2+}$, we