Furthermore, its localization is certain since there is a overlap with the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition with a greater intensity. One peak in the region at *ca.* 21000 cm^{-1} is responsible for the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition, and the other two peaks corresponding to the excitation from the ground term $^4T_{1g}(F)$, (really $^4A_{2g}$ tetragonal) to excited terms $^4E_g(P)$ and $^4A_{2g}(P)$, both from the excition of the term, $^4T_{1g}(P)$. Finally, the band at 8020 cm^{-1} is attributed to the spin-forbidden transition, $^4T_{1g}(F) \rightarrow {}^2E_g(G)$. The assignment of the bands at 12480 and 16660 cm^{-1} is unlikely to correspond to the transitions $^4T_{1g}(F) \rightarrow {}^2T_{1g}(G)$ and $^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$, respectively. From the magnitudes $B = 840$ cm^{-1} as $B_0 = 971$ cm^{-1}(14), the nephelauxetic parameter, β_{35}, = 0.86. The reduction in the electronic repulsion parameter is small in the complex, which suggest some ionic character for the ligand-metal bonding. The C.F.S.E. is 8780 cm^{-1}.

$[NiCl_2(glyH)_3H_2O]$

The spectrum displays bands at 10000, 17241 and 28571 cm^{-1} of medium intensity are attributed to spin-allowed transitions, and a shoulder at 14598 cm^{-1} attributed to a spin-forbidden transition. The three d-d bands correspond to the transitions: $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ or $^1A_{1g}(G)$, respectively. The band at 10000 cm^{-1} is quite symmetric, nevertheless the bands at 17241 and 28571 cm^{-1} are asymmetric due to splitting of the terms $^3T_{1g}(F)$ and $^3T_{1g}(P)$, from a distorted tetragonal. The 1000Dq and B values are 10000 and 1054 cm^{-1} respectively, $B_0 = 1080$ cm^{-1} (15), $\beta_{35} = 0.97$. The C.F.S.E. is 12000 cm^{-1},

$[CuCl_2(glyH)_2(H_2O)_2]$

From the work of Jorgenssen(16) it is known that there are two $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions with similar frequencies to the octahedral but with an energy difference of magnitude 3 δ/2 and a band at lower energy, corresponding to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition. The two first bands appear as an asymmetric broad band at 17540 cm^{-1}; another band, at 35710 cm^{-1}, is attributed to charge tranfer. The C.F.S.E. in this complex is 10520 cm^{-1}.

On the basis of the results a tentative model for these complexes has been obtained, although solution of the exact structure must await a full x-ray analysis.

Acknowledgements

We wish to thank Prof. Dr. W. Beck, Institut für Anorganische Chemie, University of Munich, for his help and for useful comments during the stay of Dr. Castillo at that laboratory.

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(Received January 19th, 1984) TMC 1101

Kinetics of Substitution in Two Water Soluble Cobalt(III)-Porphyrins

Jacob Abwao-Konya, Anthony Cappelli, Lynnette Jacobs, M. Krishnamurthy* and Mahalia Smith

Department of Chemistry, Howard University, Washington, D.C. 20059, U.S.A.

Summary

Kinetics of substitution of thiocyanate and pyridine in the axial positions of tetra(*p*-trimethylammoniumphenyl)porphinatocobalt(III) and tetra(*p*-sulfonatophenyl)porphinato cobalt(III) were investigated at pH 4.00 and ionic strength 0.1 M ($NaNO_3$) in aqueous solution. These reactions were found to be as facile as other such reactions of cobalt(III) porphyrins even though a new synthesis was employed in the present study. The rates of these reactions are proportional to the base strength of the parent free base porphyrin. Electrostatic attraction between the ligand and the porphyrin peripheral charges were also found to enhance the rates. The cause of labilization is believed to be primarily electronic and not steric.

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* Author to whom all correspondence should be directed.

0340–4285/84/0707–0270$02.50/0

Introduction

Since the discovery that the cobaltporphyrins are labile(1), several reports(2) have appeared on these substitution reactions. Nevertheless most of these studies suffer from a serious flaw in that the mode of synthesis of the reactant cobaltporphyrins does not assure a cobalt(III) product. Cobalt(II) porphyrins are known to bind molecular dioxygen even reversibly(3). Recently it was reported(4) that after an aqueous solution of cobalt(III) porphyrin was evaporated, the residue, on redissolving in deoxygenated water, was found to contain about 15% in the cobalt(II) form. Such contamination(5) by cobalt(II) could possibly be the cause of labile substitution reactions. In order to verify this possibility, we synthesized cobalt(III)porphyrins by chemical oxidation, and investigated some of the substitution reactions.

Experimental

A Beckman Century model Acta CIII spectrophotometer and a Radiometer model PHM 64 meter were used for titration studies. Kinetic studies were performed employing a Durrum model stopped-flow apparatus thermostatted at 25 °C. All kinetic studies were carried out at pH 4.0 (potassium hydrogenphthalate buffer, 0.01 M) and $\mu = 0.1$ M ($NaNO_3$). Plots of $\log(A_t - A_\infty)$ *vs* time were linear for over three half lives. *Pseudo*-first-order rate constants computed were reproducible within 5%.

Standard chemicals such as cobalt(II) acetate (Baker Analyzed), mercury(II) nitrate (Mallinckrodt, AR), pyridine (Allied, Instrument grade), potassium thiocyanate (Allied, Reagent grade) were used as received. Stock solutions of porphyrins, pyridine, *etc.*, were made by appropriate weighing. The water-soluble porphyrins(6), H_2TAPP and H_2TPPS, were synthesized by the literature methods.

Cobalt(III) porphyrins

In a 500 cm^3 three-necked round-bottomed flask, H_2O (200 cm^3), free base porphyrin (1.0 g) and $Hg(NO_3)_2$ (0.1 g) were mixed with constant stirring. The solution became green. A condenser, a separatory funnel and a nitrogen-gas inlet were attached to the three necks of the flask. The solution was deoxygenated by bubbling N_2, and heated to the boiling point. Cobalt acetate solution (0.1 g in 10 cm^3 H_2O) was added through the funnel and the solution changed to red immediately, indicating completion of the reaction. After *ca.* 10 min the solution was cooled, filtered, and concentrated on a steam bath. In the case of the CoTAPP derivative, a saturated solution of $NaClO_4$ was added dropwise until precipitation was completed. The perchlorate salt was filtered, washed with small quantities of ice-cold H_2O, and dried *in vacuo*. (*Caution:* Perchlorate salts of organic compounds are known to be explosive!).

For the CoTPPS derivative, the solution was passed through a column (1 cm × 50 cm) of Dowex 50W–x8 cation exchange resin, in the Na^+ form, before evaporation to dryness. The residue was purified by Soxhlet extraction with MeOH and was recovered by precipitation with Me_2CO (Found: C, 41.2; H, 2.8; N, 4.4. $Na_3[CoTPPS] \cdot 12H_2O$ calcd.: C, 41.5; H, 3.8; N, 4.4%). The number of moles of water of hydration were chosen to fit the elemental analyses, but verified by thermogravimetry employing a DuPont model 990 unit. (Found: C, 39.3; H, 3.9; N, 6.7. $[CoTAPP](ClO_4)_5 \cdot 16H_2O$ calcd.: C, 39.8; H, 5.5; N, 6%). This degree of hydration fits the elemental analyses. It could not be proved by thermogravimetry because of the danger of explosion and the fact that the quarternary ammonium compounds decompose easily on heating. Due to poor solubility, techniques such as n.m.r. could not be employed. All elemental analyses were performed by MicAnal of Arizona, USA.

Results and Discussion

In order to establish the nature of metalloporphyrin species in solution, a spectrophotometric titration was carried out varying the pH with sodium hydroxide. A plot of the absorbances of various solutions as a function of their pH shows two inflections. Similar were obtained by Ashley and Leipoldt(7). However, analysis of the curve revealed that neither of the inflections corresponds to one proton dissociation; they were always fractional and, even after allowing for experimental limitations, could not be rounded to an integral proton release. As this result indicates some sort of aggregation, we carried out these titrations in the presence of detergents such as Triton X-100, lauryl sulfate and cetylammonium sulfate. With 2% Triton, the solution pH took longer to stabilize above a pH of 8.0 and the second inflection in the titration curve changed significantly. With 4% Triton, the curve contained essentially one inflection if held long enough for the pH to stabilize (*ca.* 15 min for each addition of the base). Nevertheless the analysis of the titration curve still did not yield integral proton values, indicating that in solutions above pH 7.00, some type of hydrolytic aggregation takes place, much as reported by Pasternack and Parr(8). This necessitated all our studies being carried out below pH 6.00.

Spectrophotometric titrations were done with varying amounts of thiocyanate and of pyridine with CoTAPP. For the thiocyanate, although the spectra of solutions during initial additions exhibit an isosbestic point, it was not possible to attain saturation due to the limited solubility of the porphyrin thiocyanate salt. With pyridine, as noted by Pasternack *et al.*(9) for CoTMPyP, the Soret band of CoTAPP, without any added pyridine, does not go through the isosbestics for the rest of the curves. This indicated that the addition of second ligand is

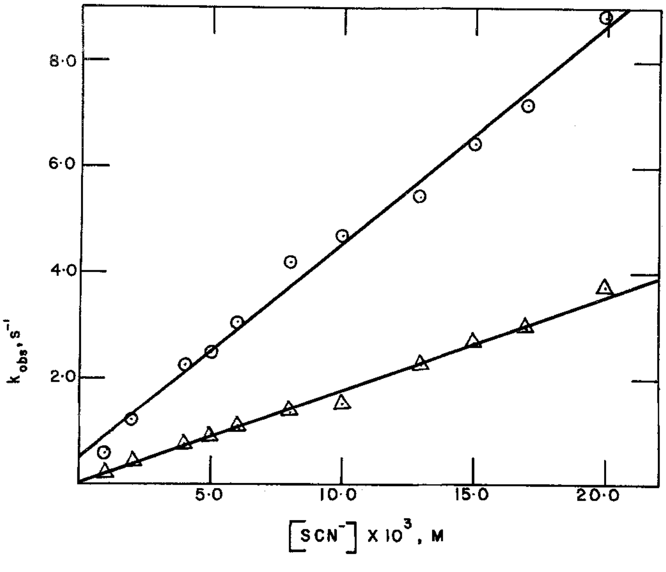

Figure 1. Plot of k_{obs} *vs* $[SCN^-]$ for SCN^- substitution in cobaltporphyrins: -⊙-⊙-: CoTAPP; -△-△-: CoTPPS.

Table 1. Summary of rate constants for the substitution of SCN^- and pyridine into different water-soluble cobaltporphyrins.

Compound	Rate constants[a)] SCN^- k_1	k_2	Pyridine k_1	k_2	k_3	k_4	Ionic strength, M
CoTAPP	499	–	428	0.0071	454	–	0.1[b)]
CoTPPS	179	–	520	0.0110	1370	–	0.1[b)]
	324	–	956	0.00304	3160	0.0377	1.0[c)]
CoTMPyP	2.10	3.1×10^{-4}	0.7	6×10^{-7}	2.8	5.8×10^{-5}	0.5[d)]
CoTCPP	450	0.15	1400	$\leqslant 10^{-3}$	2100	0.022	0.5[e)]

[a)] k_1 and k_3, $M^{-1} s^{-1}$; k_2 and k_4, s^{-1}; [b)] this work; [c)] Ref. 7; [d)] Ref. 9; [e)] Ref. 8.

faster than the first. Even the smallest addition of pyridine caused a substantial spectral change indicating that the equilibrium constant for the first ligand binding is too large for this technique to be of any value. As a result, no attempts were made to compute any equilibrium constants from the titration data. As any cobalt(II) porphyrin impurity would only affect the kinetic results and not the equilibrium data, we presumed the earlier reported results for CoTPPS to be valid.

Substitution of thiocyanate at the axial positions of cobalt porphyrins were carried out at pH 4.0. The thiocyanate concentration was varied from 1.00×10^{-3} M to 2.00×10^{-2} M. The observed *pseudo*-first-order rate constants, k_{obs}, were plotted as a function of $[SCN^-]$ in Figure 1. The linear plots with intercepts suggest the rate law to be as shown.

$$\text{Rate} = (k_1[SCN^-] + k_2)\,[\text{cobalt porphyrin}] \tag{1}$$

Such a simple rate law would fit many sets of mechanisms. A well accepted[(7, 8)] one is as follows.

$$\begin{array}{c} [(H_2O)_2\,CoTAPP]^{5-} + SCN^- \\ \rightleftharpoons \\ [(H_2O)(SCN)CoTAPP]^{6-} + H_2O \quad k_1, k_2 \end{array} \tag{2}$$

The k_1 and k_2 values thus obtained for CoTAPP and CoTPPS are summarized in Table 1.

Substitutions of pyridine were also carried out at pH 4.0, over 1.0×10^{-3} M to 2.0×10^{-2} M concentration range in total pyridine. The observed *pseudo*-first-order rate constants did not exhibit any relationship to either the total pyridine or pyridinium concentrations; but the plots of such rate constants as function of free pyridine were linear (Figure 2), suggesting a rate law similar to Equation (1) above. Corresponding rate constants for the pyridine reaction with both cobalt porphyrins are also presented in Table 1.

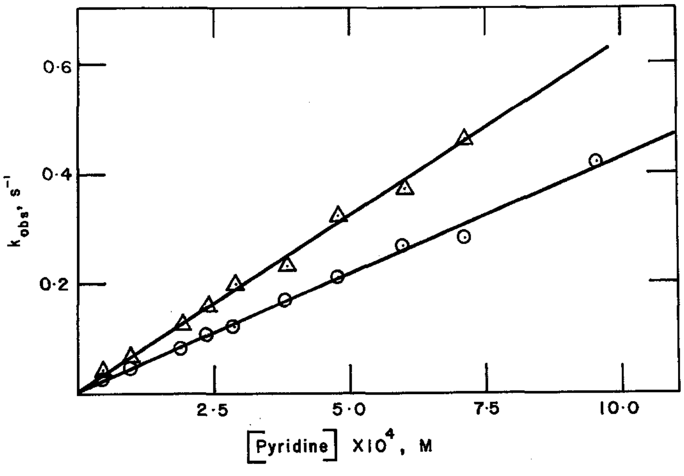

Figure 2. Plot of k_{obs} *vs* $[\text{Pyridine}]_{free}$ for the first pyridine substitution in cobaltporphyrins; –⊙–: CoTAPP; –△–: CoTPPS.

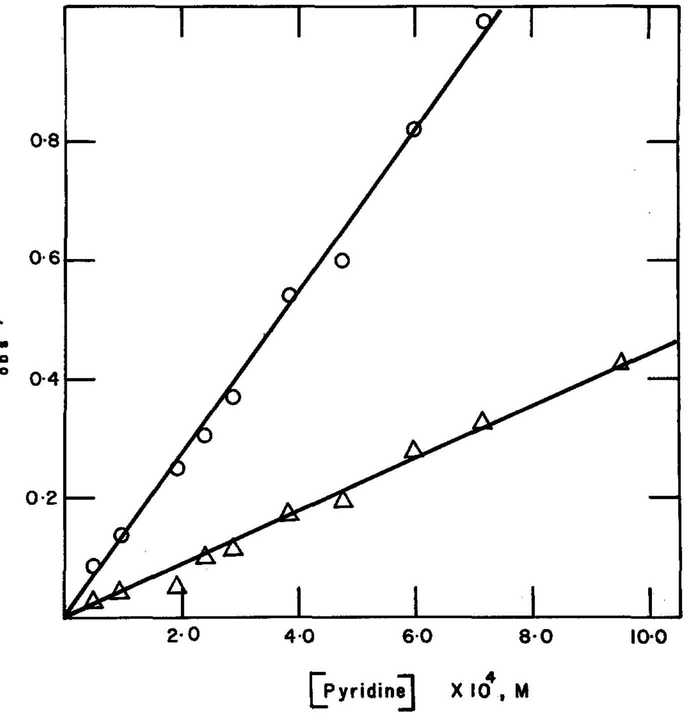

Figure 3. Plot of k_{obs} *vs* $[\text{Pyridine}]_{free}$ for the second pyridine substitution in cobaltporphyrins which were preequilibrated with pyridine; –△–: CoTAPP; –⊙–: CoTPPS.

Substitution of the second pyridine was investigated with cobalt porphyrin solutions, which were preequilibrated with a very small amount of pyridine. Here again the pyridine concentration was varied over 1.00×10^{-3} M to 2.00×10^{-2} M range. The second addition was indeed faster than the first, as inferred from the titration results. In Figure 3, the observed *pseudo*-first-rate constants are plotted as a function of free pyridine concentration. Absence of any noticeable intercept in this graph indicates either that the dissociation of the product complex does not take place or that the rate constants for such dissociation are exceedingly small. The rate constants, k_3, for this reaction are also presented in Table 1.

On the basis of this data, the following order of substitution of pyridine (both the first and second ligands) and thiocyanate into cobalt porphyrins can be arrived at: for pyridine: CoTCPP ⩾ CoTPPS > CoTAPP ⩾ CoTMPyP; for thiocyanate: CoTAPP > CoTCPP ⩾ CoTPPS ⩾ CoTMPyP. The order of basicity (as a measure of electron donating ability, pK_3 is a good indicator) for the parent free base porphyrins is: $H_2TCPP > H_2TPPS > H_2TAPP \geqslant H_2TMPyP$. Thus the order of pyridine substitution into cobalt porphyrins parallels the basicity. A similar conclusion was noted earlier in detergent solutions of cobalt porphyrins(10). However, the enhanced labilization noted for thiocyanate reaction with CoTAPP illustrates the importance of an additional factor – the electrostatic forces between the anionic ligand and the peripheral charges of the porphyrins. A plausible explanation for the lack of such enhancement with CoTMPyP could be that the positive charges are so delocalized over the *meso*-pyridine rings of the porphyrin as to be ineffective compared to the localized positive charges on the periphery of CoTAPP.

In conclusion, labilization of ligand substitutions of cobalt porphyrins is not caused by the contamination of cobalt(II). Considering the lack of such labilization with chromium(III)porphyrins(11), the most likely cause of such labilization of cobalt porphyrins is the availability of low lying energy levels in cobalt enabling enhanced internal electron transfer such as: $\mathrm{Co^{(III)}{-}P \leftrightarrow Co^{(II)}{-}P^{+}}$, similar to that proposed earlier for $\mathrm{Ni^{(III)}{-}P}$(12). Factors such as the extent of labilization being directly proportional to electron donating ability as indicated by the basicity of free base porphyrin, the reduction potential(13) of cobalt in the porphyrin complex being moderately positive compared to hexamminecobalt$^{(3+)}$, and the ease of photoreduction in aqueous solution(14), also support such a conclusion.

Acknowledgement

Financial assistance from Grant # 5 SO 6 RR0801611 from the MBS Program, DRR/NIH is gratefully acknowledged.

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(Received November 29th, 1983) TMC 1072

Benzenocarbothioamide Complexes of IIB Metal Halides

Alfonso Castiñeiras*

Departamento de Química Inorgánica, Facultad de Farmacia, Centro Coordinado del C.S.I.C., Universidad de Santiago;
Santiago de Compostela, Spain

Agueda Arquero and José R. Masaguer

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma, Canto Blanco; Madrid-34, Spain

Summary

Complexes having the empirical formula $\mathrm{M(BCTA)_2X_2}$, (M = Zn or Hg; X = Cl, Br or I) and $\mathrm{Cd(BCTA)X_2}$ (X = Cl, Br or I) are formed by reaction of benzenocarbothioamide (BCTA) with anhydrous zinc(II), cadmium(II) or mercury(II) halides and have been isolated and characterized by elemental analysis, conductance and molecular weight measurements, and by i.r., Raman and ^{1}H n.m.r. spectral studies. They are not appreciably ionized in acetonitrile solvent. The i.r. ν(CN) shift to higher a frequency and ν(CS) shift to a lower frequency indicate that BCTA is bound to the metals through sulphur. A tetrahedral structure with C_{2v} symmetry is proposed for $\mathrm{[M(BCTA)_2X_2]}$ on the basis of the i.r. and Raman data, and a dimeric tetrahedral structure with C_{2h} skeletal symmetry for $\mathrm{Cd(BCTA)X_2}$. The ^{1}H n.m.r. spectral measurements also show coordination through the sulphur atom.

Introduction

Thioamides are Lewis bases that generally co-ordinate to metals through the sulphur atom of the thiocarbonyl group. However, the nature of substituents on both the thioamide carbon and on the thioamide nitrogen may lead to different

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* Author to whom all correspondence should be directed.

0340-4285/84/0707-0273$02.50/0