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The Stability of Bis(2,4,6-tripyridyl-*s*-triazine)cobalt(II)

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The bis complex of cobalt(II) and 2,4,6-tripyridyl-*s*-triazine (TPTZ) dissociates in acid solutions according to the reactions

$$\mathrm{Co(TPTZ)_2^{2+} + 2H^+ \rightleftharpoons Co(TPTZ)^{2+} + (TPTZ)H_2^{2+}} \quad \text{(A)}$$

$$\mathrm{Co(TPTZ)^{2+} + 2H^+ \rightleftharpoons Co^{2+} + (TPTZ)H_2^{2+}} \quad \text{(B)}$$

Equilibrium constants determined spectrophotometrically for reactions A and B are 2.63 ± 0.03 and 0.603 ± 0.006 M^{-1}, respectively, at 25° and $\mu = 0.23$. Equilibrium constants for reactions C and D were redetermined under the same conditions and are $(1.52 \pm 0.005) \times 10^{-3}$ and $(1.8 \pm 1.5) \times 10^{-3}$ M, respectively. $\Delta H = 0 \pm 1$ kcal mol^{-1} for all of these

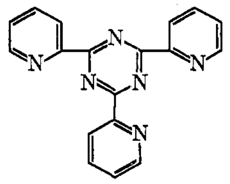
$$\mathrm{(TPTZ)H_2^{2+} \rightleftharpoons (TPTZ)H^+ + H} \quad \text{(C)}$$

$$\mathrm{(TPTZ)H^{2+} \rightleftharpoons TPTZ + H^+} \quad \text{(D)}$$

reactions. The resulting free energies of formation for the bis and mono complexes are $\Delta G_{\mathrm{II}} = -7.2 \pm 0.5$ and $\Delta G_{\mathrm{I}} = -7.9 \pm 0.5$ kcal mol^{-1}, respectively.

Introduction

The chemistry of 2,4,6-tripyridyl-*s*-triazine (abbreviated as TPTZ) and its complexes has not been thoroughly explored. The iron complexes of TPTZ have been studied by Pagenkopf and Margerum.[2] We have measured the stability of the Co$^{\mathrm{II}}$–TPTZ complexes which have not been measured previously. The chemistry of this system formally resembles that of the cobalt–terpyridine complexes[3] in aqueous solution.



TPTZ

Experimental Section

Bis(2,4,6-tripyridyl-*s*-triazine)cobalt(II) bromide hemihydrate was synthesized by using the method of Vagg, *et al.*[4] *Anal.* Calcd for $\mathrm{C_{36}H_{24}N_{12}CoBr_2}$: C, 51.2; H, 3.0; N, 19.7; Co, 7.0. Found: C, 50.7; H, 3.02; N, 20.0; Co, 6.8. TPTZ ($\mathrm{C_{18}H_{12}N_6}$) and anhydrous $\mathrm{CoBr_2}$ (G. F. Smith Chemical Co.) were used as such without further purification. Other chemicals used were of ACS reagent grade.

The bis cobalt(II) complex of TPTZ absorbs at 530 and 480 mμ (log ϵ 2.77 and 2.83) consistent with earlier observations.[4] In this region TPTZ does not absorb at the concentrations used (4×10^{-4}–10^{-5} M). Absorption peaks of TPTZ were observed at 220, 246, and 290 mμ, respectively, consistent with previous work.[2,5] Absorption measurements were made at a temperature constant to ±0.05° using a Cary Model 14 spectrophotometer. The ionic strength was kept at 0.23 M using NaCl and HCl. Absorbances reported are given corrected to 1 cm.

Observations were made at 15, 25, and 35° for both the ligand–acid and the complex–acid systems. It was found that there was no measurable change in absorption with temperature. It follows that ΔH is unmeasurably small for the $\mathrm{Co(TPTZ)_2^{2+}}$ reactions in contrast to the terpyridine system.[3]

Treatment of Data

The absorbance of $\mathrm{Co(TPTZ)_2^{2+}}$ ion measured at various concentrations without added acid was found to obey Beer's law. Assuming only the bis complex absorbs at 530 mμ, we have

$$A_0 = \epsilon_1 b[\mathrm{Co(TPTZ)_2^{2+}}] \quad (1)$$

where A_0 is the absorption observed, b is the path length of the cell, and $[\mathrm{Co(TPTZ)_2^{2+}}]$ is the concentration of the complex at equilibrium.

A plot of C/A_0 *vs.* $[\mathrm{H_t}]^2/C$ gave a straight line with noticeable curvature at small values of abscissa (Figure 1), where C is the initial concentration of the complex and $[\mathrm{H_t}]$ the total concentration of hydrogen ion added. Similar behavior is also observed for the terpyridrine system.[3] Thus, the main reaction is

$$\mathrm{Co(TPTZ)_2^{2+} + 2H^+ \overset{K_1}{\rightleftharpoons} Co(TPTZ)^{2+} + (TPTZ)H_2^{2+}} \quad (2)$$

Solving eq 1 and the equilibrium constant expression for K_1, we obtain

$$\frac{C}{A} = \frac{2}{\epsilon_1} + \frac{K_1[\mathrm{H^+}]^2}{\epsilon_1 C} + \frac{A}{\epsilon_1^2 C} \quad (3)$$

Approximate values of ϵ_1 and K_1 for the bis complex calculated from the slope and intercept of the linear portion of Figure 1 were 780 and 0.68, respectively, neglecting the last term in eq 3 and assuming $[\mathrm{H^+}] = [\mathrm{H_t}]$.

Detailed analysis of the results requires including several additional equilibria describing the system

$$\mathrm{Co(TPTZ)^{2+} + 2H^+ \overset{K_2}{\rightleftharpoons} Co^{2+} + (TPTZ)H_2^{2+}} \quad (4)$$

$$\mathrm{(TPTZ)H_2^{2+} \overset{K_3}{\rightleftharpoons} (TPTZ)H^+ + H^+} \quad (5)$$

$$\mathrm{(TPTZ)H^+ \overset{K_4}{\rightleftharpoons} TPTZ + H^+} \quad (6)$$

Assuming only $\mathrm{(TPTZ)H_2^{2+}}$ absorbs at 290 mμ, K_3

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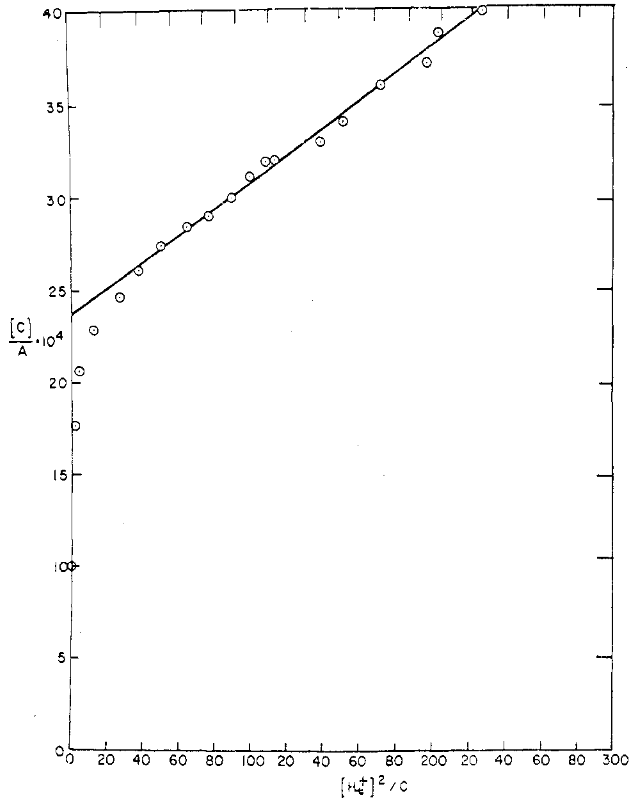

Figure 1.—Plot of variables in eq 3 showing dependence of C/A *vs.* $[H_t^+]^2/C$, at 25°. C is the total added $Co(TPTZ)_2^{2+}$ concentration and $[H_t^+]$ is hydrogen ion added.

and K_4 were redetermined using eq 5 and 6 by nonlinear least squares. Typical values of observed and predicted absorbance are listed in Table I. The values obtained for the extinction coefficient of $(TPTZ)H_2^{2+}$, K_3, and K_4 are given in Table II.

TABLE I

OBSERVED AND PREDICTED ABSORBANCE FOR THE TPTZ–ACID SYSTEM[a] AT 290 mμ, 25°, AND $\mu = 0.23\ M$

$10^3[H_t]$, M	A_o[b]	A_p[b]	$10^3[H_t]$, M	A_o[b]	A_p[b]
2.50	1.300	1.301	73.90	1.720	1.730
10.00	1.585	1.576	96.40	1.755	1.752
40.30	1.670	1.673			

[a] Every fourth observation is listed. $[TPTZ] = 4 \times 10^{-4}\ M$.
[b] A_o and A_p are observed and predicted absorbances.

Combining the equilibrium constant expressions for eq 2 and 4–6 with the mass balance equations for H, TPTZ, and $Co(TPTZ)_2^{2+}$, we obtained the system of three nonlinear equations (eq 7–9) which were solved numerically using trial values of the equilibrium constants.

$$C = [Co(TPTZ)_2^{2+}]\{1 + K_1[H^+]^2/[(TPTZ)H_2^{2+}] + K_1K_2[H^+]^3/[(TPTZ)H_2^{2+}]^2\} \quad (7)$$

$$[H_t] = [H^+] + 2[(TPTZ)H_2^{2+}] + K_3[(TPTZ)H_2^{2+}]/[H^+] \quad (8)$$

$$2C = [Co(TPTZ)_2^{2+}]\{2 + K_1[H^+]^2/[(TPTZ)H_2^{2+}]\} + [(TPTZ)H_2^{2+}]\{1 + K_3/[H^+] + K_3K_4/[H^+]^2\} \quad (9)$$

Observations were taken at 530 mμ, the $Co(TPTZ)_2^{2+}$ absorption maximum. It was evident that the mono complex does not absorb significantly at 530 mμ.

TABLE II

EQUILIBRIUM DATA FOR THE Co^{II}–TPTZ AND H–TPTZ SYSTEMS AT 25° AND $\mu = 0.23\ M$

Reaction	K, M^{-1}	Absorptivity,[c,e] $cm^{-1}\ M^{-1}$
2	2.63 ± 0.03[b]	ϵ_1^{530} 598 ± 4
4	0.603 ± 0.006	ϵ_2^{530} ≤ 5
5	$(1.52 \pm 0.005) \times 10^{-3}$ (1.8×10^{-3})[a]	ϵ_3^{290} $4.388\ (\pm 0.002) \times 10^4$
6	$(1.8 \pm 1.5) \times 10^{-3}$ (3×10^{-4})[a]	

Reaction	Free energy of formn,[d] kcal mol^{-1}
$Co^{2+} + TPTZ = Co(TPTZ)^{2+}$	$-\Delta G_I = 7.9 \pm 0.5$
$Co(TPTZ)^{2+} + TPTZ = Co(TPTZ)_2^{2+}$	$-\Delta G_{II} = 7.2 \pm 0.5$

[a] Reported in ref 2 at $\mu = 0.1$. [b] Uncertainties cited are estimates of the standard errors from the least-squares calculation. [c] The mono and bis complexes are denoted by 2 and 1, respectively. [d] The mono and bis complexes are denoted by I and II, respectively. [e] Absorptivity of the species $(TPTZ)H_2^{2+}$ at 290 mμ is denoted by ϵ_3^{290}.

A value of $\epsilon_{Co(TPTZ)^{2+}} \leq 5$ did not change the results. Co^{2+} absorption is negligible at this wavelength. To reduce the number of adjustable parameters absorptivity of $Co(TPTZ)^{2+}$ was arbitrarily chosen as 5 and was not adjusted. Thus

$$A_o = \epsilon_1[Co(TPTZ)_2^{2+}] + 5[Co(TPTZ)^{2+}]$$

where the concentration of the mono complex was obtained from the solution of eq 7–9 together with the equilibrium constant expression for K_1.

Table III shows the predicted and observed absorbances at 530 mμ for the bis complex ion and the agreement between observed and predicted absorbances demonstrates that reactions 2 and 4–6 are sufficient to describe the observations. All of the absorption data were taken together and used to adjust the absorptivity and equilibrium constant parameters simultaneously with no change in any of the parameters. Details of the nonlinear least-squares calculation have been described previously.[3,6–8]

TABLE III

OBSERVED AND PREDICTED ABSORBANCE[a] OF $Co(TPTZ)_2^{2+}$ AT 530 mμ, 25°, AND $\mu = 0.23\ M$

10^6C, M	$10^3[H]$, M	A_o	A_p[b]
32.0	1.0	0.190	0.220
32.0	3.0	0.130	0.135
32.0	4.0	0.110	0.110
32.0	7.0	0.092	0.095
16.0	5.0	0.070	0.080
4.0	5.0	0.032	0.028
400.0	0.0	2.359	2.356
100.0	0.0	0.570	0.572
25.0	0.0	0.143	0.147
6.25	0.0	0.036	0.036

[a] C, A_o, and A_p are the total concentration of $Co(TPTZ)_2^{2+}$ and the observed and predicted absorbance, respectively.
[b] Every third observation is reported.

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Results and Discussion

The equilibrium constants and absorptivities obtained in the present study are summarized in Table II, together with the free energy of formation for Co(TPTZ)$^{2+}$ and Co(TPTZ)$_2^{2+}$, ΔG_I and ΔG_{II}, calculated from our measurements. It should be noted that the large estimated error in free energy of formation is associated with the large standard error in K_4. The low estimate of ΔG_I should not be associated with the high estimate of ΔG_{II} and *vice versa*.

Pagenkopf and Margerum[2,9] determined K_3 previously and demonstrated that a second step was required to explain their kinetic data for the formation of Fe(TPTZ)$_2^{2+}$. They obtained an estimate of K_4 based on pH and photometric measurements at $\mu = 0.1$. Our values of K_3 and K_4 are concentration constants at $\mu = 0.23$ based on H$^+$ concentrations instead of pH and are somewhat different from theirs. The differences very likely can be ascribed to changes in the ionic medium and to the difficulty of determining a precise value for K_4.

All of the ΔH values are 0 within the experimental error (± 1 kcal mol^{-1}), and hence the stability of the complexes may be ascribed to large entropy increases. The bis(terpyridine)cobalt(II) complex is a low-spin system and has an overall ΔH of formation of -34 kcal mol^{-1}. We speculate that most of the large difference in entropy of formation arises from a more rigid, tightly bound structure in the latter complex as opposed to Co(TPTZ)$_2^{2+}$.

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On the Complete Assignment of Nuclear Magnetic Resonance Spectra of Glycinate Protons in Cobalt(III)-Aminocarboxylate Chelates[1]

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Complete assignments of the individual glycinate methylene protons in Co^{III}PDTA (PDTA = *dl*-1,2-propylenediamine*N,N,N',N'*-tetraacetate) and Co^{III}EDTA (EDTA = ethylenediamine-*N,N,N',N'*-tetraacetate) were accomplished by 100-MHz pmr spectroscopy. "Tickling" experiments were used to establish the identities of the overlapping AB patterns in Co^{III}PDTA. Stereospecific acid- and base-catalyzed deuterations of selected out-of-plane glycinate protons were carried out, leading to assignment of the out-of-plane glycinate proton resonances. Subsequent intramolecular scrambling of out-of-plane and in-plane glycinate groups was carried out by electrolytic reduction to the labile cobalt(II) complexes, followed by chemical reoxidation to the cobalt(III) complexes. This rapid and convenient method of scrambling enabled assignment of the in-plane glycinate protons. The magnitudes of the glycinate proton geminal coupling constants provide a valuable diagnostic for assignment of out-of-plane ($J \approx -18$ Hz) and in-plane ($J \approx -16$ Hz) AB patterns.

The use of proton magnetic resonance (pmr) in studies of the structures and reactions of aminocarboxylate chelates of cobalt(III),[3-9] rhodium(III),[9,10] palladium(II),[11,12] platinum(II),[13] and other metals has undergone steady growth. The pmr spectra of these chelates frequently include a number of overlapping AB patterns due to various pairs of nonequivalent spin-coupled glycinate protons. These complicated mixtures of AB patterns have been extremely difficult to solve completely and unambiguously. The use of H–N–C–H coupling to out-of-plane glycinate protons and the theory of anisotropic shielding has allowed a number of individual proton assignments to be made at 60 MHz for several aminocarboxylate chelates of the tetradentate and pentadentate variety. Work of this nature has recently been summarized by Legg and coworkers.[4d] There has, however, been only a single example, that of Co^{III}CyDTA, I (CyDTA = *trans*-1,2-cyclohexanediamine-*N,N,N',N'*- tetraacetate), where a complete assignment of the glycinate AB patterns of a hexadentate aminocarboxylate chelate has been accomplished, leading to identification of the chemical shifts of all eight glycinate protons.

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