

## The Cumulative Stability Constant of the Bis(1,2-ethanediamine) (1,3-propanediamine)cobalt(III) Complex Ion, $[\text{Co en}_2\text{tn}]^{3+}$

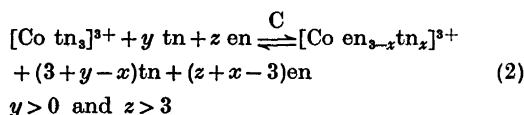
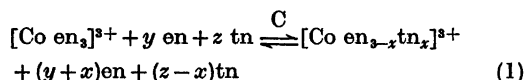
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The cumulative stability constant of  $[\text{Co en}_2\text{tn}]^{3+}$  relative to  $[\text{Co en}_3]^{3+}$  is measured in 1 M  $\text{NaNO}_3$  at 298 K. The difference,  $\log \beta_3(\text{Co en}_2\text{tn}^{3+}) - \log \beta_3(\text{Co en}_3^{3+})$ , is  $-2.12$ , giving  $\log \beta_3(\text{Co en}_2\text{tn}^{3+}) = 46.95$ . The corresponding figure for  $[\text{Co en tn}_2]^{3+}$  is tentatively given as 44.3. Equilibrium was reached from both sides, using  $[\text{Co en}_3]^{3+}$  and  $[\text{Co tn}_3]^{3+}$  as reactants, excess of the diamines, and activated carbon as catalyst. The four product species,  $[\text{Co en}_{3-x}\text{tn}_x]^{3+}$  ( $x=0, 1, 2, 3$ ), were separated by a paper chromatographic procedure.

Whereas the cumulative stability constant  $\beta_3$  of  $[\text{Co en}_3]^{3+}$  ( $\text{en}$  = ethylenediamine = 1,2-ethanediamine) has long been known,<sup>1,p,233</sup> attempts to determine  $\beta_3$  of the robust but less stable  $[\text{Co tn}_3]^{3+}$  ( $\text{tn}$  = trimethylenediamine = 1,3-propanediamine) using the Bjerrum cycle<sup>1,p,221</sup> failed due to precipitation of cobalt(II) hydroxide at increased pH.

Equilibria in robust Co(III) complex systems can be established with activated carbon as catalyst.<sup>1,p,235ff</sup> In the system  $[\text{Co en}_{3-x}\text{tn}_x]^{3+}$  ( $x=0, 1, 2, 3$ ), therefore, equilibrium conditions can be attained by adding carbon to a solution containing one of the terminal species of the series and excess amine:



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When the equilibrium is reached, further substitution will be quenched by removal of carbon, and if the concentrations of complexes and amines can be measured,  $\beta_3$  can be calculated relative to  $\beta_3$  of  $[\text{Co en}_3]^{3+}$ :

$$\frac{\beta_3(\text{Co en}_{3-x}\text{tn}_x^{3+})}{\beta_3(\text{Co en}_3^{3+})} = \frac{[\text{Co en}_{3-x}\text{tn}_x^{3+}]}{[\text{Co en}_3^{3+}]} \left( \frac{[\text{en}]}{[\text{tn}]} \right)^x \quad (3)$$

The amine concentrations can be found from

$$[\text{en}] = \frac{C_{\text{en}} - \sum_{x=0}^2 (3-x)[\text{Co en}_{3-x}\text{tn}_x^{3+}]}{1 + [\text{H}^+]K_{\text{enH}^+} + [\text{H}^+]^2K_{\text{enH}^+}K_{\text{enH}_2^+}} \quad (4)$$

and

$$[\text{tn}] = \frac{C_{\text{tn}} - \sum_{x=1}^3 [\text{Co en}_{3-x}\text{tn}_x^{3+}]}{1 + [\text{H}^+]K_{\text{tnH}^+} + [\text{H}^+]^2K_{\text{tnH}^+}K_{\text{tnH}_2^+}} \quad (5)$$

where  $C$  is the total amine concentration and  $K$  the acid dissociation constant,  $-\log K_{\text{enH}^+} = 10.17$ ,  $-\log K_{\text{enH}_2^+} = 7.49$ ,  $-\log K_{\text{tnH}^+} = 10.62$  and  $-\log K_{\text{tnH}_2^+} = 9.12$ .<sup>2</sup> Measurement of  $[\text{H}^+]$  can be done by potentiometry, and the complex species can be isolated quantitatively by a paper chromatographic method<sup>3</sup> developed in this laboratory.

### EXPERIMENTAL

*Equilibria.* Reactions were carried out in a closed vessel fitted with stirrer and glass and calomel electrodes (Radiometer G202B and K401), and placed in a thermostat at 298 K. pH was measured with a Radiometer PHM4. The glass electrode was selected on basis of linearity, which was measured with standard buffer solutions (0.025 M  $\text{KH}_2\text{PO}_4$  + 0.025

Table 1. All concentrations are in mol l<sup>-1</sup>.

	Complexes added [Co en <sub>3</sub> ] <sup>3+</sup>			[Co tn <sub>3</sub> ] <sup>3+</sup>	
<i>C</i> <sub>en</sub>	0.344	0.0769	0.321	0.0225	0.0616
<i>C</i> <sub>tn</sub>	2.953	3.529	3.626	2.697	2.233
pH corr.	11.74	11.99	12.09	11.67	11.99
[Co en <sub>3</sub> ] <sup>3+</sup>	0.0744	0.00981	0.0688	0.0166	0.0491
[Co en <sub>2</sub> tn] <sup>3+</sup>	0.0188	0.00776	0.0397	0.0059	0.0106
[Co entn <sub>2</sub> ] <sup>3+</sup>	—	0.00234	—	—	—
[en]	0.0810	0.0292	0.0348	0.0673	0.0872
[tn]	2.730	3.373	3.469	2.470	2.131
$[\beta_3(\text{Co en}_2\text{tn}^{3+})/\beta_3(\text{Co en}_3^{3+})] \times 10^3$	7.50	6.85	5.79	9.68	8.83
$[\beta_3(\text{Co entn}_2^{3+})/\beta_3(\text{Co en}_3^{3+})] \times 10^5$	—	1.79	—	—	—
log $[\beta_3(\text{Co en}_2\text{tn}^{3+})/\beta_3(\text{Co en}_3^{3+})]$	-2.13	-2.16	-2.23	-2.02	-2.05
log $[\beta_3(\text{Co entn}_2^{3+})/\beta_3(\text{Co en}_3^{3+})]$	—	-4.75	—	—	—

M Na<sub>2</sub>HPO<sub>4</sub>, pH=6.86; 0.01 M borax, pH=9.18; sat. Ca(OH)<sub>2</sub>, pH=12.45). pH as measured in the reaction vessel was calibrated by measurements on 0.1, 0.01 and 0.001 F HCl at constant ionic strength *I*=1. This pH was corrected for influence of Na<sup>+</sup> of the 1 M NaNO<sub>3</sub> medium.<sup>4</sup>

Stock solutions of amines were 1 M in NaNO<sub>3</sub> and, respectively, 0.591 M in en and 4.73 in tn.

Stock solutions were pipetted into the vessel, and a convenient pH of 10–12 established by addition of 1 M HNO<sub>3</sub>. Total volume ranged from 13 to 67 ml. 1–1.4 mmol accurately weighed [Co en<sub>3</sub>]Cl<sub>3</sub> or [Co tn<sub>3</sub>]Cl<sub>3</sub> and 0.15–1.0 g activated carbon were added to the vessel. After stirring for 48 h pH was measured and carbon removed by filtration and washing.

**Separations.** The equilibrium solutions were concentrated at room temperature under a stream of air. When the original volume exceeded 35 ml, NaNO<sub>3</sub> was precipitated with abs. ethanol and removed prior to renewed evaporation. The concentrated solutions underwent chromatographic separation as described elsewhere.<sup>3</sup> In the present case, two eluents were employed: 90% phenol:1-butanol:pyridine:benzene:acetone:water:80% acetic acid. No. 1, 30:14:14:14:14:0.5:0; No. 2, 30:14:14:14:14:1.5:2.5 by volume. Eluent No. 1 removed the bulk of the nitrates (48 h); No. 2 separated the complexes (48 h).

**Analyses.** Molecular weights of the complexes were obtained from Co analyses. The complexes were fumed to dryness with conc. H<sub>2</sub>SO<sub>4</sub>, diluted with H<sub>2</sub>O, and Co(II) determined with excess EDTA and backtitration with Zn(II).<sup>5</sup> The absolute molar amounts of complexes in the equilibrium mixtures were estimated from the weights and molecular weights of the chromatographic fractions and converted to concentrations by division with the total reaction volume. The data are presented in Table 1.

## RESULTS AND DISCUSSION

Table 1 shows that equilibrium has been reached from both sides, and that  $\log \beta_3(\text{Co en}_2\text{tn}^{3+}) - \log \beta_3(\text{Co en}_3^{3+}) = -2.12 \pm 0.08$ . The corresponding value for  $[\text{Co en tn}_2]^{3+}$ , -4.75, is reasonable, though merely indicative, as only one determination was made. It is experimentally very difficult to obtain a better estimate, and hardly possible for  $[\text{Co tn}_3]^{3+}$ . Such experiments would require very high concentrations of tn and therefore large reaction volumes, which due to the salt medium would further complicate the chromatography.

Absolute values of  $\beta_3$  may be estimated from a recent determination<sup>6</sup> of  $\beta_3(\text{Co en}_3)^{3+} = 49.07$  in 1 M KCl at 298 K. (Bjerrum's value<sup>1</sup>, p. 233 of 48.69 was measured at 303 K.) This gives  $\beta_3(\text{Co en}_2\text{tn}^{3+}) = 46.95$  and  $\beta_3(\text{Co en tn}_2)^{3+} \approx 44.3$ .

It may be relevant to compare our result with the measurements of Poulsen and Bjerrum<sup>2</sup> on  $[\text{Ni en}_x]^{2+}$  and  $[\text{Ni tn}_x]^{2+}$  complexes. In these labile systems, all consecutive stability constants could be measured, and from them we find that  $\log \beta_3(\text{Ni tn}_3)^{2+} - \log \beta_3(\text{Ni en}_3)^{2+} = -6.27$ . One-third of this value, -2.1, agrees well with our result, which suggests an intrinsic stability difference between six-membered and five-membered diamine chelate rings, to some extent independent of the metal and of the number of chelate rings.

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Received September 7, 1976.