

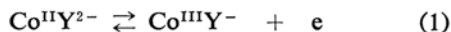
# Stability Constants of Some Substitution-inert Cobalt(III) Complexes

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(Received May 8, 1965)

Only a few investigations have been made on the stability constants of cobalt(III) complexes.<sup>1)</sup> This is because cobalt(III) forms mostly substitution-inert complexes; the formation of such complexes discourages considerably the determination of the stability constant. In this communication, the stability constants of cobalt(III) complexes with ethylenediaminetetraacetate (edta<sup>4-</sup>), propylenediaminetetraacetate (pdta<sup>4-</sup>) and trimethylenediaminetetraacetate (trdta<sup>4-</sup>), which are all substitution-inert, are presented, and compared with the stability constants of some divalent metal ions reported previously.<sup>2)</sup>

The equilibrium potentials of the reaction



were measured at the dropping mercury electrode with the solutions which contain varied concentrations of  $\text{Co}^{\text{II}}\text{Y}^{2-}$  and  $\text{Co}^{\text{III}}\text{Y}^{-}$ , where  $\text{Y}^{4-}$  denotes edta<sup>4-</sup>, pdta<sup>4-</sup> or trdta<sup>4-</sup> anion. From these values, the standard oxidation-reduction potentials of Eq. 1 ( $E_{\text{CoY}}^{\circ}$ ) were calculated. These values agreed to the half-wave potentials of the reduction waves of  $\text{Co}^{\text{III}}\text{Y}^{-}$  and the oxidation waves of  $\text{Co}^{\text{II}}\text{Y}^{2-}$ . The stability constants of  $\text{Co}^{\text{III}}\text{Y}^{-}$  ( $K_{\text{Co(III)Y}}$ ) were calculated by using the values of  $E_{\text{CoY}}^{\circ}$ , the stability constants of  $\text{Co}^{\text{II}}\text{Y}^{2-}$  ( $K_{\text{Co(II)Y}}$ )<sup>2)</sup> and the standard oxidation-reduction potential of the  $\text{Co(aq.)}^{2+} - \text{Co(aq.)}^{3+}$  couple (+1.842 V. vs. NHE).<sup>3)</sup> The results are given in Table I.

The stability constant of  $\text{Co}^{\text{III}}\text{edta}^{-}$  obtained in this study is in satisfactory agreement with that reported by Reilley et al.<sup>4)</sup> The stability constant of  $\text{Co}^{\text{III}}\text{pdta}^{-}$  is larger than that of  $\text{Co}^{\text{III}}\text{edta}^{-}$  by 1.5 in log  $K$  unit. This tendency, which agrees essentially with that reported previously,<sup>2)</sup> is considered to be attributed to the inductive effect of the methyl group of

TABLE I. THE STABILITY CONSTANTS OF COBALT(III) COMPLEXES WITH ETHYLENEDIAMINETETRAACETATE, PROPYLENEDIAMINETETRAACETATE AND TRIMETHYLENEDIAMINETETRAACETATE\*

Couple	$E_{\text{CoY}}^{\circ}$ V. vs. SCE	log $K_{\text{Co(II)Y}^{2-}}$	log $K_{\text{Co(III)Y}^{-}}$
$\text{Co}^{\text{II}}\text{edta}^{2-} - \text{Co}^{\text{III}}\text{edta}^{-}$	+0.13	15.71	40.6
$\text{Co}^{\text{II}}\text{pdta}^{2-} - \text{Co}^{\text{III}}\text{pdta}^{-}$	+0.12	17.07	42.1
$\text{Co}^{\text{II}}\text{trdta}^{2-} - \text{Co}^{\text{III}}\text{trdta}^{-}$	+0.05	14.48	40.7

\* The measurements were made with the solution containing 0.05 M acetate buffer (pH 4.6 to 5.4) at ionic strength 0.2 ( $\text{KNO}_3$ ) and 25°C.

coordinated pdta<sup>4-</sup> ion.<sup>2,5)</sup> On the other hand, the stability constants of  $\text{Co}^{\text{III}}\text{edta}^{-}$  and  $\text{Co}^{\text{III}}\text{trdta}^{-}$  are almost the same in magnitude. This supports the previous conclusion that the decrease in the size of metal ion favors the formation of trimethylenediaminetetraacetato complex;<sup>2)</sup> the ionic radius of cobalt(III) is smaller than those of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), and lead(II). In addition, it should be noted that cobalt(III) gives a stability constant considerably larger than chromium(III),<sup>6)</sup> manganese(III)<sup>7)</sup> and iron(III)<sup>8)</sup> in the case of EDTA complexes and also than iron(III)<sup>9)</sup> in the case of TRDTA complexes. This may relate to the fact that EDTA forms a spin-paired complex with cobalt(III),<sup>10)</sup> but not with chromium<sup>10)-</sup>(III), manganese(III),<sup>11)</sup> and iron(III).<sup>10)</sup> The details of the study will be reported later.

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