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

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Only a few investigations have been made on the stability constants of cobalt(III) complexes.[1] 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 ($edta^{4-}$), propylenediaminetetraacetate ($pdta^{4-}$) and trimethylenediaminetetraacetate ($trdta^{4-}$), which are all substitution-inert, are presented, and compared with the stability constants of some divalent metal ions reported previously.[2]

The equilibrium potentials of the reaction

$$Co^{II}Y^{2-} \rightleftarrows Co^{III}Y^{-} + e \qquad (1)$$

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

The stability constant of $Co^{III}edta^{-}$ obtained in this study is in satisfactory agreement with that reported by Reilley et al.[4] The stability constant of $Co^{III}pdta^{-}$ is larger than that of $Co^{III}edta^{-}$ by 1.5 in log K unit. This tendency, which agrees essentially with that reported previously,[2] is considered to be attributed to the inductive effect of the methyl group of coordinated $pdta^{4-}$ ion.[2,5] On the other hand, the stability constants of $Co^{III}edta^{-}$ and $Co^{III}trdta^{-}$ are almost the same in maguitude. This supports the previous conclusion that the decrease in the size of metal ion favors the formation of trimethylenediaminetetraacetato complex;[2] 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),[6] manganese(III)[7] and iron(III)[8] in the case of EDTA complexes and also than iron(III)[9] in the case of TRDTA complexes. This may relate to the fact that EDTA forms a spin-paired complex with cobalt(III),[10] but not with chromium[10]-(III), manganese(III),[11] and iron(III).[10] The details of the study will be reported later.

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

Couple	E°_{CoY} V. vs. SCE	log $K_{Co(II)Y}$[2]	log $K_{Co(III)Y}$
$Co^{II}edta^{2-}$-$Co^{III}edta^{-}$	+0.13	15.71	40.6
$Co^{II}pdta^{2-}$-$Co^{III}pdta^{-}$	+0.12	17.07	42.1
$Co^{II}trdta^{2-}$-$Co^{III}trdta^{-}$	+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 (KNO_3) and 25°C.

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1) L. G. Sillén and A. E. Martell, "Stability Constants," Chemical Society, London (1964).
2) H. Ogino, This Bulletin, 38, 771 (1965).
3) A. A. Noyes and T. J. Deahl, *J. Am. Chem. Soc.*, 59, 1337 (1937).
4) C. N. Reilley, W. G. Scribner and C. Temple, *Anal. Chem.*, 28, 450 (1956).
5) J. H. Grimes, A. J. Huggard and S. P. Wilford, *J. Inorg. Nucl. Chem.*, 25, 1225 (1963).
6) R. L. Pecsok, L. D. Shields and W. P. Schaefer, *Inorg. Chem.*, 3, 114 (1964).
7) N. Tanaka, T. Shirakashi and H. Ogino, This Bulletin, 38 (1965), in press.
8) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, 34, 576 (1951).
9) F. L'Eplattenier and G. Anderegg, ibid., 47, 1792 (1964).
10) W. Klemm, *Z. anorg. Chem.*, 252, 225 (1944).
11) Y. Yoshino, A. Ouchi, Y. Tsunoda and M. Kojima, *Can. J. Chem.*, 40, 775 (1962).