APPENDIX 1 : Stability of the complexes and statistical effects.

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There are two common ways to express on a quantitative basis the stability of ternary complexes [1-3]. The two methods are independent of the basicity of the ligands , A and B. Some of the general definitions used in both the methods are as follows.

Ligand A can combine with the metal ion in the following ways :*

$$M + A \rightleftharpoons MA \qquad K^{M}_{MA} = [MA] / ([M][A]) \qquad (1)$$

$$MA + A \rightleftharpoons MA_2 \qquad K^{MA}_{MA_2} = [MA_2] / ([MA][A]) \qquad (2)$$

$$M + 2A \rightleftharpoons MA_2 \qquad \beta^{M}_{MA_2} = [MA_2] / ([M][A]^2) \qquad (3)$$

Equations (1) - (3) hold analogously for ligand B. Formation of a ternary complex can be considered to be taking place in three different ways.

$$M + A + B \rightleftharpoons MAB \qquad \beta^{M}_{MAB} = [MAB] / ([M][A][B]) \qquad (4)$$

$$MA + B \rightleftharpoons MAB \qquad K^{MA}_{MAB} = [MAB] / ([MA][B]) \qquad (5)$$

$$MB + A \rightleftharpoons MBA \qquad K^{MB}_{MBA} = [MAB] / ([MB][A]) \qquad (6)$$

Hence ,

$$\log K^{MA}_{MAB} = \log \beta^{M}_{MAB} - \log K^{M}_{MA} \qquad (7)$$

$$\log K^{MB}_{MBA} = \log \beta^{M}_{MAB} - \log K^{M}_{MB} \qquad (8)$$

The ternary complexes MAB and MBA [cf. eqs. 5 and 6] are identical for labile species in solution.

* Charges are omitted in all the equations for clarity.

(i) The one approach compares the difference in stability $\Delta \log K$ e.g. for the reaction between CuA or $Cu^{2+}(aq)$ and the ligand B. On the basis of the properties of a cyclic system [1, 4] one can define $\Delta \log K$ as in eq.9. Consequently the influence of both ligands in a ternary complex is mutual and of the same size ; both ligands are either stabilized or destabilized in their coordination to the same metal ion. The difference , $\Delta \log K$, is the result from the substraction of two constants and must therefore also be a constant. This corresponds to the equilibrium indicated in eq. 10.

$$\Delta \log K = \log K^{MA}_{MAB} - \log K^{M}_{MB} = \log K^{MB}_{MBA} - \log K^{M}_{MA} \qquad 9$$

$$MA + MB \rightleftharpoons MAB + M \qquad 10$$

When the first ligand combines with a given multivalent (hydrated) metal ion , it has more coordination positions available for bonding than the second ligand. Hence , $\log K^{M}_{MA} > \log K^{MA}_{MA_2}$ usually holds and one expects to observe negative values for $\Delta \log K$. The difference , $\log K^{MA}_{MA_2} - \log K^{M}_{MA}$, is generally about - 0.5 to - 0.8 log units for monodentate ligands and about - 1 to - 2 log units for bidentate ligands [5]. A more satisfactory approach is to determine statistical values for $\Delta \log K$. In the case where A and B are bidentate ligands, there are twelve edges of a regular octahedron (Oh) available for the first entering ligand but only five for the second [6] i.e. the statistical factor is 5/12 and , accordingly , $\Delta \log K_{Oh} = - 0.4$. For a square - plane (sp) a factor of $\frac{1}{4}$, i.e. $\Delta \log K_{sp} = - 0.6$ is obtained. However , for the distorted octahedron (do) of Cu^{2+}_{aq} the statistical value is more difficult to assess · Considering the Jahn - Teller inversion to be rapid [7], there are eight (or even twelve) equivalent attacking positions for the first ligand while the value for the second ligand can vary from one to four (or even five) depending on the relative rates of inversion. Hence, the statistical value is between 1/8 (or 1/12) and 4/8 and $\Delta \log K_{do}$ = - 0.9 (or - 1.1) to - 0.3. In case of $Cu^{2+}(aq)$ and the ligands that introduce a strong ligand field, the statistical expression $\Delta \log K_{do/Cu} = -0.9$ is considered to be the most appropriate one [8]. Hence, an experimentally determined value of $\Delta \log K > -0.9$ indicates that in eq. **(10)** the ternary complex is favoured.

(ii) The other approach is based on the " disproportionation " constant, X as defined by eq. **11** ; log X may be calculated according to eqs. (**12**) or (**13**).

$$MA_2 + MB_2 \rightleftharpoons 2MAB ; X = [MAB]^2 / ([MA_2][MB_2]) \qquad \mathbf{11}$$

$$\log X = 2 \log \beta^{M}_{MAB} - (\log \beta^{M}_{MA_2} + \log \beta^{M}_{MB_2}) \qquad \mathbf{12}$$

$$\log X = (\log K^{MB}_{MBA} - \log K^{MA}_{MA_2}) + (\log K^{MA}_{MAB} - \log K^{MB}_{MB_2}) \qquad \mathbf{13}$$

For statistical reasons the value expected for X [eq. **(11)**] is 4, i.e. log X = 0.6[9-11], and the statistical value for one of the terms within brackets in eq. **(11)** is 0.3 log units. Hence , under purely statistical conditions one would expect the ternary complex to be formed to the extent of 50% while the binary parent complexes should occur to the extent of 25% each.

Each of the above two methods has its own merits and demerits and preference to either approach has to be given depending on the kind of study. The main advantage of the log X formulation is its firm statistical basis. This advantage is lost while using $\Delta \log K$ formulation since the statistical value depends upon the coordination number of the metal ion and the denticity of the ligand. However, the calculation of log X requires the knowledge of $K^{MA}_{MA_2}$ and $K^{MB}_{MB_2}$. For many systems containing large ligands these constants are often unknown and their direct determination impossible [3, 12, 13].

Electrostatic effects contribute differently to the $\Delta \log K$ and $\log X$ formulation depending upon the charge [2]. To a first approximation electrostatic factors cancel and do not contribute to mixed complex stability in the $\Delta \log K$ formulation when either ligand possesses a zero charge. However, they cancel in the $\log X$ expression only when the charges of the two ligands in the mixed complex are equal to each other. Thus in a mixed complex of 2,2'-bipyridyl and a negatively charged ligand, the electrostatic contribution to mixed complex stability is absent in $\Delta \log K$, but likely to be appreciable in $\log X$. The presence of electrostatic factors also implies an ionic strength dependence of $\Delta \log K$ and $\log X$ [2]. The $\log X$ values are appreciably influenced by the change in ionic strength (I) whereas $\Delta \log K$ values are less dependent upon I.

Steric hindrance between the two ligands in a MA_2 or MB_2 complex results in the distortions from a tetragonal geometry (in Cu^{2+}). However, this distortion may be absent in the ternary complexes as in the complexes of Cu containing bipyridyl [2, 14]. In the $\log X$ formation the stability of the mixed complex MAB is compared to that of the pure 2:1 complexes MA_2 and MB_2. In the cases where the geometry of the binary 2:1 and the mixed complex is different, e.g. in case of bipyridyl, the nontetragonal pure 2:1 complex is an inappropriate reference state for the mixed tetragonal complexes. For bipyridyl in a tetragonal reference state $\log K^{Cu}_{Cu A_2} \approx 0$. Thus for the ligands that suffer steric hindrance in their pure 2:1 complexes, the values of $\log X$ are increased by an amount that is irrelevant to the intrinsic tendency toward mixed complex formation.

Because the pure 2:1 complexes MA_2 and MB_2 are additional species not on the pathway for formation of the mixed complex MAB extraneous factors that enter into $K^{M}_{MA_2}$ and $K^{M}_{MB_2}$ appear in log X and give a misleading assessment of the instrinsic tendency toward mixed complex formation. This serious deficiency does not occur in the Δ log K formulation and for this reason it is the preferred method for comparisons.

References :

1. H. Sigel , Chimia , 1967 , **21** , 489.
2. R.B. Martin and R. Prados , J. Inorg. Nucl. Chem., 1974, **36** , 1665.
3. R. Griesser and H. Sigel , Inorg. Chem., 1970 , **9** , 1238.
4. H. Sigel , K. Becker and D.B. Mc Cormick , Biochim. Biophys. Acta 1967 , **148** , 655.
5. L.G. Sillen and A.E. Martell : Stability Constants of Metal Ion Complexes. Spec. Publ. No. 17 , The Chemical Society , London 1964 ; Suppl. No.1, London 1971.
6. R.F. Pasternack and H. Sigel , J. Am. Chem. Soc., 1970 , **92** , 6146.
7. D.B. Moss , C. - T. Lin and D.B. Rorabacker , J.Am. Chem. Soc. 1973 , **95** , 5179.
8. H. Sigel , Angew. Chem. Int. Ed. Engl. 1975 , **14(6)** , 394.
9. R. De Witt and J.I. Watters . J. Am. Chem. Soc. , 1954 , **76** , 3810.
10. S. Kida , Bull. Chem. Soc. Jpn., 1956 , **29** , 805.
11. V.S. Sharma and J. Schubert , J. Chem. Educ. , 1969 , **46** , 506.
12. H. Sigel · Structural Aspetcs of Mixed Ligand Complex Formation in solution, Vol. 2 (1973) of Metal Ions in Biol. Syst., ed. H. Sigel , Marcel Dekker, New York.
13. H. Sigel , R. Griesser , and B. Prijis , Z. Naturforsch , 1972 , **27b** , 353.
14. I.M. Procter , B.J. Hathaway and P.G. Hodgson , J. Inorg. Nucl. Chem., 1972 , **34** , 3689.