The Absence of Stereoselectivity in Planar Complexes of Optically Active 1,2-Diamines

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STEREOSELECTIVE effects in the formation of octahedral complexes from transition-metal ions and optically active 1,2-diamines have been much studied. Stereoselectivity in planar or tetragonal complexes, however, is not well documented although there are examples suggesting its existence.[1] A potentiometric study of copper(II) complexes of optically active α-amino-acids showed no difference in stability between the species $Cu(+L)_2$, $Cu(-L)_2$ and $Cu(+L)(-L)$ (where L is the ligand).[2] A reported difference, using a spectrophotometric method,[3] has not been confirmed.[4] Calculations by Corey and Bailar show that the α-amino-acid chelate ring is almost planar so that large differences in stability between the species $M(+L)_2$ [or $M(-L)_2$] and $M(+L)(-L)$ are not to be expected.[5] The chelate rings formed by 1,2-diamines, however, were shown to be puckered and the estimated difference in energy between the species $M(+L)_2$ and $M(+L)(-L)$ is 1 kcal. (corresponding to a difference in stability constant of *ca.* 0·73 log units at 25°) assuming all the other considerations (including solvation) to be equal.[5]

We have studied potentiometrically the 1:2 complexes formed between copper and (+)-, (−)-, and (±)-1,2-diaminopropane (pn), (+) and (±)-2,3-diaminobutane (bn), and (+)-, (−)-, and (±)-stilbenediamine and between nickel(II) and (+)- and (±)-diaminobutane. Three optically pure samples of diaminopropane were used; resolved by us, by Dr. Gillard (University of Kent), and Dr. Ugo (University of Milan). Other ligands were resolved by Dr. Ugo. The optically active samples of stilbenediamine weighed only a few milligrams and contained some carbonate so stability constants could not be calculated accurately. However, the formation curve of the copper complex of the racemic mixture in 40% aqueous dioxan, prepared from equal quantities of the (+)- and (−)-forms, was exactly midway between the curves for the (+)- and (−)-forms separately; the latter were calculated assuming analytical purity for the original samples.

In all cases the acid dissociation constants of the hydrochlorides of the (+)-, (−)-, and (±)-species were the same within ±0·015 pK units as expected and in no case did we find a significant difference in stability between the $M(+L)_2$, $M(-L)_2$, or the $M(+L)(-L)$ species. Stability constants were calculated using Irving and Rossotti's correction term method over the range $\bar{n}$ = 0·3 to 1·7.[6] The results are shown in the Table where the ranges quoted correspond to the standard deviations over four to seven separate titrations. Stability constants of the complexes with the racemic ligands have been measured previously by Basolo, Chen, and Murmann (working at an ionic strength of 0·5M-KNO_3).[7] Their results for the diaminopropane complexes are very close to ours but for diaminobutane complexes they found somewhat higher constants. The maximum difference in our results corresponds to difference in stability between the $M(+L)_2$ and $M(+L)(-L)$ species of about 0·1 kcal. for the nickel bis-complex and less for the copper complexes, rather than the 1 kcal. expected. This difference is within experimental error. Assuming the bis-complexes with copper to be approximately planar it is possible that small differences in solvation (*i.e.* entropy changes) may compensate for the enthalpy differences predicted by Corey and Bailar.

Stability constants at 25° and μ = 0·10 M

	$\log K_{CuL}$	$\log K_{CuL_2}$
(+)-pn	10·71 ± 0·02	9·22 ± 0·02
(−)-pn	10·73 ± 0·02	9·27 ± 0·02
(±)-pn	10·71 ± 0·02	9·23 ± 0·02
(+)-bn	10·87 ± 0·02	9·30 ± 0·02
(±)-bn	10·86 ± 0·01	9·27 ± 0·02

	$\log K_{NiL}$	$\log K_{NiL_2}$
(+)-bn	7·35 ± 0·03	6·09 ± 0·04
(±)-bn	7·39 ± 0·01	6·16 ± 0·03

A planar configuration for the nickel bis-complexes is less certain than for copper but visible spectra of the bis-complexes of the (+)- and (±)-forms of both diaminopropane and diaminobutane were found to be completely indistinguishable. Had the *cis*- and *trans*- isomers of the species $[Ni(bn)_2(H_2O)_2]^{2+}$ existed in different ratios in the (+)-L [or (−)-L] solution and the racemic mixture, spectral differences would be expected.[8]

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