The Conformation of Bis(amino-acidato)copper(II) Complexes

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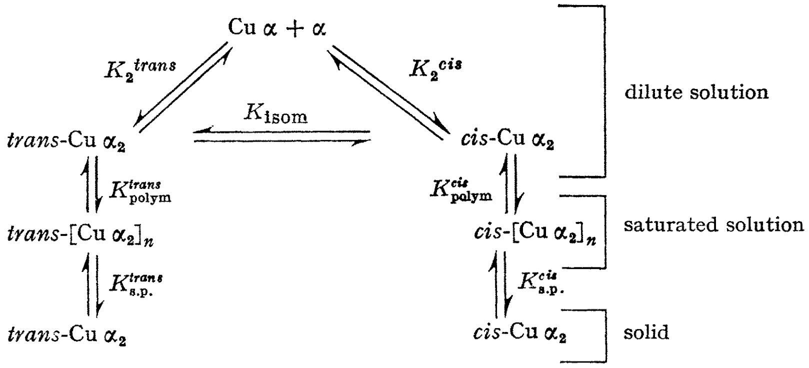
THE recent separation and crystallographic identification[1] of the *cis*- and *trans*-isomers of the optically active bis(α-alaninato)copper(II) complex invalidates previous assumptions, based on electronic spectra, that the only conformation of the Cu^{II} chromophore in bis(amino-acidato)-copper(II) complexes in solution, is *trans*. A rigorous examination of these complexes must encompass all the possible equilibria, as outlined in the following scheme. (The constants are self-explanatory.)



We report on the use of circular dichroism (c.d.) spectra as a method for establishing the preferred molecular conformation of kinetically labile complexes in solution. This is achieved by comparing the c.d. spectrum in the *d–d* transition region of the solid, dispersed in a potassium halide disc, with that of its aqueous solution. Mason and his co-workers[2] have applied this technique to the (+)-tris-ethylenediaminecobalt(III) salts and found good agreement between the solid and solution phases for a number of anions and site symmetries. We have found similar agreement for a variety of kinetically inert complexes. Consequently, where the solid-state c.d. spectrum and the solution c.d. spectrum are identical, the species giving rise to this spectrum must be the same.

Using this criterion, we have unequivocally established that for the 1:2 complexes of Cu^{II} with the bidentate ligands, L-isoleucine, L-valine, and L-tyrosine, the predominant species in solution is *trans* and, from the similarity of c.d. spectra (curves in the Figure are typical examples), this is the conformation in the solid state also for these complexes. The basis of this assignment is the known[3] *trans*-conformation of crystalline bis-(L-tyrosinato)copper(II).

The c.d. spectra of the various forms of bis-(α-*alaninato*)-copper(II) reveal that (i) the predominant species in solution† is *trans*, (ii) the c.d. spectrum of the solid *trans*-isomer is virtually enantiomeric to that of its solution, and

† All solutions were adjusted to pH 8·0—9·0 so that the complexes are of the bis-type only.[4]

(iii) the optical activity of the *cis*-isomer is considerably less than that of the *trans*-isomer. The reason for (ii) is not known, the preliminary crystal report[5] reveals only that the conformation is *trans* and that the complex is polymeric, which may be of significance to the present work. Clearly, more data are needed on this aspect. The optical activity of saturated solutions in equilibrium with *trans*-solid *A* (lower left-hand equilibrium of scheme) was identical to that of dilute solutions *B* prepared from either isomer, whereas the optical activity of 'aged' saturated solutions in equilibrium with *cis*-solid *C* (lower right-hand equilibrium of scheme) was less (*ca.* 25%) than that of *A* and *B*. For all three solutions the band positions in the c.d. and electronic spectra were identical. Clearly, some of the *cis*-form must be present in *C* according to the equilibrium scheme, and the lower optical activity of this solution can be attributed to the presence of this isomer, in line with the observation (iii) above. Furthermore, the implication that *cis*-isomer is present in a negligible amount in *A* and *B* is in keeping with the conclusion, from the c.d. spectra, that the *trans*-isomer is the predominant species for bis-(α-alaninato)-copper(II) in solution.

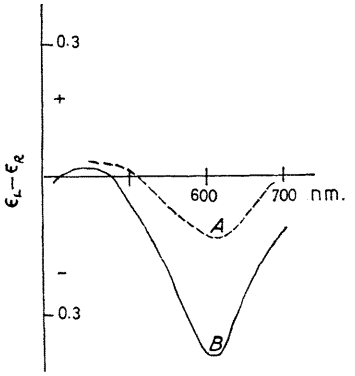


FIGURE. *Circular dichroism spectra of bis-*(L-*tyrosinato*) *copper*(II) *phases*: *A*, *solid* (*not to scale*); *B*, *aqueous solution* pH 8·6.

The application of this technique to other kinetically labile systems is to be given in a fuller report. We thank Dr. van der Helm for making his results available prior to publication.

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