51. Stereoselectivity in Reactions of Metal Complexes. VI[1]).

Kinetic Study of the Interconversion of *cis*-N and *trans*-N (S)-Aspartato-N-acetato(amino-acidato)cobalt(III) Complexes

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(24. IX. 76)

Summary

The *cis*-N/*trans*-N interconversion of the title compound containing glycine and (*R*)- or (*S*)-leucine has been studied by polarimetric and spectrophotometric techniques. Equilibrium constants were determined on the basis of kinetic and thermodynamic data. It is shown that the chirality of the bidentate amino-acid has a pronounced influence on the *cis-trans* equilibrium of these systems. Possible mechanisms of the interconversion reaction are discussed.

In a previous paper [1], we described the synthesis and the separation of the *cis*-N and *trans*-N isomers of mixed-ligand cobalt(III) complexes with (*S*)-aspartic-N-monoacetic acid ((*S*)-AMA) and different amino-acids as secondary bidentate ligands. During this work we have noticed that the solutions of the pure isomers are not stable and changes are taking place until an equilibrium mixture containing both isomers is finally produced. Furthermore, hydroxocomplexes are formed at higher pH-values as a result of partial dechelation of the quadridentate ligand (Fig. 1). By analogy with the structure found for $[Co((S)$- or (R)-$AMA)_2]^{3-}$ described previously, it is probably the 6-membered chelate ring which is opening.

In this paper we report some results about the kinetics of interconversion and the equilibrium between the two isomers *cis*-N- and *trans*-N-$[Co((S)$-$AMA)(AA)]^-$.

Fig. 2 shows the variation of the specific rotation, as a function of time, for the two isomers *cis*-N- and *trans*-N-$[Co((S)$-$AMA)(gly)]^-$. The curves demonstrate clearly two successive reaction steps. The formation of an intermediate is also evident from the visible spectra (Fig. 3).

The rates of the two reaction steps are sufficiently different to allow the determination of initial reaction rates for the isomerisation. The results obtained from

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[1]) Part V: see [1].

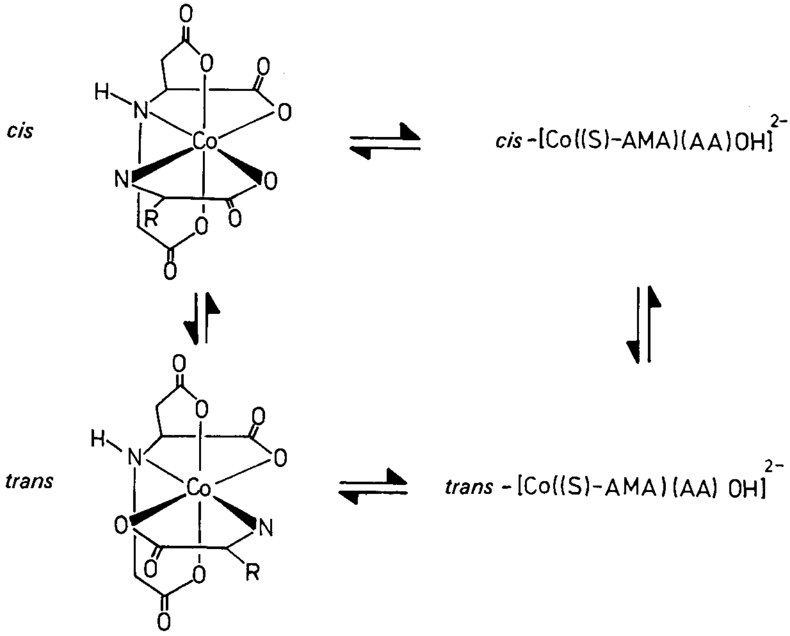

Figure 1

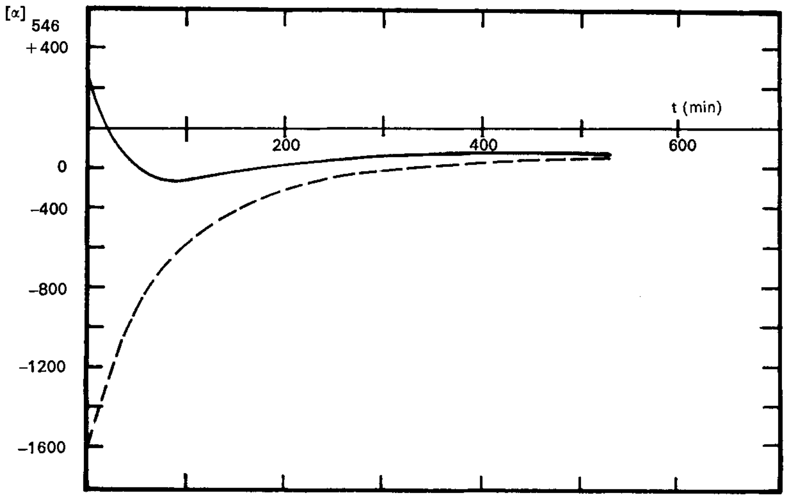

Fig. 2. *Variation of the specific rotation, as a function of time, for the two isomers* cis-*N*-(– – – –) *and* trans-*N*-[*Co*((S-*AMA*) *gly*]$^-$ (——) (pH=9.50, 55°)

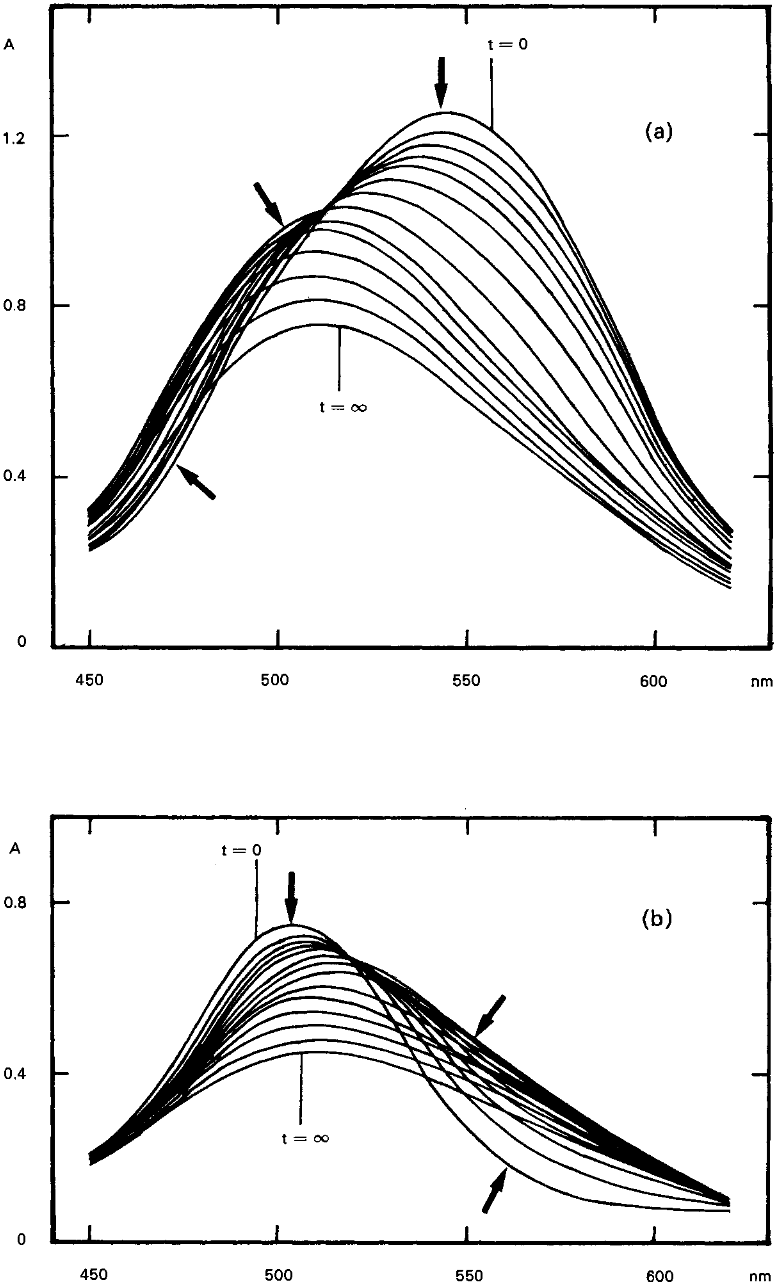

Fig. 3. *Variation of absorption for*

(a) cis-*N*-[*Co*((S)-*AMA*) *gly*]$^-$ ($c = 8.03 \cdot 10^{-3}$ mol/l; pH = 9.24, 55°)
(b) trans-*N*-[*Co*((S)-*AMA*) *gly*]$^-$ ($c = 5.24 \cdot 10^{-3}$ mol/l; pH = 9.28, 55°)
(time intervals variable)

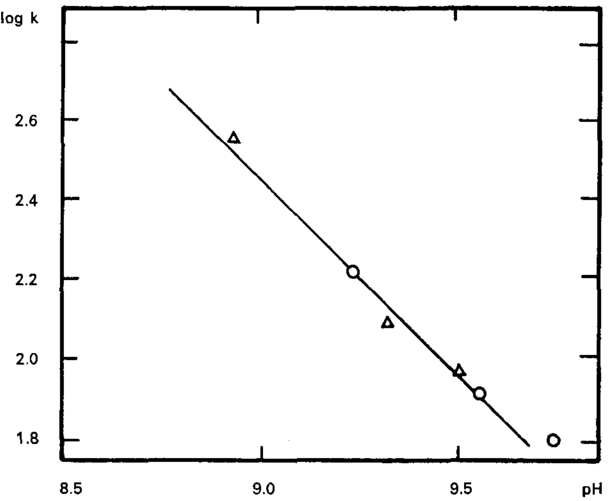

Fig. 4. *Isomerisation rate as a function of pH.* Polarimetric (*Δ*) and spectrophotometric (o) measurements; t = 55° (*k* in $\min^{-1}$)

polarimetric and spectrophotometric measurements are in good agreement and the rate of isomerisation is first order in $[OH^-]$ (Fig. 4).

The formation of hydroxocomplexes does not occur at pH $\leqslant$ 8. Fig. 5 shows the evolution of CD. and VIS. spectra of *cis*-N- and *trans*-N-[Co((*S*)-AMA)gly]$^-$ samples after three months at room temperature.

The isosbestic point of the VIS. spectra and the isorotatory point of the CD. spectra strongly suggest the presence of only two compounds, *cis*-N and *trans*-N. Chromatographic separation of each mixture on a Sephadex G 10 column (h = 125 cm; ⌀ = 4 cm; elution with water) further confirms the presence of both isomers only.

From these spectroscopic measurement we can determine the relative stability of the two isomers (*cf.* Table).

In order to study the influence of the substituents and of the absolute configuration of the amino-acid on the relative stability of the geometrical isomers, analogous measurements were carried out with complexes containing (*R*)- or (*S*)-leucine. The complexes with these amino-acids were chosen because of their slow rate of dechelation (Fig. 6).

The measurements were performed in NH_4^+/NH_3 as well as glycine/glycinate buffers. Both the initial rates of the isomerisation and the equilibrium *cis:trans* ratios were identical in either buffer medium. The results are given in the Table.

The equilibrium constants obtained from kinetic data and equilibrium composition coincide within experimental error for all three examples. The relative yields of the syntheses correspond approximatively to the equilibrium composition in the case of glycine, but not in the case of leucine. The chirality of leucine shows a strong influence on the relative stability of the geometrical isomers. Since the rate of isomerisation of the complex containing leucine is the same in glycinate as in ammonia buffers, it follows that the reaction takes place probably with chelate ring opening

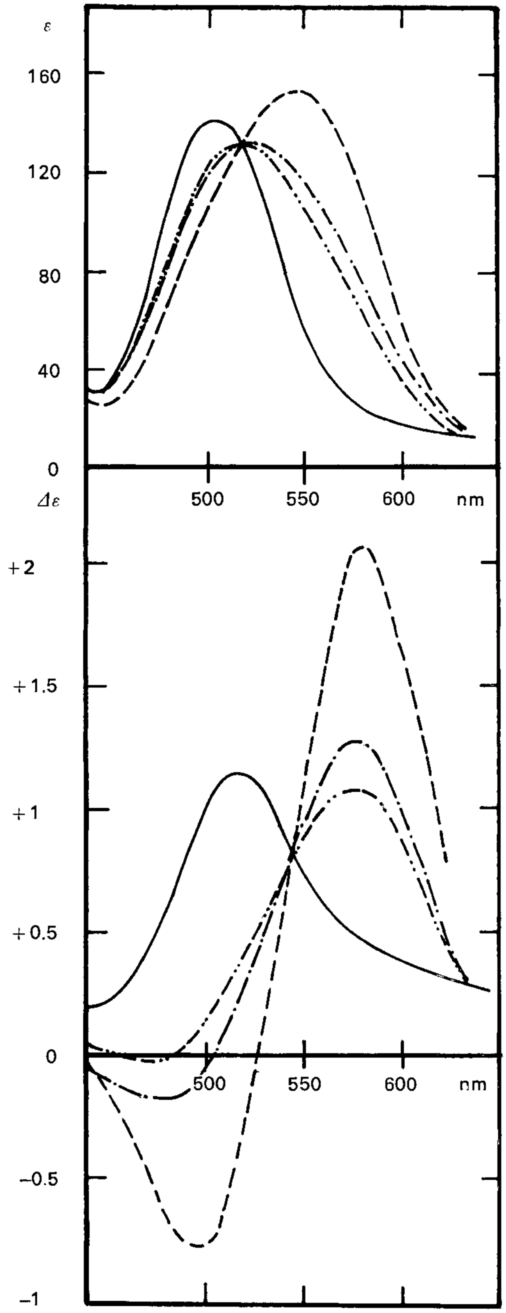

Fig. 5. *Evolution of CD.- and VIS. spectra of* cis-*N- and* trans-*N*-[*Co*((S)-*AMA*) *gly*]$^-$ *solutions* (pH = 8, room temperature) (——) *trans-N*; (– – – –) *cis*-N; (–·–·–) Mixture obtained from the *cis*-N; (–··–··–) Mixture obtained from the *trans*-N

but without complete dissociation of the amino-acid. Two interpretations would agree with the kinetic data: a) direct substitution of the carboxylate group of the amino-acid by OH^- and b) acid dissociation of the N–H group of the quadridentate

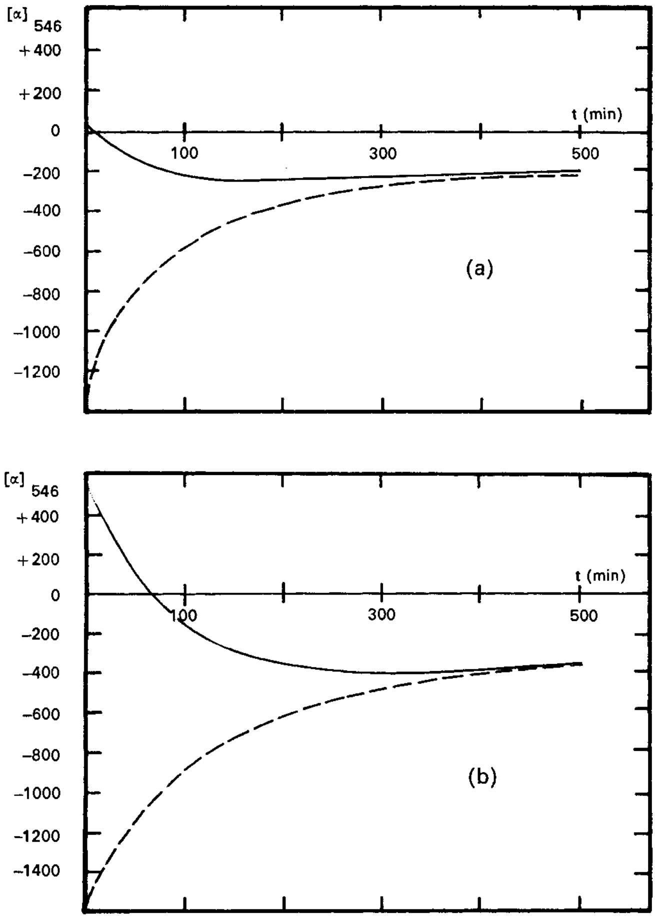

Fig. 6. *Variation of the specific rotation as a function of time, for*
(a) cis-*N*- (----) *and* trans-*N*-(*Co*((S)-*AMA*)((S)-*leu*)$]^-$ (——)
(b) cis-*N*- (----) *and* trans-*N*-[*Co*((S)-*AMA*)((R)-*leu*)$]^-$ (——) (pH=9.50, 55°)

Table. Cis/trans *ratios and relative rates of isomerisation of complexes of the type* [*Co*((S)-*AMA*)(*AA*)$]^-$

AA	[*cis*]/[*trans*] in the product of synthesis[a]	in the equilibrium mixture	v_0(*cis*)[d] / v_0(*trans*)
glycine	1.37	1.25[b]	1.2
(*R*)-leucine	1.31	0.93[c]	0.93
(S)-leucine	0.92	2.85[c]	2.69

[a] Ref. [1].

[b] From CD. measurements (pH=7.9; room temperature).

[c] pH=9.50; 55°. Equilibrium composition from specific rotation at infinite time. Specific rotation *vs.* time curves were corrected by extrapolation for the contribution of the second reaction step.

[d] v_0=initial rate, pH=9.50, 55°.

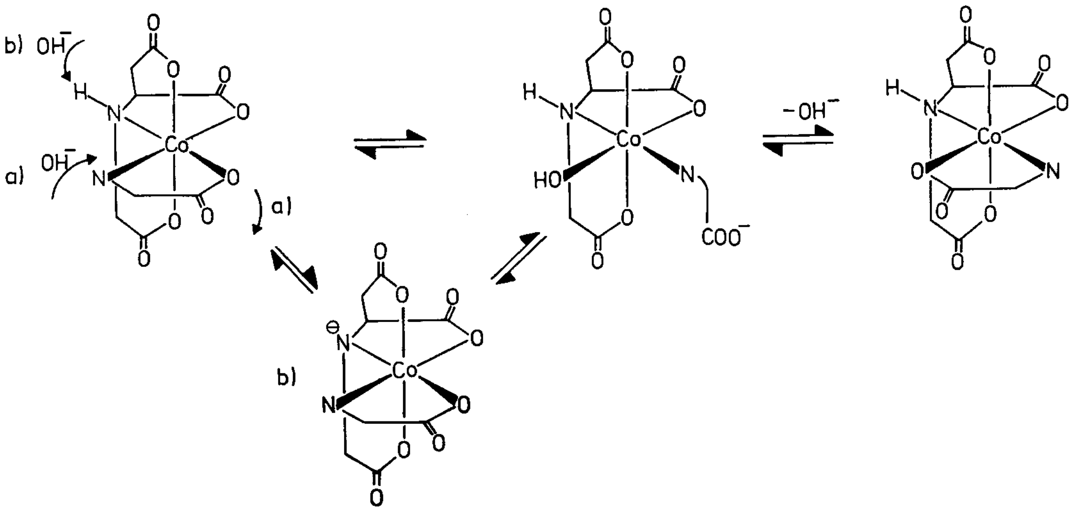

Figure 7

ligand decreasing the positive charge on the central atom, thus favouring the dechelation of the amino-acid (Fig. 7).

A definitive choice between these two possibilities would be premature. Further studies using in particular a quadridentate ligand with a methyl substituent on the nitrogen atom are in progress.

REFERENCES

[1] *G. Colomb & K. Bernauer*, Helv. *60*, 241 (1977).