

## OUTER-SPHERE INTERACTION OF (S)-ASPARAGINE AND (S)-GLUTAMINE WITH $[\text{Co}(\text{NH}_3)_6]^{3+}$ ION AND ITS POSSIBLE ROLE IN LIGAND SUBSTITUTION

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Optical activity of the achiral cation  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is induced both by (S)-AsnONa and (S)-GlnONa, as shown by a negative Cotton effect in the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition region. An outer-sphere interaction by three-point attachment of the amides can explain the fact that substitution reaction of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  with the mentioned amides in an alkaline medium is unusually slow as compared with other amino acids.

Substitution reaction of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation with (S)-asparagine (Asn) and (S)-glutamine (Gln) in the presence of charcoal affords specifically<sup>1,2</sup>  $\Lambda$ -mer- $[\text{Co}((\text{S})\text{-Asn})_3]$  and  $\Lambda$ -fac- $[\text{Co}((\text{S})\text{-Gln})_3]$ , respectively. The specific coordination of (S)-asparagine results from masking of the hydrophilic  $\text{NH}_2$  groups by hydrogen bonding with the amide group. Such interaction is sterically favoured only in the case of the  $\Lambda$ -mer isomer<sup>2</sup>. Similarly, in the case of the ternary complexes  $[\text{Co}(\text{en})_2(\text{S})\text{-Asn}]^{2+}$  and  $[\text{Co}(\text{en})((\text{S})\text{-Asn})_2]^+$  (but not the analogous complexes of Gln), isomers with favourable steric conditions for an interligand hydrogen bonding were formed preferentially<sup>3</sup>. In these and other cases<sup>4,5</sup> the geometry of the second coordination sphere clearly affects that of the primary sphere<sup>6</sup>. In an attempt to obtain the remaining  $[\text{Co}((\text{S})\text{-Asn})_3]$  isomers by substitution of the  $\text{NH}_3$  groups in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in an alkaline medium in the absence of charcoal, no substitution was observed even on prolonged heating<sup>7</sup>. We also have found<sup>7</sup> that reaction of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  with (S)-Asn or (S)-Gln afforded the  $\Lambda$ -fac- $[\text{Cr}((\text{S})\text{-Asn})_3]$  or  $[\text{Cr}((\text{S})\text{-Gln})_3]$  isomers. The observed fact indicates that, in the absence of charcoal, the  $\text{NH}_3$  groups of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in solutions containing the two amides are stabilized towards substitution. Moreover, the preference of the isomers depends considerably on the quality of the substituted ligands (cf. Co(III) and Cr(III)). These facts, and particularly the resistance of the  $\text{NH}_3$  groups to substitution, can be explained by formation of probably spatially oriented hydrogen bonds between the  $\text{NH}_3$  hydrogen atoms and (S)-asparagine or (S)-glutamine. According to Mason and Norman<sup>8</sup>, in a solution containing excess of an optically active compound, the

cation  $[\text{Co}(\text{NH}_3)_6]^{3+}$  exhibits a Cotton effect in the  $d-d$  transition region, induced by formation of an ion pair with mutually preferred orientation of both species. We have utilized this fact for the detection of interactions between  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and (*S*)-Asn or (*S*)-Gln using circular dichroism. The found values (for (*S*)-Asn:  $\Delta\epsilon = -3.67 \cdot 10^{-3}$ ; for (*S*)-Gln:  $\Delta\epsilon = -3.40 \cdot 10^{-3}$ ; both at 470 nm) show that both amides induced optical activity of the achiral chromophore  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transitions region. In both cases we observed a negative Cotton effect, typical for amino acids of the (*S*)-configuration<sup>9</sup>. Since the CD spectrum of the ion pair  $[\text{Co}(\text{NH}_3)_6]^{3+}-(\text{S})\text{-Asn}$  (*S*)-Gln) has a similar character as the CD spectra of  $[\text{Co}(\text{NH}_3)_6]^{3+}-(\text{AB})$  systems (where AB = (*S*)- $\alpha$ -amino acid), the negative Cotton effect should be induced by the same type of interactions<sup>10</sup>, *i.e.* by hydrogen bonding between the  $\text{NH}_3$  groups and the  $\text{COO}^{(-)}$  group of (*S*)-Asn or (*S*)-Gln. However, unlike other amino acids, both amides can be bonded in a combined manner, *e.g.* in a bidentate fashion through  $\alpha\text{-COO}^{(-)}$  and one or two  $\text{NH}_3$  groups, or in a terdentate manner involving the hydrogen bond to the amide linkage. The chelate rings of the terdentate ligand can assume several conformations one of which, with the carboxyl oxygen atoms and the  $\text{CH}_2$  group in the negative sector ( $\text{NH}_2$  and  $\text{CONH}_2$  groups in the positive sector), is depicted in Fig. 1. The carboxyl oxygen atoms are fixed above the nodal plane in the negative sectors by the  $\text{NH}_3 \cdots \text{O}=\text{C}-\text{NH}_2$  hydrogen bonding. As already mentioned, this arrangement is not the only possible conformation and for some other ones we should assume even a positive Cotton effect. Since the experimentally observed Cotton effect was negative, we assume that (*S*)-Asn as well as (*S*)-Gln prefer only the conformation shown in Fig. 1. This behaviour, related obviously with optimum steric requirements in the neighbourhood of the  $\text{NH}_3 \cdots \text{O}=\text{C}-\text{NH}_2$  hydrogen bond, cannot be unequivocally explained even using the molecular model. The experimentally observed greater stability of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  to substitution in the presence of (*S*)-Asn or (*S*)-Gln, supporting the concept of three-point attachment of the amide, agrees with the general trend of

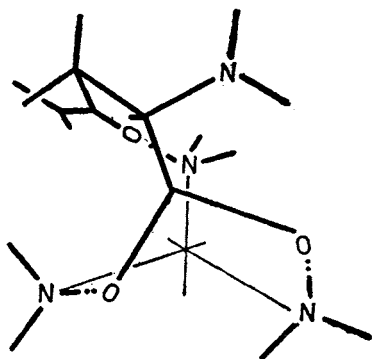


FIG. 1  
Orientation of (*S*)-asparagine in the ion pair  
 $[\text{Co}(\text{NH}_3)_6]^{3+}-(\text{S})\text{-Asn}$

stabilities of metal complexes, decreasing in the order terdentate ligand > bidentate ligand.

### EXPERIMENTAL

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  was prepared according to ref.<sup>11</sup>; (S)-Asn ( $[\alpha]_{546} + 36.7^\circ$  in 5M-HCl) and (S)-Gln ( $[\alpha]_{546} + 37.0^\circ$  in 5M-HCl) were Fluka products. The CD spectra were measured on a Jouan Roussel Dichrograph. The interaction between  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (M) and (S)-AsnONa (L) or (S)-GlnONa (L) was studied in solutions of concentration  $c_M = 0.1 \text{ mol dm}^{-3}$  and  $c_L = 0.5 \text{ mol dm}^{-3}$ .

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