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Absence of Tridentate Coordination of (S)-Glutamic Acid in [Co(dien)((S)-Glutamato-2)]$^+$ Ion

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Diethylenetriamine can generally coordinate in two different geometries which depend on the mutual stereochemical requirements of coordinated multidentate ligands. Legg and Cooke [1] studied the stereochemistry of [Co(dien)(Asp)]$^+$ (Asp means aspartic acid anion) and found that (R)- or (S)-aspartic acid acts as tridentate ligand spanning rigidly only a face of the octahedron. Motivated by the homological character of glutamic acid we describe here the behaviour of glutamic acid in the mixed [Co(dien)((S)-Glu)]$^{n+}$ (Glu means glutamic acid anion) complex cation.

For the preparation of [Co(dien)((S)-Glu)]$^{n+}$ the procedure described by Legg and Cooke [1] was used. Chromatographic separation (Dowex 50WX8 in Na$^+$ cycle, 0.3 *M* $NaClO_4$ as eluting agent) gave several bands which were collected and concentrated *in vacuo.* The $NaClO_4$ deposited was continuously removed by filtration. The filtrate obtained was evaporated to dryness and extraction of the remaining solid with ethanol yielded the product as a residue insoluble in ethanol. Only the product obtained from the third fraction showed reasonable electronic absorption spectrum, ^{1}H-NMR spectrum and optical activity. *Anal.*: for [Co(dien)(H_2O)((S)-GluONa)]$(ClO_4)_2$ (m.w. 547.1) calcd. 19.76% C; 4.05% H; 10.24% N. Found 19.17% C; 4.08% H; 10.30% N.

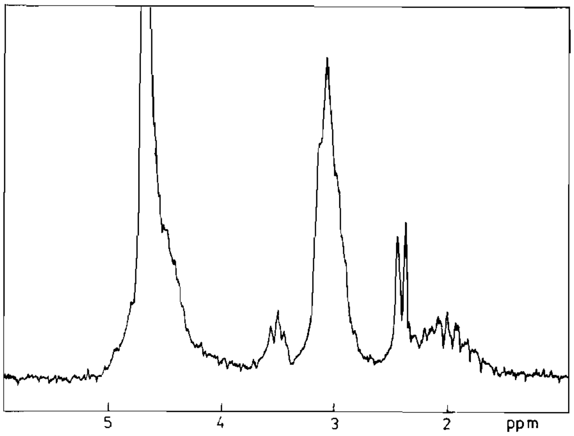


Fig. 1. ^{1}H-NMR spectrum of [Co(dien)(H_2O((S)-GluONa)] $(ClO_4)_2$ (Varian XL-100).

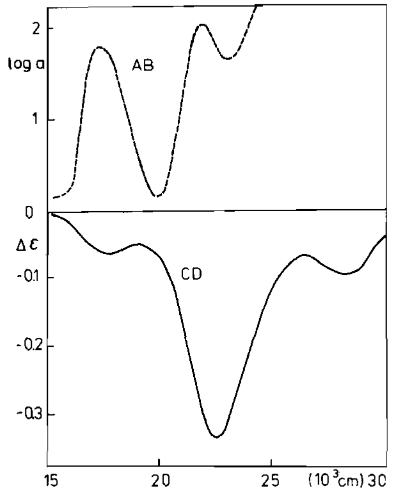
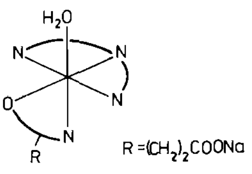


Fig. 2. Electronic absorption (Specord UV–VIS, C. Zeiss, Jena) and circular dichroism spectra (Roussel Jouan 185 Model II) of [Co(dien)(H_2O)((S)-GluONa)] $(ClO_4)_2$.



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When glutamic acid coordinates in [Co(dien)((S)-Glu)]$^+$ as tridentate ligand forming 5- and 7-membered chelate rings, dien must adopt facial arrangements. However, results [2, 3] show that from the two facultative dispositions (*fac* and *mer*) meridional topology is preferred. Thus the facial coordination of dien should be enforced by the second tridentate ligand. Experimental results (*vide supra*) indicate that in the complex under investigation, (S)-glutamic acid behaves here as a bidentate ligand with a dangling–$(CH_2)_2$–COONa group, in which the sixth coordination site is occupied by water (I). Bidentate coordination has been estimated by ^{1}H-NMR and circular dichroism spectra. In Fig. 1, the ^{1}H-NMR spectrum of [Co(dien)(H_2O)((S)-GluONa]$^{2+}$ is summarized. If tridentate coordination should occur the –$(CH_2)_2$–COO^- group should be axially disposed which in turn requires extreme equatorial position of α-CH and thus a great downfield shift of methine

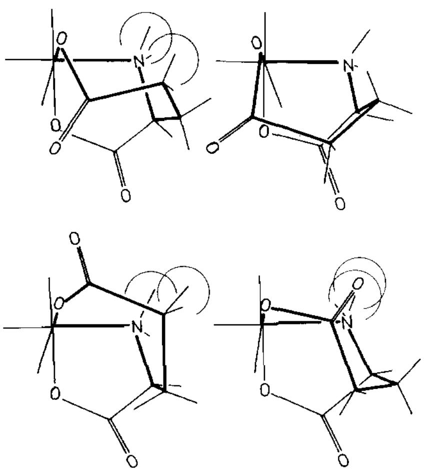

Fig. 3. Steric situations arising from the different conformations of (S)-glutamic acid acting as a tridentate ligand.

proton should be observed. However, the α-CH proton exhibits resonances at 3.50 ppm (D_2O, sodium 2,2-dimethyl-2-silapentane-5-sulfonate as external standard) which is very close to methine proton resonances found in $[Co(en)_2((S)\text{-}Glu)]_2^{2+}$ in which glutamic acid acts as bidentate ligand [4] (ethylene protons of dien exhibit resonance centered at 3.08 ppm, while β- and γ-CH_2 protons resonate at 2.42 and 2.02 ppm, respectively. Individual signals were assigned from the signal integrated intensity). Additional evidence for bidentate coordination of (S)-glutamic acid can be obtained from the circular dichroism spectrum (Fig. 2). Meridional coordination of (S)-glutamic acid causes the complex to have no configurational chirality and the observed optical activity in the $^1A_{1g} \rightarrow {}^1T_{1g}$ spectral region is only the result of the vicinal effect of coordinated (S)-glutamic acid.

Furthermore, bidentate coordination of (S)-glutamic acid leads to the mixed $[Co(dien)(H_2O)((S)\text{-}GluONa]^{2+}$ complex, in which the CoN_4O_2 chromophore gives rise to two geometrical arrangements where both oxygen atoms can occupy *cis* or *trans* positions. From the electronic absorption spectrum (Fig. 2) it follows that the complex obtained does not show any splitting of the first band suggesting that both oxygen atoms are *cis* (I).

The preferred bidentate behaviour can be explained on the basis of both internal entropy loss accompanying 7-membered flexible ring formation [5] and glutamic acid side chain conformational considerations. To coordinate as tridentate ligand the $-(CH_2)_2-COO^-$ group must be axially disposed and the 5-membered chelate ring must adopt λ or envelope conformation. While in the case of tridentate (S)-aspartic acid a 6-membered chelate ring can be arranged in two rigid conformations differing from each other in the mutual position of carboxyl C=O groups; lengthening of the side chain in the case of (S)-glutamic acid causes the number of 7-membered chelate ring conformations to increase. In principle a 7-membered ring can exist [6] in four basic conformations: boat, twist-boat, chair and twist-chair. Reference to Dreiding molecular models shows that (S)-glutamic acid can adopt two of them, *i.e.* two boat and two chair forms (Fig. 3). From these models it further also follows that in three of four conformations steric repulsions between eclipsed $-CH_2$ and $-NH_2$ groups and between C=O and $-NH_2$ groups occur. In the fourth, boat conformation, all linkages are eclipsed, *i.e.* in unfavourable conformation.

From the study of molecular models we conclude thus that purely on conformational ground (taking unfavourable entropy effect also into account) (S)-glutamic acid cannot act as tridentate ligand because serious steric interactions prevent the $-(CH_2)_2-COO^-$ group from coordinating.

References

1 J. I. Legg, and D. W. Cooke, *J. Am. Chem. Soc., 89,* 6854 (1967).
2 F. R. Keene and G. H. Searle, *Inorg. Chem., 11,* 148 (1972).
3 F. R. Keene and G. H. Searle, *Inorg. Chem., 13,* 2173 (1974).
4 J. I. Legg and J. Steele, *Inorg. Chem., 10,* 2177 (1971).
5 D. Shaw, *J. Am. Chem. Soc., 97,* 3856 (1975).
6 J. B. Hendrickson, *J. Am. Chem. Soc., 83,* 4537 (1961).