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Specific Behaviour of (S)-Asparagine and (S)-Glutamine in Mixed Ethylenediamine Complexes of the Types $[Co(en)_2(AB)]^{2+}$ and $[Co(en)(AB)_2]^+$

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Complexes of the general types $[Co(en)_2((S)\text{-}AB)]^{2+}$ and $[Co(en)((S)\text{-}AB)_2]^+$, where AB represents asparagine or glutamine, have been prepared and studied by electronic absorption, circular dichroism and ^1H NMR spectroscopies. With the exception of the cis*(O)–*cis*(N)-$[Co(en)((S)\text{-}Asn)_2]^+$ isomer which favours Δ configuration, Λ-isomers with equatorially disposed ligand side chains predominate. Stereoselective formation of the Λ-isomers of $[Co(en)((S)\text{-}AB)_2]^+$ depends primarily on the geometry of the coordination sphere which makes possible the formation of different numbers of internal hydrogen bonds through $-CONH_2$ and ethylenediamine or asparagine (glutamine) NH_2 groups. A lower degree of stereoselectivity has been observed in the case of glutamine, due to the relief of strain in formation of hydrogen bonds which profoundly discriminates between Λ and Δ asparagine isomers. Evidence for hydrogen bonding has been obtained from both the study of CD spectra measured in different solvents, and the temperature dependence of the chemical shift of an NH proton peak of the* trans*(O)-$[Co(en)((S)\text{-}Asn)_2]^+$ ion.*

Introduction

We are studying cobalt(III) chelate systems of bidentate amino acids *i.e.* (S)-asparagine and (S)-glutamine, ligands capable of forming hydrogen bonds as a source of possible stereoselectivity. Recently [1] it was found that these ligands form Λ-tris(amino-acidato)cobalt(III) isomers. Further studies have shown [2] that other isomers are also formed, but some isomer discrimination can be ascribed to amidic group hydrogen bonding. Continuing the investigation of metal complexes of these ligands, we describe in this paper mixed ethylenediamine–asparagine and glutamine complexes with regard to isomer formation and metal complex geometry.

*In this paper AB denotes bidentate amino acid.

Experimental

Reagents

(S)-asparagine ($[\alpha]_D$ = +39° in 5 mol dm^{-3} HCl) was a product of Koch-Light, and (S)-glutamine ($[\alpha]_D$ = +35.5 in 3 mol dm^{-3} HCl) was supplied by International Enzymes (Windsor, Berkshire, England). *Trans*-$[CoCl_2(en)_2]Cl$ was prepared according to the literature [3].

Preparation and Separation of $[Co(en)_{3-n}(AB)_n]^{(3-n)}$, n = 1 or 2

To an aqueous solution containing 3.9 g (0.026 mol) of (S)-asparagine and 1.10 g (0.026 mol) NaOH, 5.7 g (0.020 mol) of *trans*-$[CoCl_2(en)_2]Cl$ was added and the mixture was heated to 50 °C and stirred for 20 minutes. The reaction mixture, after cooling to laboratory temperature, was diluted to 500 ml with water and applied to the top of a Dowex 50WX4 (200–400 mesh, H^+ cycle) cation exchange column (25 × 5 cm). Elution with water gave a solution of Λ-mer-[Co((S)-asparaginato)$_3$]. Further elution at a rate of 1–2 ml/min with 0.1 mol dm^{-3} $NaClO_4$ gave six red-coloured bands, assigned according to the order of elution as A_1, A_2, A_3, A_4, A_5 and A_6. These were collected and evaporated to small volumes. Excess $NaClO_4$ was filtered off. Further evaporation and addition of an ethanol–ether (1:1)

TABLE I. Elemental Analyses of the Complexes Prepared.

Fract. No.		%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
A_1	Λ-[Co(en)((S)-Asn)$_2$]$ClO_4 \cdot 2H_2O$	23.24	23.80	5.07	4.86	16.26	15.97
A_2	Δ-[Co(en)((S)-Asn)$_2$]$ClO_4 \cdot 2H_2O$	23.24	23.27	5.07	4.99	16.26	15.72
A_3	Λ-[Co(en)((S)-Asn)$_2$]$ClO_4 \cdot 0.5H_2O$	24.52	25.17	4.73	4.77	17.16	17.10
A_4	Λ-[Co(en)((S)-Asn)$_2$]$ClO_4 \cdot H_2O$	24.13	24.26	4.86	4.99	16.89	17.03
A_5	Λ-[Co(en)$_2$((S)-Asn)]$(ClO_4)_2 \cdot 0.5C_2H_5OH$	20.31	21.11	4.92	5.09	15.79	16.35
A_6	Δ-[Co(en)$_2$((S)-Asn)]$(ClO_4)_2 \cdot H_2O \cdot 0.5C_2H_5OH$	19.65	19.68	5.12	5.02	15.27	14.90
G_1	Δ-[Co(en)((S)-Gln)$_2$]$ClO_4 \cdot 1.5H_2O$	26.90	27.12	5.46	5.09	15.69	15.58
G_2	Λ-[Co(en)((S)-Gln)$_2$]$ClO_4 \cdot H_2O$	27.36	28.18	5.36	5.37	15.95	15.80
G_3	Λ-[Co(en)((S)-Gln)$_2$]$ClO_4 \cdot 3H_2O$	25.61	25.46	5.73	5.72	14.93	14.88
G_4	Δ-[Co(en)((S)-Gln)$_2$]$ClO_4 \cdot 1.5H_2O$	26.90	27.15	5.46	5.66	15.69	15.75
G_5	Δ-[Co(en)((S)-Gln)$_2$]$ClO_4 \cdot H_2O$	27.36	27.50	5.36	5.39	15.95	15.99
G_6	Λ-[Co(en)((S)-Gln)$_2$]$ClO_4 \cdot 0.5H_2O \cdot 0.5C_2H_5OH$	28.87	28.86	5.59	5.67	15.54	15.95
G_7	Δ-[Co(en)$_2$((S)-Gln)]$(ClO_4)_2 \cdot 0.5H_2O \cdot 0.5C_2H_5OH$	21.63	21.68	5.27	5.30	15.14	15.48
G_8	Λ-[Co(en)$_2$((S)-Gln)]$(ClO_4)_2 \cdot 0.5C_2H_5OH$	22.30	21.99	5.47	5.17	16.25	15.89

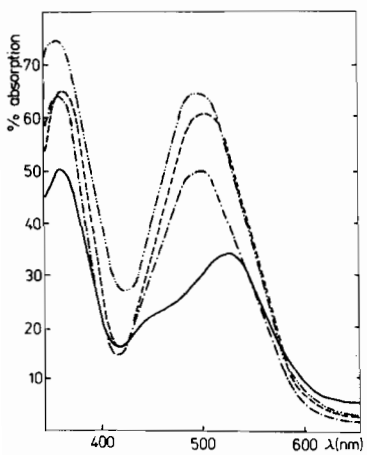

Fig. 1. The electronic absorption spectra of Λ-*trans*(O)-[Co(en)((S)-Gln)$_2$]$^+$ (———), Λ-*cis*(O)-C_2-[Co(en)((S)-Gln)$_2$]$^+$ (–•–•–), Λ-*cis*(O)-C_1-[Co(en)((S)-Gln)$_2$]$^+$ (-------), Δ-[Co(en)$_2$((S)-Gln)]$^{2+}$ (–••–).

mixture provided the desired complexes. These were air-dried.

The same procedure was used in the case of (S)-glutamine, where after chromatography eight bands (G_1 to G_8) were obtained.

Results and Discussion

Elemental analyses given in Table I show that the compositions of the A_1–A_4 complexes are similar to those of G_1 to G_6 and can be formulated as [Co(en)(AB)$_2$]$ClO_4 \cdot nH_2O$. On the other hand, the compositions of the complexes A_5, A_6, G_7 and G_8 are [Co(en)$_2$(AB)]$(ClO_4)_2 \cdot nH_2O$.

With regard to the CoN_4O_2 chromophore, the complexes A_1–A_4 and G_1–G_6 exist in three geometrical isomers: *trans*(O)–*cis*(N), C_1-*cis*(O)–*cis*(N) and C_2-*cis*(O)–*trans*(N). The geometrical isomers prepared were identified using their electronic absorption and ^{1}H NMR spectra (*vide infra*). The electronic spectra, which are illustrated for the three isomers in Fig. 1, are composed of two bands corresponding to the d–d transitions: $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. The symmetry of the first band can be used for differentiation between the *trans*(O) and *cis*(O) isomers. Thus isomers whose spectra showed tetragonal splitting of the first band corresponding to a $^1T_{1g}$ state were assigned as *trans*(O) isomers (A_1, G_1 and G_2). On the other hand, complexes having symmetrical bands differ from each other in the ratio of their respective extinction coefficients, as reported by Matsuoka *et al.* [4]. The C_1-*cis*(O)-isomers show lower values for $\epsilon_1:\epsilon_2$ ratio (see Table II). Applying these arguments, it was possible to assign the topology of individual isomers. The geometry of individual isomers was also supported by their ^{1}H NMR spectra.

Based on the symmetry of the individual isomers, different numbers of signals were expected for the *trans*(O), C_1-*cis*(O) and C_2-*cis*(O) isomers. Both α-CH and β(γ)-CH_2 protons are in identical geometric and magnetic environments in the case of the *trans*-(O) and the C_2-*cis*(O) isomers, while the C_1-*cis*(O) isomers give two sets of α-CH triplets and -CH_2 doublets. Figure 2 shows the *trans*(O)-[Co(en)-(Asn)$_2$]$^+$, *trans*(O)-[Co(en)(Gln)$_2$]$^+$ and [Co(en)$_2$-

TABLE II. Absorption and Circular Dichroism Data of the $[Co(en)_{3-n}(AB)_n]^{3-n}$ Isomers Prepared.

Isomer	Absorption λ (nm) ϵ_{max}, (M^{-1} cm^{-1})		Ratio ϵ_{max}	CD	
				λ (nm)	$\Delta\epsilon$ (M^{-1} cm^{-1})
Λ-*trans*(O)-$[Co(en)((S)\text{-}Asn)_2]^+$	360	136	1.54	353	−0.54
	530	98		538	+3.08
Λ-*cis*(O)-C_1-$[Co(en)((S)\text{-}Asn)_2]^+$	358	152	1.08	352	−0.20
	500	140		505	+2.76
Δ-*cis*(O)-C_1-$[Co(en)((S)\text{-}Asn)_2]^+$	358	147	1.09	350	+0.26
	500	135		514	−2.53
Λ-*cis*(O)-C_2-$[Co(en)((S)\text{-}Asn)_2]^+$	360	167	1.34	358	−1.12
	500	124		513	+3.66
Λ-$[Co(en)_2((S)\text{-}Asn)]^{2+}$	347	131		348	.....
	487	102		490	+2.65
Δ-$[Co(en)_2((S)\text{-}Asn)]^{2+}$	346	122		362	−0.12
	487	98		503	−2.38
Λ-*trans*(O)-$[Co(en)((S)\text{-}Gln)_2]^+$	363	139	1.60	355	−0.37
	530	87		535	+2.96
Δ-*trans*(O)-$[Co(en)((S)\text{-}Gln)_2]^+$	362	136	1.62	351	+0.29
	530	87		540	−2.04
Λ-*cis*(O)-C_1-$[Co(en)((S)\text{-}Gln)_2]^+$	358	143	1.08	359	−0.19
	501	132		503	+2.70
Δ-*cis*(O)-C_1-$[Co(en)((S)\text{-}Gln)_2]^+$	358	139	1.10	363	+0.13
	500	126		501	−2.49
Λ-*cis*(O)-C_2-$[Co(en)((S)\text{-}Gln)_2]^+$	358	152	1.38	360	−1.00
	500	110		502	+3.52
Δ-*cis*(O)-C_2-$[Co(en)((S)\text{-}Gln)_2]^+$	358	170	1.34	359	+0.23
	499	127		506	−2.59
Λ-$[Co(en)_2((S)\text{-}Gln)]^{2+}$	347	133		358	−0.06
	487	109		502	+2.21
Δ-$[Co(en)_2((S)\text{-}Gln)]^{2+}$	347	138		356	−0.07
	488	108		505	−1.76

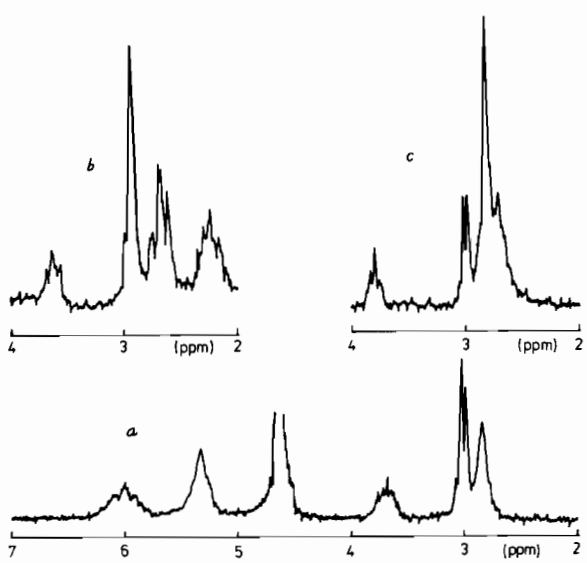

Fig. 2. ^1H NMR spectra of Λ-*trans*(O)-$[Co(en)((S)\text{-}Asn)_2]^+$ (a), Λ-*trans*(O)-$[Co(en)((S)\text{-}Gln)_2]^+$ (b), Λ-$[Co(en)_2((S)\text{-}Asn)]^{2+}$ (c).

(Asn)]$^{2+}$ spectra. From this figure it can be seen that the ethylenediamine protons resonate around 2.8 ppm. The others, *i.e.* α-CH proton (X from ABX) and the $-CH_2$ protons of Asn or Gln (AB portion), which were assigned both on the basis of their integrated intensities and the comparison of absorption of these protons in similar complexes [5], absorb between 2.56–3.68 ppm respectively.

The complexes prepared were chromatographically resolved into $(+)_{578}$- and $(-)_{578}$-isomers. Their asymmetric features are attributed to the configurational, conformational and vicinal effects. These contributions cause the isomers to be diastereoisomers, the absolute configurations of which were assigned from both the sign of the dominant CD band (examples in Fig. 3) in the visible range of the spectrum using (+)-$[Co(en)_3]^{3+}$ as a standard, and with extrapolations from the D_3 symmetry to approximately C_2 for these complexes. Since the $(+)_{578}$-isomers show positive major CD bands in the $^1T_{1g}$ region, these isomers were assigned the Λ-configuration. On the other hand, the $(-)_{578}$-isomers with negative major CD bands were assigned the Δ-confi-

TABLE III. Formation Ratios (%) of $[Co(en)_{3-n}(AB)_n]^{3-n}$ and $[Co((S)\text{-}pn)_{3-n}(AB)_n]^{3-n}$.

	trans(O) Λ:Δ	*cis*(O)-C_1 Λ:Δ	*cis*(O)-C_2 Λ:Δ
$[Co((S)\text{-}pn)((S)\text{-}Asp)_2]^{+}$ [a]	81.0:19.0	14.3:85.7	⩽100:⩾0 [b]
$[Co(en)((S)\text{-}Asp)_2]^{+}$ [c]	78.5:21.5	10.4:89.6	<100:>0 [d]
$[Co(en)((S)\text{-}Asn)_2]^{+}$	100.0:0	28.0:72.0	100.0:0
$[Co(en)((S)\text{-}Gln)_2]^{+}$	53.0:47.0	52.0:48.0	75.0:25.0
	Λ:Δ		
$[Co(en)_2((S)\text{-}Asp)]^{2+}$ [c]	60.0:40.0		
$[Co((S)\text{-}pn)_2((S)\text{-}Asp)]^{2+}$ [a]	49.0:51.0		
$[Co(en)_2((S)\text{-}Glu)]^{2+}$ [e]	70.0:30.0		
$[Co(en)_2((S)\text{-}Glu)]^{2+}$ [f]	53.0:47.0		
$[Co(en)_2((S)\text{-}Asn)]^{2+}$	81.0:19.0		
$[Co(en)_2((S)\text{-}Gln)]^{2+}$	59.0:41.0		

[a] Y. Kojima and M. Shibata, *Inorg. Chem.*, *10*, 2382 (1971). [b] Only 2.0% of the production of the Λ-*cis*(O)-C_2 isomer; no Δ could be measured. [c] Ref. 11. [d] Only 3.1% of the Λ-*cis*(O)-C_2 isomer and only trace of the Δ isomer were observed. [e] Ref. 5. [f] D. A. Buckingham, J. Dekkers, A. M. Sargeson and L. Marzilli, *Inorg. Chem.*, *12*, 1207 (1973).

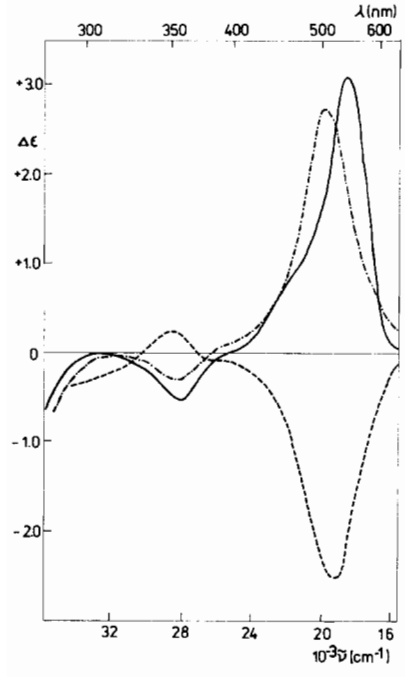

Fig. 3. The CD spectra of Λ-*trans*(O)-$[Co(en)((S)\text{-}Asn)_2]^{+}$ (———), Λ-*cis*(O)-C_1-$[Co(en)((S)\text{-}Asn)_2]^{+}$ (–·–), Δ-*cis*(O)-C-$[Co(en)((S)\text{-}Asn)_2]^{+}$ (– – –).

guration. For the determination of the absolute configurations, circular dichroism data were mainly used, but the ^1H NMR data served also for the differentiation of complex chirality, through the utilization of different steric situations at the α-carbon atoms of the diastereoisomers [6].

Structural Effects

From the literature [7] it follows that the degree of stereospecific coordination of the aliphatic amino acids in $[Co(en)_2(AB)]^{2+}$ is low based on the Λ:Δ ratios. Since amino acid chelate rings are nearly planar [8] there are no substantial interactions between the amino acids and the ethylenediamine rings in the Λ and Δ isomers, which in turn would lead to stereospecific coordination of the amino acids. As can be seen from Table III, coordination of AB favours the Λ-isomer in the case of amino acids bearing a polar side chain. In many cases the observed predominance of the Λ-isomer in the reaction mixture was ascribed to the possible formation of a hydrogen bond between the polar amino acid side chain and the NH_2 group of the bidentate diamine which would discriminate between diastereoisomers (see for example ref. [9]). Although it seems that the formation of the hydrogen bond plays an important role, a study of molecular models does not reveal unambiguously why hydrogen bonding in the Λ-$[Co(en)_2(AB)]^{2+}$ isomer should be preferred.

The other reason for stereoselective coordination of AB could be nonbonding. The observed Λ:Δ ratio of 7:3 for $[Co(en)_2((S)\text{-glutamic acid})]^{2+}$ relative to 6:4 for (S)-aspartic acid where steric factors predominate is the reverse of the stereoselectivity observed in our $[Co(en)_2(Asn \text{ or } Gln)]^{2+}$ complexes. The Λ:Δ ratio is surprisingly higher for aspargine than for

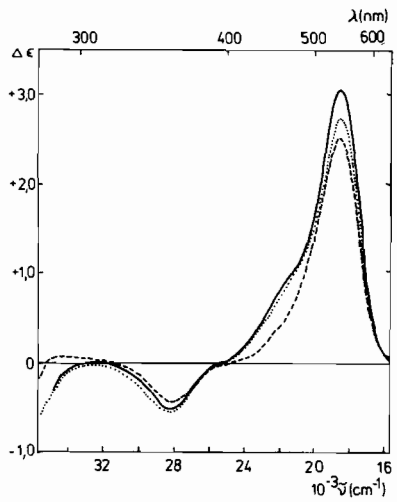

Fig. 4. The CD spectra of Λ-*trans*(O)-[Co(en)((S)-Asn)$_2$]$^+$ in H_2O (———), 0.1 mol dm^{-3} HCl (·····), in DMSO (------).

glutamine, whereas the reverse would be expected if steric crowding played any important role.

Both asparagine and glutamine represent ligands capable of hydrogen bonding through their -$CONH_2$ groups, which in their tris-bidentate cobalt(III) complexes, assuming 'three-point' binding influences such as solvent–solute interactions [2], leads to the preferred formation of Λ-mer-Co((S)-Asn)$_3$. However, it should be emphasized that for effective hydrogen bonding such factors as optimum bond distance and angle must be ensured [10].

A detailed study of Dreiding molecular models does not show any substantial difference between the Λ and Δ isomers of [Co(en)$_2$(Asn or Gln)]$^{2+}$ as far as hydrogen bonding is concerned, ignoring any hydrogen bonding between -$CONH_2$ and NH_2 groups of ethylenediamine or amino acid*. Thus the origin of the observed predominance of Λ-isomers remains obscured.

Generally, complexes of the [Co(en)(AB)$_2$]$^+$ type display a greater variety of stereochemistries than do the [Co(en)$_2$(AB)]$^{2+}$ complexes. The [Co(en)(AB)$_2$]$^+$ complexes differ from each other in symmetry, in the degree of steric interactions, and finally in the ability to hydrogen bond. From these three aspects the results summarized in the Table III should be considered. The yields given in Table III are governed by thermodynamic factors and thus the relative yields of isomers may be related to their stabilities. With the exception of *cis*(O)–*cis*(N) isomers, Λ-isomers with equatorially-disposed ligand side chains predominate. It would seem at first glance that the preference for Λ-isomers is the result of nonbonding interactions imposed by the presence of two *cis*-amide side chains in [Co(en)(AB)$_2$]$^+$. This situation is similar to that in tris(amino-acidato)cobalt(III) complexes, where nonbonding interactions between two alkyl side chain groups favour Λ-isomers over Δ-isomers by about 4 kJ mol^{-1} [12]. However, the synthesis of all expected isomers of the [Co(AB)$_3$] type (see for example refs. [13, 14]) shows that this value is insufficient to assert stereoselective formation of only Λ-isomers. From the study of Dreiding models it follows that differences exist between Λ and Δ isomers as far as the construction of hydrogen bonds is concerned. Two internal hydrogen bonds can be formed between the carbonyl parts of the -$CONH_2$ groups and the amino acid -NH_2 groups of the (S)-Asn ligands in the case of the Λ-*trans*(O)–*cis*(N)-[Co(en)((S)-Asn)$_2$]$^+$ isomer, which is consistent with the exclusive isolation of the Λ-isomer for this *trans*(O)–*cis*(N) configuration. Two internal hydrogen bonds can be formed between the carbonyl parts of the -$CONH_2$ groups and ethylenediamine NH_2 groups in the case of the Λ-*trans*(N)–*cis*(O)-[Co(en)((S)-Asn)$_2$]$^+$ isomer and once again, only the Λ isomer is observed experimentally. The analogous Δ isomers can only form such hydrogen bonds when the rings are distorted significantly from their ground state configurations. However, for the Λ and Δ-*cis*(N)–*cis*(O)-[Co(en)((S)-Asn)$_2$]$^+$ isomers, both isomers are able to form internal hydrogen bonds without appreciable distortion. The Δ isomer can form two hydrogen bonds and Λ only one, which is consistent with the experimental predominance of the Δ isomer.

When the side chain is lengthened, as from Asn to Gln, the formation of hydrogen bonds, which can only form with strain in the isomers of the Asn complexes, is now relatively strain-free, and experimentally these isomers are observed for the [Co(en)((S)-Gln)$_2$]$^+$ species.

Evidence for hydrogen bonding to solvents is obtained from the detailed study of the CD spectra of the Λ-*trans*(O)–*cis*(N)-[Co(en)((S)-Asn)$_2$]$^+$ isomer. As can be seen in Fig. 4 this isomer shows one CD band in the first absorption band region with a shoulder on the shorter wavelength side of this major peak. This shoulder at around 22,000 cm^{-1} is not evident in DMSO. Furthermore the peak at around 18,600 cm^{-1} in hydrogen bonding solvents is shifted to 18,700 cm^{-1} in DMSO. Furthermore in the nonhydrogen bonding solvent there are some differences in the 32,000 cm^{-1} to 36,000 cm^{-1} region.

The ^{1}H NMR spectrum of Λ-*trans*(O)–*cis*(N)-[Co(en)((S)-Asn)$_2$]$^+$ does not show full deuterium

*A study of the crystal and molecular structure of Λ-[Co(en)$_2$((S)-Asn)]$^{2+}$ suggests that in this isomer intramolecular interactions occur only between the -$CONH_2$ and the asparagine -NH_2 groups [11].

exchange of the asparagine NH_2 protons. It could be indicative for both intra- and intermolecular hydrogen bonding. However, the temperature dependence of chemical shift *i.e.* $d\delta/dT$ of the NH_2 protons (k = 0.0018 and 0.0014, respectively) shows insignificant upfield shifts, from which it follows that these protons are shielded by an intramolecular hydrogen bond [15–17]. Intermolecular hydrogen bonding should produce larger shifts.

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