TRIS[SARCOSINATO-O,N(—1)]COBALT(III).
A METAL COMPLEX WITH FORCED CONFIGURATION
OF NITROGEN ATOMS

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Because of the strong interchelate interactions of N—CH$_3$ groups, only the *mer* isomers of the tris[sarcosinato-O,N(−1)]cobalt(III) were isolated. They were chromatographically resolved into the Λ and Δ isomers on a starch column and the configurations of the latter were determined from the sign of the Cotton effect. Nonbonding interactions among the N—CH$_3$ groups excluded the existence of isomers with *SSS* snd *RRR* configurations of the secondary nitrogen atoms and combinations thereof. The Λ-(*SRR*), Λ-(*SRS*) and Δ-(*RRS*) isomers were identified using ^{1}H-NMR spectroscopy.

The stereochemistry of diastereoisomeric complexes depends on a number of factors, including nonbonding interactions among alkyl groups or among these groups and hydrogen atoms of the same or a neighbouring ring[1]. In cobalt(III) amino acid complexes, these interactions are chiefly manifested in the different relative stabilities of the geometric isomers[2]. On the other hand, the difference in the stability of diastereoisomers is relatively small, provided that inter- or intramolecular hydrogen bonding does not play a role in the complex. The interactions, whose strength depends on the steric volume of the alkyl group, may increase the stability of an isomer with equatorial disposition of the side chain, where it is important whether the chain is straight or branched. The results obtained so far indicate[3] that (*S*)-α--monoamino-monocarboxylic acids give a somewhat higher yield of Λ-isomers. The minimum difference in the stability of the diastereoisomers is caused by a low degree of puckering of the chelate rings.

It can be expected that, with sarcosine, whose nitrogen atom becomes chiral on coordination, the effect of alkyl groups will be more pronounced; moreover, it is then necessary to determine whether sarcosine will be coordinated stereospecifically and to discover the number of isomers formed. The present work is intended as a solution of these problems.

EXPERIMENTAL

Chemicals and instruments: Sarcosine and the other chemicals were obtained from the firm Lachema. The electronic absorption spectra were measured on an Optica-Milano CF-4 spectrophotometer and the optical rotatory dispersion on a Jasco UV-5 instrument. The ^{1}H-NMR spectra were obtained on a Varian XL-100 instrument, using sodium 2,2-dimethyl-2-silapentane 5-sulphonate as an external standard.

Complex preparation: To a suspension of 0·01 mol of $Co(OH)_3$ in water were added 0·03 mol of sarcosine. The mixture was heated with stirring to 60°C for 5 h, cooled to laboratory temperature, filtered and the filtrate passed through a Dowex 50 WX8 column (50—100 mesh, H^+- -cycle). The complex was obtained by evaporation of the eluate. For $C_9H_{18}N_3O_6Co . 2 H_2O$ (359·3) calculated: 30·09% C, 6·17% H, 11·71% N; found: 30·42% C, 6·17% H, 11·86% N.

Resolution of the mer-*Tris[sarcosinato*-O,N(− 1)]*cobalt*(III) *on a Starch Column*

An amount of 400 g of potato starch was suspended in c. 1 000 ml of water and stirred. The suspension was allowed to settle for 60 minutes, the supernatant was decanted off and this procedure was repeated until the decanted liquor was transparent. The starch suspension was then transferred into a 85 × 2·5 cm column. After percolation of water, a concentrated solution containing 1 g of the complex was placed on the top of the column and the column was then washed with water; a single broad band was formed on the column. 3 ml fractions were automatically collected from the column and their optical rotation was measured. The $(-)_{578}$ isomer was eluted first.

RESULTS AND DISCUSSION

Chirality of cobalt(III) complexes can originate from configurational, vicinal and conformational contributions[4]. While the latter contribution is negligble with amino acid complexes, configurational chirality and the vicinal effect play a substantial role in the overall chirality of the complex. The vicinal effect can then be caused by a chiral carbon atom or a donor one. The tris[sarcosinato-O,N(− 1)]cobalt(III) is an example of $Co(AB)_3$ type complexes with configurational chirality and chirality forced by coordination of the donor atom, as the sarcosine nitrogen atom becomes chiral on coordination. Non-symmetrical ligand character (N- and O-donor atoms), configurational chirality and the presence of three chiral-centres result in 32 isomeric forms for the tris[sarcosinato-O,N(− 1)]cobalt(III).

It follows from the electronic absorption spectrum (Fig. 1.) that the donor atoms are meridionally arranged in the complex (splitting of the band corresponding to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition for microsymmetry C_{2v} (ref.[5]). In no case was the presence of a facial isomer detected in the reaction mixture. The specific formation of the *mer* isomer is given, as follows from the Dreiding models, by exceptionally strong non-bonding interactions among the N—CH_3 groups, if the donor atoms are facially arranged. The number of isomers is thus reduced to sixteen *mer* forms: Λ-(*SSS*), Λ-(*SSR*), Λ-(*SRR*), Λ-(*RRR*), Λ-(*RRS*), Λ-(*RSS*), Λ-(*RSR*), Λ-(*SRS*), Δ-(*SSS*), Δ-(*SSR*), Δ-(*SRR*), Δ-(*RRR*), Δ-(*RRS*), Δ-(*RSS*), Δ-(*RSR*), Δ-(*SRS*). (Symbols Λ

and Δ denote absolute complex configurations[6] and symbols S and R the configurations of the secondary nitrogen atoms[7].)

In view of the character of the complex, the isomers were resolved chromatographically. Separation into Λ and Δ isomers was unsuccessful on an Al_2O_3 column; however, the resolution was effected on a starch column. The $(-)_{578}$ isomer was eluted first. The absolute configuration of the $(-)_{578}$ and $(+)_{578}$ isomers was determined from the sign of the Cotton effect observed in the region of the $^1T_{1g} \leftarrow {^1A_{1g}}$ spectral transition[8] (Fig. 2) and on the basis of the octant rule[9]: isomers with a negative Cotton effect or with a negative octant sign have the Δ-configuration, while the Λ-configuration is assigned to isomers with a positive Cotton effect or octant sign. Since there is a correlation between the order of the eluted isomers and their configuration[10], it is also possible to employ this fact for the determination of the absolute complex configuration.

The methyl group of a secondary nitrogen atom in sarcosine can be axial or equatorial with respect to the C_3-pseudoaxis of the complex. The former case corresponds to absolute configuration R and the latter to S (for the Λ-configuration, while the reverse is true for the Δ-configuration). These various arrangements of the $N—CH_3$ groups lead to interactions between two $N—CH_3$ groups and between an $N—CH_3$ group and the hydrogen atom of a secondary nitrogen atom of a neighbouring ring. In addition, there are also interactions with the CH_2 group of the acetate ring. The above interactions can occur within the individual chelate rings and as interchelate interactions among three chelate rings. However, in view of the configuration, only
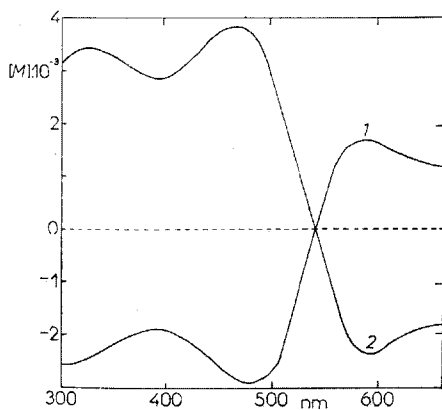

FIG. 1

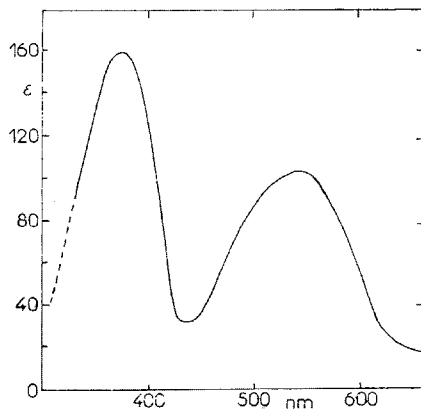Electronic Absorption Spectrum of the *mer*-Tris[sarcosinato-O,N(−1)]cobalt(III)

FIG. 2

Optical Rotatory Dispersion of the $\Lambda(S_1R_2R_3)$ (*1*) and Δ-$(R_1R_2S_3)$ (*2*) Isomers of the *mer*-Tris[sarcosinato-O,N(−1)]cobalt(III)

interactions in one pair of these rings can be considered. The study of the Dreiding models has shown that isomers with configurations SSS and RRR can be excluded, whether the complex configuration is Λ or Δ, as very strong interactions among the $(S_1S_2,\ R_1R_3)$ N—CH_3 groups then occur (Fig. 3). Possible interactions between an N—CH_3 group and the hydrogen atom of an NH group of a neighbouring ring depend on the conformation of the N(H)—$C(H_3)$ bond and are minimal when this bond exhibits the synperiplanar conformation. With the Λ-isomers, an isomer with the R_1S_3 configuration can also be excluded for steric reasons (interaction of N—CH_3 groups, Fig. 3). On elimination of Λ-isomers with which the above interactions would be irremovable, *i.e.* $S_1S_2S_3$, $R_1R_2R_3$, $S_1S_2R_3$, $R_1S_2R_3$, $R_1R_2S_3$ and $R_1S_2S_3$, it can be concluded that the Λ-isomers can only exist in the following forms: Λ-$(S_1R_2R_3)$ and Λ-$(S_1R_3S_3)$ (Fig. 3) with equatorial-axial-axial and equatorial--axial-equatorial N—CH_3 groups. Both isomers are quite free of interactions of the N—CH_3 group and their existence is equally probable in view of the steric conditions. A similar situation exists with the Δ-isomers; the existence of isomers with SSS and RRR nitrogen atom configurations is also sterically excluded. If all the above-discussed interactions are considered, the existence of only two isomers can be expected, with $R_1S_2S_3$ and $R_1R_2S_3$ secondary nitrogen atom configurations and with the corresponding equatorial-axial-axial and equatorial-equatorial-axial arrangements.

In order to determine the configuration of the secondary nitrogen atoms, proton magnetic resonance spectra or the resonance of the N—CH_3 groups were measured. Two Λ-isomers were isolated chromatographically; they differ in the number of peaks corresponding to the N—CH_3 protons. As the spectra were measured in D_2O where rapid exchange of the N-H protons takes place, the signal observed for the N—CH_3 group is a singlet. The ^{1}H-NMR spectrum of the Λ-isomer, which was isolated second, exhibited two singlets with $\delta = 2\cdot72$ and $2\cdot84$ p.p.m. $(J = 7$ Hz$)$ and an intensity ratio of $2 : 1$ (the less intense signal lies at a lower field). These signals were assigned to the N—CH_3 protons on the basis of the integral intensity. The presence of two N—CH_3 signals indicates that two kinds of N—CH_3 group are present in the molecule. In fact, the three chelate rings in the *mer* isomer are not geometrically and magnetically equivalent: on rotation of one chelate ring by 180° a *fac* isomer is formed; from this it follows that two chelate rings lie symmetrically with respect to the three-fold pseudoaxis of rotation and will yield similar proton signals. This is valid for the N-CH_3 group located in the mutual *trans* position. Since the chemical shift is a function of neighbouring groups, it will, of course, also depend on the configuration of the secondary nitrogen atom, with which the orientation of the N—CH_3 group with respect to the other groups affecting the chemical shift is also connected. The resonance observed at the higher field $(2\cdot72$ p.p.m., a signal with twice the intensity$)$ corresponds to the geometrically and magnetically identical N—CH_3 protons. As the signals of the axial protons are upfield shifted

to a higher field compared to the equatorial protons[11], the signal at 2·72 p.p.m. (double intensity) can be assigned to the protons of two axial N—CH₃ groups, whose nitrogen atom has absolute configuration *R*. On the other hand, the signal located at 2·84 p.p.m. can be assigned to the protons of the equatorial N—CH₃ group with
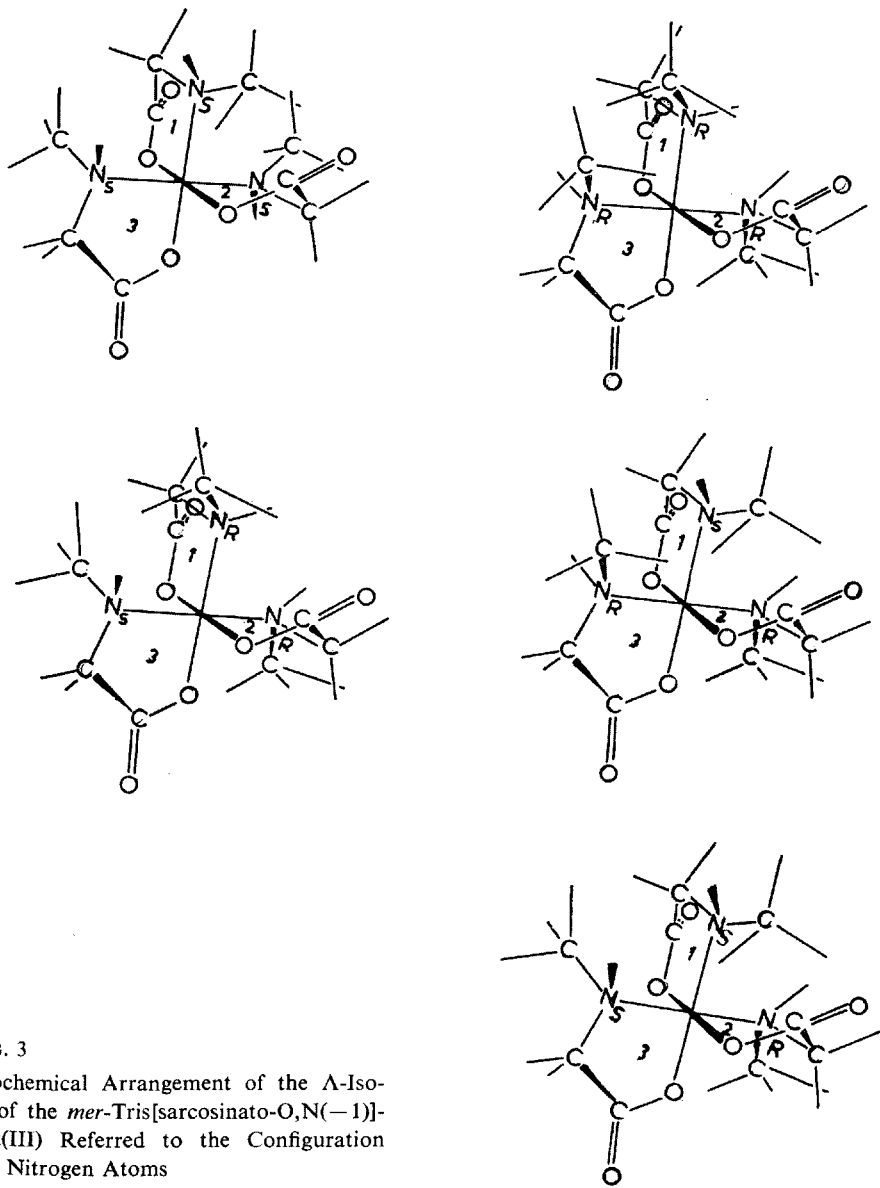

FIG. 3

Stereochemical Arrangement of the Λ-Isomers of the *mer*-Tris[sarcosinato-O,N(—1)]-cobalt(III) Referred to the Configuration of the Nitrogen Atoms

nitrogen atom configuration S. On the basis of these arguments, the Λ-isomer, eluted second of the pair of Λ-isomers, can be ascribed configuration Λ-$(S_1 R_2 R_3)$.

On the other hand, the Λ-isomer eluted first exhibited three singlets, $\delta = 3 \cdot 03$, $2 \cdot 86$ $(J = 9$ Hz$)$ and $2 \cdot 68$ $(J = 7$ Hz$)$ p.p.m. with a $1 : 1 : 1$ intensity ratio, which were ascribed to the $N—CH_3$ group protons on the basis of the integral intensity. As has been pointed out, two signals corresponding to two geometrically and magnetically different $N—CH_3$ groups should be present in the ^{1}H-NMR spectrum; however, this is possible provided that these groups are oriented in the same way with respect to the three-fold pseudoaxis of rotation. As the study of the Dreiding models indicated that an isomer with the $S_1 R_2 S_3$ nitrogen atom configuration is permissible, it is possible to ascribe the spectrum with the three $N—CH_3$ group signals to this isomer.

With the only Δ-isomer isolated, three signals corresponding to resonance of the $N—CH_3$ group protons were observed in the ^{1}H-NMR spectrum; $\delta = 2 \cdot 44$, $2 \cdot 34$ $(J = 7$ Hz$)$ and $2 \cdot 20$ $(J = 7$ Hz$)$ p.p.m. (with a $1 : 1 : 1$ intensity ratio). The singlet at $\delta = 2 \cdot 34$ p.p.m. is further splitted $(J = 2$ Hz$)$. The presence of three $N—CH_3$ group signals excludes the existence of an isomer with nitrogen atom configuration $R_1 S_2 S_3$. On the other hand, the different configuration of trans-nitrogen atoms $(R_2 S_3)$ should be manifested by two signals for these protons. This isomer can thus be ascribed configuration Δ-$(R_1 R_2 S_3)$.

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