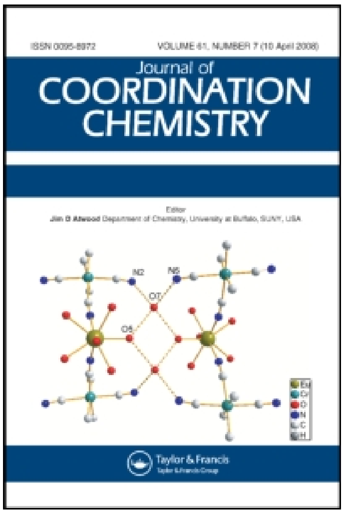

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SOME COBALT(III) COMPLEXES OF S-AZETIDINE-2-CARBOXYLIC ACID

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SOME COBALT(III) COMPLEXES OF S-AZETIDINE-2-CARBOXYLIC ACID[1]

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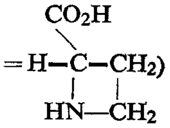
One isomer of $[Co(S\text{-}azet)_3]$ (S-azet = S-azetidine-2-carboxylate ion) has been isolated and assigned the Λ-facial configuration from absorption and circular dichroism (CD) spectra. Both optical isomers of $[Co(en)_2S\text{-}azet]I_2$ were isolated and their absolute configurations assigned. Two isomers assigned as Λ (+)-β_2-SS- and Δ-(-)-β_1-RR–$[Co(trien)S\text{-}azet]I_2$ were isolated in the case of the triethylenetetraamine complex. The complexes are closely related to the corresponding S-proline complexes.

INTRODUCTION

Sargeson and Searle[3] prepared *trans*, α and β isomers of triethylenetetraamine disubstituted complexes of cobalt(III). There are two β isomers of $[Co(trien)aa]^{2+}$ (aa = amino acid anion). Marzilli and Buckingham[4] isolated the β_2 isomer (N of amino acid *trans* to –NH of trien) with sarcosine and both β_1 (N of amino acid *trans* to $-NH_2$ of trien) and β_2 isomers with glycine. They recognized the possibilities of conformational isomerism of coordinated trien, but believed that only the more stable conformation of trien was obtained. Concurrently Lin and Douglas[5] isolated β_1 and β_2 isomers, including the conformational isomers in the latter case, for a series of amino acids. One of the amino acids included was S-proline which is of interest because of the 5-membered heterocyclic ring which makes the chelate ring rather rigid. In complexes of the types $[Co(aa)_3]$[6, 7] and $[Co(en)_2(aa)]X_2$,[8] proline differs from other amino acids in showing stereoselectivity and in the circular dichroism (CD) spectra of the complexes. Lin and Douglas[5] used the expected stereoselectivity of proline in conjunction with the CD spectra in making assignments of the geometrical and conformational isomers of $[Co(trien)S\text{-}prol]^{2+}$. The assignments[5] for the Λ-(+)-β_2-SS and Δ-(−)-β_2-RR isomers have been confirmed by X-ray crystal structure studies.[9]

S-Azetidine-2-carboxylic acid (S-azetH =  has a 4-membered ring instead of the 5-membered pyrolidine ring in proline. It is of interest as a ligand because of the expected rigidity of the chelate ring formed in bonding to a metal ion.

EXPERIMENTAL

Spectral data

Absorption spectra were obtained using a Cary 14 spectrophotometer. CD curves were obtained with a Roussel-Jouan Dichrograph using a Sylvania Sun Gun lamp in the visible region. Two cm cells with quartz end plates were used for measurements. The concentrations of the solutions measured ranged from 0.002 to 0.008 M for CD and absorption spectra. All measurements were at room temperature.

Analyses

Elemental analyses were performed by Alfred Bernhardt, Elbach, West Germany.

Syntheses and Resolutions

S-Azetidine-2-carboxylic acid was purchased from Nutritional Biochemical Corp., Cleveland, Ohio.

The (+) or (−) sign for the complexes studied indicates the sign of the dominant CD peak.

Preparation and resolution of β_1*-(−)-RR and* β_2*-(+)-SS-[Co(trien) S-azet]*I_2 *and [Co(S-azet)*$_3$*] complexes* The preparation of these complexes followed the preparative prodedure for β_2-(−)-RR-[Co(trien) (S-prol)]I_2.[5] The small scale preparation and the need to avoid the possibility of base hydrolysis of S-axetH[10] required some modification.

One hundred and one milligrams of S-azetH was dissolved in 2 ml of water on a water bath (40°). A warm solution of 400 mg of NaOH in 2 ml of water was poured into the azetH solution, then 315 mg of *cis*-α-[Co(trien)Cl_2]Cl[3] was added quickly and the resulting solution was heated on a water bath (*ca.* 50°), with constant stirring, for 20 min while the color of the solution changed from violet to red. The CD measurement of the reaction mixture showed a Cotton effect curve. The solution was cooled in the refrigerator over night and the impurities were removed by filtration. An excess of solid NaI (*ca.* 0.4 g) was added with stirring. The solution was concentrated by an air stream until crystals appeared on the surface and then it was cooled in the refrigerator over night. A red solid was collected by filtration. The solid was washed with an excess of ethanol to remove excess NaI and then dissolved in a small amount of warm water. The solution stood in the refrigerator over night. A purplish pink fibrous type of precipitate of (+)-[Co(S-azet)$_3$] was obtained. The product was recrystallized several times from hot water. The final yield was about 30 mg. $\Delta\epsilon_{max} = +2.85$ (18,400 cm^{-1}). *Anal.* Calcd for $CoC_{12}H_{18}N_3O_6$: C, 40.10; H, 5.01; N, 11.69. Found: C, 39.83; H, 4.82; N, 11.36.

The filtrate was concentrated with an air stream until some solid appeared on the surface, then it was cooled in the refrigerator over night. More tris-azet complex was filtered off. To the filtrate more NaI was added with stirring and it was evaporated with an air stream. The dried solid was washed with an excess of ethanol to remove excess NaI. The solid was treated with absolute methanol. The more soluble part was richer in the β_2-(+)-isomer and the less soluble part was richer in the β_1-(−)-isomer. With the same technique, the more soluble portion was evaporated to dryness with an air stream and then dissolved in absolute methanol. The less soluble portion was washed with an excess of absolute methanol several times. The final products for CD and spectral study were recrystallized one time from hot water. The $\Delta\epsilon_{max}$ of the major CD peaks: −2.24 (19,300 cm^{-1}) for (−)-β_1-RR-[Co(trien)-S-azet]I_2; and $\Delta\epsilon = +1.92$ (20,800 cm^{-1}) for (+)-β_2-SS-[Co(trien) S-azet]I_2. *Anal.* Calcd for $CoC_{10}H_{24}N_5O_2I_2$: C, 21.46; H, 4.30; N, 12.34; I, 45.44. Found: C, 21.88; H, 4.75; N, 12.46; I, 45.46.

Preparation and Resolution of S-azetidine-2-carboxylatobis-(ethylenediamine)cobalt(III) Iodide

This compound was prepared by the general method as described by Liu and Douglas.[11] Some modifications were made for the small scale preparation and to avoid base hydrolysis of *azetH*.[10] One hundred and one milligrams of S-azetH was dissolved in a warm solution (*ca.* 40°) of 400 mg of NaOH in 3 ml of water. Solid *trans*-[Co(en)$_2Cl_2$]Cl (290 mg) was added quickly and the resulting solution was allowed to react on a water bath (*ca.* 50°), with constant stirring, for 10 min. The color of the solution changed from green to orange-red and CD measurement of the reaction mixture showed optical activity. The solution was cooled in the refrigerator over night and filtered to separate the orange-yellow crystals ([Co en$_3$]Cl_3). An excess of NaI was added to the filtrate. The filtrate was cooled in the refrigerator over night and filtered to separate the red crystals, which showed no optical activity.

The filtrate was dried by an air stream and washed with an excess of ethanol. The solid residue was (±)-[Co(en)$_2$ S-azet]I_2 which was recrystallized one time from warm water for the CD and absorption spectral measurements.

The unresolved complex was separated by the different solubilities of the two optical isomers in absolute methanol. The unresolved complex was partially dissolved in a few ml of absolute methanol. The more soluble part was richer in the (+)-isomer and the less soluble part was richer in the (−)-isomer. The same technique was repeated and the methanol solutions obtained by partial dissolution of the complex were evaporated to dryness by an air stream. Two optical isomers were separated in fairly pure form. Because of the small amount of final product obtained, only one crystallization from water was performed for the

CD and absorption spectra measurement. The $\Delta\epsilon$ value for the dominant CD peak: was −1.65 (19,300 cm^{-1}) for the (−)-isomer and +1.45 (19,750 cm^{-1}) for the (+)-isomer. *Anal.* Cald for $CoC_8H_{22}N_5O_2I_2$: C, 18.01; H, 4.11; N, 13.13; I, 47.65. Found: C, 18.19; H, 4.21; N, 13.18; I, 47.37.

RESULTS AND DISCUSSION

[Co(S-azet)$_3$]

The purplish-pink tris-S-azet complex is sparingly soluble in water. The first absorption band is more intense than the second (Figure 1), as is true of most of the facial isomers of amino acid complexes,[7, 12] although the second band is more intense for both the facial and meridional isomers of [Co(S-proline)$_3$].[7] The half-width of the first band is about the same as that of the correspondingly narrow band for facial isomers of other [Co(aa)$_3$] complexes, without the apparent splitting of the broader first band shown by the corresponding meridional isomers. The peak positions of the two visible absorption bands agree closely with those of fac-[Co(S-prol)$_3$].[7] The sign pattern of the CD peaks in the first band region is that expected for a Λ configuration.[7] Denning and Piper obtained three isomers of [Co(S-prol)$_3$], but not the Λ-mer-isomer. Molecular models indicate that this isomer is also unlikely for [Co(S-azet)$_3$] because of unfavourable steric interaction. The one isomer obtained can be confidently assigned as Λ-fac-[Co(S-azet)$_3$] with a dominant positive CD peak in the first band region. Only one isomer was obtained, but one cannot conclude that the others could not be obtained in view of the very small scale preparation.

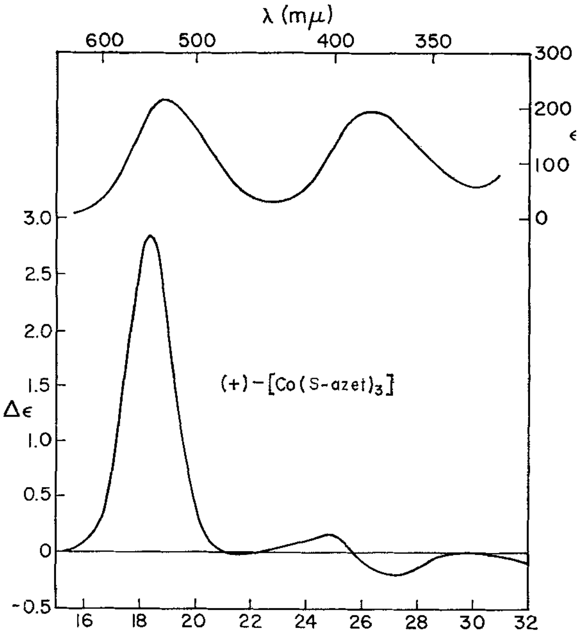


FIGURE 1 Circular dichroism and electronic absorption spectra for the only isomer of [Co(S-azet)$_3$] isolated.

[Co(en)$_2$S-azet]I$_2$

Both isomers were obtained in the preparation of [Co(en)$_2$S-azet]I$_2$. The CD curve (Figure 2) for the unresolved complex is very nearly the average of the curves for the resolved isomers, indicating that the two isomers were formed in nearly equal amounts. The solubilities of the isomers in ethanol differed sufficiently for their separation without the use of a resolving agent. No stereoselectivity is shown in this case although only the Δ-[Co(en)$_2$-S-prol]I$_2$ isomer was isolated.[8] Stereoselectivity has also been reported in related complexes of N-substituted amino acids[13, 14] and glutamic acid.[15] Other complexes of the type [Co(en)$_2$aa]$^{2+}$ generally show a single CD peak at slightly lower energy than the position of the maximum of the first absorption band or this dominant CD peak plus a weaker one at higher energy and of opposite sign. The less soluble isomer shows the latter pattern with a dominant negative CD peak and a weak positive peak at higher energy (Figure 2). The negative sign of the dominant peak permits the assignment of the Δ configuration.[8] The more soluble isomer can be assigned the Λ configuration because of the dominant positive CD peak in the usual position, but is unusual in showing a weak peak of opposite sign at still lower energy. This pair of isomers is the first of the type [Co(en)$_2$aa]$^{2+}$ to reveal three CD peaks in the first band region. This is the usual pattern[8, 11] of "vicinal effect" curves—those obtained by cancellation of the contributions of the Δ and Λ spiral configurations. The present "vicinal effect" curve, as indicated by the CD curve of the unresolved complex, shows only two peaks, but presumably it is because of the unusual intensities of the three transitions, as indicated by the appearance of the lowest energy peak at all. Also the highest energy peak appears only for the Δ-isomer, while it appears only for the Λ-isomer in other cases.[8, 11]

The presence of three components in the first band region appears to be general for compounds of the type [Co(en)$_2$aa]$^{2+}$ with the central component dominant and its sign indicative of the absolute configuration as related to the sign of the E$_a$ component of [Co(en)$_3$]$^{3+}$.

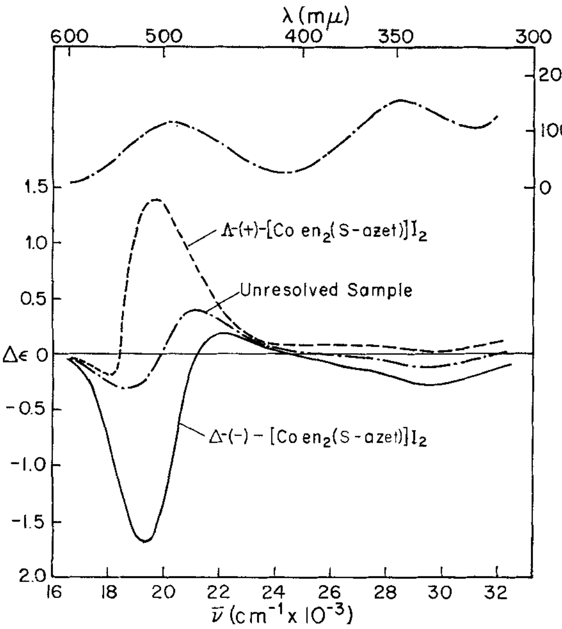


FIGURE 2 Circular dichroism and electronic absorption spectra for the isomers of [Co en$_2$(S-azet)]I$_2$.

Two different types of vicinal effect CD curves were obtained for β-[Co(trien) S-prol]$^{2+}$ complex ions.[5] One for the β$_2$-(RR and SS)-[Co(trien)-S-prol]$^{2+}$ ion was similar to that of the [Co(NH$_3$)$_4$-S-prol]$^{2+}$ ion, which exhibits three CD peaks (—, +, —) in the first ligand band region.[16] This is a common type for many complexes of S-amino acids.[11, 16] The other for the β$_1$-(RR and SS)-[Co(trien) S-prol]$^{2+}$ ion is similar to that of (—)$_{436}$-[Co(NH$_3$)$_4$R-sarcosine]$^{2-}$ ion, which exhibits two CD peaks (—, +) in the first ligand field region.[17] The vicinal effect CD curve for the [Co(en)$_2$S-azet]$^{2+}$ ion (figure 2) is also similar to that of (—)$_{436}$-[Co(NH$_3$)$_4$R-sarcosine]$^{2+}$ ion, i.e., similar to that of the β$_1$-(RR and SS)-[Co(trien) S-prol]$^{2+}$ ion. No "vicinal effect" CD curve is available for β-[Co(trien)S-azet]$^{2+}$ (*vide infra*) because only one β$_1$-isomer and one β$_2$-isomer were obtained.

[Co(trien)S-azet]I$_2$

Only two isomers of [Co(trien)S-azet]I$_2$ were isolated. However, one cannot conclude that S-azet exhibits stronger stereoselectivity than S-proline since only one preparative method was used and small amounts of other isomers could have been lost in the small scale preparation. Both isomers of [Co(en)$_2$S-azet]I$_2$ were isolated.

The two isomers of [Co(trien)S-azet]I$_2$ gave different absorption spectra (Figure 3), corresponding to those of the β$_1$ and β$_2$ isomers[5] of [Co(trien)S-prol]I$_2$. The isomer with the more intense and lower energy first band was assigned the β$_1$ configuration (N of azet *trans* to —NH$_2$ of trien) and the other isomer was assigned the β$_2$ configuration. Only the RR and SS conformations[18] of trien were obtained[5] for [Co(trien)S-prol]$^{2+}$.

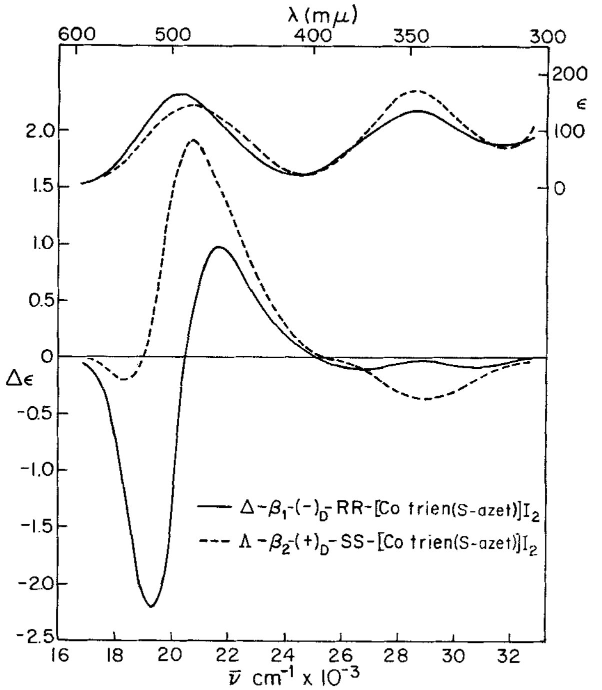


FIGURE 3 Circular dichroism and electronic absorption spectra for the two isomers isolated of β-[Co(trien)(S-azet)]I$_2$.

The assignments made[5] for the Λ-(+)-β$_2$-SS and Δ-(—)-β$_2$-RR isomers have been confirmed by X-ray crystal structure studies.[9] The CD curves for isomers with the RS and SR trien conformations were much different from those for RR and SS isomers and different from those of the S-azet complexes reported here.

The CD curves for Λ-β_1–SS– and Λ-β_2–SS–[Co(trien)S-prol)]I_2[5] differ only slightly and are of the same form as the (+) isomer of [Co(trien)S-azet]I_2 (Figure 3). The absorption spectrum permits this to be assigned as a β_2-isomer, and hence as the Λ-β_2–SS isomer. The other isomer of the S-azet complex shows a CD spectrum not at all similar to that of Δ–β_2(RR)–[Co(trien)S-prol]I_2[5] and the absorption spectrum indicated it to be a β_1-isomer. The first, dominant, negative CD peak of this isomer is similar in position, intensity, and width to the corresponding peak for Δ-β_1–RR–[Co(trien)S-prol]I_2 and the CD curves are similar in the second absorption band region also. These CD curves differ in that there is a prominent, negative, second CD peak for the S-azet complex, while the CD curve is weakly negative in this region for the S-prol complex. This difference is attributed to differences in contributions caused by the different rigid rings of S-proline and S-azetidine-2-carboxylic acid. The second isomer is assigned as Δ-β_1–(−)–RR–[Co(trien)S-azet]I_2. It is interesting to note the similarities of the CD spectra of the two isomers of [Co(trien)S-azet]I_2 reported here to the two isomers of $[Co(en)_2azet]^{2+}$ (Figure 2). The only isomer reported, Δ-[Co(en)$_2$S–prol]I_2, also gives a CD spectrum most similar to that of Δ–β_1–RR–[Co(trien)S-prol]I_2. For amino acids such as S-alanine, the closest correspondence in CD curves is between Λ-[Co(en)$_2$S–aa]$^{2+}$ [11] and Λ-SS–β_2–[Co(trien)S–aa]$^{2+}$, and between Δ-[Co(en)$_2$S-aa]$^{2+}$ [11] and Δ-RR–β_1–[Co(trien)S–aa]$^{2+}$.

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