

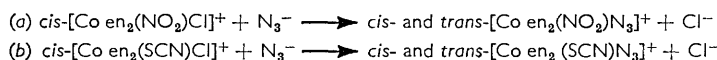
20. *The Preparation and Properties of Some New Azidobis(ethylenediamine)cobalt(III) Complexes. Part I. Preparation and Properties of the Azidonitro-, Azidoisothiocyanato- and Azidoammine Derivatives.*

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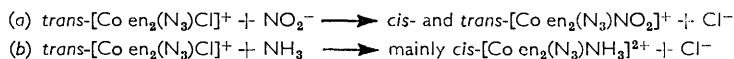
A series of salts corresponding to each of the cations *cis*- and *trans*-[Co en₂(SCN)N₃]⁺, *cis*- and *trans*-[Co en₂(NO₂)N₃]⁺, and *cis*-[Co en₂(NH₃)N₃]²⁺ has been prepared. The configurations of the *cis*-series have been proved by the isolation of an optically active enantiomorph of each. The visible, ultraviolet, and infrared absorption spectra have been investigated. The configurational assignments are supported by infrared measurements.

INTEREST in the study of substitution in diacidobis(ethylenediamine)cobalt(III) complexes by azide ions has increased recently.¹ In order to follow such reactions it is essential to know the chemical and physical properties of the azido-complexes formed. This necessitates their preparation since so far very few have been fully characterised. The complexes [Co(NH₃)_{6-n}(N₃)_n]⁽³⁻ⁿ⁾⁺ (*n* = 1—3)² and the *cis*- and *trans*-isomers of [Co en₂(N₃)₂]⁺, [Co en₂(N₃)Cl]⁺, and [Co en₂(N₃)H₂O]²⁺ have been prepared and characterised.³ In this paper the preparation and properties of *cis*- and *trans*-[Co en₂(SCN)N₃]⁺, *cis*- and *trans*-[Co en₂(NO₂)N₃]⁺, and *cis*-[Co en₂(NH₃)N₃]²⁺ salts are reported for the first time.

Two main methods have been used to prepare these complexes: (1) replacement of a labile chlorine atom in the corresponding chloro-complex by azide:



(2) Replacement of the labile chloro-group of *trans*-[Co en₂(N₃)Cl]ClO₄ by the required group (NO₂⁻ or NH₃):



The second steps involving the formation of diazido-complexes do not interfere to an appreciable extent, since in these conditions the nitro- and isothiocyanato-groups are not very labile.

The asymmetry of the *cis*-cations has been demonstrated by the preparation and partial fractional crystallisation of the α-(+)-bromocamphor-π-sulphonates. Apparent molar rotations have been measured at various wavelengths in aqueous solution. Optical rotatory dispersion curves were obtained by correcting the observed values for the anionic contribution. Since the objective was to distinguish between *cis*- and *trans*-isomers rather than to effect complete resolutions, the preparation and fractional crystallisation was not pursued further. The molecular rotations measured are given in Fig. 3.

¹ Brown and Ingold, *J.*, 1953, 2680; Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379, 5382; Tobe and Watts, personal communication.

² Linhard and Flygare, *Z. anorg. Chem.*, 1950, **262**, 328; Linhard, Weigel, and Flygare, *ibid.*, 1950, **263**, 233; Linhard and Weigel, *ibid.*, p. 245.

³ Staples and Tobe, *J.*, 1960, 4812.

The rotations were measured on a Stanley photoelectric polarimeter. The rotations actually measured were in the range 0.160–0.004°, the accuracy of the instrument being ±0.001°.

The visible and ultraviolet absorption spectra have been measured and the results are shown in Figs. 1 and 2. Replacement of the chloro- by an azido-group considerably increases the molar extinction coefficient of the peak in the visible region. In the visible

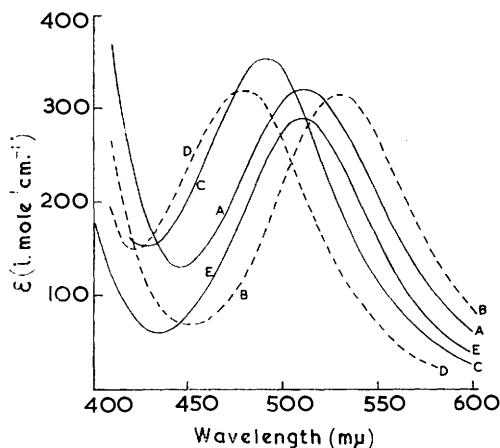


FIG. 1.

FIG. 1. Visible absorption spectra of (A) *cis*-[Co en₂N₃(SCN)]₂S₂O₆, (B) *trans*-[Co en₂N₃(SCN)]ClO₄, (C) *cis*-[Co en₂N₃(NO₂)]ClO₄, (D) *trans*-[Co en₂N₃(NO₂)]ClO₄, and (E) *cis*-[Co en₂N₃(NH₃)]S₂O₆.

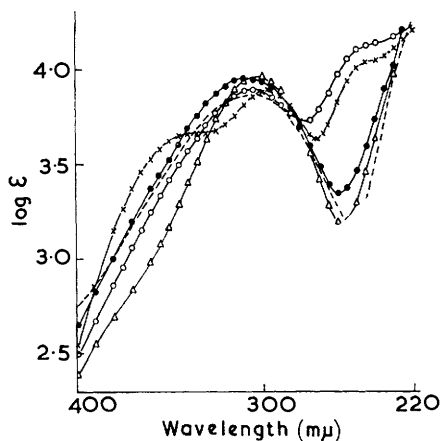


FIG. 2.

FIG. 2. Near-ultraviolet absorption spectra of (o) *cis*-[Co en₂N₃(NO₂)]ClO₄, (x) *trans*-[Co en₂N₃(NO₂)]ClO₄, (●) *trans*-[Co en₂N₃(SCN)]ClO₄, (---) *cis*-[Co en₂N₃(NH₃)]S₂O₆. Δ *cis*-[Co en₂N₃(NH₃)]S₂O₆.

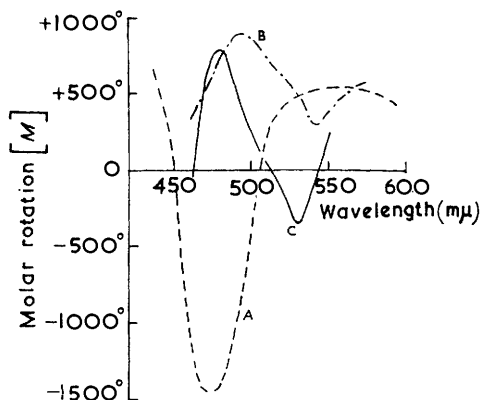


FIG. 3. Optical rotatory dispersion curves for (A) (+)-*cis*-[Co en₂N₃(NO₂)]⁺, (B) (+)-*cis*-[Co en₂N₃(SCN)]⁺, and (C) (+)-*cis*-[Co en₂N₃(NH₃)]²⁺.

region the absorption spectra of salts of a common complex cation are identical. This property has been used as a criterion for isomeric purity.

The infrared absorption spectra have also been investigated over the range 2.5–15.0 μ. Some characteristic frequencies are given in Table 1. The frequencies of the asymmetric stretching vibration of the azido-group suggest that the three nitrogen atoms are collinear. The infrared spectra also support the configurational assignments which have been made on the basis of the isolation of an optically active enantiomorph of the *cis*-isomer. Baldwin

has shown⁴ that the frequency of the NH₂ bending vibration, which occurs in the 1600 cm.⁻¹ region, may be correlated with the configuration of the complex. For complexes of the type *trans*-[Co en₂AB]X single, sharp bands occur in the range 1605—1575 cm.⁻¹ whereas the bands are much more complex for the *cis*-compounds and occur over the range 1634—1527 cm.⁻¹. The results for our complexes are shown in Table 1. Table 2 shows the results of some previous reports of azide bands for comparison.

TABLE 1.
Some characteristic frequencies (cm.⁻¹) for infrared absorption by some azidobis(ethylenediamine)cobalt(III) complexes.

Compound	N ₃	NH ₂ bending	Co-ordinated SCN
<i>cis</i> -[Co en ₂ (NO ₂)N ₃]ClO ₄	2045s 2066sh	1565s 1580m 1610sh 1647sh	
<i>cis</i> -[Co en ₂ (NO ₂)N ₃] ₂ S ₂ O ₆	2066s	1585s 1623sh	
<i>trans</i> -[Co en ₂ (NO ₂)N ₃]ClO ₄	2070s	1603s	
<i>trans</i> -[Co en ₂ (NO ₂)N ₃]NO ₃	2058s	1603s	
<i>cis</i> -[Co en ₂ (SCN)N ₃] ₂ S ₂ O ₆	2049s 2070sh	1597m 1647sh	2160
<i>cis</i> -[Co en ₂ (SCN)N ₃]NO ₃	2041s	1592m 1613sh	2132
<i>trans</i> -[Co en ₂ (SCN)N ₃]ClO ₄	2058s	1608s	2128
<i>trans</i> -[Co en ₂ (SCN)N ₃]I	2049s	1595s	2137
<i>trans</i> -[Co en ₂ (SCN)N ₃]SCN	*	1603s	2165
<i>cis</i> -[Co en ₂ (NH ₃)N ₃] ₂ S ₂ O ₆	2037sh 2075s	1577s 1597s 1634sh 1650sh	

In addition, the following peaks for co-ordinated SCN were measured: *cis*-[Co en₂(SCN)Cl]NO₃ 2123; *trans*-[Co en₂(SCN)Cl]SCN 2137 (ionised SCN 2049); *trans*-[Co en₂(SCN)Cl]ClO₄ 2137 cm.⁻¹.

* As the asymmetric stretching frequency of the co-ordinated azido-group and that of the ionic thiocyanate occur at the same wavelength (*ca.* 2060 cm.⁻¹) it was not possible to assign the two parts of a peak occurring at 2058 and 2049 cm.⁻¹ unambiguously without a detailed isotopic investigation.

TABLE 2.
Azide absorption bands (cm.⁻¹) reported previously.

	Ref.		Ref.		Ref.			
<i>cis</i> -[Co en ₂ (N ₃)Cl]ClO ₄	2041	3	NaN ₃	2128	<i>a</i>	HN ₃ (gas)	2140	<i>b</i>
<i>trans</i> -[Co en ₂ (N ₃)Cl]ClO ₄	2033	3	KN ₃	2041	<i>a</i>	HN ₃ (solid)	2169	<i>b</i>
<i>cis</i> -[Co en ₂ (N ₃) ₂]ClO ₄	2028, 2075	3	NH ₄ N ₃	2041	<i>a</i>	CH ₃ N ₃ (gas)	2143	<i>c</i>
<i>trans</i> -[Co en ₂ (N ₃) ₂]ClO ₄	2020	3						

(*a*) Gray and Waddington, *Trans. Faraday Soc.*, 1957, **53**, 901. (*b*) Dows and Pimentel, *J. Chem. Phys.*, 1955, **23**, 1258. (*c*) Eyster and Gillette, *ibid.*, 1940, **8**, 369.

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EXPERIMENTAL

Preparations.—*cis*-Chloronitrobis(ethylenediamine)cobalt(III) chloride,⁵ *cis*-chloroiso-thiocyanatobis(ethylenediamine)cobalt(III) chloride,⁵ and *trans*-chloroazidobis(ethylenediamine)-cobalt(III) perchlorate³ were prepared by methods described in the literature.

cis-Azidoisothiocyanatobis(ethylenediamine)cobalt(III) dithionate. *cis*-Chloroiso-thiocyanatobis(ethylenediamine)cobalt(III) chloride (10.3 g.) was dissolved in warm water (30 ml.), a solution of sodium azide (2.2 g.) in water (10 ml.) was added, and the mixture was gently heated to the b. p. The filtered solution was cooled and saturated sodium dithionate was added. After 2 hr. red crystals of *cis*-azidoisothiocyanatobis(ethylenediamine)cobalt(III) dithionate were filtered off, washed with alcohol and ether, and dried over P₂O₅. These crystals were recrystallised from hot water by addition of saturated sodium dithionate solution until the visible absorption spectrum was reproducible (yield 2.0 g.) (Found: N₃⁻, 11.6; SCN⁻, 16.0; Cl⁻, 0.0. C₁₀H₃₂Co₂N₁₆O₆S₄ requires N₃⁻, 11.7; SCN⁻, 16.1; Cl⁻, 0.0%).

cis-Azidoisothiocyanatobis(ethylenediamine)cobalt(III) nitrate. A warm, aqueous solution of the dithionate (2 g.) in water (20 ml.) was treated with solid ammonium nitrate (5 g.). Red

⁴ Baldwin, *J.*, 1960, 4369.

⁵ Werner, *Annalen*, 1912, **386**, 1.

crystals (1.0 g.) of the *nitrate* were filtered off, washed with alcohol and ether, and dried (P_2O_5) (Found: N_3^- , 12.4; SCN^- , 16.8; C, 17.35; H, 4.6; N, 37.15; S, 9.4. $C_5H_{16}CoN_9O_3S$ requires N_3^- , 12.3; SCN^- , 17.0; C, 17.6; H, 4.7; N, 37.0; S, 9.4%). This salt was also prepared by adding solid ammonium nitrate to the reaction mixture instead of sodium dithionate.

Action of ammonium α -(+)-bromocamphor- π -sulphonate on cis-azidoisocyanobis(ethylenediamine)cobalt(III) chloride. *cis*-Chloroisothiocyanatobis(ethylenediamine)cobalt(III) chloride (6 g.) was dissolved in warm water (12 ml.), a solution of sodium azide (1.3 g.) in water (5 ml.) was added, and the mixture was heated to the b. p., filtered, and cooled. Solid ammonium α -(+)-bromocamphor- π -sulphonate (5 g.) was added and after 15 min. pink crystals (1.0 g.) were filtered off, washed with alcohol and ether, and dried.

These crystals were left in alcohol overnight to ensure the removal of any resolving agent present, then collected again, washed with alcohol and ether, and dried (P_2O_5) (Found: C, 30.8; H, 5.3; SCN^- , 9.9; N_3^- , 7.0. $C_{15}H_{30}BrCoN_8O_4S_2$ requires C, 30.6; H, 5.1; SCN^- , 9.8; N_3^- , 7.1%). Further batches of the *salt* were obtained from the mother-liquor and were similarly treated. The rotatory dispersion curves of different batches were the same, within the limits of experimental error. The rotatory dispersion curves obtained indicate that the complex ion was, at least partially, resolved. As it has not yet been possible to convert this salt into the perchlorate it is not possible to say whether or not the complex was fully resolved.

trans-Azidoisothiocyanatobis(ethylenediamine)cobalt(III) thiocyanate. The aqueous filtrate from the precipitation of *cis*-azidoisothiocyanatobis(ethylenediamine)cobalt(III) dithionate was treated with solid potassium thiocyanate; purple crystals of the *trans*-thiocyanate were precipitated almost immediately. These were recrystallised from hot water, washed with alcohol and ether, and dried over P_2O_5 . This recrystallisation was repeated until a constant absorption spectrum was obtained (yield, 3.5 g.) (Found: N_3^- , 12.3; ionic SCN^- , 17.3; total SCN^- , 34.3; C, 21.3; H, 4.75; N, 37.2; S, 18.9; Cl^- , 0.0. $C_6H_{16}CoN_8S_2$ requires N_3^- , 12.5; ionic SCN^- , 17.3; total SCN^- , 34.4; C, 21.35; H, 4.75; N, 37.4; S, 19.0%).

trans-Azidoisothiocyanatobis(ethylenediamine)cobalt(III) perchlorate. The thiocyanate of this series (5 g.) was dissolved in warm water (80 ml.), and solid sodium perchlorate was added. Dark purple crystals of the *trans*-perchlorate (3.0 g.) were filtered off, washed with alcohol and ether, and dried. This compound was recrystallised from warm water until the absorption spectrum was constant (Found: N_3^- , 11.0; SCN^- , 15.5; Cl^- , 0.0; C, 15.8; H, 4.5; N, 29.6; S, 8.6. $C_5H_{16}ClCoN_8O_4S$ requires N_3^- , 11.1; SCN^- , 15.3; Cl^- , 0.0; C, 15.9; H, 4.4; N, 29.6; S, 8.5%).

cis-Azidoamminebis(ethylenediamine)cobalt(III) dithionate. To *trans*-chloroazidobis(ethylenediamine)cobalt(III) perchlorate (2.0 g.) liquid ammonia (20 ml.) was added dropwise. After 0.5 hr. the flask was allowed to warm to room temperature. After 24 hr., when the excess of ammonia had evaporated, the solid from five such experiments was washed with alcohol, dried, and ground with 0.25M-acetic acid (10 ml.). A purple residue was filtered off, washed with alcohol and ether, and dried. This was impure *trans*-diazidobis(ethylenediamine)cobalt(III) perchlorate. The aqueous filtrate was treated with solid sodium dithionate, and purplish-red crystals of *cis*-azidoamminebis(ethylenediamine)cobalt(III) dithionate (1.2 g.) were filtered off washed with alcohol and ether, and dried (Found: N_3^- , 10.3%; Cl^- , 0.0; equiv., 197. $C_4H_{19}CoN_8O_6S_2$ requires N_3^- , 10.5%; equiv., 199).

cis-Azidonitrobis(ethylenediamine)cobalt(III) perchlorate. *cis*-Chloronitrobis(ethylenediamine)cobalt(III) chloride (14.8 g.) was dissolved in warm water (50 ml.), and sodium azide (3.25 g.) was added. The solution was warmed to the b. p., then allowed to cool, and solid sodium dithionate was added. Orange crystals were filtered off, washed with alcohol and ether, and dried over P_2O_5 . These were a mixture of *cis*- and *trans*-azidonitro-dithionate which proved very difficult to separate. The aqueous filtrate was treated with solid sodium perchlorate and after a few minutes a red crystalline precipitate of *cis*-azidonitrobis(ethylenediamine)cobalt(III) perchlorate (2.6 g.) was filtered off, washed with alcohol and ether, dried over P_2O_5 , and recrystallised from hot water until the visible absorption spectrum was constant (Found: N_3^- , 11.2; Cl^- , 0.0; C, 13.1; H, 4.6. $C_4H_{16}ClCoN_8O_6$ requires N_3^- , 11.4; C, 13.1; H 4.7%).

Action of ammonium α -(+)-bromocamphor- π -sulphonate on cis-azidonitrobis(ethylenediamine)cobalt(III) perchlorate. The perchlorate (1.0 g.) was dissolved in warm water (10 ml.), and solid ammonium α -(+)-bromocamphor- π -sulphonate (5 g.) was added to the filtered solution. On cooling, pink-orange crystals of the *cis*- α -(+)-bromocamphor- π -sulphonate were precipitated.

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These were filtered off, washed with alcohol and ether, left in alcohol overnight, washed with ether, and dried (yield 0.6 g.) (Found: C, 28.6; H, 5.3; N_3^- , 7.6. $C_{14}H_{30}BrCoN_8O_6S$ requires C, 28.9; H, 5.2; N_3^- , 7.5%). Further batches of the salt were obtained from the mother-liquor. The rotatory dispersion curves of each batch were the same within the limits of experimental error and indicated that the complex was at least partly resolved.

trans-Azidonitrobis(ethylenediamine)cobalt(III) nitrate. *trans-Chloronitrobis(ethylenediamine)cobalt(III) nitrate* (16.4 g.) was heated with water (45 ml.), sodium azide (3.25 g.) was added, and the solution was heated until all the solid had dissolved. Orange-red crystals of *trans-azidonitrobis(ethylenediamine)cobalt(III) nitrate* were precipitated on cooling. These crystals were filtered off, washed with alcohol and ether, and dried. The aqueous filtrate was treated with solid ammonium nitrate and a second, bigger crop of crystals was filtered off, washed, and dried over P_2O_5 (total yield 6.2 g.). This salt was recrystallised from hot water until the absorption spectrum was reproducible. (Found: N_3^- , 12.7; Cl^- , 0.0; C, 14.4; H, 4.9. $C_4H_{16}CoN_8O_6$ requires N_3^- , 12.8; Cl^- , 0.0; C, 14.6; H, 4.9%).

trans-Azidonitrobis(ethylenediamine)cobalt(III) perchlorate. *trans-Azidonitrobis(ethylenediamine)cobalt(III) nitrate* (5 g.) was dissolved in warm water (50 ml.), and solid sodium perchlorate was added. Orange-red crystals were filtered off, washed with alcohol and ether, and dried. This salt (3.5 g.) was recrystallised from water until a constant visible absorption spectrum was obtained (Found: N_3^- , 11.3; Cl^- , 0.0; C, 13.0; H, 4.2. $C_4H_{16}ClCoN_8O_6$ requires N_3^- , 11.4; Cl, 0.0; C, 13.1; H, 4.4%).

Analytical Procedures.—(a) *Equivalent weight.* The complex (~0.1 g.; accurately weighed), dissolved in the minimum amount of cold water, was passed through a column of Amberlite IR-120 resin in its sodium form, then through Amberlite IR-120 in its hydrogen form, and this second effluent was titrated with borax solution (Methyl Red). The complex could not be passed through a resin in its hydrogen form because the azido-groups are displaced by high concentrations of acid.

(b) *Halogen and pseudohalogen determination.* The azidoamine- and azidoisothiocyanato-derivatives were analysed by a procedure previously described.³ To the complex (0.05–0.1 g.; accurately weighed) 4N-sodium hydroxide (10 ml.) was added. The solutions were left overnight, then sufficient glacial acetic acid was added to adjust the pH to 5.0–4.5. The halide, azide, and thiocyanate ions present were titrated potentiometrically with silver nitrate solution, a calomel half-cell and a silver electrode with an agar-ammonium nitrate bridge being used.

This procedure was, however, modified for the azidonitro-analogues. The reaction between alkali and these complexes is slow and in order to avoid loss of azide-containing vapours when the solutions were warmed in a water-bath, the experiments were performed in sealed Pyrex tubes. The resulting solutions were neutralised with dilute acetic acid to pH 7.4–7.5, a calomel half cell and a glass electrode being used. This careful pH control was essential because azide and nitrite ions react rapidly in acid solution to give nitrogen. The azide present was then titrated potentiometrically with silver nitrate solution. It has been shown, by using synthetic mixtures of sodium azide and sodium nitrite, that the results can be up to 2% low by this method. This probably accounts for the somewhat low analyses of the azidonitro-compounds.

Spectral Measurements.—The visible and ultraviolet absorption spectra were measured with a Unicam S.P. 500 spectrophotometer with silica cells. The infrared spectra were measured in the form of potassium bromide discs on a Perkin-Elmer Infracord spectrometer.

Measurement of Optical Rotation.—The optical rotations were measured on a Stanley photoelectric polarimeter with 1 dm. tube.