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Isomers of the Bis(1,4,7-triazacyclodecane)cobalt(III) and (1,4,7,11,14,17-Hexaazacycloeicosane)cobalt(III) Ions: Preparations, Characterizations and Isomerization

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Cobalt(III) complex formation, using tacd·3HBr from the Richman–Atkins synthesis for cyclic polyamines, gives the trans *and* cis *isomers of [Co(tacd)$_2$]$^{3+}$ in the equilibrium ratio 96:4 (perchlorates, 80°). Two other complexes are also formed, and these have been characterized (^{13}C and ^{1}H n.m.r. and visible spectroscopy) as single isomers* mer,cis-*[Co(hace)]$^{3+}$ and* cis-*[Co(dtah)]$^{3+}$ (dtah = 1,16-diamino-3,7,10,13-tetraazahexadecane). These hexamine ligands hace and dtah are therefore co-products with tacd in the Richman–Atkins synthesis, and they coordinate stereospecifically. The* cis $\rightleftarrows$ trans *[Co(tacd)$_2$]$^{3+}$ isomerization is catalyzed by base or charcoal, and the mechanism proposed is intramolecular bond-rupture of a Co–*sec*-NH bond and subsequent rearrangement of a trigonal-bipyramidal intermediate. This isomerization proceeds in Na$_3$PO$_4$ solution to give 100%* trans, *and use of this enables pure [Co(hace)]$^{3+}$ to be obtained by chromatographic separation from the preparative mixture. The ion-exchange chromatographic elution order of the four complexes is rationalized in terms of differential ion-associations.*

Introduction

To extend studies of isomerization reactions of CoN$_6^{3+}$ complexes [1], we wished to examine the system [Co(tacd)$_2$]$^{3+}$ (tacd = 1,4,7-triazacyclodecane). On coordination, this macrocyclic ligand gives a six-membered chelate ring analogous to that formed by 1,3-diaminopropane (tn), and two five-membered rings (en), all coupled. Two geometric

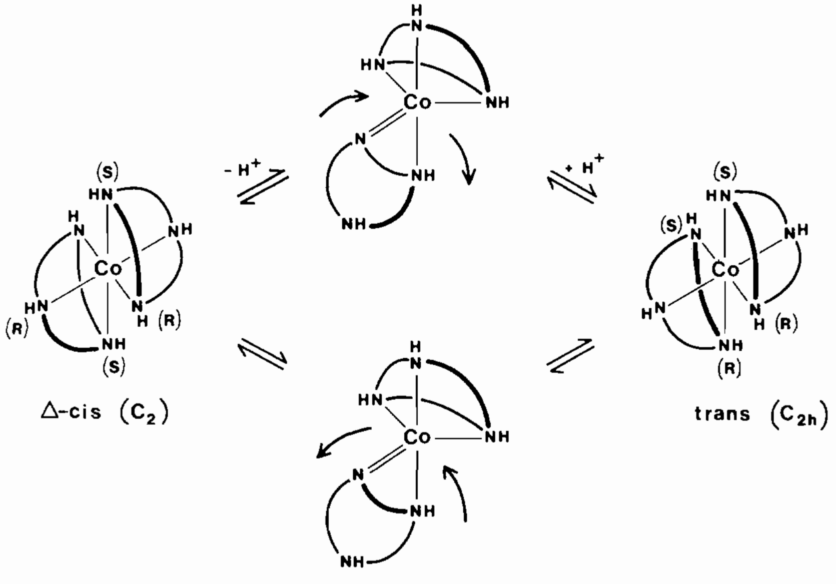

Fig. 1. Geometric isomers of [Co(tacd)$_2$]$^{3+}$, and possible trigonal-bipyramidal intermediates leading to the *cis* → *trans* change. The six-membered chelate rings (tn) are shown thickened. The absolute configurations of the optical forms of the *cis* isomer are defined as the chirality of the octahedron edges spanned by the two (tn) rings: Δ is right-handed. R and S are the absolute configurations at the asymmetric coordinated *sec*-nitrogen atoms.

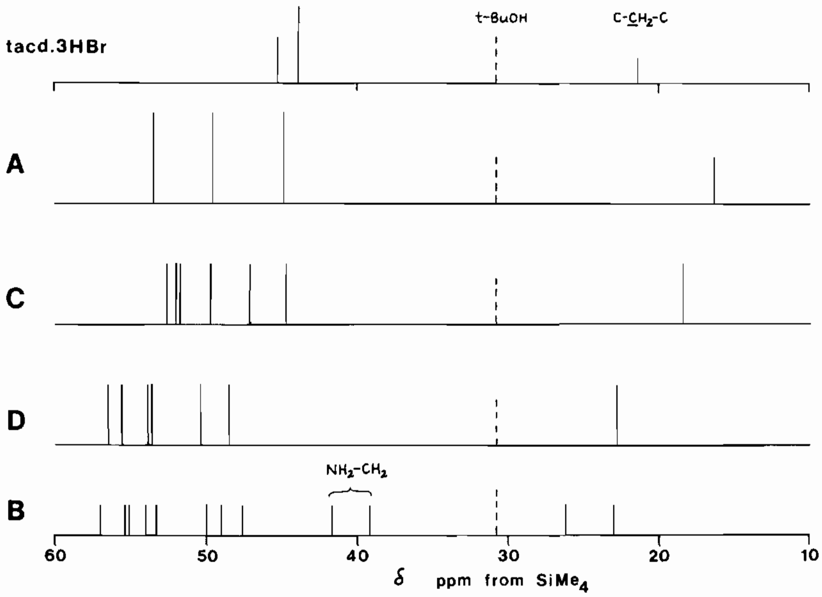

Fig. 2. 20.1 MHz ^{13}C n.m.r. spectra in D_2O: (A), *trans*-[Co(tacd)$_2$](ClO$_4$)$_3$; (C), *cis*-[Co(tacd)$_2$](ClO$_4$)$_3$; (D), *mer,cis*-[Co(hace)](ClO$_4$)$_3$; (B), *cis*-[Co(dtah)](ClO$_4$)$_3$.

isomers are possible, in which the (tn) rings from the two ligands are disposed *cis* (chiral) and *trans* to each other (Fig. 1), and the *cis* can further exist as optical isomers. The complex has been reported previously but isomers were not separated [2].

The ligand tacd·3HBr was obtained by the Richman–Atkins cyclization procedure [3]. We found this to be a difficult preparation from which it was difficult to obtain a product with an acceptable ^{13}C n.m.r. spectrum, and when this ligand product was employed to synthesize the [Co(tacd)$_2$]$^{3+}$ isomers two other complexes were also obtained. Following our preliminary report [4], this article describes the preparation, separation, and characterizations of these four complexes, and the isomerization of [Co(tacd)$_2$]$^{3+}$.

Results and Discussion

Preparation and Isolation of Complexes

The [Co(tacd)$_2$]$^{3+}$ complex was prepared by substitution of tacd in [Co(NH$_3$)$_5$Br]$^{2+}$ in the presence of catalytic charcoal at 80°, and the four complexes produced are designated (A) to (D) according to the order of their elution from SP-Sephadex cation-exchange resin columns with Na_3PO_4 eluent. (A) and (C) are the *trans* and *cis*-[Co(tacd)$_2$]$^{3+}$ isomers respectively, (D) is one isomer of [Co(hace)]$^{3+}$ (hace = 1,4,7,11,14,17-hexaazacycloeicosane), and (B) is one isomer of [Co(dtah)]$^{3+}$ (dtah = 1,16-diamino-3,7,10,13-tetraazahexadecane). These identifications are discussed in following sections. The separation of all four complexes was not possible directly, but by using the isomerizations (A) $\rightleftarrows$ (C) and enhancement of (A) by ion-association, the four complexes were eventually isolated as their pure perchlorate salts.

From the preparative solution, three bands of complexes were separated chromatographically on SP-Sephadex resin. From the first two of these (A), yellow, and (B), orange, were obtained as the pure perchlorates by work-up on a weak-acid cation-exchange resin. The product from the third orange band, isolated as perchlorate, was a mixture of the two complexes (C) and (D) as demonstrated by the ^{13}C n.m.r. spectrum which showed two sets of seven equal resonances in the intensity ratio (C):(D) *ca.* 1:3. From this ratio and the amounts of products isolated from the three bands, the molar ratio of the four products is (A):(B):(C):(D) = 86:2:3:9.

Isomerization of *cis* to *trans*-[Co(tacd)$_2$]$^{3+}$ (C) → (A), is essentially complete in Na_3PO_4 solution, and this reaction at 80° was used to remove (C) from the above (C) + (D) mixture; the (A) and (D) can be readily separated chromatographically, to give pure (D).

The pure (C) isomer was obtained by equilibrating (A) on charcoal at 80°, and the resulting equilibrium mixture of (A):(C) *ca.* 96:4 was separated on SP-Sephadex resin. The interconversion of (A) and (C), and the n.m.r. evidence below, establish these

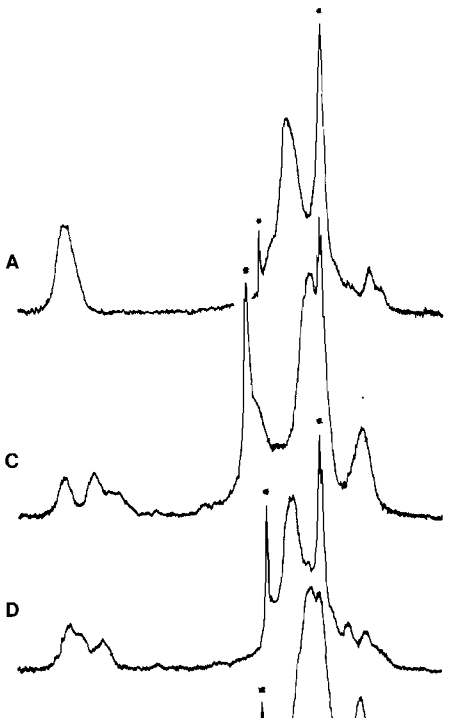

Fig. 3. 60 MHz ^{1}H n.m.r. spectra of complexes (A) to (D) in d$_6$-dimethyl sulphoxide. Asterisks denote solvent signals.

as the isomers of $[Co(tacd)_2]^{3+}$, and their proportions above correspond with those obtained from the preparation at the same temperature.

Assignments of Configurations of the $[Co(tacd)_2]^{3+}$ *Isomers*

The clean ^{13}C n.m.r. spectra of (A) and (C) (Fig. 2) account for the seven carbons in the tacd ligands. The four peaks in ratio 2:2:2:1 from (A) give the molecular symmetry as C_{2h}, while the spectrum of (C) consists of seven equal peaks giving the molecular symmetry as C_2. Both spectra are characterized by a single resonance upfield due to the central methylene carbon of the (tn) ring as in tacd·3HBr, tn, and $[Co(tn)_3]^{3+}$ [5]. These results establish (A) and (C) as the *trans* and *cis* isomers respectively.

There is substantial evidence that the conformations of en and tn chelate rings interconvert rapidly in solution [6–9], so that in the present system the ^{13}C n.m.r. spectra probably reflect averaged conformations [10], and the effective molecular symmetries thus indicated are those based on planar chelate rings (Fig. 1).

The ^{1}H n.m.r. spectra of (A) and (C) in d$_6$-dimethyl sulphoxide (Fig. 3) have broad overlapping NH resonances and three broad overlapping CH_2 bands showing little resolution [11, 12]. (C) shows three NH resonances (1:1:1) corresponding to the three stereochemically distinct NH groups in the *cis* geometry. The *trans* structure has two stereochemically different NH groups (ratio 2:1), although these are not resolved in the single broad NH resonance, albeit slightly unsymmetric, given by (A). The three broad methylene proton peaks are attributed to the $N–CH_2–C–CH_2–N$, $N–CH_2–CH_2–N$, and $N–C–CH_2–C–N$ protons (at low to high field respectively) from their ratio (*ca.* 4:8:2) and from comparisons with other six-membered chelate ring systems [12, 13], and the lack of resolution in these peaks is consistent with rapidly interconverting ring conformations.

(A) and (C) have yellow and orange colours respectively, and we take these and the different visible absorption spectra (Fig. 4) to be characteristic of the *trans* and *cis* geometries.

Characterization of mer,cis-$[Co(hace)]^{3+}$, *(D)*

From the chromatography behaviour, (D) and (B) were both evidently CoN_6^{3+} complexes. (D) has properties very similar to those of $[Co(tacd)_2]^{3+}$: the elemental analysis indicates $C_{14}N_6$; the ^{13}C n.m.r. shows seven equal resonances, with one at high field due to $N–CH_2–CH_2–CH_2–N$; and the ^{1}H n.m.r. shows three NH resonances, but no NH_2 indicating that the ligand is macrocyclic.

However, (D) remained unchanged under conditions where isomerizations of CoN_6^{3+} complexes occur (with charcoal, or base, or Na_3PO_4) so that it could not be another isomer of $[Co(tacd)_2]^{3+}$ (*i.e.* a conformational isomer or NH diastereoisomer). (D) is therefore a single geometric isomer of $[Co(hace)]^{3+}$. This implies that the dimeric cyclic amine hace was present in the ligand sample obtained from the Richman–Atkins synthesis, and a similar situation has been reported by Margulis and Zompa in that the planned synthesis of $[Ni(tacd)_2](ClO_4)_2$ gave instead crystals of one isomer of $[Ni(hace)](ClO_4)_2·(Me_2NCHO)$ [14].

Three geometric isomers are possible for $[Co(hace)]^{3+}$, and diastereoisomers arise from the different possible orientations of NH bonds at the secondary nitrogens which couple meridional pairs of chelate rings (Fig. 5). The seven equal resonances in the clean ^{13}C n.m.r. spectrum in D_2O (both neutral and basified with NaOH to pH 12) show that only one of the six possible species is present (different NH diastereoisomers give different ^{13}C n.m.r. resonances [10, 15]), and together with the non-observance of any isomerization this implies that the coordination of hace is highly stereospecific. The ^{13}C n.m.r. spectrum and the ^{1}H n.m.r. spectrum (three different NH) show

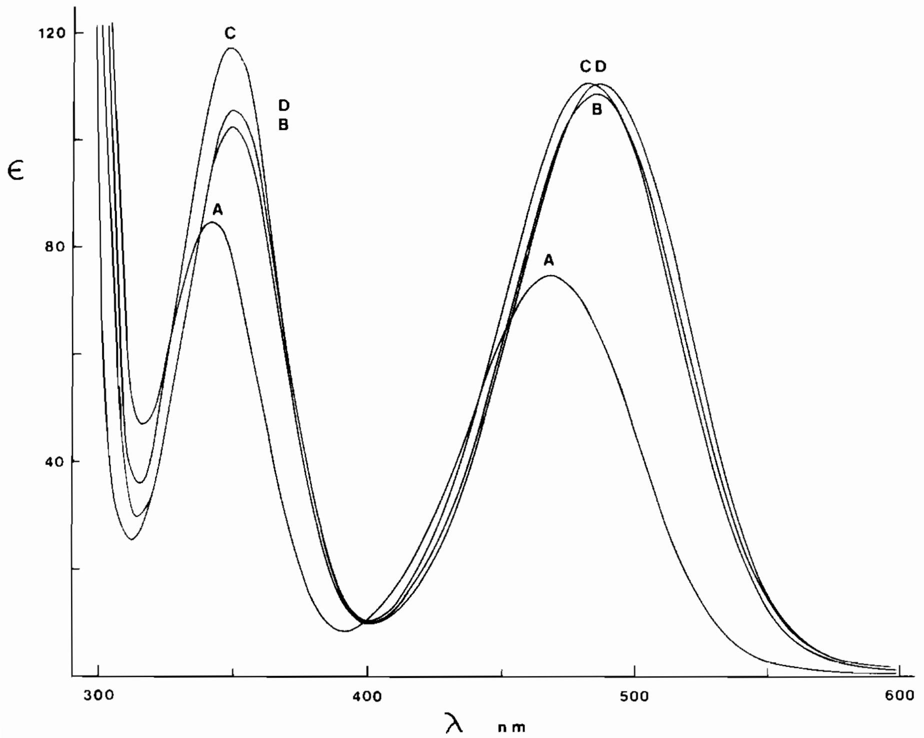

Fig. 4. Visible absorption spectra of complexes (A) to (D) in water.

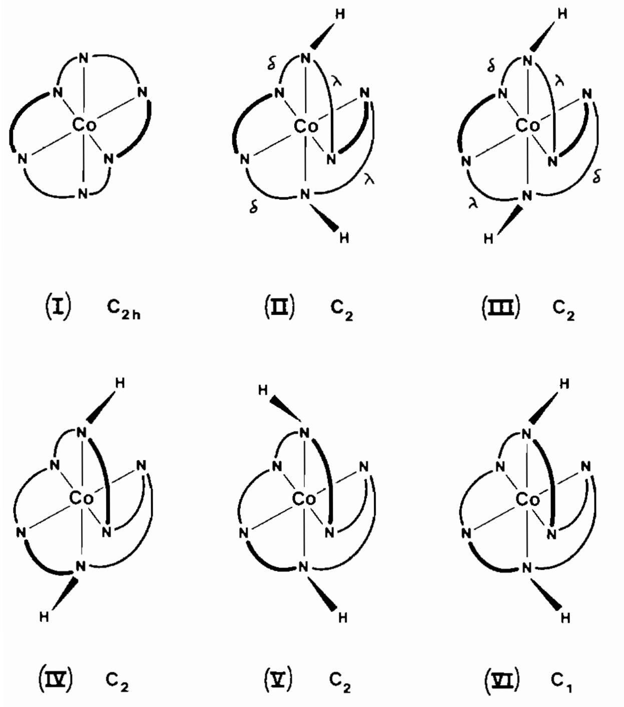

Fig. 5. Possible geometries and diastereoisomers for [Co(hace)]$^{3+}$, (D). Symmetries are based on planar rings or on the fixed en ring conformations δ or λ for the *mer*-[Co(dien)$_2$]$^{3+}$ moiety in (II) and (III).

also that the symmetry is two-fold eliminating structures (I) and (VI) (Fig. 5), and the close similarity of the visible absorption spectrum to that of *cis*-[Co(tacd)$_2$]$^{3+}$ (C) indicates *cis* geometry (IV) or (V). That (C) and (D) chromatograph almost together is also consistent with their similar *cis* geometry. The structure found for [Ni(hace)]·(ClO$_4$)$_2$·(Me$_2$NCHO) was (IV) [14]. Conformational analyses of the [Co(hace)]$^{3+}$ and [Co(tacd)$_2$]$^{3+}$ systems will be reported elsewhere [16].

Characterization of cis-*[Co(dtah)]*$^{3+}$*, (B)*

From the elemental analysis and the ^{13}C n.m.r. spectrum, (B) contained twelve carbons. The ^1H n.m.r. spectrum showed three broad overlapping NH peaks in ratio 2:1:1, and three broad resonances, ratio 2:1:1, at higher fields due to NH_2. The integration ratio $NH:NH_2:CH_2$ = 4:4:24 gives two NH_2 groups in the complex ion, so that the ligand is non-macrocyclic.

The twelve equal ^{13}C resonances show that (B) is a single complex isomer of C_1 symmetry. There are eight *C*H_2–NH–*C*H_2 resonances whose chemical shifts correspond closely with those of (D), and one of the two upfield N–C–*C*H_2–C–N resonances also corresponds closely with that of (D). The two resonances at around δ 40 ppm, which have no correspondences in the other complexes, are assigned as

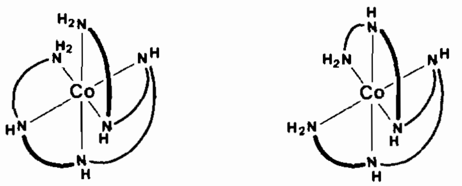

Fig. 6. Possible structures for *cis*-$[Co(dtah)]^{3+}$, (B).

NH_2–CH_2– [5, 17]. These properties indicate that (B) has a structure similar to *mer,cis*-$[Co(hace)]^{3+}$ (D) but less an ethylene bridge, and the linear hexamine dtah must have been present in the tacd• 3HBr sample used in the synthesis of the complexes.

The formulation $[Co(tacd)(adp)]^{3+}$ (adp = NH_2–CH_2–CH_2–CH_2–NH–CH_2–CH_2–NH_2), which is also consistent with the n.m.r. spectra, is excluded by subsequent work on the Richman–Atkins tacd• 3HBr product: ion-exchange has separated two differently charged fractions tacd•3HCl and hexamine• 6HCl [4], and (B) and (D) were produced only from the latter fraction.

The close similarity of the visible absorption spectra of (B) and (D) confirm that they have similar arrangements of the chelate rings about the cobalt, particularly of the (tn) rings. Two geometric isomers are possible for a *cis* arrangement of the two (tn) rings in (B) (Fig. 6) and two and four NH diastereoisomers are possible for these respectively, but the present evidence does not allow the structure of (B) to be decided amongst these six possible diastereoisomers. The failure to detect other isomers of (B) indicates that the coordination of dtah, like hace, is highly stereospecific.

The present results demonstrate that significant amounts of other polyamines may be co-products in the Richman–Atkins synthesis for cyclic amines, and that these may not be easily removed by recrystallization procedures [4]. Notwithstanding the content of higher amines in the present Richman–Atkins tacd•3HBr sample, the methods described are efficient for obtaining the pure $[Co(tacd)_2]^{3+}$ isomers, since isomerization of (A) is required to obtain (C) in reasonable amounts. (B) and (D) would be obtained more efficiently however by using only the hexamine component from ion-exchange separation of the ligand.

Ion-association with Phosphate

The R_x (relative R_F) values for the elutions with Na_3PO_4 of (A), (B), (C) and (D) are 2.9_2, 1.9_2, 1.6_9* and 1.5_5* respectively, relative to the slowly moving reference complex *s-fac*-$[Co(medien)_2]^{3+}$ [medien = 2,2′-methyliminodi(ethylamine) or 4-methyldiethylenetriamine] [18].

In seeking to account for this elution order in terms of the differential associations of the complex cations with the eluent anions [18], Dreiding molecular models were examined. These suggest that for each of the geometric isomers of $[Co(tacd)_2]^{3+}$ chair conformations of the two (tn) rings give the least overall non-bonded interactions, and that the two (en) rings in each coordinated ligand are enantiomeric to give the least ring strain. With these conformational arrangements, for each geometric isomer N–H bonds are available only in pairs to hydrogen-bond simultaneously to a PO_4^{3-} anion. There are two pairs for each isomer, the pairs being at opposite ends of the molecular C_2 axis in the *trans* isomer (and related by the molecular mirror plane) and at one end of the molecular C_2 axis in the *cis* isomer (and related by that axis). Other conformational arrangements examined all lead to the conclusion that ion-association is restricted to NH interactions pairwise for the two isomers; there seems no possibility that three N–H bonds can be disposed to associate trigonally with a PO_4^{3-} ion in the manner proposed for the $[Co(dien)_2]^{3+}$ isomers [18].

The greater degree of association of PO_4^{3-} with the *trans* isomer, as indicated by its first elution, can be rationalized on the basis that the two sets of associations on opposite sides of the *trans* molecule are more favourable than the associations on one side of the *cis* molecule where the two PO_4^{3-} ions would be in closer proximity.

This greater ion-association of PO_4^{3-} with the *trans*-$[Co(tacd)_2]^{3+}$ was exploited in the preparative chemistry, PO_4^{3-} effecting a shift in the equilibrium position *trans:cis* from 96:4 to essentially 100% *trans*.

For the *s-fac* and *u-fac* isomers of $[Co(dien)_2]^{3+}$ and $[Co(dien)(medien)]^{3+}$, the proposed trigonal associations of NH with PO_4^{3-} lead to stronger associations as reflected in higher R_x values than those above. However, associations seem to be restricted to NH pairs in the isomers *mer*-[Co(dien)-(medien)]$^{3+}$ (R_x = 1.35) and *s-fac*-$[Co(medien)_2]^{3+}$ ($R_x \equiv 1.00$) [18], and the stronger associations than these which are indicated for both $[Co(tacd)_2]^{3+}$ isomers may be related to the greater acidity of *sec*-NH than NH_2 protons.

With the complexes *mer,cis*-$[Co(hace)]^{3+}$ (D) and *cis*-$[Co(dtah)]^{3+}$ (B) of similar geometry, the elution of (B) before (D) could be due to some trigonal association with (B) since additional NH bonds are available from the more flexible terminal (en) rings.

Isomerization

All four complexes were completely inert in acidic solution; no changes were detectable in 0.1 *M* $HClO_4$ after four days at 80°. (A) and (C) interconverted however under conditions of charcoal in water to the

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*The degree of separation between (C) and (D) is insufficient for their separation on a preparative scale.

equilibrium proportions (A):(C) *ca.* 95:5, equilibration being attained by *ca.* 1 hr (80°). With homogeneous 0.1 *M* Na_3PO_4 solution (pH 10.7 at 80°), equilibration of (C) required *ca.* 24 hr (80°) to leave a trace only of (C), and the isomerization in 0.05 *M* $Na_2B_4O_7$ (pH 8.9) was considerably slower, requiring *ca.* 10 days (80°). Clearly the isomerization is base-catalyzed.

These conditions for the isomerization of $[Co(tacd)_2]^{3+}$ parallel those for the isomerizations of $[Co(en)_3]^{3+}$ (racemization) [19], $[Co(dien)_2]^{3+}$ and $[Co(dien)(medien)]^{3+}$ [1] suggesting similar mechanisms. Under homogeneous conditions the reactions have been shown to be intramolecular, at least for the bis(tridentate) complexes, and of the two mechanistic possibilities [1], a twist process initially seemed attractive for $[Co(tacd)_2]^{3+}$ in that a twist of one of the macrocyclic ligands 120° around its face of the octahedron would involve little distortions of the ligands. However this mechanism offers no obvious explanation for the observed base dependence, whereas a bond-rupture process does so. In the present system this would require dissociation of a coordinated secondary amine nitrogen, and while we are not aware of isomerizations where dissociations of *sec*-NH have been required [20, 21], an analogous dissociation of a coordinated thioether has been proposed for the charcoal-catalyzed racemization of *u-fac*-$[Co(daes)_2]^{3+}$ [daes = di(2-aminoethyl)sulphide] [22].

For a bond-rupture process, five different trigonal-bipyramidal intermediates can arise from Δ-*cis*-$[Co(tacd)_2]^{3+}$. Two of these are pathways for the *cis* → *trans* conversion as in Fig. 1, two others (both symmetrical) lead to direct Δ → Λ inversion, and a fifth gives no change. *Cis* → *trans* change through either of the trigonal-bipyramids shown in Fig. 1 would require inversions of the configurations at both coordinated nitrogen centres of the partly dissociated tacd (designated R or S in Fig. 1), and this implies a base dependence for the N–H deprotonation which must precede each inversion. The by-products apparent on chromatography of the homogeneous reaction solution in Na_3PO_4 give support for this bond-rupture proposal [1].

The interconversion of $[Co(tacd)_2]^{3+}$ with charcoal was a clean reaction; no hydrolysis by-products nor cobalt(II) were evident in the solution after removal of the charcoal, although the possibility of these species being completely adsorbed on the charcoal can not be excluded. However cobalt(II) has not been detectable in some other charcoal-catalyzed isomerizations, and there is now substantial evidence [1, 19, 22, 23] that cobalt(III)–cobalt(II) electron-exchange processes are unimportant for such reactions. Detailed work has indicated that the charcoal-catalyzed racemization of $[Co(en)_3](ClO_4)_3$ in basic solution occurring on the charcoal surface proceeds through the conjugate base and a five-coordinate intermediate, and that an electron-exchange process becomes significant only for solutions containing added $[Co(en)_3]^{2+}$ + en [19]. This mechanism of OH^--induced deprotonation followed by dissociation and rearrangement of a trigonal-bipyramid intermediate satisfies the observations on $[Co(tacd)_2]^{3+}$. With Co(II) not detectable, complete dissociation of ligands, as occurs with $[Co(dien)(medien)]^{3+}$ on charcoal [1], seems less likely here. The particular catalytic role of the charcoal remains unclear [19, 22].

Experimental

Spectra

20.10 MHz ^{13}C n.m.r. spectra in D_2O, broad-band proton decoupled, were obtained on a Bruker WP-80DS spectrometer locked to deuterium. An 8192 data table was used. A capillary of t-butyl alcohol provided a reference signal 618.9 Hz, δ 30.79 for CH_3 (measured for a t-butyl alcohol capillary against $SiMe_4$ as internal reference in $CDCl_3$).

^1H n.m.r. spectra of the complexes in d_6-dimethyl sulphoxide ($SiMe_4$ internal reference) were obtained on a Varian T-60 spectrometer. Chemical shifts δ of resonances were (A): 1.8, 3.0, 3.3 (CH_2); 6.3 (NH). (C): 2.0, 2.8, 3.6 (CH_2); 5.6, 5.8_5, 6.3 (NH). (D): 2.0, 3.0, 3.3 (CH_2); 5.7, 6.1, 6.2 (NH). (B): 1.9, 2.7, 3.3 (CH_2); 4.0, 4.2, 4.9 (NH_2); 5.5_5, 5.8_5, 6.2_5 (NH).

Visible absorption spectra were recorded on a Zeiss DMR-10 spectrophotometer.

Ligand Preparation

The tacd·3HBr was synthesized by the Richman-Atkins method and contained hace and dtah [4]. The preparation, and the ion-exchange separation, will be described more fully elsewhere.

Preparation and Separation of trans-*$[Co(tacd)_2]^{3+}$ and* cis-*$[Co(dtah)]^{3+}$*

A mixture of $[Co(NH_3)_5Br]Br_2$ (7.68 g, 0.02 mol), tacd·3HBr (15.44 g), $LiOH{\cdot}H_2O$ (5.04 g) and catalytic charcoal (2.5 g of BDH "granulated charcoal for gas absorption", freshly ground) in water (300 ml) was heated over a steam bath (80°) for 4 hr. The charcoal was filtered off, and the solution was absorbed on a column (3.2 × 12 cm) of Biorex-70 weak-acid cation-exchange resin, 50–100 mesh, Na^+ form, when a pink by-product component passed through the column. The orange mixture of complexes was eluted off with 0.1 *M* $HClO_4$ and the effluent was neutralized with NaOH. This solution was divided and applied to six columns (4.5 × 46 cm) of SP-Sephadex C-25 cation-exchange resin, Na^+ form, and these were eluted with 0.1 *M* Na_3PO_4 when the complexes separated in three bands. The first eluted, major, yellow, band contained *trans*-[Co(tacd)$_2$]$^{3+}$ (A); the second, weak, orange band contained *cis*-[Co(dtah)]$^{3+}$ (B); the third orange band contained a mixture of *cis*-[Co(tacd)$_2$]$^{3+}$ (C) and *cis*-[Co(hace)]$^{3+}$ (D). Carmine and purple bands preceding and postceding the above three bands contained reaction by-products.

The combined effluents from the six columns, of each band, were worked up as follows. The effluent, diluted, was applied to a column of Biorex-70 resin, Na^+ form, to remove Na_3PO_4. The complex was eluted off with 0.1 *M* $HClO_4$, and this effluent was evaporated to near dryness and ethanol was added to complete the precipitation of complex-perchlorate. The product was filtered off, washed with ethanol, and dried at 70° to constant weight. Yields of perchlorate salts: (A) as yellow plates (the least soluble complex) 9.27 g, 72%. (C) and (D) mixture as orange powder 1.33 g, 10%. ^{13}C n.m.r. gave the ratio (C):(D) as 1:2.8 and 1:3.4 in the products isolated from two separate preparations. Crude (B) as orange powder 0.26 g, 2%. (The (B) effluents from several 0.02 mol-scale preparations were worked up collectively.) (B) thus isolated contained small amounts of the other complexes (^{13}C n.m.r.) due to incomplete chromatographic separation. 0.9 g of (B) was rechromatographed on a 4.5 X 40 cm column of SP-Sephadex with 0.1 *M* Na_3PO_4. A small amount of (A) which separated first, and the last portion of the (B) orange band which contained some (C) and (D), were discarded. The effluent of (B) was worked up and crystallized as the perchlorate salt as above, and the ^{13}C n.m.r. spectrum confirmed purity. *Anal.* Calcd. for $[Co(C_7H_{17}N_3)_2](ClO_4)_3$: C, 26.1; H, 5.3; Cl, 16.5; N, 13.1. Found for (A): C, 26.0; H, 5.1; Cl, 16.4; N, 12.8%. Calcd. for $[Co(C_7H_{17}N_3)_2](ClO_4)_3 \cdot H_2O$: C, 25.4; H, 5.5; Cl, 16.1; N, 12.7. Found for (C) and (D) mixture: C, 25.2; H, 5.3; Cl, 16.3; N, 12.4%. Calcd. for $[Co(C_{12}H_{32}N_6)](ClO_4)_3$: C, 23.3; H, 5.2; Cl, 17.2; N, 13.6. Found for (B): C, 23.3; H, 5.2; Cl, 17.2; N, 13.6%.

Mer,cis-*[Co(hace)](ClO$_4$)$_3$, (D)*

The mixture of (C) and (D) perchlorates from above (1.20 g) was reacted in 0.1 *M* Na_3PO_4 (50 ml) in a stoppered flask (nitrogen atmosphere) at 80° for 9 hr when the orange solution gradually darkened. The solution was diluted six-fold and adsorbed on a 4.5 X 44 cm column of SP-Sephadex resin and eluted with 0.1 *M* Na_3PO_4. The (A) isomer formed from (C) separated in a yellow band ahead of the unchanged (D) in an orange band. By-products appeared in grey, orange and brown bands following (D). The effluents of (A) and (D) were worked up and crystallized as perchlorates by the Biorex-70 resin procedure. Yield of (A) 0.24 g, pure by ^{13}C n.m.r. Yield of (D) 0.58 g. *Anal.* Calcd. for $[Co(C_{14}H_{34}N_6)](ClO_4)_3 \cdot H_2O$: C, 25.4; H, 5.5; Cl, 16.1; N, 12.7. Found for (D): C, 25.2; H, 5.2; Cl, 16.5; N, 12.7%.

Cis-*[Co(tacd)$_2$](ClO$_4$)$_3$, (C)*

Trans-[Co(tacd)$_2$](ClO$_4$)$_3$ (A) (5.00 g) and charcoal (2.0 g) in water (100 ml) were stirred magnetically in a stoppered flask (nitrogen atmosphere) at 80° for 4 hr. After the charcoal was filtered off, Co(II) could not be detected in the solution. The solution was applied to columns 4.5 X 44 cm of SP-Sephadex and eluted with 0.1 *M* Na_3PO_4. Bands of unchanged (A), and (C), were obtained as perchlorates using the Biorex-70 resin procedure. There were no by-product bands. Yields of (C) 0.18 g, (A) recovered 4.10 g, giving the equilibrium ratio (A):(C) = 96:4. (C) does not react in 0.1 *M* Na_3PO_4 under the conditions of the chromatographic separation. *Anal.* Calcd. for $[Co(C_7H_{17}N_3)_2](ClO_4)_3$: C, 26.1; H, 5.3; Cl, 16.5; N, 13.1. Found for (C): C, 26.5; H, 5.4; Cl, 16.8; N, 13.0%.

Separate Preparation of cis-*[Co(dtah)]$^{3+}$ and* mer,cis-*[Co(hace)]$^{3+}$*

Complexes were prepared by the above substitution method using the hexamine fraction (as hexamine·6HCl) from the ion-exchange separation of crude tacd·3HBr [4]. Sephadex chromatography separated a carmine band ahead of two orange bands. These orange complexes had R_x values 1.9_2 and 1.5_4 (determined separately on small columns [18]), identical with those of (B) and (D) prepared from the crude tacd·3HBr. The amounts of the two complexes isolated as perchlorates gave the molar ratio (D):(B) as 5.0:1, similar to their ratio in the preparation from crude tacd·3HBr. However the sample of hexamine·6HCl used contained hace and dtah in similar proportions [4], so that more of dtah was lost in the form of hydrolyzed species than of hace. The ^{13}C n.m.r. spectra of the two complexes were identical with those of (B) and (D) (vide supra), and the single bands obtained on chromatography and the ^{13}C n.m.r. spectra confirmed that only one isomeric species was detected for each complex.

Isomerization Reactions

These were examined by heating solutions of a complex *ca.* 0.04 *M* (typically 0.06 g in 3 ml), sometimes with freshly ground charcoal (0.03 g, "BDH granulated for gas absorption"), under nitrogen atmospheres in stoppered flasks in a bath at 80° with occasional shaking. Small samples were withdrawn at various times, charcoal was filtered off, and the solutions were chromatographed on small columns of SP–Sephadex resin with 0.1 *M* Na_3PO_4.

The results of these experiments at 80° with *cis*-[Co(tacd)$_2$](ClO$_4$)$_3$ (C) are listed.

Conditions	*Results*
0.1 *M* $HClO_4$	No change detectable after 7 days.
D_2O	No change detectable after 1 day (^{13}C n.m.r.)
0.05 *M* $Na_2B_4O_7$, pH 8.9	(A):(C) ~ 50:50 at 1 day, ~90:10 at 5 days.
0.1 *M* Na_3PO_4, pH 10.7	(A):(C) ~ 50:50 at 2 hr, ~90:10 at 6 hr, trace only (C) at 24 hr.
0.1 *M* Na_3PO_4 at 20°	No (A) detectable after 4 days.
Charcoal in water	Identical proportions (A):(C) ~ 95:5 at 1 and 24 hr.
Charcoal in 0.1 *M* $HClO_4$	Equilibrium not attained by 24 hr, (A):(C) ~ 65:35.

After solutions of (D) in 0.1 *M* Na_3PO_4, with and without charcoal, or in water with charcoal, had stood for 1 day at 80°, no other isomers were detected on chromatographic analysis, but purplish bands of hydrolysis products were evident from the reactions in Na_3PO_4 after extended times.

From (B) in 0.1 *M* Na_3PO_4 at 80° no isomerization was detectable, but substantial hydrolysis to purple products had occurred at 2 hr, and no (B) remained after 2 days. With charcoal in water at 80° no isomerization was detectable at 2 hr.

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References

1 G. H. Searle, F. R. Keene and S. F. Lincoln, *Inorg. Chem., 17,* 2362 (1978).

2 H. Koyama and T. Yoshino, *Bull. Chem. Soc. Japan, 45,* 481 (1972).

3 J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc., 96,* 2268 (1974).

4 M. E. Angley, M. Dwyer, S. F. Lincoln, G. H. Searle, R. J. Geue and F. R. Keene, *Inorg. Chim. Acta Letters, 45,* L91 (1980).

5 S. Bagger, O. Bang and F. Woldbye, *Acta Chem. Scand. Ser. A, 27,* 2663 (1973).

6 T. G. Appleton and J. R. Hall, *Inorg. Chem., 9,* 1807 (1970).

7 P. G. Beddoe, M. J. Harding, S. F. Mason and B. J. Peart, *Chem. Commun.,* 1283 (1971).

8 M. Kojima, M. Fujita and J. Fujita, *Bull. Chem. Soc. Japan, 50,* 898 (1977).

9 M. Kojima and J. Fujita, *Bull. Chem. Soc. Japan, 50,* 3237 (1977).

10 Y. Yoshikawa, *Chem. Letters,* 109 (1978).

11 J. L. Sudmeier and G. L. Blackmer, *J. Am. Chem. Soc., 92,* 5238 (1970).

12 D. A. Buckingham, L. Durham and A. M. Sargeson, *Aust. J. Chem., 20,* 257 (1967).

13 I. R. Jonasson, S. F. Lincoln and D. R. Stranks, *Aust. J. Chem., 23,* 2267 (1970).

14 T. N. Margulis and L. J. Zompa, *J. Chem. Soc. Chem. Commun.,* 430 (1979).

15 R. W. Hay, B. Jeragh, S. F. Lincoln and G. H. Searle, *Inorg. Nucl. Chem. Letters, 14,* 435 (1978).

16 M. Dwyer and G. H. Searle, unpublished work.

17 G. H. Searle, S. F. Lincoln, F. R. Keene, S. G. Teague and D. G. Rowe, *Aust. J. Chem., 30,* 1221 (1977).

18 G. H. Searle, *Aust. J. Chem., 30,* 2625 (1977).

19 P. D. Totterdell and M. Spiro, *J. Chem.Soc. Dalton,* 1324 (1979).

20 C. K. Poon and M. L. Tobe, *Inorg. Chem., 7,* 2398 (1968).

21 G. H. Searle and A. M. Sargeson, *Inorg. Chem., 12,* 1014 (1973).

22 A. Hammershoi and E. Larsen, *Acta Chem. Scand. Ser. A, 32,* 485 (1978).

23 R. J. Mureinik and M. Spiro, *J. Chem. Soc. Dalton,* 2480, 2493 (1974).