Stability of β-[Co(trien)(dipeptide)](ClO$_4$)$_2$ Complexes to Alkaline Hydrolysis. Samples of each of the β-[Co(trien)(dipeptide)](ClO$_4$)$_2$ complexes (15 mg) were taken up in water (5 ml) and their pH's adjusted by potentiometric titration to pH 10, 11, 12, and 13, using 0.01 *M* NaOH. After the required time intervals had elapsed, the samples were quenched to pH 8.0 with dilute $HClO_4$.

A sample of each of the products was diluted to a final concentration of 1×10^{-6} mol/ml with pH 2.2 dilution buffer (0.2 *M* NaCit). One milliliter of each of the samples was used for amino acid analysis in the normal manner.

Recovery of Amino Acids and Dipeptides Following Displacement from Their Complexes by Sodium Cyanide. [Co(trien)(amino acid)]$^{2+}$ species (lys, arg, phe, leu, asp) (1×10^{-6} mol) were dissolved in a minimum volume of hot water and, on cooling, slightly greater than 2 equiv of solid sodium cyanide was added. The solutions were warmed to 40° for 15 min before being allowed to cool and diluted to 100 ml with pH 2.2 dilution buffer. Amino acid analysis of 1.0 ml of solution gave a quantitative yield of the amino acid in each case (lys, 1.01; arg, 0.94; phe, 1.00; leu, 1.01; asp, 1.08).

The dipeptides were recovered using a similar procedure to that outlined above. Initial experiments for dipeptide displacement by NaCN gave mixtures of dipeptide and amino acid products, indicating simultaneous hydrolysis and displacement (*e.g.*, for β-[Co(trien)(glygly)]$^{2+}$ at 40° in, NaCN (0.1 *M*), pH 10.64: glycine, 37.3%; glycylglycine, 62.7%). The use of buffered solutions of NaCN or NaCN–H^+ eliminated this problem, giving quantitative recovery of the dipeptides and no contamination by the C-terminal amino acids.

Quantitative Hydrolysis and Cyanide Displacement from β-[Co(trien)(dipeptide)](ClO$_4$)$_2$. The cobalt(III)–dipeptide complexes of glycylglycine, glycyl-L-alanine, glycyl-DL-leucine, and glycyl-L-phenylalanine at 100 times the normal sample concentration for amino acid analysis (*i.e.*, 1×10^{-6} mol/ml) were applied to the resin bed to detect the presence of free amino acid impurities (Table II). To a further sample of each of the complexes was added acidified NaCN (0.1 *M*) and the samples were warmed to 40° for 2 hr. The excess cyanide was removed by freeze-drying and the remaining samples were diluted to 1×10^{-8} mol/ml for amino acid analysis.

A sample (10 mg) of each of the cobalt(III)–peptide complexes was hydrolyzed by adding 20 ml of Na_2HPO_4 (0.5 *M*) and sufficient NaOH (1.0 *M*) to give a final pH of 10.8 ± 0.1. The samples were left to stand at room temperature for 150 min ($>9t_{1/2}$ for hydrolysis), before diluting the samples to a final concentration of 1×10^{-8} mol/ml with 0.2 *M* NaCit. The quantitative recovery of the C-terminal amino acid was used as a measure of quantitation of base hydrolysis.

The quantitative recovery of the N-terminal amino acid was measured following cyanide displacement of the amino acids from the base-hydrolyzed samples. To a 10-ml sample of the hydrolyzed solution of the complexes was added a 10-fold excess of solid NaCN and the solutions were acidified with HCl (1.0 *M*). The solutions were warmed at 40° for 3 hr before removing excess HCN *in vacuo*. The samples were made up to 95 ml with dilution buffer, the pH adjusted to ~2 with NaOH (1.0 *M*) and the volume made up to 100 ml. A sample (10 ml) was made up to 100 ml with pH 2.2 dilution buffer to give a final concentration of 1×10^{-8} mol/ml for analysis.

Amino acid analysis in the presence of cobalt(III)–tetramine complexes of amino acids and dipeptides causes the accumulation of these products on the resin bed. The complexes cannot be removed using the normal Beckman regeneration cycle (*i.e.*, NaOH, 0.2 *M*, 30 min, 30 psi; NaOH, 0.2 *M*, Na^+, pH 3.25, 60 min, 200 psi). The columns can be regenerated by pumping with 1.0 *M* sodium citrate buffer (pH 4.3, 6 hr, 225 psi) and NaOH (0.2 *M*, 60 min, 30 psi) and reequilibrated with sodium citrate buffer (0.2 *M*, pH 3.25, 175 psi, 180 min).

Acknowledgment. This work was supported in part by the award of an Australian National University Scholarship to K. W. B. The Authors wish to thank the Microanalytical Unit of The Australian National University for the Co, C, H, N, and halogen analyses. We wish to thank Drs. D. A. Buckingham and A. M. Sargeson for helpful discussion.

Registry No. *cis*-β$_2$-[Co(trien)(L-ala)](ClO$_4$)$_2$, 51151-90-7; *cis*-β$_2$-[Co(trien)(L-arg)](ClO$_4$)$_2$·HClO$_4$, 50859-42-2; *cis*-β$_2$-[Co(trien)(L-asp)](ClO$_4$)$_2$ (5-ring), 50932-68-8; *cis*-β$_2$-[Co(trien)(gly)](ClO$_4$)$_2$, 51022-67-4; *cis*-β$_2$-[Co(trien)(L-glu)](ClO$_4$)$_2$, 50859-44-4; *cis*-β$_2$-[Co(trien)(L-his)](ClO$_4$)$_2$, 50859-46-6; *cis*-β$_2$-[Co(trien)(L-ile)](ClO$_4$)$_2$, 51095-79-5; *cis*-β$_2$-[Co(trien)(L-leu)](ClO$_4$)$_2$, 51151-98-5; *cis*-β$_2$-[Co(trien)(L-lys)](ClO$_4$)$_2$, 50859-48-8; *cis*-β$_2$-[Co(trien)(L-met)](ClO$_4$)$_2$, 50859-50-2; *cis*-β$_2$-[Co(trien)(L-phe)](ClO$_4$)$_2$, 51151-92-9; *cis*-β$_2$-[Co(trien)(L-pro)](ClO$_4$)$_2$, 51095-81-9; *cis*-β$_2$-[Co(trien)(sar)](ClO$_4$)$_2$, 15053-83-5; *cis*-β$_2$-[Co(trien)(L-ser)](ClO$_4$)$_2$, 50859-52-4; *cis*-β$_2$-[Co(trien)(L-thr)](ClO$_4$)$_2$, 50859-54-6; *cis*-β$_2$-[Co(trien)(L-tyr)](ClO$_4$)$_2$, 51095-83-1; *cis*-β$_2$-[Co(trien)(L-val)](ClO$_4$)$_2$, 51152-00-2; *cis*-β$_2$-[Co(trien)(*S*-benzyl-L-cys)](ClO$_4$)$_2$, 50859-56-8; *cis*-β$_2$-[Co(trien)(cysteic acid)](ClO$_4$)$_2$, 50932-70-2; *cis*-β$_2$-[Co(trien)(*O*-benzyl-L-tyr)](ClO$_4$)$_2$, 50859-58-0; *cis*-β$_2$-[Co(trien)(*N*-ε-carbobenzoxy-L-lys)]$^{2+}$, 50859-59-1; *cis*-β$_2$-[Co(trien)(nitro-L-arg)]$^{2+}$, 50859-60-4; *cis*-β$_2$-[Co(trien)(*im*-benzyl-L-his)]$^{2+}$, 50859-61-5; *cis*-β$_2$-[Co(trien)(L-glu γ-benzyl ester)]$^{2+}$, 50859-62-6; *cis*-β$_2$-[Co(trien)(*O*-benzyl-L-ser)]$^{2+}$, 50859-63-7; *cis*-β$_2$-[Co(trien)(L-asp β-benzyl ester)]$^{2+}$, 50859-64-8; *cis*-β$_2$-[Co(trien)(glygly methyl ester)](ClO$_4$)$_3$, 51063-11-7; *cis*-β$_2$-[Co(trien)(glygly ethyl ester)](ClO$_4$)$_3$, 51019-38-6; *cis*-β$_2$-[Co(trien)(glygly isopropyl ester)](ClO$_4$)$_3$, 51019-40-0; *cis*-β$_2$-[Co(trien)(glygly)](ClO$_4$)$_2$, 51019-42-2; *cis*-β$_2$-[Co(trien)(gly-L-ala)](ClO$_4$)$_2$, 50859-66-0; *cis*-β$_2$-[Co(trien)(gly-DL-leu)](ClO$_4$)$_2$, 50859-68-2; *cis*-β$_2$-[Co(trien)(gly-L-phe)](ClO$_4$)$_2$, 50859-70-6; *cis*-β$_2$-[Co(trien)(L-asp)](ClO$_4$)$_2$ (6-ring), 50859-72-8; *cis*-β$_2$-[Co(trien)(OH)(OH$_2$)]$^{2+}$, 50859-73-9.

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Dissymmetric Arsine Complexes. Preparation and Properties of a Series of Cobalt(III) Complexes Containing a Linear Quadridentate Arsine

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The linear quadridentate arsine tetars, $(CH_3)_2As(CH_2)_3As(C_6H_5)(CH_2)_2As(C_6H_5)(CH_2)_3As(CH_3)_2$, exists in meso and racemic forms which form stable cobalt(III) complexes. An extensive series of these complexes of both ligands have been prepared in their various topological isomers as well as the optically active forms of the stereospecifically coordinated racemic ligand. Both thermodynamic and kinetic methods have been used to prepare the various isomers and the isomeric equilibria have been measured in all cases. It was found that the meso ligand generally prefers the trans topology, whereas the racemic ligand is flexible in the isomers it can form. All the systems are very prone to catalytic substitution and topological equilibration which occur *via* labile Co(II) species. These problems are discussed in detail and methods for dealing with these are given.

Hitherto the study of the relationships between the circular dichroism spectra and the absolute configurations of transition metal complexes has been restricted to complexes containing "hard" donor atoms such as nitrogen and oxygen. While, except for the exciton circular dichroism of interligand transitions,[1] these relationships are far from clear, some gen-

eral correlations seem to hold within very restricted and closely related systems. The d-d circular dichroisms of bis- and tris-bidentate octahedral complexes seem to show consistent patterns which may eventually be unified under common regional rules.[2] For systems with multidentate chelates[3] and those owing their dissymmetry only to conformational isomerism,[4] tentative rules have been proposed, but the complexity[4] of these systems is such as to preclude any convincing correlations to be made and, worse, at present it is not obvious which experiments would be definitive. In view of this it seems opportune to raise a previously unexplored problem, namely, the nature of the circular dichroism displayed by complexes containing "soft" donor atoms such as arsenic and phosphorus.

We were interested in preparing dissymmetric metal complexes containing arsenic and phosphorus donor atoms for the purpose of making systems suitable for asymmetric synthesis. This and some of the subsequent papers are somewhat of a digression from this theme and are concerned with the preparation of these chiral complexes and the circular dichroism they display. It will be seen that the systems show a complexity far greater than might have been anticipated and that the circular dichroism data provide a powerful probe into the electronic state of the central metal atom. Indeed the modification of the electronic state of the metal atom is a central issue in considerations of organometallic reactivity.

In a previous paper[5] we described the preparation of a linear quadridentate arsine (tetars) which exists in meso and racemic forms (Figure 1). It was shown how these two isomers could be separated by means of their Co(III) complexes and how the stereospecifically coordinated racemic ligand could be resolved as its cobalt complex. All the possible topological isomers of the $[Co(tetars)Cl_2]^+$ ion were isolated and their equilibria studied. This system thus potentially provides a large number of optically active complexes where the variations in circular dichroism with varying topologies and permutations of substituents attached to the cobalt atom can be studied within a fixed chirality of the two inner arsenic atoms.

We describe here the preparations, characterizations, and topological equilibria of an extended series of Co(III) complexes derived from these two isomeric ligands. The difficulties in handling these complexes which exhibit behavior characteristic of both organometallic and conventional "Werner" complexes will be discussed in some detail.

1. Stereochemistry

As was pointed out previously,[5] the racemic ligand can coordinate in the cis-α, the cis-β, or the trans topology, while the meso ligand is restricted to the cis-β and trans topologies. These are shown in Figure 2. Molecular models indicate that the racemic ligand will coordinate completely stereospecifically because of the directing properties of the inner chiral arsenic atoms (Figure 2). The chirality of the inner two arsenic atoms of the meso ligand prevents the formation of the cis-α topology but it makes the two axial X groups of the [Co-(*R*,*S*-tetars)X_2]$^+$ inequivalent. All these predictions are supported by experiment.[5]

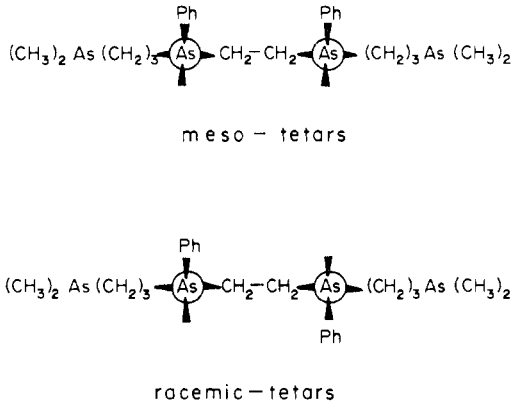

Figure 1.

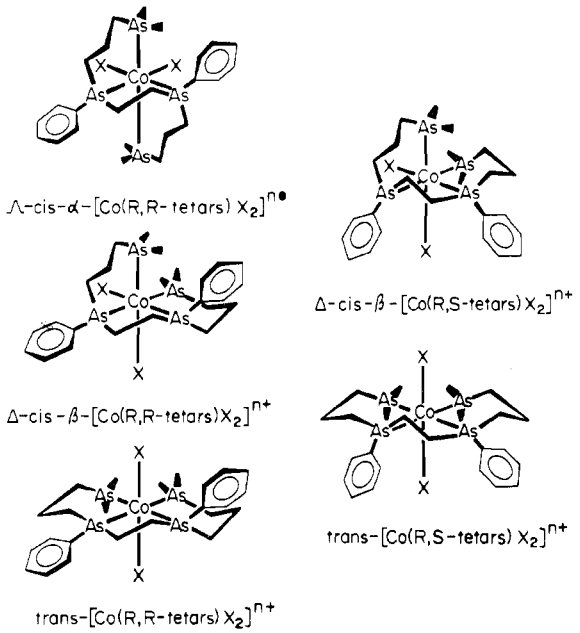

Figure 2. The five geometric isomers of $[Co(tetars)X_2]^{n+}$; the racemic tetars isomers are shown on the left and the meso on the right.

The methyl proton nmr signals clearly distinguish isomers for a given ligand. Thus for the racemic tetars-Co complexes of the type $[Co(R,R:S,S\text{-tetars})X_2]^{n+}$, the *cis*-$\alpha$ complex should show two methyl proton resonances of equal area, the cis-β should show four methyl resonances, and the trans should show two resonances of equal area. The cis-α and trans complexes are distinguished by the fact that one of the (degenerate) methyl proton resonances should occur upfield near TMS because of the diamagnetic shielding by the phenyl groups whereas the trans isomer should show two methyl resonances in the "normal" region. The meso ligand should give four methyl proton resonances for the cis-β topology and, because the inner ring is rapidly flipping, the trans isomer should show two methyl resonances of equal area. Again all these predictions have been verified by experiment.[5]

2. General Synthetic Methods

Under all the conditions used here no inversion of the arsenic atoms occurs and hence complexes of the meso and racemic ligands can be treated separately. The optically active and racemic complexes in some cases have quite different solubility properties which require different conditions for their isolation and we give these in some detail in the Experimental Section. This detail in many cases is quite

(1) B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969).
(2) F. S. Richardson, *Inorg. Chem.*, **11**, 2366 (1972).
(3) J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2697 (1966).
(4) B. Bosnich and J. M. Harrowfield, *J. Amer. Chem. Soc.*, **94**, 3425 (1972).
(5) B. Bosnich, W. G. Jackson, and S. B. Wild, *J. Amer. Chem. Soc.*, **95**, 8269 (1973).

important because of the tendency of many of the complexes to interconvert catalytically during crystallization which gives a spurious value for the topological distribution. The topological distribution of the reaction mixtures, however, can be determined quite accurately and reproducibly by nmr.

For the substitution of the two octahedral positions of the cobalt complexes we have used two starting materials, either the dichloro or diaquo complexes. In aqueous alcohol solutions the most stable isomer is the *cis*-α-dichloro species for the racemic ligand and the *trans*-dichloro species for the meso ligand and these isomers have been used as starting materials. In very few cases can kinetic proportions be obtained and, generally, only then when stoichiometric amounts of reactants are used. If topological equilibration is prevented, the reactions proceed with steric retention. When excess of the incoming ligand is used and most noticeably when the ligand is mildly reducing, rapid catalytic topological equilibration occurs, no doubt caused by the participation of labile Co(II) species. This distinction of mechanisms, as it turns out, is irrelevant for the substitution of most of the dichloro complexes of the meso ligand where the most stable product has the same configuration as the reactant, but the catalytic interconversion of the racemic ligand complexes leads to a miscellaneous assortment of topologies depending in a subtle way on the nature of the X group.

While the ubiquitous catalytic pathway is useful for establishing the thermodynamic proportions of isomers, it is a hindrance in the kinetic control of the production of isomers. We have, however, circumvented this problem to some extent by using the diaquo complexes which are even more susceptible to reduction but which substitute their aquo groups extremely rapidly. And if the conditions are arranged so that the product is precipitated as soon as it is formed, the catalysis in many cases can be suppressed. The aquo complexes have a further advantage in that the $[Co(R,S\text{-tetars})(OH_2)_2]^{3+}$ ion exists exclusively in the cis-β topology in water or dilute perchloric acid solutions, and since substitution was found to proceed with topological retention, this complex provided a kinetic entry into the cis-β complexes of the meso ligand which thermodynamically prefers trans complexes with charged unidentate ligands.

The diaquo complexes of the racemic ligand are somewhat more complicated topologically although we have used them to advantage in obtaining isomers which are in small proportions or not present at all under thermodynamic conditions. If the diaquo complex is crystallized from concentrated perchloric acid, brown crystals of *cis*-β-$[Co(R,R:S,S\text{-tetars})(OH_2)_2](ClO_4)_3$ are deposited. We infer this from the fact that when acetonitrile reacts with the solid, the kinetically stable *cis*-β-$[Co(R,R:S,S\text{-tetars})(CH_3CN)_2](ClO_4)_3$ complex is formed exclusively. If, however, the diaquo complex is crystallized from 5 *M* $HClO_4$, brick red crystals of *cis*-α-$[Co(R,R:S,S\text{-tetars})(OH_2)_2](ClO_4)_3$ are deposited; the acetonitrile reaction gives exclusively *cis*-α-$[Co(R,R:S,S\text{-tetars})(CH_3CN)_2](ClO_4)_3$. A similar situation obtains for the optically active complexes although these tend to be more soluble. In aqueous perchloric acid solutions ranging from 5 to 0.01 *M* the diaquo complexes form an equilibrium mixture consisting of cis-α (55%) and cis-β (45%) (by nmr). If either the solid *cis*-α- or *cis*-β-diaquo complexes are dissolved in dilute perchloric acid solutions, equilibration occurs rapidly and smoothly in 15 min and the reaction proceeds from either side with sharp, steady isosbestic points at 522 and 423 mμ. In concentrated perchloric acid equilibration is complete within the time of mixing starting with either the cis-α or cis-β complexes but now, as far as we can estimate from the variation and shape of the spectra, the equilibrium lies almost completely to the *cis*-β-diaquo side. The various spectra including the circular dichroism are shown in Figure 3. This acid catalysis of the rate of exchange and isomerization of diaquo complexes has been observed before.[6]

3. Complexes of the Meso Ligand

Anation of *trans*-$[Co(R,S\text{-tetars})Cl_2]Cl$ with simple anionic ligands (Br^-, N_3^-, NCS^-, NO_2^-) when approximately stoichiometric amounts are used proceeds smoothly in hot water or water–alcohol solutions. The corresponding *trans*-$[Co(R,S\text{-tetars})X_2]^+$ complexes are produced and easily isolated. With excess anion, the substitution is catalyzed; the rate shows an induction period and then rapid substitution occurs but again, only trans products are formed. Anation by cyanide ion is exceedingly rapid under all conditions and is undoubtedly catalytic. If more than about 5 equiv of cyanide is used, the ligand itself is stripped off the cobalt. No cis-β isomers have been observed for any of these reactions.

For each of the anions (except CN^-), substitution of the first chloride ligand in *trans*-$[Co(R,S\text{-tetars})Cl_2]^+$ ion proceeds under uncatalyzed conditions at a similar rate for each anion, presumably by a dissociative mechanism. In view of the different environments of the two chlorides in this complex, this suggests that the first act of substitution involves the release of the same chloride ligand in all cases. We have not attempted to isolate all the initially formed *trans*-$[Co(R,S\text{-tetars})Cl(X)]^+$ isomers, but in the cases of N_3^-, NO_2^-, and NCS^- substitution, particularly NCS^-, there is a sufficient difference in rate between the two successive chloride displacement steps to allow a significant accumulation of the intermediate *trans*-$[Co(R,S\text{-tetars})Cl(X)]^+$ complexes. Indeed, we have monitored the reaction by nmr and found that one isomer of the *trans*-$[Co(R,S\text{-tetars})Cl(X)]^+$ species is formed exclusively (>90%) during the course of substitution. (We have shown elsewhere[5] that the two *trans*-$[Co(R,S\text{-tetars})NO_2Cl]^+$ isomers show different nmr spectra; we find that, during reaction, only methyl resonances corresponding to *trans*-dichloro and *trans*-di-X and two sharp resonances for the *trans*-chloro-X species are observed.) We have isolated and characterized *trans*-$[Co(R,S\text{-tetars})Cl(X)]^+$ ($X^- = N_3^-$, NO_2^-) species and it seems likely that both these are the same isomer but we do not know which one.

We now turn to the preparation of the *cis*-β-$[Co(R,S\text{-tetars})X_2]^{n+}$ complexes which are not formed by the above methods. The *cis*-β-$[Co(R,S\text{-tetars})(OH_2)_2](ClO_4)_3$ complex was prepared by treating the *cis*-β-carbonato complex with 12 *M* $HClO_4$.

The *cis*-β-$[Co(R,S\text{-tetars})(OH_2)_2]^{3+}$ complex when dissolved in acetonitrile at 20° rapidly (~5 min) generates the *cis*-β-$[Co(R,S\text{-tetars})(CH_3CN)_2]^{3+}$ ion as the exclusive isomeric product.[7,8] This complex is readily isolated. The cis-β complex slowly isomerizes to the trans isomer in acetonitrile and, at 60°, gives at equilibrium 70% trans and 30% cis-β. These experiments, together with the nmr data, confirm that the diaquo complex exists exclusively as the cis-β isomer in both the solid and aqueous perchloric acid solutions. The *trans*-

(6) W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961).

(7) It is interesting to note that acetonitrile preferentially coordinates even in 1:1 water–acetonitrile solutions of the diaquo complex to give a quantitative yield of the *cis*-β-bis(acetonitrile) complex. The acetonitrile ligand is not readily substituted by anions except under catalytic conditions and no solvent exchange occurs in CD_3CN after 1 day at room temperature (by nmr). In amine–cobalt(III) chemistry, acetonitrile is, in contrast, an excellent leaving group and a poor ligand.[8]

(8) *E.g.*, see R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966), and our unpublished observations.

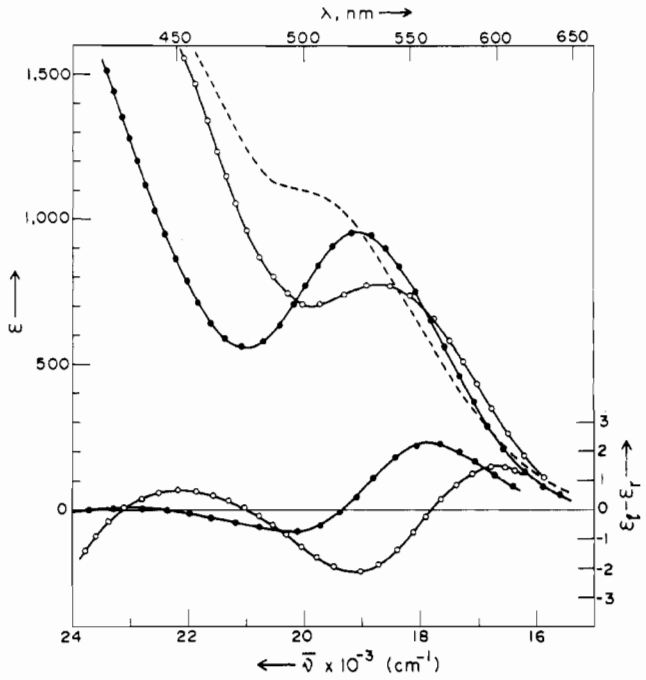

Figure 3. The absorption and circular dichroism spectra of $[Co(tetars)(OH_2)_2]^{3+}$: *cis*-$[Co(R,R\text{-tetars})(OH_2)_2]^{3+}$ in 12 *M* $HClO_4$ (open circles) and 1 *M* $HClO_4$ (solid circles); *cis*-β-$[Co(R,S\text{-tetars})(OH_2)_2]^{3+}$ in 1 *M* $HClO_4$ (dashes).

bis(acetonitrile) isomer can be isolated pure from the equilibrium mixture but can also be prepared by aerial oxidation of $Co(ClO_4)_2$ and *R,S*-tetars in acetonitrile. The rates of interconversion of the *trans*- and *cis*-β-bis(acetonitrile) complexes are very sensitive to their purity; they are more prone to catalytic interconversion in concentrated acetonitrile solutions than in dilute solutions. Unless due care is taken to obtain the compounds in a state of high purity, attempts at isolating the isomers by fractional crystallization is made very difficult. This problem is also encountered with other ligands.

Through anation of the *cis*-β-diaquo complex in water or freshly prepared dimethyl sulfoxide solutions, we have obtained the *cis*-β-dichloro and *cis*-β-dibromo complexes. In both cases the anation is exceedingly rapid, and in dilute solution, the product is exclusively the cis-β isomer, but increasing amounts of the trans isomer are formed as the reaction solutions are made more concentrated and if the preparations are not carried out rapidly. The dibromo compound is the more sensitive to catalytic isomerization but both complexes are readily separated from their more soluble trans isomers and once pure are conveniently stable to isomerization. These two isomers can also be prepared by dissolving the *cis*-β-carbonato complex in the appropriate concentrated acid.

Retention of configuration in the anation of the diaquo complex appears to be the general rule but we have been unable to isolate pure samples of the cis-β isomers of other unidentate anions we have tried, N_3^-, NO_2^-, NCS^-, and CN^-. Although products containing variable proportions of the cis-β isomers could be obtained, the samples were so sensitive to catalytic isomerization that attempts to purify and isolate the cis-β complexes were unsuccessful. Attempts to isolate the *cis*-β-dinitro complex by reaction between NO^+ ions and the *cis*-β-diaquo complex, a process that probably does not involve metal–ligand bond cleavage,[9] were not successful although the transient pink (nitrito) complex and the desired *cis*-β-dinitro (yellow) complex were observed during reaction. Azide ions react with the diaquo complex to give the brown *cis*-β-diazido complex but this suddenly, and apparently spontaneously, isomerizes to the green trans isomer in the solid state.

We suppose that the problem with many of these complexes is that they are somewhat unstable with respect to the Co(III) state and that, even if none of the Co(II) catalyst is formed during the substitution process, it will be produced as a result of internal reduction of the metal and the oxidation of the bound ligand. This suggestion is supported by a number of observations. Thus the orange *cis*-β-oxalato complex, which was isolated pure, spontaneously decomposes completely in water solution giving Co(II), free arsine, and presumably carbon dioxide. Similar spontaneous decomposition occurs with the red-violet amino acid complexes. These complexes can be contrasted with the cobalt–amine complexes which, generally, will spontaneously reduce only under very forcing conditions.[10]

The only other cis-β isomers prepared contained chelating ligands CO_3^{2-}, $C_2O_4^{2-}$, and $acac^-$, the complexes of which could be prepared from either the *cis*-β-diaquo or *trans*-dichloro complexes.

Finally, we have prepared most of the *trans*-$[Co(R,S\text{-tetars})X_2]^+$ ions, where X is an anionic unidentate ligand, by aerial oxidation of $Co(ClO_4)_2$, the free *R,S*-tetars, and 2 mol of the anion in methanol. In all cases the exclusive product was the trans isomer.

The nmr data for the trans and cis-β complexes of the meso arsine are given in Table I. Included, also, are some data for the cis-β isomers of NO_2^- and NCS^- which were not obtained free of the trans species but which can be identified by the characteristic four-line nmr methyl proton signals. It will be noted that two methyl proton signals are observed for the methyl groups of the CH_3CN and acac ligands. This is expected for the unsymmetrical cis-β complexes. Two methyl proton signals are also expected for the CH_3CN ligands in *trans*-$[Co(R,S\text{-tetars})(CH_3CN)_2]^{3+}$ ion because the two axial coordination sites are different. This is observed (Table I).

The absorption spectra of the cis-β complexes will be given elsewhere in conjunction with those of the corresponding isomers of the racemic ligand. We show the first visible absorption band of the *trans*-$[Co(R,S\text{-tetars})X_2]^{n+}$ ions in Figure 4. It will be seen that the spectra follow the spectrochemical series but that, unlike the analogous amine complexes, the intensities are somewhat higher and the strong charge-transfer bands appear at lower energy. The lower energy "d–d" band of $[Co(diars)_3](ClO_4)_3$ (diars = *o*-phenylenebis(dimethylarsine)) occurs at 431 mμ[11] and of all the X groups, only CN^- has a stronger ligand field than the arsine. The NO_2^- ligand is about the same as the arsine. The clearly resolved bands of the Br^-, Cl^-, and N_3^- complexes probably represent the $^1A_{1g} \rightarrow {}^1E_g$ transition derived from $^1A_{1g} \rightarrow {}^1T_{1g}$. For the other ligands NCS^-, CH_3CN, NO_2^-, and CN^- which are closer to arsenic in ligand field strengths, the "d–d" absorption bands seen in Figure 4 probably consist of both the (overlapped) $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions.

4. Complexes of the Racemic Ligand

The *cis*-α-$[Co(R,R:S,S\text{-tetars})Cl_2]Cl$ complex is substituted with bromide ions (3–5 equiv) in refluxing water–ethanol

(9) R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, 78, 4886 (1956).

(10) S. Lum, L. Ereshefsky, and C. S. Garner, *J. Inorg. Nucl. Chem.*, 35, 1591 (1973), and references therein.

(11) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 7, 1154 (1968).

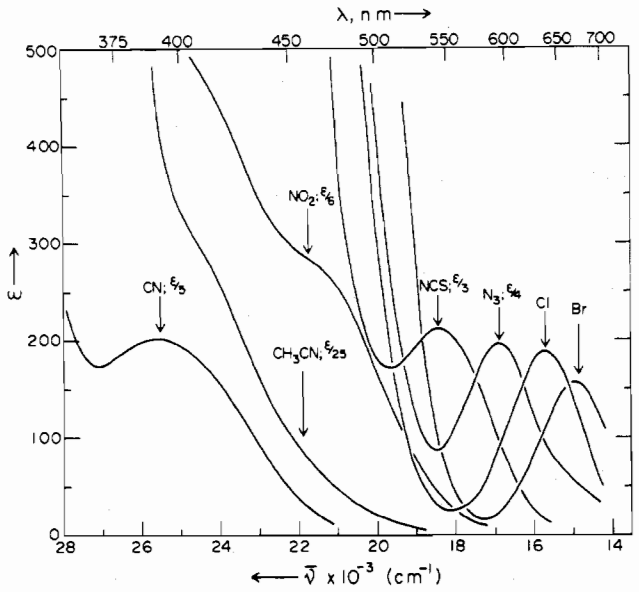

Figure 4. The lower energy absorption spectra of *trans*-[Co(*R*,*S*-tetars)X_2]$^{n+}$. All were measured in methanol solution except that for X = CH_3CN which was done in acetonitrile.

Table I. Nmr Spectra of [Co(*R*,*S*-tetars)X_2]$^{n+}$ Methyl Proton Resonances

X	δ^a Cis-β	Trans
Cl^-	107, 96, 89, 75	100, 94
Br^-	113, 99, 95, 89	105, 103
NO_2^-	112, 103, 87, 71	127, 34
NCS^-	106, 104, 84, 80	111, 94
CN^-		107, 105
N_3^-		118, 98
OH_2 [b]	122, 94, 94, 82	
CH_3CN [c]	123, 113, 107, 85 (176, 83)	122, 100 (169, 127)
½ acac$^-$ [d]	134, 101, 97, 87, 64, 57	
½ CO_3^{2-}	94, 92, 89, 61	
½ $Cl(NO_2)^{2-}$, I		101, 98
½ $Cl(NO_2)^{2-}$, II		108, 86
½ $Cl(N_3)^{2-}$, I		106, 97

[a] δ is given in Hz downfield from TMS (internal) at 60 Mc. All spectra are in DMSO-d_6 except for X = OH_2. [b] Acidified D_2O, internal DSS reference. [c] Coordinated CH_3CN methyl resonances shown in parentheses were assigned by deuteration studies. [d] Separate acac methyl resonances not assigned.

(1:1) solution with complete retention of topology to give the green *cis*-α-dibromo complex. With excess bromide (>20 equiv), substitution is rapid and catalytic but only the cis-α product is produced even under equilibrium conditions in methanol, ethanol, water, and acetonitrile. Thus both the kinetic and thermodynamic reactions give the same result. This is generally not so for other anions. Substitution of the parent *cis*-α-dichloro complex with NO_2^- (3–5 equiv) in water–ethanol (1:1) gives exclusively the deep yellow-brown *cis*-α-dinitro complex. If a large excess of NO_2^- (≥20 equiv) is used, the reaction is rapid and catalytic and initially gives the *cis*-α-dinitro complex exclusively which can be isolated at this stage. If, however, the reaction is continued after the complete NO_2^- substitution, the reaction again suddenly "takes off" catalytically with rapid isomerization to the *trans*-dinitro complex which can also be isolated. There are no significant amounts of the *cis*-β-dinitro species observed in any of these stages of reaction.

Unlike the two reactions above, the reactions between the *cis*-α-dichloro complex and the anions N_3^-, NCS^- CN^-, and CO_3^{2-} could not be properly controlled to produce one topological isomer in significant proportions over the others. This was because the topological equilibria were established at comparable rates to the substitution reactions. The NCS^- substitution occurs in two distinct steps of which the first yielded the *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl(NCS)]$^+$ complex. Because of the very slow substitution of the second chloride, this half-substituted complex could be isolated quantitatively. The rate-inhibiting effect of the NCS^- ligand is well known in amine–cobalt(III) chemistry.[12] The second stage of substitution leading to the *cis*-α-$(NCS)_2$ complex was overlapped by isomerization to the *cis*-β- and *trans*-diisothiocyanato isomers. Addition of excess NCS^- did not appear to catalyze the two initial steps in the substitution but seemed to speed up the attainment of the isomer equilibrium which was found to be 30% *cis*-α-, 10% *cis*-β-, and 60% *trans*-$(NCS)_2^+$. We have obtained all these isomers pure from the equilibrium mixture by a combination of fractional crystallization and ion exchange. This, however, is even more complicated than it appears because catalytic isomeric interconversion occurs during the crystallization process, the proportions of isomers obtained depending on the rate of precipitation of any one isomer. Once pure, the isomers are quite stable. This difficulty is not peculiar to this complex and was encountered with the carbonato, diazido, and dicyano isomers prepared from the *cis*-α-dichloro complex. In the carbonato preparation, the product obtained after quenching the reaction immediately after complete chloride substitution was found to be a mixture consisting of 25% *cis*-α and 75% *cis*-β-carbonato complexes. The two isomers were fractionally crystallized from the mixture. If the reaction is allowed to continue after this stage, an equilibrium mixture of isomers is produced consisting of 95% *cis*-β- and 5% *cis*-α-carbonato complexes.

The cyanide and azide anations of the *cis*-α-dichloro complex, irrespective of the anion concentration, were always rapid and catalyzed and always gave equilibrium proportions of isomers. The cyanide reaction with the *cis*-α-dichloro complex is very rapid and gave a distribution of 35% *cis*-α- and 65% *trans*-dicyano complexes. A cleaner reaction occurs starting with the *cis*-α-dibromo complex where the isomer distribution is the same. In neither of the reactions was any of the *cis*-β-dicyano complex detected. The separation of these two isomers is complicated by their interconversion but is readily achieved by the method given in the Experimental Section.

The azide reaction gives about equal proportions of *cis*-α- and *cis*-β-diazido complexes and about 10% *trans*-diazido. Both the cis isomers were obtained pure by fractional crystallization although problems of interconversion were again encountered. The resulting final filtrate was a characteristic green color of the *trans*-diazido species which was also detected by nmr but attempts to isolate it failed because of isomeric interconversion to the less soluble cis species during crystallization. Ion exchange resulted in the appearance of a fast-running green band but, before elution could be effected, it suddenly turned to the brown color of the *cis*-diazido species.

The above reactions did not always produce all the desired isomers or, if they did, some were in such low concentrations or had solubility characteristics which made their isolation difficult. We therefore resorted to two different methods of

(12) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 167.

which the first involved the *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)CO_3]-ClO_4 complex as the starting material. Treatment of this solid complex with cold, concentrated HCl or HBr gave the *cis*-β-dichloro or *cis*-β-dibromo complexes, respectively, in about 80% yield. Similarly the reaction between the solid *cis*-β-diaquo complex and the two acids gives a quantitative yield of the *cis*-β-dichloro and *cis*-β-dibromo complexes. The reaction with the solid *cis*-α-diaquo complex gives the *cis*-α complexes.

As was pointed out earlier the diaquo complexes exist as a rapidly equilibrating mixture of isomers in water consisting of roughly equal amounts of the *cis*-α and *cis*-β ions. Using stoichiometric amounts of the anions Cl^-, Br^-, NO_2^-, NCS^-, and CO_3H^-, rapid reactions occurred with the equilibrated diaquo species in water. In every case the anated products consisted of roughly equal amounts of the *cis*-α and *cis*-β isomers. This suggests that the anation proceeds with retention of configuration. If greater than stoichiometric amounts of anion are used, particularly with NO_2^-, isomer equilibration occurs, presumably because of catalysis. We have used this method, of controlled anation of the diaquo complexes, as an alternate route to the synthesis of the *cis*-α-carbonato, -diisothiocyanato, and -dinitro isomers and the *cis*-β-diisothiocyanato isomer and as the only route to the thermodynamically unstable *cis*-β-dinitro isomer. Separations were effected by fractional crystallization where the complexes showed little tendency to interconvert, presumably because the mild conditions used for the reaction minimized the production of catalyst.

Anation of the diaquo complexes with CN^- was slow even when the system was buffered. The reaction appears to be catalytic under all circumstances tried, as only the thermodynamically stable cis-α and trans complexes were formed.

The only reaction of the diaquo species which did not give roughly equal proportions of the cis-α and cis-β products under conditions where catalysis was suppressed was the N_3^- reaction. This gave a preponderance of the cis-α isomer (~85%) over the cis-β form; the proportions were not those representing complete topological equilibration. We suppose the reason for this is that the basic azide ions are involved in substituting hydroxoaquo and possibly hydroxoazido substrates which may rapidly equilibrate to give different proportions of the cis-α and cis-β isomers from those existent for the diaquo complexes. This is supported by the observation that the reaction proceeds through the colors pink-red (hydroxoaquo) to violet (hydroxoazido (?)) to brown (diazido).

Attempts at obtaining some of the unstable trans complexes by oxidation of $Co(ClO_4)_2$, the arsine, and 2 mol of the unidentate ligand failed in all cases except for the chloro species.[5] Thermodynamic proportions of isomers were obtained presumably because of catalysis.

In Table II we list the nmr methyl proton signals of the various isomers. It will be seen that the data confirm the structures. Of particular interest is the consistent high-field shifts of two signals in the cis-α complexes and one in the cis-β complexes as is expected because of the diamagnetic shielding by the phenyl groups. These data are essentially independent of solvent, concentration, and counteranion.

5. Complexes of the Optically Active tetars Ligand

The optically active isomers were prepared by virtually the same methods as just described for the racemic isomers. However, catalytic interconversion during precipitation and different solubility relationships between isomers necessitated in many cases new separation methods. Some of the differences are not trivial; for example, the active *cis*-α- and *cis*-β-diazido complexes seemed to crystallize in the same unit cell unless special precautions were taken. We give the special details in the Experimental Section.

Table II. Nmr Spectra of [Co(*R*,*R*-tetars)X_2]$^{n+}$ Methyl Proton Resonances

X	δ[a] Cis-α	Cis-β	Trans
Cl^-	91, 24	106, 99, 84, 12	99, 92
Br^-	102, 25	109, 106, 93, 14	
NO_2^-	90, 36	106, 104, 75, 18	115, 113
NCS^-	90, 34	112, 99, 86, 18	111, 93
CN^-	104, 34		110, 103
N_3^-	89, 35	106, 100, 87, 14	109, 100
OH_2[b]	94, 49	118, 115, 88, 25	
CH_3CN[c]	103, 44 (172)	116, 114, 97, 26 (159, 139)	
$^1/_2$ CO_3^{2-}	74, 38	87, 84, 80, 46	
$^1/_2$ $Cl(NCS)^{2-}$	91, 89, 36, 23		
$^1/_2$ $Cl(CH_3CN)^-$[c]		110, 102, 93, 25 (145)	
OH^-[b]	76, 27	98, 93, 83, 14	

[a] δ is given in Hz downfield from TMS (internal) at 60 Mc. Except for X = OH_2 and OH^-, all spectra are in DMSO-d_6. [b] In acidified D_2O, internal DSS reference. [c] Coordinated CH_3CN methyl resonances are shown in parentheses and were assigned by deuteration studies.

We have shown previously that the racemic tetars ligand is completely stereospecific.[5] The absolute configuration of the ligand is known from an X-ray determination.[13] All the absolute configurations of the complexes are therefore correlated and known. No inversion at arsenic occurs under the conditions of preparation. All the compounds are optically pure because the initial resolution was carried to equal and opposite maximum rotation and interconversion between complexes after extensive fractional crystallization always gave a material with an identical rotation before and after an interconversion cycle. Furthermore, the morphologies of the racemic crystals are always quite distinct from those of the optically active analogs.

6. Isomer Proportions

The isomer proportions are given in Table III for the complexes of the meso ligand while those of the racemic ligand are shown in Table IV. Isomer equilibration was achieved *via* the catalytic paths and, in a number of cases, the values were checked by starting with different isomers; the results were the same. The catalytic reaction can be set off by simply refluxing a particular compound in the presence of the corresponding free anion; most will catalytically equilibrate spontaneously. The proportions were measured by nmr integration of the methyl proton signals and are accurate to about 5%. Little side product (~1%), mainly Co(II) and free arsine, is formed during equilibration.

A number of arresting features are seen from the results. The first is that the meso ligand strongly favors trans topologies whereas the racemic analog appears to be flexible in the topologies it takes up. The second is that, for both ligands, the tripositively charged complexes show a general preference for the cis isomers. This is particularly evident for the meso ligand where the only cis topologies observed, with unidentate ligands, are the diaquo and bis(acetonitrile) complexes at equilibrium. It may be that in these cases, solvation plays a dominant role in the topological outcome. The cis complexes are probably more highly solvated than the trans complexes, and, if it is assumed that the cis-trans solva-

(13) N. C. Payne, private communication.

Table III. Equilibrium Proportions of $[Co(R,S\text{-tetars})X_2]^{n+}$ Isomers

X	Solvent	% trans	% cis-β
H_2O	H_2O	0	100[a]
CH_3CN	CH_3CN	80	20[a]
		70	30[b]
Cl^-, Br^-, I^-, NO_2^-, CN^-, N_3^- NCS^-	H_2O, CH_3OH, C_2H_5OH, CH_3CN	100	0

[a] At 30°. [b] At 60–80°. All others refer to the reflux temperature of the solvent.

Table IV. Equilibrium Proportions of $[Co(R,R\text{-tetars})X_2]^{n+}$ Isomers

X	Solvent	% cis-α	% cis-β	% trans
Cl^-	H_2O	80	20	0
	CH_3CN	85	15	0
	CH_3OH	75	5	20
Br^-	H_2O, CH_3OH, CH_3CN, C_2H_5OH	100	0	0
NO_2^-	1:1 C_2H_5OH-H_2O	4	0	96
NCS^-	1:2 C_2H_5OH-H_2O	25	10	65
N_3^-	1:2 C_2H_5OH-H_2O	43	42	15
	CH_3CN	76	16	8
CN^-	CH_3OH	40	0	60
$1/2\ CO_3^{2-}$	10:1 H_2O-CH_3OH	5	95	
CH_3CN	CH_3CN[a]	60	40	0
H_2O	H_2O[b]	55	45	0

[a] At 60–80°. [b] At 30°. All others refer to the reflux temperature of the solvent.

tion difference is greater for the tripositively charged species than for the unipositively charged complexes, this larger solvation difference may be responsible for tilting the topological balance.

It has become common to discuss conformation and topological equilibria in terms of internal nonbonding interactions. These techniques are quite useful when decisions about conformations are required but are generally inadequate when topological equilibria are considered. The results in Tables III and IV are difficult to interpret simply in terms of nonbonding interactions because it is not obvious why, for example, the dibromo complex of the racemic ligand should strongly favor the *cis*-α topology while its dinitro analog should give the trans isomer. We prefer not to speculate on these results except to suggest that electronic effects associated with the metal–ligand bonds may play an important role in the topological equilibria.

7. Experimental Section

The nmr spectra were measured on Varian T60 and HA100 spectrometers at 29° using 0.1 *M* complex solutions and generally an internal TMS reference. Optical rotations were measured on 10^{-4} to 10^{-5} g/g solutions with a Perkin-Elmer 141 digital recording polarimeter at 30°. Absorption spectra and circular dichroism spectra were recorded on Unicam SP820 and Roussel-Jouan instruments, respectively. A Yellow Springs Instrument Co. Model 31 conductivity bridge was used to obtain conductivities at 20° on 10^{-3} to 10^{-4} *M* solutions. In all these measurements due care was taken to ensure that no changes in topology or general chemical constitution occurred from the solid to the solution phase.

Isomer Proportions. These were determined by nmr by integrating the methyl proton signals. The methods were essentially the same for both the kinetically and thermodynamically controlled reactions. Typically, a reaction mixture was diluted with ice water containing excess sodium perchlorate and the complexes were completely extracted into methylene chloride. The extract was dried and pumped to dryness at room temperature and the residue analyzed in an appropriate solvent. In this way the results were quite reproducible.

The diaquo equilibria were measured in acidic D_2O and the equilibrium and the kinetic distributions of the acetonitrile complexes were measured without extraction in deuterated acetonitrile.

Carbonato Complexes. ***cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)CO_3]ClO_4.** *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl_2]Cl[5] (5.0 g) in methanol (100 ml) and water (500 ml) was heated on a steam bath to 80°. Sodium carbonate (0.82 g) in water (10 ml) was then added. The blue solution rapidly turned red and a flocculent light green side product was deposited. After the reaction was heated for 1 hr, the solution was cooled and filtered; sodium perchlorate (13 g) in water (25 ml) was added to the filtrate which, at once, was filtered again. The red solution was extracted into methylene chloride (eight 100-ml portions). The extracts were dried ($MgSO_4$) and pumped to dryness to give a glassy red solid (3.7 g; 95% cis-β, 5% cis-α). This was dissolved in hot methanol (650 ml) and upon cooling at 0° for 3 hr red blocks deposited (3.0 g). These were collected and a further 0.5 g was obtained after the addition of a large volume of ether. The combined fractions were recrystallized from methanol (600 ml) by the addition of ether (2 l.) to give the pure *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)CO_3]$ClO_4 \cdot CH_3OH$ complex (3.3 g; $\Lambda = 77$ ohm^{-1} cm^2 mol^{-1}, methanol). The methanol solvate was confirmed by nmr.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)CO_3]ClO_4 \cdot CH_3OH$: C, 35.6; H, 4.6; Cl, 4.1. Found: C, 35.7; H, 4.7; Cl, 4.1.

This complex (1.0 g) was recrystallized from hot water (120 ml) after the addition of sodium perchlorate (2.0 g). It deposited as orange-red flakes, or red blocks if the crystallization was carried out slowly. In either case the unsolvated complex was formed (0.8 g).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)CO_3]ClO_4$: C, 35.6; H, 4.5; Cl, 4.3. Found: C, 35.3; H, 4.6; Cl, 4.3.

***cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)CO_3]ClO_4.** *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl_2]ClO_4 (5.0 g) in methanol (100 ml) and water (500 ml) was treated with Na_2CO_3 (0.82 g) for *exactly* 3 min at 80°. The red solution was cooled in ice and then filtered, excess $NaClO_4$ was added, and the complex was extracted into CH_2Cl_2. After removal of the solvent, the residue (3.6 g; 40% cis-α) was dissolved in hot ethanol (900 ml) and ether (500 ml) was added. The solution deposited 2.3 g of the cis-β complex after 12 hr at 0°. This was collected and ether (1700 ml) was added to the filtrate which was cooled at 0° for several hours, giving the slightly impure *cis*-α-carbonato complex (1.1 g) as deep red needles. These were collected, taken up in hot methanol (100 ml), and diluted with ether (100 ml). After 1.5 hr at 0° the solution deposited 0.15 g of impure *cis*-α complex which was collected; a further 150 ml of ether was added to the filtrate which, after 10 hr at 0°, deposited 0.8 g of pure *cis*-α-carbonato complex ($\Lambda = 75$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)CO_3]ClO_4$: C, 35.6; H, 4.5; Cl, 4.3. Found: C, 35.5; H, 4.6; Cl, 4.4.

Δ-*cis*-β-[Co(*R*,*R*-tetars)CO_3]ClO_4. Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]Cl (3.0 g) was treated with Na_2CO_3 (0.52 g) in the same manner as the racemic analog. The residue (2.2 g), obtained by CH_2Cl_2 extraction, was twice recrystallized from acetonitrile (100 ml) by the slow addition of ether (300 ml). The red blocks (2.0 g) of the pure Δ-*cis*-β-carbonato complex were collected and washed with acetonitrile–ether (1:5) and then ether. (This active complex deposits as a gel from common protic solvents; $[\alpha]D$ −87 (±40)°, $[\alpha]_{436}$ +308 (±30)°, methanol.)

Anal. Calcd for $[Co(C_{24}H_{38}As_4)CO_3]ClO_4$: C, 35.6; H, 4.5; Cl, 4.3. Found: C, 35.4; H, 4.6; Cl, 4.3.

Λ-*cis*-α-[Co(*R*,*R*-tetars)CO_3]ClO_4. A filtered solution of Λ-*cis*-α- or Δ-*cis*-β-[Co(*R*,*R*-tetars)$(OH_2)_2$]$(ClO_4)_3 \cdot H_2O$ (1.0 g) in water (35 ml) containing a little acetone was allowed to equilibrate at 20° for 15 min. Sodium bicarbonate (0.9 g) in water (15 ml) was added to this isomeric diaquo mixture (55% cis-α, 45% cis-β); there was an immediate red to violet-pink color change. After 1 min the solution had become orange-red. Sodium perchlorate (2 g) was then added to produce a gelatinous orange precipitate. A dry glass of carbonato complex (0.8 g; 40% cis-α, 60% cis-β) was obtained by methylene chloride extraction (three 40-ml portions), drying (Na_2SO_4), and pumping off the solvent. Fractional crystallization from acetonitrile (20 ml) by the successive additions of ether gave fraction 1 (0.45 g; 25 ml of ether, 18 hr at 0°, >90% cis-β), fraction 2 (0.1 g; a further 30 ml of ether, 10 hr at 0°, >80% cis-β), and a final fraction (0.18 g of a sticky pink solid, >95% *cis*-α, after a further 150 ml of ether). The final fraction (0.18 g) was reprecipitated from methanol–ether and recrystallized from water (30 ml, 10°) by slowly adding saturated aqueous sodium perchlorate. The pink-red needles (0.1 g) of the pure Λ-cis-α isomer were collected and washed quickly with ice water and finally excess ether ($[\alpha]D$ +284 (±25)°, $[\alpha]_{578}$ +328 (±30)°, $[\alpha]_{546}$ +425 (±40)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)CO_3]ClO_4$: C, 35.6; H, 4.5; Cl, 4.3. Found: C, 35.5; H, 4.5; Cl, 4.4.

Diaquo Complexes. ***cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)$(OH_2)_2$]$(ClO_4)_3$.** The *cis*-α- or *cis*-β-carbonato complex (5.0 g) was dissolved in perchloric acid (70%, 25 ml) at 20° to give a deep brown solution. The mixture was warmed briefly and then run through a fine-porosity sintered-glass filter. The brown product was collected from the fil-

trate after 1 hr at 0° and washed quickly with perchloric acid (70%) followed by excess ether, leaving a dry brown crystalline solid (6.0 g; $\Lambda = 500$ ohm^{-1} cm^2 mol^{-1}, water). This complex consistently crystallized with 0.25 mol of perchloric acid in the crystal.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(OH_2)_2](ClO_4)_3 \cdot 0.25HClO_4$: C, 27.6; H, 4.1; Cl, 11.0. Found: C, 28.0; H, 4.1; Cl, 11.2.

cis-α-**[Co(*R*,*R*:*S*,*S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$.** The method closely followed that given immediately above except that water (25 ml) was added immediately following filtration of the brown reaction mixture. The solution rapidly turned pink, and on cooling, the clumps of pink-red needles which had separated were collected and washed with perchloric acid (5 *M*) and then with ether. Recrystallization from warm water (100 ml) by the addition of perchloric acid (70%, 100 ml) gave the pure cis-α isomer (5.0 g; $\Lambda = 418$ ohm^{-1} cm^2 mol^{-1}, water). If the cis-β isomer described above is recrystallized in this way, it also yields the pure *cis*-α-diaquo complex.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(OH_2)_2](ClO_4)_3 \cdot 2H_2O$: C, 27.3; H, 4.4; Cl, 10.1. Found: C, 27.3; H, 4.2; Cl, 10.1.

Δ-*cis*-β-**[Co(*R*,*R*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$.** Water (3 ml) was slowly added to Δ-*cis*-β-$[Co(R,R\text{-tetars})CO_3]ClO_4$ (1.0 g) in perchloric acid (70%, 12 ml) and brown needles (1.15 g) separated on cooling. These were collected and washed with perchloric acid (8 *M*) and then ether. The active diaquo complex is soluble in 12 *M* perchloric acid unlike its racemic form and was recrystallized from this solvent (15 ml) by the careful addition of water (3 ml). Deep red-brown needles were obtained (1.0 g) ($[\alpha]_D$ +205 (±40)°, $[\alpha]_{546}$ −520 (±50)°, $[\alpha]_{436}$ −425 (±40)°, 5×10^{-2} *M* $HClO_4$, equilibrated 30 min at 30°).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(OH_2)_2](ClO_4)_3 \cdot H_2O$: C, 27.8; H, 4.3; Cl, 10.3. Found: C, 27.1; H, 4.2; Cl, 10.6.

Λ-*cis*-α-**[Co(*R*,*R*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$.** This preparation followed that given immediately above except that 20 ml of water was added to the $HClO_4$ solution. Red crystals (1.2 g) were obtained. Recrystallization of this or the Δ-cis-β isomer above from perchloric acid (12 *M*, 15 ml) by the addition of water (20 ml) gave the pure Δ-cis-α complex (1.0 g). The crystals were collected and washed with 5 *M* perchloric acid followed by excess ether. Optical rotations and visible and CD spectra in equilibrated 5×10^{-2} *M* $HClO_4$ solution (30°) were identical with those given above for the Δ-cis-β complex.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(OH_2)_2](ClO_4)_3 \cdot 2H_2O$: C, 27.3; H, 4.4; Cl, 10.1. Found: C, 27.3; H, 4.3; Cl, 10.1.

cis-β-**[Co(*R*,*S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$.** This preparation, from *cis*-β-$[Co(R,S\text{-tetars})CO_3]ClO_4$ (3.0 g), was very similar to that described for the cis-α racemic isomer above. Large brown needles (3.6 g) separated from the perchloric acid (5 *M*, 40 ml) solution. These were collected and washed with perchloric acid (5 *M*) followed by ether. Recrystallization from perchloric acid (70%, 25 ml) by the addition of water (25 ml) afforded the pure *cis*-β-diaquo isomer (3.4 g; $\Lambda =$ 390 ohm^{-1} cm^2 mol^{-1}, water).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(OH_2)_2](ClO_4)_3 \cdot 2H_2O$: C, 27.3; H, 4.4; Cl, 10.1. Found: C, 27.1; H, 4.3; Cl, 10.1.

All the solid diaquo isomers slowly decompose on storage but may be restored to purity by recrystallization from hot perchloric acid solution. Contact with methanol or ethanol rapidly produces crystalline and isolable yellow cobalt(II) derivatives.

Dichloro Complexes. These isomers have been described previously.[5] Reported here are more efficient methods of preparation.

cis-β-**[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]ClO$_4$. Method 1.** *cis*-β-$[Co(R,R:S,S\text{-tetars})CO_3]ClO_4$ (1.0 g) was slurried with hydrochloric acid (50 ml, 10 *M*, 0°). The complex dissolved to a deep brown solution from which fine brown crystals deposited on the addition of sodium perchlorate (3 g) in water (20 ml, 0°). The crystals (0.8 g; 75% cis-β, 25% cis-α) were filtered and washed with ethanol–ether (1:1) and then with ether. Brown needles (0.5 g) were obtained on recrystallization from acetone (500 ml) and ether (300 ml). A second recrystallization gave the pure cis-β isomer (0.48 g).

Method 2. Hydrochloric acid (5 *M*, 10 ml) was added to an equilibrated aqueous solution of *cis*-α- or *cis*-β-$[Co(R,R:S,S\text{-tetars})(OH_2)_2](ClO_4)_3$ (1.2 g in 50 ml). Alternatively DMSO (10 ml) may be used as the solvent. The initial red solution rapidly became deep brown-blue. Sodium perchlorate (2 g) in water (10 ml) was added to the well cooled product mixture to precipitate the dichloro complex (0.8 g; 60% cis-β, 40% cis-α). The pure cis-β isomer (0.4 g) was then obtained as described in method 1.

Δ-*cis*-β-**[Co(*R*,*R*-tetars)Cl$_2$]ClO$_4$.** Both methods above were closely followed. From Δ-*cis*-β-$[Co(R,R\text{-tetars})CO_3]ClO_4$ (1.0 g) and Δ-*cis*-β-$[Co(R,R\text{-tetars})(OH_2)_2](ClO_4)_3$ (1.2 g), methods 1 and 2 gave respectively 0.55 and 0.45 g of the pure Δ-*cis*-β-dichloro isomer.

The racemic and active *cis*-β-dichloro isomers prepared as above were identical with those characterized previously.[5]

Dibromo Complexes. *cis*-α-**[Co(*R*,*R*:*S*,*S*-tetars)Br$_2$]Br. Method 1.** *cis*-α-$[Co(R,R:S,S\text{-tetars})Cl_2]Cl$ (1.0 g) in a mixture of methanol (50 ml), hydrobromic acid (48%, 30 ml), and water (20 ml) was heated on a steam bath for 45 min. The resulting deep green solution was extracted with methylene chloride (three 50-ml portions), and the dried (Na_2SO_4) extracts were taken to dryness. The residue was again heated in methanolic hydrobromic acid for 45 min, cooled, and extracted. The solid product in methanol (20 ml) and acetone (20 ml) deposited shiny black-green prisms on slow dilution with ether. The product was filtered, washed with acetone–ether (1:10) and ether, and again recrystallized (0.8 g; $\Lambda = 66$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]Br$: C, 31.2; H, 4.1; Br, 25.9. Found: C, 31.4; H, 4.1; Br, 26.0.

The perchlorate salt obtained by metathesis in methanol-aqueous sodium perchlorate was recrystallized twice from acetonitrile or boiling methanol by addition of ether (0.8 g; $\Lambda = 104$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]ClO_4$: C, 30.6; H, 4.1; Br, 16.9; Cl, 3.8. Found: C, 30.6; H, 4.0; Br, 16.9; Cl, 3.8.

Method 2. Cobalt bromide (1.0 g) in methanol (100 ml) was treated with *R*,*R*:*S*,*S*-tetars[5] (2.86 g) in ether (100 ml). Air was drawn through the then deep green-black solution for 45 min. Hydrobromic acid (5 ml, 48%) was then added, and following a further passage of air (5 min), the solution was pumped to dryness (4 g, 100% cis-α). The pure cis-α complex (3.8 g) was obtained on recrystallization as in method 1.

cis-β-**[Co(*R*,*R*:*S*,*S*-tetars)Br$_2$]ClO$_4$.** *cis*-β-$[Co(R,R:S,S\text{-tetars})CO_3]ClO_4$ (1.0 g) and cold hydrobromic acid (20 ml, 48%) were allowed to react as in method 1 given earlier for the preparation of the *cis*-β-dichloro complex. The initial deep brown-green solution rapidly deposited crystals which were taken up in acetone (200 ml, 0°). Upon the addition of sodium perchlorate (2 g) in cold water (300 ml) a green precipitate of the perchlorate salt deposited. The entire mixture was extracted with methylene chloride (three 75-ml portions). The green-brown extract was pumped to dryness, taken up in acetone, and reprecipitated by the addition of excess aqueous sodium perchlorate. The product (0.9 g; 75% cis-β, 25% cis-α) was collected, washed with cold water, and pumped dry. Brown-green, almost black blocks (0.6 g; $\Lambda = 102$ ohm^{-1} cm^2 mol^{-1}, methanol) of the pure cis-β isomer were obtained on two recrystallizations from acetone (450 ml) and ether (450 ml).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]ClO_4$: C, 30.6; H, 4.1; Br, 16.9; Cl, 3.8. Found: C, 30.7; H, 4.2; Br, 16.8; Cl, 3.7.

Λ-*cis*-α-**[Co(*R*,*R*-tetars)Br$_2$]Br.** This isomer was prepared from Λ-*cis*-α-$[Co(R,R\text{-tetars})Cl_2]Cl$ (1.0 g) by reaction with HBr in methanol as was described above for the racemic *cis*-α-dibromo complex. Recrystallization was effected from methanol (15 ml) and acetone (45 ml) by the slow addition of ether (400 ml). Black-green needles (0.88 g) were obtained.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]Br$: C, 31.2; H, 4.1; Br, 25.9. Found: C, 31.2; H, 4.2; Br, 25.3.

The perchlorate salt was also obtained ($[\alpha]_{578}$ −386 (±15)°, $[\alpha]_{546}$ −2180 (±20)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]ClO_4$: C, 30.6; H, 4.1; Br, 16.9; Cl, 3.8. Found: C, 30.9; H, 4.9; Br, 16.7; Cl, 3.7.

Δ-*cis*-β-**[Co(*R*,*R*-tetars)Br$_2$]ClO$_4$.** Δ-*cis*-β-$[Co(R,R\text{-tetars})CO_3]ClO_4$ (1.0 g) was treated with cold HBr (48%, 20 ml) and an isomeric mixture of dibromo complexes (0.9 g; 75% Δ-cis-β, 25% Λ-cis-α) was obtained by the method described for the *cis*-β-dibromo isomer of the racemic ligand. The pure Δ-cis-β isomer (0.5 g) was obtained after one fractionation from boiling methanol (180 ml) and ether (180 ml) and a final recrystallization from acetonitrile–ether. Small, shiny brown-black blocks were formed ($[\alpha]_D$ −201 (±60)°, $[\alpha]_{578}$ −352 (±60)°, $[\alpha]_{546}$ −854 (±40)°, $[\alpha]_{436}$ −1859 (±40)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]ClO_4$: C, 30.6; H, 4.1; Br, 16.9; Cl, 3.8. Found: C, 30.6; H, 4.3; Br, 16.8; Cl, 3.8.

trans-**[Co(*R*,*S*-tetars)Br$_2$]ClO$_4$. Method 1.** *trans*-$[Co(R,S\text{-tetars})Cl_2]Cl$ (1.0 g) was treated twice with HBr in aqueous methanol in the same way as that described for the preparation of the *cis*-α-dibromo complex. The *trans*-$[Co(R,S\text{-tetars})Br_2]Br$ so obtained was recrystallized from methanol (25 ml) and ether (100 ml) as golden plates or green golden blocks depending upon the rate of crystallization (plates, fast; blocks, slow). The collected product (0.8 g; $\Lambda = 71$ ohm^{-1} cm^2 mol^{-1}, methanol) was washed with methanol–ether (1:10) and ether.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)Br_2]Br$: C, 31.2; H, 4.1; Cl, 25.9. Found: C, 31.4; H, 4.4; Cl, 26.1.

The perchlorate salt obtained by metathesis from methanol–aqueous sodium perchlorate solution was recrystallized from acetone (60 ml) and ether (150 ml) as olive green needles (0.8 g; $\Lambda = 85$ ohm^{-1} cm^2 mol^{-1}, methanol; $\Lambda = 122$ ohm^{-1} cm^2 mol^{-1}, acetonitrile).

Method 2. *cis*-β-[Co(*R*,*S*-tetars)CO_3]ClO_4 (1.0 g) in methanol (50 ml) or *cis*-β-[Co(*R*,*S*-tetars)$(OH_2)_2$]$(ClO_4)_3 \cdot 2H_2O$ (1.2 g) in water (80 ml) was treated carefully with cold hydrobromic acid (48%, 10 ml). In each case, a deep brown solid (70% cis-β, 30% trans) of the dibromo perchlorate precipitated rapidly. Methanol (30 ml) was added and the resultant mixture was gently refluxed for 30 min to effect the complete cis-β to trans isomerization, recognized by a distinct deep brown to golden yellow color change. The trans isomer was quantitatively extracted into methylene chloride (three 25-ml portions) after the addition of sodium perchlorate (2 g). The solvent was pumped from the dried (Na_2SO_4) extracts, and the yellow residue was recrystallized as in method 1; yield 0.8 g.

cis-β-[Co(*R*,*S*-tetars)Br_2]ClO_4. An isomeric mixture of the cis-β and trans isomers (1.0 g; 75% cis-β, 25% trans) was obtained as described immediately above. Complete catalyzed cis-β to trans isomerization can be prevented by careful recrystallization of this mixture from cold acetonitrile by slow dilution with ether. Brown-black crystals (0.6 g; $\Lambda = 92$ ohm^{-1} cm^2 mol^{-1}, methanol) of the less soluble and pure cis-β isomer were obtained by two recrystallizations from this solvent mixture.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)Br_2]ClO_4: C, 30.6; H, 4.1; Br, 16.9; Cl, 3.8. Found: C, 30.4; H, 4.1; Br, 16.7; Cl, 3.7.

Bis(acetonitrile) Complexes. *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$. *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)$(OH_2)_2$]$(ClO_4)_3$ (0.5 g) in acetonitrile (30 ml) was allowed to stand at 20°. The initial red solution rapidly became orange (5 min) and finally yellow-brown. After 1.5 hr, ether (150 ml) was added to precipitate the product as yellow-brown crystals. The collected complex (0.4 g; >90% cis-α) was washed with acetonitrile–ether (1:10) and ether. Recrystallization, twice from acetonitrile (35 ml) by addition of ethanol (30 ml) and ether (50 ml), gave yellow-brown prisms (0.25 g). A final recrystallization was required from acetonitrile (20 ml) and aqueous sodium perchlorate (2 g, 80 ml); the yellow plates (0.2 g; $\Lambda = 346$ ohm^{-1} cm^2 mol^{-1}, acetonitrile) were filtered and washed with methanol and then ether.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CH_3CN)_2$]$(ClO_4)_3$: C, 31.6; H, 4.2; N, 2.6; Cl, 10.0. Found: C, 31.4; H, 4.3; N, 2.7; Cl, 10.1.

cis-β-[Co(*R*,*R*:*S*,*S*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$. Using *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)$(OH_2)_2$]$(ClO_4)_3 \cdot 0.25HClO_4$ (0.5 g) in acetonitrile (30 ml), the method followed that given immediately above for the cis-α isomer. The crude product (0.5 g; >90% cis-β) derived from the initial ether precipitation was recrystallized twice from acetonitrile (30 ml) and ether. The first fraction from the final recrystallization of fine yellow threadlike crystals (0.2 g; $\Lambda = 361$ ohm^{-1} cm^2 mol^{-1} acetonitrile), was the pure cis-β isomer; it was collected and washed with cold acetone followed by ether.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CH_3CN)_2$]$(ClO_4)_3$: C, 31.6; H, 4.2; N, 2.6; Cl, 10.0. Found: C, 31.6; H, 4.2; N, 2.6; Cl, 10.0.

Λ-*cis*-α-[Co(*R*,*R*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$. Λ-*cis*-α- or Δ-*cis*-β-[Co(*R*,*R*-tetars)$(OH_2)_2$]$(ClO_4)_3 \cdot H_2O$ (0.5 g) in acetonitrile (30 ml) was refluxed for 30 min. The resultant yellow solution was pumped to dryness (0.55 g; 60% cis-α, 40% cis-β). The yellow residue was quickly reprecipitated from acetonitrile (15 ml) by the addition of aqueous sodium perchlorate (2 g, 90 ml). The crystals were collected, washed with cold water and excess ether, and fractionally crystallized from acetonitrile (30 ml) by the slow addition of ether. Fraction 1 (0.2 g; 30 ml of ether, 12 hr at 0°) was collected and washed with acetonitrile–ether (1:5) and ether. The filtrate was set aside. Recrystallization of this fraction from acetonitrile (15 ml) by the slow addition of ether (15 ml) afforded the pure cis-α isomer as shiny yellow-brown blocks (0.18 g) which were collected and washed with ethanol and ether ($[\alpha]_{436}$ −317 (±5)°, acetonitrile).

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CH_3CN)_2$]$(ClO_4)_3$: C, 31.6; H, 4.2; N, 2.6; Cl, 10.0. Found: C, 31.5; H, 4.4; N, 2.5; Cl, 9.9.

Δ-*cis*-β-[Co(*R*,*R*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$. To the filtrate from the acetonitrile fractionation set aside in the preparation immediately above was added excess ether. A yellow solid (0.3 g; mainly Δ-cis-β) was obtained. This material yielded pure the Δ-cis-β isomer on two recrystallizations from acetonitrile (10 ml) by addition of ether (10 ml). The yellow needles (0.1 g) were collected and washed with ethanol and ether ($[\alpha]_{436}$ −418 (±20)°, acetonitrile).

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CH_3CN)_2$]$(ClO_4)_3$: C, 31.6; H, 4.2; N, 2.6; Cl, 10.0. Found: C, 31.6; H, 4.2; N, 2.7; Cl, 9.8.

trans-[Co(*R*,*S*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$. A solution of *cis*-β-[Co(*R*,*S*-tetars)$(OH_2)_2$]$(ClO_4)_3 \cdot 2H_2O$ (0.5 g) in acetonitrile (50 ml) was refluxed for 40 min. The brown solution which had become yellow deposited orange-yellow needles on slow addition of ether (250 ml). After 1 hr at 0°, these crystals (0.45 g, mainly trans) were collected, washed with ethanol and ether, and recrystallized twice from acetonitrile (25 ml) by the addition of methanol (25 ml) followed by ether (75 ml). Well-formed needles (0.25 g; $\Lambda = 309$ ohm^{-1} cm^2 mol^{-1}, acetonitrile) of pure trans isomer were obtained. Orange blocks rather than needles deposit if recrystallization is carried out from acetonitrile–ether. In both cases the complex crystallizes as a solvate; this was verified by nmr.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CH_3CN)_2$]$(ClO_4)_3 \cdot CH_3CN$: C, 32.6; H, 4.3; N, 3.8; Cl, 9.6. Found: C, 32.4; H, 4.5; N, 3.7; Cl, 9.5.

cis-β-[Co(*R*,*S*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$. A method identical with that described immediately above was followed except the initial reflux was omitted. Instead, the solution was allowed to stand at 20° for 30 min. The crude product (0.5 g; >95% cis-β) obtained by ether precipitation was recrystallized from acetonitrile (50 ml) by the slow addition of aqueous sodium perchlorate (2 g, 200 ml). A second recrystallization of the product (0.4 g) from acetonitrile (25 ml) and ethanol (100 ml) afforded the pure isomer as pearly yellow plates (0.35 g; $\Lambda = 337$ ohm^{-1} cm^2 mol^{-1}, acetonitrile). A solvate was obtained which was confirmed by nmr.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CH_3CN)_2$]$(ClO_4)_3 \cdot CH_3CN$: C, 32.6; H, 4.3; N, 3.8; Cl, 9.6. Found: C, 32.6; H, 4.5; N, 3.7; Cl, 9.7.

Dicyano Complexes. *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)$(CN)_2$]ClO_4. A solution of *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl_2]Cl (1.0 g) or preferably *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Br_2]Br (1.1 g) in methanol (20 ml) was treated with sodium cyanide (0.063 g) in water (20 ml). A yellow solution developed in 20 min with the dichloro reactant and developed almost instantly commencing with the dibromo complex. There is less side product in the latter case. The solution was filtered, sodium perchlorate (2 g) in water (25 ml) was added, and as yellow crystals began to form, the entire mixture was extracted with methylene chloride (three 25-ml portions). The solvent was pumped from the dried (Na_2SO_4) extracts and the yellow residue (0.85 g; 35% cis-α, 65% trans) was dissolved in hot methanol (70 ml). Large clear yellow blocks separated after cooling at 0° for 12 hr. Ether (10 ml) was added and after a further 24 hr at 0°, the crystals were collected. Further 10-ml portions of ether were added to the cold filtrate periodically over about 5 hr until small amounts of fine yellow-green needles began to deposit. These crystals were filtered at once. Excess ether (100 ml) was then added immediately to the filtrate and the yellow-green solid (0.3 g, mainly trans) which precipitated was set aside. The combined less soluble fractions (0.45 g; mainly cis-α) were recrystallized from hot methanol (40 ml) solution as large yellow prisms. The addition of ether yielded further pure fractions as needles (0.4 g; $\Lambda = 78$ ohm^{-1} cm^2 mol^{-1}, methanol). It is important to note that the less abundant and less soluble cis-α isomer will only deposit first if crystallization is performed slowly, and under such conditions considerable trans to cis-α conversion occurs. In rapid crystallizations, the trans isomer will deposit first.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CN)_2$]ClO_4: C, 37.4; H, 4.6; N, 3.4; Cl, 4.2. Found: C, 37.5; H, 4.7; N, 3.4; Cl, 4.5.

trans-[Co(*R*,*R*:*S*,*S*-tetars)$(CN)_2$]ClO_4. The crude trans isomer (0.3 g) obtained above was recrystallized quickly from hot methanol (40 ml) by the addition of ether (60 ml). A second recrystallization from a hot filtered methanol solution removed a (yellow) insoluble side product. Well-formed needles of pure trans complex (0.25 g; $\Lambda = 77$ ohm^{-1} cm^2 mol^{-1}, methanol) were obtained by the addition of ether.

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CN)_2$]ClO_4: C, 37.4; H, 4.6; N, 3.4; Cl, 4.2. Found: C, 37.6; H, 4.6; N, 3.5; Cl, 4.6.

Λ-*cis*-α-[Co(*R*,*R*-tetars)$(CN)_2$]ClO_4. Λ-*cis*-α-[Co(*R*,*R*-tetars)Br_2]Br (1.1 g) was treated with sodium cyanide (0.063 g) in aqueous methanol (1:1, 40 ml) as described in the racemic isomer preparation above. The residue (0.8 g) obtained from the CH_2Cl_2 extract was fractionally crystallized from hot methanol (50 ml) by slowly adding ether. The first fraction (0.5 g; mainly Λ-cis-α) was collected, the filtrate was immediately diluted with excess ether, and the yellow crystals which deposited were set aside. Recrystallization of the first fraction from hot methanol (60 ml) and ether (40 ml) gave deep yellow needles (0.3 g) of the pure Λ-cis-α isomer. Addition of excess ether to this filtrate gave more crystals which were collected and set aside ($[\alpha]_{436}$ +298 (±30)°, $[\alpha]_{365}$ −260 (±25)°, methanol).

Anal. Calcd for [Co($C_{24}H_{38}As_4$)$(CN)_2$]ClO_4: C, 37.4; H, 4.6; N, 3.4; Cl, 4.2. Found: C, 37.7; H, 4.8; N, 3.3; Cl, 4.6.

trans-[Co(*R*,*R*-tetars)$(CN)_2$]ClO_4. The two batches of crystals set aside in the preparation immediately above contained the impure trans isomer. They were combined (0.3 g) and then recrystallized from hot methanol (35 ml) and ether (70 ml) to give fine canary yellow needles of the pure trans isomer. The crystals (0.2 g) were collected and washed with methanol–ether (1:4) and ether ($[\alpha]_{436}$ −507 (±25)°, $[\alpha]_{365}$ +200 (±20)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(CN)_2]ClO_4$: C, 37.4; H, 4.6; N, 3.4; Cl, 4.2. Found: C, 36.6; H, 4.7; N, 3.3; Cl, 4.4.

trans-**[Co(*R,S*-tetars)(CN)$_2$]ClO$_4$.** The method was identical with that described for the racemic ligand complexes; *trans*-[Co(*R,S*-tetars)Cl_2]Cl (0.5 g) or the corresponding dibromo bromide (0.55 g) was treated with 2.5 equiv of CN^- ions in aqueous methanol and precipitated with aqueous $NaClO_4$. The crude product (0.45 g; 100% trans) was recrystallized twice from hot methanol (50 ml) by dilution with ether (30 ml) and gave long yellow needles (0.4 g; $\Lambda = 76$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(CN)_2]ClO_4$: C, 37.4; H, 4.6; N, 3.4; Cl, 4.2. Found: C, 37.4; H, 4.8; N, 3.5; Cl, 4.6.

Diisothiocyanato Complexes. *cis*-**α-[Co(*R,R*:*S,S*-tetars)(NCS)$_2$]ClO$_4$. Method 1.** *cis*-α-[Co(*R,R*:*S,S*-tetars)Cl_2]Cl (1.0 g) in ethanol (50 ml) and water (40 ml) containing sodium thiocyanate (1.0 g) was refluxed on a steam bath for 20 hr. Sodium perchlorate (2 g) in water (300 ml) was then added to the deep orange solution which was cooled and extracted with CH_2Cl_2 (three 50-ml portions). The CH_2Cl_2 was removed giving a red solid (0.9 g; 30% *cis*-α-, 10% *cis*-β-, and 60% *trans*-diisothiocyanato complexes). This material in boiling methanol (400 ml) deposited orange-brown plates (0.38 g) of the less soluble and pure cis-α isomer on cooling for 4 hr at 0°. These crystals were collected and washed quickly with cold ethanol and ether; the filtrate containing mainly the trans isomer was retained and purified by ion-exchange chromatography. The cis-α isomer was recrystallized from boiling methanol (0.36 g; $\Lambda = 83$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.8; H, 4.2; N, 3.2; S, 7.4; Cl, 4.0.

Method 2. A mixture of $Co(ClO_4)_2$ in methanol and equimolar amounts of *R,R*:*S,S*-tetars in ether and sodium thiocyanate in water gives on aerial oxidation (30 min) and addition of excess perchloric acid (2 *M*) a solution of the mixed isomeric composition similar to that obtained in method 1. The pure cis-α isomer was obtained from this mixture in similar yield by the same work-up procedure.

Method 3. The pure cis-α isomer could be obtained in about 40% yield as a side product in the preparation of the cis-β isomer described below.

cis-**β-[Co(*R,R*:*S,S*-tetars)(NCS)$_2$]ClO$_4$.** Sodium thiocyanate (0.5 g) in water (20 ml) was added to an equilibrated (15 min) solution of *cis*-α- or *cis*-β-[Co(*R,R*:*S,S*-tetars)$(OH_2)_2](ClO_4)_3$ (0.6 g) in water (60 ml). A rapid pink-red to orange-red color change was perceptible. Acetone (50 ml) was added to dissolve the little $(NCS)_2$ complex that had deposited. After 3 min sodium perchlorate (2 g) in water (300 ml) was added to ensure complete precipitation, and after 1 hr at 0° the red-brown perchlorate salt (0.38 g; 50% *cis*-α, 50% *cis*-β) was collected, washed with water, ethanol–ether (1:4), and finally ether. The two isomers were separated by fractional crystallization as follows. The product (0.38 g) in hot methanol (150 ml) was cooled whence fine red needles deposited (cis-β). The addition of ether (200 ml) causes more needles to crystallize together with a little cis-α as red blocks after 18 hr at 0°. The crystals were collected and recrystallized from methanol (150 ml) and ether (150 ml) to give the pure cis-β isomer as well-formed red needles (0.18 g; $\Lambda = 81$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.8; H, 4.1; N, 3.0; S, 7.1; Cl, 4.0.

trans-**[Co(*R,R*:*S,S*-tetars)(NCS)$_2$]ClO$_4$.** Following method 1 given for the preparation of *cis*-α-$(NCS)_2^+$, the isomeric mixture (~0.8 g; 30% cis-α, 10% cis-β, 60% trans) was obtained. The mixture (0.8 g) in methanol was absorbed on a 30 × 2 cm column of cation-exchange resin (Dowex 50W-X2, 200–400 mesh, H^+ form, 100 g) and eluted slowly with 0.05 *M* LiCl solution in methanol. Four cleanly separated bands developed, the fastest moving of which was the brown trans isomer. This fraction was collected and pumped to near dryness (25 ml). Sodium perchlorate (2 g) in water (50 ml) was added to produce fine brown crystals (0.45 g) which were collected, washed with cold water, and pumped dry. Two recrystallizations from acetonitrile (35 ml) and ether (120 ml) yielded long deep red-brown needles of pure trans isomer (0.4 g; $\Lambda = 131$ ohm^{-1} cm^2 mol^{-1}, acetonitrile).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.5; H, 4.2; N, 3.2; S, 7.1; Cl, 4.2.

Λ-*cis*-α-**[Co(*R,R*-tetars)(NCS)$_2$]ClO$_4$.** The methods given for the racemic isomer were used without essential modification; the solubility relationships between the three active isomers are similar to those encountered for the racemic isomers, and the pure Λ-cis-α isomer was obtained by methanol–ether fractional crystallization of the isomeric mixture as shiny red-brown blocks ($[\alpha]D$ +590 (±30)°, $[\alpha]_{546}$ +654 (±30)°, $[\alpha]_{436}$ −270 (±80°), methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.7; H, 4.2; N, 3.2; S, 7.3; Cl, 3.8.

Δ-*cis*-β-**[Co(*R,R*-tetars)(NCS)$_2$]ClO$_4$.** Δ-*cis*-β-[Co(*R,R*-tetars)$(OH_2)_2](ClO_4)_3 \cdot H_2O$ (0.5 g) in water (20 ml) was treated with sodium thiocyanate (0.4 g) in water (10 ml) by the method described for the racemic analog and isolated as the ClO_4^- salt (0.35 g; 50% cis-α, 50% cis-β). This solid in hot methanol (90 ml) deposited orange plates (0.1 g; pure cis-β) on cooling for 5 hr at 0°. These crystals were collected and washed with ether. By working up the filtrate more cis-β complex may be obtained as well as the pure cis-α complex. The combined cis-β product (0.14 g) was recrystallized to purity from hot methanol (30 ml) and ether (120 ml). Orange-red flakes or needles (0.12 g) were obtained ($[\alpha]D$ +66 (±20)°, $[\alpha]_{546}$ −38 (±15)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.8; H, 4.6; N, 3.2; S, 7.3; Cl, 4.0.

trans-**[Co(*R,R*-tetars)(NCS)$_2$]ClO$_4$.** A mixture of $(NCS)_2^+$ isomers (0.8 g; 30% cis-α, 10% cis-β, 60% trans) was prepared from Λ-*cis*-α-[Co(*R,R*-tetars)Cl_2]Cl (1.0 g) exactly as described for the racemic complex. The trans isomer was again separated by ion exchange. The product precipitated as the perchlorate salt was recrystallized twice from acetonitrile (60 ml) by the slow addition of ether (250 ml) and obtained as long red-fawn needles (0.35 g; $[\alpha]D$ +122 (±20)°, $[\alpha]_{578}$ +151 (±30)°, $[\alpha]_{546}$ +216 (±40)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.7; H, 4.4; N, 3.2; S, 7.0; Cl, 4.1.

trans-**[Co(*R,S*-tetars)(NCS)$_2$]ClO$_4$.** *trans*-[Co(*R,S*-tetars)Cl_2]Cl (1.0 g) in methanol (50 ml) and water (50 ml) containing sodium thiocyanate (0.9 g) was refluxed 3 hr on a steam bath to effect complete catalytic chloride substitution. The cooled deep orange-red solution deposited large needles of *trans*-[Co(*R,S*-tetars)$(NCS)_2$]NCS (0.8 g) which after 2 hr at 20° were filtered and washed with water and ether. The perchlorate salt was obtained by metathesis from hot methanol solution by the addition of aqueous sodium perchlorate. These red-brown plates were recrystallized from hot methanol (250 ml) and ether. The pure complex (0.8 g; $\Lambda = 78$ ohm^{-1} cm^2 mol^{-1}, methanol) was collected after 10 hr at 0° and was washed with ethanol–ether (1:2) followed by ether.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NCS)_2]ClO_4$: C, 34.7; H, 4.3; N, 3.1; S, 7.1; Cl, 3.9. Found: C, 34.6; H, 4.2; N, 3.2; S, 7.0; Cl, 4.0.

Dinitro Complexes. *cis*-**α-[Co(*R,R*:*S,S*-tetars)(NO$_2$)$_2$]ClO$_4$. Method 1.** *cis*-α-[Co(*R,R*:*S,S*-tetars)Cl_2]Cl (0.5 g) in ethanol (25 ml) and water (75 ml) containing sodium nitrite (0.13 g) was heated on a steam bath for 20 min. Sodium perchlorate (2 g) in water (300 ml) was added to the cooled orange-red product solution and after 10 hr at 0° the precipitated fine crystals (0.5 g; 100% cis-α) were collected and washed with cold water followed by ether. The product was recrystallized twice from boiling methanol (200 ml) by the slow addition of ether and yielded deep orange-red blocks (0.35 g; $\Lambda = 88$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.3; N, 3.2; Cl, 4.0. Found: C, 32.9; H, 4.4; N, 3.2; Cl, 4.0.

Method 2. Sodium nitrite (0.5 g) in cold water (10 ml) was added with stirring to a solution of *cis*-β-[Co(*R,R*:*S,S*-tetars)$(OH_2)_2](ClO_4)_3 \cdot 0.25\ HClO_4$ (0.6 g) in water (5 ml) containing acetone (5 ml) at 0°. A rapid sequence of color changes, red (diaquo) to pink (nitrito) to yellow (nitro), was observed. After 10 min at 0°, acetone (50 ml; 0°) was added and the then clear yellow solution was filtered into aqueous sodium perchlorate (2 g, 300 ml) whence fine yellow crystals separated. The product (0.4 g; 50% cis-α, 50% cis-β, trace of trans) was collected and washed with cold water and excess ether. The complex was dissolved at once in boiling methanol (50 ml) and filtered. Large red-yellow blocks (0.2 g; cis-α) separated on standing for 12 hr at 0°, together with a little of the cis-β (orange blocks) and trans (yellow needles) isomers. The cis-α isomer was separated mechanically by swirling the mixed crystals with ether and decanting the suspension containing the lighter cis-β and trans crystals. Two recrystallizations from boiling methanol (50 ml) by the addition of ether (50 ml) yielded the pure cis-α complex (0.15 g).

cis-**β-[Co(*R,R*:*S,S*-tetars)(NO$_2$)$_2$]ClO$_4$.** A mixture of cis-α and cis-β isomers (0.4 g) was prepared exactly as described immediately above. DMSO or water may be used in place of acetone–water as solvent with equivalent results. The isomeric mixture in acetonitrile (35 ml) deposited small orange blocks (0.1 g; cis-β) on addition of ether (50 ml). A second fraction (0.15 g; mainly cis-β) was obtained on further addition of ether (35 ml). This second fraction was recrystallized once from acetonitrile (20 ml) and ether (40 ml) to

remove the cis-α component. After 3 hr at 0°, these orange blocks (0.08 g) were collected and washed with ether, and then the combined cis-β complex (0.18 g) was recrystallized again from acetonitrile (35 ml) by the slow addition of ether (70 ml) to give the pure cis-β isomer (0.1 g; $\Lambda = 84$ ohm^{-1} cm^2 mol^{-1}, methanol; $\Lambda = 118$ ohm^{-1} cm^2 mol^{-1}, acetonitrile).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.3; N, 3.2; Cl, 4.0. Found: C, 33.2; H, 4.3; N, 3.4; Cl, 4.4.

trans-**[Co(*R,R*:*S,S*-tetars)(NO$_2$)$_2$]ClO$_4$.** Sodium nitrite (0.88 g) in water (20 ml) was added to *cis*-α-[Co(*R,R*:*S,S*-tetars)Cl$_2$]Cl (0.5 g) in ethanol (20 ml) and the mixture was refluxed for 4 hr on a steam bath. The then yellow solution was cooled and the product was precipitated as fine yellow crystals (0.45 g; mainly trans) by the addition of aqueous sodium perchlorate (2 g, 400 ml). After 18 hr at 0°, these were collected, washed with cold water and ether, and recrystallized twice from boiling methanol (100 ml) by the slow addition of ether (0.35 g; $\Lambda = 81$ ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.3; N, 3.2; Cl, 4.0. Found: C, 32.4; H, 4.3; N, 3.2; Cl, 4.2 (blocks); C, 32.8; H, 4.2 (needles).

Λ-*cis*-α-**[Co(*R,R*-tetars)(NO$_2$)$_2$]ClO$_4$.** This was prepared by a method identical with method 1 given for the racemic analog; deep red-yellow blocks (0.15 g) were obtained by two recrystallizations from hot methanol (130 ml) of the crude product (0.4 g) from Λ-*cis*-α-[Co(*R,R*-tetars)Cl$_2$]Cl (0.5 g). Further fractions of the pure isomer (0.15 g) were obtained as needles by the slow addition of ether to the filtrates ([α]D +105 (±25)°, $[\alpha]_{546}$ +176 (±30)°, $[\alpha]_{436} = -492$ (±50)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.3; N, 3.2; Cl, 4.0. Found: C, 31.5; H, 4.1; N, 3.0; Cl, 4.8.

Δ-*cis*-β-**[Co(*R,R*-tetars)(NO$_2$)$_2$]ClO$_4$.** This preparation exactly followed that given for the racemic complex; Δ-*cis*-β-[Co(*R,R*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$·H$_2$O (0.6 g) was used in place of racemic diaquo as starting complex. The yellow product mixture (0.4 g; 50% cis-α, 50% cis-β) in acetonitrile (20 ml) yielded the following fractions on addition of ether: fraction 1 (0.12 g; orange blocks, mainly Δ-cis-β; 30 ml of ether, 10 hr at 0°), fraction 2 (0.2 g; red-orange crystals; 70% Λ-cis-α, 30% Δ-cis-β; 50 ml of ether, 1 hr at 0°), and fraction 3 (0.06 g; mainly Λ-cis-α; excess ether). Fraction 1 was recrystallized from acetonitrile (15 ml) by the slow addition of ether (30 ml). The orange blocks (0.1 g) of pure Δ-cis-β were collected and washed with acetonitrile–ether (1:4) and finally ether ([α]D +77 (±2)°, $[\alpha]_{578}$ +96 (±2)°, $[\alpha]_{546}$ +182 (±2)°, $[\alpha]_{436}$ −604 (±25)°, acetonitrile).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.3; N, 3.2; Cl, 4.0. Found: C, 33.6; H, 4.4; N, 3.1; Cl, 4.3.

trans-**[Co(*R,R*-tetars)(NO$_2$)$_2$]ClO$_4$.** From Λ-cis-α-[Co(*R,R*-tetars)Cl$_2$]Cl (0.5 g), the procedure was identical with that described for the racemic isomer. The crude complex (0.4 g; mainly trans) was recrystallized twice from hot methanol (60 ml) by the addition of ether (180 ml) (0.3 g; [α]D +193 (±10)°, $[\alpha]_{578}$ +274 (±5)°, $[\alpha]_{546}$ +196 (±8)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.3; N, 3.2; Cl, 4.0. Found: C, 33.1; H, 4.4; N, 3.2; Cl, 4.3.

trans-**[Co(*R,S*-tetars)(NO$_2$)$_2$]ClO$_4$.** A mixture of *trans*-[Co(*R,S*-tetars)Cl$_2$]Cl (1.0 g) in methanol (50 ml) and sodium nitrite (0.88 g) in water (50 ml) was refluxed for 4 hr on a steam bath. A solution of sodium perchlorate (2 g) in water (10 ml) was added to the still hot yellow-brown product solution and a precipitate formed immediately. The mixture was returned to the steam bath and sufficient methanol added to bring about complete dissolution. After 2 hr, the solution was cooled and glistening orange-brown plates (0.96 g) settled on standing 18 hr at 0°. These were collected, washed with water and ether, and pumped dry. Recrystallization from boiling methanol (180 ml) afforded golden crystals (0.85 g; $\Lambda = 83$ ohm^{-1} cm^2 mol^{-1}, methanol) by slowly diluting the solution with ether.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(NO_2)_2]ClO_4$: C, 32.9; H, 4.4; N, 3.2; Cl, 4.0. Found: C, 32.8; H, 4.4; N, 3.0; Cl, 4.2.

Diazido Complexes. *cis*-α-**[Co(*R,R*:*S,S*-tetars)(N$_3$)$_2$]ClO$_4$.**

Method 1. *cis*-α- or *cis*-β-[Co(*R,R*:*S,S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$ (0.6 g) in water (50 ml) was allowed to stand at 20° for 15 min. Sodium azide (0.15 g) in water (50 ml) was then added slowly with stirring. The deep red solution rapidly turned pink-red with stirring (hydroxo-aquo (?)) and then deep brown-red as crystals began to separate. Acetone (50 ml, 0°) was added to give a clear brown solution which was filtered into cold aqueous sodium perchlorate (2 g, 200 ml). Fine brown crystals (0.5 g) separated almost quantitatively. These were collected, washed with cold water and ether, and pumped dry. This complex was slowly reprecipitated from acetonitrile solution with aqueous sodium perchlorate as shiny uniform brown plates (0.48 g; 83% cis-α, 17% cis-β). Rapid recrystallization from acetonitrile solution (70 ml) by dilution with ether (150 ml) yielded brown-black plates (0.38 g) which were collected after 30 min at 0°. Fractions which deposited on further standing or on further addition of ether contained the cis-β isomer. The first fraction was again quickly recrystallized from acetonitrile (70 ml) and ether (150 ml) to give the pure cis-α isomer (0.35 g; $\Lambda = 90$ ohm^{-1} cm^2 mol^{-1}, methanol) as small black-violet prisms.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(N_3)_2]ClO_4$: C, 33.2; H, 4.4; N, 9.7; Cl, 4.1. Found: C, 33.1; H, 4.3; N, 9.6; Cl, 4.6.

Method 2. Solutions of *cis*-α-[Co(*R,R*:*S,S*-tetars)Cl$_2$]Cl (1.0 g) in ethanol (50 ml) and sodium azide (0.82 g) in water (30 ml) were mixed and the clear blue solution was then heated at 80° for 1 hr giving a deep brown mixture of the diazido isomers. The complex (0.95 g; 45% cis-α, 45% cis-β, 10% trans) was obtained as the perchlorate salt as described in method 1. The cis-α and cis-β isomers were separated as follows. Typically, an isomeric mixture (2.0 g) of this composition was dissolved in acetonitrile (225 ml) and the cis-α component caused to crystallize quickly by the addition of ether (500 ml). Without delay, these crystals were filtered off and washed with acetonitrile–ether (1:4) and ether. A large excess of ether (3 l.) was immediately added to the filtrate and washings, yielding a fine brown crystalline precipitate (0.9 g). This solid was retained for the isolation of the cis-β isomer; the green (trans) supernatant liquid was discarded since only cis-α–cis-β isomeric mixtures were obtainable from this. The first fraction of complex from the initial fractionation procedure was recrystallized as described in method 1 to give the pure cis-α isomer (0.7 g).

cis-β-**[Co(*R,R*:*S,S*-tetars)(N$_3$)$_2$]ClO$_4$.** The second fraction of complex (0.9 g, mainly cis-β) from above was refractionated from acetonitrile (65 ml) by the addition of ether and gave the following: fraction 1 (0.24 g; brown-black needles, pure cis-β; 120 ml of ether; 30 min at 0°) and fraction 2 (0.65 g; fine brown crystals, cis-α–cis-β mixture; 500 ml of ether; 30 min at 0°). Fraction 2 in acetonitrile (50 ml) yielded a second crop of pure cis-β isomer (0.1 g) by addition of ether (120 ml) and one seed crystal of the pure isomer; these crystals were collected after 45 min at 0°. All fractions were washed with acetonitrile–ether (1:4) followed by ether. The combined fractions of cis-β isomer (0.34 g) were given a final recrystallization from acetonitrile (30 ml) and ether (120 ml). Almost black needles (0.2 g; $\Lambda = 86$ ohm^{-1} cm^2 mol^{-1}, methanol) were obtained. It is important to note that this separation procedure is reproducible if carried out quickly and exactly as described. The slightly less soluble cis-α isomer crystallizes more quickly than the cis-β form; however, the more soluble cis-β isomer is the more stable isomer in acetonitrile (76%, 80°) and unless due care is taken, the isomers interconvert while in an impure form and tend to cocrystallize slowly.

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(N_3)_2]ClO_4$: C, 33.2; H, 4.4; N, 9.7; Cl, 4.1. Found: C, 33.3; H, 4.3; N, 9.5; Cl, 4.3.

Λ-*cis*-α-**[Co(*R,R*-tetars)(N$_3$)$_2$]ClO$_4$.** Using Δ-*cis*-β-[Co(*R,R*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$·H$_2$O (0.6 g) reactant and following method 1 given above for the racemic isomer, a mixture (0.48 g; 83% Λ-cis-α, 17% Δ-cis-β) of the active diazido perchlorates was obtained. The product was crystallized from acetonitrile (35 ml) by the addition of ether: fraction 1 (0.25 g; red-brown plates, pure cis-β isomer; 60 ml of ether; 2 hr at 0°) and fraction 2 (0.15 g; brown-black chunky crystals, mainly cis-α; excess ether; 30 min at 0°). This second fraction was recrystallized from methanol–acetone (1:1, 40 ml) by the slow addition of ether (110 ml) to give shiny black-violet needles (0.12 g) of the pure Λ-*cis*-α isomer as a methanol solvate (confirmed by nmr) ([α]D −125 (±30)°, $[\alpha]_{436}$ −824 (±40)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(N_3)_2]ClO_4 \cdot 0.5CH_3OH$: C, 33.2; H, 4.6; N, 9.5; Cl, 4.0. Found: C, 33.4; H, 4.6; N, 9.7; Cl, 4.3.

Δ-*cis*-β-**[Co(*R,R*-tetars)(N$_3$)$_2$]ClO$_4$.** The first fraction (0.25 g) from the preparation immediately above was recrystallized from acetonitrile and ether as large red-brown plates (0.22 g) of the pure isomer. This complex may be prepared more directly and in higher yield by following method 2 described for the racemic cis-α isomer; Λ-*cis*-α-[Co(*R,R*-tetars)Cl$_2$]Cl (1.0 g) was used as starting complex. The perchlorate salt of the isomeric mixture (0.9 g; 45% Λ-cis-α, 45% Δ-cis-β, 10% trans) so obtained was slowly crystallized from warm acetonitrile (50 ml) by gradually diluting this solution with ether (60 ml). The Δ-cis-β isomer is less soluble and crystallizes as the acetonitrile solvate (verified by nmr); by allowing slow crystallization (2 days, 0°), substantial Λ-cis-α to Δ-cis-β transformation occurs. A final recrystallization from acetonitrile and ether yielded plates or needles (0.35 g; [α]D +524 (±25)°, $[\alpha]_{578}$ +637 (±20)°, $[\alpha]_{546}$ 1120 (±20)°, methanol).

Anal. Calcd for $[Co(C_{24}H_{38}As_4)(N_3)_2]ClO_4 \cdot CH_3CN$: C, 34.3; H, 4.5; N, 10.8; Cl, 3.9. Found: C, 32.9; H, 4.5; N, 10.2; Cl, 4.3.

The active cis-α and cis-β isomers show the reverse order of solubilities in acetonitrile compared to their racemic counterparts, presumably because the Δ-cis-β isomer selectively forms a solvate. Because of this and also the catalytic isomer interconversion, the Λ-cis-α isomer could not be obtained isomerically pure from acetonitrile. It is purified from methanol as its methanol solvate provided it is >85% pure. If the Λ-cis-α isomer is <85% pure, brown needles containing exactly equal amounts of Λ-cis-α and Δ-cis-β isomers, apparently in the same crystal, deposit from methanol.

trans-**[Co(*R*,*S*-tetars)(N$_3$)$_2$]ClO$_4$.** A mixture of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (1.0 g) in methanol (50 ml) and sodium azide (0.65 g) in water (50 ml) was refluxed for 1 hr on a steam bath. The resultant deep olive green solution was filtered and sodium perchlorate (2 g) in water (200 ml) added slowly yielding black-green plates. The crystals (0.9 g) were collected after 2 hr at 0°, washed with water and ether, and recrystallized twice from acetone by the addition of aqueous sodium perchlorate (0.85 g; Λ = 92 ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for [Co(C$_{24}$H$_{38}$As$_4$)(N$_3$)$_2$]ClO$_4$: C, 33.2; H, 4.4; N, 9.7; Cl, 4.1. Found: C, 33.2; H, 4.4; N, 9.7; Cl, 4.3.

Miscellaneous Complexes. *cis*-α-**[Co(*R*,*R*:*S*,*S*-tetars)Cl(NCS)]ClO$_4$.** A solution of sodium thiocyanate (0.25 g) in water (50 ml) was added to *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]Cl (0.5 g) in ethanol (25 ml) and the mixture heated at 80° for 15–20 min. The blue solution which had become a deep wine red was filtered, and a violet solid precipitated almost quantitatively (0.5 g; 100% *cis*-α-Cl(NCS)$^+$) on addition of excess aqueous sodium perchlorate. This was filtered, washed with cold water and ether, and recrystallized twice from acetonitrile or boiling methanol by slowly adding ether. Violet plates (0.4 g; Λ = 84 ohm^{-1} cm^2 mol^{-1}, methanol) were obtained.

Anal. Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl(NCS)]ClO$_4$: C, 34.2; H, 4.4; N, 1.60; S, 3.7; Cl, 8.1. Found: C, 34.2; H, 4.4; N, 1.68; S, 3.6; Cl, 8.6.

Λ-*cis*-α-**[Co(*R*,*R*-tetars)Cl(NCS)]ClO$_4$.** Using an analogous procedure to that described above for the racemic isomer and using Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]Cl (0.5 g) as reactant, fine shiny violet flakes (0.4 g) of the pure complex were obtained ([α]D +652 (±20)°, [α]$_{578}$ +597 (±20)°, [α]$_{436}$ −201 (±20)°, methanol).

Anal. Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl(NCS)]ClO$_4$: C, 34.2; H, 4.4; N, 1.60; S, 3.7; Cl, 8.1. Found: C, 34.2; H, 4.4; N, 1.65; S, 3.5; Cl, 8.4.

cis-β-**[Co(*R*,*R*:*S*,*S*-tetars)Cl(CH$_3$CN)](ClO$_4$)$_2$.** Silver perchlorate (0.22 g) in acetonitrile (25 ml) was added to *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]ClO$_4$ (0.84 g) also in acetonitrile (75 ml) and the mixture was refluxed for 6 hr. The initially blue solution which had become red was filtered to remove silver chloride, and ether (150 ml) was added. Unreacted *cis*-α-dichloro complex quickly deposited and this was filtered off. The crude red complex was reclaimed from the filtrate by the addition of excess ether. A second reprecipitation from acetonitrile and ether yielded fine red crystals which were collected and washed with ether. The pale blue filtrate contained *cis*-α-dichloro complex and was discarded. The product (0.4 g; exclusively one isomer of *cis*-β-Cl(CH$_3$CN)$^{2+}$) was taken up in acetone (10 ml) from which it immediately reprecipitated as well-formed red crystals. A final recrystallization from acetonitrile–acetone (4:1) yielded orange-red blocks (0.3 g; Λ = 280 ohm^{-1} cm^2 mol^{-1}, acetonitrile) on slow dilution with ether.

Anal. Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl(CH$_3$CN)](ClO$_4$)$_2$: C, 32.5; H, 4.3; N, 1.46; Cl, 11.1. Found: C, 32.5; H, 4.4; N, 1.60; Cl, 11.2.

trans-**[Co(*R*,*S*-tetars)Cl(N$_3$)]ClO$_4$, Isomer I.** Sodium azide (0.5 g) in cold water (20 ml) was added to *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (0.5 g) in methanol. Green plates of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]N$_3$ deposited, and after 30 min at 0°, they were collected, washed with cold water, and quickly recrystallized from methanol–ether to remove traces of excess azide ion. The product (0.45 g) was refluxed in methanol (100 ml) for 50 min and the initially bright grass green solution deepened in color. The solution was cooled and sodium perchlorate (2 g) in water (300 ml) was added. Fine green-black crystals (0.45 g) separated almost quantitatively, and this solid was reprecipitated from hot methanol (100 ml) with excess aqueous sodium perchlorate. The collected crystals were washed with methanol–ether (1:10) and ether. Fractional crystallization from boiling methanol (100 ml) by the slow addition of ether gave the following: fraction 1 (0.1 g; pure *trans-meso*-diazido complex, green-black plates; cooling only; 12 hr at 0°), fraction 2 (0.2 g; *trans*-diazido and *trans*-chloroazido isomer I; green-black plates and long black needles, respectively; 100 ml of ether; 12 hr at 0°), and fraction 3 (0.1 g; green plates, *trans*-dichloro and *trans*-chloroazido isomer I; excess ether). Fraction 2 was easily separated mechanically into needles and plates; the needles (0.1 g) were recrystallized twice from boiling methanol and ether to give the pure *trans*-[Co(*R*,*S*-tetars)Cl(N$_3$)]ClO$_4$ isomer I as very long, thin, deep olive-green needles (0.08 g).

Anal. Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl(N$_3$)]ClO$_4$: C, 33.4; H, 4.4; N, 4.9; Cl, 8.2. Found: C, 34.3; H, 4.4; N, 4.9; Cl, 8.6.

cis-β-**[Co(*R*,*S*-tetars)(acac)](ClO$_4$)$_2$. Method 1.** A solution of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (0.8 g) in methanol (80 ml) and acetylacetone (0.13 g) in sodium hydroxide solution (1.30 ml, 1 *M*; 30 ml water) was refluxed for 1.5 hr on a steam bath. The green solution became a deep red-brown and a brown insoluble side product deposited. The solution was filtered and the side product washed with a little methanol and water. Sodium perchlorate (2 g) in water (200 ml) was added to the red filtrate and washings, and the entire mixture was extracted with methylene chloride (four 50-ml portions). The solvent was pumped from the dried (Na_2SO_4) extracts leaving a red glass. This solid dissolved and then immediately crystallized upon the addition of methylene chloride (5 ml); ether (5 ml) was added and the crystals were collected after 1 hr at 0°. Two recrystallizations of the product (0.4 g) from boiling methanol (65 ml) yielded red plates on slow dilution with ether (100 ml) (0.3 g; Λ = 164 ohm^{-1} cm^2 mol^{-1}, methanol).

Anal. Calcd for [Co(C$_{24}$H$_{38}$As$_4$)(C$_5$H$_7$O$_2$)](ClO$_4$)$_2$: C, 35.4; H, 4.6; Cl, 7.2. Found: C, 35.6; H, 4.8; Cl, 7.4.

Method 2. A material identical (nmr and visible spectra) to that obtained by method 1 was prepared from *cis*-β-[Co(*R*,*S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$·2H$_2$O (0.4 g) in water (30 ml) by adding dropwise a solution of acetylacetone (0.041 g) in aqueous sodium hydroxide solution (4.1 ml, 0.1 *M*; 30 ml of water). The red solution rapidly became orange; sodium perchlorate (2 g) in water (200 ml) was added, and the pure acac isomer (0.1 g) was then isolated as described in method 1. More decomposition was evident in this synthetic method.

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Registry No. *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]Cl, 50805-06-6; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)CO$_3$]ClO$_4$, 50805-08-8; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]ClO$_4$, 50805-10-2; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)CO$_3$]ClO$_4$, 50805-12-4; Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]Cl, 50805-13-5; Δ-*cis*-β-[Co(*R*,*R*-tetars)CO$_3$]ClO$_4$, 50804-57-4; Δ-*cis*-β-[Co(*R*,*R*-tetars-(OH$_2$)$_2$](ClO$_4$)$_3$, 50804-59-6; Λ-*cis*-α-[Co(*R*,*R*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$, 50804-61-0; Λ-*cis*-α-[Co(*R*,*R*-tetars)CO$_3$]ClO$_4$, 50804-63-2; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$, 50804-65-4; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$, 50804-67-6; *cis*-β-[Co(*R*,*S*-tetars)CO$_3$]ClO$_4$, 50804-69-8; *cis*-β-[Co(*R*,*S*-tetars)(OH$_2$)$_2$](ClO$_4$)$_3$, 50883-37-9; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]ClO$_4$, 50804-71-2; Δ-*cis*-β-[Co(*R*,*R*-tetars)Cl$_2$]ClO$_4$, 50804-73-4; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Br$_2$]Br, 50804-74-5; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Br$_2$]ClO$_4$, 50804-76-7; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)Br$_2$]ClO$_4$, 50804-78-9; Λ-*cis*-α-[Co(*R*,*R*-tetars)-Br$_2$]Br, 50804-79-0; Λ-*cis*-α-[Co(*R*,*R*-tetars)Br$_2$]ClO$_4$, 50804-81-4; Δ-*cis*-β-[Co(*R*,*R*-tetars)Br$_2$]ClO$_4$, 50804-83-6; *trans*-[Co(*R*,*S*-tetars)-Cl$_2$]Cl, 50883-38-0; *trans*-[Co(*R*,*S*-tetars)Br$_2$]ClO$_4$, 50804-85-8; *trans*-[Co(*R*,*S*-tetars)Br$_2$]Br, 50804-86-9; *cis*-β-[Co(*R*,*S*-tetars)Br$_2$]-ClO$_4$, 50804-88-1; CH$_3$CN, 75-05-8; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)(CH$_3$-CN)$_2$](ClO$_4$)$_3$, 50804-90-5; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)(CH$_3$CN)$_2$]-(ClO$_4$)$_3$, 50804-92-7; Λ-*cis*-α-[Co(*R*,*R*-tetars)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 50838-07-8; Δ-*cis*-β-[Co(*R*,*R*-tetars)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 50932-78-0; *trans*-[Co(*R*,*S*-tetars)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 50883-32-4; *cis*-β-[Co(*R*,*S*-tetars)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 50883-34-6; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)-(CN)$_2$]ClO$_4$, 50804-09-6; *trans*-[Co(*R*,*R*:*S*,*S*-tetars)(CN)$_2$]ClO$_4$, 50804-11-0; Λ-*cis*-α-[Co(*R*,*R*-tetars)(CN)$_2$]ClO$_4$, 50804-13-2; *trans*-[Co(*R*,*R*-tetars)(CN)$_2$]ClO$_4$, 50804-15-4; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)-(NCS)$_2$]ClO$_4$, 50804-17-6; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)(NCS)$_2$]ClO$_4$, 50804-19-8; *trans*-[Co(*R*,*R*:*S*,*S*-tetars)(NCS)$_2$]ClO$_4$, 50804-21-2; Λ-*cis*-[Co(*R*,*R*-tetars)(NCS)$_2$]ClO$_4$, 50804-23-4; Δ-*cis*-β-[Co(*R*,*R*-tetars)(NCS)$_2$]ClO$_4$, 50804-25-6; *trans*-[Co(*R*,*R*-tetars)(NCS)$_2$]-ClO$_4$, 50804-27-8; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-29-0; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-31-4; *trans*-[Co-(*R*,*R*:*S*,*S*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-33-6; Λ-*cis*-α-[Co(*R*,*R*-tetars)-(NO$_2$)$_2$]ClO$_4$, 50804-35-8; Δ-*cis*-β-[Co(*R*,*R*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-37-0; *trans*-[Co(*R*,*R*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-39-2; *trans*-[Co(*R*,*S*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-41-6; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)-(N$_3$)$_2$]ClO$_4$, 50804-43-8; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)(N$_3$)$_2$]ClO$_4$, 50804-45-0; Λ-*cis*-α-[Co(*R*,*R*-tetars)(N$_3$)$_2$]ClO$_4$, 50804-47-2; Δ-*cis*-β-[Co(*R*,*R*-tetars)(N$_3$)$_2$]ClO$_4$, 50804-49-4; *trans*-[Co(*R*,*S*-tetars)-(N$_3$)$_2$]ClO$_4$, 50804-51-8; *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl(NCS)]ClO$_4$, 50804-53-0; Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl(NCS)]ClO$_4$, 50804-55-2; *cis*-β-[Co(*R*,*R*:*S*,*S*-tetars)Cl(CH$_3$N)](ClO$_4$)$_2$, 50803-90-2; *trans*-[Co(*R*,*S*-tetars)Cl$_2$]N$_3$, 50803-92-4; *trans*-[Co(*R*,*S*-tetars)Cl(N$_3$)]-ClO$_4$, 50803-94-6; Hacac, 123-54-6; *cis*-β-[Co(*R*,*S*-tetars)(acac)]-(ClO$_4$)$_2$, 50803-96-8; *trans*-[Co(*R*,*S*-tetars)(CN)$_2$]ClO$_4$, 50803-98-0;

cis-β-[Co(*R*,*S*-tetars)Cl_2]$^+$, 50803-99-1; *cis*-β-[Co(*R*,*S*-tetars)$(NO_2)_2$]$^+$, 50804-00-7; *cis*-β-[Co(*R*,*S*-tetars)$(NCS)_2$]$^+$, 50804-01-8; *trans*-[Co(*R*,*S*-tetars)$(NCS)_2$]$^+$, 50804-02-9; *trans*-[Co(*R*,*S*-tetars)Cl(NO_2)]$^+$, 50804-03-0; *trans*-[Co(*R*,*R*-tetars)Cl_2]$^+$, 50804-04-1; *trans*-[Co(*R*,*R*-tetars)$(N_3)_2$]$^+$, 50804-05-2; Λ-*cis*-α-[Co(*R*,*R*-tetars)$(OH)_2$]$^+$, 50804-06-3; Δ-*cis*-β-[Co(*R*,*R*-tetars)$(OH)_2$]$^+$, 50804-07-4.

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Dissymmetric Arsine Complexes. Synthesis, Chemistry, and Configurational Stability of *cis*-Bis(*o*-phenylenebis(dimethylarsine))cobalt(III) Complexes

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Systematic methods for preparing *cis*-[Co(diars)$_2$X$_2$]$^{n+}$ (diars = *o*-phenylenebis(dimethylarsine)) complexes are given. The *cis*-[Co(diars)$_2$Cl$_2$]$^+$ ion has been resolved into its pure optical isomers and from these the optical isomers of the diaquo, carbonato, dinitrato, dinitro, and hydroxoaquo complexes have been isolated. It is shown by chemical interconversion reactions that all are optically pure and substitution of the diaquo complex proceeds with complete chiral retention. In the absence of catalysis all these complexes are remarkably inert to racemization. The rate constant for loss of optical activity of the *cis*-[Co(diars)$_2$Cl$_2$]ClO$_4$ complex in dilute dry methanol at 54.9° is found to be 30% faster than that for cis → trans isomerization.

In the preceding paper[1] we described the preparation of an extensive series of dissymmetric cobalt(III)-arsine complexes derived from a stereospecific quadridentate tetra(tertiary arsine) ligand. As we shall see in subsequent papers, the circular dichroism that these complexes show is exceedingly complex. We therefore sought a simpler model system to investigate so that the general characteristics of the circular dichroism spectra of dissymmetric arsine complexes could be analyzed as a prelude to the more complicated systems. Of all the arsine ligand complexes that are conveniently prepared, the bis(*o*-phenylenebis(dimethylarsine))cobalt(III) complexes (Figure 1) seemed to present themselves as the least complicated as well as having the electronic features necessary for a nonempirical determination of their absolute configurations.

The first reported[2] complexes of this ligand coordinated to a cobalt(III) center were of the type [Co(diars)$_2$X$_2$]$^+$, X$^-$ = Cl$^-$, Br$^-$, I$^-$, and NCS$^-$, and all had the trans configuration. Subsequently, two reports[3,4] described the preparations of some *cis*-[Co(diars)$_2$X$_2$]$^+$ complexes which involved the use of Ag$^+$ ions to remove the halogens from the complexes. These methods of entry into the cis complexes, however, amount to little more than recipes and are devoid of the necessary systematic preparative features necessary for dealing with a series of optically active complexes and interrelating their configurations. On the basis of our previous experience,[1] it occurred to us that the reason the silver method worked was that solvento complexes were produced and these were stable in the cis geometry and anated with retention. These previous reports also noted that the stability of these cis species was capricious in the sense that although cis species were isolated, they, without apparent inducement, quickly and erratically reverted to the trans isomers. Thus the problem of using diars as a model compound in the study of the optical activity of its cobalt(III) complexes is not a simple one.

(1) B. Bosnich, W. G. Jackson, and S. B. Wild, *Inorg. Chem.*, **13**, 1121 (1974).
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(3) T. M. Dunn, R. S. Nyholm, and S. Yamada, *J. Chem. Soc.*, 1564 (1962).
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It is the purpose of this paper to describe systematic preparative methods which give both the racemic and optically active complexes with full retention of geometry and chirality. In addition we offer an explanation and supporting evidence for the capricious instability of the cis complexes.

1. Preparations

The green *trans*-[Co(diars)$_2$Cl$_2$]Cl complex is easily prepared by the addition of hydrochloric acid to an aerially oxidized aqueous alcohol solution of cobalt acetate and 2 mol of diars. This complex reacts with lithium carbonate in aqueous methanol to give a high yield of the very water-soluble orange *cis*-[Co(diars)$_2$CO$_3$]Cl salt which is unstable in water in the presence of chloride ions and tends to revert to the *trans*-dichloro complex. It was obtained as the perchlorate salt after extraction into methylene chloride. Upon the addition of concentrated perchloric acid to this carbonato complex, crystals of the *cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ complex deposit.

The nmr spectrum of the *cis*-diaquo ion in dilute aqueous perchloric acid solutions shows the characteristic four-line methyl proton spectrum and there is no evidence for the *trans*-diaquo isomer after 1 month at room temperature. The addition of 1 equiv of hydroxide ions to an aqueous solution of the *cis*-diaquo complex deposits the rather insoluble *cis*-[Co(diars)$_2$OH(OH$_2$)](ClO$_4$)$_2$ complex. These two complexes are starting materials which give easy entry into the preparations of cis complexes.

The aquo group of the *cis*-hydroxoaquo complex is very much more labile than the hydroxo group and it thus may be possible selectively to substitute the cis octahedral positions one at a time by simply adjusting the pH of the solution. We have not pursued this problem of preparing *cis*-[Co(diars)$_2$XY]$^{n+}$ complexes except for the *cis*-[Co(diars)$_2$OH(CH$_3$CN)](ClO$_4$)$_2$ complex which is prepared by dissolving the *cis*-hydroxoaquo complex in acetonitrile. The orange product shows an nmr pattern typical of a *cis*-[Co(diars)$_2$XY]$^{n+}$ species (Table I).

The aquo groups of the *cis*-diaquo species are also very labile and, in all cases, appear to be substituted with steric retention. Thus, in acetonitrile, the *cis*-diaquo complex