

Dissymmetric Arsine Complexes. Monomeric and Dimeric Dioxygen Complexes of Cobalt

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Tertiary arsine complexes of cobalt form stable monomeric and dimeric dioxygen adducts. Reaction of oxygen with formally cobalt(I)-arsine complexes produces "sideways" bonded dioxygen adducts. The cobalt(III)-diaquoarsine complexes react with hydrogen peroxide to give the same monomeric adducts. This latter reaction proceeds rapidly by a catalytic pathway and more slowly by what appears to be a "simple" substitution process where optical activity is retained when the active $cis\text{-}[\text{Co}(\text{diars})_2(\text{OH})_2]^{3+}$ ion is used as the substrate. The robust chemical behavior of these monomeric complexes is similar to other analogous cobalt(III)-arsine compounds and their visible electronic absorption spectra clearly indicate that the species are best regarded as cobalt(III)-peroxide complexes. The significance of this conclusion in relation to bond length data is briefly discussed. Reaction of oxygen with cobalt(II) arsines leads to the production of dimeric dioxygen-bridge adducts, the absorption spectra and chemical properties of which indicate that these too are Co(III) species but with a peroxide bridging ligand. The monomeric dioxygen adducts react with sulfur dioxide to give the bidentate sulfato complexes which have been prepared and characterized, some in optically active forms. Dimeric (formally) Co(II) complexes containing Co-Co bonds disproportionate in the presence of strong bases to give Co(I) species which react with oxygen to give the "sideways" bonded dioxygen adducts.

The current interest¹⁻³ in dioxygen complexes of transition metal ions derives, in part, from the biochemical problems associated with oxygen uptake, transport, and reactivity in living systems. A number of approaches have been adopted in order to understand the subtle stereochemical and electronic features which operate in biological systems. Of these, the most prevalent is the design of so-called model systems. The immediate appeal and advantages of this approach are obvious although the method is inherently limiting in the sense that a model presupposes a reasonably detailed knowledge of the system itself. Another approach is to remove the inherent restrictions of the model systems and simply to explore the diversity of structures and reactivities of a set of dioxygen complexes of a particular class of compounds. The advantage of this latter method is that it provides a fuller understanding of the potential complexity of the problem although at times it may suffer the disadvantage of having only glancing relevance to the biological problem. We believe, at present, that the complexity of dioxygen complexes is such as to require further investigation in certain areas. It is the purpose of this article to describe the preparations, properties, electronic structures, and reactivities of a particular class of dioxygen complexes of cobalt which hitherto have not been investigated, namely, those with tertiary arsine ligands.

The use of arsines rather than the more common nitrogen and/or oxygen donor atom systems is somewhat more difficult because of the ready oxidation of trivalent arsenic and the catalytic behavior of the cobalt complexes but is, at present, perhaps more fruitful because of the diversity of dioxygen complexes that can be prepared. The only other reports using "soft" donor atoms as ligands with cobalt are the recent observations of Vaska,^{4,5} who described complexes with phosphines as ligands. We have found that the type of dioxygen complex formed with these arsine systems depends on the oxidation state of the cobalt-arsine substrate and to some extent on its structure. The oxidation states

we have employed to study their oxygen reactivity are (formally), Co(I), Co(II), and Co(III). The methods for preparing the Co(I) derivatives is the subject of a future paper and the syntheses of the Co(III) precursors are described elsewhere.⁶⁻⁸

The three arsine ligands used are shown in Figure 1 where it will be noted that tetars exists in stable racemic ($R,R:S,S$ -tetars) and meso (R,S -tetars) forms which have been separated and the racemic isomer has been resolved.⁶

1. Dioxygen Complexes Derived from "Cobalt(I)" Arsines

When $cis\text{-}\alpha\text{-}[\text{Co}(R,R:S,S\text{-tetars})\text{Cl}_2]\text{Cl}$ is dissolved in neutral methanol-water mixtures and treated with NaBH_4 , a transient straw yellow solution is produced which rapidly absorbs oxygen to produce a cherry red solution. The red product is the $cis\text{-}\beta\text{-}[\text{Co}(R,R:S,S\text{-tetars})\text{O}_2]^+$ ion; a single-crystal X-ray structure of the optically active ($-$)- $cis\text{-}\beta\text{-}[\text{Co}(R,R\text{-tetars})\text{O}_2]\text{ClO}_4$ complex shows it contains a "sideways" bonded dioxygen moiety.⁹ A similar reaction occurs with the $trans\text{-}[\text{Co}(R,S\text{-tetars})\text{Cl}_2]\text{Cl}$ complex but the red $cis\text{-}\beta\text{-}[\text{Co}(R,S\text{-tetars})\text{O}_2]\text{ClO}_4$ is unstable and slowly decomposes in solution to give cobalt(II)-arsine complexes and arsine oxides. Because of this, attempts at recrystallizing this complex to purity from a variety of solvents were unsuccessful. There is, however, little doubt about the constitution of the product because the visible absorption spectrum of freshly prepared solutions of the initially isolated product was very similar to that of the stable $cis\text{-}\beta\text{-}[\text{Co}(R,R:S,S\text{-tetars})\text{O}_2]\text{ClO}_4$ species and the nmr spectrum of a similarly prepared solution gave the characteristic four-line methyl proton spectrum of a $cis\text{-}\beta$ complex (Table I). The NaBH_4 reduction of the $trans\text{-}[\text{Co}(\text{diars})_2\text{Cl}_2]\text{Cl}$ complex is complicated because of the production of the very insoluble Co(II) complex $[\text{Co}(\text{diars})_2\text{Cl}_2]$, although by the very rapid addition of NaBH_4 a very small amount of the brown $cis\text{-}[\text{Co}(\text{diars})_2\text{O}_2]\text{ClO}_4$ complex can be isolated. We assume that, in all these reactions, the borohydride ion reduces the complexes

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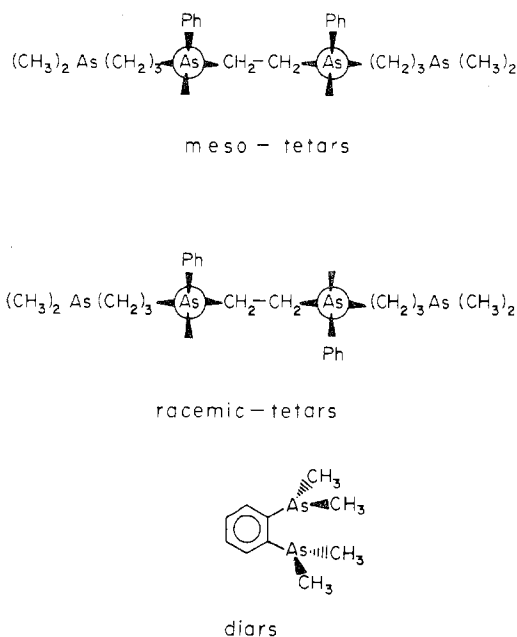


Figure 1.

Table I. Nmr Data of the As-CH₃ Protons

Complex	Solvent	δ , ^a Hz
<i>cis</i> - β -[Co(<i>R,R:S,S</i> -tetars)O ₂]-ClO ₄	CD ₂ Cl ₂	104, 73, 65, 65
<i>cis</i> - β -[Co(<i>R,S</i> -tetars)O ₂]ClO ₄	DMSO- <i>d</i> ₆	100, 70, 62, 61
	CDCl ₃	104, 73, 66, 64
<i>cis</i> -[Co(diars) ₂ O ₂]ClO ₄	DMSO- <i>d</i> ₆	105, 85, 75, 47
	CDCl ₃	112, 99, 78, 53
<i>cis</i> - α -[Co(<i>R,R:S,S</i> -tetars)SO ₄]-ClO ₄ -CH ₃ CN	DMSO- <i>d</i> ₆	117, 111, 77, 75
<i>cis</i> - β -[Co(<i>R,R:S,S</i> -tetars)SO ₄]-ClO ₄	DMSO- <i>d</i> ₆	111, 88, 74.5, 74
<i>cis</i> - β -[Co(<i>R,S</i> -tetars)SO ₄]ClO ₄	DMSO- <i>d</i> ₆	108, 95, 89, 71
<i>cis</i> -[Co(diars) ₂ SO ₄]ClO ₄	DMSO- <i>d</i> ₆	137, 119, 97, 57

^a Relative to TMS as an internal standard at 30° and 60 MHz.

^b Free CH₃CN resonance.

to Co(I) species which are reactive to oxygen. This assumption is supported by the following observations.

Among others, the stable hydride complexes *trans*-[Co(*R,R:S,S*-tetars)HX]ClO₄ (X⁻ = Cl⁻, Br⁻, I⁻), *trans*-[Co(*R,S*-tetars)HI]ClO₄, and *trans*-[Co(diars)₂HCl]ClO₄ have been isolated. Their preparation and properties will be discussed elsewhere. If the hydrogen atom in these complexes is regarded as a proton, or more precisely if it can be induced to react as a proton, the complexes under these conditions can be considered as Co(I) derivatives.¹⁰ When these complexes are suspended in methanol in the presence of catalytic amounts of triethylamine, they absorb atmospheric oxygen to give almost quantitative yields of the *cis*-[Co(As)₄O₂]⁺ species. No detectable oxygen uptake occurs in acidic media. We therefore suppose that the function of the base is to remove a proton from the metal to give a reactive Co(I) species which rapidly picks up oxygen. Because of the extreme reactivity and the apparent general instability of these Co(I) species we were unsuccessful in our attempts to isolate them.

A similar reaction occurs with the highly reactive species *cis*-[Co(diars)₂(H₂)₂]ClO₄ which has been isolated and fully

characterized. This compound reacts with oxygen in neutral methanol solutions to give the *cis*-[Co(diars)₂O₂]ClO₄ complex quantitatively with the liberation of 1 molar equiv of hydrogen gas. This reaction is not detectably reversible under 1 atm of hydrogen; in fact there is no change in the absorption spectrum of the *cis*-[Co(diars)₂O₂]ClO₄ complex in methanol after it has been kept under hydrogen for 24 hr. As far as the reaction with oxygen is concerned, the dihydrido species therefore appears to behave as if one hydrogen atom is a proton and the other a hydride.¹¹ If both hydrogen atom ligands could be removed as protons, the *cis*-[Co(diars)₂(H)₂]⁺ ion could then be regarded as a derivative of Co(-I) with the interesting prospect of a four-electron transfer to oxygen. Addition of strong base to the *cis*-[Co(diars)₂(H)₂]-ClO₄ complex in methanol, however, does not change the course of the reaction with oxygen; the same *cis*-[Co(diars)₂O₂]ClO₄ complex is produced in both neutral and basic media. These same dioxygen complexes may be prepared by a distinctly different route.

2. Dioxygen Complexes Derived from Cobalt(III)-Arsine Complexes

The cobalt(III)-diaquo complexes *cis*-[Co(diars)₂(H₂O)₂](ClO₄)₃,⁸ *cis*- β -[Co(*R,S*-tetars)(H₂O)₂](ClO₄)₃, and *cis*-[Co(*R,R:S,S*-tetars)(H₂O)₂](ClO₄)₃, the last existing as a roughly equal mixture of *cis*- α and *cis*- β isomers at equilibrium in water,⁷ react in neutral water solutions with hydrogen peroxide to give the dioxygen complexes *cis*-[Co(diars)₂O₂]ClO₄, *cis*- β -[Co(*R,S*-tetars)O₂]ClO₄, and (exclusively) *cis*- β -[Co(*R,R:S,S*-tetars)O₂]ClO₄, respectively. All these complexes are identical with the corresponding species formed by the reactions of the "Co(I)" complexes and oxygen. On a preparative scale these hydrogen peroxide reactions are undoubtedly catalytic; they are characterized by an induction period whereafter the reaction "takes off" and the substitution becomes exceedingly rapid. Furthermore, isomeric equilibration occurs as evidenced by the fact that only the *cis*- β -[Co(*R,R:S,S*-tetars)O₂]⁺ isomer is produced despite the fact that both *cis*- α - and *cis*- β -diaquo isomers are present as starting materials and the H₂O₂ reaction is much faster than the *cis*- α - to *cis*- β -diaquo isomerization. If optically active⁸ *cis*-[Co(diars)₂(H₂O)₂](ClO₄)₃ is used, complete racemization occurs under catalytic conditions. Catalysis of this kind is not unusual for these cobalt(III)-arsine complexes^{7,8} and we have observed similar catalysis with such mildly reducing anions as Br⁻ and the oxalate dianion. We suppose, therefore, that the catalytic substitutions with H₂O₂ involve the production of catalytic amounts of labile cobalt(II)-arsine complexes which catalyze the reactions *via* an electron-transfer mechanism. Presumably a small amount of H₂O₂ is oxidized during the induction period.

In very dilute water solutions (10⁻⁴ M) using 1 equiv of H₂O₂, the catalytic pathway can be suppressed to some extent. The reaction still proceeds but much more slowly and apparently by a "simple" substitution process. This we infer from the fact that if optically active *cis*-[Co(diars)₂(H₂O)₂](ClO₄)₃ is used, optically active *cis*-[Co(diars)₂O₂]ClO₄ can be isolated [($\epsilon_1 - \epsilon_r$)_{550m μ} = -0.075; ($\epsilon_1 - \epsilon_r$)_{475m μ} = +0.1]. The *cis*-[Co(diars)₂O₂]ClO₄ is probably not optically pure but the result clearly indicates that at least part of the reaction involves a "simple" substitution at a Co(III) complex

(10) We will show elsewhere that, as far as their absorption spectra are concerned, they are best regarded as Co(III) species and, hence, species with hydridic ligands.

(11) This apparent dichotomy is revealed in its reactions with acids which suggest the hydridic nature of one of the hydrogen atom ligands. Thus, for example, HCl reacts with the "dihydride" to give *trans*-[Co(diars)₂HCl]⁺ with the liberation of 1 mol of hydrogen gas. We will discuss these reactions in more detail elsewhere.

because if Co(II), or even Co(I), were involved, we would expect complete racemization as is observed in the catalyzed reactions. Whether the "simple" substitution involves cleavage of the O-O bond or addition of the intact O-O bond of H_2O_2 must await isotopic labeling experiments for a decision.

These dioxygen complexes are quite robust. Thus the *cis*- β -[Co(*R,R*:*S,S*-tetars) O_2] ClO_4 complex can be recrystallized from boiling water without decomposition and the optically active *cis*-[Co(diars) $_2O_2$] ClO_4 complex does not racemize in water solutions except when induced by Co(II) catalysis. The instability of the *cis*-[Co(*R,S*-tetars) O_2] ClO_4 complex is probably due to the preference of the meso tetars ligand for a planar arrangement when the complex has an overall (single) positive charge.⁷ In solutions containing coordinating anions, the complexes slowly decompose to give eventually Co(II), free arsine, and arsine oxides. In acid solutions, a rapid reaction occurs with the *cis*- β -[Co(*R,R*:*S,S*-tetars) O_2] ClO_4 complex. The addition of perchloric acid causes a rapid (~2 sec) pink to violet change in color which is then followed by the production of Co(II), free arsine, and arsine oxide. Attempts at removing the dioxygen ligand under reduced pressure (0.01 mm) and/or heating the solid complexes led to complete decomposition.

In methylene chloride, both the *cis*-[Co(diars) $_2O_2$] ClO_4 and *cis*- β -[Co(*R,R*:*S,S*-tetars) O_2] ClO_4 complexes react "instantly" with dissolved SO_2 to give *cis*-[Co(diars) $_2SO_4$]- ClO_4 and *cis*- β -[Co(*R,R*:*S,S*-tetars) SO_4] ClO_4 , respectively; none of the *cis*- α -[Co(*R,R*:*S,S*-tetars) SO_4] ClO_4 ion is formed. Of necessity, these reactions were followed by nmr and the products were not isolated because the presence of SO_2 subsequently led to reduction. There is, however, no doubt that the first formed products are the sulfato complexes and that no *cis*- α SO_4^+ complex is formed because we have prepared, isolated, and fully characterized the *cis*- α , *cis*- β , and *cis*-(diars) $_2SO_4^+$ complexes (see Experimental Section and Table I).

The robust chemistry displayed by these dioxygen complexes is characteristic of cobalt(III)-arsinic complexes and on this basis we conclude that their chemistry indicates a cobalt(III) peroxide charge distribution. This chemical observation is supported by the electronic spectra of these diamagnetic complexes. In Figure 2 we show the visible absorption spectra of the *cis*-[Co(diars) $_2(H_2O)_2$] $^{3+}$, *cis*-[Co(diars) $_2O_2$] $^+$, and the Δ -*cis*- β -[Co(*R,R*-tetars) O_2] $^+$ ions and the associated circular dichroism of the last. All three absorption spectra are very similar in both position and intensity suggesting that the electronic state of the Co atom is similar in all three cases. Cobalt(III) complexes containing arsenic donor atoms in general show more intense "d-d bands" and a reduction of the free ion interelectronic repulsion parameters^{6,12,13} but the upper state d-electron manifolds retain much of their crystal field spectroscopic characteristics and provide a useful basis for interpretation.^{6,12,13} Thus, the two transitions of the *cis*-[Co(diars) $_2(H_2O)_2$] $^{3+}$ ion are assigned to the $^1A_{1g} \rightarrow ^1T_{1g}$ (480 $m\mu$) and $^1A_{1g} \rightarrow ^1T_{2g}$ (410 $m\mu$) transitions of an "octahedral" spin-paired Co(III) complex. The two dioxygen complexes also show a lower energy transition in almost the same position and with almost the same intensity as the first band of the diaquo complex; the higher energy band is partly obscured in the dioxygen adducts by the intrusion of charge-

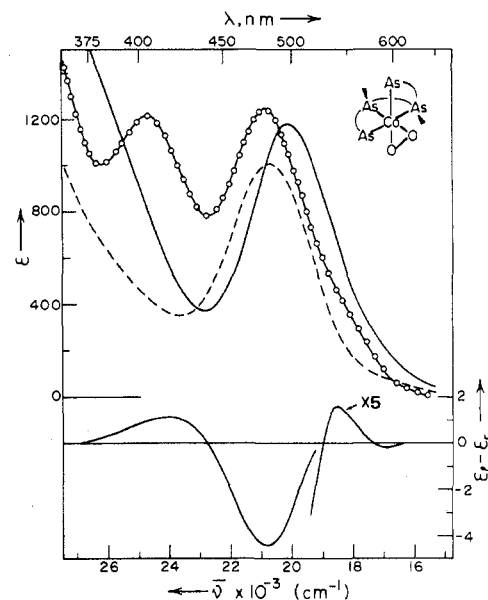


Figure 2. Visible absorption spectra of *cis*-[Co(diars) $_2(OH)_2$]- ClO_4 in 0.5 M $HClO_4$ (—○—○—) and *cis*-[Co(diars) $_2O_2$] ClO_4 in CH_3OH (---) and the absorption and circular dichroism spectra of (—) Δ -*cis*- β -[Co(*R,R*-tetars) O_2] ClO_4 in water (—). The structure of the last complex is shown in the inset.

transfer bands. Accordingly, if the lower band of the dioxygen complexes is assigned to the $^1A_{1g} \rightarrow ^1T_{1g}$ transition, this threefold degeneracy may be revealed in the circular dichroism. This is so (Figure 2). Thus, if we use the absorption spectra as a criterion and if it is acceptable to define the oxidation state of Co in the diaquo species as Co(III), then the assignment of cobalt(III) peroxide to these dioxygen complexes seems inescapable and consistent with their chemical properties.

The above assignment of an integral oxidation state to the dioxygen complexes is to some extent a departure from current descriptions of the bonding offered for these complexes^{1,5,14} and we briefly comment on the matter. Previous discussions have centered on structural information relating to coordination angles and coordinated O-O bond lengths which are said to be either "long" or "short" relative to the uncoordinated O_2 , O_2^- , or O_2^{2-} species. Indeed, within a closely related series of complexes of the same metal, there is a correlation between O-O bond length and reversible oxygen uptake.^{15,16}

However, another and probably a more salient comparison of bond lengths can be adopted. The generally accepted classical criteria of oxidation state, namely, electronic spectra and magnetism, support the view that the peroxochromium complexes are best described as species containing "sideways" bonded peroxide ligands. The O-O bond lengths in these complexes are about 1.42 Å,¹⁷ there being only one which is unusually "long," 1.47 Å.¹⁷ The coordinated O-O bond lengths of Vaska's⁵ phosphine-cobalt complex and the present tetars complex⁹ are both 1.42 Å. Thus, on the basis of coordinated O-O bond length, our

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cobalt(III) (coordinated) peroxide formulation is consistent with the chromium complexes and is probably a valid criterion of oxidation state for "sideways" bond species of the first transition series.

We note in passing that there are complexes of the second and third transition series where the O-O bond lengths are 1.42 Å or longer and where reversible oxygen exchange occurs.^{14,18} However, bond length comparisons, assembled by whatever index, are unlikely to be the sole measure of reversibility; a primary consideration must be the ease with which an internal redox reaction between the (coordinated) metal and the dioxygen ligand can occur. Since the primary process of separating an oxygen molecule from a wholly or partially oxidized metal must involve the transference of charge from the dioxygen moiety back to the metal, the position of the dioxygen to metal charge-transfer band may provide a useful criterion for reversibility for a given metal. That some reversible oxygen carriers do indeed involve reductive elimination between integral oxidation states is clearly indicated by the superoxide-cobalt(III) species studied by Basolo¹⁹ and we suspect this is true of hemoglobin despite the apparent diamagnetism of the oxygenated form.

Another criterion of oxidation state that has been used is the O-O stretching frequency. The complexes described here decompose rapidly in a laser beam and the infrared spectra, in both the solid and CH₂Cl₂ solutions, are dominated by ligand transitions in the O-O stretching region. A comparison of the infrared spectra of the dioxygen adducts with those of the corresponding dichloro complexes did not allow us to make a definite assignment of the O-O stretch.

3. Dioxygen Complexes Derived from "Cobalt(II)"-Arsine Complexes

By starting with cobalt(II)-arsine complexes a different type of dioxygen complex is formed. When Co(ClO₄)₂ and either of the tetars ligands are mixed in methanol or acetonitrile solutions, a very rapid reaction occurs in the presence of oxygen and the solutions turn deep red-brown. The resultant dioxygen adducts are extremely difficult to isolate because of the presence of large amounts of arsine oxides and Co(II) salts and because of the instability of the products in the presence of Co(II) catalysts. We have only isolated the adduct of the meso ligand in a pure state; the corresponding complex of the optically active *R,R*-tetars ligand could be isolated as a pink powder which gave the expected nmr spectrum (Table II) but which could not be induced to form acceptable crystals. A similar but crystalline adduct using the diars ligand was obtained by aerial oxidation of the [Co(diars)₂(ClO₄)₂]²⁰ complex in acetonitrile.

The nmr data of these adducts are given in Table II where it will be seen that the number and positions of the arsenic methyl proton resonances are consistent^{7,8} with *trans*-[Co(*R,S*-tetars)XY]ⁿ⁺ and *trans*-[Co(diars)₂XY]ⁿ⁺ species. We therefore suggest that these complexes are the classic dioxygen-bridged dimers of cobalt,²¹ namely, *trans,trans*-[(CH₃CN)(*R,S*-tetars)Co-O-O-Co(*R,S*-tetars)(CH₃CN)](ClO₄)₄

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Table II. Nmr Data of the As-CH₃ Protons of the Dioxygen Dimers

<i>trans,trans</i> -[CH ₃ CN-(L)CoO ₂ Co(L)CH ₃ CN]·(ClO ₄) ₄	Solvent	δ, ^a Hz
L = <i>R,R</i> : <i>S,S</i> -tetars ^c	DMSO- <i>d</i> ₆	106, 94, 88, 82 (107) ^b
L = <i>R,R</i> -tetars ^c	DMSO- <i>d</i> ₆	100, 95, 87, 82 (112) ^b
L = <i>R,S</i> -tetars	DMSO- <i>d</i> ₆	106, 89 (124) ^b
L = (diars) ₂ ^d	DMSO- <i>d</i> ₆	125, 132

^a Relative to TMS as an internal standard at 30° and 60 MHz. ^b Coordinated CH₃CN resonances. ^c The racemic and active tetars ligands give different spectra for their complexes and the racemic compound appears to give only one isomer. However, the compounds could not be obtained as acceptable crystals. ^d The coordinated CH₃CN resonance occurs under the residual solvent absorption (~130 Hz).

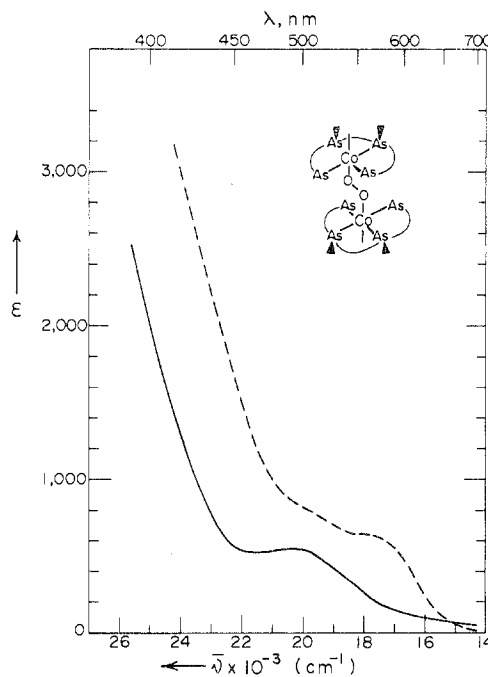


Figure 3. Visible absorption spectra of the *trans,trans*-[CH₃CN(L)-CoO₂Co(L)CH₃CN](ClO₄)₄ complexes: L = (diars)₂, —; L = *R,S*-tetars, ----. The inset shows the proposed structure of the *R,S*-tetars dimer where the exo,exo positioned phenyl groups are represented as wedges.

and *trans,trans*-[(CH₃CN)(diars)₂Co-O-O-Co(diars)₂(CH₃CN)](ClO₄)₄. The molecular weight of the former in CH₃CN is consistent with this formulation. The complex derived from the *R,S*-tetars ligand has three isomeric forms²² depending on whether the relative orientations of the phenyl groups are exo,exo, exo,endo, or endo,endo. We suppose that the isomer isolated is the exo,exo form because molecular models suggest it is the least sterically hindered. This is shown schematically in Figure 3. However, the yield is low and it is possible that one of the less stable forms has been isolated.

Both the robust chemical behavior and the visible absorption spectra (Figure 3) of these complexes indicate that they are best regarded as Co(III) complexes linked by a peroxide bridge. The relatively weak absorption bands at low energies occur in the expected⁶ positions for a *trans*-[Co(As)₄(CH₃CN)OH]²⁺ chromophore and represent the split ¹A_{1g} → ¹T_{1g} octahedral transition. The tail of the strong band

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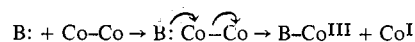
which intrudes into the visible region probably represents the peroxide-cobalt(III) charge-transfer transition.

The bridged peroxy complexes when pure are quite stable in aqueous solutions and can be recrystallized from hot water. The addition of strong acids to aqueous solutions leads to an immediate color change from red-brown to orange, and if 1 equiv of base is added immediately after the acid addition, the color reverts back to red-brown and the unchanged starting material can be isolated. We assume that the color change is due to protonation of the peroxide bridge which, initially, is not cleaved by the acid. However, if the complexes are boiled in water for 5 min or heated to 80° with acid for a few minutes, the peroxide bridge does cleave. The analysis of the reaction products of these cleavage reactions is complicated because both Co(III) complexes and Co(II) complexes are formed and the latter catalyze substitution of the Co(III) species. Thus, the reaction with HCl does not give the expected *trans*-chloroacetonitrilecobalt(III) product but rather the *trans*-dichloro complex and Co(II) complexes which presumably catalyze the substitution of the acetonitrile ligand.

4. Dioxygen Complexes Derived from Co-Co Dimers

There is a third method of preparing the "sideways" bonded dioxygen adducts. The addition of a strong base (B) to the dimers²² *trans,trans*-[CH₃CN(*R,S*-tetars)Co-Co(*R,S*-tetars)-CH₃CN]⁴⁺, *trans,trans*-[CH₃CN(*R,R*-tetars)Co-Co(*R,R*-tetars)CH₃CN]⁴⁺, and *trans,trans*-[H₂O(diars)₂Co-Co(diars)₂-OH]⁴⁺ dissolved in acetonitrile or acetone leads to the production of the "sideways" bonded adducts in less than 50% yield in terms of total cobalt. The other products are mainly Co(III) complexes substituted with acetonitrile and methylamine, if methylamine is used as the base, as well as aquo species and a small amount of Co(II). A full analysis of these products was not carried out except to confirm the presence of cobalt(III)-arsine complexes as the other major product.

We assume these reactions involve the heterolytic cleavage of the Co-Co bond to produce Co(III) complexes and the oxygen-sensitive Co(I) species



The speed of these reactions depends on the concentration and strength of the base. Thus weak bases such as triphenylphosphine and pyridine are not effective but triethylamine, hydroxide, and methylamine cause rapid reactions in aqueous acetonitrile.

5. Experimental Section

Instrumentation. The nmr spectra were measured using a Varian T-60 spectrometer at 29° with TMS as an internal reference. Absorption and circular dichroism spectra were taken using a Unicam SP820 recording spectrophotometer and a Roussel-Jouan Dichrographe II, respectively. Conductivities were obtained with a Yellow Springs Instrument Co. Model 31 conductivity bridge and optical rotations were measured using a Perkin-Elmer 141 digital recording polarimeter.

Gas Analysis. The amounts of oxygen absorbed and hydrogen released in the reaction of *cis*-[Co(diars)₂(H₂)ClO₄] with oxygen were analyzed by Raman spectroscopy as follows. Methanol (100 ml) was added to a 500-ml two-necked round-bottom flask containing a magnetic stirrer. One of the flask's ground-glass joints contained a stopper; the other, positioned vertically, contained an ~4-cm clear-glass finger through which the laser beam (4880 Å) passed. The instrumental configuration was such that the incident laser beam direction was *z*, that of the glass finger was *y*, and the scattered light cone was collected along *x*. The O₂ (of air) Raman signal was then measured for the band at ~1550 cm⁻¹. Without changing any of the instrument settings or the position of the reaction flask, *cis*-[Co-

(diars)₂(H₂)ClO₄ (1 g) in a plastic boat was added through the side arm and the flask was stoppered immediately. While the solution was stirred, the decrease in the O₂ signal and the increase in the H₂ signal at ~4395 cm⁻¹ were measured. When no further change was observed, the flask was filled with H₂ and the signal recorded. In this way, the amount of O₂ absorbed with H₂ released could be measured from the respective areas of the Raman bands to an accuracy of about 5%. It was found that 1 molar equiv of O₂ was absorbed and the same amount of H₂ released. The *cis*-[Co(diars)₂(H₂)ClO₄] complex is very insoluble in methanol and the rate of absorption of O₂ is essentially governed by its rate of dissolution. There is essentially no change in pressure during the course of reaction. It should be pointed out that this simple method of accurately measuring the gaseous mixture requires some sophistication of the normal Raman setup. For the present work a lock-in detection was used and the laser beam was chopped by a Pockel's cell driven by the amplified signal of the lock-in amplifier.

Product Analysis. The hydrido complexes *trans*-[Co(*R,R,S,S*-tetars)HI]ClO₄, *trans*-[Co(*R,S*-tetars)HI]ClO₄, *trans*-[Co(diars)₂-HCl]ClO₄, and *cis*-[Co(diars)₂(H₂)ClO₄] (0.5 g) were suspended separately in methanol and stirred in air. A few drops of triethylamine was added and the reaction was allowed to proceed to completion (~4 hr). Water (500 ml) containing NaClO₄ (2 g) was then added and the mixture extracted with CH₂Cl₂ until no color remained in the aqueous phase. The extracts were dried (Na₂SO₄) and pumped to dryness at 40°. The homogeneous residues were then analyzed by nmr and visible absorption spectra. All the reactions produce the "sideways" bonded dioxygen adducts to the extent of about 95%. The remaining product consists of Co(II) and free arsine oxides. The former is effectively removed by the extraction procedure which transfers the Co(III) species quantitatively from the aqueous phase.

SO₂ Reactions. Sulfur dioxide was bubbled through CD₂Cl₂ for 1 min and then added to preweighed samples of the dioxygen complexes in nmr tubes. The nmr spectra were measured at once. The characteristic spectra of the bidentate SO₄²⁻ complexes are observed in high resolution for about 1 min, whereafter the resolution collapses due to the production of Co(II) species.

cis-β-[Co(*R,R,S,S*-tetars)O₂]ClO₄. **Method 1.** Sodium borohydride (0.10 g) was added in small portions to an ice-cold, stirred solution of *cis-α*-[Co(*R,R,S,S*-tetars)Cl₂]Cl⁶ (0.50 g) in ethanol (20 ml) and water (20 ml). The blue solution rapidly became straw yellow and then crimson. After the addition of NaBH₄ was complete, the solution was stirred in air for 10 min at 0° and NaClO₄ (2 g) was added to give a pink precipitate. The mixture was stirred for a further 5 min, filtered, and washed with water, ethanol-ether (1:10) and finally ether. The product was taken up in acetone, reprecipitated with aqueous NaClO₄, and collected. Two recrystallizations, the first from hot methanol (80 ml) and ether (300 ml) and the second from methanol (20 ml) and acetone (10 ml) by the slow addition of ether, gave chunky pink-red blocks of the pure complex (0.28 g; λ = 78 ohm⁻¹ cm² mol⁻¹, 1.39 × 10⁻³ M in methanol at 25°; FW = 816 (calcd), 850 ± 50 (found, ebulliometry in CH₃CN)).

Anal. Calcd for [Co(C₂₄H₃₈As₄O₂)ClO₄]: C, 35.2, H, 4.8; Cl, 4.3. Found: C, 35.3; H, 4.6; Cl, 4.3.

Method 2. *cis-β*- or *cis-α*-[Co(*R,R,S,S*-tetars)(H₂O)₂](ClO₄)₃⁷ (0.60 g) in acetone (10 ml) and water (50 ml) was treated with a dropwise addition of H₂O₂ (5 ml; 30%) in water (25 ml). There was an immediate color change from amber-red to deep pink and the product began to precipitate out of solution. After stirring of the mixture for 5 min, NaClO₄ (2 g) in water (10 ml) was added. The product was filtered and isolated by method 1 (0.31 g).

Δ-cis-β-[Co(*R,R*-tetars)O₂]ClO₄. **Method 1.** *Δ-cis-α*-[Co(*R,R*-tetars)Cl₂]Cl⁶ (0.5 g) was allowed to react with NaBH₄ in the manner described for the racemic analog. To the resulting deep red solution was added NaClO₄ (2 g) in water (30 ml) and the mixture was extracted with CH₂Cl₂ (two 50-ml portions). The complex in the CH₂Cl₂ extracts vigorously decomposes if the extract is dried with MgSO₄, and hence the combined extract was filtered through paper a number of times to remove the excess water and then pumped to dryness. The crude product was recrystallized twice from hot water to give fine pink-brown crystals. A final crystallization from methanol (20 ml) by the slow addition of ether gave chunky red blocks (0.15 g; [α]_D -216 (±15)°, [α]₅₇₈ -235 (±15)°, [α]₅₄₆ -420 (±20)°, [α]₄₃₆ +859 (±20)°, 1.62 × 10⁻⁴ g/g in methanol, 25°).

Anal. Calcd for [Co(C₂₄H₃₈As₄O₂)ClO₄]: Co, 7.3; C, 35.2; H, 4.8; As, 37.2; Cl, 4.3; O, 11.9. Found: Co, 7.4; C, 35.3; H, 4.7; As, 36.4; Cl, 4.3; O, 11.9.

Method 2. *Δ-cis-β*-[Co(*R,R*-tetars)(H₂O)₂](ClO₄)₃·H₂O (0.60 g) was treated with H₂O₂ in the same way as given in method 2 for

the racemic compound and worked up by method 1 given for the active form (0.25 g).

cis-[Co(diars)₂O₂](ClO₄)₃. Three drops (~0.15 ml) of 30% hydroperoxide was added to an efficiently stirred solution of *cis*-[Co(diars)₂(H₂O)₂](ClO₄)₃ (0.25 g) in warm water (5 ml). Within 5 min, small brown crystals began to separate. The reaction mixture was left to stand at room temperature in the dark for 1 hr, after which the crystals were collected, washed quickly with ice water followed by ether, and air-dried. The complex was recrystallized from warm water by the careful addition of aqueous NaClO₄ and cooling (0.1 g; $\Lambda = 83 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $8.16 \times 10^{-4} M$ in methanol at 25°).

Anal. Calcd for [Co(C₂₀H₃₂As₄)O₂](ClO₄): C, 31.5; H, 4.2; Cl, 4.7. Found: C, 32.0; H, 4.3; Cl, 4.9.

By using the optically active diaquo complex, the weakly active *cis*-[Co(diars)₂O₂](ClO₄)₃ can be isolated.

trans,trans-[CH₃CN(*R,S*-tetars)Co-O-O-Co(*R,S*-tetars)CH₃CN](ClO₄)₄. The (meso) *R,S*-tetars (5.8 g) was dissolved in ether (20 ml) under N₂, and a fresh solution of Co(ClO₄)₂·6H₂O (3.4 g) in acetonitrile (40 ml) was added to the stirred arsine solution. A deep brown-yellow solution resulted which intensified in color as air was drawn through it for 5 min. A large quantity of ether was then added, and the resulting chocolate brown solid was collected and washed with acetonitrile-ether (1:3) and then ether. It was taken up in acetonitrile-acetone (1:1) and fractionally crystallized by the addition of ether. The first fractions, which were bright yellow, were mainly *trans*-[Co(*R,S*-tetars)(CH₃CN)₂](ClO₄)₃ and a little of the *cis*- β -bis(acetonitrile) complex. The middle fraction was yellow-brown and the last fraction was deep brown; these were worked up separately. The middle fraction was fractionally crystallized from acetonitrile by the slow addition of ether; the first fractions were deep brown blocks, and the latter fractions became progressively contaminated with the yellow bis-acetonitrile complexes and were discarded. The deep brown blocks from the latter fractions derived from the initial reaction mixture and the same crystals derived from the fractionation of the middle fraction were combined and twice crystallized from acetonitrile by the slow addition of ether to give shining red-brown needles (1.15 g; $\Lambda = 516 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, 3.38×10^{-4} and $1.02 \times 10^{-4} M$ in acetonitrile at 25°; FW = 1882.2 (calcd), 2000 \pm 200 (found), in acetonitrile by "osmometry" over the concentration range 1×10^{-3} – $5 \times 10^{-3} M$, using *cis*-[Co(diars)₂(CH₃CN)₂](ClO₄)₃ and *cis*- and *trans*-[Co(diars)₂Cl₂](ClO₄)₂ as reference compounds).

Anal. Calcd for [Co(C₂₄H₃₆As₄)(CH₃CN)O](ClO₄)₂: Co, 6.3; C, 33.2; H, 4.4; N, 1.5; Cl, 7.5. Found: Co, 6.3; C, 33.3; H, 4.6; N, 1.6; Cl, 7.8.

trans,trans-[CH₃CN(diars)₂Co-O-O-Co(diars)₂CH₃CN](ClO₄)₄·4H₂O. A solution of diars (2.86 g) in acetonitrile (15 ml) was added to a freshly prepared solution of Co(ClO₄)₂·6H₂O (1.38 g) in acetonitrile (10 ml). This solution was stirred as H₂O₂ (1.4 g; 30%) in acetonitrile (25 ml) was added dropwise over 5 min. The solution became warm and the color changed from deep green to deep brown. It was pumped down to a volume of about 5 ml and filtered into a separating funnel; NaClO₄ (5.0 g) in water (50 ml) was then added to the filtered solution which was repeatedly extracted with CH₂Cl₂ until there was very little brown color in the aqueous phase. The deep brown CH₂Cl₂ extracts were dried (Na₂SO₄) and pumped down to an oily residue which was taken up in acetonitrile (10 ml) and CH₂Cl₂ (50 ml) and filtered under gravity. Ether (30 ml) was slowly added and the solution was left to stand at room temperature for 0.5 hr before the flocculent white solid was filtered off. More ether was added to the filtrate until the solution just became cloudy. It was set aside for 3 days at 5° and the deep brown blocks were collected and washed with CH₂Cl₂-ether (1:2) and finally ether. They were recrystallized from CH₂Cl₂-acetonitrile (5:1; 60 ml) by the slow addition of ether (30 ml). A final crystallization from acetonitrile by the slow addition of aqueous NaClO₄ gave shiny black plates (0.5 g; $\Lambda = 474 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $5 \times 10^{-4} M$ in acetonitrile at 25°).

Anal. Calcd for [Co(C₂₀H₃₂As₄)(CH₃CN)O](ClO₄)₂·2H₂O: C, 28.6; H, 4.3; Cl, 7.7; N, 1.5; O, 19.1. Found: C, 29.4; H, 4.7; Cl, 7.9; N, 1.5; O, 19.2.

This compound can also be prepared in low yield by exposing *trans*-[Co(diars)₂(ClO₄)₂] in acetonitrile to oxygen. However, catalytic disproportionation occurs and the oxygen adduct is converted to the bis(acetonitrile)cobalt(III) complexes.

cis- α -[Co(*R,R*:*S,S*-tetars)SO₄](ClO₄)₂·CH₃CN. *cis*- α - or *cis*- β -[Co(*R,R*:*S,S*-tetars)(H₂O)₂](ClO₄)₃ (0.6 g) was dissolved in water (35 ml) containing acetone (5 ml) and allowed to equilibrate (~10 min). Sodium sulfate (1.0 g) in water (10 ml) was added to

this diaquo mixture (55% *cis*- α , 45% *cis*- β); there was a rapid but barely perceptible color change. Sodium perchlorate (2 g) was added and the deep red solution was extracted with CH₂Cl₂ (four 35-ml portions). The extract was dried (Na₂SO₄) and pumped to dryness giving 0.42 g of a mixture of isomers (50% *cis*- α , 50% *cis*- β). The residue was taken up in acetonitrile (60 ml); ether (60 ml) was slowly added, and the mixture was allowed to stand for 24 hr at 0°. The red blocks (0.14 g; mainly *cis*- α) were collected and washed with ethanol-ether (1:2) and finally ether. The maroon filtrate (without the washings) was set aside for the isolation of the *cis*- β isomer. The crude *cis*- α complex was recrystallized from acetonitrile (45 ml) by the addition of ether (80 ml) and re-formed as deep red plates (0.11 g) of the pure *cis*- α isomer as the acetonitrile solvate (verified by nmr; $\Lambda = 123 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $7.34 \times 10^{-4} M$ in acetonitrile at 25°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)SO₄](ClO₄)₂·CH₃CN: C, 33.9; H, 4.5; N, 1.52; S, 3.5; Cl, 3.9. Found: C, 33.8; H, 4.7; N, 1.46; S, 3.7; Cl, 4.3.

cis- β -[Co(*R,R*:*S,S*-tetars)SO₄](ClO₄)₂. To the filtrate set aside after the isolation of the *cis*- α isomer was added ether (80 ml). Small violet crystals separated after 24 hr at 0°. These (0.15 g; mainly *cis*- β) were collected and washed as described for the *cis*- α isomer. Recrystallization from acetonitrile (30 ml) and ether (50 ml) afforded small well-formed maroon-violet needles (0.12 g; $\Lambda = 116 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $7.37 \times 10^{-4} M$ in acetonitrile at 25°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)SO₄](ClO₄)₂: C, 32.7; H, 4.4; S, 3.6; Cl, 4.0. Found: C, 33.2; H, 4.6; S, 3.6; Cl, 4.4.

Δ -*cis*- α -[Co(*R,R*-tetars)SO₄](ClO₄)₂. From Δ -*cis*- β -[Co(*R,R*-tetars)(H₂O)₂](ClO₄)₃·H₂O (0.6 g), a mixture of Δ -*cis*- α and Δ -*cis*- β sulfato complexes (0.43 g) was obtained by the method described for the racemic isomers. This mixture in acetonitrile (40 ml) deposited shiny chunky red crystals (0.14 g) on addition of ether (40 ml) and after standing for 40 hr at 0°. The crystals (mainly *cis*- α) were collected and the filtrate was set aside. They were recrystallized from warm acetonitrile (40 ml) by slowly adding ether (100 ml) and re-formed as red crystals (0.1 g) of the CH₃CN solvate (confirmed by nmr; $[\alpha]_D + 441 (\pm 20)^\circ$, $[\alpha]_{578} + 488 (\pm 20)^\circ$, $[\alpha]_{546} + 147 (\pm 15)^\circ$, $[\alpha]_{436} - 604 (\pm 20)^\circ$, in acetonitrile at 25°, $1.29 \times 10^{-4} \text{ g/g}$).

Anal. Calcd for [Co(C₂₄H₃₈As₄)SO₄](ClO₄)₂·CH₃CN: C, 33.9; H, 4.5; N, 1.52; S, 3.5; Cl, 3.9. Found: C, 34.1; H, 4.7; N, 1.59; S, 3.3; Cl, 4.2.

Δ -*cis*- β -[Co(*R,R*-tetars)SO₄](ClO₄)₂. Ether (40 ml) was added to the filtrate set aside after isolation of the *cis*- α isomer, and the brown-violet clumps of needles (0.15 g) which deposited after 24 hr at 0° were collected and washed with ether. This material was recrystallized from acetonitrile (20 ml) by the slow addition of ether (60 ml). Fibrous violet needles of the pure Δ -*cis*- β isomer were obtained (0.1 g; $[\alpha]_D - 148 (\pm 15)^\circ$, $[\alpha]_{578} - 87 (\pm 15)^\circ$, $[\alpha]_{546} - 531 (\pm 25)^\circ$, $[\alpha]_{436} + 479 (\pm 20)^\circ$, in acetonitrile at 25°, $1.15 \times 10^{-4} \text{ g/g}$).

Anal. Calcd for [Co(C₂₄H₃₈As₄)SO₄](ClO₄)₂: C, 32.7; H, 4.4; S, 3.6; Cl, 4.0. Found: C, 32.3; H, 4.9; S, 3.6; Cl, 4.3.

cis- β -[Co(*R,S*-tetars)SO₄](ClO₄)₂. Sodium sulfate (0.5 g) in water (20 ml) was slowly added with stirring to *cis*- β -[Co(*R,S*-tetars)(H₂O)₂](ClO₄)₃·2H₂O⁷ (0.35 g) in water (20 ml) and acetone (2 ml). The initially orange-brown solution rapidly turned carmine red. Sodium perchlorate (2 g) in water (50 ml) was added, and the red crystals, which had deposited after 1 hr at 0°, were collected and washed with ice water and finally ether. The product was reprecipitated from acetone-water (1:1) by the addition of excess sodium perchlorate. Finally the complex (0.2 g) was recrystallized from boiling methanol (40 ml) as red-brown needles (0.1 g). A second crop of pure complex (0.05 g) was obtained by diluting the filtrate with ether (75 ml) and allowing the solution to stand for 10 hr at 0° ($\Lambda = 75 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $3.56 \times 10^{-4} M$ in methanol at 25°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)SO₄](ClO₄)₂: C, 32.7; H, 4.4; S, 3.6. Found: C, 33.1; H, 4.4; S, 3.8.

cis-[Co(diars)₂SO₄](ClO₄)₂. Sodium sulfate (0.4 g) in water (5 ml) was added to a solution of *cis*-[Co(diars)₂(H₂O)₂](ClO₄)₃ (0.3 g) in warm water (3 ml). Large red crystals began to form and these were redissolved by gently heating the solution on a steam bath. The solution was allowed to stand at 5° for 16 hr, and the crystals were then filtered and washed with a little ice water followed by a large volume of ether (0.25 g). The complex was recrystallized from acetonitrile (30 ml) by the addition of ether (70 ml), and after cooling at 5° for 16 hr, splendid orange plates were collected and washed with acetonitrile-ether (1:2) and then ether (0.2 g; $\Lambda = 73 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $4 \times 10^{-4} M$ in methanol at 25°).

Anal. Calcd for [Co(C₂₀H₃₂As₄)SO₄](ClO₄)₂: C, 29.1; H, 3.9; Cl, 4.3; S, 3.9. Found: C, 29.5; H, 4.0; Cl, 4.4; S, 3.8.

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Registry No. *cis*- α -[Co(*R,R,S,S*-tetars)Cl₂]Cl, 50805-06-6; *cis*- β -[Co(*R,R,S,S*-tetars)O₂]ClO₄, 52195-72-9; *cis*- β -[Co(*R,R,S,S*-tetars)-(H₂O)₂](ClO₄)₃, 50804-65-4; *cis*- α -[Co(*R,R,S,S*-tetars)(H₂O)₂](ClO₄)₃, 50804-67-6; H₂O₂, 7722-84-1; Δ -*cis*- α -[Co(*R,R*-tetars)Cl₂]Cl, 50805-13-5; Δ -*cis*- β -[Co(*R,R*-tetars)O₂]ClO₄, 52225-11-3; Δ -*cis*- β -[Co(*R,R*-tetars)(H₂O)₂](ClO₄)₃, 50804-59-6; *cis*-[Co(diars)₂(H₂O)₂]-

(ClO₄)₃, 50804-95-0; *cis*-[Co(diars)₂O₂]ClO₄, 52195-74-1; *trans,trans*-[CH₃CN(*R,S*-tetars)CoOOCo(*R,S*-tetars)CH₃CN](ClO₄)₄, 52195-76-3; *trans,trans*-[CH₃CN(diars)₂CoOOCo(diars)₂CH₃CN](ClO₄)₄, 52195-78-5; *cis*- α -[Co(*R,R,S,S*-tetars)SO₄]ClO₄, 52195-80-9; *cis*- β -[Co(*R,R,S,S*-tetars)SO₄]ClO₄, 52225-13-5; Λ -*cis*- α -[Co(*R,R*-tetars)SO₄]ClO₄, 52225-15-7; Δ -*cis*- β -[Co(*R,R*-tetars)SO₄]ClO₄, 52225-17-9; *cis*- β -[Co(*R,S*-tetars)(H₂O)₂](ClO₄)₃, 50883-37-9; *cis*- β -[Co(*R,S*-tetars)SO₄]ClO₄, 52225-19-1; *cis*-[Co(diars)₂SO₄]ClO₄, 52195-82-1; *cis*- β -[Co(*R,S*-tetars)O₂]ClO₄, 52304-81-8; *trans,trans*-[CH₃CN(*R,R,S,S*-tetars)CoOOCo(*R,R,S,S*-tetars)CH₃CN](ClO₄)₄, 52248-64-3; *trans,trans*-[CH₃CN(*R,R*-tetars)CoOOCo(*R,R*-tetars)CH₃CN](ClO₄)₄, 52247-98-0.

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Synthesis and Stereochemistry of Cobalt(III) Complexes of 1,3-Diamino-2-propanol and Related Ligands

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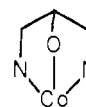
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trans-[Co(2-tmO)₂]X (I) (2-tmOH is 1,3-diamino-2-propanol, X⁻ is Cl⁻, Br⁻, ClO₄⁻) has been prepared. Its stereochemistry was determined by carbon-13 nmr. Earlier reports on the composition of this compound are in error. Complexes derived from I were *trans*-[Co(2-tmO)(2-tmOH)]Cl₂, *trans*-[Co(2-tmOH)₂]Cl₃, *cis*-[Co(2-tmOH)(2-tmOH)Cl]Cl₂, and *trans*-[Co(2-tmOH)₂Cl₂]Cl. The stereochemistry of each of these compounds was also determined by carbon-13 nmr. A convenient preparation of 2,3-diamino-1-propanol (1-tmOH) was developed and the complexes *trans*-[Co(1-tmOH)₂]Br₂ and [Co(1-tmOH)₃]Br₃ were prepared. Hydrolysis reactions of diacido complexes were studied. No complexes in which 1-tmOH served as a tridentate ligand were isolated. A previous assumption concerning the stereochemistry of [Co(tmNH₂)₂]³⁺ (tmNH₂ is 1,2,3-triaminopropane) was confirmed by carbon-13 nmr measurements.

Introduction

Our introduction to the chemistry reported in this paper came when we attempted to utilize Co³⁺ as a blocking agent for the amino groups in 1,3-diamino-2-propanol.¹ For this purpose we needed the tris(diamine)cobalt(III) complex. All our attempts to prepare this complex were frustrated by formation of [Co(2-tmO)₂]⁺ (I) although several synthetic routes were utilized. In this complex the ligand is bound in tridentate fashion. A report on the preparation of the tris(diamine) complex of 2-tmOH is in error.² In fact there have been other, earlier reports on cobalt(III) complexes of this ligand.³ In each case the complex obtained initially was incorrectly formulated.⁴

Very few studies have been made on complexes of potentially tridentate ligands of the 1,2,3-trisubstituted propane type.⁵ The behavior of 2-tmOH as a tridentate ligand was surprising to us in view of the chelate ring strain which should exist in a structure of the type⁶



We were, however, aware of recent reports on complexes of hydroxyamines which show a number of novel compositions and a variety of equilibria involving the hydroxyl groups. Most of the work, up to this time, has been concerned with 2-aminoethanol⁷ and 2-(2-aminoethylamino)ethanol (etolen),⁸ which contain primary alcohol functions. When one considers the number of hydroxylic compounds that are present in natural systems, it is surprising how little research has been done on their metal complexes. Because of the paucity of data on complexes of 1,2,3-tridentate ligands and on potentially chelating alcohols we undertook a thorough investigation of the title complex. Acid-base equilibria which exist for this complex allow the formation of a large number of interesting species. Carbon-13 nmr was particularly useful for assignment of stereochemistry to these species. Complexes of the isomeric ligand 2,3-diamino-1-propanol (1-tmOH) are also reported. Alcohols are not normally considered to be good ligands but the work reported here, as well as that al-

(1) Hereafter 1,3-diamino-2-propanol is abbreviated 2-tmOH; its alkoxide form is 2-tmO. In metal-complexed form the alkoxide is always coordinated while 2-tmOH indicates coordination of the protonated form.

(2) W. C. Drinkard and H. F. Bauer, *J. Amer. Chem. Soc.*, **82**, 5031 (1960).

(3) (a) F. G. Mann, *J. Chem. Soc.*, 2904 (1927); (b) J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Chem.*, **17**, 331 (1939).

(4) As [Co(2-tmOH)₂(OH)₂]⁺. This complex was reported to lose 2 mol of water upon heating to give *trans*-[Co(2-tmO)₂]⁺.

(5) The only complete study, which includes assignment of stereochemistry, is that on the Co^{III}L₂⁺ complexes of H₂NCH₂CH₂(NH₂)CO₂⁻: W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

(6) An examination of molecular models indicates that meridional binding of a ligand of this type is impossible contrary to what is sometimes assumed. See H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Van Nostrand, New York, N. Y., 1960, p 155.

(7) (a) H. Yoneda and S. Kida, *J. Amer. Chem. Soc.*, **82**, 2139 (1960); V. V. Udovenko and A. N. Gerasenkova, *Russ. J. Inorg. Chem.*, **11**, 1105 (1966); V. V. Udovenko and L. G. Reiter, *ibid.*, **15**, 958 (1970); V. V. Udovenko, O. N. Stepanenko, and B. G. Eroshok, *Russ. J. Inorg. Chem.*, **17**, 1409 (1972); (b) K. Ohashi, J. Fujita, B. Shimoyama, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 2422 (1968); Y. Kuge and S. Yamada, *ibid.*, **42**, 2552 (1969); R. L. Dotson, *J. Inorg. Nucl. Chem.*, **34**, 3131 (1972).

(8) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **82**, 2992 (1960); B. Das Sarma, G. J. Tennenhouse, and J. C. Bailar, Jr., *ibid.*, **90**, 1362 (1968); J. A. Broomhead, *ibid.*, **90**, 4480 (1968); B. Das Sarma, and J. C. Bailar, Jr., *ibid.*, **91**, 5958 (1969); J. Bassett, R. Grzeskowiak, and B. L. O'Leary, *J. Inorg. Nucl. Chem.*, **32**, 386 (1970).