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Dissymmetric Arsine Complexes. Cobalt Hydrides and Cobalt Dioxygen Complexes

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Cobalt hydrido and "sideways" bonded dioxygen complexes have been prepared. The complexes contain two linear quadridentate arsine ligands, one of which is flexible in the topologies it can adopt while the other forces a cis-α topology of the complexes. It is found that the protic and hydridic character of the hydrido ligands is modified by the imposition of a cis-α topology. The "sideways" bonded dioxygen complexes are best described as cobalt(III) peroxide species and their stability is essentially unaffected when the coordination angle trans to the dioxygen moiety is less than 90°.

Conventional cobalt complexes, namely, those with "hard" donor ligands, are decomposed to the metal in the presence of hydride ions, and the dioxygen complexes, which are usually derived from the divalent oxidation state, invariably give either the μ-peroxo dimers or superoxo monomers.[1,2] With "soft" donor atoms, such as phosphorus or arsenic, or with the cyanide ligand, by contrast, hydride ion reduction generally produces hydrido complexes of varying stability[3–8] and the now-accessible cobalt(I) state reacts with oxygen to give "sideways" bonded dioxygen complexes of remarkable stability.[9,10] It is evident from the high intensities of the d–d transitions and the drastically reduced (free-ion) interelectronic repulsions,[11–13] that the d orbitals of the metal have become more diffuse and polarizable when the metal is surrounded by soft ligands, and it has been suggested[8,13] that it is this property which gives rise to the stability of the hydrides, the "sideways" bonded dioxygen species, the accessibility of the cobalt(I) state, and the consequent organometallic reactivity. Given that these electronic conditions are fulfilled, there remains an intriguing stereochemical feature which may determine the reactivity of the hydrides and the stability of the dioxygen complexes.

Both of the "sideways" bonded dioxygen–cobalt complexes which have had their (crystal) structures determined, one with phosphine[9] and the other with arsine ligands,[14] are grossly distorted octahedra. In particular, the donor atom–cobalt angle trans to the cobalt–dioxygen plane is large (~110°) (see Figure 4) and similar to the corresponding angles observed for rhodium and iridium dioxygen complexes.[15,16] This has led to the inference that the bonding and oxidation state of these species may be unusual and that the bonding may be described by schemes reminiscent of the Chatt–Dewar model for ethylene binding.

The other stereochemical aspect relates to the dichotomous chemical reactivity of dihydrocobalt complexes, where it is observed for the *cis*-$[\mathrm{Co(diars)_2(H)_2}]^+$ ion (diars = *o*-phenylenebis(dimethylarsine)) that, after the first hydrido ligand is induced to react as a hydride, the trans monohydrido species so formed displays no hydridic character under normal conditions.[8] The second hydrido ligand reacts as a proton. This probably also obtains for the (diphos)$_2$ analogue of Sacco,[5] although it has not been investigated in the same detail. The question then arises as to whether this dichotomous reactivity is a consequence of the cis to trans rearrangement which occurs after the release of the first hydride.

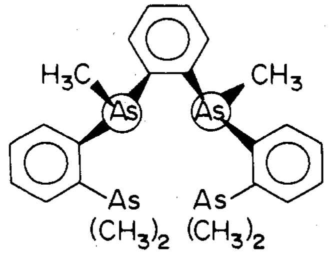
This paper describes some of the hydrido and dioxygen complexes of cobalt associated with two linear quadridentate arsine ligands, one of which is flexible in the topologies it can adopt and the other is rigid and forces a cis arrangement of the two remaining octahedral positions, while, at the same time, the arsenic–cobalt–arsenic angle trans to the two substitutional sites cannot expand beyond 90°.

1. Stereochemistry

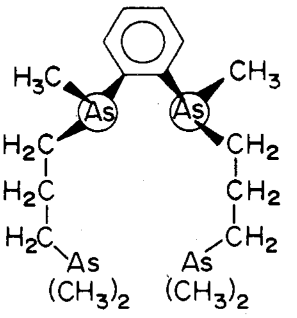
The structures of the two arsines used are shown in Figure 1, and it will be noted that both have racemic configurations of the inner arsenic atoms, which are geometrically stable under the present experimental conditions. We have shown elsewhere[17] that the racemic fars ligand can adopt any of the cis-α, cis-β, and trans topologies about an octahedral metal center, and there appears to be no strong preference for any one of these. The racemic qars ligand, by contrast, is inflexible and only adopts the symmetrical cis-α geometry.[17] Indeed, so strong does this preference seem to be, that the crystal structure of $[\mathrm{Pd}(R,R{:}S,S\text{-qars})\mathrm{Cl}]\mathrm{ClO_4}$ resembles a cis-α octahedral complex with a vacant site.[18] Moreover, the inner arsenic–palladium–arsenic angle is 82°.

2. Hydrides

When the deep green *cis*-α-$[\mathrm{Co}(R,R{:}S,S\text{-fars})\mathrm{Br_2}]\mathrm{Br}$ complex is reduced with $\mathrm{BH_4^-}$ ions in neutral aqueous methanol, a transient straw yellow solution is produced which rapidly fades in the presence of oxygen to produce the deep brown "sideways" bonded dioxygen adduct *cis*-β-$[\mathrm{Co}(R,R{:}S,S\text{-fars})\mathrm{O_2}]^+$. The straw yellow solution contains *trans*-$[\mathrm{Co}(R,R{:}S,S\text{-fars})(\mathrm{H})\mathrm{Br}]^+$ which, under the basic reaction conditions, is deprotonated to give a Co(I) species which reacts with oxygen. If, however, the reduction is carried out under acidic conditions, with acetic acid, the deprotonation is suppressed and the yellow *trans*-$[\mathrm{Co}(R,R{:}S,S\text{-fars})(\mathrm{H})\mathrm{Br}]\mathrm{ClO_4}$ complex can be isolated. In acidic or neutral solutions



racemic – Qars



racemic – Fars

Figure 1. Structures of the arsines *R*,*R*:*S*,*S*-qars (top) and *R*,*R*:*S*,*S*-fars (bottom).

this hydrido complex is unreactive to oxygen, but it does slowly decompose in both solutions and in the solid state to give arsine and Co(II). This is probably a Co(II)-catalyzed decomposition which is characteristic of cobalt(III) arsine complexes, even without hydrido ligands.[13] Addition of excess BH_4^- does not produce a stable dihydrido species.

When, however, the *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl$_2$]Cl complex is treated with excess BH_4^- in acidic methanol solution, the off-yellow *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$ complex can be isolated and is conveniently stable under nitrogen. The stability of dihydrido species when the system contains only *o*-phenylene chelate bridges and their instability when trimethylene chelate bridges are present are similar to the difference[8] observed between the tetars and diars ligands, of which only the latter gives stable dihydrocobalt complexes. This, in part, may be related to the rigidity of the *o*-phenylene link which leads to a greater general stability of the complexes, but also, it is probable[8] that the production of the very unstable Co(I) species is suppressed, by virtue of the lower acidity of the dihydrido species when only *o*-phenylene linkages are present.

Under similar conditions to those required for the preparation of the *trans*-[Co(*R*,*R*:*S*,*S*-fars)(H)Br]$^+$ ion, the *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl$_2$]$^+$ ion is reduced to the bright orange-yellow *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)Cl]$^+$ ion which, as its perchlorate salt, is stable as the solid for only a few minutes under nitrogen at 25° and in solutions very rapidly decomposes. In the presence of oxygen, the decomposition partly involves the release of HCl and the production of the dioxygen complex. There thus appears to be an inherent instability associated with *cis*-hydridohalogenocobalt arsine complexes which is not observed[8] with the trans species. This instability has also been observed with the [Co(ttas)(H)Cl]ClO$_4$ complex, where ttas is the tripod ligand As(CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$)$_3$[19] which fixes the hydrido and chloro ligands in cis positions.

There is also a distinct difference between the reactivities of the *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$ and *cis*-[Co(diars)$_2$(H)$_2$]ClO$_4$ complexes with acids (HX) where the latter gives off only 1 equiv of H$_2$ and produces the corresponding *trans*-[Co(diars)$_2$(H)X]$^{n+}$ ions. At low temperatures, 5 *N* HCl reacts with *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]$^+$ to produce first the yellow *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)Cl]$^+$ ion which, upon warming, reacts further to release a second equivalent of H$_2$ and *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl$_2$]$^+$ is quantitatively produced. A similar two-step reaction occurs under analogous conditions when 5 *N* HClO$_4$ is used and maroon *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H$_2$O)$_2$](ClO$_4$)$_3$ is eventually precipitated. Thus, unlike the topologically flexible [Co(diars)$_2$(H)$_2$]$^+$ ion, both hydrido ligands of *cis*-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]$^+$ can be induced to react as hydrides.

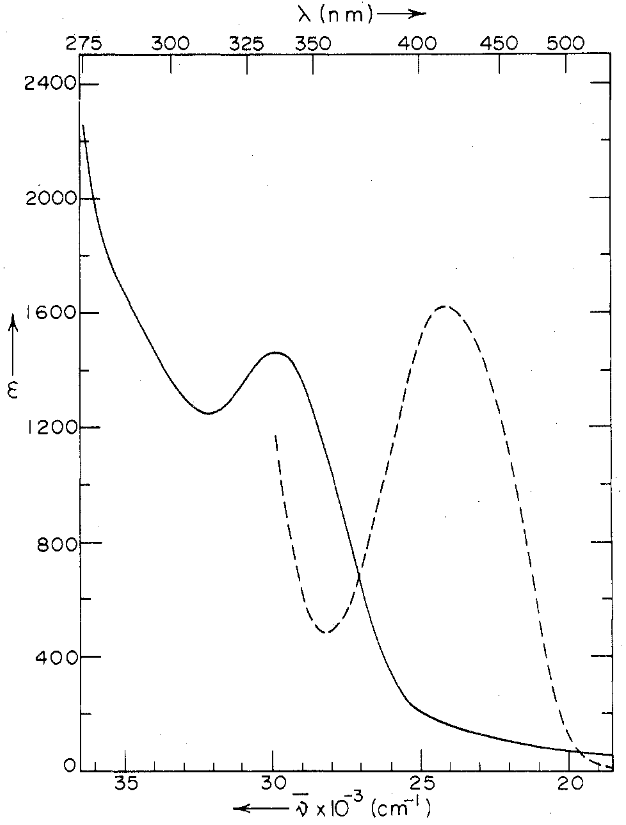


Figure 2. Visible absorption spectra of *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$ (——) in methanol and *trans*-[Co(*R*,*R*:*S*,*S*-fars)(H)Br]ClO$_4$ (- - - -) in acetone. Both were measured under hydrogen.

The precise reasons for the hydridic character and the instability of *cis*-hydrido–X complexes and the protic character and stability of the trans species are not obvious except that, in the former, the hydrido ligand is forced trans to a strong-field arsenic donor atom which may have a labilizing influence. Whatever the reasons, however, these modifications in hydrido ligand reactivity may be significant in the design of hydrogenation catalysts, which generally behave as if one hydrido ligand transfers as a hydride and then the second inserts as a proton into the incipiently formed metal–carbon bond.

Figure 2 shows the absorption spectra of the two hydrido complexes. The clearly resolved absorption bands of the two complexes represent the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions of cobalt(III) systems.[8] This same band of the [Co(diars)$_3$]$^{3+}$ ion occurs at 23200 cm^{-1} (431 mμ)[12] and, as can be seen, replacing two (strong field) arsenic donor atoms with two hydrides causes this band to shift some 7000 cm^{-1} to higher energies. Thus the hydrido ligand in these cobalt(III) species exerts the highest known crystal field, suggesting that the cobalt–hydride bond is strongly covalent despite its high (kinetic) reactivity.

3. Dioxygen Complexes

There are two distinct ways of preparing the "sideways" bonded dioxygen complex *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)O$_2$]ClO$_4$. One involves the reaction of *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)-

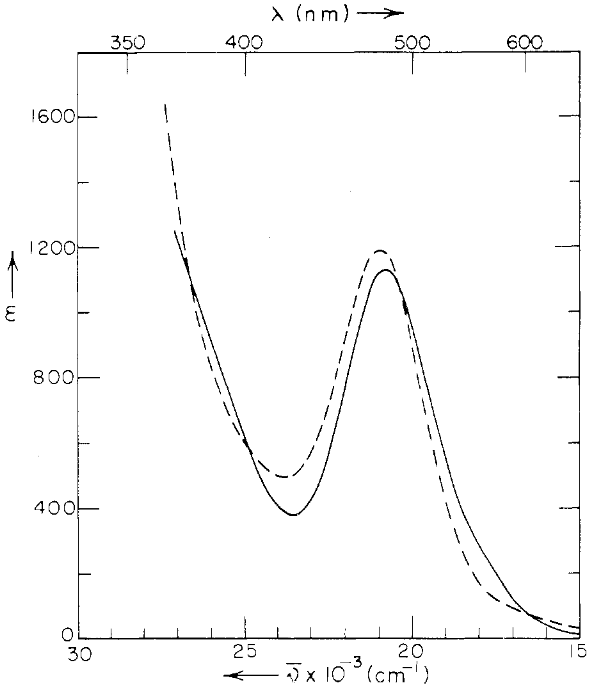


Figure 3. Visible absorption spectra of *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)-O_2]ClO_4 (——) and *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)O_2]ClO_4 (- - - -). Both are in methanol solutions.

$(H_2O)_2](ClO_4)_3$[20] with excess H_2O_2 in aqueous solution

$$cis\text{-}\alpha\text{-}[Co(R,R{:}S,S\text{-fars})(H_2O)_2]^{3+} + H_2O_2 \rightarrow cis\text{-}\beta\text{-}[Co(R,R{:}S,S\text{-fars})O_2]^{+} + 2H_3O^{+}$$

This reaction is catalytically controlled[10] and is accompanied by considerable decomposition. The other, much cleaner, reaction involves the generation of a very reactive Co(I) species from the *trans*-[Co(*R*,*R*:*S*,*S*-fars)(H)Br]$^+$ ion by the action of base (triethylamine)

$$trans\text{-}[Co^{III}(R,R{:}S,S\text{-fars})(H)Br]^{+} + B \rightarrow [Co^{I}(R,R{:}S,S\text{-fars})Br]^{0} + BH^{+}$$

The Co(I) species then reacts with oxygen to give the "sideways" bonded adduct

$$[Co^{I}(R,R{:}S,S\text{-fars})Br] + O_2 \rightarrow cis\text{-}\beta\text{-}[Co(R,R{:}S,S\text{-fars})O_2]^{+} + Br^{-}$$

The *cis*-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]$^+$ ion reacts somewhat differently from the *cis*-[Co(diars)$_2$(H)$_2$]$^+$ analog with O_2. In neutral protic or aprotic solvents, the latter spontaneously releases 1 equiv of H_2 and absorbs 1 equiv of O_2 to form [Co(diars)$_2O_2$]$^+$.[10] The qars analogue, presumably because the hydrido ligands are not as acidic, does not spontaneously absorb oxygen to any extent, but rather, the reaction requires base to initiate the removal of a (single) proton before rapid and complete oxygen uptake occurs. Since 1 equiv of hydrogen is liberated during the base-catalyzed reaction, we conclude that a cobalt(I)–hydrido species, *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)H]^0, is the entity involved in the oxygen uptake.

The observation that both hydrido ligands in the *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]$^+$ ion can also be induced to react as hydrides with acids provided the basis for a second route to the "sideways" bonded dioxygen species. Since H_2O_2 is mildly acidic, it was anticipated that this would induce the release of two hydrides (eq 1) to produce a Co(III) complex which

$$cis\text{-}\alpha\text{-}[Co(R,R{:}S,S\text{-qars})(H)_2]^{+} + H_2O_2 \rightarrow cis\text{-}\alpha\text{-}[Co(R,R{:}S,S\text{-qars})O_2]^{+} + 2H_2 \qquad (1)$$

would then react with the incipiently formed O_2^{2-} ion. This proved to be the case.

Both complexes are subject to catalytic decomposition in the presence of Co(II) impurities but the pure complexes are very stable in neutral media. Of the two, the qars–O_2 complex is the more stable. The high stability, which resembles that observed for normal Werner complexes, suggests that they are best regarded as peroxocobalt(III) complexes. This is confirmed by their absorption spectra which are shown in Figure 3. These d–d absorption bands ($^1A_{1g} \rightarrow {}^1T_{1g}$) occur at similar energies and are of similar intensity as observed for the corresponding $^1A_{1g} \rightarrow {}^1T_{1g}$ bands of cobalt(III) arsine complexes containing two oxygen donor atoms. There is no reason to suppose, therefore, that, either chemically or electronically, these dioxygen complexes are in any peculiar sense different from, for example, the corresponding carbonato complexes.

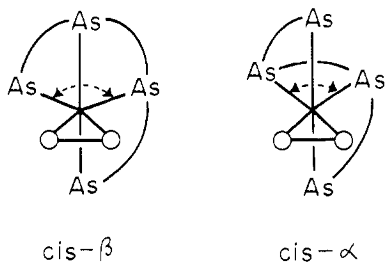


Figure 4. "Sideways" bonded dioxygen complexes formed by linear quadridentate arsines in the cis-β and cis-α topologies. The figures are meant to illustrate, diagrammatically, how the cis-β complexes can expand the coordination angle trans to the dioxygen moiety and how the cis-α topology constrains this angle by means of the chelate bridge linking the inner two arsenic atoms. The angles in question are indicated by dotted braces.

Table I. NMR Data at 60 MHz

Complex	(As–CH_3),[a] Hz	Solvent (30°)
cis-β-[Co(*R*,*R*:*S*,*S*-fars)-CO_3]ClO_4	76.7, 89.0, 90.0, 96.6, 104.8, 105.5	CD_3CN
cis-α-[Co(*R*,*R*:*S*,*S*-fars)-$(H_2O)_2$]$(ClO_4)_3$	80.4, 101.0, 120.9	D_2O-$HClO_4$[b]
cis-β-[Co(*R*,*R*:*S*,*S*-fars)-O_2]ClO_4	64.5, 72.7, 76.5, 85.4, 98.1, 104.1	CD_3CN
trans-[Co(*R*,*R*:*S*,*S*-fars)-(H)Br]ClO_4	101.4, 102.7,[c] 105.6, 108.5, 123.3	CF_3COOH
cis-α-[Co(*R*,*R*:*S*,*S*-qars)-$(H)_2$]ClO_4	100.0, 106.2, 116.5	DMSO-d_6
cis-α-[Co(*R*,*R*:*S*,*S*-qars)-O_2]ClO_4	84.7, 91.3, 143.7	CD_2Cl_2

[a] All values relative to internal TMS except those for D_2O where internal DSS was used. [b] One drop of concentrated $HClO_4$. [c] Represents six protons.

The fars–O_2 complex adopts exclusively the cis-β topology, presumably so that the angle trans to the dioxygen moiety can expand (Figure 4) but this cannot be crucial electronically nor can it be crucial insofar as the stability is concerned, because the qars complex, in which the trans angle cannot expand beyond 90°, has an almost superimposable absorption spectrum (Figure 3) and it is the most stable of all the cobalt–arsine–("sideways")dioxygen complexes so far prepared.[10]

4. Stereochemistry

In most cases the NMR methyl proton signals unambiguously determine the topologies of these complexes simply on the basis of symmetry. Table I lists the chemical shifts of these resonances for the various complexes prepared. It will be seen that, except for the [Co(*R*,*R*:*S*,*S*-fars)(H)Br]$^+$ ion, the assignments are unambiguous in the absence of accidental equivalence. The trans assignment for the bromohydrido species is based on the fact that all of the monohydrido complexes formed by both tetars and diars ligands have a trans topology.[8] Moreover, the hydride chemical shift of this monohydrido species (τ 36.8 in DMSO-d_6) is characteristic of *trans*-[Co(As)$_4$(H)X]$^{n+}$ complexes, and in conformity with the (paramagnetic shielding) theory of hydrido chemical shifts,[21] this trans hydrido resonance occurs at higher fields than the (equivalent) cis hydrido resonances in *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$ (τ 26.7 in DMSO-d_6).

5. Experimental Section

The instrumentation and the methods of product analysis were the same as those described in detail elsewhere.[8,10]

***cis*-β-[Co(*R*,*R*:*S*,*S*-fars)CO$_3$]ClO$_4$·NaClO$_4$.** To a warm solution of *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Cl$_2$]ClO$_4$[17] (0.5 g) in water (30 ml) and methanol (10 ml) was added a solution of Na$_2$CO$_3$ (0.09 g) in water (1 ml). The resultant solution was heated on a steam bath for 10 min, during which time the initial violet color changed gradually to a deep red. The solution was filtered and NaClO$_4$ (5 g) was added to the filtrate, which was pumped down at 40° to a volume of about 2–3 ml. After cooling of the solution in ice, the small red needles were collected and washed with ether.

The product was taken up in acetonitrile (15 ml); it was filtered, and the solution was diluted with ether (15 ml). After 3 days at 5° the resultant red blocks were collected, washed with 20% acetonitrile in ether, and finally washed with ether. A second recrystallization from acetonitrile–ether gave the pure carbonato complex (0.3 g). [The compound is explosive when heated and satisfactory analysis has been difficult to obtain.] Anal. Calcd for [Co(C$_{18}$H$_{34}$As$_4$)CO$_3$]ClO$_4$·NaClO$_4$: C, 25.6; H, 3.8; Cl, 8.0; O, 19.8. Found: C, 26.1; H, 3.9; Cl, 8.2; O, 20.7.

***cis*-β-[Co(*R*,*R*:*S*,*S*-fars)(H$_2$O)$_2$](ClO$_4$)$_3$.** Concentrated perchloric acid (5 ml) was poured onto solid *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)CO$_3$]ClO$_4$·NaClO$_4$ (1.0 g.) in a large boiling tube. The substance reacted with vigorous effervescence and, after this had subsided, the deep burgundy solution was filtered (sinter) and *then* diluted with water (5 ml). The resulting mixture was warmed for a few minutes on a steam bath and after it was allowed to stand at 5° for 2 hr, the deep red-violet plates were collected and washed with a large amount of ether.

The compound was taken up in concentrated perchloric acid (8 ml) and *then* slowly diluted with water (8 ml). After 1 day at 5°, the pure diaquo complex was collected and washed with cold 6 *N* HClO$_4$ and then with ether (0.8 g). Λ_M = 331 ohm^{-1} cm^2 mol^{-1} (9.79 × 10^{-4} *M* in H$_2$O at 26.5°). Anal. Calcd for [Co(C$_{18}$H$_{34}$As$_4$)(H$_2$O)$_2$](ClO$_4$)$_3$: C, 22.9; H, 4.1; Cl, 11.3. Found: C, 23.2; H, 4.3; Cl, 11.4.

***trans*-[Co(*R*,*R*:*S*,*S*-fars)(H)Br]ClO$_4$.** *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Br$_2$]Br[17] (0.25 g) was dissolved in methanol (10 ml) and glacial acetic acid (0.5 ml) and stirred under nitrogen as NaBH$_4$ (0.05 g) in methanol (10 ml) was added at a rapid drop rate. The color of the solution changed from the original deep green to a straw yellow. Immediately after the BH$_4^-$ addition was completed, a solution of NaClO$_4$ (2 g) dissolved in deoxygenated water (75 ml) was added over a period of 2 min. Fine yellow crystals separated from the solution. After stirring of the mixture for 5 min, these were collected and washed with water, then with 10% methanol in ether, and, finally, with ether.

The product was recrystallized from acetone by the slow addition of ether. After 10 hr at 0°, the resultant golden-yellow needles were filtered and washed with 10% acetone in ether and then with ether (0.15 g). Stability: the solid is only stable for a few hours at 25°. Λ_M = 140 ohm^{-1} cm^2 mol^{-1} (8.00 × 10^{-4} *M* in acetone at 25°). Anal. Calcd for [Co(C$_{18}$H$_{34}$As$_4$)(H)Br]ClO$_4$: C, 27.4; H, 4.5; Cl, 4.5; Br, 10.1. Found: C, 27.3; H, 4.6; Cl, 4.7; Br, 10.4.

***cis*-β-[Co(*R*,*R*:*S*,*S*-fars)O$_2$]ClO$_4$. Method 1.** To a stirred solution of *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)(H$_2$O)$_2$](ClO$_4$)$_3$[20] (1.0 g) in water (20 ml) was added 30% H$_2$O$_2$ (4 ml). The mixture was allowed to stand at 25° for 10 min and the now deep brown solution was extracted with CH$_2$Cl$_2$ (three 40-ml portions). The brown extracts were gravity filtered and then pumped to dryness at 30° leaving a brown solid. This was taken up in CH$_2$Cl$_2$ (25 ml) and CH$_3$CN (5 ml) and crystallized by adding ether to the cloud point. After the solution was allowed to stand at 5° for 5 days, the brown needles were collected and washed with ether. A second recrystallization from CH$_2$Cl$_2$ and ether yielded small lustrous brown needles of the dioxygen complex (0.2 g).

Method 2. To a solution of *trans*-[Co(*R*,*R*:*S*,*S*-fars)(H)Br]ClO$_4$ (0.2 g) in methanol (10 ml) was added 2 drops of triethylamine and the solution was stirred in air for 10 min. The brown solution was diluted with NaClO$_4$ (2 g) in water (100 ml) and extracted with CH$_2$Cl$_2$ and purified as described in method 1 (0.1 g). Λ_M = 83 ohm^{-1} cm^2 mol^{-1} (8.31 × 10^{-4} *M* in H$_2$O at 26.5°). Anal. Calcd for [Co(C$_{18}$H$_{34}$As$_4$)O$_2$]ClO$_4$: C, 29.2; H, 4.6; Cl, 4.8; O, 13.0; As, 40.5. Found: C, 29.4; H, 4.8; Cl, 4.9; O, 12.8; As, 40.8.

***cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$.** *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl$_2$]Cl[17] (0.25 g) was dissolved in methanol (10 ml) and concentrated hydrochloric acid (0.25 ml). The solution was brought to 60° under nitrogen and vigorously stirred as NaBH$_4$ (0.3 g) in methanol (25 ml) was added at a rapid drop rate. After about 10 ml of the BH$_4^-$ solution was added, the initial violet solution turned orange-yellow (*cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)Cl]$^+$) and then turned darker yellow-brown at the end of the addition. Immediately following the BH$_4^-$ addition, a hot solution of NaClO$_4$ (1.25 g) in deoxygenated water (35 ml) was added to the vigorously stirred reaction mixture. Stirring was continued as the mixture was allowed to cool slowly to 30°. The off-yellow crystals were collected and washed first with water, then with 25% methanol in ether (50 ml), and finally with ether.

The product was taken up in hot methanol (25 ml) containing NaBH$_4$ (0.05 g) and was quickly filtered into a hot solution of NaClO$_4$ (1 g) in water (25 ml). The whole mixture was allowed to cool slowly to 25° under the hydrogen generated from the BH$_4^-$ in the aqueous methanol. Fine pale needles of the pure dihydrido complex were formed. These were collected and washed as before (0.2 g). The solid product is stable for only a few hours and was analyzed at once. Λ_M = 83 ohm^{-1} cm^2 mol^{-1} (9.49 × 10^{-4} *M* in methanol at 26° under N$_2$). Anal. Calcd for [Co(C$_{24}$H$_{30}$As$_4$)(H)$_2$]ClO$_4$: C, 37.0; H, 4.1; Cl, 4.6. Found: C, 36.8; H, 4.2; Cl, 4.5.

***cis*-α-[Co(*R*,*R*:*S*,*S*-qars)O$_2$]ClO$_4$. Method 1.** Triethylamine (0.1 ml) was added to a stirred solution of *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$ (0.4 g) in methanol (125 ml). The solution was exposed to the air and vigorously stirred for 10 min during which time a deep red-brown solution was formed. Ether (200 ml) was then added and the solution was allowed to stand at 5° for 24 hr. Small deep brown blocks were formed. These were collected and washed with 10% methanol in ether and finally with ether. The pure dioxygen complex was obtained after recrystallization from warm methanol by the slow addition of ether (0.15 g).

Method 2. *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H)$_2$]ClO$_4$ (0.4 g) was dissolved in methanol (125 ml) and a 6% H$_2$O$_2$ (5 ml) solution in methanol (25 ml) was added to it. Vigorous evolution of hydrogen occurred and the solution turned a deep red-brown. After 5 min, the reaction was complete and the product was isolated as described above (0.2 g). Λ_M = 65 ohm^{-1} cm^2 mol^{-1} (1.12 × 10^{-3} *M* in methanol at 25°). Anal. Calcd for [Co(C$_{24}$H$_{30}$As$_4$)O$_2$]ClO$_4$: C, 35.6; H, 3.7; Cl, 4.4; As, 37.1. Found: C, 35.6; H, 3.7; Cl, 4.3; As, 37.0.

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Registry No. *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)CO$_3$]ClO$_4$, 55648-79-8; *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)(H$_2$O)$_2$](ClO$_4$)$_3$, 57395-92-3; *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)(H$_2$O)$_2$](ClO$_4$)$_3$, 57456-85-6; *trans*-[Co(*R*,*R*:*S*,*S*-fars)(H)Br]ClO$_4$, 57395-94-5; *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)O$_2$]ClO$_4$, 57427-76-6; *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)(H$_2$)]ClO$_4$, 57395-96-7; *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)O$_2$]ClO$_4$, 57395-98-9; *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Cl$_2$]ClO$_4$, 55648-81-2; *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Br$_2$]Br, 55648-82-3; *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl$_2$]Cl, 55648-83-4; H$_2$O$_2$, 7722-84-1; HCl, 7647-01-0.

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Assignment of Mechanism to Titanium(III) Reductions of Cobalt(III) Complexes. Hard and Soft Theory as a Means of Assessing Bridging Ligands for Inner-Sphere Electron Transfer

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The hexaaquotitanium(III) reductions of the cobalt(III) complexes $Co(NH_3)_5X^{(3-n)+}$, with $X^{n-} = F^-, Cl^-, Br^-, I^-, SO_4^{2-}$, NH_3, H_2O, and DMN (*N,N*-dimethylnicotinamide), $Co(bpy)_3^{3+}$, and the μ-superoxo complex $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ have been studied at 25 °C, $I = 0.5$ M (LiCl). The dependence of second-order rate constants, k_{obsd}, on [H+] has been investigated over the range 0.05–0.44 M and is of the general form $k_{obsd} = k_0 + k_1[H^+]^{-1}$, where k_1 is effective in all cases, but k_0 is detected only for $Co(NH_3)_5I^{2+}$ and the μ-superoxo complex. For the complex $X^{n-} = F^-$ the [H+] dependence takes the form $1/k_{obsd} = a + b[H^+]$, where the magnitude of the parameters a and b is indicative of precursor complex formation. From a comparison of rate constants with those for $Ru(NH_3)_6^{2+}$ and V^{2+} reductions of the same complexes (log–log plots), it is concluded that the Ti(III) reductions of $Co(NH_3)_5SO_4^+$, $Co(NH_3)_5(O_2CCH_3)^{2+}$, and the μ-superoxo complex are also inner sphere and that other reactions studied are outer sphere. Potential bridging ligands in these and other reactions can be assessed in terms of the hard and soft acid–base concept.

Recently Martin and Gould[1] have investigated the Ti(III) reduction of carboxylatopentaamminecobalt(III) complexes and from the rate constant pattern concluded that carboxylate functions as a bridging ligand for inner-sphere electron transfer. From the [H+] dependence Birk[2] has obtained evidence for precursor complex formation (and therefore an inner-sphere mechanism) in the Ti(III) reduction of $Co(NH_3)_5N_3^{2+}$. Information on the Ti(III) reductions of $Co(NH_3)_5Cl^{2+}$, and *cis*- and *trans*-$Co(en)_2Cl_2^+$ has been obtained by Orhanovic and Earley,[3] but inner- or outer-sphere assignments remain in some doubt. At the same time we have been studying the Ti(III) reduction of other $Co(NH_3)_5X^{(3-n)+}$ complexes, $Co(bpy)_3^{3+}$ and $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$, with a view to assigning inner- or outer-sphere mechanisms. The Ti(III) reductions of vanadium(IV) and -(V)[4,5] have previously been reported from these laboratories. Other Ti(III) redox studies have also been reported.[6-8]

Experimental Section

Titanium(III) Solutions. Titanium metal sponge (Johnson and Matthey Chemicals Ltd., 0.5 g) was dissolved in concentrated hydrochloric acid (10 ml) maintained at 40–50 °C (ca. 6 h) in air-free conditions. Excess solid was removed using a porosity No. 4 filter, and the solution was diluted sixfold with N_2-degassed water. The Ti(III) was standardized by addition of an excess of Ce(IV) and back-titrating with Fe(II) in 1 M H_2SO_4 using ferroin as indicator. The absorption coefficient, ϵ 3.97 M^{-1} cm^{-1} at 502 nm, was used for subsequent standardizations. The hydrogen ion concentration was determined by passing aliquot portions down a column of Amberlite IR 120(H) cation-exchange resin. The [H+] of the eluent solution was determined by titration with 0.1 M NaOH. Stock solutions had [Ti(III)] = 0.08–0.17 M and [H+] = 0.4–1.0 M, with [Ti(IV)] ≤ 1% of the [Ti(III)]. Solutions were stored in air-free conditions at 0 °C for up to 2 weeks.

Table I. Details of Uv–Visible Spectra of Cobalt(III) Complexes (from Ref 19 Except As Stated)

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$Co(NH_3)_5F^{2+}$	352^a	38	511	45
$Co(NH_3)_5Cl^{2+}$	362^a	45	530	47.3
$Co(NH_3)_5Br^{2+}$			551^a	53
$Co(NH_3)_5I^{2+}$	388	2700	580^a	79
$Co(NH_3)_5H_2O^{3+}$	345^a	44	492	47
$Co(NH_3)_5SO_4^{+\ b}$	357^a	34.8	517	65.5
$Co(NH_3)_5(DMN)^{3+\ c}$	334^a	86.5	475	63.2
$Co(NH_3)_6^{3+}$	339^a	47	473^a	58
$Co(bpy)_3^{3+\ d}$			448^e	67.9
$[(NH_3)_5Co]_2O_2^{5+\ f}$	297^a	2.45×10^4	670^a	890

[a] Wavelength used for kinetic studies. [b] Reference 13. [c] Reference 18. [d] Reference 24. [e] Kinetics followed at 420 nm (ϵ 57.1 M^{-1} cm^{-1}). [f] See, e.g., A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 36 (1970).

Cobalt(III) Complexes. The complexes $Co(NH_3)_5F^{2+}$,[9] $Co(NH_3)_5Cl^{2+}$,[10] $Co(NH_3)_5Br^{2+}$,[11] $Co(NH_3)_5I^{2+}$,[12] $Co(NH_3)_5SO_4^+$,[13] $Co(NH_3)_5H_2O^{3+}$,[14] $Co(NH_3)_6^{3+}$,[15] $Co(bpy)_3^{3+}$,[16] and $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ [17] were prepared as chloride salts, and $Co(NH_3)_5(DMN)^{3+}$ was prepared as the perchlorate salt.[18] Uv–visible spectra were in good agreement with existing literature values, Table I.

Other Reagents. Solutions of chromium(II) perchlorate, $LiClO_4$, and $HClO_4$ were prepared as described previously.[20] Lithium chloride (Hopkin and Williams Reagent grade) was recrystallized twice. The hydrochloric acid was Analar grade reagent.

Rate Measurements. All reactions conform to the stoichiometric equation

$$Ti(III) + Co(III) \rightarrow Ti(IV) + Co(II) \qquad (1)$$

except with the μ-superoxo complex where the reduction $\mu(O_2^-) \rightarrow \mu(O_2^{2-})$ occurs. Reactions were monitored by following absorbance (A) changes at peak positions of the oxidant, Table I. The Ti(III) reactant was in large (generally >10-fold) excess. Plots of log ($A_t - A_\infty$) against time were linear to >80% reaction for all but Co-