

and an excess of ligand TTP (0.3 g, 0.00112 mol) were stirred together in nitromethane (50 ml) for about 4 hr. The resulting mixture was filtered giving an orange filtrate which was concentrated to about 10 ml. Upon addition of ether, an orange microcrystalline product separated. The complex was purified by recrystallization from a minimum amount of hot acetonitrile.

Method 2. *cis*-[Co(TTP)Cl₂]₂BF₄ was dissolved with stirring in hot water, and an excess of sodium nitrite was added. The dark red-violet solution, which turned orange almost immediately, was allowed to boil for 30 min. The solution was then cooled and filtered, and the water was removed by evaporation. The orange microcrystalline product was purified by recrystallization from hot acetonitrile.

Anal. Calcd for [Co(C₁₀H₂₀S₄)(NO₂)₂]₂BF₄: C, 23.72; H, 3.98; N, 5.53. Found: C, 23.63; H, 4.07; N, 5.29.

***trans*-Dichloro(13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)-cobalt(III) Perchlorate.** Cobalt(II) perchlorate hexahydrate was stirred in nitromethane with an excess of the ligand TTX. The resulting red-brown solution was filtered, and ether was added to the filtrate. The red-brown microcrystalline product which separated, [Co(TTX)](ClO₄)₂, was isolated by filtration and redissolved in nitromethane. An excess of lithium chloride was added and the mixture was stirred for 10 min. The resulting green solution was filtered, and the filtrate was concentrated to a few milliliters. Addition of ether to this solution caused a green microcrystalline product to separate. The complex was collected and purified by recrystallization from nitromethane and washing with ether.

Anal. Calcd for [Co(C₁₅H₂₂S₄)Cl₂](ClO₄): C, 32.18; H, 3.95; Cl, 18.99. Found: C, 32.18; H, 3.86; Cl, 18.83.

***trans*-Dibromo(13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)-cobalt(III) Perchlorate.** When the red-brown complex [Co(TTX)](ClO₄)₂ was stirred with an excess of lithium bromide in nitromethane for 30 min, a green-brown complex could be isolated in a manner similar to that given for the chloro complex.

Anal. Calcd for [Co(C₁₅H₂₂S₄)Br₂](ClO₄): C, 27.77; H, 3.41; Br, 24.63; Cl, 5.46. Found: C, 27.64; H, 3.44; Br, 24.50; Cl, 5.33.

Preparation of Rhodium Complexes. *cis*-Dichloro(1,4,8,11-tetrathiacyclohexadecane)rhodium(III) Chloride. Rhodium(III) chloride (K + K) was dissolved in a minimum amount of water and filtered into a boiling ethanol solution containing an excess of the ligand TTP. The resulting clear yellow solution was filtered, and most of the solvent was removed. Upon addition of ether a bright yellow microcrystalline product separated. The complex was filtered and washed with acetone and ether before drying.

Anal. Calcd for [Rh(C₁₀H₂₀S₄)Cl₂]Cl: C, 25.13; H, 4.21; Cl, 22.25. Found: C, 25.34; H, 4.38; Cl, 21.95.

***cis*-Dichloro(13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)-rhodium(III) Chloride.** The procedure given above for *cis*-[Rh(TTP)Cl₂]Cl was used substituting the ligand TTX.

Anal. Calcd for [Rh(C₁₅H₂₂S₄)Cl₂]Cl: C, 33.37; H, 4.10; Cl, 19.70. Found: C, 33.22; H, 4.27; Cl, 19.53.

***cis*-Dibromo(1,4,8,11-tetrathiacyclohexadecane)rhodium(III) Bromide.** The procedure above was repeated using rhodium(III) bromide. The complex isolated is a bright yellow crystalline product.

Anal. Calcd for [Rh(C₁₀H₂₀S₄)Br₂]Br: C, 19.65; H, 3.29; Br, 39.22. Found: C, 19.50; H, 3.40; Br, 38.98.

***cis*-Diiodo(1,4,8,11-tetrathiacyclohexadecane)rhodium(III) Iodide.** Rhodium(III) chloride was dissolved in a minimum amount of water and treated with an excess of lithium iodide. This solution was then filtered into a boiling ethanol solution containing an excess of the ligand TTP. The volume of the resulting red-brown solution was reduced. The red-brown crystals which formed were collected and recrystallized from ethanol to which lithium iodide had been added.

Anal. Calcd for [Rh(C₁₀H₂₀S₄)I₂]I: C, 15.96; H, 2.68; I, 50.37. Found: C, 16.51; H, 2.87; I, 47.37.

***cis*-Dichloro(1,4,8,11-tetrathiacyclohexadecane)rhodium(III) Tetrafluoroborate.** A few drops of 48% tetrafluoroboric acid was added to an ethanol solution of [Rh(TTP)Cl₂]Cl. There was an immediate separation of a light yellow complex. This complex was insoluble in ethanol but could be successfully recrystallized from acetonitrile.

Anal. Calcd for [Rh(C₁₀H₂₀S₄)Cl₂]BF₄: C, 22.69; H, 3.81; Cl, 13.39. Found: C, 22.80; H, 3.87; Cl, 13.68.

Dimer of 1,4,8,11-Tetrathiacyclohexadecane)rhodium(III) Trichloride. Rhodium(III) chloride was dissolved in a minimum amount of water and filtered into a cold ethanol solution of the ligand TTP. There was an immediate separation of a tan colored solid which was insoluble in hot water, ethanol, and other common organic solvents.

Anal. Calcd for [Rh₂(C₁₀H₂₀S₄)₂Cl₆]: C, 25.13; H, 4.21; Cl, 22.35. Found: C, 25.21; H, 4.55; Cl, 23.19.

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Registry No. 1,11-Dioxa-4,8-dithiaundecane, 16260-48-3; TTU, 25676-62-4; [Co(TTP)](BF₄)₂, 52392-77-5; [Co(CH₃CN)₆](BF₄)₂, 15170-09-9; *cis*-[Co(TTP)Cl₂]₂BF₄, 52392-93-5; *cis*-[Co(TTP)Br₂]₂BF₄, 52392-90-2; *trans*-[Co(TTP)I₂]₂(C₆H₅)₄, 52392-92-4; *cis*-[Co(TTP)Cl₂]₂(ClO₄), 52392-82-2; *cis*-[Co(TTP)(NCS)₂]₂(C₆H₅)₄, 52392-84-4; [Co(TTP)C₂O₄]₂(ClO₄), 52392-88-8; *cis*-[Co(TTP)(NO₂)₂]₂BF₄, 52392-86-6; *trans*-[Co(TTX)Cl₂]₂(ClO₄), 52392-95-7; *trans*-[Co(TTX)Br₂]₂(ClO₄), 52392-97-9; *cis*-[Rh(TTP)Cl₂]Cl, 52393-01-8; *cis*-[Rh(TTX)Cl₂]Cl, 52392-75-3; *cis*-[Rh(TTP)Br₂]Br, 52393-02-9; *cis*-[Rh(TTP)I₂]I, 52392-98-0; *cis*-[Rh(TTP)Cl₂]₂BF₄, 52393-00-7; [Rh(TTP)Cl]_xCl_{1-x}, 52392-80-0.

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Dissymmetric Arsinic Complexes. Preparation, Properties, and Electronic Structures of Cobalt-Arsinic Complexes Containing Co-Co Bonds

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Cobalt(III)-diaquo complexes of the type *cis*-[Co(As)₄(OH₂)₂]³⁺ are reduced in primary alcohols and give Co-Co dimers *trans,trans*-[H₂O(As)₄Co-Co(As)₄OH₂]⁴⁺. Three arsines were used, namely, the quadridentate ligands *R,R,S,S*-tetars (and *R,R*-tetars) and *R,S*-tetars and the bidentate chelate diars. The tetars complexes form stable acetonitrile adducts whereas the diars dimer appears to contain quasi-five-coordinate Co atoms. These diamagnetic complexes are stable in solution in the absence of catalysis, but their stability seems to be kinetically controlled because spontaneous dimerization of the monomeric cobalt(II) arsines does not occur. Evidence is presented which suggests that the alcohol reductions involve a hydrido intermediate. A number of observations support a quasi crystal field interpretation of the visible absorption spectra of the dimers; in essence it is assumed that the "d-d" transitions are localized on each Co atom except for the levels derived from the Co-Co bond. The consequences of this scheme in relation to the bonding in these complexes is briefly discussed.

Of all the transition elements which might be expected to form stable metal-metal bonds, those of Co(II) appear to be

the least studied. There are a variety of reasons for this but probably the main inconvenience is associated with the well

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known fact that most Co(II) complexes absorb atmospheric oxygen very rapidly. A second, more important reason is related to the potential stability of the metal-metal bonded dimer. If the ligand field strength of the ligands is not sufficient to achieve a spin-paired state in the Co(II) monomers, we would not expect stable metal-metal bonded dimers to be formed unless, by so doing, the dimer collapses into a diamagnetic state. It follows, therefore, that the systems most likely to form stable metal-metal bonds are Co(II) complexes surrounded by strong-field ligands which, initially, pair the Co(II) monomer to its (spin) doublet state. Indeed, the two thoroughly authenticated complexes containing Co^{II}-Co^{II} bonds are the [Co₂(CN)₁₀]⁶⁻ and [Co₂(CNC-H₃)₁₀]⁴⁺ ions which both contain strong-field ligands, and both these ions dissociate in solution to give (paramagnetic) five-coordinate Co(II) complexes (or six-coordinate species with a weakly held solvent molecule) which are spin paired.^{3,4} It has been known for some time that chelating arsine ligands produce Co(II) complexes in the doublet ground state,⁵ and, if our supposition is correct, we would expect these to form stable dimers.

This has proved to be the case, and it is the purpose of this article to describe the preparation and properties of some of these complexes. In particular, we offer what we believe is a cogent interpretation of the "d-d" spectra of the dimers which provides an insight into their stability. The three arsines we have used are shown in Figure 1, where it will be noted that (meso) *R,S*-tetars and (racemic) *R,R:S,S*-tetars exist in stable optical and geometric forms and that the latter has been resolved.^{6,7} We shall deal with the complexes of the tetars ligands first because they are less complicated than the diars system.

1. Dimers of the tetars Ligands

If either the meso or racemic tetars ligands are added to cobaltous perchlorate in methanol or acetonitrile solutions, the cobalt(II) complexes are very unstable and exceedingly sensitive to oxygen with which they react to give peroxo-cobalt(III) dimers. We will discuss these in the following paper. Although some Co-Co dimerization may occur in these solutions, we have not been able to isolate either the dimers or monomers in a pure state by simply mixing the metal and ligand in solution. The diaquocobalt(III) species *cis-β*-[Co(*R,S*-tetars)(H₂O)₂](ClO₄)₃⁷ and *cis-α*- or *cis-β*-[Co(*R,R:S,S*-tetars)(H₂O)₂](ClO₄)₃⁷ are reduced to the deep yellow Co(II) complexes by the addition of zinc dust in acetonitrile. In the presence of excess zinc, these solutions remain reasonably stable in air, but once the zinc is removed, they rapidly absorb oxygen.

In view of the above observations, it is perhaps surprising that we have been able to prepare the dimers quite easily by another method of reduction. The *cis*-diaquocobalt(III) complexes, of either ligand, dissolve in most primary alcohols to give amber-red solutions which turn yellow and deposit deep yellow solids. The speed with which this reaction occurs depends on the alcohol, occurring within 10 sec in meth-

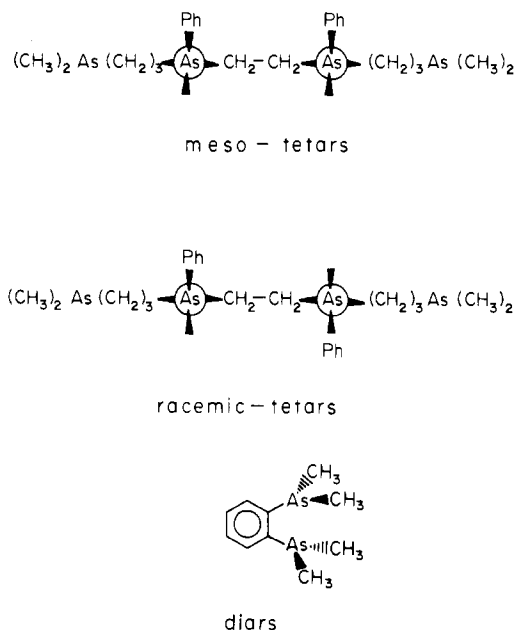


Figure 1.

anol and becoming progressively slower for the higher primary homologs. The yellow solids, which only slowly absorb oxygen in solution, are diamagnetic both in the solid state and in solutions and analyze for the stoichiometry [Co(tetars)(H₂O)](ClO₄)₂⁸ (the perchlorate ions are known to be free in solution from conductance measurements). These complexes are therefore (formally) Co(II) species formed by the oxidation of the alcohols presumably to the corresponding aldehydes although we have not been able positively to identify the organic products to enable us to discuss the mechanism of reduction. (We have, however, identified formaldehyde (carbazole) in the reaction product of the diars reaction with methanol.)

Unlike the monomeric complexes, these Co(II) species have a stability comparable to that of the Co(III) analogs. Thus in acetonitrile, the aquo groups in both complexes can be replaced to produce the acetonitrile adducts [Co(tetars)-(CH₃CN)](ClO₄)₂ which have been isolated. The coordinated acetonitrile does not exchange with CD₃CN solvent after 3 hr at 30° (nmr). Attempts at replacing the aquo groups with anionic ligands, such as Cl⁻ and NCS⁻ in acetone solutions, however, led to decomposition. If excess Cl⁻ or NCS⁻ was added initially or after decomposition had occurred, the characteristic blue-green tetrahedral Co(II) species [CoX₄]²⁻ were produced after a few minutes in warm acetone. We therefore suppose that these complexes are (formally) Co(II) dimers linked by a Co-Co bond which quenches the paramagnetism of the monomeric units. The nmr spectra of these complexes support this supposition as well as confirm that the tetars ligands are in a planar arrangement. In addition, molecular weight determinations in acetonitrile confirm the dimeric formulation.

We have shown elsewhere^{6,7} that the monomeric Co(III) species *trans*-[Co(*R,S*-tetars)X₂]ⁿ⁺ as well as both isomers of the species *trans*-[Co(*R,S*-tetars)XY]ⁿ⁺ gives only two methyl proton signals of equal area presumably because of

(8) The presence of coordinated water in this and the other dimer aquo adducts is an assumption. We have observed the (broad) ~3500-cm⁻¹ water band in the ir spectra of the solids, but this, of course, does not prove the presence of coordinated water. The chemical evidence suggests that, in the tetars dimers, the water is probably coordinated but that it is quite possible in the case of the diars dimers that each cobalt atom is essentially five-coordinate.

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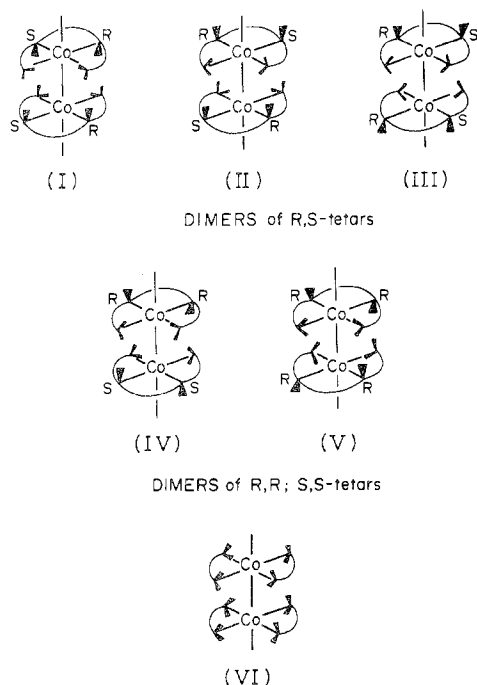


Figure 2. Schematic representation of the various dimer isomers. The large wedges represent phenyl groups; the smaller ones, methyl groups.

rapid conformational flipping of the chelate rings. Assuming this obtains in the dimers and that, on an nmr time scale, there are no stable rotamers through rotation about the Co-Co bond, there are three distinct structural isomers for the *trans*-meso ligand arrangement: an endo,endo disposition of the phenyl groups (I), an endo,exo phenyl group arrangement (II), and an exo,exo phenyl group arrangement (III) (Figure 2). On this basis, symmetry arguments determine that I and III should give two methyl proton signals of equal area and II should give four methyl proton signals of equal area. Furthermore, the two remaining coordination sites (one on each cobalt atom) are equivalent in structures I and III but inequivalent in II. Table I lists the methyl proton signals of the meso ligand dimer complexes where it will be seen that, for both the aquo and acetonitrile adducts, only two arsenic methyl proton resonances are observed and that the acetonitrile has only a single (coordinated) acetonitrile methyl proton resonance. It is interesting that only one isomer is produced exclusively because even if over 95% of the quantitatively produced product is isolated, the same nmr spectrum is observed and there is no (nmr) evidence of other isomers. We assume that the isomer obtained is III (exo,exo) because, as molecular models indicate, this topology is the least sterically congested particularly with respect to neighboring phenyl group interactions. A similar topological exclusiveness is observed for the racemic ligand.

In Figure 2 we show the two dimer isomers of the racemic tetars ligand (a third is the optical antipode of V). In both the meso (IV) and chiral (V) topologies, the two remaining coordination sites are equivalent and both isomers should show four arsenic methyl proton resonances. These conclusions hold whether the chelate rings are conformationally labile on an nmr time scale or not and provided there are no stable rotamers about the Co-Co bond. We have prepared the dimer from both the racemic diaquo complex and the optically pure active diaquo species. In both cases over 95% yields could be obtained and, starting with either aquo complex, the identical (four-line) nmr spectrum for the arsenic

methyl protons and a single acetonitrile methyl resonance was obtained (Table I). There was no nmr evidence for any other isomers. The isomer obtained in both cases, therefore, is V (or its antipode). This result seems reasonable from an inspection of molecular models which suggest that there is much more crowding of the phenyl groups in IV than in V. That phenyl group interactions contribute to instability is supported by the observation that the *R,S*-tetars dimers are more stable than those of *R,R*-tetars; the former (in III) has no endo-phenyl interactions while the latter has two (Figure 2).

It should be pointed out that experience^{6,7} suggests a four-line arsenic methyl proton spectrum and the chemical shifts given in Table I could only be obtained for a *trans*-XY species of the racemic ligand. If one or both the ligands in either dimer were in cis topologies, more arsenic as well as acetonitrile methyl proton resonances would occur than is observed.

2. Absorption and Circular Dichroism Spectra of the Dimers

In Figure 3 we show the visible absorption spectra of three dimers, *trans,trans*-[CH₃CN(*R,S*-tetars)Co-Co(*R,S*-tetars)-CH₃CN](ClO₄)₄, *trans,trans*-[CH₃CN(*R,R*-tetars)Co-Co(*R,R*-tetars)CH₃CN](ClO₄)₄, and *trans,trans*-[H₂O(*R,R*-tetars)Co-Co(*R,R*-tetars)H₂O](ClO₄)₄, and the circular dichroism associated with the last two. In order to interpret these spectra, we adopt a quasi crystal field approach where it is assumed that the transitions occurring in the region 29,000–14,000 cm⁻¹ involve states localized on one or other of the equivalent cobalt atoms and that the only transitions involving charge transfer between the metal atoms involve the antibonding upper state derived from the σ Co-Co bond. With these assumptions, it is convenient⁹ to label the states according to their transformation properties in the point group D_{4h} and it is assumed that these classifications will provide approximate selection rules for the system.

In Figure 4 we show a qualitative molecular orbital diagram which specifies these assumptions more precisely; only the metal d-orbital interactions are shown, and those derived from the metal s and p overlap are not included. Since, by assumption, the "d-d" transitions are localized, except for the state derived from the Co-Co bond, the diagram shows the states for one Co atom. The z axis lies along the metal-metal bond which is formed by overlap of the d_{z^2} orbitals of Co atoms 1 and 2; the bonding orbital (a_{1g}) thus formed

(9) A similar but somewhat less severe set of selection rules is obtained if the states are classified according to the D_{4d} point group. Using similar assumptions to those given for the D_{4h} classification, the d-orbital MO levels are as follows: bonding, $\{(1/\sqrt{2})(d_{z^2(1)} + d_{z^2(2)})\}^2$, a_1 , and $\{d_{x^2-y^2}, d_{xy}\}^4$, e_2 ; nonbonding, $\{d_{xz}, d_{yz}\}^4$, e_3 ; antibonding, $\{d_{x^2-y^2}, d_{xy}\}^4$, e_2 , and $\{(1/\sqrt{2})(d_{z^2(1)} - d_{z^2(2)})\}^2$, b_2 . The "d-d" transitions are ${}^1A_1 \rightarrow {}^1E_3$ and ${}^1A_1 \rightarrow {}^1E_1$ derived from $e_3 \rightarrow e_2$ and ${}^1A_1 \rightarrow {}^1E_1$ from $e_3 \rightarrow b_2$. The transition to 1E_3 is magnetic dipole allowed and the two transitions to 1E_1 are electric dipole allowed and polarized perpendicular to the Co-Co bond axis. The two ${}^1A_1 \rightarrow {}^1E_1$ excitations, however, are different in the sense that the one derived from $e_3 \rightarrow b_2$ is allowed in the zero-order ($g \rightarrow u$) whereas the other, derived from $e_3 \rightarrow e_2$, is a $g \rightarrow g$ transition acquiring u character by mixing with odd-parity 1E_1 states of the system. We thus expect the former to be more strongly allowed than the latter although experience⁶ with arsine-cobalt systems suggests that extinction coefficients as high as 500 or more could be obtained by the mixing mechanism. Thus the D_{4d} classification predicts three "d-d" bands of weak (${}^1A_1 \rightarrow {}^1E_3$), medium (${}^1A_1 \rightarrow {}^1E_1$; $e_3 \rightarrow e_2$), and high (${}^1A_1 \rightarrow {}^1E_1$; $e_3 \rightarrow b_2$) intensity. It could be argued that this is a preferable classification scheme on the supposition that the dimers are staggered, and, indeed, an equally cogent interpretation of the observed spectra can be given on this basis. We, however, are not persuaded that the observed spectra allow for a clear-cut distinction between the two schemes to be made and we have adopted the D_{4h} classification because it offers what seems, to us, a clearer pictorial representation of our arguments.

Table I. Nmr Data of the As-CH₃ Protons for the Dimers

<i>trans,trans</i> -[(D)(L)Co-Co(L)(D)] ⁴⁺	Solvent	δ, ° Hz
D = H ₂ O; L = (diars) ₂	Concd HClO ₄ ^b	132, 149
	DMSO- <i>d</i> ₆	113, 139
	CD ₃ CN	113, 132
D = H ₂ O; L = <i>R,S</i> -tetars	CD ₂ Cl ₂	90, 106
	CDCl ₃	96, 106
	DMSO- <i>d</i> ₆	94, 104, 160 ^c
D = CH ₃ CN; L = <i>R,S</i> -tetars	CD ₃ CN	93, 101, 153 ^c
	DMSO- <i>d</i> ₆	92, 108
D = (CH ₃) ₂ SO; ^d L = <i>R,S</i> -tetars	DMSO- <i>d</i> ₆	74, 93, 96, 107, 130 ^c
D = CH ₃ CN; L = <i>R,R</i> -tetars ^e	DMSO- <i>d</i> ₆	60, 78, 107, 119
D = (CH ₃) ₂ SO; ^d L = <i>R,R</i> -tetars	DMSO- <i>d</i> ₆	

^a At 60 MHz relative to internal TMS at 29°. ^b The unchanged complex can be quantitatively recovered by dilution with water. No hydride resonances were found. ^c CH₃CN resonances. ^d Formed in deuterated DMSO solvent by dissolution of the aquo adducts. ^e Same spectrum is obtained if racemic materials are used.

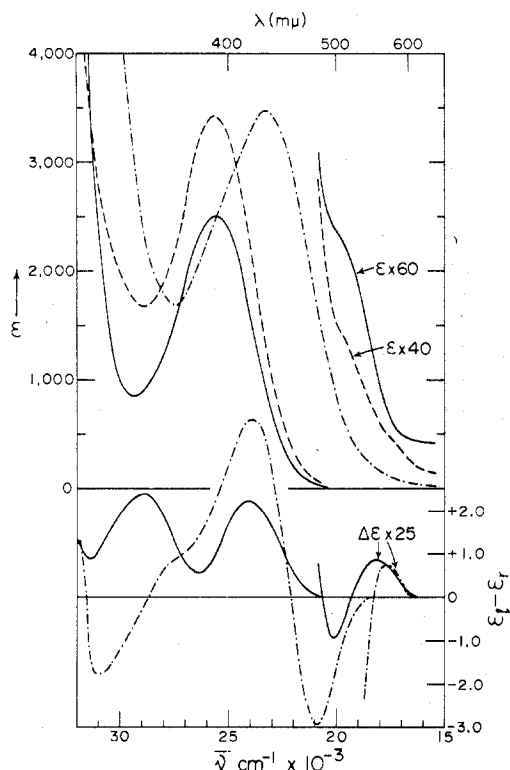


Figure 3. Visible absorption spectra and associated circular dichroism spectra of the tetras Co-Co dimers: *trans,trans*-[CH₃CN(*R,R*-tetars)Co-Co(*R,R*-tetars)CH₃CN]⁴⁺, —; *trans,trans*-[CH₃CN(*R,S*-tetars)Co-Co(*R,S*-tetars)CH₃CN]⁴⁺, - - - -; *trans,trans*-[H₂O(*R,R*-tetars)Co-Co(*R,R*-tetars)H₂O]⁴⁺, - · - · - ·. The spectra of the acetonitrile adducts were measured in acetonitrile and those of the aquo adduct in methylene chloride.

allows the unpaired electron of each Co to pair. The $d_{x^2-y^2}$ orbital (of Co(1)) interacts with the As atoms in the octahedral plane and forms the (filled) molecular orbital b_{1g} . The bonding orbitals have their antibonding counterparts b_{1g}^* and a_{2u}^* ; the relative positions of these are suggested by experiment. We assume the d_{xy} and d_{xz} , d_{yz} orbitals to be essentially nonbonding although both the acetonitrile ligand and the arsenic donor atoms have vacant π orbitals which formally could bond to these orbitals and tend to stabilize them. However, because these d orbitals are filled on both Co atoms and because the two sets lie in close proximity to each other, interaction between these levels will be destabilizing. Furthermore, since the two e_g sets point more directly at one another than the two b_{2g} orbitals, we would expect the former to be more destabilized than the latter and we assume this to be the major source of discrimination between the e_g and b_{2g} levels in each Co atom. Thus, in essence, we have supposed that Co(2) is a (paramagnetic)

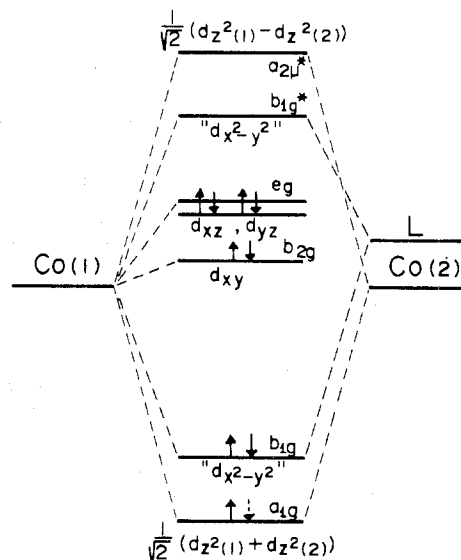


Figure 4. Qualitative molecular orbital diagram for one of the cobalt atoms of the Co-Co dimers. Only the d-orbital interactions of the cobalt atom are shown. The ordering of the nonbonding and antibonding states is suggested from experiment.

substituent bonded to Co(1) (or *vice versa*) and that the possible states derived from mixing between the b_{1g} , b_{2g} and e_g states of one metal with the corresponding states of the other metal are unimportant in assigning the spectrum in the visible region.

According to the above scheme, there should be four "d-d" transitions (or six if the e_g level is split), of which only one, $^1A_{1g} \rightarrow ^1E_u$ ($e_g \rightarrow a_{2u}^*$), is (electric dipole) allowed, and, if the above ordering is correct, the lowest energy transition should be the magnetic dipole allowed excitation $^1A_{1g} \rightarrow ^1E_g$ ($e_g \rightarrow b_{1g}^*$). The acetonitrile adducts clearly show a strong absorption band ($\epsilon > 3000 M^{-1} cm^{-1}$) at $25,500 cm^{-1}$ and some evidence of unresolved shoulders on the higher energy side. At lower energies, both spectra clearly show very weak shoulders at around $19,500 cm^{-1}$. We assign the major strong band at $25,500 cm^{-1}$ to the allowed $^1A_{1g} \rightarrow ^1E_u$ transition and the weak shoulder at $19,500 cm^{-1}$ to the forbidden $^1A_{1g} \rightarrow ^1E_g$ transition. The positive circular dichroism band at $18,500 cm^{-1}$ is associated with this latter transition, but it is not clear whether the negative band at $20,000 cm^{-1}$ is to be regarded as the other component of a plus-minus couplet due to splitting of the 1E_g upper state or to other transitions under the absorption manifold.

These assignments of the $^1A_{1g} \rightarrow ^1E_u$ and $^1A_{1g} \rightarrow ^1E_g$ transitions on the basis of intensity are supported by the spectrum of the aquo adduct. According to the scheme in Figure 4, we would expect that substitution in the axial po-

sitions would affect the a_{2u}^* level much more than the b_{1g}^* level. Hence, we expect the ${}^1A_{1g} \rightarrow {}^1E_u$ transition to shift to lower energies when the spectrochemically weaker⁷ aquo group replaces the acetonitrile ligand; the ${}^1A_{1g} \rightarrow {}^1E_g$ transition, however, should be essentially unaffected by axial substitution. Figure 3 shows that the strong absorption band is shifted to lower energies in the aquo adduct and that the weak low-energy shoulder of the acetonitrile adducts is not resolved in the aquo adduct. The circular dichroism, however, reveals that the first (positive) band is unshifted by substitution.

The other two "d-d" bands, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}^*$) and ${}^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}^*$), both of which are (electric dipole) forbidden, presumably lie under the strong absorption. Their presence is revealed by the circular dichroism spectra but it is not clear whether the two minima in the acetonitrile adduct at 26,500 and 31,500 cm^{-1} should be regarded as negative circular dichroism bands which are "carried" positive by the positive bands or simply regions of weak (positive) circular dichroism. We are inclined to the former view. However, the two (CD) peaks at 24,000 and 29,000 cm^{-1} are definite absorption bands, and if we assign the 24,000- cm^{-1} band to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition and the other to the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ excitation, a predicted result is observed. Thus, the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ band is unshifted in going from the acetonitrile to the aquo complexes. The fate of the other band, which should shift to lower energies, is ambiguous because of the intrusion of a strong negative band, which is probably a charge-transfer transition, in the aquo adduct.

The above interpretation of the Co-Co dimer spectra is somewhat different from that given for the isoelectronic $\text{Mn}_2(\text{CO})_{10}$ complex where the dominant low-energy band is the $d\sigma \rightarrow d\sigma^*$ transition of the Mn-Mn bond.¹⁰

We have chosen the present interpretation because it does not seem likely that π -bonding effects would be sufficient to stabilize the d_{xz}, d_{yz} set of orbitals to the extent of approaching the energy of the σ (a_{1g}) orbital. If this were so, we would expect to observe two strong transitions; there is evidence for only one. It is reasonable, therefore, to assign the allowed transition to a promotion emanating from the "nonbonding" set of orbitals rather than the $d\sigma$ (a_{1g}) orbital. If strong π bonding occurs as in low-valent metal carbonyls, however, it is possible that the $d\pi$ orbitals could approach the $d\sigma$ (a_{1g}) orbital in energy.

It is therefore appropriate to mention briefly which metal-metal bonded systems are likely to be susceptible to one or other of the interpretations. We believe that if a straightforward crystal field interpretation is sufficient to interpret the "d-d" spectroscopic properties of the (spin-paired) monomers or, what is usually easier to obtain, the spectroscopic properties of the next highest oxidation state, e.g., $[\text{Co}(\text{CN})_5]^{3-} \rightarrow [\text{Co}(\text{CN})_6]^{3-}$, then the quasi crystal field approach adopted here will apply. If strong π bonding is an important consideration in interpreting the low-energy transitions of the monomers or the complexes of the next oxidation state, e.g., $\text{Mn}(\text{CO})_5 \rightarrow \text{Mn}(\text{CO})_5\text{X}$, as in the case of the low-valent carbonyls, then Gray's interpretation will apply. There, of course, may be intermediate systems but most complexes tend to classify themselves fairly well in these two categories.

From the spectra shown¹¹ by the Co(III) $[\text{Co}(\text{CN})_5\text{X}]^{3-}$

(10) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem. Soc.*, **92**, 3653 (1970).

(11) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968).

ions ($X^- = \text{CN}^-, \text{NCS}^-, \text{N}_3^-$), which at low energies show essentially "d-d" transitions, we suggest that the spectrum of the $[\text{Co}_2(\text{CN})_{10}]^{6-}$ ion can be interpreted by the scheme given here and we suspect that it will be applicable to most Co(II) and Rh(II) metal-metal bonded dimers.

One observation which derives from the molecular orbital diagram is that the two Co atoms, which share a pair of electrons *via* a Co-Co bond, have closed-shell configurations and can be regarded as derivatives of Co(III). This is supported by the stability of these systems compared to the corresponding Co(II) species and indicated by the fact¹ that the (equatorial) Co-CN bond lengths in $[\text{Co}_2(\text{CN})_{10}]^{6-}$ are the same as in $[\text{Co}(\text{CN})_6]^{3-}$. The first step in the decomposition of these dimers appears to be homolytic cleavage of the Co-Co bond (to give unstable Co(II) species) and not the dissociation of the ligands. Apart from ligand steric effects, one probable source of instability in the metal-metal bond is the repulsion of the filled d_{xz}, d_{yz} orbitals on each cobalt atom. Presumably if these electrons can be delocalized on the ligands, as in, for example, $\text{Mn}_2(\text{CO})_{10}$, this repulsion will be alleviated.

3. Co(II) Complexes of the diars Ligand

The Co(II) complexes of the diars ligand are more stable than those of the tetars ligands and tend to be insoluble in most common solvents. They are therefore easily isolated.³ The addition of 2 equiv of diars to $\text{Co}(\text{ClO}_4)_2$ in methanol leads to the formation of the yellow complex $[\text{Co}(\text{diars})_2(\text{ClO}_4)_2]$,¹² which is paramagnetic in the solid state (1.9 BM). This monomeric¹² complex is soluble in acetonitrile in which it forms a green solution and is paramagnetic. The found magnetic moment is low, however, being about 1.1 BM in 0.11 *M* solutions, although the green solid which has been isolated from these solutions and has the constitution $[\text{Co}(\text{diars})_2(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ gives the expected moment of 1.8 BM. Because of the small paramagnetic shift observed and solubility limitations, accurate concentration-dependent magnetic moments could not be obtained for the green acetonitrile solutions. The *trans*- $[\text{Co}(\text{diars})_2(\text{ClO}_4)_2]$ complex is unstable in DMSO solutions, in which the arsine is slowly removed at 25° to form $\text{Co}^{\text{II}}\text{-DMSO}$ complexes exclusively in dilute solutions (~ 0.01 *M*), and, at higher concentrations (~ 0.1 *M*), an equilibrium between the complex and the $\text{Co}^{\text{II}}\text{-DMSO}$ complexes is established. Unlike the case of the acetonitrile solutions where resolution is lost, a very sharp nmr spectrum is obtained in freshly prepared DMSO solutions; the observed single methyl proton resonance has a width of 1.5 Hz at half-height at 60 MHz. The spectrum, however, is shifted upfield relative to external TMS, and a magnetic moment (which increases with time because of dissociation) of about 2.0 BM is obtained on a freshly prepared solution of 0.16 *M* concentration. Thus in DMSO the $[\text{Co}(\text{diars})_2(\text{ClO}_4)_2]$ appears to be monomeric whereas in acetonitrile there is some, but not very convincing, evidence of dimerization. The compound is not sufficiently soluble in other common solvents to allow for exploring the possibility of dimer formation in other solutions.

If, however, *cis*- $[\text{Co}(\text{diars})_2(\text{OH}_2)_2](\text{ClO}_4)_3$ is reduced in primary alcohols, a very bright yellow material is produced; it is diamagnetic in the solid and in solution. Its molecular weight in acetonitrile indicates a dimer and it analyzes for the formula $[\text{Co}(\text{diars})_2\text{OH}_2](\text{ClO}_4)_2$. We therefore conclude that the compound is the Co-Co dimer *trans,trans*- $[\text{H}_2\text{O}(\text{diars})_2\text{Co-Co}(\text{diars})_2\text{OH}_2](\text{ClO}_4)_4$. The *trans,trans* topo-

(12) F. W. B. Einstein and G. A. Rodley, *J. Inorg. Nucl. Chem.*, **29**, 347 (1967).

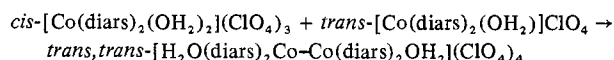
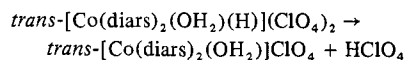
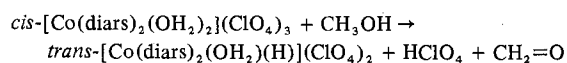
logy of the diars ligands (Figure 2(VI)) is supported by the nmr of the methyl proton resonances of which only two of equal area are observed in both DMSO and acetonitrile (Table I).

Unlike the tetars dimers, acetonitrile does not form a stable adduct with the diars dimer. Addition of ether to acetonitrile solutions produces crystals which contain varying amounts of acetonitrile depending on the conditions of precipitation. In fact, we have isolated samples from acetonitrile-ether solutions which had no detectable (nmr) amounts of water or acetonitrile. It therefore appears that the dimer contains quasi-five-coordinate Co atoms. The chemical evidence indicates that this complex is much more stable than the tetars dimers with respect to Co-Co fission; the stability order is diars > *R,S*-tetars > *R,R*-tetars. This is probably due, in part, to the greater steric hindrance between ligands experienced in the tetars systems (Figure 2). The quasi-five-coordinate properties of the diars dimer may be due to the ability of the strong Co-Co bond to transfer, by σ donation, electron density into the axial positions. This suggestion seems plausible if we view the Co-Co bond as a result of addition of a strong Lewis base, Co(I), to a strong Lewis acid, Co(III), *via* orbitals of the same quantum number. The tendency to five-coordination in Co(III) has been observed with strong-field ligands; perhaps the most notable cases are the $[\text{Co}(\text{CN})_5\text{X}]^{2-}$ ions which undergo classic $\text{S}_{\text{N}}1$ limiting substitution reactions.¹³

That the axial positions of the diars dimer are only slightly perturbed in solution is indicated by the absorption spectra (Figure 5). It will be seen that the spectra are similar to those found for the tetars dimers except that the absorption maxima appear at lower energies and are somewhat less intense. Also the weak band at lower energies is not clearly resolved. It will be noted that in going from acetonitrile solutions to the presumably oxygen-donating DMSO solutions there is very little change in the spectrum, which would be anticipated if the Co atoms are quasi-five-coordinate. The appearance of the absorption maxima at lower energies for the diars dimer in acetonitrile compared to those of the tetars-acetonitrile adduct dimers suggests that the average axial crystal field strength due to the Co-Co bond and the (strong field) acetonitrile ligand is greater than the combined effect of the Co-Co bond and the weakly perturbing acetonitrile ligands despite the increased strength of the Co-Co bond in the diars dimer.

These spectra are quite distinct from those observed for dilute ($10^{-2} M$) acetonitrile solutions of the paramagnetic *trans*- $[\text{Co}(\text{diars})_2(\text{ClO}_4)_2]$ complex which show two broad absorption manifolds, one at around $700 m\mu$ (ϵ 14.4) and another centered at $400 m\mu$ ($\epsilon \sim 300$). The dimers show no absorption from the strong visible band out to $850 m\mu$.

The detailed mechanism of formation of these dimers in primary alcohols is not understood but the general stoichiometry seems to be as follows for the methanol reaction with the *cis*- $[\text{Co}(\text{diars})_2(\text{OH}_2)_2](\text{ClO}_4)_3$ complex



(13) (a) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962); (b) A. Haim, R. J. Grassie, and W. K. Wilmarth, *Advan. Chem. Ser.*, No. 49 (1965).

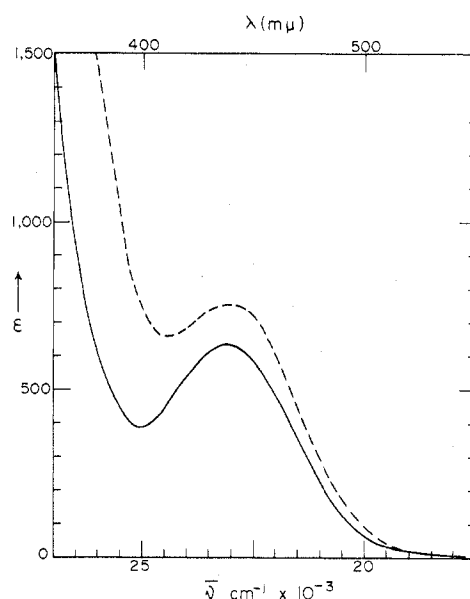


Figure 5. Visible absorption spectra of *trans,trans*- $[\text{H}_2\text{O}(\text{diars})_2\text{-Co-Co}(\text{diars})_2\text{H}_2\text{O}]^{4+}$ in acetonitrile (—) and dimethyl sulfoxide (---).

That is, the function of the alcohol is to reduce the cobalt(III)-diaquo complex to the hydrido-aquo species with the formation of formaldehyde. The hydrido-aquo species is weakly acidic with respect to the Co-H bond and releases the Co(I) species which then reacts with a Co(III) complex to form the Co-Co bond. Whether the complexes have coordinated water or methanol is not known but the facts are as follows: (1) 2 molar equiv of HClO_4 is released during the reaction and the reaction mixture (see Experimental Section) has a pH of about 2 at completion, (2) formaldehyde was detected (carbazole reaction) for the methanol reduction, and (3) the *trans*- $[\text{Co}(\text{diars})_2(\text{OH}_2)(\text{H})](\text{ClO}_4)_2$ has been prepared independently and it does behave as a weak acid releasing the Co(I) complex which picks up oxygen (see following paper). The general stoichiometry of the reaction is therefore supportable but the mechanistic details of Co-Co bond formation must be subtle because we have mixed equivalent amounts of *trans*- $[\text{Co}(\text{diars})_2(\text{OH}_2)(\text{H})](\text{ClO}_4)_2$ ¹⁴ and *cis*- $[\text{Co}(\text{diars})_2(\text{OH}_2)_2](\text{ClO}_4)_3$ in acetone, the only inert solvent in which the two are soluble; upon the addition of a catalytic amount of pyridine, to remove the hydride as a proton, an "instantaneous" reaction takes place. The product, however, is the monomeric *trans*- $[\text{Co}(\text{diars})_2(\text{ClO}_4)_2]$ complex.

The general reaction scheme found for the diars system probably also applies to the tetars complexes but the fact that the monomers do not dimerize spontaneously despite the strong Co-Co bond suggests that the dimers are kinetically rather than thermodynamically stable. All the dimers are subject to catalytic disproportionation into Co(II) monomers in the presence of an, as yet, unidentified catalyst which is formed during the preparations if care is not taken. The methods given in the Experimental Section have been found to be reliable in this regard.

(14) This hydrido-aquo complex is quite different in its properties when compared to the dimer. Thus, the hydride decomposes in DMSO and the dimer is stable; the hydride is insoluble in concentrated HClO_4 and the dimer is very soluble; the hydride forms a stable isolated adduct with acetonitrile and the dimer does not; the hydride picks up oxygen in dilute aqueous pyridine and the dimer does not. These facts, and others, together with the molecular weight determinations, establish that the dimer is not the hydrido-aquo complex. The corresponding tetars-hydrido-aquo complexes could not be isolated because of their rapid decomposition.

4. Experimental Section

Instrumentation. The nmr spectra were recorded using a Varian T-60 spectrometer at 29°. Absorption and circular dichroism spectra were measured using a Unicam SP820 recording spectrophotometer and a Roussel-Jouan Dichrographe II, respectively. Conductivities and optical rotations were obtained using a Yellow Springs Instrument Co. Model 31 conductivity bridge and a Perkin-Elmer 141 digital recording polarimeter. Solid magnetic moments were obtained by the Gouy method and the solution moments were obtained by the Evans method¹⁵ using TMS as the internal and external references. The molecular weights were determined by "osmometry" using a Mechrolab Inc. Model 301A vapor pressure osmometer. The osmometer was standardized using *cis*- and *trans*-[Co(diars)₂Cl₂](ClO₄)₂ and *cis*-β-[Co(diars)₂(CH₃CN)₂](ClO₄)₃ over a concentration range of 1 × 10⁻³ to 5 × 10⁻⁴ M. Excellent straight lines were obtained for the plot of resistance change vs. concentration for both the reference and sample complexes in acetonitrile. The *cis*- and *trans*-dichloro complexes gave superimposable straight lines as did the dimers and the dimeric dioxygen complex (see following paper). Assuming the *cis*- and *trans*-dichloro complexes are fully dissociated 1:1 electrolytes over the concentration range (conductance measurements support this), the plots for the four-particle bis-acetonitrile complex and those for the five-particle dimers correspond exactly to the theoretically predicted values throughout the concentration range.

Preparation of the Arsinates. The preparation of the *R,R,S,S*-tetraars, *R,R*-tetraars, and *R,S*-tetraars followed procedures given elsewhere⁶ and Feltham's method¹⁶ was used for the diars preparation.

trans,trans-[H₂O(*R,S*-tetraars)Co-Co(*R,S*-tetraars)H₂O](ClO₄)₄. Treatment of *cis*-β-[Co(*R,S*-tetraars)(OH₂)₂](ClO₄)₃·2H₂O with either ethanol or methanol gives an identical product which contains no alcohol; the ethanol reaction is probably the more convenient. Finely ground *cis*-β-[Co(*R,S*-tetraars)(OH₂)₂](ClO₄)₃·2H₂O (0.6 g) was added in small portions to absolute ethanol (250 ml) at 60° with vigorous stirring. The solid dissolved to give a brown solution which rapidly turned bright yellow. After the addition was complete, the solution was brought to the boil and filtered while hot. A large volume of ether was added slowly to the filtrate which then began to deposit fine deep yellow crystals which were collected after 12 hr at 0° and washed with ethanol and then ether (0.38 g; Λ = 542 ohm⁻¹ cm² mol⁻¹, 5.56 × 10⁻⁴ M in methanol at 25°). *Anal.* Calcd for [Co(C₂₄H₃₈As₄)(H₂O)](ClO₄)₂: C, 32.0; H, 4.5; Cl, 7.9. Found: C, 32.8; H, 4.8; Cl, 8.0.

trans,trans-[CH₃CN(*R,S*-tetraars)Co-Co(*R,S*-tetraars)CH₃CN](ClO₄)₄. Dissolution of the yellow diaquo adduct in acetonitrile gives a deep yellow solution which rapidly lightens in color and shortly thereafter deposits canary yellow plates of the acetonitrile adduct; the addition of ether completes the crystallization. The yield is quantitative. A more direct method of preparation is as follows. Finely ground *cis*-β-[Co(*R,S*-tetraars)(OH₂)₂](ClO₄)₃·2H₂O (1.6 g) was added in small portions to well-stirred boiling methanol (100 ml). After the addition, the yellow solution was boiled for a further 3 min and acetonitrile (15 ml) added. The hot solution was filtered and a large volume of ether added. After 1 hr at 0° the small yellow blocks were collected, washed with ethanol, and then with ether. These were recrystallized from acetonitrile by the addition of ether to give yellow plates (1.25 g; Λ = 564 ohm⁻¹ cm² mol⁻¹, 2.13 × 10⁻⁴ M in acetonitrile at 25°; FW = 1850.3 (calcd), 2000 ± 200 (found, 4:1 electrolyte by "osmometry" in acetonitrile); μ_{eff}(dimer) = 0.7 BM at 28°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)(CH₃CN)](ClO₄)₂: C, 33.8; H, 4.5; N, 1.51; Cl, 7.7. Found: C, 33.5; H, 4.8; N, 1.56; Cl, 7.8.

trans,trans-[CH₃CN(*R,R,S,S*-tetraars)Co-Co(*R,R,S,S*-tetraars)CH₃CN](ClO₄)₄. This dimer was prepared from either *cis*-β- or *cis*-α-[Co(*R,R,S,S*-tetraars)(OH₂)₂](ClO₄)₃ (0.4 g) by reduction in boiling methanol (80 ml) followed by the addition of acetonitrile (15 ml) as described for the *R,S*-tetraars complex. The fine yellow needles obtained after the addition of a large volume of ether were recrystallized twice from acetonitrile (3 ml) and methanol (10 ml) by the addition of excess aqueous sodium perchlorate (0.22 g; Λ = 522 ohm⁻¹ cm² mol⁻¹, 3.39 × 10⁻⁴ in acetonitrile 25°; μ_{eff}(dimer) = 0.8 BM at 28°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)(CH₃CN)](ClO₄)₂: C, 33.8; H, 4.5; N, 1.51; Cl, 7.7. Found: C, 33.8; H, 4.5; N, 1.42; Cl, 7.6.

(15) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(16) R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometal. Chem.*, 7, 285 (1967).

trans,trans-[CH₃CN(*R,R*-tetraars)Co-Co(*R,R*-tetraars)CH₃CN](ClO₄)₄. This optically active complex was prepared by a similar method to the one given for the racemic analog. It crystallized as yellow needles ([α]_D²⁵ + 189 (±12)°, [α]_D³⁶⁵ - 233 (±15)°, 1.59 × 10⁻⁴ g/g in acetonitrile 30°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)(CH₃CN)](ClO₄)₂: C, 33.8; H, 4.5; N, 1.51; Cl, 7.7. Found: C, 33.7; H, 4.8; N, 1.69; Cl, 7.5.

trans,trans-[H₂O(*R,R*-tetraars)Co-Co(*R,R*-tetraars)H₂O](ClO₄)₄·2(CH₃)₂CO. Finely ground *cis*-α-[Co(*R,R*-tetraars)(OH₂)₂](ClO₄)₃ (0.3 g) was added in small portions to a well-stirred boiling solution of ethanol (25 ml) and water (1 ml). The resulting yellow-brown solution was kept boiling for a further 3 min. It was quickly cooled and ether (200 ml) was added without delay. The brown-yellow crystals were collected and recrystallized from acetone by the addition of ether (0.1 g). The presence of two molecules of acetone was confirmed by nmr ([α]_D + 43 (±4)°, [α]_D⁵⁷⁸ + 41 (±4)°, 7.02 × 10⁻⁴ g/ml in CH₂Cl₂ at 28°).

Anal. Calcd for [Co(C₂₄H₃₈As₄)(H₂O)](ClO₄)₂·2(CH₃)₂CO: C, 33.8; H, 4.8; Cl, 7.4. Found: C, 34.2; H, 4.8; Cl, 7.6.

trans-[Co(diars)₂(ClO₄)₂]. Cobalt perchlorate hexahydrate (0.64 g) in hot methanol (20 ml) was treated with diars (1.0 g) in hot methanol (20 ml) under nitrogen. The solution rapidly turned deep brown and began to deposit brown crystals. After boiling of the reaction mixture for a few minutes, the product was collected and washed with methanol and then ether and dried at 100° (0.95 g; μ_{eff} = 1.94 BM at 28°).

Anal. Calcd for [Co(C₁₀H₁₆As₂)₂](ClO₄)₂: C, 28.9; H, 3.9; Cl, 8.5. Found: C, 28.4; H, 4.0; Cl, 8.7.

This brown compound is soluble in acetonitrile to give a green solution from which green crystals may be isolated by the slow addition of ether. This green compound appears to have the constitution [Co(diars)₂(CH₃CN)₂](ClO₄)₂·CH₃CN and a magnetic moment μ_{eff} ≈ 1.8 BM at 28° but satisfactory microanalysis could not be obtained because the CH₃CN molecules effloresce from the solid at room temperature. The solid is only stable in an atmosphere of acetonitrile. The compound dissolves in DMSO to give the same nmr spectrum as that obtained for the [Co(diars)₂(ClO₄)₂] complex; three molecules of CH₃CN are released upon dissolution. Similarly the addition of methanol converts the green complex to the brown.

trans,trans-[H₂O(diars)₂Co-Co(diars)₂H₂O](ClO₄)₄. *cis*-[Co(diars)₂(OH₂)₂](ClO₄)₃¹⁷ (1.0 g) was dissolved in warm water (10 ml) and then diluted with methanol (90 ml). The red-brown solution was filtered through paper at once and the filtrate was gently heated on a steam bath for 15 min. The color gradually lightened to yellow and fine yellow needles began to deposit. After cooling, these were collected and washed with methanol and then ether (0.6 g; Λ = 605 ohm⁻¹ cm² mol⁻¹, 5 × 10⁻³ M in acetonitrile at 25°; μ_{eff}(dimer) = 0.7 BM at 28°; FW = 1742 (calcd), 1900 ± 200 (found, 4:1 electrolyte in acetonitrile by "osmometry"). [The formula weight assumes the presence of two loosely coordinated acetonitrile groups.]

Anal. Calcd for [Co(C₁₀H₁₆As₂)₂H₂O](ClO₄)₂: C, 28.3; H, 4.0; As, 35.0; Cl, 8.4. Found: C, 28.4; H, 4.1; As, 35.0; Cl, 8.4. Microanalytical data for the oxygen content were unsatisfactory because of the explosive nature of the ClO₄⁻ ions. The value obtained was 15.9% which compares with the expected values of 17.0 for the aquo adduct or 15.4 for the anhydrous material.

Acknowledgments. We thank the National Research Council of Canada and the Chemistry Department of the University of Toronto for financial support.

Registry No. *cis*-β-[Co(*R,S*-tetraars)(OH₂)₂](ClO₄)₃, 50883-37-9; ethanol, 64-17-5; *trans,trans*-[H₂O(*R,S*-tetraars)CoCo(*R,S*-tetraars)H₂O](ClO₄)₄, 52195-88-7; *trans,trans*-[CH₃CN(*R,S*-tetraars)CoCo(*R,S*-tetraars)CH₃CN](ClO₄)₄, 52195-90-1; *cis*-β-[Co(*R,R,S,S*-tetraars)(OH₂)₂](ClO₄)₃, 50804-65-4; *cis*-α-[Co(*R,R,S,S*-tetraars)(OH₂)₂](ClO₄)₃, 50804-67-6; methanol, 67-56-1; *trans,trans*-[CH₃CN(*R,R,S,S*-tetraars)CoCo(*R,R,S,S*-tetraars)CH₃CN](ClO₄)₄, 52248-00-7; *cis*-α-[Co(*R,R*-tetraars)(OH₂)₂](ClO₄)₃, 50804-61-0; *trans,trans*-[CH₃CN(*R,R*-tetraars)CoCo(*R,R*-tetraars)CH₃CN](ClO₄)₄, 52248-02-9; *trans,trans*-[H₂O(*R,R*-tetraars)CoCo(*R,R*-tetraars)H₂O](ClO₄)₄, 52248-66-5; *trans*-[Co(diars)₂(ClO₄)₂], 17444-52-9; *cis*-[Co(diars)₂(OH₂)₂](ClO₄)₃, 50804-95-0; *trans,trans*-[H₂O(diars)₂CoCo(diars)₂H₂O](ClO₄)₄, 52195-92-3.

(17) B. Bosnich, W. G. Jackson, and J. McLaren, *Inorg. Chem.*, 13, 1133 (1974).