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Complexes of *cis*-1,2-Bis(dimethylarsino)ethylene. I. Iron and Cobalt

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The preparations of *cis*-1,2-bis(dimethylarsino)ethylene, *cis*-edas, and several of its transition metal derivatives are reported. The transition metal complexes which have been prepared include $[Fe(cis\text{-edas})_3][ClO_4]_2$, $[Fe(cis\text{-edas})_3][ClO_4]_3$, *trans*-$[FeCl_2(cis\text{-edas})_2][FeCl_4]$, *trans*-$[CoBr_2(cis\text{-edas})_2]Br$, $[Cu(cis\text{-edas})_2][ClO_4]$, and $[PdCl(cis\text{-edas})_2][ClO_4]$. The visible spectra of the iron(II) and cobalt(III) compounds are discussed, and the weak transitions which are observed are assigned to the d–d transitions of octahedral and *trans*-octahedral complexes with spin-paired d^6 electron configurations. The visible spectra of the other complexes are also reported.

Introduction

Since the preparation of *o*-phenylenebis(dimethylarsine) by Chatt and Mann,[2] transition metal complexes of tertiary arsines have been extensively investigated. The studies of complexes of *o*-phenylenebis(dimethylarsine) by Nyholm and coworkers are particularly noteworthy in this regard.[3] The transition metal complexes of *o*-phenylenebis(dimethylarsine) are usually spin paired and have many interesting spectral and magnetic properties[4–7] which have proved useful for investigating the transition metal–arsenic bond. However, the presence of the aromatic ring complicates many of the spectral features of interest including the ultraviolet and infrared spectra, nmr spectra, etc. Accordingly, it was desirable to obtain a bidentate ligand with structural features and chemical properties similar to those of *o*-phenylenebis(dimethylarsine) but with less complicated spectral properties. The preparation of this bidentate arsenic ligand and its complexes is reported below.

Experimental Section

Materials and Analyses.—Technical grade cacodylic acid obtained from Ansul was recrystallized from water before use. Dimethyliodoarsine was prepared from the recrystallized cacodylic acid using the method of Burrows and Turner,[8] with an over-all yield of 60% based on the crude cacodylic acid. Dry tetrahydrofuran was used as obtained from Fisher Scientific Co., while *cis*-dichloroethylene was obtained from Eastman. The elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo.

Preparation of Compounds.—All of the reactions involving these volatile toxic arsenic compounds were carried out under nitrogen in an efficient hood. It is essential that the tetrahydrofuran used in the preparation of $NaAs(CH_3)_2$ be extremely dry, since any hydroxyl groups present result in the hydrolysis of $NaAs(CH_3)_2$ with a consequent decreased yield of product. During the preparation of the transition metal complexes, the solutions were kept under nitrogen to avoid oxidation of the arsine ligand. However, once prepared, most of the complexes could be recrystallized in the air without oxidation.

***cis*-1,2-Bis(dimethylarsino)ethylene.**—$NaAs(CH_3)_2$ (0.5 mol) in 0.4 l. of tetrahydrofuran was prepared as previously described.[9,10] *cis*-Dichloroethylene (24 g) was added dropwise over a period of 2–3 hr. The temperature was maintained at 40° by the dropping rate of dichloroethylene. After the addition of *cis*-dichloroethylene was complete, the reaction mixture was allowed to stir 1 hr more, 25 ml of methanol was added, and then most of the tetrahydrofuran was removed by distillation at atmospheric pressure. Next, 750 ml of water was added, and the water-insoluble organic layer was separated by use of a separatory funnel. (*Caution!* This layer is extremely flammable and malodorous.) After separating this oily layer, the oil was filtered and fractionated by vacuum distillation. The product was obtained in 30–40% yield based on $As(CH_3)_2I$ and consisted of approximately 10% *cis*-1,2-bis(dimethylarsino)ethylene and 90% *trans*-1,2-bis(dimethylarsino)ethylene; bp 90–93° (24 mm); $n^{25}{}_D$ 1.5567. The *cis* and *trans* isomers could not be separated by distillation. *Anal.* Calcd for $C_2H_2[As(CH_3)_2]_2$: C, 30.53; H, 5.98. Found: C, 29.5; H, 5.98. The mass sepctrum shows a parent peak at 236 mass units.

Dichlorobis[*cis*-1,2-bis(dimethylarsino)ethylene]iron(III) Tetrachloroferrate(III).—1,2-Bis(dimethylarsino)ethylene (1 g) was added to 1 g of $FeCl_3$ in 10 ml of ethanol. A bright crimson precipitate formed immediately and was separated by filtration. Recrystallization of this precipitate from 10 ml of ethanol resulted in 0.12 g of complex. *Anal.* Calcd for $[FeCl_2(C_2H_2(As(CH_3)_2)_2)_2][FeCl_4]$: C, 18.1; H, 3.5; Cl, 26.7. Found: C, 18.1; H, 4.1; Cl, 25.7.

Tris[*cis*-1,2-bis(dimethylarsino)ethylene]iron(II) Perchlorate.—$Fe(ClO_4)_2 \cdot 6H_2O$ (1 g) was dissolved in 5 ml of absolute ethanol and 2 ml of 1,2-bis(dimethylarsino)ethylene was added. The solution was heated on a boiling water bath for several minutes. As the volume of solvent was reduced, an orange solid precipitated. Boiling was continued for 10 min and then 10 ml of ethanol was added and the solution was filtered. The complex was recrystallized from water and dried at 60° under vacuum for 24 hr. *Anal.* Calcd for $[Fe(C_2H_2(As(CH_3)_2)_2)_3][ClO_4]_2$: C, 22.5; H, 4.4; Cl, 7.4. Found: C, 22.6; H, 5.0, Cl, 7.4.

Tris[*cis*-1,2-bis(dimethylarsino)ethylene]iron(III) Perchlorate.—$[Fe(edas)_3][ClO_4]_2$ (1 g) was dissolved in 25 ml of concentrated HNO_3 and 5 ml of dilute $NaClO_4$ solution was added. The solution was then evaporated to approximately 5 ml on a hot plate. The dark green product (0.45 g) was precipitated, washed with water, and dried at 60° under vacuum for 48 hr. The complex was recrystallized from concentrated HNO_3 by adding a dilute solution of $NaClO_4$ until precipitation occurred.

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The dry solid is stable but can be dissolved only in concentrated HNO_3 without decomposition. *Anal.* Calcd for $[Fe(C_2H_2(As(CH_3)_2)_2)_3][ClO_4]_3$: C, 20.4; H, 4.0; Cl, 10.0. Found: C, 20.9; H, 4.1; Cl, 9.9.

Bis[*cis*-1,2-bis(dimethylarsino)ethylene]copper(I) Perchlorate.—$Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 g) was dissolved in 5 ml of methanol, and 0.2 g of 1,2-bis(dimethylarsino)ethylene was added dropwise. A white precipitate was immediately formed and isolated by filtration yielding 0.05 g of white complex. The compound was insoluble in all common solvents except dimethyl sulfoxide in which it decomposed. *Anal.* Calcd for $[Cu(C_2H_2(As(CH_3)_2)_2)_2][ClO_4]$: C, 22.7; H, 4.4; Cl, 5.6. Found: C, 22.7; H, 4.4; Cl, 6.0.

***trans*-Dichlorobis[*cis*-1,2-bis(dimethylarsino)ethylene]cobalt(III) Bromide.**—1,2-Bis(dimethylarsino)ethylene (2.5 g) was added to 3 g of $CoBr_2$ in 80% methanol–ether. The mixture was heated to 55° and air was bubbled through the solution for 48 hr. The volume of solvent was maintained throughout the reaction. Over this period of time, the color of the solution changed from yellow to dark green. The volume of the solution was reduced until green crystals began to appear; then the solution was cooled and filtered to yield 0.45 g of product. The complex was recrystallized from methanol. *Anal.* Calcd for $[CoBr_2(C_2H_2(As(CH_3)_2)_2)_2]Br$: C, 18.7; H, 3.6. Found: C, 18.4; H, 3.8.

Chlorobis[*cis*-1,2-bis(dimethylarsino)ethylene]palladium(II) Perchlorate.—To a solution containing 1.55 g of K_2PdCl_4 dissolved in 16 ml of water and 30 ml of ethanol was added 2.25 g of 1,2-bis(dimethylarsino)ethylene. After filtering, 110 ml of water was added, the solution was boiled, and 70% $HClO_4$ was added dropwise to yield a brown powder. This brown complex was recrystallized from 2:1 acetone–water. *Anal.* Calcd for $[PdCl(C_2H_2(As(CH_3)_2)_2)_2]ClO_4$: C, 20.2; H, 4.0; Cl, 9.9. Found: C, 22.2; H, 4.4; Cl, 9.6.

***cis*-1,2-Bis(dimethylarsino)ethylene.**—$[FeCl_2(\textit{cis}\text{-edas})_2][FeCl_4]$ (3.0 g) was added to 6.0 g of triphenylphosphine in a distillation apparatus, and the mixture was heated until the triphenylphosphine had melted (75°) and all of the iron complex had dissolved. The system was evacuated, and then the temperature of the triphenylphosphine melt was gradually increased to between 150 and 170°. The iron complex decomposed at this temperature, liberating 1.4 g of the *cis*-1,2-bis(dimethylarsino)ethylene ligand which was collected in a liquid-nitrogen trap. The nmr spectrum of the distillate indicated that there was no *trans* compound present. The nmr spectrum showed two singlets at τ 8.95 and 3.05.

Physical Measurements.—The infrared spectra were obtained using a Perkin-Elmer Model 337 infrared spectrophotometer. The reflectance spectra were measured on a Zeiss PMQ II especially equipped with a lead sulfide detector for measurements from 4000 to 12,000 cm^{-1}, while the solution spectra were obtained using a Cary Model 14. The nmr spectra were obtained using a Varian A-60 nmr spectrometer with internal TMS standard.

Results and Discussion

The preparation of the mixture of the *cis* and *trans* isomers of 1,2-bis(dimethylarsino)ethylene has been reported previously.[10] However, only two transition metal complexes, $TiBr_4(\textit{cis}\text{-edas})$ and $Pt(\textit{cis}\text{-edas})_2{}^{2+}$, have been isolated and characterized.

The reaction of $As(CH_3)_2{}^-$ with 1,2-dihaloethylenes has been studied under a variety of conditions which differ markedly from those used by Bennett. None of these reactions using different temperatures, solvents, dihaloethylenes, and alkali metals, including lithium and sodium, led to significant increases in the yield of the *cis* isomers. These results have not been described in detail, but the preparation of 1,2-bis(dimethylarsino)ethylene described above represents the optimum conditions for the production of *cis*-1,2-bis(dimethylarsino)ethylene found thus far.

The pure *cis* isomer can easily be prepared from the *cis–trans* mixture by formation of the iron complex $[FeCl_2(\textit{cis}\text{-edas})_2][FeCl_4]$. In ethanol or ether, the mixture of *cis* and *trans* isomers reacts with $FeCl_3$ to form an insoluble red precipitate which consists entirely of the *cis*-1,2-bis(dimethylarsino)ethylene chelate of iron(III). If they are formed, the iron(III) complexes of the *trans* isomer remain in solution and do not contaminate the insoluble $[FeCl_2(\textit{cis}\text{-edas})_2][FeCl_4]$. The ligand *cis*-1,2-bis(dimethylarsino)ethylene can be regenerated from its iron(III) complex by treatment with molten triphenylphosphine at 150° (0.1 mm), with over-all yields of at least 80%. Most of the compounds described above have been prepared from the *cis–trans* mixture, but for reactions in which the presence of the *trans* isomer interferes with the isolation and purification of the *cis* complexes, the pure *cis* isomer can be used advantageously in place of the *cis–trans* mixture.

Reaction of $Fe(ClO_4)_2 \cdot 6H_2O$ in ethanol with *cis*-1,2-bis(dimethylarsino)ethylene readily yields an orange compound with the composition $[Fe(\textit{cis}\text{-edas})_3][ClO_4]_2$. There are two steric arrangements which are possible for this complex: (a) the usual "octahedral" complex in which the six arsenic atoms are arranged at the corners of an octahedron (D_3 point group) and (b) the trigonal-prismatic arrangement which has been observed for several sulfur complexes (D_{3h} point group).[11] In contrast with the sulfur complexes, a trigonal-prismatic arrangement of the arsenic groups would not be expected, since such an arrangement would entail a great deal of crowding of the rather bulky methyl groups attached to the arsenic atoms. This steric effect is not a consideration in the sulfur complexes since there are no additional groups attached to the sulfur atoms in those complexes.

The visible spectrum of $[Fe(\textit{cis}\text{-edas})_3][ClO_4]_2$ should give direct evidence regarding the steric arrangement of these ligands. A trigonal-prismatic arrangement should give rise to a ligand field with trigonal (D_{3h}) symmetry, while an octahedral disposition of the six arsenic atoms should lead to the usual octahedral ligand field, with perhaps a small trigonal component.

The visible spectra of the complexes of *o*-phenylenebis(dimethylarsine), das, have been extensively investigated.[12–14] The visible spectra of the spin-paired d^6 complexes $Fe(das)_3{}^{2+}$ and $Co(das)_3{}^{3+}$ are conveniently described by a ligand field with octahedral symmetry.[13] On the other hand, the diamagnetism and visible spectrum of $Ni(das)_3{}^{2+}$ were accounted for by assuming that the complex has trigonal (D_{3h}) quantization.

The visible spectrum of $Fe(\textit{cis}\text{-edas})_3{}^{2+}$ was obtained from the diffuse reflectance of the pure solid and in

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solution in methanol. The spectrum of Fe(*cis*-edas)$_3{}^{2+}$ is very similar to that previously obtained for Fe(das)$_3{}^{2+}$ (Figure 1). No significance should be ascribed to the minor shifts in the positions of the absorption maxima between Fe(das)$_3{}^{2+}$ and Fe(*cis*-edas)$_3{}^{2+}$, since there are factors other than electronic effects which can easily cause shifts of 100–800 cm^{-1}. The extinction coefficients for Fe(*cis*-edas)$_3{}^{2+}$ are much smaller than those of Fe(das)$_3{}^{2+}$ which are well within the range usually found for d–d transitions. A very weak transition near 14.5 kK was observed in the reflectance spectra (Table I) of Fe(das)$_3{}^{2+}$ and Fe(*cis*-edas)$_3{}^{2+}$, while the two more intense transitions were near 21.5 and 27 kK.

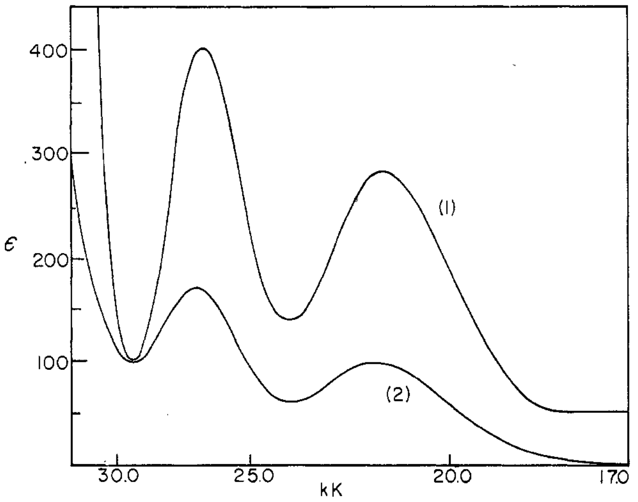

Figure 1.—The visible spectra of (1) [Fe(das)$_3$][ClO$_4$]$_2$ in dimethyl sulfoxide and (2) [Fe(*cis*-edas)$_3$][ClO$_4$]$_2$ in methanol.

Table I

Electronic Spectra of the d^6 Complexes of *cis*-1,2-Bis(dimethylarsino)ethylene

Compound	Symmetry	Absorption max, kK (ϵ_{max}, M^{-1} cm^{-1})		
	O$_h$	^{3}T$_1$	^{1}T$_1$	^{1}T$_2$
	D$_{4h}$	(^{3}E) (^{3}A$_2$)	(^{1}E) (^{1}A$_2$)	(^{1}E and ^{1}B$_2$)
[Fe(*cis*-edas)$_3$][ClO$_4$]$_2$		14.7[a]	21.5 (100)	27.4 (170)
[Fe(das)$_3$][ClO$_4$]$_2$		14.5[a]	21.4 (230)	26.6 (350)
trans-[CoBr$_2$(*cis*-edas)$_2$]Br		...	15.5 (90), 21.6 (sh)	...
trans-[CoBr$_2$(das)$_2$]-[ClO$_4$]		...	15.7 (87), ...[b]	...

[a] Observed in reflectance only. [b] Obscured by charge-transfer bands.

These spectra are typical of those usually observed for octahedral spin-paired d^6 complexes. The first electronic transition which is observed in the reflectance spectrum is extremely weak and can only be assigned to the lowest energy spin-forbidden transition $^1A_1 \rightarrow {}^3T_1$. The two transitions of modest intensity at 21.5 and 27.4 kK are the two spin-allowed transitions $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$, respectively. The only other transition expected for an octahedral d^6 complex is $^1A_1 \rightarrow {}^3T_2$. This transition is not usually observed in d^6 complexes, since it has a very low intensity and is normally obscured by the $^1A_1 \rightarrow {}^1T_1$ transition. There is no evidence of any large splitting of any of these bands, which indicates the absence of a large trigonal field in these arsine complexes.

The cobalt(III) complexes can be prepared by first treating *cis*-1,2-bis(dimethylarsino)ethylene with the appropriate cobalt(II) salt in alcohol, followed by air oxidation in acidic solutions of the cobaltous complex. Under these conditions, a series of green complexes of cobalt(III) is formed. When CoBr$_2$ is used, the green complex [CoBr$_2$(*cis*-edas)$_2$]Br is easily isolated and purified. The spectrum of this d^6 complex is reported in Table I. The spectrum of this cobalt(III) complex is almost identical with that of the green cobalt complex CoBr$_2$(das)$_2{}^{2+}$ which has been shown by X-ray structural investigations to have a *trans*-octahedral arrangement of the ligands around the cobalt.[14] There is one absorption band with an extinction coefficient of 90 at 15.5 kK in [CoBr$_2$(*cis*-edas)$_2$]Br. This transition is to be compared with a similar absorption band at 15.7 kK with a molar extinction coefficient of 87 in *trans*-[CoBr$_2$(das)$_2$][ClO$_4$]. The other transitions in the two compounds are also almost identical. Thus, this series of green cobalt(III) complexes of *cis*-1,2-bis(dimethylarsino)ethylene almost certainly has a *trans*-octahedral arrangement of ligands.

The reflectance spectra of the iron(III) complexes of *cis*-1,2-bis(dimethylarsino)ethylene were also obtained and are compared with those of *o*-phenylenebis(dimethylarsine) in Table II. As in the case of the cobalt complexes, the spectra of the iron(III) complexes of *cis*-1,2-bis(dimethylarsino)ethylene are almost indistinguishable from those of *o*-phenylenebis(dimethylarsine) and must also be octahedrally coordinated.

Table II

Spectral Properties of Iron(III) Complexes of *cis*-1,2-Bis(dimethylarsino)ethylene

Compound	Color	Electronic absorption max, kK
[Fe(*cis*-edas)$_3$][ClO$_4$]$_3$	Orange	4.0,[a] 15.7, 17.2, 19.2, 24.0
[Fe(das)$_3$][ClO$_4$]$_3$	Orange	...,[b] 15.7, 17.2, 19.2, ...
trans-[FeBr$_2$(*cis*-edas)$_2$][ClO$_4$]	Green	5.0,[a] 14.0, 16.4, 18.2, 24.0
trans-[FeBr$_2$(das)$_2$]-[ClO$_4$]	Green	5.0,[a] 13.7, 16.0, 17.8, 23.0
trans-[FeCl$_2$(*cis*-edas)$_2$][FeCl$_4$]	Red	...,[b] 18.2, 19.8, 27.4
trans-[FeCl$_2$(das)$_2$]-[FeCl$_4$]	Red	...,[b] 18.0, 19.5, 26.0

[a] Observed in reflectance only. [b] Not observed.

The palladium(II) complex can be prepared using methods analogous to those used for the preparation of the platinum(II) complexes. The perchlorate salt is separated from the complex mixture of compounds of the *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene by addition of perchlorate ion. The palladium(II) complex which was isolated has a composition indicating it to be pentacoordinate as are the platinum complex of *cis*-1,2-bis(dimethylarsino)ethylene and the platinum and palladium complexes of *o*-phenylenebis(dimethylarsine).

No copper(II) derivatives of *o*-phenylenebis(dimethylarsine) have been reported although they have been isolated for short periods of time.[15] To determine whether the copper(II) complexes of *cis*-1,2-bis(dimethylarsino)ethylene would be stable, several reactions between copper(II) salts and *cis*-1,2-bis(dimethylarsino)ethylene were carried out, wherein the reaction of copper(II) perchlorate is typical. The copper(II) derivatives of *cis*-1,2-bis(dimethylarsino)ethylene are apparently even less stable than those of *o*-phenylenebis(dimethylarsine), since it proved impossible to isolate any copper(II) complexes, even for short periods of time. The copper(I) perchlorate prepared from this reaction is white and insoluble in all of the solvents with which it does not react, and consequently has not been further characterized.

Conclusions

Pure *cis*-1,2-bis(dimethylarsino)ethylene is an excellent bidentate chelating ligand. It readily forms complexes with the first-, second-, and third-row transition elements in both high and low oxidation states. The complexes of iron(II), iron(III), cobalt(III), and palladium(II) are remarkably stable. The metal derivatives of *cis*-1,2-bis(dimethylarsino)ethylene can be handled in the presence of air and water without appreciable decomposition. The iron complex $[Fe(cis\text{-edas})_3][ClO_4]_3$ is particularly stable in contrast with $[Fe(das)_3][ClO_4]_3$ which decomposes on standing.

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[15] R. D. Feltham, unpublished results.

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Pentacoordinate Complexes. II.[1] The Electron Spin Resonance Spectrum of Pentakis(methyl isocyanide)cobalt(II) and a Comparison with Pentacyanocobaltate(II)

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The esr spectrum of $Co(CH_3NC)_5^{2+}$ in ethylene glycol–water glasses and solutions has been investigated in the temperature range 77–300°K. The *g* values observed are consistent with a square-pyramidal structure for this complex. Evidence is presented for increased unpaired electron delocalization in the $Co(CH_3NC)_5^{2+}$ ion in comparison with the pentacyano complex $Co(CN)_5^{3-}$; this may explain the difference in chemical reactivity of the two complexes. Optical spectra for $Co(CH_3NC)_5^{2+}$ are also reported.

Introduction

Pentacoordinated transition metal ions have been the subject of recent studies concerned with elucidating the molecular structure of these complexes in solution.[3-5] The two most likely geometries for such ions are the trigonal bipyramid and the square pyramid, of D_{3h} and C_{4v} symmetry, respectively.

Recently, Alexander and Gray[4] have shown that the optical and esr spectra of $Co(CN)_5^{3-}$ can be explained by assuming a square-pyramidal ground-state geometry for this complex. As part of a continuing study of pentacoordinated Co(II) ions,[1] we have investigated the physical properties of the low-spin pentakis(methyl isocyanide)cobalt(II) ion using optical and esr methods. The results of this study, which indicate that the symmetry of $Co(CH_3NC)_5^{2+}$ is also C_{4v}, provide the basis for some interesting comparisons of the physical and chemical properties of the two ions.

Experimental Section

Materials.—Baker Analyzed reagent grade chemicals were used. Methyl isocyanide was prepared according to the method of Casanova, *et al.*,[6] and redistilled twice to ensure purity. The uv spectrum of the product in water showed no band at 940 mμ which is characteristic for quinoline used in the synthesis. Gas chromatographic analysis of the methyl isocyanide also showed no trace of quinoline or acetonitrile. The preparation of $Co_2(CH_3NC)_{10}(NO_3)_4$ was accomplished by adding a small excess of CH_3NC to the cobaltous salt in absolute ethanol at 0° under nitrogen in the absence of light. The resultant red solid was washed with ethanol and used immediately or stored in Dry Ice.

Analysis.—Optical spectra of the complex in aqueous solution were recorded on a Cary Model 14 spectrophotometer to verify the purity of the sample. No evidence for the presence of quinoline was observed. Gas chromatographic analysis showed no trace of acetonitrile and thus ruled out the possibility of a Co(II)-catalyzed isomerization of CH_3NC to CH_3CN.

Esr Spectra.—A Varian V-4502 X-band esr spectrometer and 9-in. magnet equipped with Fieldial were employed. Field

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