

## Stereochemistry of $\beta$ -Diketone Complexes of Cobalt(III). XI. Synthesis and Properties of Some cyano Bis(Acetylacetonato)cobalt(III) Complexes

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*K{cis[Co acac<sub>2</sub>(CN)<sub>2</sub>], [PPh<sub>4</sub>]{cis[Co acac<sub>2</sub>(CN)<sub>2</sub>], trans and cis[Co acac<sub>2</sub>py(CN)] have been synthesized and characterized. The complex cis[Co acac<sub>2</sub>(CN)<sub>2</sub>}<sup>-</sup> does not show any isomerization or solvolysis in chloroform or dimethylsulfoxide or water. The complexes cis and trans[Co acac<sub>2</sub>py(CN)] cannot be interconverted in refluxing chloroform or benzene. Although no isomerization is noted in dimethylsulfoxide solution for either isomer, the trans isomer does undergo solvolysis with partial loss of pyridine.*

### Introduction

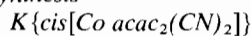
Previous work<sup>1</sup> has shown that complexes of the type [Co acac<sub>2</sub>(py)X] undergo intramolecular *cis*  $\rightleftharpoons$  *trans* isomerization in chloroform solution. The rate of isomerization is dependent on X. The reaction of the  $\pi$  donor N<sub>3</sub><sup>-</sup> complex is much more rapid than that of the  $\pi$  acceptor, NO<sub>2</sub><sup>-</sup>. Since CN<sup>-</sup> is a very good  $\pi$  acceptor we set out to study its complexes in order to test our notion of the effect of anion on reactivity. Only one complex of this kind, K{cis[Co acac<sub>2</sub>(CN)<sub>2</sub>]} has appeared in the literature to date.<sup>2</sup> We wish to report here the synthesis, characterization and reactivity of two new complexes, *cis* and *trans*[Co acac<sub>2</sub>py(CN)].

### Experimental

#### Materials

The starting material [Co acac<sub>3</sub>] was prepared by the method of Bryant and Fernelius.<sup>3</sup> All other materials were reagent grade and used without further purification. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

#### Synthesis

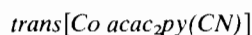


The following is a modification and simplification of the synthesis reported by Nishikawa and co-workers.<sup>2</sup> The yield has been more than doubled. A solution of

8.00 g of [Co acac<sub>3</sub>] (0.0224 mol) in 160 ml of methanol was placed in an ice bath. After the addition of 2.88 g of potassium cyanide (0.0448 mol) and 2.0 g of Norit A activated charcoal, the reaction mixture was stirred at 0°C for six hours. The solution was filtered, the filtrate was placed in a large evaporating dish and evaporated to dryness, and the residue was washed with chloroform to remove any unreacted [Co acac<sub>3</sub>]. The chloroform-insoluble residue was extracted with acetone until the acetone extracts were colorless, and a five-fold excess of diethyl ether was added to the acetone solution. The mixture was kept at 0°C for 24 hours, at which point the flocculent pink precipitate was filtered and air dried. The weight of the pure product was 3.64 g, giving a 47% yield based on the initial weight of [Co acac<sub>3</sub>]. *Anal.* calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>CoK, K[Co acac<sub>2</sub>(CN)<sub>2</sub>]: C, 41.38; H, 4.02; N, 8.04. Found: C, 41.07; H, 4.19; N, 7.93.



A 0.5 g sample of K{cis[Co acac<sub>2</sub>(CN)<sub>2</sub>]} (0.0014 mol) was dissolved in 20 ml of water. Upon addition of 0.6 g of tetraphenylphosphonium bromide (0.0014 mol), a red precipitate immediately formed. This product was filtered and air dried. Recrystallization was accomplished by dissolving the crude product in chloroform and adding sufficient petroleum ether to induce cloudiness. The mixture was kept at 0°C for four to five hours and the crystalline product was filtered and air dried. The yield was 0.90 g, a 95% yield based on the weight of the initial potassium salt. *Anal.* calcd for C<sub>36</sub>H<sub>36</sub>N<sub>2</sub>O<sub>5</sub>PCo, [PPh<sub>4</sub>][Co acac<sub>2</sub>(CN)<sub>2</sub>]·H<sub>2</sub>O: C, 64.86; H, 5.41; N, 4.21. Found: C, 65.06; H, 5.01; N, 4.13.



A solution of 5.00 g of [Co acac<sub>3</sub>] (0.0140 mol) in 120 ml methanol was placed in an ice bath and treated with 0.91 g of potassium cyanide (0.0140 mol), 2.0 g of Norit A activated charcoal, and 4.4 ml of pyridine (0.0560 mol). The reaction mixture was stirred at 0°C for 18 hours, at which point it was filtered and the filtrate was evaporated to dryness. The residue

was extracted with chloroform and filtered. The chloroform extract, total volume ~80 ml, was deposited on a 2.5 cm column packed to a height of 45 cm with 60–100 mesh florasil (Floridin Co.). Elution with 200 ml of chloroform resulted in removal of traces of the unreacted [Co acac<sub>3</sub>]. Treatment of the column with 90% benzene–10% methanol resulted in the movement of one red and one yellow–orange band down the column. The red fraction, which came off the column first, was collected and evaporated to dryness. The product, a mixture of *trans* and *cis* isomers at this point, was dissolved in chloroform and a 4-fold excess of petroleum ether was added. After 18 hours at 0°C, the mixture was filtered and the product was air dried. The weight of the red crystalline product was 0.20 g, a 4% yield based on the weight of the initial [Co acac<sub>3</sub>]. *Anal.* calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>Co, [Co acac<sub>2</sub>py(CN)]: C, 53.04; H, 5.25; N, 7.73. Found: C, 52.86; H, 5.31; N, 7.67. M.P. 184°C.

#### *cis*[Co acac<sub>2</sub>py(CN)]

The filtrate from the recrystallization of the *trans* [Co acac<sub>2</sub>py(CN)] preparation was evaporated to dryness at room temperature. The red product weighed 0.10 g, a 2% yield based on the weight of the initial [Co acac<sub>3</sub>]. *Anal.* calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>Co, [Co acac<sub>2</sub>py(CN)]: C, 53.04; H, 5.25; N, 7.73. Found: C, 52.83; H, 4.96; N, 7.60. M.P. 173°C.

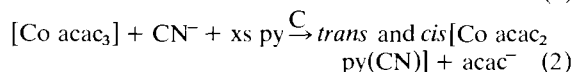
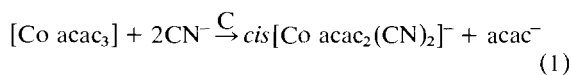
#### Measurements

Spectral measurements were carried out as previously described.<sup>1</sup>

### Results and Discussion

#### Synthesis

The synthetic scheme utilized in this work can be represented by



The chelate replacement reaction does not take place in the absence of charcoal. The charcoal catalysis most likely involves the intermediacy of a labile Co(II) complex.<sup>4</sup>

The product isolated in (1) is isomerically pure and no *trans* isomer can be isolated from the reaction mixture. However, under the reaction conditions, both *cis* and *trans* isomers might be expected to form. The initial products might then isomerize to the thermodynamically stable isomer. The by-products isolated from the reaction mixture in addition to the starting material were [Co<sub>2</sub>acac<sub>4</sub>(OH)<sub>2</sub>], and K<sub>3</sub>[Co(CN)<sub>6</sub>]

and an unidentified Co(II) salt. Under the same reaction conditions as (1), except with Co(III)/CN<sup>-</sup> of 1, no [Co acac<sub>2</sub>H<sub>2</sub>O(CN)] was isolated.

The synthesis of [Co acac<sub>2</sub>py(CN)] is accomplished by a simple modification of the dicyanide preparation. By reducing the CN<sup>-</sup>/Co(III) ratio to one and adding a four-fold excess of pyridine, a small yield of the desired product is obtained. Use of only a stoichiometric amount of pyridine significantly lowers the yield. The main by-products in reaction (2) are *cis* [Co acac<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> and a water soluble Co(II) salt. The product isolated is a mixture of the *trans* and *cis* isomers as would be expected from the nature of the reaction. In this reaction control of the temperatures near 0°C is important since carrying it out at room temperature results in the formation of little or no product.

#### Spectroscopy

The infrared spectra, 4000–400 cm<sup>-1</sup>, were determined with the complexes in potassium bromide disks, while the spectra in the 2200–2000 cm<sup>-1</sup> region were determined using chloroform solutions. The spectra show absorptions typical of the coordinated acetylacetonate anion, tetraphenylphosphonium cation and pyridine.<sup>5</sup> The medium intensity C≡N stretch appears at 2130 ± 5 cm<sup>-1</sup> for all the complexes. This is in the region found for other Co(III) complexes with cyanide ligands.<sup>6</sup> Although two C≡N<sup>-</sup> stretching absorptions are expected in the *cis*[Co acac<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup>, only one band is seen in the solid and in solution. This failure to resolve the bands is not noted for *cis*[Co en<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> where ν(CN) are seen at 2137, 2128 cm<sup>-1</sup>.<sup>7</sup>

The nmr spectra of the various complexes were determined in several solvents and the chemical shifts are listed in Table I. The number of methine and methyl resonances observed supports the assignment of stereochemistry for the complex.<sup>8</sup> The resonances of the acetylacetonate protons are shifted from those of other anion complexes of this type. For example, the methyl resonance of *trans*[Co acac<sub>2</sub>py(CN)] is 0.07 ppm upfield from that of *trans*[Co acac<sub>2</sub>py(N<sub>3</sub>)]. Similarly, the methyl splitting for *cis*[Co acac<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> is much larger than that of the *cis*[Co acac<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup> or *cis*[Co acac<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, *i.e.*, 0.38 ppm *versus* 0.08 ppm. The chemical shifts of the methine resonances are not much affected by the change in anion. The effect of CN<sup>-</sup> on the methyl resonance is probably related to magnetic anisotropy effects of this unsaturated ligand rather than to ground state *cis* or *trans* effects.<sup>8,9</sup>

The positions of the absorption maxima of solutions of the complexes are given in Table II. The assignments are consistent with previous work.<sup>1</sup> The visible spectra show one prominent absorption at 19.1–20.0 kK and a shoulder at ~27 kK. These absorptions can be assigned to the ligand field transitions of <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> of the pseudooctahedral cobalt(III).

TABLE I. Proton Magnetic Resonance Data (ppm) for Cyanide Complexes.

Complex	Isomer	Solvent	Resonance <sup>a</sup>	
			CH <sub>3</sub>	C-H
K[Co acac <sub>2</sub> (CN) <sub>2</sub> ]	<i>cis</i>	D <sub>2</sub> O	-1.90 -2.23	-5.55
	<i>cis</i>	DMSO-d <sub>6</sub>	-1.70 -2.02	-5.35
[P(Ph) <sub>4</sub> ][Co acac <sub>2</sub> (CN) <sub>2</sub> ]	<i>cis</i>	CDCl <sub>3</sub>	-1.79 -2.17	-5.36
[Co acac <sub>2</sub> py(CN)]	<i>trans</i>	CDCl <sub>3</sub>	-2.04	-5.38
		DMSO-d <sub>6</sub>	-1.98	-5.42
	<i>cis</i>	CDCl <sub>3</sub>	-2.05 -2.07 -2.13	-5.37 -5.53
		DMSO-d <sub>6</sub>	-2.00 <sup>b</sup> -2.07	-5.47 -5.63
			-2.12	

<sup>a</sup> Chemical shifts relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate for D<sub>2</sub>O and DMSO-d<sub>6</sub> and tetramethylsilane for CDCl<sub>3</sub>. <sup>b</sup> Intensity ratio 3:3:6 for -2.00, -2.07, and -2.12 respectively.

In general the frequency of the first band is consistent with the high ligand field strength of the cyanide ion. For example, the *trans*[Co acac<sub>2</sub>py(CN)] complex shows a maximum at 19.5 kK while the corresponding weaker field anions, NO<sub>2</sub><sup>-</sup> and N<sub>3</sub><sup>-</sup> complexes show maxima at 18.7 and 17.2 kK, respectively. Further the *cis*[Co acac<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> shows a maximum at 19.1 kK while the azide complex has a maximum at 15.6. It is interesting to note, however, that the dicyanide complex shows a band which is red shifted from the *cis* cyanopyridine by 900 cm<sup>-1</sup>. An unexpected low frequency shift has been previously ascribed to the presence of isocyanide linkage isomers.<sup>10</sup> The isocyanide ligand possesses a ligand field strength comparable to that of ammonia.<sup>11</sup> Therefore, the maxima for *cis*[Co acac<sub>2</sub>(NC)<sub>2</sub>]<sup>-</sup> should be close to that of *cis*[Co acac<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.<sup>5</sup> Actually the latter complex displays a maximum at 18.3 kK, some 800 cm<sup>-1</sup> lower in energy

than the dicyanide.<sup>4</sup> The frequency of the charge transfer band  $t_{2g} \rightarrow \pi^*$  is comparable (within 300 cm<sup>-1</sup>) to that of the NO<sub>2</sub><sup>-</sup> and N<sub>3</sub><sup>-</sup> complexes. This may be taken as evidence for an absence of significant  $\pi$  mixing of the anion with the  $t_{2g}$  metal orbitals in the ground state. On the other hand, the  $\sigma_L \rightarrow e_g$  charge transfer band is blue shifted from the bands of the corresponding NO<sub>2</sub><sup>-</sup> and N<sub>3</sub><sup>-</sup> bands. This most likely arises from the destabilization of the  $e_g$  metal orbital by the good sigma donor cyanide ligand. The expected blue shift of all the charge transfer bands is seen in going from the *trans* to *cis* isomer.<sup>1</sup>

#### Isomerization and Solvolysis

Aqueous solutions of *cis*[Co acac<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> do not show any solvolysis or isomerization even when heated to 80°C for 24 hours. Prolonged refluxing does, however, lead to decomposition. It is interesting to note that heating of D<sub>2</sub>O solutions of the complex leads to D-H exchange of the methine proton of the acetylacetonate ligand.<sup>12</sup> The tetraphenylphosphonium salt of the complex was prepared in order to attempt isomerization in chloroform solution. Surprisingly, refluxing the complex (60°C) in chloroform for 72 hours does not lead to isomerization. No solvolysis or isomerization is noted for the complex in DMSO at room temperature for several days. Finally, charcoal catalysis does not appear to lead to isomerization in aqueous solution at room temperature. On the other hand heating of these mixtures leads to decomposition. After separation of the *cis* and *trans*[Co acac<sub>2</sub>py(CN)] several isomerization reactions were attempted. Refluxing either of the isomers in CHCl<sub>3</sub> for 30 hours did not lead to any observable isomerization. Similarly prolonged heating (~300 hours) in chloroform only leads to decomposition of *trans*[Co acac<sub>2</sub>py(CN)] to [Co acac<sub>3</sub>] and a Co(II) complex. Likewise refluxing the *trans* complex in benzene (~80°C) for 72 hours yields only [Co acac<sub>3</sub>] and [Co acac py<sub>2</sub>(CN)<sub>2</sub>]. Dissolution of *trans*[Co acac<sub>2</sub>py(CN)] in DMSO yields an equilibrium mixture of the original complex and *trans*[Co acac<sub>2</sub>CN(DMSO)]. The nmr spectrum in DMSO-d<sub>6</sub> shows two methine resonances at -5.42 and -5.47 ppm and two methyl resonances at -1.98

TABLE II. Electronic Absorption Maxima (kK) of Cyanide Complexes in Chloroform.

Complex	Isomer	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>	$t_{2g} \rightarrow \pi^*$	$\pi \rightarrow e_g$	$\delta_L \rightarrow e_g$
[P(Ph) <sub>4</sub> ][Co acac <sub>2</sub> (CN) <sub>2</sub> ]	<i>cis</i>	19.1 (1.85) <sup>a</sup>	30.9 (3.82)	b	b
[Co acac <sub>2</sub> py(CN)]	<i>trans</i>	19.5 (2.17)	30.4 (3.83)	34.8 (4.04)	38.9 (4.30)
[Co acac <sub>2</sub> py(CN)]	<i>cis</i>	20.0 (2.16)	30.9 (3.82)	35.2 (4.04)	39.7 (4.38)

<sup>a</sup> Log  $\epsilon_{max}$  in parentheses. <sup>b</sup> Obscured by cation absorption.

and  $-2.08$  ppm with the latter in the ratio 2:1. The low field methine and methyl lines are assigned to the DMSO complex since addition of excess pyridine to the solution decreases the intensity of these lines while enhancing the others. In contrast, no solvolysis is noted for DMSO solution of the *cis*[Co acac<sub>2</sub>py(CN)]. Finally, no isomerization is noted for either the *cis* or *trans*[Co acac<sub>2</sub>py(CN)] in DMSO over several weeks at room temperature.

The most interesting result of this work is the observation that the complexes do not undergo facile isomerization reaction like the other anion complexes. For example, while the half-time for isomerization at 60°C in CHCl<sub>3</sub> is 0.8 hr for [Co acac<sub>2</sub>py(NO<sub>2</sub>)] and <0.05 hr for [Co acac<sub>2</sub>py(N<sub>3</sub>)],<sup>1</sup> no isomerization is noted for the *trans* or *cis* cyanide complex in 30 hr. The isomerizations most likely proceed via an intramolecular chelate ring opening mechanism with the formation of a trigonal bipyramid. The azide reaction is rapid because the anion is a  $\pi$  donor which stabilizes the reaction intermediate. On the other hand cyanide is a  $\pi$  acceptor which tends to destabilize the intermediate. The failure to observe isomerization of *cis*[Co acac<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> in refluxing chloroform after 72 hours is in marked contrast to the results on *cis*[Co acac<sub>2</sub>(NO<sub>2</sub>)]<sup>-</sup>. In the latter case the half-time to reach equilibrium is 0.7 hr.<sup>12</sup> The apparent lack of reactivity of the dicyanide complex may be due to the above mentioned anion effect or it may be related to an equilibrium effect. If the *trans*  $\rightleftharpoons$  *cis* equilibrium is to the right ( $K_{eq} > 20$ ) then no *trans* isomer will be detected by the nmr method. This latter point can be cleared up by observations on the, as yet unknown, *trans* dicyanide.

The contrast in the ability to undergo solvolysis reactions in water or DMSO for the *cis* and *trans* isomers is related to a strong octahedral *trans* effect in

this type of complex.<sup>6</sup> In general the anions are strongly held and dissociation only occurs if it is *trans* to another anion. Therefore the *trans* isomers lead to replacement of the ligand (anion or pyridine) *trans* to the cyanide while the *cis* isomers do not undergo solvolysis.

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