

The spectrochemical order of the ligands according to X is generally found to be $F \sim OC_2H_5 > CH_3 \sim C_6H_5 \sim CF_3$. The π interaction between the substituent lone pair with the phosphorus-sulfur $d\pi$ system apparently dominates the inductive effect of the substituent (e.g., F vs. CF_3). This would be expected to produce a synergic effect in the reverse sense to that postulated for transition metal carbonyl compounds, although not so readily discernible in the P-S stretching frequencies. The nephelauxetic series of the ligands ordered according to X in order of B' is $F \sim OC_2H_5 < CH_3 \sim C_6H_5 \sim CF_3$, indicating greater electronic delocalization with those substituents found to produce the largest

phosphorus coupling constants in the epr spectra of the vanadyl complexes.⁷

Acknowledgments.—We thank Dr. R. M. Tuggle for his X-ray investigation of $CoOS_3P_2(CH_3)_4$ and Dr. M. J. Bennett and Mr. R. H. Sumner for permission to use Figure 1 prior to publication. We are indebted to Miss J. K. Schneider and Dr. A. R. Sanger for their preparation of the $HS_2P(CF_3)_2$ acid and to Drs. A. R. Sanger and A. J. Tomlinson for helpful discussions. We thank the National Research Council of Canada and the University of Alberta for the financial support of this work.

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Stereochemistry of β -Diketone Complexes of Cobalt(III). X. Synthesis and Spectroscopy of Some Azide Complexes of Bis(acetylacetonato)cobalt(III)¹

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Received December 9, 1971

$K\{trans-[Co(acac)_2(N_3)_2]\}$, $[PPh_4]\{cis- \text{ and } trans-[Co(acac)_2(N_3)_2]\}$, $cis- \text{ and } trans-[Co(acac)_2N_3py]$, and $cis-[Co(acac)_2N_3NH_3]$ have been synthesized and characterized. The stereochemistry of the complexes was assigned with the aid of their proton magnetic resonance spectra. In addition, infrared and ultraviolet-visible spectra of the materials were determined and the absorption bands assigned. The complexes undergo a facile $trans \rightleftharpoons cis$ isomerization reaction in solution at 34°.

Previous work with bis(acetylacetonato)cobalt(III) complexes has centered around nitro compounds of the type $cis-$ and $trans-[Co(acac)_2NO_2L]^{n-}$, where L is NO_2^- ,² an amine,³ or water.² In contrast to the inert diamine complexes^{4,5} $cis-$ and $trans-[Co(acac)_2L_2]^+$, the nitro derivatives are stereochemically labile.⁶ This observation has promoted the study of complexes of other anions. Comparisons of the reactivities for a series of anion complexes of the type $cis-$ and $trans-[Co(acac)_2XL]^{n-}$ will contribute toward understanding the mode of reaction of low ligand field complexes of cobalt(III).⁷ We wish to report here the synthesis, characterization, and reactivity of the new azide complexes $cis-$ and $trans-[Co(acac)_2N_3L]^{n-}$ where L is N_3^- , pyridine, or ammonia and $n = 1$ or 0. A structural representation of the complexes is given in Figure 1.

Experimental Section

Materials.—The starting material $[Co(acac)_2]$ was prepared by the method of Ellern and Ragsdale.⁸ All other materials were reagent grade and used without further purification.

Syntheses. $K\{trans-[Co(acac)_2(N_3)_2]\}$.—Two grams of $[Co(acac)_2]$ (0.0078 mol) was dissolved in 125 ml of methanol. After the addition of 2.5 g of potassium azide (0.0308 mol) and

2 ml of glacial acetic acid (0.0348 mol), 2 ml of 30% hydrogen peroxide solution (0.0176 mol) was added dropwise. The reaction mixture was stirred at 25° for 2 hr, at which point the precipitated crude product was filtered and air-dried. The green-brown product was dissolved in ~20 ml of water and 0.5 g of sodium azide and 2.0 g of potassium chloride (~0.4 M in N_3^- and ~1.6 M in K^+) were added. The solution was filtered and kept at 0° for 2–3 days. The crystalline product was filtered and air-dried. A typical yield was 1.05 g, 35% based on the original cobalt(II) complex. *Anal.*⁹ Calcd for $C_{10}H_{14}O_4N_6CoK$, $K[Co(acac)_2(N_3)_2]$: C, 31.58; H, 3.71; N, 22.10. Found: C, 31.47; H, 3.83; N, 21.47.

$[PPh_4]\{trans-[Co(acac)_2(N_3)_2]\}$.—The addition of 1.2 g of $[P(Ph)_4]Br$ (0.0029 mol) to a solution of 1.0 g of $K\{trans-[Co(acac)_2(N_3)_2]\}$ (0.0026 mol) in a minimum of water (~20 ml) resulted in the immediate formation of a finely divided precipitate of the tetraphenylphosphonium salt of the complex. This was washed several times with water and air-dried. A typical yield was 1.25 g, 60% based on the initial weight of the potassium salt. *Anal.* Calcd for $C_{34}H_{38}O_4N_6P_4Co$, $[PPh_4][Co(acac)_2(N_3)_2]$: C, 59.99; H, 5.04; N, 12.35. Found: C, 59.86; H, 5.05; N, 12.56; mp 152°.

$[PPh_4]\{cis-[Co(acac)_2(N_3)_2]\}$.—One gram of $[PPh_4]\{trans-[Co(acac)_2(N_3)_2]\}$ was dissolved in a minimum of acetone (~30 ml) and kept at 25° for 15 min. The emerald green crystals of the *cis* isomer which formed were filtered, washed quickly with a small portion of acetone, and air-dried. The yield was 0.50 g, 50% based on the original *trans* isomer. *Anal.* Calcd for $C_{34}H_{34}O_4N_6P_4Co$, $[PPh_4][Co(acac)_2(N_3)_2]$: C, 59.99; H, 5.04; N, 12.35. Found: C, 59.84; H, 5.01; N, 12.28; mp 161°.

$trans-[Co(acac)_2N_3py]$.—Two grams of $[Co(acac)_2]$ (0.0078 mol) was dissolved in 200 ml of water. One gram of sodium azide (0.0156 mol) and 2 ml of pyridine (0.0248 mol) were added, followed by the dropwise addition of 2 ml of 30% hydrogen peroxide solution (0.0176 mol). The reaction mixture was stirred at 25° for 2 hr, and the precipitate which formed was filtered and air-dried. The crude product was purified by dissolving in a

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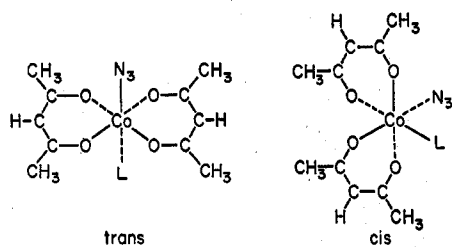
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Figure 1.—Structural representation of $[\text{Co}(\text{acac})_2\text{N}_3\text{L}]^{n-}$.

minimum of chloroform and reprecipitated by addition of a fourfold excess of petroleum ether (bp 30–60°). The yellow-brown product was filtered, washed twice with 20-ml portions of petroleum ether, and air-dried. The final yield was 1.05 g, 35% based on the original cobalt(II) complex. *Anal.* Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4\text{N}_4\text{Co}$, $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$: C, 47.63; H, 5.06; N, 14.81. Found: C, 47.26; H, 4.28; N, 14.55; mp 137°.

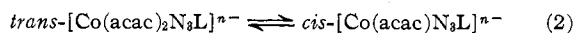
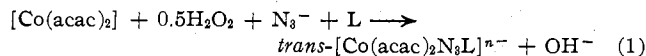
cis- $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$.—A solution of 1.0 g of *trans*- $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$ in 25 ml of chloroform was kept at 25° for 3 hr. This solution was streaked on 20 × 20 cm glass plates coated to 0.25-mm thickness with silica gel (Brinkman Silplate 22). The plates were developed with 90% benzene–10% methanol. The top component was removed by scraping off the streak and extracting the complex from the silica gel with methanol. The methanol was stripped off *in vacuo* at room temperature. The *cis* isomer, 90% pure at this point, was redissolved in chloroform and the thin-layer separation was repeated. After extraction from the silica gel with methanol and evaporation to dryness, the pure *cis* isomer was isolated. The yield was 0.09 g, a 9% recovery. *Anal.* Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4\text{N}_4\text{Co}$, $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$: C, 47.63; H, 5.06; N, 14.81. Found: C, 47.41; H, 5.02; N, 14.83; mp 145°.

cis- $[\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3]$.—Two grams of $[\text{Co}(\text{acac})_2]$ (0.0078 mol) was dissolved in 125 ml of methanol. After 0.75 g of sodium azide (0.0117 mol) and 2 ml of concentrated ammonium hydroxide (0.0296 mol) were added, 2 ml of 30% hydrogen peroxide solution (0.0176 mol) was immediately added dropwise. The reaction was allowed to proceed for 1 hr at 25° with stirring, at which point the solution was slowly evaporated to dryness. The dry residue was extracted with chloroform, dried over Drierite, and filtered. A twofold excess of petroleum ether was added, and the product was filtered and air-dried. A typical yield was 0.85 g, 34% based on the weight of the original cobalt(II) complex. *Anal.* Calcd for $\text{C}_{10}\text{H}_{17}\text{O}_4\text{N}_4\text{Co}$, $[\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3]$: C, 37.99; H, 5.41; N, 17.33. Found: C, 37.71; H, 5.34; N, 17.02; mp 146°.

Spectroscopy.—Proton magnetic resonance spectra were obtained with a Hitachi Perkin-Elmer R-20 high-resolution spectrometer at 60 MHz, at 34°. Chemical shifts, to ±0.01 ppm, were measured relative to an internal standard with a frequency counter. Samples were dissolved to 4% (w/v) in the appropriate deuterated solvents (from Diaprep, Inc.) and the internal standards were tetramethylsilane for chloroform solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate for water and dimethyl sulfoxide solutions. Ultraviolet and visible absorption spectra were obtained with a Cary 14 recording spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 457 spectrophotometer in the 4000–400-cm⁻¹ range with the materials in potassium bromide pellets. Chloroform solution spectra were obtained with a Perkin-Elmer 237B spectrophotometer with the complexes in 0.1-mm NaCl cavity cells.

Results and Discussion

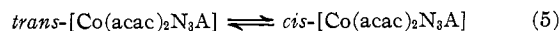
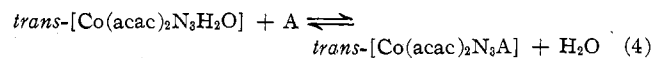
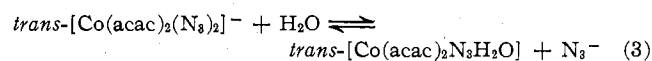
Synthesis.—The synthetic scheme utilized in this work can be represented by



where L = N₃⁻, py, or NH₃ (n = 1, 0). The reactions are completed in a few hours at room temperature with about 35% yield of product obtained. Under the conditions given in the Experimental Section, two by-products of reaction 1, *i.e.*, the dimers $[\text{Co}_2(\text{acac})_4$

(OH)₂]¹⁰ and $[\text{Co}_2(\text{acac})_4(\text{N}_3)_2]$,¹¹ are minimized. In the case of $\text{K}\{\text{trans-}[\text{Co}(\text{acac})_2(\text{N}_3)_2]\}$ and *trans*- $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$ the product precipitates from methanol and aqueous solution, respectively. For the ammonia complex the *trans* isomer is not precipitated from aqueous solution and only *cis*- $[\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3]$ is isolated *via* extraction of the reaction mixture with chloroform. It is assumed that the soluble *trans* isomer in the reaction mixture isomerizes *via* reaction 2 to the more stable *cis* form during the course of the isolation procedure. The materials isolated *via* reaction 1 are isomerically pure. Since the cobalt(III) complexes are formed *via* the oxidation of labile cobalt(II) compounds, it is reasonable to assume that both the *cis* and *trans* isomers are formed. The initial products then would isomerize to the thermodynamically stable isomer in that solvent or to the least soluble compound which precipitates from solution.

The *trans*- $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$ and *cis*- $[\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3]$ can also be prepared by the addition of the amine to *trans*- $[\text{Co}(\text{acac})_2(\text{N}_3)_2]^-$ in water. Presumably this proceeds *via* the sequence



where A is pyridine or ammonia. A scheme similar to reactions 3–5 has been observed for the reaction of *trans*- $[\text{Co}(\text{acac})_2(\text{NO}_2)_2]^-$.^{2,6} The *trans*- $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$ is insoluble in aqueous solution, and therefore isomerization cannot occur. More generally, the *cis* isomers are obtained *via* the isomerization (reaction 2) of *trans*- $[\text{Co}(\text{acac})_2(\text{N}_3)_2]^-$ in acetone and *trans*- $[\text{Co}(\text{acac})_2\text{N}_3\text{py}]$ in chloroform. Since the potassium salt of the former complex is insoluble in acetone, the corresponding tetraphenylphosphonium salt was used as starting material. The isomerization reaction of the pyridine complex leads to the formation of an equilibrium mixture which can be separated *via* preparative tlc techniques.¹² The azide complexes are green crystalline solids which are stable at room temperature. In contrast to the other solid complexes, however, the salts $[\text{PPh}_4][\text{Co}(\text{acac})_2(\text{N}_3)_2]$ and *cis*- $[\text{Co}(\text{acac})_2\text{N}_3\text{NH}_3]$ readily decompose at 100°.

The salt $\text{K}\{\text{trans-}[\text{Co}(\text{acac})_2(\text{N}_3)_2]\}$ does not show any redox decomposition at neutral pH in water over a period of weeks. However, the *trans* isomer rapidly undergoes other reactions in water to yield an equilibrium mixture of products. The initial equilibrium is reached in 5 min at 34°. The pmr spectra of D₂O solutions show three methine resonances at -5.77, -5.73, and -5.62 ppm as well as three methyl resonances at -2.30, -2.22, and -2.12 ppm. A reasonable assignment would be that the low-field methine and methyl resonances arise from *trans*- $[\text{Co}(\text{acac})_2\text{N}_3\text{H}_2\text{O}]$, the midfield lines from *trans*- $[\text{Co}(\text{acac})_2(\text{N}_3)_2]^-$, and the high-field methine and methyl lines from *cis*-

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[Co(acac)₂(N₃)₂]⁻. The second methyl line of the latter complex is assumed to be under the *trans* methyl. From the relative intensity of the resonances, the ratio of the three species is approximately 1:4:3. Addition of excess N₃⁻ reduces the intensity of the *trans*-[Co(acac)₂N₃H₂O] line but does not affect the relative intensity of the lines of the two other species. The equilibrium mixture is most likely formed *via* the rapid solvolysis, reaction 3, as well as a rapid isomerization, reaction 2. The overall pattern of behavior of the azide complexes is analogous to that of [Co(acac)₂(NO₂)₂]⁻ in aqueous solution.^{2,13} For example, rapid solvolysis of the *trans* complex leads to the formation of *trans*-[Co(acac)₂NO₂H₂O]. However, the ratio of the dianion complex to the aquo complex is ~2.3 in the nitro cases while a somewhat higher value ~4 is observed for the azide system. In addition to this the *trans* ⇌ *cis* isomerization of [Co(acac)₂(NO₂)₂]⁻ appears to be slower than for [Co(acac)₂(N₃)₂]⁻ under approximately the same conditions.¹³ After a few days at room temperature the methine resonances of the [Co(acac)₂(N₃)₂]⁻D₂O solution disappear, presumably *via* exchange with the solvent. In addition new methyl resonances grow in at -2.36, -2.24, and -2.17 ppm in a 1:1:2 pattern. This is consistent with the slow formation of *cis*-[Co(acac)₂N₃H₂O]. Unfortunately, the isolation of *cis*- and *trans*-[Co(acac)₂N₃H₂O] which are needed to check the aqueous solution scheme proposed above has not been carried out. All attempts have led to the isolation of only [Co₂(acac)₄(N₃)₂].¹¹

In contrast to the complicated behavior in D₂O, *cis*- and *trans*-[Co(acac)₂(N₃)₂]⁻ undergo a simple isomerization reaction in DMSO. Starting from either isomer an equilibrium mixture of the two species is formed. No solvolysis is observed and the addition of excess N₃⁻ does not affect the isomerization. The *trans* to *cis* equilibrium constant is 0.8 and the *t*_{1/2} to reach equilibrium, is 3 hr at 34°. The lack of solvolysis by DMSO for [Co(acac)₂(N₃)₂]⁻ is in marked contrast to the behavior of *trans*-[Co(acac)₂(NO₂)₂]⁻. For the latter material it appears that the equilibrium ratio of [Co(acac)₂(NO₂)₂]⁻ to [Co(acac)₂NO₂DMSO] is about ~4.5. The difference in the extent of the aqueous and DMSO solution solvolysis for the nitro and azide complexes indicates that the preference of the azide ion is for a *trans* azide rather than a solvent molecule (water or DMSO) and that this is greater than the similar preference of the nitrite ion. The small difference in behavior of the nitro and azide complexes may be related to a somewhat greater octahedral *trans* effect of NO₂⁻ than of N₃⁻.¹⁴ In this case the strong σ -donating nitrogen ligand prefers a weaker donor oxygen atom of the solvent *trans* to it rather than another anion.

The PPh₄ salts of *cis*- and *trans*-[Co(acac)₂(N₃)₂]⁻ both isomerize in chloroform at 34° to give an equilibrium mixture of the two isomers, with a *trans* to *cis* equilibrium constant of 0.5 and a half-time of 0.5 hr. Similar measurements for the [Co(acac)₂(NO₂)₂]⁻ isomers yield an equilibrium constant of 2.0 and an isomerization half-time of 2.3 hr at 35°. An isomerization in chloroform is observed for both *cis*- and *trans*-

[Co(acac)₂N₃py]. At 29° the *trans* to *cis* equilibrium constant is 2.49 with a half-time of 40 min. The equilibrium constant for the reaction of [Co(acac)₂NO₂py] is 0.59 and the half-time is 86 hr. It appears from both cases above that the isomerization of the azide complexes is considerably faster than for the nitro complexes. It is most likely that isomerization in cobalt(III) β -diketone complexes involves the formation of a trigonal-bipyramidal intermediate *via* chelate ring opening.¹⁶ The faster rate for the azide complexes¹⁷ is then consistent with an increased stabilization of the trigonal bipyramid by the π -electron-donating azide ion in contrast to the π -electron-accepting nitrite ion.¹⁷ Finally the *cis*-[Co(acac)₂N₃NH₃] does not show any isomerization reaction in chloroform and the pyridine and ammonia complexes both show no solvolysis or isomerization in DMSO.

Spectroscopy.—The visible-ultraviolet absorption, infrared, and nuclear magnetic resonance spectra of the various materials were determined. Although all of them are needed for characterization, only the proton magnetic resonance spectra are useful in assigning stereochemistry.¹⁸ It is readily seen that in the *trans* isomer all the acetylacetonate methyl and methine groups are related to each other by symmetry elements of the molecule and are therefore equivalent. Pmr spectra of the *trans* isomers should then show one methyl and one methine resonance in the intensity ratio 6:1. Figure 2 shows a typical spectrum of a *trans* isomer. The symmetry of the complexes is reduced for the *cis* isomers. For the *cis*-[Co(acac)₂(N₃)₂]⁻, the two methine protons are equivalent while the methyl protons are divided into two sets of methyl groups. The pmr spectrum for this isomer shows one methine and two methyl resonances in the ratio 1:3:3. For the complex *cis*-[Co(acac)₂N₃L], where L = pyridine or ammonia, neither the methyl groups nor the methine protons are related to each other by a symmetry element of the molecule. The expected spectrum shows four methyl resonances and two methine resonances in the ratios 3:3:3:3:1:1. This is nicely borne out in the spectrum of *cis*-[Co(acac)₂N₃py]. In the case of *cis*-[Co(acac)₂N₃NH₃], however, only three methyl resonances are resolved, in the ratio 6:3:3, while the methine resonances overlap each other to give a single resonance. The stereochemistry of all the complexes reported here has been assigned using the nmr method. Further, the relative amounts of the isomers in mixtures and of the solvolysis products can be estimated by determining the area under each resonance and the intensity of the various proton resonances.

The nmr spectral data for the complexes in DMSO-*d*₆ and CDCl₃ are summarized in Table I and typical spectra are shown in Figure 2. The spectrum of the K-{*trans*-[Co(acac)₂(N₃)₂]} salt in DMSO-*d*₆ is identical with the spectrum of the corresponding tetraphenylphosphonium salt. The chemical shifts of the methyl protons fall in the range -1.98 to -2.10 ppm in DMSO and -2.08 to -2.25 ppm in CDCl₃. Similarly the methine proton resonances fall in the range -5.35 to -5.50 ppm in DMSO and -5.32 to -5.57 in CDCl₃.

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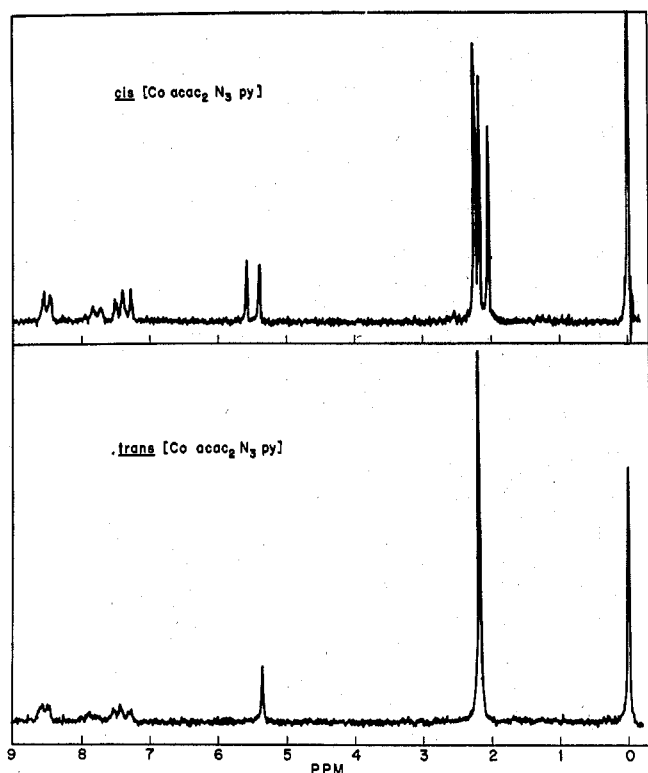


Figure 2.—Proton magnetic resonance spectra of azidopyridine-bis(acetylacetonato)cobalt(III) in deuteriochloroform.

TABLE I
PROTON MAGNETIC RESONANCE DATA
(PPM) FOR AZIDE COMPLEXES

Complex	Isomer	Solvent	Resonance	
			CH ₃	C-H
[PPh ₄][Co(acac) ₂ (N ₃) ₂]	Trans	DMSO- <i>d</i> ₆	-2.05	-5.35
	Trans	CDCl ₃	-2.10	-5.32
	Cis	DMSO- <i>d</i> ₆	-2.02	-5.42
			-1.98	
	Cis	CDCl ₃	-2.15	-5.38
			-2.08	
[Co(acac) ₂ N ₃ py]	Trans	DMSO- <i>d</i> ₆	-2.08	-5.40
			-2.15	-5.35
	Cis	DMSO- <i>d</i> ₆	-2.17	-5.65
			-2.15	-5.47
	Cis	CDCl ₃	-2.08	
			-2.02	
			-2.25	-5.57
			-2.23	-5.40
			-2.17	
			-2.05	
	Cis	DMSO- <i>d</i> ₆	-2.10	-5.50
			-2.05	
-2.00				
-2.18			-5.50	
-2.17				
-2.08				

The position of the resonance is only slightly dependent on the ligand. For example, in the compounds *trans*-[Co(acac)₂N₃L]ⁿ⁻ the methyl and methine lines shift upfield by 0.03–0.05 ppm in going from py to N₃⁻. By taking the average chemical shift of the methyl lines and of the methine lines, the various *cis* isomers can also be compared. A small upfield shift of 0.04–0.12 ppm is noted in going from L equals NH₃ or py to N₃⁻. The upfield shift observed may be related to the expected effect of the increase in negative charge on the complex.¹⁹

Comparing the *cis*-*trans* isomer pairs, it is seen that the methyl and methine resonances shift downfield, 0.02 to 0.06 ppm, when going from the *trans* to the *cis* isomers. This small downfield shift is in the direction expected for an increase in dipole moment in going from the *trans* to the *cis* isomer.¹⁹ In addition to the small electric field effects, a general solvent shift of 0.05 to 0.13 ppm downfield for the methyl protons in going from CDCl₃ to DMSO is noted. Conversely the methine resonances shift 0.05 to 0.08 ppm upfield with the change in solvent. The splitting of the non-equivalent methyl proton resonances in the *cis* isomers is dependent on the solvent and is about 0.04–0.15 ppm in DMSO and somewhat larger in CDCl₃, 0.07–0.20 ppm. The splitting also seems to be dependent on the ligand. For example, the methyl splitting in CDCl₃ is 0.07 for N₃⁻, 0.10 for NH₃, and 0.20 for py. The methine proton resonance is also substantially split for the py complex. This can be related to magnetic anisotropy of the pyridine ring and to changes in solvation.¹⁸ In addition to the resonances which arise from the methyl and methine protons of the acetylacetonate ligand, amine proton resonances are also seen. The aromatic proton resonances of pyridine give rise to six lines in the -7.2 to -8.7 ppm region for both isomers in both solvents. The ammonia protons give rise to a broad resonance at -2.67 ppm in CDCl₃ and -3.45 ppm in DMSO.

The variation in the nmr spectra noted here for the azide complexes is analogous to observations made on the corresponding nitro complexes.¹⁸ It is interesting to note that a small downfield shift is generally noted in going from NO₂⁻ to N₃⁻. For example the proton chemical shifts of [Co(acac)₂N₃py] are 0.02–0.04 ppm downfield from [Co(acac)₂NO₂py]. A similar observation is made for the NH₃ complexes. The downfield shifts of the azide complexes may be related to the magnetic anisotropy effects of the π system in the anion.¹⁴ As noted previously,¹⁸ there appears to be no compelling reason to assign changes in pmr chemical shifts in these complexes to ground-state *cis* and *trans* effects of the azide and nitro ligands.

The infrared spectra, 4000–400 cm⁻¹, were determined with the complexes in potassium bromide disks while the spectra in the 1800–2200-cm⁻¹ region were determined using chloroform solutions. The spectra show absorptions typical of the coordinated acetylacetonate anion, azide ion, and the amine.²⁰ The intense azide asymmetric stretch appears at 2030 cm⁻¹ for *cis*- and *trans*-[Co(acac)₂N₃py] and *cis*-[Co(acac)₂N₃NH₃] in solution and in the solid state and [PPh₄]{*trans*-[Co(acac)₂(N₃)₂]} shows only a single absorption at 2010 cm⁻¹ while [PPh₄]{*cis*-[Co(acac)₂(N₃)₂]} shows two absorptions at 2030 and 2010 cm⁻¹ both in solution and in the solid state. This low-symmetry splitting has also been observed for *cis*-[Co(en)₂(N₃)₂]⁺.²¹ The azide symmetric stretching absorption is probably obscured by an acetylacetonate band at 1285 cm⁻¹. An additional band does appear at 1275 cm⁻¹ for *cis*-[Co(acac)₂(N₃)₂]⁻. Aside from the differences noted above, the ir spectra are all similar and there are no other striking differences between the *cis* and *trans* isomers.

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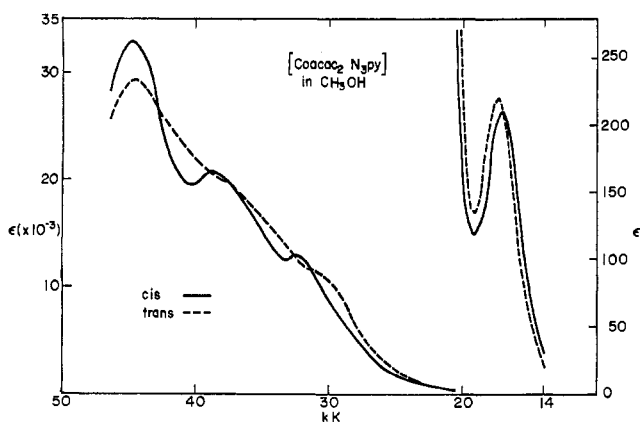


Figure 3.—Absorption spectra of azidopyridinebis(acetylacetonato)cobalt(III) in methanol.

Electronic absorption spectra were determined with the complexes in several solvents. Typical spectra are shown in Figure 3 and the absorption maxima are listed in Table II. The spectrum of the trans isomer

the absorption frequency between NO_2^- , NH_3 , py, and N_3^- points out the relatively weak ligand field of N_3^- in comparison with other nitrogen donors. The relative position of N_3^- in the low end of the spectrochemical series may arise from the ability of the anion to act as a π donor to the metal.²¹ Conversely a recent spectral study provides no evidence for the azide to act as a π acceptor in octahedral cobalt(III) complexes.²³ A difference in the frequency of the ligand field band is also noted for the cis-trans pairs. For example, *cis*- $[\text{Co}(\text{acac})_2(\text{N}_3)_2]^-$ absorbs at $\sim 500 \text{ cm}^{-1}$ higher energy than does the trans isomer. The difference for the pyridine complexes is somewhat smaller, $< 200 \text{ cm}^{-1}$. The intensity of the absorption of the cis-trans pairs also seems to be about the same.

The ultraviolet spectra show a relatively weak band at 29–33 kK and two strong absorptions at 37.5–39.5 and 44.4–44.8 kK. The low-energy, low-intensity band can be assigned to a metal-to-acetylacetonate ligand $t_{2g} \rightarrow \pi^*$ charge transfer.⁶ The frequency order is $\text{py} > \text{NH}_3 > \text{N}_3^-$ for the cis isomer and the spread is 300–500 cm^{-1} . The red shift observed for the azide ligand

TABLE II
ELECTRONIC ABSORPTION MAXIMA (kK) OF AZIDE COMPLEXES

Complex	Isomer	Solvent	${}^1A_{1g} \rightarrow {}^1T_{1g}$	$t_{2g} \rightarrow \pi^*$	$\sigma_L \rightarrow e_g^*$	$\pi \rightarrow \pi^*$
[PPh ₄][Co(acac) ₂ (N ₃) ₂]	Trans	CHCl ₃	15.6 (2.54) ^a	29.9 (4.22)		
		DMSO	15.6 (2.58)	29.0 (4.06)		
	Cis	DMSO	16.1 (2.57)	31.1 (4.24)		
		CHCl ₃	16.0 (2.48)	31.2 (4.11)		
[Co(acac) ₂ N ₃ py]	Trans	DMSO	17.2 (2.46)	~30		
		CH ₃ OH	17.4 (2.34)	31.1 (4.04)	38.0 (4.29)	44.4 (4.42)
		CHCl ₃	17.2 (2.44)	30.2 (3.95)	~38	
	Cis	DMSO	17.2 (2.37)	31.5 (3.96)		
		CH ₃ OH	17.2 (2.32)	~32.6 (4.11)	38.8 (4.31)	44.8 (4.53)
		DMSO	17.0 (2.36)	31.5 (4.10)		
[Co(acac) ₂ N ₃ NH ₃]	Cis	CH ₃ OH	17.2 (2.02)	~33	38.9 (4.04)	44.8 (4.22)
		DMSO	17.0 (2.36)	31.5 (4.10)		
		CHCl ₃	17.1 (2.32)	~32	39.5 (4.31)	

^a Log ϵ_{max} in parentheses.

of [PPh₄][Co(acac)₂(N₃)₂] is identical with that of the corresponding K⁺ salt in DMSO. Solution spectra taken of [Co(acac)₂(N₃)₂]⁻ in water and methanol are not listed since extensive solvolysis and isomerization are noted in these solvents. In the solvents listed the complexes appear to be stable in the time it takes to record the spectra.

The visible spectra show one prominent absorption at 15.6–17.5 kK as well as a shoulder at ~ 25 kK. These absorptions can be assigned to the ligand field transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ of the pseudooctahedral cobalt(III). Even though the low symmetry of the complexes gives rise to splitting of the octahedral levels, only broad unresolved absorptions are observed. The frequency of the ligand field maxima does vary with the complex *cis*- or *trans*-[Co(acac)₂N₃L]ⁿ⁻. For example, in DMSO and chloroform solution the frequency order is $\text{py} \geq \text{NH}_3 > \text{N}_3^-$ with a difference between py and N_3^- of $\sim 1000 \text{ cm}^{-1}$. This corresponds to the expected ligand field order.²² Comparing the azide complexes with the corresponding nitro complexes,²³ it is seen that the absorptions in chloroform for the N_3^- complex are $\sim 1400 \text{ cm}^{-1}$ lower in energy than for the NO_2^- complexes. The large difference in

might arise from the destabilization of the t_{2g} level which arises from the π -donating ability of N_3^- . This effect is also seen when the frequency of the $t_{2g} \rightarrow \pi^*$ charge-transfer band in *trans*-[Co(acac)₂(N₃)₂]⁻ is compared to that of [Co(acac)₂(NH₃)₂]⁺. The band is observed at ~ 4 kK higher energy for the amine complex.⁴ The two highest energy ultraviolet bands are only recorded for the stable methanol solutions of *cis*- and *trans*-[Co(acac)₂N₃py] and *cis*-[Co(acac)₂N₃NH₃]. The absorption of [PPh₄]⁺ prevents accurate determination of the bands of [Co(acac)₂(N₃)₂]⁻ in this region. The band at 37.5–39.5 kK has been assigned $\sigma_L \rightarrow e_g^*$ acetylacetonate ligand-to-metal charge transfer while the band at 44.4–44.8 kK is associated with an acetylacetonate ligand $\pi \rightarrow \pi^*$ transition. The former represents a new assignment of this band to a charge-transfer rather than a ligand $\pi \rightarrow \pi^*$ transition. The new assignment results from spectral studies of mono-, bis-, and tris(acetylacetonato)cobalt(III) complexes.²⁴ The frequency of the bands seems to be independent of the ligand. However, there appears to be a substantial blue shift in the charge-transfer bands in going from the trans to the cis isomer. This effect which is noted for all bis(acetylacetonate) complexes of cobalt(III)⁶ may be related to the mixing of higher excited states (involving 4p orbitals of cobalt) into

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the excited state of the trans isomer and the ground state of the cis isomer. This mechanism which would destabilize the affected levels has been suggested to rationalize the substantial blue shift of the charge-transfer transition observed when going from the *trans*- to *cis*-[Ru(NH₃)₄(py)₂]²⁺.²⁵ It is interesting to compare the ultraviolet spectra of the azide complexes to those of the corresponding nitro complexes. It appears that the $\sigma_L \rightarrow e_g^*$ transition energies are ~ 800 cm⁻¹ higher in energy for the azide complexes.^{8,12} Considering the weaker ligand field of N₃⁻ the opposite

trend would be expected. However the presence of an azide-to-metal charge-transfer absorption in this region²⁸ may give rise to apparent band shifts. In fact, the ultraviolet spectra for the azide complexes are considerably broader and less well defined than for the nitro complexes.

Acknowledgment.—The authors wish to acknowledge the support of this research by the National Science Foundation *via* Grant GP-23464. The authors wish to acknowledge the assistance of Mr. Dirk Hill in the isolation of some of the materials. We are also grateful to Professor R. D. Archer, University of Massachusetts, for generously supplying unpublished work.

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Complexes of Binucleating Ligands. V. Some Copper(II) and Nickel(II) Complexes of Two Related Sulfur-Containing Ligands

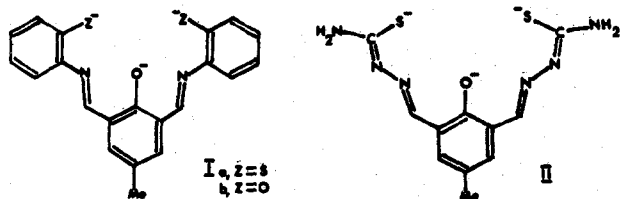
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Received November 29, 1971

The synthesis and some properties are described of an extensive series of binuclear copper(II) and nickel(II) complexes derived from the two sulfur-containing binucleating ligands 2-hydroxy-5-methylisophthalaldehyde di-2'-mercaptoanil and 2-hydroxy-5-methylisophthalaldehyde dithiosemicarbazone (derived trianions hereafter represented as L³⁻ and Q³⁻, respectively). The complexes have the general form LM₂X or QM₂X, where X represents a range of monoanionic species incorporated at an accessible bridging site built into the complexes; examples are quoted where X⁻ = OH⁻, 1/2O²⁻, RO⁻, RS⁻, NH₂⁻, NHR⁻, NR₂⁻, C₆H₅N₃⁻, *i.e.* pyrazolate anion, N₃⁻, NCO⁻, and Cl⁻.

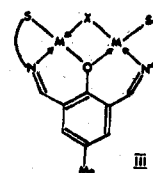
Introduction

The results presented here form part of a long-term project directed toward the synthesis and study of complexes of binucleating ligands¹ designed to bind two metal ions in close proximity. One aspect of this work, to which we are devoting considerable attention, concerns the potential capacity of complexes of appropriately designed binucleating ligands to trap and possibly, in some cases, to activate a range of anionic and neutral species at an in-built accessible bridging site between the two metallic centers. These studies have now been extended to binucleating ligands containing sulfur donor atoms in the hope that they might show enhanced affinity, compared with analogous ligands containing nitrogen and oxygen donor atoms, for "soft" cations, in particular those of the second and third transition series. Reported here are preliminary model studies on some nickel(II) and copper(II) complexes of two trianionic ligands, Ia (hereafter



L³⁻), formally derived from 2-hydroxy-5-methylisophthalaldehyde di-2'-mercaptoanil, and II (hereafter

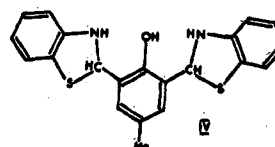
Q³⁻), derived from 2-hydroxy-5-methylisophthalaldehyde dithiosemicarbazone. The primary purpose of these model studies was to determine whether the ligands did indeed impose the desired binuclear arrangement(III) and, if so, to study the gross stereo-



chemical features of the complexes and the range of groups, X⁻, which could be accommodated at the bridging site.

Results and Discussion

Ligands.—Condensation of *o*-aminobenzenethiol with 2-hydroxy-5-methylisophthalaldehyde in ethanol yielded colorless, 2,6-di(2'-benzothiazolanyl)-*p*-cresol (IV) (hereafter LH₃), rather than the di-Schiff base



related to Ia which would be expected to be deeply colored, *e.g.*, 2-hydroxy-5-methylisophthalaldehyde di-2'-hydroxyanil (hereafter referred to as RH₃ where the

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