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Isomeric Tetracyanoethylene Adducts of *N,N′*-Ethylenebis(acetylacetoniminato)cobalt(II)

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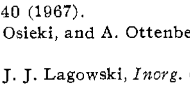
The reaction of tetracyanoethylene (TCNE) with *N,N′*-ethylenebis(acetylacetoniminato)cobalt(II), Co(acacen), in various solvents is described. A microcrystalline air-sensitive reaction product has been isolated in the presence of pyridine (py), in a green and a purple form, either of which can be converted to the other. Elemental analysis, molecular weight data, magnetic moment measurement, solution and powder electronic absorption spectra, and mull ir spectra are used to characterize both species as being isomers of identical composition, [Co(acacen)py]$_2$TCNE. Possible structures for both the green and purple isomers in solution and in the solid state are discussed and structures involving coordination through the N atoms of TCNE are tentatively assigned to both isomers in the solid state. A reaction product isolated in the absence of pyridine is characterized as a Co(acacen)–TCNE polymer.

Introduction

Tetracyanoethylene (TCNE) has been observed to undergo different types of reactions with transition metal complexes and this has been the subject of an excellent review by Baddley.[2] Reactions with some metalocene complexes such as ferrocene[3] and cobaltocene[4] result in the formation of a charge-transfer complex. Salt formation has been postulated for the product of the reaction between dibenzenechromium and TCNE.[5] Certain low-valent transition metal complexes such as $IrBr(CO)(P(C_6H_5)_3)_2$,[6] $Pt(P(C_6H_5)_3)_2HCl$,[7] $Pt(P(C_6H_5)_3)_4$,[8] $Pd(P(C_6H_5)_3)_4$,[9] etc., react with TCNE to yield a product with a cyclopropane-like structure involving coordination of C–C double bond to the metal. Herberhold[10] has isolated a series of compounds $M(CO)_5TCNE$ (M = Cr, Mo, W) in which the olefinic linkage presumably occupies only one coordination site. Coordination through a nitrile nitrogen rather than through the π-olefinic bond is also possible. Such a structure has recently been found for $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$.[11]

Thus far, reactions of TCNE with complexes exhibiting a porphyrin-like chelate structure have not been reported. We wish to describe such a reaction between TCNE and *N,N′*-ethylenebis(acetylacetoniminato)cobalt(II) [Co(acacen)] in various solvents. The product of this reaction is of additional interest in that it exists in two different isomeric forms of identical composition.



Co(acacen)

Experimental Section

Materials.—All solvents were carefully dried and stored under nitrogen. Pyridine was refluxed over and distilled from CaH_2. The reagents 2,4-pentanedione, ethylenediamine, and anhydrous cobalt(II) iodide were obtained commercially and used without further purification. The TCNE was a generous gift from E. I. du Pont de Nemours & Co. and was vacuum sublimed (*ca.* 1 mm) at 60° twice to yield large white crystals.

Preparation of Complexes.—All preparations, manipulations, and storage of these complexes were carried out under an atmosphere of prepurified nitrogen.

Co(acacen).—The Schiff base *N,N′*-ethylenebis(acetylacetonimine) was prepared by the literature method of Martell, Belford, and Calvin.[12] The cobalt complex was prepared by a modification of the method of Everett and Holm.[13] *Anal.* Calcd for Co(acacen): C, 51.25; H, 6.45; N, 9.96. Found: C, 51.26; H, 6.58; N, 9.92.

[Co(acacen)py]$_2$TCNE.—A solution of TCNE, 0.32 g (2.49 mmol), in 15 ml of toluene was added dropwise to a solution of Co(acacen), 0.68 g (2.44 mmol), in 25 ml of toluene to which 0.5 ml (6.2 mmol) of pyridine had been added. A dark green precipitate was formed almost immediately. The solid was isolated by filtration, washed repeatedly with toluene and then pentane, and dried in an oil pump vacuum. The yield was quantitative, giving a forest green microcrystalline product. The dry microcrystals decompose to a brown solid on exposure to air for a few minutes. *Anal.* Calcd for [Co(acacen)py]$_2$TCNE: C, 56.56; H, 5.42; N, 16.50. Found: C, 55.70; H, 5.53; N, 17.03.

These green microcrystals readily dissolve in methylene chloride, chloroform, acetone, and pyridine to give a reddish brown solution. The compound is insoluble in hydrocarbon solvents such as benzene and hexane and only very sparingly soluble in toluene. Recrystallization of this product was accomplished by using a methylene chloride–hexane (2:1, v/v) mixed solvent, resulting in the isolation of a purple microcrystalline solid. This product was dried in an oil pump vacuum after washing with cold methylene chloride–hexane. *Anal.* Calcd for [Co(acacen)py]$_2$TCNE: C, 56.56; H, 5.42; N, 16.50. Found: C, 55.10; H, 5.32; N, 17.60. This purple solid can also be prepared directly by performing the synthesis in a methylene chloride–hexane mixed solvent. As was observed with the green solid, exposure to the air resulted in immediate decomposition to a brown solid.

[Co(acacen)TCNE]$_n$.—A solution of TCNE, 0.93 g (7.26 mmol), in 40 ml of benzene was added dropwise to a solution of Co(acacen), 2.0 g (7.12 mmol), in 200 ml of benzene at 50°. A dark precipitate formed immediately which was isolated by filtration, washed with benzene, and dried in an oil pump vacuum. *Anal.* Calcd for Co(acacen)TCNE: C, 52.81; H, 4.40; N, 20.53. Found: C, 51.93; H, 4.27; N, 20.66. Recrystallization was not possible as the product is insoluble or only very sparingly

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[2] W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2**, 7 (1968).

[3] (a) O. W. Webster, W. Mahler, and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 3678 (1962); (b) M. Rosenblum, R. W. Fish, and R. W. Bennett, *ibid.*, **86**, 5166 (1964); (c) R. L. Collins and R. Pettit, *J. Inorg. Nucl. Chem.*, **29**, 503 (1967); (d) E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Amer. Chem. Soc.*, **89**, 4540 (1967).

[4] R. L. Brandon, J. H. Osieki, and A. Ottenberg, *J. Org. Chem.*, **31**, 1214 (1966).

[5] J. W. Fitch, III, and J. J. Lagowski, *Inorg. Chem.*, **4**, 864 (1965).

[6] J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968), and references therein.

[7] C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 798 (1968), and references therein.

[8] W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

[9] P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

[10] M. Herberhold, *Angew. Chem., Int. Ed. Engl.*, **7**, 305 (1968).

[11] M. F. Rettig and R. M. Wing, *Inorg. Chem.*, **8**, 2685 (1969).

[12] A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).

[13] G. N. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 2442 (1966).

soluble in a wide range of solvents including toluene, ethanol, methylene chloride, acetone, THF, acetonitrile, and pyridine.

Analyses and Physical Measurements.—Elemental analyses and molecular weight measurements were performed in an inert atmosphere by Dr. Alfred Bernhardt of the Max Planck Institute für Kohlenforschung, Höhenweg, West Germany.

Magnetic measurements were made on a Faraday balance at room temperature and liquid nitrogen temperature. The sample bucket and microbalance were enclosed in a glass envelope purged with helium.

Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 221 spectrophotometer. The mulls were prepared in a glove bag and the KBr plates were sealed with paraffin prior to removal to the atmosphere.

Ultraviolet–visible absorption spectra were obtained using a Cary 14 spectrophotometer. Solid-state powder absorption spectra were obtained from Nujol mulls sealed between quartz plates with paraffin in a glove bag. Solution spectra were obtained under anaerobic conditions by purging 10-mm cuvettes sealed with serum caps with nitrogen and filling with syringes.

Results

A TCNE adduct of Co(acacen) has been prepared under varying conditions. Preparations using benzene or toluene as a solvent result in the immediate precipitation of an intractable solid which contains Co and TCNE in a 1:1 ratio. These products could not be further purified and are presumed to be polymeric in nature. When the reaction is carried out in the presence of a Lewis base such as pyridine, a product containing cobalt, TCNE, and pyridine in a 2:1:2 ratio, respectively, is isolated.[14] For reasons which will become evident later, we will refer to reaction products from solutions containing pyridine as dimers.

The solvent plays an important role in determining the nature of the adduct isolated in the presence of pyridine. A green microcrystalline solid is obtained from toluene. A purple complex of identical composition (as shown by elemental analysis and molecular weight) is isolated from a more polar methylene chloride–hexane solvent mixture. It is possible successfully to convert one colored species to another by recrystallizing the green complex from methylene chloride or the purple complex from toluene.[15] These reactions are summarized as

$$\begin{tikzcd}
 & & {[\mathrm{Co(acacen)py}]_2\mathrm{TCNE}\ \text{green}} \arrow[dd, shift right, "\mathrm{CH_2Cl_2}"', "\mathrm{C_6H_{12}}"] \\
{[\mathrm{Co(acacen)TCNE}]_n} & \mathrm{Co(acacen)} + \mathrm{TCNE} \arrow[l, "\mathrm{C_6H_6}"'] \arrow[ur, "\mathrm{C_6H_5CH_3}", "+\mathrm{py}"'] \arrow[dr, "\mathrm{CH_2Cl_2}", "+\mathrm{py}\quad \mathrm{C_6H_{12}}"'] & \\
 & & {[\mathrm{Co(acacen)py}]_2\mathrm{TCNE}\ \text{purple}} \arrow[uu, shift right, "\mathrm{C_6H_5CH_3}"']
\end{tikzcd}$$

Electronic spectra of the green and purple adducts shown in Figure 1 were obtained in the solid state as Nujol mulls. In both spectra, the weak absorption band at 1180 nm found in the parent complex, Co(acacen), has disappeared. Previous authors[16] have found this absorption band at *ca.* 1200 nm to be characteristic of a cobalt ion in a square-planar ligand environment; hexacoordinate cobalt does not exhibit this absorption. Presumably in both the green and purple adducts, the cobalt atom has achieved a coordination number of 6. The parent Co(acacen) complex does not exhibit any absorption maxima in the 500–1100-nm region, while the green and purple adducts exhibit maxima at 675 and 590 nm, respectively. Similar bands appear in the ferrocene–TCNE (975 and 1150 nm in KBr mull)[3b] and $\mathrm{Cr(CO)_5TCNE}$ (760–820 nm, solvent dependent)[10] complexes and are assigned by these authors to metal→TCNE charge-transfer transitions. A similar assignment can tentatively be made in the spectra of the adducts reported here (see Figure 1). The higher energy absorptions shown in Figure 1 are essentially those found in the parent Co(acacen) moiety.

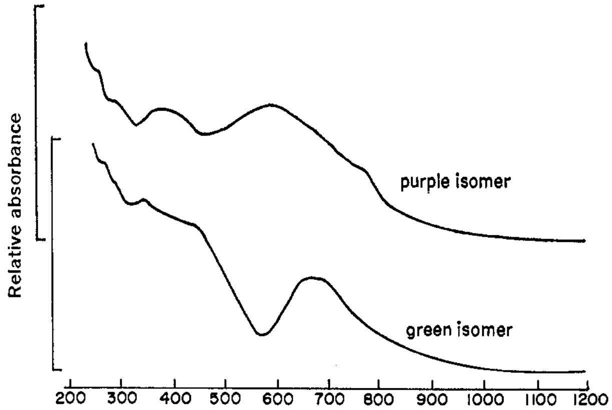

Figure 1.—Electronic absorption spectra of $[\mathrm{Co(acacen)py}]_2$-TCNE in Nujol. Purple isomer absorption maxima in nm: 225 (sh), 285 (sh), 370, 590, and 775 (sh). Green isomer absorption maxima in nm: 240 (sh), 280 (sh), 345, 470 (sh), and 675.

Both the green and purple adducts, when dissolved in methylene chloride or toluene, give identical electronic spectra in the same solvent. This is supporting evidence that both adducts are isostructural when dissolved in the same solvent. The absorption spectra in methylene chloride exhibit a broad band in the visible region with closely spaced vibrational maxima at 340, 383, 395, 400, 410, 419, 429, 438, 448, 460, and 470 nm (see Figure 2). Webster and coworkers report[3a] a

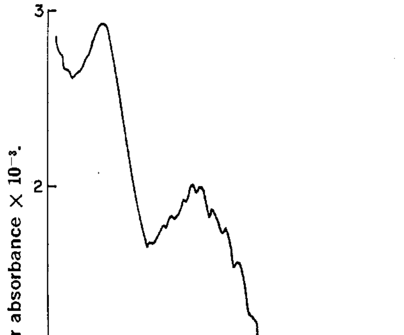

Figure 2.—Electronic spectrum of $[\mathrm{Co(acacen)py}]_2\mathrm{TCNE}$ (green or purple isomer) in methylene chloride. Absorption maxima in nm: 340, 383, 395, 400, 410, 419, 429, 438, 448, 460, and 470.

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[14] The slight deviation of the experimental analyses from that calculated for $[\mathrm{Co(acacen)py}]_2\mathrm{TCNE}$ is probably due to the extreme air sensitivity of these compounds. All analytical samples were stored under vacuum in sealed-glass ampoules; exposure to air results in immediate decomposition.

[15] Quantitative recrystallization from low polarity solvents such as toluene is not possible, due to the low solubility of both adducts. However, sufficient amounts of material for analysis can be dissolved and recovered from toluene.

[16] S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966); H. Nishkawa and S. Yamada, *Bull. Chem. Soc. Jap.*, **37**, 8 (1964); S. Yamada and H. Nishikawa, *ibid.*, **38**, 683 (1965).

similarly complex spectrum in the 350–500-nm region when the TCNE adduct of ferrocene is dissolved in acetonitrile. The presence of these closely spaced maxima was taken by these authors as evidence for the presence of the TCNE radical anion in solution.[3a] Presumably in a polar solvent such as methylene chloride both the green and purple TCNE adducts of Co(acacen) undergo some degree of dissociation to yield the TCNE radical anion (further evidence for dissociation in polar solvents is shown below in the results of molecular weight determinations). The toluene spectra of the green and purple adducts are identical but do not exhibit the characteristic TCNE radical anion absorptions. The occurrence of different spectra in methylene chloride and toluene is not surprising, since the nature of the solvent seems to determine which colored adduct is isolated.

Further evidence indicating identical composition for the two adducts and dissociation in polar solvents to give identical species is obtained from molecular weight data. Results obtained in *N*,*N*-dimethylformamide (DMF)[17] for the purple and green adducts are 154 and 155, respectively. This agrees with the calculated average molecular weight of 169 for the following dissociation reaction in DMF

$$\underset{\text{green or purple adduct}}{[\mathrm{Co(acacen)py}]_2\mathrm{TCNE}]} \longrightarrow 2\mathrm{Co(acacen)} + 2\mathrm{py} + \mathrm{TCNE}$$

Gill and coworkers[18] reported that pyridine, when acting as a ligand, exhibits a strong ir absorption at 1600 cm^{-1}. Both colored adducts described here exhibit such an ir absorption band. Further justification for assigning this absorption to coordinated rather than free pyridine in these adducts comes from the fact that drying powdered samples *in vacuo* (conditions which should remove pyridine molecules of crystallization) does not alter the intense band at 1600 cm^{-1}.

Structural differences between the solid purple and green adducts are apparent from their infrared spectra. A sensitive probe for determining complex formation in TCNE adducts is the cyanide stretching region of the spectrum. The C≡N bond force constants are sensitive to the release of additional electron density to the TCNE moiety. Table I lists the ir absorption bands in the C≡N stretching region for both adducts and uncomplexed TCNE. Note that on complex formation the C≡N stretching frequency shifts to lower energy and that there is a significant difference between the spectra of the green and purple adducts. These spectra are shown in Figure 3.

Both the green and purple adducts are diamagnetic as shown by measurement on a Faraday balance at room and liquid nitrogen temperatures. This indicates that in the solid state the single unpaired electron on the parent Co(acacen) moiety[19] becomes paired on reaction with TCNE. This must come about by interaction between two Co(acacen) moieties, since mere transfer of an electron to the TCNE to give Co(III) and TCNE$^-$ would still result in an odd number of electrons and a paramagnetic compound.

TABLE I

INFRARED SPECTRA IN THE C≡N STRETCHING REGION[a]

TCNE	[Co-(acacen)-TCNE]$_n$	[Co-(acacen)-py]$_2$-TCNE purple isomer	[Co-(acacen)-py]$_2$-TCNE green isomer	(π-C$_5$H$_5$)-VBr·TCNE[b]	TCNE$^-$ [c]	TCNE^{2-}
2262 s						
		2248 w	2241 w			
	2235 w					
2230 m						
2212 m	2212 s			2211 w	2208	
		2202 s				
			2190 s	2192 s		
	2180 sh	2180 s	2180 sh		2183	
		2170 s				
		2158 sh	2152 s	2152 s		2160
	2135 sh					
		2120 sh		2128 s		
			2108 sh			2095

[a] Nujol mull spectra expressed in cm^{-1}. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] M. F. Rettig and R. M. Wing, *Inorg. Chem.*, **8**, 2685 (1969); KBr pellet. [c] O. W. Webster, W. Mahler, and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 3678 (1962); KBr pellet.

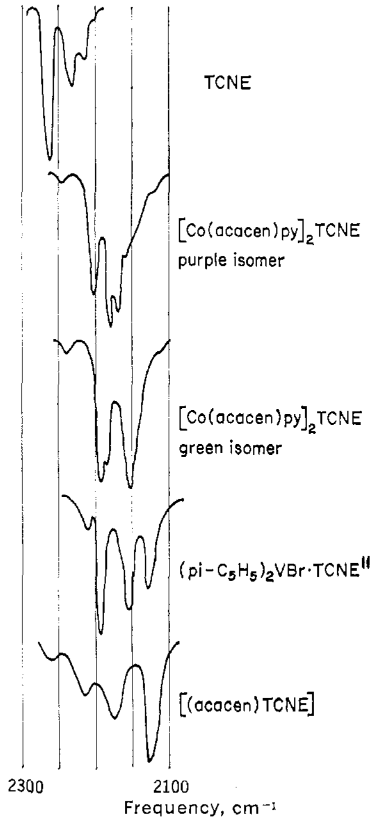

Figure 3.—Nujol mull infrared spectra.

Elemental analysis has established that Co, TCNE, and pyridine are present in the green and purple adducts in the ratio 2:1:2, respectively. This stoichiometry is substantiated by the observed diamagnetism of the complexes (a minimum requirement that there be an even number of cobalt atoms per molecular unit) and molecular weights in DMF. Electronic spectral data (see above) indicate that cobalt is in an octahedral environment, and infrared spectra show that pyridine is present as coordinated pyridine. These data, when considered together, strongly support formulating the green and purple adducts as dimers with the formula [Co(acacen)py]$_2$TCNE. A polymeric structure of this

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[17] Molecular weight determinations in less polar solvents where dissociation of the complex is less likely were not possible due to low solubility of the complexes.

[18] N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

[19] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970).

stoichiometry would not fulfill the requirement that the pyridine in addition to the TCNE be present as a ligand.

Discussion

Thus far we have established that when a TCNE adduct of Co(acacen) is prepared in the presence of pyridine, the complex contains 2 mol of cobalt/mol of TCNE and this adduct is capable of existing in a green and a purple form. Further experimental evidence is given which indicates that the adducts are dimers with the molecular formula [Co(acacen)py]$_2$TCNE. Since the green and purple solids have been shown to have identical composition and exhibit similar behavior in solution, they are presumably different isomeric forms of the same complex. The exact structure of these isomers has not been determined directly, but a good deal can be inferred about the probable modes of bonding and molecular geometry from the available data.

TCNE–metalocene complexes are thought to involve little or no direct interaction between the transition metal and cyanocarbon. That is, TCNE does not occupy a site in the inner coordination sphere of the metal. X-Ray analysis of the ferrocene charge-transfer complex indicates there is little or no change in bond distances on going from the free to complexed TCNE moiety.[3d] These charge-transfer type complexes are characterized by the presence of a doublet ir absorption in the C$\equiv$N stretching region (2260 and 2225 cm^{-1}).[3b]

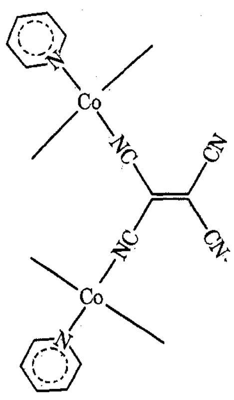
A charge-transfer type of structure for [Co(acacen)py]$_2$TCNE would involve a sandwich arrangement with a TCNE layer lying parallel between two Co(acacen)py moieties. However, such a complex would not afford very reasonable possibilities for different isomeric structures and indeed our experimental results do not favor this mode of bonding. Charge-transfer complexes of TCNE are also well known with organic aromatic molecules such as substituted benzenes.[20] *N,N'*-Ethylenebis(acetylacetonimine) when complexed to cobalt and in its free uncomplexed form can be viewed as two pseudoaromatic rings linked by an ethylene bridge. TCNE, when allowed to react with the free uncomplexed Schiff base, yields a neutral colored solid product. The C$\equiv$N stretching region of the ir spectrum of this solid, however, is significantly different from that found for either colored isomer of the Co(acacen)–TCNE adduct (see Figure 3). Based on these results and the difficulty of envisioning isomers of different geometry without merely rotating the TCNE moiety 90° about the Co–Co axis, we do not favor formulating the compounds described here as sandwich-like charge-transfer complexes.

A second mode of bonding found in transition metal–TCNE complexes is the cyclopropane-like structure found in IrBr(CO)(P(C$_6$H$_5$)$_3$)$_2$(TCNE),[6] Pt(P(C$_6$H$_5$)$_3$)$_2$(TCNE),[7] and Pd(P(C$_6$H$_5$)$_3$)$_2$(TCNE).[9] The analogous structure for the isomers reported here is a TCNE carbon–cobalt σ linkage between two Co(acacen)py groups. The experimentally observed diamagnetism supports this structure. However, since this mode of bonding involves formation of a TCNE C–C single bond with resulting free rotation about the C–C axis, there is no possibility for different isomeric forms. The existence of the TCNE radical anion in methylene chloride solution and complete dissociation in DMF also seem less plausible with this type of structure, as it would require cleavage of the carbon–cobalt σ bond.

A third mode of TCNE bonding to a transition metal is coordination through the cyanide group nitrogen atoms to the metal. This has been observed by Rettig and Wing in (π-C$_5$H$_5$)$_2$VX·TCNE (X = Cl, Br, I).[11] Infrared spectra appear to provide strong evidence for bonding through the nitrogen in these compounds, and this is substantiated by X-ray analysis for the case where X = Br.[11]

Infrared spectra of the green and purple isomers reported here are very similar to those reported for (π-C$_5$H$_5$)$_2$VX·TCNE in the C$\equiv$N stretching region (see Table I and Figure 3). These spectra are similar in that there is a shift of absorption of the cyanide groups to lower frequencies from that of free TCNE. There is also an increase in the number of ir-active C$\equiv$N stretching frequencies, presumably due to a lowering of the symmetry of the TCNE ligand upon coordination. Rettig and Wing[11] assigned the intense absorption at 2192 cm^{-1} to a nitrogen-bonded C$\equiv$N stretching frequency. The green isomer reported in the present study exhibits an identical absorption and presumably in the purple isomer this band is found at a slightly higher frequency, 2202 cm^{-1}.

A dimeric structure involving nitrogen coordination affords three possibilities for geometric isomers as shown in I–III.



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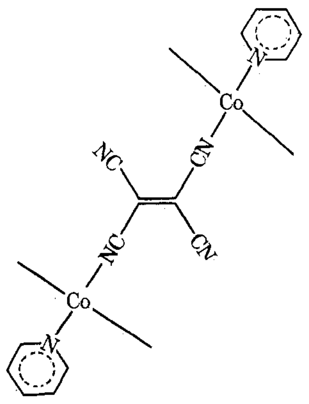

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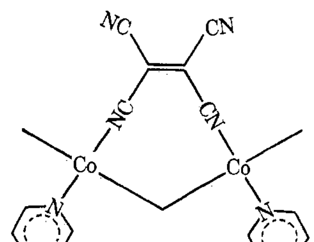

III

Structure III can be considered less probable than I or II for steric reasons. Using the bond angles and bond lengths reported by Bekoe and Trueblood[21] for crystalline TCNE, one can calculate an approximate nearest-neighbor N–N distance for the two coordinated N atoms of TCNE in I and III. These calculations indicate that neighboring coordinated N atoms in I are *ca.* 0.5 Å farther apart than in III. This results in

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(20) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964.

(21) D. A. Bekoe and K. N. Trueblood, *Z. Kristallogr., Kristallogeometrie, Kristallophys., Kristallchem.*, **113**, 1 (1960).

excessive steric crowding of the adjacent Co(acacen) moieties in III, rendering it a less plausible structure than I. One can arrive at a similar conclusion by the use of molecular models. Structure I most certainly represents a more polar molecule than does II and on this basis we tentatively assign I to the purple isomer isolated from the more polar methylene chloride solvent and II to the green isomer.

Structures I and II can account for a diamagnetic electronic configuration by enabling the TCNE to act as a "bridge," thereby providing a suitable molecular orbital for the unpaired electron on each cobalt(II) ion to become paired. This does not necessarily imply that in the solid state there is a complete transfer of electron density from the Co(acacen)py moiety to the TCNE ligand. The mull ir spectrum of the green or purple isomer does not agree with the published spectrum of TCNE^{-} [3a,11] or TCNE^{2-} [11] (see Table I). However, apparently complete electron transfer does occur in methylene chloride solution as the electronic solution spectrum of both isomers indicates the presence of TCNE$^{\cdot-}$ in this solvent (see Figure 2 and Results).

Coordination through the nitrogen atoms as shown in I above should give rise to an ir-active $C{=}C$ stretching frequency.[11] However, due to strong absorptions in this region by the Schiff base ligand, positive identification of such a band is not possible.

Nitrogen coordination as described above provides a reasonable mechanism by which a polymeric species involving a continuous chain of alternating TCNE–Co(acacen) groups could be formed. Such is a possible structure for the intractable solid isolated from benzene or toluene solutions in the absence of pyridine. Elemental analysis gives [Co(acacen)TCNE]$_n$ as the approximate stoichiometry and ir absorptions in the $C{\equiv}N$ stretching region are similar to those observed for the well-behaved green and purple isomers (see Table I).

In conclusion, our results support formulating the purple and green complexes of composition [Co(acacen)py]$_2$TCNE as geometric isomers having I and II, respectively, as their most probable structures.

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Stereochemistry of β-Diketone Complexes of Cobalt(III). VI. Synthesis and Spectroscopy of *cis*- and *trans*-Nitroaminebis(acetylacetonato)cobalt(III)

By L. J. Boucher* and N. G. Paez

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cis- and *trans*-nitroaminebis(acetylacetonato)cobalt(III) complexes, where amine is ammonia, methylamine, dimethylamine, trimethylamine, piperidine, and aniline, have been synthesized and characterized. The stereochemistry of the complexes can be 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. In chloroform solution all the trans complexes isomerize to form only the cis isomers, with the rate of conversion dependent on the amine. The aniline complex isomerizes several orders of magnitude faster than the other complexes and also shows a slow conversion in the solid state.

The synthesis and characterization of a large number of amine complexes of the type *trans*-Co(acac)$_2$NO$_2$L[1] have been reported.[2] Although many heterocyclic amine derivatives are known,[3] no alkylamine complexes have been previously characterized. A brief report of the trans → cis isomerization of the pyridine complex and the isolation of the only previously known cis isomer of this type has appeared.[4] To determine the effect of the donor strength of the amine on the isomerization and ligand-exchange reactions of the Co(acac)$_2$NO$_2$L complexes, we have first prepared and characterized the cis,trans isomer pairs for a number of alkylamines. The complexes reported here are listed in Table I and a structural representation is shown in Figure 1.

Experimental Section

Materials.—The starting material, Na[*trans*-Co(acac)$_2$(NO$_2$)$_2$], was prepared as previously described.[2] The amines used were reagent grade (Eastman Organic Chemicals) and used without further purification.

Synthesis. ***trans*-Co(acac)$_2$NO$_2$L.**—Four grams (1.1×10^{-2} mol) of Na[Co(acac)$_2$(NO$_2$)$_2$] were dissolved in 100 ml of distilled water and 2 g of the liquid amine ligand (>2-fold excess) added. Aqueous solutions of methylamine (40%), trimethylamine (25%), dimethylamine (25%), and ammonia (25%) were used. The resulting mixture was stirred at room temperature for 10 min (4 hr for ammonia) and then filtered. In the case of the ammonia and aniline reactions, the desired product precipitated out of solution. The red-brown powder was collected on a funnel and washed with 50 ml of distilled water and air dried (yield ~75%). In the case of the other amines the desired product remained in solution. The aqueous reaction mixture was extracted with 100 ml of chloroform (four times). The deeply colored chloroform layer was separated and evaporated to dryness. The residue was taken up in a small amount of chloroform and the product was precipitated by the addition of petroleum ether (bp 30–60°). The red-brown powder was collected and air dried (yield ~40%).

***cis*-Co(acac)$_2$NO$_2$L.**—One gram of the corresponding trans isomer was dissolved in 75 ml of chloroform and the resulting

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[1] acac = 2,4-pentanedionato (acetylacetonato).

[2] L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

[3] C. Varnelyi and A. Kezsmarky, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **14**, 79 (1969).

[4] L. J. Boucher and N. G. Paez, *Inorg. Chem.*, **9**, 418 (1970).