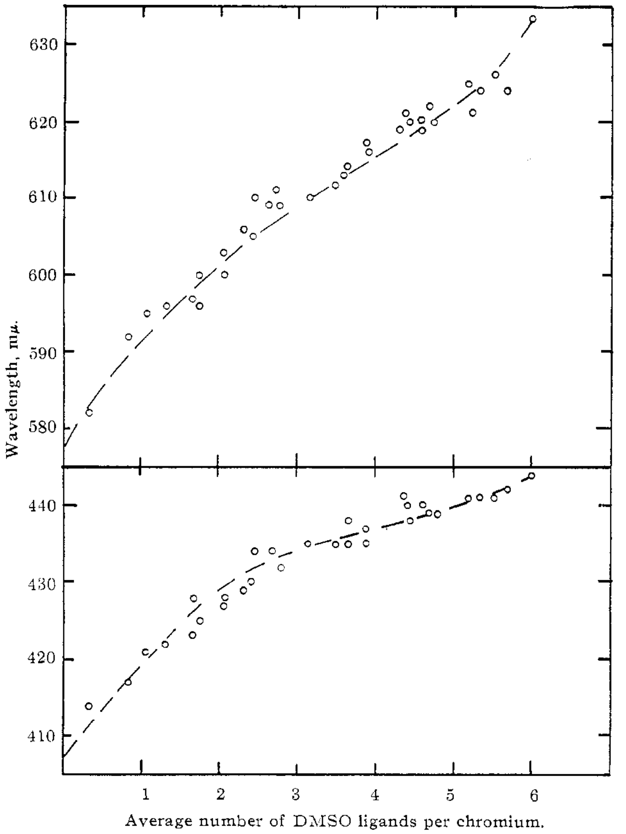

Figure 1.—The position of the absorption maximum as a function of the average number of DMSO ligands in the series of compounds $Cr(H_2O)_n(DMSO)_{6-n}^{3+}$.

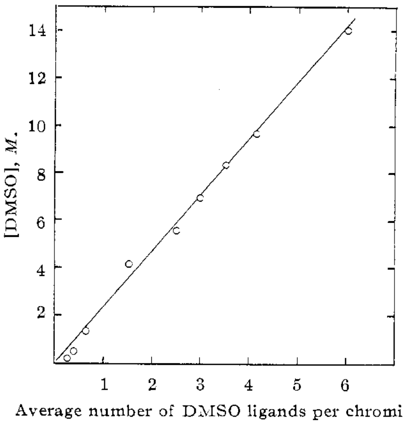

Figure 2.—The average number of DMSO ligands per chromium at equilibrium as a function of the concentration of DMSO in aqueous solution.

one may estimate the average number of DMSO ligands from the wavelengths of the maxima in the absorption spectrum.

Figure 2 shows a plot of the equilibrium ligand DMSO:Cr ratio *vs.* the DMSO concentration at 40.0°. This plot appears to be very nearly linear, with the greatest deviations at low DMSO concentration. This linear relation implies that the stepwise formation constants for $Cr(DMSO)_6^{3+}$ are all of the same order of magnitude. If this were not so, a linear relationship would not be observed.

An investigation of the kinetics of aquation of $Cr(DMSO)_6^{3+}$ and the solvolysis of $Cr(H_2O)_6^{3+}$ in DMSO produced ambiguous results. This was a direct result of the inability to isolate intermediate species and the lack of information concerning the activities of $Cr(H_2O)_n(DMSO)_{6-n}^{3+}$, DMSO, and water in the DMSO–water solutions.

Contribution from the Department of Chemistry,
University of California,
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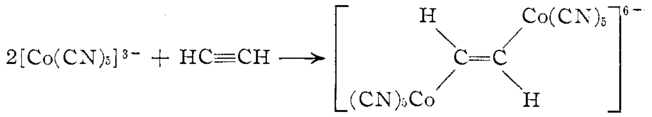
The Pentacyanocobaltate(II) Ion and Acetylenic Compounds

By Michael E. Kimball, John P. Martella,[1] and William C. Kaska

Received September 7, 1966

The interaction of pentacyanocobaltate(II) ion in aqueous solution with organic and inorganic compounds has led to some novel complexes with cobalt–carbon[2,3] and cobalt–metal bonds.[4] For example, in 1959 Griffith and Wilkinson[5] reported that acetylene and $[Co(CN)_5]^{3-}$ yield I, a moderately stable adduct with cobalt–carbon bonds



I

We wish to report on our studies with $[Co(CN)_5]^{3-}$ and acetylenic systems.

Experimental Section

Materials.—Baker Analyzed reagent chemicals were used throughout. Prepurified nitrogen was passed through a water solution of $[Co(CN)_5]^{3-}$ to remove oxygen. Distilled water was deaerated under vacuum or by bubbling nitrogen through the solvent. Dimethyl acetylenedicarboxylate was obtained from Aldrich Chemical Co. and distilled before use. Dicyanoacetylene was prepared according to Blomquist and Winslow.[6] Methyl propiolate was prepared by oxidation[7] of propargyl alcohol followed by esterification of the resultant acid. Tetracyanoethylene was purchased from Aldrich Chemical Co. and sublimed before use. Diphenylacetylene, 1-phenylpropyne, 1-propyne, perfluorobutyne, and allene were used as received. All of the reactions of $[Co(CN)_5]^{3-}$ were performed in the general manner described below.

Reaction of Pentacyanocobaltate(II) Ion with Dimethyl Acetylenedicarboxylate.—A deaerated aqueous solution (*ca.* 40 ml) which contained 2.38 g (0.01 mole) of $CoCl_2 \cdot 6H_2O$ was added to a magnetically stirred aqueous solution (*ca.* 30 ml) which contained 3.6 g (0.055 mole) of KCN, under nitrogen at 0°. The green solution was stirred for 3 min, whereupon 0.71 g (0.005 mole) of $CH_3CO_2C{\equiv}CCO_2CH_3$ in 2 ml of deaerated methanol was

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[1] NSF undergraduate summer research participant.

[2] J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **87**, 5361 (1965).

[3] J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.* (Amsterdam), **3**, 421 (1965).

[4] A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

[5] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1629 (1959).

[6] A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 156 (1945).

[7] V. Wolf, *Ber.*, **86**, 735 (1953).

added. The reaction solution became yellow-orange; it was stirred for 4 min whereupon 200 ml of chilled, deaerated ethanol was added. The solution became cloudy, and a red oil separated which slowly crystallized. The solid was redissolved in 10 ml of water and methanol was added until bright yellow crystals formed (56% yield). The solid was dried under vacuum over P_2O_5 for 2 days.

Anal.[8] Calcd for $K_6[Co_2(CN)_{10}C_6H_6O_4]\cdot 2H_2O$: C, 24.49; H, 1.67; N, 18.22; Co, 15.42. Found: C, 24.42; H, 1.63; N 17.94; Co, 14.95.

Spectra.—The infrared spectra were measured as Nujol mulls and in aqueous solution in Irtran-2 cells with a Beckman IR-7 instrument.

Results

Table I summarizes the results obtained from the interaction of $[Co(CN)_5]^{3-}$ with acetylenic compounds.

TABLE I

Acetylenic compounds which yield isolable adducts	Acetylenic compounds which yield nonisolable adducts
$CH_3CO_2C{\equiv}CCO_2CH_3$	$C_6H_5\ C{\equiv}CC_6H_5$[c]
$C_2H_5CO_2C{\equiv}CCO_2C_2H_5$[a]	$C_6H_5C{\equiv}CH$[b]
$HC{\equiv}CCO_2CH_3$[a]	$CH_3C{\equiv}CH$[b]
$NCC{\equiv}CCN$	$H_2C{=}C{=}CH_2$[c]
$HC{\equiv}CH$	$F_3CC{\equiv}CCF_3$[c]

[a] The product is air stable but hygroscopic. [b] A definite color change of the $[Co(CN)_5]^{3-}$ solution occurred from green to yellow. [c] No definite color change of the $[Co(CN)_5]^{3-}$ solution occurred.

The pentacyanocobaltate(II) ion in aqueous solution reacts with dimethyl acetylenedicarboxylate to yield an air-stable, brilliant yellow, crystalline compound.[9] The complex is very soluble in water, but insoluble in ethanol and other organic solvents. Treatment of $[Co(CN)_5]^{3-}$ adducts with iodine is most helpful in labeling cobalt–carbon bonds.[10] Thus iodination of the adduct in water at 0° in the absence of light led to *trans*-dimethyl iodofumarate, when 1 equiv of iodine was used. Two equivalents of iodine under the same conditions led to *trans*-dimethyl diiodofumarate.[11] Although daylight does not affect the nature of the adduct in the solid state or in solution, the absence of light and low temperature during iodinolysis reduce the possibility of adduct isomerization. A titration showed consumption of 2 equiv of $[Co(CN)_5]^{3-}$ per mole of $CH_3CO_2C{\equiv}CCO_2CH_3$. The yellow adduct did not react with additional $[Co(CN)_5]^{3-}$, nor did it react with additional $CH_3CO_2C{\equiv}CCO_2CH_3$. The nmr spectrum of the adduct in D_2O shows only one resonance signal, 3 ppm upfield from H_2O. The chemical shift is very dependent upon the concentration of the adduct and the temperature of the solution. The nmr spectrum of the methyl propiolate adduct shows two resonance signals; the vinyl hydrogen atom resonance occurs at 2 ppm downfield from H_2O and the methyl hydrogen atom resonance at 4 ppm upfield from H_2O.

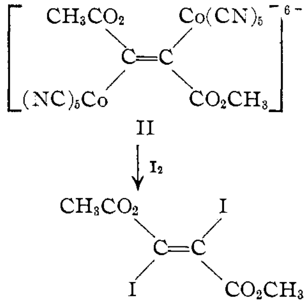
The infrared spectrum of adduct II shows peaks at 2132 and 2107 cm^{-1}, which is a region of the spectrum characteristic of cyanide stretching vibrations. A spectrum of the adduct in water showed one peak at 2146 cm^{-1}. Polarographic records of the adduct in water at 25° and pH 10 show two separate waves. These are consistent with Vlček's[12] reported results with $[Co(CN)_5X]^{3-}$ derivatives. After 3 days at 25–30° there are three waves in the polarogram; one of these waves arises from the presence of cyanide ion. Magnetic susceptibility measurements indicate the adduct is diamagnetic.

Discussion

There are several interesting features that may be emphasized from Table I. Although a moderately air- and moisture-stable complex, I, may be isolated from the reaction of $[Co(CN)_5]^{3-}$ and acetylene, no definite products could be isolated with 1-propyne. Moreover, no reaction occurred with allene[13] and isomers of 1-propyne. Indeed, it seems significant that stable $[Co(CN)_5]^{3-}$ adducts are isolated with acetylenic and olefinic systems only if certain electron-withdrawing groups are attached to the C≡C or C=C bond.[14] These include cyano and carbomethoxy. It certainly does seem unusual that $F_3CC{\equiv}CCF_3$[15] shows no evidence of reaction with $[Co(CN)_5]^{3-}$ since one might also expect that the CF_3 group is more electron withdrawing than H.

Under the assumption that the isolation of *trans*-dimethyl diiodofumarate reflects the stereochemistry of the cobalt adduct before iodinolysis, our observations suggest the following formulation and stereochemistry of the adduct

$$2[Co(CN)_5]^{3-} + CH_3CO_2C{\equiv}CCO_2CH_3 \longrightarrow$$



II

The similar reduction of acetylenic compounds with Cr^{II} has been studied by Castro and Stephens.[16] They suggest a mechanism which involves direct attack by the solvated metal moiety on the acetylenic system. Bottei and Joern[17] have reported that Cr^{II} reacts at

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(8) Analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany.

(9) We have also observed that $[HCo(CN)_5]^{3-}$ and $[Ni_2(CN)_6]^{4-}$ also yield hygroscopic but air-stable adducts with dimethyl acetylenedicarboxylate. This work will be reported later.

(10) J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **86**, 2311 (1964).

(11) This product has the same properties as noted by W. Peter, *Ann.*, **369**, 128 (1909).

(12) A. A. Vlček, *Pure Appl. Chem.*, **10**, 61 (1965).

(13) Likewise, $[Co(CN)_5]^{3-}$ does not react with ethylene: M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 6624 (1965).

(14) J. E. Huhey, *J. Org. Chem.*, **31**, 2356 (1966), has recently compiled a table of "group electronegativities" and polar substituent constants.

(15) Mays and Wilkinson,[13] have reported a stable adduct with $F_2C{=}CF_2$, but no reaction occurs with $F_3CC{\equiv}CCF_3$. We have isolated a stable adduct with $(NC)_2C{=}C(CN)_2$, although diethyl maleate and diethyl fumarate show no evidence of reaction with $[Co(CN)_5]^{3-}$. Carboalkoxy groups also activate the N=N bond since we have observed that $C_2H_5CO_2N{=}NCO_2C_2H_5$ forms a stable adduct.

(16) C. E. Castro and R. D. Stephens, *J. Am. Chem. Soc.*, **86**, 4358 (1964).

(17) R. S. Bottei and W. A. Joern, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, 65V.

different rates with acetylenedicarboxylic acid, the monoanion of acetylenedicarboxylic acid and the dianion of acetylenedicarboxylic acid. They have also detected a Cr^{II} complex, of unknown geometry, with acetylenedicarboxylic acid.

We have observed, however, that the dianion of acetylenedicarboxylic acid gave no evidence of reaction with $[Co(CN)_5]^{3-}$ at pH 13.30. A reaction did occur, as evidenced by a color change, when the pH was lowered to 10–11.[18]

Acknowledgment.—M. E. K. and W. C. K. gratefully acknowledge support of this work by the research committee of The University of California, Santa Barbara, Calif.

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(18) Preliminary kinetic studies of $[Co(CN)_5]^{3-}$ and $CH_3CO_2C{\equiv}CCO_2CH_3$ show the kinetics to be complicated. The reaction rate is drastically reduced when the alkoxy carbon chain is increased.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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A New Method for the Preparation of Fluorodisulfate Salts

BY DARRYL D. DES MARTEAU AND GEORGE H. CADY

Received August 26, 1966

The only reported fluorodisulfate salt is that of potassium. It was prepared by the reaction of potassium fluoride with excess sulfur trioxide.[1]

$$KF + 2SO_3 = KS_2O_6F = KSO_3F + SO_3$$

The white crystalline compound was unstable and decomposed completely to potassium fluorosulfate and sulfur trioxide when heated to 100° for 4 hr. Calcium fluorodisulfate has been suggested as an intermediate in the reaction of calcium fluoride with sulfur trioxide.[2]

Potassium, sodium, and, probably, ammonium fluorodisulfates have now been produced by reaction of peroxydisulfuryl difluoride with the corresponding peroxydisulfates, the potassium and sodium salts being

$$M_2[O_3SOOSO_3] + FO_2SOOSO_2F = 2M[O_3SOSO_2F] + O_2$$

$$2M[O_3SOSO_2F] = 2M[SO_3F] + 2SO_3 \quad (M = K, Na, or NH_4)$$

obtained in high yield. The ammonium salt was impure and was obtained in approximately 15% yield.

Experimental Section

Reagents.—Peroxydisulfates of sodium, potassium, and ammonium were obtained from commercial sources and were dried by warming *in vacuo*. Peroxydisulfuryl difluoride ($S_2O_6F_2$) was prepared by the reaction of fluorine with sulfur trioxide using a procedure similar to that of Shreeve and Cady.[3] [Since a by-product of this process, SO_3F_2 (bp −31.3°), is now known to probably be explosive, it is advisable to collect only that part of the product which condenses in a trap at −78°. Most of the gaseous SO_3F_2 is carried through the trap by a stream of nitrogen used in the process and discarded in a fume hood. Peroxydisulfuryl difluoride alone is not explosive, but it can form explosive mixtures with various reducing agents.]

Preparation and Analysis.—The reactions were carried out in a Pyrex-glass bulb fitted with a Fischer-Porter glass valve closed by a Teflon stem. $S_2O_6F_2$ was condensed onto the dried, powdered peroxydisulfate at −183° and the mixture was then allowed to warm to room temperature. A slow reaction took place near room temperature liberating oxygen. An approximate 10:1 mole ratio of $S_2O_6F_2$ to $M_2S_2O_8$ was used in each case. The reactions were very slow and became slower with time, probably owing to surface effects. Oxygen was removed periodically by pumping on the reaction vessel at −183°. After no further oxygen was observed to form [21 days for 1.7384 g of $K_2S_2O_8$, 4 days for 1.0339 g of $Na_2S_2O_8$, 8 days for 1.0356 g of $(NH_4)_2S_2O_8$], the excess $S_2O_6F_2$ was removed by pumping at room temperature until the rate of weight loss was only a few milligrams per hour. The products could not be pumped to constant weight because the unstable fluorodisulfate salts dissociated slowly into SO_3 and $MOSO_2F$ at room temperature. For the above samples of $K_2S_2O_8$ and $Na_2S_2O_8$ the weights of product were 2.743 and 1.718 g, respectively (theory: 2.807 and 1.756 g). For the sample of $(NH_4)_2S_2O_8$ the weight of product was 1.169 g (1.789 g, theory) and corresponded to approximately 15% $NH_4S_2O_6F$ mixed with 85% NH_4SO_3F. The products were then heated to 135° maximum and pumped to constant weight. After this treatment the above samples weighed 1.760, 1.073, and 1.035 g, respectively, corresponding closely to the theoretical weights 1.770, 1.060, and 1.063 g, respectively, for KSO_3F, $NaSO_3F$, and NH_4SO_3F. Other runs were similar to those just described. $KOSO_2F$, $NaOSO_2F$, and NH_4OSO_2F were then hydrolyzed in 1 *N* sodium hydroxide for 10 hr at 100° and the resulting solutions were analyzed for sulfur and fluorine. Sulfur was determined gravimetrically as barium sulfate and fluorine volumetrically by the method of Willard and Winter.[4] The sulfur trioxide was identified qualitatively by its physical properties, by tendency to liberate iodine from aqueous potassium iodide, and by giving a positive test for sulfate after hydrolysis. Oxygen was identified by its mass spectrum and volatility at −183°. The infrared spectrum of the excess peroxydisulfuryl difluoride remaining after reaction corresponded to $S_2O_6F_2$ containing a trace of SiF_4. Analytical data for the runs given above are summarized in Table I.

TABLE I
ANALYTICAL DATA

	Cation		
	Na^+	K^+	NH_4^+
Moles of O_2[a]	0.98	0.99	1.02
Moles of SO_3[b]	0.99	1.00	1.01
F[c] found, wt %	16.2	13.6	16.0
F calcd, wt %	15.6	13.8	16.2
S[c] found, wt %	26.2	22.5	27.6
S calcd, wt %	26.3	23.2	27.3

[a] Per mole of $M_2S_2O_8$ consumed. [b] Per mole of MS_2O_6F decomposed by heating. [c] Analysis of $MOSO_2F$.

X-Ray powder photographs were taken for samples of $KOSO_2F$ and KS_2O_6F prepared by the method given above and by the method of Lehmann and Kolditz.[1] The two methods gave materials having essentially the same patterns. These are given in the Ph.D. thesis of the junior author.[5] When the patterns were compared with those reported by Lehmann and Kolditz,[1] the extent of agreement was incomplete. Professor Kolditz has also com-

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(1) H. A. Lehmann and L. Kolditz, *Z. Anorg. Allgem. Chem.*, **272**, 69 (1953).

(2) E. L. Meutterties and D. D. Coffman, *J. Am. Chem. Soc.*, **80**, 5914 (1958).

(3) J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963).

(4) H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(5) D. D. Des Marteau, Thesis, University of Washington, 1966.