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Reaction of Potassium Hexacyanoferrate(III) with Molten Sulfur at 200° C. Evidence for the Thiofulminate Ligand

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Potassium hexacyanoferrate(III) reacts with molten sulfur at 200° C to give, after appropriate work-up of the reaction mixture, a dark green, paramagnetic material which contains sulfur. The experimental evidence – solubility and reaction characteristics and analytical, magnetic, and infrared data – indicate that the dark green substance is polymeric and contains thiofulminate (←CNS) ligand. Repeated extraction of the dark green material with water at 55° C, followed by filtration and treatment of the filtrate with 1,4-dioxane, gives a pale yellow compound. On the basis of elemental analysis, infrared, magnetic susceptibility and conductance data, and thermal stability experiments, the yellow compound is assigned the formula $K_3Fe(CN)_4(CNS)_2$ *and is also believed to contain the thiofulminate ligand.*

Introduction

The cyanide ligand with its unshared pair of electrons on the nitrogen atom has basic character.[1] Thus, for example, the iron(II) complexes, $[Fe(phen)_2(CN)_2]$ and $[Fe(bipy)_2(CN)_2]$ (phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine) can be protonated on the cyanide groups and in this regard they are stronger bases than their iron(III) analogs.[2] An increase in basicity is observed if the iron is replaced by ruthenium(II) or osmium(II); the proton affinities follow the order $[Fe(phen)_2(CN)_2] < [Ru(phen)_2(CN)_2] < [Os(phen)_2(CN)_2]$. This trend is attributed to increasing back-bonding from electrons in metal *d*-orbitals to the π-electron system of the aromatic amine with increasing atomic number of the metal.[3] A number of Lewis acid adducts of transition-metal–cyano complexes have been prepared,[4] *e.g.*, $K_2[Ni(CN \cdot BF_3)_4]$; $[Fe(phen)_2(CN \cdot BF_3)_2]$; $Fe(phen)_2(CN)_2 \cdot GeF_4$; $Fe(phen)_2(CN)_2 \cdot 2GeF_4$.

The ability of elemental sulfur to function as a Lewis acid is well known and requires no documentation. Important examples of such behavior include the vigorous conversion of trialkylphosphines to trialkylphosphine sulfides and of cyanide ion to thiocyanate ion.

The study described in this paper had as its objective the formation and characterization of a new type of thiocyanate ligand (the thiofulminate ligand), ←CNS, through the addition of a sulfur atom to the nitrogen atom of ligated ←CN in potassium hexacyanoferrate(III). This complex would appear to be a good candidate for the proposed addition since the cyanide groups are joined by strong σ bonds to the iron and the latter is in a sufficiently stable state to resist oxidation by sulfur. We believe that this communication provides persuasive evidence that our objective was attained.

Experimental

Materials

Nitrogen, obtained from Linde or Air Products Co., was purified by first passing it over hot copper turnings (*ca.* 350° C) and then through drying towers containing Linde 4A molecular sieves. Acetonitrile and 1,4-dioxane (both from J.T. Baker Chemical Co.) were used without further purification. They were stored over Linde 4A molecular sieves and were deaerated prior to use by passing oxygen-free nitrogen through them for about 30 min. Reagent grade carbon disulfide (Fisher Scientific Co.) was used without further purification. Commercial grade absolute ethanol was purified by distillation from magnesium ethoxide. Sublimed sulfur (Mallinckrodt Chemical Works) was used without further treatment (stated purity, 99.9%). Potassium hexacyanoferrate(III) (J.T. Baker Chemical Co.), with a stated purity of 99.9%, was used without additional purification.

Analytical Procedures

The potassium content of the dark green water-insoluble product to be described later was determined by flame photometry at the Kansas Geological Survey, Lawrence, Ks. In water-soluble compounds, the element was analyzed for precipitation of the tetraphenylborate salt.[5] Microanalyses for hydrogen, carbon, nitrogen, and sulfur were carried out by Chemalytics, Inc. Some of the microanalyses for hydrogen, carbon, and nitrogen were performed by Ms. Kathy Widiger on a F & M model 185 C, H and N analyzer. Iron was determined by a standard titrimetric procedure as described by Fritz and Schenk.[6]

Infrared Spectra

Reported spectra were taken in KBr pellets on a Perkin–Elmer infrared spectrometer, Model 421. There was no evidence for reaction of the potassium bromide with the products to be described as evidenced by the fact that essentially identical spectra were obtained in Nujol mulls.

Magnetic Susceptibility Measurements

These measurements were made at room temperature, *ca.* 25° C, by the Faraday method, using the susceptibility of $Hg[Co(SCN)_4]$ as a standard. Measurements were made at four different field strengths in order to determine whether the products exhibited ferromagnetic behavior. Diamagnetic corrections were made with the use of the constants listed by Selwood.[7]

Conductance Measurements

The molar conductances of $10^{-3}M$ aqueous solutions of the yellow, water-soluble product (described later) were measured at 25° C with a Beckman Industrial Instruments Division Model RC-16B2 conductivity bridge and a conventional dip-type cell. The cell constant was found by measuring the resistance of a $10^{-2}M$ potassium chloride solution, for which the specific conductivity is known to be 1.413×10^{-3} $\text{ohm}^{-1}\ \text{cm}^{-1}$ at 25° C.

Preparation and Isolation of Dark Green Product

The optimum temperature for reaction between potassium hexacyanoferrate(III) and molten sulfur was found in preliminary experiments to be 200° C. At this temperature, the iron complex is stable toward decomposition; molten sulfur exhibits its maximum viscosity and consists primarily of highly polymerized chains (average length, $5\text{–}8 \times 10^5$ atoms) with free radical ends.[8]

The reaction was carried out in a 100-ml round-bottomed flask fitted with a single standard taper 24/40 female joint. A glass cap (standard taper 24/40 male joint) equipped with gas inlet and outlet tubes was used to close the flask. Teflon sleeves were used on the joint to prevent seizure and to avoid contamination of the reaction mixture by a lubricant.

In a typical reaction, 9.0840 g (0.0276 mol) of finely ground $K_3[Fe(CN)_6]$ and 50.0 g (1.56 g-atoms) of sulfur were mixed intimately and added to the reaction flask, which was then flushed with oxygen-free nitrogen for about 15 min. The flask was placed in an oil bath which had been heated to 200° C, and the mixture was maintained at this temperature for 36 hr. During this time nitrogen was passed continuously through the reaction flask and into a $1M$ NaOH solution to test for the possible liberation of cyanogen. No cyanogen was detected. Periodically, during the 36-hr heating time, the reaction vessel was removed from the oil bath and allowed to cool to below 159° C. The decrease in viscosity of the sulfur on cooling permitted the mixture to be stirred, after which it was returned to the oil bath for additional heating at 200° C.

Following the reaction period, the mixture was allowed to cool to 140–150° C, and was then filtered quickly under a stream of nitrogen. It was next stirred with carbon disulfide to remove residual sulfur. Any last traces of sulfur were removed from the resulting brown solid by sublimation at 135° C under a pressure of 0.05 mm of Hg. Following complete removal of sulfur, the brown solid was extracted with 100 ml of acetonitrile in a Soxhlet extractor. The acetonitrile extract was dark red in color ($FeNCS^{2+}$ was shown to be present) and extraction was continued until the solvent coming through the extractor thimble was colorless. A light green solid remained in the thimble.

To remove unreacted $K_3[Fe(CN)_6]$, the light green solid was stirred with three 75-ml portions of water, the stirring times being of approximately 20-min duration. The undissolved dark green material was dried *in vacuo* over $CaCl_2$; weight, 1.8287 g. At this point in the various experiments carried out, the green solid was subjected to complete elemental analysis, an infrared spectrum taken, and the magnetic susceptibility measured.

Isolation of Yellow Product

In the specific run being described, after the infrared spectrum showed the green material to be identical to that obtained in all previous runs, the entire amount of product was suspended in 75 ml of water in a 100-ml round bottomed flask and the mixture was stirred at 55° C for 24 hr. Nitrogen was passed continuously through the flask during this time. The dark green solid was filtered through a sintered glass filter of fine porosity. The resulting green filtrate was in turn passed through a Millipore filter of 10 mμ porosity. A yellow-green filtrate that exhibited an absorption maximum at 23.8 kK (420 mμ) in the visible region was obtained. Remaining on the filter was a thin film of dark blue solid, which gave an infrared spectrum with absorption peaks at 2071(vs), 587(m), and 485 cm^{-1}(s). These absorptions agree well with those obtained for Prussian blue.

The green material remaining on the sintered glass filter was suspended in another 75-ml portion of water, stirred for 24 hr at 55° C, and filtered through a sintered glass filter of fine porosity. The resulting filtrate was then passed through a clean Millipore filter. The process of suspending the dark green solid in 75-ml portions of water, followed by appropriate filtrations, was continued until Millipore filtration gave a colorless filtrate, a condition which was fulfilled after six or seven extractions at 55° C. In contrast to its fine, powdery consistency prior to extraction with water, the dark green material was rather gummy after six or seven extractions. It is interesting to note that although no additional colored extracts could be obtained from the dark green solid after six or seven extractions, the infrared spectrum of the solid remaining was identical to a spectrum taken before extractions.

The combined Millipore filtrates (all of which gave the same visible spectrum with a peak at 23.8 kK) were reduced to a volume of about 50 ml on a rotovac. Two hundred milliliters of deaerated 1,4-dioxane was then added to the solution. A pale yellow precipitate formed after the solution was stirred. The yellow solid was filtered under a stream of nitrogen on a sintered glass filter of medium porosity, washed with ethyl ether, and dried *in vacuo* for 24 hr; yield 0.237 g. The product was stored in a black-surfaced desiccator under nitrogen since it appeared to be air and light sensitive. The infrared spectrum was taken and the magnetic susceptibility determined. Since only a small amount of yellow solid could be obtained from each sample of dark green product, it was not possible to obtain a complete set of elemental analyses on the product of each individual run. Therefore, microanalyses for carbon, nitrogen, and sulfur were generally obtained on each yellow product, and in addition, an analysis for one other element, *e.g.,* iron or potassium, was performed.

The Effect of Heat on the Yellow Product

On being exposed to air and light for several days, the yellow solid changed in color to yellow–orange. Extraction of the yellow–orange solid with carbon disulfide gave an extract which was shown to contain elemental sulfur.

To test further the stability of the yellow product, about 0.1 g of the material was placed in a test tube fitted with a standard taper 24/40 female joint and the tube was closed with a glass cap (standard taper 24/40 male joint) equipped with gas inlet and outlet tubes. The tube and its contents were immersed in an oil bath and heated at various temperatures while a continuous stream of nitrogen was maintained throughout the apparatus. After the heating period, an infrared spectrum of the solid was taken. The yellow solid proved to be thermally stable at 60° C, but at 80° C an infrared absorption peak at 1108 cm^{-1}, *characteristic of the yellow solid,* diminished noticeably in intensity, and after 12 hr of heating at 100° C disappeared altogether. The solid remaining was extracted with carbon disulfide and the extract solution was shown to contain elemental sulfur. The solid that was insoluble in carbon disulfide was subsequently heated at 145° C for 24 hr. A pale yellow solid, identified as sulfur, sublimed onto the upper, cooler part of the apparatus. An infrared spectrum was taken on the material remaining after removal of sulfur.

Results and Discussion

The Dark Green Product

Elemental analyses of the dark green products from five different experiments gave the following empirical formulas: $K_{1.31}Fe_{1.00}(CN)_{4.62}S_{0.54}\cdot 0.40H_2O$; $K_{1.27}Fe_{1.00}(CN)_{4.45}S_{0.39}\cdot 0.38H_2O$; $K_{1.51}Fe_{1.00}(CN)_{4.38}S_{0.42}\cdot 0.30H_2O$; $K_{1.41}Fe_{1.00}(CN)_{4.34}S_{0.57}\cdot 0.36H_2O$; and $K_{1.35}Fe_{1.00}(CN)_{4.23}S_{0.40}\cdot 0.26H_2O$. In each case, analysis accounted for essentially 100% of the product, with the water content being calculated from determination of hydrogen. The presence of water in the green material was confirmed by the infrared spectrum which showed, among other absorptions (see below), bands at 3400 (s, br), 1610(s), and 803 cm^{-1}(w). The peak at 803 cm^{-1} is in the region (880–650 cm^{-1}) normally attributed to coordinated water. Added support for the presence of the latter comes from the fact that the three absorption peaks cited remained even after the green solid was heated *in vacuo* at 100° C.

The absorption spectrum of the product was identical from run to run. In addition to the water bands noted, absorption peaks were found at 2071(vs), 2045(sh), 2028(sh), 1215(s), 590(m), 490(s), and 455 cm^{-1} (s, sh(?)). The starting compound, $K_3[Fe(CN)_6]$, exhibited bands at 2500(m), 2116(vs), 2074(m), 507(m), and 383 cm^{-1}(s).

The insolubility in water, the varying analytical results from product to product even though practically all of the product was accounted for in each case, and the identity of the infrared spectra strongly suggest that the green material is polymeric. The question arises regarding the nature of the binding of the sulfur in the material. Two pieces of evidence argue against sulfur being present as coordinated sulfide. First, no peaks are observed in the infrared region, 400–230 cm^{-1}, where metal–sulfur stretching frequencies normally occur.[9] Second, if sulfur is assumed to be present as sulfide and the carbon and nitrogen as cyanide (and iron as Fe(III), there is very poor charge balance on the basis of the empirical formulas given in Table I. That iron does not exist in an oxidation state higher than three in the green material is shown by the fact that treatment with dilute hydrochloric acid resulted in no oxygen (or chlorine) evolution.

We propose that the sulfur exists in the form of the coordinated *thiofulminate* ion, $\leftarrow CNS^-$. Several observations strongly suggest that such an assignment is indeed correct. Charge-balance data for the empirical formulas listed in Table I fit quite well the assumption that sulfur is bound to cyanide. Deviations from perfect

TABLE I. Elemental Analyses of Dark Green Products from Reactions of $K_3Fe(CN)_6$ with Sulfur at 200° C.

	(1)	*(2)*	*(3)*	*(4)*	*(5)*
%K	19.99 ± 0,02	20.62 ± 0.42	23.78 ± 0.03	22.08 ± 0.24	22.18 ± 0.24
Fe	21.55 ± 0.03	23.22 ± 0.05	22.15 ± 0.06	22.45 ± 0.01	23.38 ± 0.02
C	20.81 ± 0.11	21.51 ± 0.03	20.65 ± 0.02	20.32 ± 0.09	20.62 ± 0.08
N	25.64 ± 0.07	26.68 ± 0.09	25.28 ± 0.05	25.13 ± 0.00	25.53 ± 0.01
H_2O^a	2.77	2.86	2.15	2.59	1.97
S	6.67	5.19	5.46	7.33	5.37
Total	97.43	100.08	99.83	99.90	99.05
C/N	0.95	0.94	0.95	0.94	0.94
Empirical Weight:	254.3	240.3	247.8	248.8	236.3

Empirical formulas	Corresponding to *(1)* above:	$K_{1.31}Fe_{1.00}(CN)_{4.62}S_{0.54}\cdot 0.40H_2O$
	Corresponding to *(2)* above:	$K_{1.27}Fe_{1.00}(CN)_{4.45}S_{0.39}\cdot 0.38H_2O$
	Corresponding to *(3)* above:	$K_{1.51}Fe_{1.00}(CN)_{4.38}S_{0.42}\cdot 0.30H_2O$
	Corresponding to *(4)* above:	$K_{1.41}Fe_{1.00}(CN)_{4.34}S_{0.57}\cdot 0.36H_2O$
	Corresponding to *(5)* above:	$K_{1.35}Fe_{1.00}(CN)_{4.23}S_{0.40}\cdot 0.26H_2O$

[a] $\%H_2O$ was calculated on the basis of %H

charge balance for the five formulas are: (1) −0.31; (2) −0.18; (3) +0.13; (4) +0.07; and (5) +0.12. The strong absorption peak at 1215 cm^{-1} is found in neither S-bonded or N-bonded thiocyanato complexes and is in the region (780–1500 cm^{-1}) in which N–S double bond stretching bands are found.[10] Moreover, one might expect that the infrared spectrum of coordinated thiofulminate would be roughly analogous to that of coordinated fulminate, ←CNO. Typically, the latter ligand exhibits an N–O stretching band in the region 1050–1205 cm^{-1} [11] and it is thus not unreasonable to assign our band at 1215 cm^{-1} to an N–S stretch. Although we have attributed the absorption peak at 803 cm^{-1} to coordinated water, one might argue that the absorption is due to the C–S stretch of N-bonded thiocyanate.[12] Simple qualitative tests ruled out that possibility. The dark green solid was suspended in 85% phosphoric acid and the mixture heated to a gentle boil while nitrogen was passed continuously over the mixture and through a 1*M* sodium hydroxide solution. Hydrogen sulfide was liberated, but there was no trace of either cyanide or thiocyanate ions in the neutralized sodium hydroxide trap solution. The phosphoric acid solution in the reaction vessel was neutralized with sodium hydroxide and tested for cyanide ion (negative), thiocyanate ion (negative), and ammonium ion (positive). As a control, tetramethylammonium hexathiocyanato-N-ferrate(III), prepared by a minor modification of the method of Forster and Goodgame,[13] was treated in the same manner as the dark green substance. The observations were identical to those for the dark green solid except in one very important respect: thiocyanate ion was found in the neutralized sodium hydroxide trap solution, indicating that hydrogen thiocyanate had been liberated. On the basis of these results, the presence of sulfur as thiocyanate in the dark green solid would appear to be ruled out.

The effective magnetic moments (taken at room temperature, *ca.* 25° C) of the dark green products ranged from 4.23 to 4.44 B.M. based on the empirical formulas shown in Table I. The values are much too high for Fe(III) (with a d^5 configuration) in a strong octahedral field. Although low-spin octahedral complexes of metal ions with a $t_{2g}{}^5$ configuration usually have considerable orbital contribution to their magnetic moments near room temperature, the maximum moments observed for such iron(III) complexes are in the vicinity of 2.3 B.M. A possible explanation for our high values is that some of the iron(III) ions are surrounded predominantly by the strong-field cyanide ions, while others are linked to weaker field CNS^- ions. The thiofulminate ion would probably not differ markedly from the thiocyanate ion, which is considered a ligand of intermediate field strength, in its capacity to cause *d*-orbital splitting. The presence of a ligand of intermediate field strength could cause some of the iron(III) ions to adopt the high spin $t_{2g}{}^3\ e_g{}^2$ configuration. There is also the possibility that water molecules, which also fall about midway in the spectrochemical series, are coordinated to some of the iron(III) ions.

The Yellow Compound

The experimental evidence is strong that the yellow compound should be formulated as $K_3Fe(CN)_4(CNS)_2$.

Elemental analytical data and charge-balance calculations agree excellently with the formula. *Anal.* Calcd for $K_3Fe(CN)_4(CNS)_2$: K, 29.82; Fe, 14.20; C, 18.32; N, 21.36; S, 16.30. Found: K, 29.76 ± 0.13, 29.60 ±

0.09; Fe, 14.45 ± 0.13, 14.06 ± 0.11; C, 18.69, 19.10, 18.73, 18.93, 18.74, 18.87; N, 21.32, 21.14, 21.28, 21.65, 21.15, 21.34; S, 14.80, 15.20, 14.69; 16.27, 15.96; ^{14}C/N, 1.02, 1.05, 1.03, 1.02, 1.03, 1.03. The molar conductances of $10^{-3}M$ aqueous solutions of the yellow product from two runs were 426 and 434 ohm^{-1} cm^{-1} at room temperature, values within the range (400–450 ohm^{-1} cm^{-1}) expected for a 3:1 electrolyte.

The yellow compound is paramagnetic. Compounds obtained from four different dark green products had effective magnetic moments in the range 2.61–2.73 B.M. at room temperature. These values are between those expected for substances with one and two unpaired electrons. As has been pointed out above, the maximum moment found for low-spin octahedral iron(III) complexes is about 2.3 B.M. The higher values found for the yellow compound are consistent with the presence of some weaker field ligand, such as CNS^- would be expected to be, in addition to the strong field cyanide ligand.

Perhaps the most compelling evidence for the proposed formula comes from infrared and thermal stability information. The yellow compound showed the following absorptions: 2115(s); 2093(m); 2072(s); 2062(s); 2040(vs); 2025(vs); 1108(s); 610(m); 578(s); and 383 cm^{-1}(m). *No bands are found in 690–720 cm^{-1} and the 780–860 cm^{-1} regions where C–S stretches for S-bonded and N-bonded thiocyanate, respectively, are normally observed.*[12] The strong absorption band at 1108 cm^{-1} can, by the arguments used for the 1215 cm^{-1} band in the dark green product, be assigned to an N–S stretch. Although the peak at 383 cm^{-1} falls in the region expected for metal–sulfur stretching frequencies, a peak at the same frequency is exhibited by $K_3[Fe(CN)_6]$ and is attributed to Fe–CN bonding.[15] Also, the possibility of metal–sulfide bonding is eliminated by charge-balance considerations and the high solubility of the compound in water. That the sulfur is bound rather weakly in the yellow compound is demonstrated by the ready release of the *free element* at temperatures in the neighborhood of 100° C. The complete disappearance of the strong absorption band at 1108 cm^{-1} after a 24-hr heating period at 145° C is accompanied by the appearance of bands which we found to be characteristic of $K_3[Fe(CN)_6]$, *i.e.*, at 2500 and 507 cm^{-1}.

At this point, a word is in order regarding the comparative thermal stability of the dark green product relative to that of the yellow compound. No decomposition is observed up to 200° C; at 225° C, some elemental sulfur is set free and a brown water-insoluble material remains. Marked changes occur in the infrared spectrum, with perhaps the most significant change being the disappearance of the strong band at 1215 cm^{-1} and the appearance of new bands at 1110(s) (*cf.*, 1108 cm^{-1}(s) for the yellow compound) and 1047 cm^{-1}(m). The shift to lower frequencies, coupled with the thermal stability data, suggests that the thiofulminate ligand is a bridging group in the dark green product.

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