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Solid-State Reactions of Iron(II) Hexacyanochromate(III)

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Received June 22, 1967

Cyanide linkage isomerism has been found to occur in the solid state for the polymeric complex of approximate composition $Fe_3[Cr(CN)_6]_2$. The combination of infrared spectroscopy, X-ray powder diffraction, magnetic susceptibilities, and Fe^{57} Mössbauer spectroscopy indicates that four distinct structures occur at different stages in the isomerization of this solid. The initial face-centered-cubic material contains $Fe^{2+}—N≡C—Cr^{3+}$ linkages and has interstitial Fe^{2+}. In the first reaction step the interstitial Fe^{2+} displaces Cr^{3+} from the carbon octahedra to give a half-isomerized complex with both Fe^{2+} and Cr^{3+} in the carbon octahedra and Cr^{3+} in interstitial sites. In the presence of air, this complex undergoes further rearrangement and partial oxidation. The oxidized compound can then be reduced to give the true linkage isomer, *e.g.*, the complex containing $Cr^{3+}—N≡C—Fe^{2+}$ linkages with Fe^{2+} in interstitial sites.

Introduction

In 1964 Shriver, *et al.*,[2] prepared a complex with the apparent composition $KFeCr(CN)_6$ containing $Fe^{2+}—N≡C—Cr^{3+}$ linkages. Calculation of site preference energies for this system led to the prediction that it would be unstable with respect to isomerization to $KCrFe(CN)_6$, containing $Fe^{2+}—C≡N—Cr^{3+}$ linkages. Upon heating, this compound was found to change from brick red to green, and the cyanide stretching frequency changed from 2168 to 2092 cm^{-1}. It appeared that, in effect, a cyanide "flip" had occurred.[3]

This study was undertaken in order to establish exactly what changes were, in fact, occurring in the system, and, hopefully, to establish a mechanism for the rearrangement. It was felt that the combination of a number of techniques, including infrared spectroscopy, X-ray powder diffraction, magnetic susceptibilities, and Fe^{57} Mössbauer spectroscopy, would serve to characterize the system.

At the beginning of this research we felt that the Mössbauer effect would prove to be the most powerful tool in elucidating the changes which were taking place. Unfortunately, the samples give diffuse spectra which, in general, cannot be thoroughly resolved. As a result, the Mössbauer spectra serve mainly as corroborative evidence for conclusions reached on the basis of other techniques.

Experimental Section

Preparation of Compounds.—$K_3Cr(CN)_6$ was prepared by the method of Schlessinger[4] or used as received from A. D. Mackay, Inc.

The unisomerized complex was prepared by the slow addition, at 0°, of a solution of $K_3Cr(CN)_6$ to a stirred solution containing an excess of $FeSO_4 \cdot 7H_2O$. A light brown precipitate formed immediately, and this was rapidly vacuum filtered under nitrogen. The precipitate was washed several times with H_2O, followed by several washings with 95% ethanol, and was finally washed with anhydrous ether. The solid was then dried of any remaining ether under vacuum at 5°. This method left a considerable amount of water in the complex but was necessary because more rigorous drying procedures led to extensive isomerization.

The complex of approximate composition $Cr_4[Fe(CN)_6]_3$ was prepared in a nitrogen atmosphere by the addition of $K_4Fe(CN)_6$ solution to an excess of Cr^{2+} to give a light blue precipitate which became light green after exposure to air. A ratio of 1.37 for Cr to Fe was found for this green material. This method of synthesis was chosen because the direct reaction of the substitution-inert Cr^{3+} ion with $Fe(CN)_6{}^{4-}$ leads to an ill-defined product.

Analyses.—C, H, and N analyses were performed by Miss Hilda Beck of this department and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Iron was determined by potentiometric titration with dichromate. Chromium was determined spectrophotometrically as $CrO_4{}^{2-}$ at 372 mμ using a Cary Model 14 spectrophotometer. The chromium was separated from iron in a two-step process. After oxidation in base, the ferric hydroxide precipitate was filtered from the solution. This precipitate was dissolved in concentrated HCl, and after reduction of the Cr(VI), the iron was removed by anion-exchange chromatography using Dowex 1-X8 resin.

Iron to chromium ratios from the chemical analyses were verified by X-ray fluorescence measurements. A GE XRD-5 diffractometer was used with a tungsten anode and a LiF crystal analyzer. $[(H_2NCH_2CH_2NH_2)_3Cr][Fe(CN)_6]$ was used as a calibrant and ratios were determined from peak area measurements using both $K\alpha$ and $K\beta$ radiation.

Weight losses (see Table I) were determined by heating samples in the Faraday balance to about 100° for 1 day under a helium flow and observing the weight change. Although water is the principal species removed, part of the weight loss is undoubtedly due to ethanol or ether. For this reason, the total percentage is probably high by as much as 1% in some cases.

Physical Measurements.—Infrared spectra were taken on Nujol mulls between KBr plates using a prism-grating Beckman IR-9. In addition, samples were run as Nujol mulls on polyethylene plates in the region 300–500 cm^{-1} using a Beckman IR-10. X-Ray powder diffraction data were collected on film in a 114.6-mm Debye–Scherrer camera. A Picker 6147 X-ray generator was used with vanadium-foil-filtered Cr $K\alpha$ radiation (λ 2.2909 A). Fe^{57} Mössbauer spectra were obtained on an automated constant-velocity NSEC Model B spectrometer using a 3-mCi Co^{57} in palladium source. Operation of the instrument was checked periodically with sodium nitroprusside and iron standard absorbers. All data in this paper are relative to $\delta = 0$ for $Na_2Fe(CN)_5NO \cdot 2H_2O$. The automation of the spec-

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[1] (a) Department of Chemistry; NASA Fellow, 1965–1966; NSF Predoctoral Fellow, 1966–1968; (b) Department of Chemistry; Alfred P. Sloan Fellow; (c) Department of Materials Science.

[2] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

[3] Some other systems which appear to involve cyanide linkage isomerism have been reported: J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965); J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965); J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, private communication.

[4] G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N. Y., 1962, p 82.

TABLE I

ANALYTICAL DATA ON FOUR SAMPLES OF IRON CHROMICYANIDE

Sample	Fe	Cr	N	C[a]	H	Wt loss	Total[b]	Fe:Cr[c]	N:Cr
1	19.38	11.20	18.75	16.75	3.43	28.45	94.53	1.61	6.23
2	24.54	14.01	19.85	20.53	3.10	9.66	88.59	1.63	5.27
3	21.29	12.40	19.95	20.86	3.65	17.52	92.02	1.60	5.99
4	20.13	11.86	18.77	17.61	3.65	25.73	94.10	1.58	5.99
							Av 92.31	1.61	5.87

[a] Carbon analyses are occasionally high owing to the incomplete removal of ether from the sample. [b] The hydrogen analysis is excluded from this total. [c] This ratio was determined from wet analyses; X-ray fluorescence results on three of these samples give an average ratio of 1.63.

trometer and the general method for the treatment of the data have been described previously.[5] The Mössbauer data were approximated as Lorentzian curves through the use of a local modification of Davidon's variable metric minimization program.[6] In this method the number of peaks is specified along with their approximate velocities, intensities, and half-widths. These last three quantities are then varied by the program to obtain the best fit to the data. Powdered samples were pressed between aluminum foil sheets and clamped in brass plates. Low temperatures were achieved by placing these plates in a polystyrene foam cavity and blowing cold nitrogen across the sample. Temperature control, regulated by varying the rate of boiling of liquid nitrogen was ±2°. Magnetic susceptibilities were measured by the Faraday method. Samples in open quartz buckets were suspended from a Cahn RM automatic electrobalance into a 6-in. Varian electromagnet with truncated pole pieces. The sample was encased by a double-walled elliptical dewar which permitted temperature control and which also allowed a helium flow to be passed through the sample cavity. The system was calibrated using $HgCo(SCN)_4$.[7,8] (Noting the discrepancy between ref 7 and 8, we have used the same treatment as Cotton, *et al.*[9]) Low temperatures were obtained by boiling liquid nitrogen and passing the cold gas through the dewar, and high temperatures were obtained using heated air in a similar fashion. For all samples, deflections were measured at a minimum of 12 temperatures over a temperature range from about −150 to +100° (except for the unisomerized sample, where the upper limit was +30°). Curie–Weiss law parameters were determined from the least-squares fit of $1/\chi_g$ *vs.* T(°K). Susceptibilities were corrected for diamagnetic contributions using values given by Figgis and Lewis.[10]

Results

A major difficulty in this study was to establish the composition of the material. $K_3Cr(CN)_6$ is apparently strongly absorbed by the precipitate, so unless the preparation is carried out in an excess of Fe^{2+} the composition is somewhat variable. Both chemical analysis and X-ray fluorescence analysis (Table I) established the ratio of iron to chromicyanide as 1.6/1.0. In order to maintain electroneutrality, then, some other anion must be present. The only possibilities here are SO_4^{2-} or OH^-, and analytical tests for SO_4^{2-} indicated that none was present. The presence of OH^- may be indicated by a sharp band in the infrared spectrum at about 3650 cm^{-1}, which is distinct from the broad water band at 3400 cm^{-1}.[11] Thus, the compound may be formulated as $Fe_{1.6}[Cr(CN)_6](OH)_{0.2}$. In addition, there is always a significant amount of water present. Although heating under vacuum will remove most of this, it appears impossible to remove all of it.

In the case of the unisomerized and half-isomerized material the X-ray powder patterns may be completely indexed on the basis of a face-centered-cubic unit cell. In the case of the oxidized, reduced, and $Cr_4[Fe(CN)_6]_3$ samples the patterns appeared to be simple cubic with a unit cell approximately half the size of the other compounds. For the sake of uniformity these apparent unit cell parameters are doubled in all discussions. The lattice parameters, corrected by the use of NaCl as an internal standard, are: unisomerized, 10.65;[12] half-isomerized, 10.50; oxidized, 10.07; reduced, 10.19; and $Cr_4[Fe(CN)_6]_3$, 10.06; all ±0.02 A.

The magnetic susceptibilities (Table II) are somewhat variable, owing to differences in composition and water content. As described in the Discussion, μ_{eff} values are calculated on the basis of the analytical data, and thus are subject to less scatter than the gram-susceptibilities.

TABLE II

MAGNETIC DATA

Sample	$10^6\chi_g$(av), cgs[a]	θ(av), °K[a]	μ_{eff}(av), BM[a,b]
Unisomerized	74 ± 3	−23 ± 4	5.31 ± 0.06
Half-isomerized	53 ± 3	52 ± 3	5.34 ± 0.07
Oxidized	29 ± 1	37 ± 16	3.9 ± 0.2
Reduced	36 ± 0.9	11 ± 6	4.96 ± 0.06

[a] The limits of error represent standard deviations for four different preparations of the unisomerized material and three preparations for each remaining material. χ values represent data at 300°K. [b] The significance of the μ_{eff} values is given in the discussion.

The infrared spectral data are summarized in Table III along with probable assignments.

For all samples of iron (II) hexacyanochromate(III) and its reaction products the peaks of the Mössbauer spectra were broad, with full widths at half-height in the range 0.5–0.7 mm/sec. This breadth is not due to instrumental or sample thickness effects, but it does correlate with the somewhat diffuse X-ray powder patterns which indicate that the individual crystallites

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(5) H. Marcus, L. H. Schwartz, and M. E. Fine, *Am. Soc. Metals, Trans. Quart.*, **59**, 468 (1966).

(6) W. C. Davidon, USAEC Report ANL-5990 (1959).

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(8) B. N. Figgis and R. S. Nyholm, *ibid.*, 338 (1959).

(9) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

(10) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

(11) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 73.

(12) This value represents a lower limit, since in all cases some isomerization has undoubtedly taken place.

TABLE III

INFRARED SPECTRAL DATA[a]

Complex	$\nu_{C\equiv N}$	ν_{M-C}, δ_{M-C-N}	ν_{O-H}
Unisomerized	2170 s	488 s, 370 s	3650 m
Half-isomerized	2170 m 2100 m	490 s, 370 s	3650 w
Oxidized	2100 s	525 s, b	
Reduced	2100 s	525 s, b	
$Cr_4[Fe(CN)_6]_3$	2098 s	525 s, b	

[a] Frequencies are all in cm^{-1}: s, strong; m, medium; w, weak; b, broad. In addition, absorptions due to water at *ca.* 3400 and *ca.* 1600 cm^{-1} are observed for most samples.

are small or somewhat inhomogeneous. Because the Mössbauer spectra could not, in general, be completely resolved, all of the isomer shift and quadrupole splitting parameters could not be extracted from the data. For this reason, the information obtained from the spectra will be discussed separately for each compound. Because the cryostat used was rather primitive, temperature could not be easily preselected. As a result, the figures and data reported here cover a range of approximately 25°. Any error introduced by this temperature variation is likely to be insignificant, particularly when compared to the intrinsic error caused by the diffuse patterns and broad half-widths. Furthermore, examination of all of the complexes between the approximate temperature limits of −30 and −100° showed in most cases no significant variations in the peak positions, indicating that the second-order Doppler shifts for these compounds are small and that comparison of spectra obtained at somewhat different temperatures should not debilitate any conclusions reached. For example, the spectrum of the unisomerized complex, which exhibited the largest temperature dependence, had a total spread of isomer shift values of 0.034 and 0.065 mm/sec for the outer and inner peaks, respectively, between the temperature limits of −45 and −100°. The temperature variation of the quadrupole splittings was more pronounced, since it involved a range of 0.34 and 0.46 mm/sec for the same temperatures.

Discussion

In the face-centered-cubic lattice which is common to Prussian blue and its analogs, one metal is octahedrally coordinated by the carbon end of cyanide and the other by the nitrogen end.[13] This arrangement gives rise to interstitial sites which will accommodate any excess ions. In the present case the analytical data (Table I) indicate that there is 0.3 interstitial metal ion for each lattice metal ion.

Unisomerized Complex.—The unisomerized complex forms immediately upon the reaction of $K_3Cr(CN)_6$ and any Fe^{2+} salt. When dried, it is a light brown to orange powder. The infrared spectrum is similar to that of $K_3Cr(CN)_6$, with all three major bands shifted to higher frequencies by about 30 cm^{-1}, a shift which is common upon cyanide bridge formation.[2,14] In particular, the cyanide stretching frequency at 2170 cm^{-1} indicates that the species is a chromicyanide, and not a ferrocyanide, for which the cyanide stretching frequency would be expected at about 2100 cm^{-1}. Using known ionic radii, it is possible to estimate a lattice constant for this system on the assumption that it contains $Fe^{2+}—N\equiv C—Cr^{3+}$ linkages. Using the lattice parameters for the Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} chromicyanides[15] and the Goldschmidt ionic radii[16] for these ions, it is possible to obtain an average $Cr(CN)_6^{3-}$ radius of 4.55 A. Coupling this value with the ionic radius of Fe^{2+} leads to an expected lattice constant for the unisomerized complex of 10.62 A, in close agreement with the observed value of 10.65 A.

The Mössbauer spectrum of this system, although difficult to resolve, indicates that all iron is present as high-spin Fe^{2+}.[17] Figure 1 shows a resolved spectrum

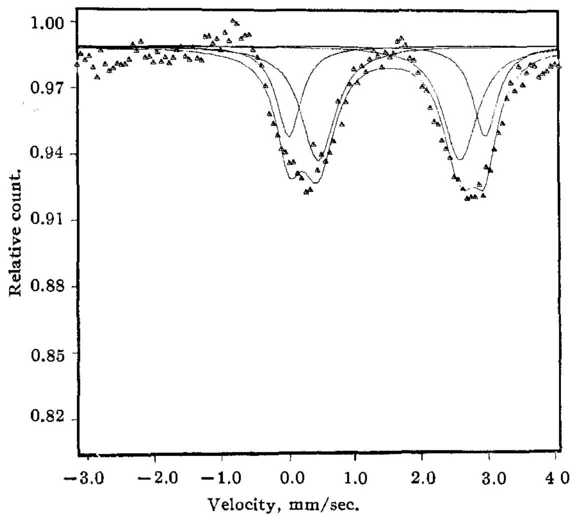

Figure 1.—Mössbauer spectrum of the unisomerized complex at −67°. In the curve-fitting process the two outer peaks and the two inner peaks were constrained to be equal in half-width and intensity.

at −67°, and the following assignments can be made. The weaker, outside peaks are a quadrupole-split pair with the isomer shift (δ) equal to +1.48 mm/sec and quadrupole splitting (ΔE) equal to 2.92 mm/sec. The inner peaks constitute another quadrupole-split pair with $\delta = +1.52$ mm/sec and $\Delta E = 2.11$ mm/sec. These peaks are assigned to Fe^{2+} in interstitial sites and nitrogen octahedra, respectively. This assignment is confirmed by the intensities, which are found to be in the ratio 0.60/1.00, in exact agreement with the ratio predicted from the analytical data. Although the Debye temperature and, hence, the recoil-free fraction are expected to change from one site to another, these changes should not markedly affect the relative intensities. As a result, the intensities within a given pattern should serve as at least a semiquantitative measure of the

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(13) D. F. Shriver in "Structure and Bonding," Vol. 1, Springer-Verlag, Berlin, 1966, p 32.

(14) G. Emschwiller, *Compt. Rend.*, **238**, 1414 (1954); D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

(15) A. Ferrari, M. E. Tani, and E. Morisi, *Acta Cryst.*, **15**, 90 (1962).

(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 43.

(17) For a general review of the structural implications of Mössbauer spectra see: V. I. Gol'danski, "The Mössbauer Effect and Its Applications in Chemistry," Consultants Bureau, New York N. Y., 1964.

amount of a particular absorbing species. This hypothesis is substantiated by the data of Fluck, Kerler, and Neuwirth,[18] who found approximately correct relative intensities for iron in the carbon and nitrogen sites of Prussian blue. Furthermore, the agreement we find on samples where we are reasonably sure of the structures indicates that it is probably valid to carry intensity arguments over to the forms where our other data are less conclusive.

The interstitial Fe^{2+} is expected to have a greater quadrupole splitting than Fe^{2+} in the nitrogen holes, which have octahedral symmetry. If the Fe^{2+} in the nitrogen sites was in a site of rigorous cubic symmetry, we would expect little or no quadrupole splitting. However, since these materials contain a large fraction of interstitial ions as well as a significant amount of water, the local symmetry may be less than cubic. As a result, the rather large quadrupole splitting does not appear to be unreasonable. Since Fe–N bonds are weaker than Fe–C bonds, it is to be expected that the distortions caused by interstitials will be more pronounced for the nitrogen octahedra than the carbon octahedra.

Since it is meaningless to speak of an effective magnetic moment for systems containing more than one paramagnetic center, the data were treated in terms of gram-susceptibilities by the following method. Cr^{3+} is orbitally nondegenerate so that its magnetic moment is expected to fall near the spin-only value, and measured magnetic moments for Cr^{3+} compounds are found to fall in a narrow range around 3.8 BM.[19] Using this value and some specific temperature (300°K was used in all cases), along with the analytical data for chromium in the complex, it is possible to calculate the contribution made by chromium to the total gram-susceptibility. This value is subtracted from the observed gram-susceptibility at 300°K (which is obtained from the Curie–Weiss law determined for the system) to give the gram-susceptibility due to the iron. At this point some assumption must be made about the distribution of different iron species in the system. Based on these assumptions and the analytical data for iron, one can then obtain an effective magnetic moment per paramagnetic iron. This value can be compared with an expected moment to check the validity of the assumed structure.

For the unisomerized complex, the gram-susceptibility, χ_g, is found to be about 74×10^{-6} cgs at 300°K with $\theta = -23$°K in $\chi_g = C/(T + \theta)$. If it is assumed that all iron present is paramagnetic and equivalent, then the effective magnetic moment for iron is found to be about 5.3 BM. The variation in values for several different preparations was from 5.25 to 5.37 BM, but such a variation is expected, since small but variable degrees of isomerization have taken place in all samples. In any case, these values are quite close to the expected magnetic moment of 5.4 BM for high-spin Fe^{2+}.

The above data lead us to the conclusion that the unisomerized complex has Cr^{3+} in the carbon holes, Fe^{2+} in the nitrogen holes, and the appropriate number of high-spin Fe^{2+} ions in interstitial sites.

Half-Isomerized Complex.—If the unisomerized complex is allowed to remain under an inert atmosphere at room temperature for a few days or if it is heated to 50° for about 3 hr in an inert atmosphere, a new complex results which is characterized visually by a slight darkening to a light brown. This complex appears to result from the exchange of Fe^{2+} and Cr^{3+} between the interstitial sites and the carbon octahedra; thus it corresponds to a complex which is approximately half-isomerized. Since originally there is only enough iron present in interstitial sites to be able to occupy 60% of the carbon holes, 40% of the carbon holes will still contain Cr^{3+}. The following evidence is offered in support of these conclusions.

The infrared spectrum shows two peaks of roughly equal intensity in the cyanide stretching region at 2170 and 2100 cm^{-1}. The band at 2170 cm^{-1} has already been established as corresponding to $Cr(CN)_6^{3-}$, and the band at 2100 cm^{-1} is in the region where $Fe(CN)_6^{4-}$ is known to absorb in similar complexes.[2] Thus, the complex is a mixture of ferrocyanide and chromicyanide.

The Mössbauer spectra obtained here were again difficult to resolve, particularly in the region near +0.5 mm/sec. (This region of +0.5 mm/sec relative to nitroprusside, which corresponds to an actual velocity of about 0 with the Co^{57} in Pd source used, is the least reliable portion of the spectrum, owing to both instrumental errors and geometric effects.) However, a few generalizations can be made. If the reaction taking place can be represented schematically by Fe^{2+} (interstitial) $\rightarrow$ Fe^{2+} (carbon hole), then the product is expected to show Mössbauer absorption in the region near +0.2 mm/sec. Thus, we expect to find an increase in absorption in the region near +0.2 mm/sec at the expense of the region near +2.5 mm/sec, and this is found to be the case. Figure 2 shows a typical spectrum with an attempted resolution. Some specific things can be said about the observed Mössbauer spectrum. We expect the relative area of the remaining absorption at +2.5 mm/sec to be roughly $^1/_2(1.00 - 0.38) = 0.31$. The average relative area for this peak from five separate spectra was found to be 0.34, in fairly close agreement with the expected value. Also, for two samples at −52 and −75° the position of this peak was +2.57 mm/sec, nearly identical with the peak ascribed to Fe^{2+} in nitrogen holes in the unisomerized complex. Resolution of the spectrum in the low-velocity region was poor, giving a peak near +0.45 mm/sec (which again is consistent with Fe^{2+} in the nitrogen holes) but giving another peak, presumably ferrocyanide, at about +0.03 mm/sec, which is more negative than the expected value for a ferrocyanide by about 0.15 mm/sec.

By using the same method of analysis as used for the

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(18) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 277 (1963).

(19) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 126 (1964).

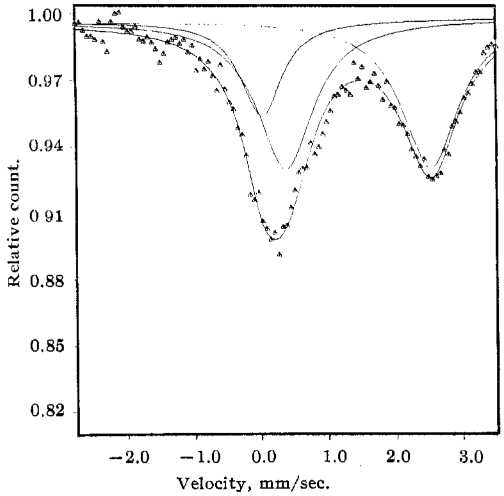

Figure 2.—Mössbauer spectrum of the half-isomerized complex at −52°. The two high-velocity peaks were constrained to be equal in half-width and intensity.

unisomerized complex, one finds that the magnetic data support the postulated structure of the half-isomerized complex. The observed gram-susceptibility at 300°K is about 53 × 10^{-6} cgs, and θ equals +52°K. If the assumption is made that complete isomerization has occurred, then the values obtained for the effective magnetic moment of iron in the complex are too high to be reasonable. If, on the other hand, the assumption is made that the Fe^{2+} which originally occupied interstitial sites has displaced Cr^{3+} from carbon holes, then 38% of the iron will exist as ferrocyanide and will therefore be diamagnetic. The remaining 62% will be in nitrogen holes (the argument would not be changed if any of it now occupied interstitial sites) and will still be paramagnetic. Based on these assumptions, the effective magnetic moment per iron is found to have an average value of 5.34 BM, in close agreement with the expected value.

The lattice parameter determined for this system represents a change in the expected direction, but it is not particularly revealing. The value of 10.50 A is intermediate between the values for the unisomerized and reduced complexes and probably reflects a contraction due to a smaller ionic radius for $Fe(CN)_6^{4-}$ than for $Cr(CN)_6^{3-}$.

Oxidized Complex.—If either of the previous complexes is heated to about 80° or higher in air for a few hours, a dark green complex results. This can be shown to be an oxidation product which requires both water and oxygen for its formation. These requirements and the reality of the oxidation can be shown by the following experiments. A dry sample which had been sealed off under nitrogen was still a light brown color after several weeks at 100°. Upon exposure to the atmosphere, this sample immediately turned green. Also, a sample heated in a vacuum system showed no change when pure oxygen was admitted, and measurements indicated that no oxygen was consumed, but upon exposing the sample to the atmosphere it turned green. Similarly, a sample heated in oxygen-free water showed no color change until opened to the atmosphere. As further proof of oxidation it was found that this green complex could be reversibly reduced by either alcoholic hydrazines or aqueous $Na_2S_2O_4$.

The oxidized complex is the easiest to work with because there are no problems with its stability, but it remains the most perplexing part of this system. The available evidence is tentatively interpreted in terms of a completely isomerized compound which has interstitial Fe^{3+} in some unusual coordination environment with spin equal to $^3/_2$.

The infrared spectrum shows only a single band in the cyanide stretching region, at 2100 cm^{-1}. This is the expected frequency for a ferrocyanide complex and rules out the possibility of a ferricyanide, for which the expected frequency would be about 2160 cm^{-1}. This peak, although broad, is symmetrical, and there is no evidence for any absorption remaining at 2170 cm^{-1}. The infrared data reveal nothing about what occupies the nitrogen holes, but the fact that there is no observable change in the cyanide stretching frequency upon reduction indicates that the Fe^{3+} being reduced is probably in interstitial sites. A peculiar feature of the infrared spectrum is the apparent disappearance of one low-frequency absorption. Rather than the two bands ($\nu_{\text{M-C}}$ and δ_{MCN}) observed for the unisomerized and half-isomerized complexes, there appears to be only one low-frequency band in the oxidized complex, a broad band at about 525 cm^{-1}. This may be two overlapping bands, but, if so, they could not be resolved.

The lattice constant for this complex, 10.07 A, is reasonable, if not enlightening. Attempts to predict a value are complicated by the problem of obtaining an ionic radius for $Fe(CN)_6^{4-}$. Probably the most reliable value for a $Fe(CN)_6^{4-}$ complex is Prussian blue, which has a = 10.18 A.[20] Using this value and the Goldschmidt ionic radius for Fe^{3+}, an ionic radius of 4.55 A for $Fe(CN)_6^{4-}$ is obtained. However, the use of the (probably less reliable) lattice constants for the Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ferrocyanides[21] along with the ionic radii (except using the Cu^{2+} radius given by Knox[22]) gives an ionic radius for ferrocyanide of 4.32 ± 0.03 A. Depending upon which radius is chosen, then, the predicted value for Cr^{3+}–$Fe(CN)_6^{4-}$ is either 10.20 or 9.74 A, a significant spread about the observed value of 10.07 A. The most important information available from this lattice constant determination is the fact that it is quite close to the value of 10.06 A which is found for the species $Cr_4[Fe(CN)_6]_3$, which almost certainly contains Cr^{3+}—N≡C—Fe^{2+} linkages.

The Mössbauer spectrum of the oxidized complex consists of a broad, essentially flat plateau from about 0 to 1.0 mm/sec (Figure 3). This spectrum may be resolved into three peaks at about 0, +0.5, and +1.0 mm/sec. The only thing which can be said conclu-

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(21) R. Rigamonti, *Gazz. Chim. Ital.*, **68**, 803 (1938).

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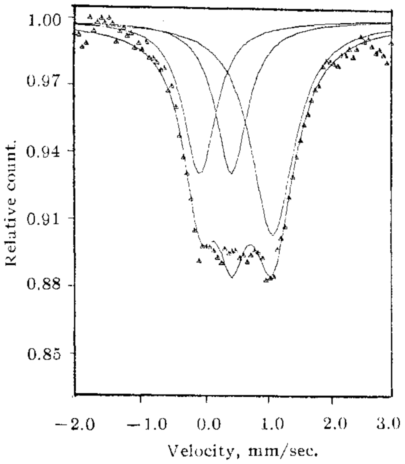

Figure 3.—Mössbauer spectrum of the oxidized complex at −75°. The two low-velocity peaks were constrained to be equal in half-width and intensity.

sively is that there is no high-spin Fe^{2+} present, since there is no absorption in the region 2–3 mm/sec. Assignment beyond this point is speculative, but no single peak can be assigned to either a ferro- or ferricyanide, on the basis of isomer shift expectations.[23]

The magnetic susceptibility at 300°K for the oxidized complex is found to be about 29×10^{-6} cgs, with $\theta = +37$°K. (Attempts to allow the sample to oxidize in the Faraday balance gave slightly higher susceptibilities and varying values of θ, in the range +60 to +80°. This is apparently due to incomplete oxidation in the relatively inaccessible region containing the sample. This conclusion is substantiated by visual inspection of the sample which indicates that oxidation is not complete.) From the infrared evidence there is Fe^{2+} in all carbon holes and therefore it is the remainder of the iron, in the nitrogen holes or in interstitial sites, which has been oxidized, and this is substantiated by semiquantitiative experiments which indicate that 35–40% of the total iron in this complex could be reduced. By the usual methods of analysis, then, the effective magnetic moment per paramagnetic iron is 3.9 BM, a value close to the spin-only moment for a species with three unpaired electrons. Such a system is not entirely without precedent. This system, which presumably exists as an oxide (hydroxide can probably be ruled out by the absence of an OH stretching band in the infrared), is in some ways similar to the system studied by Robin, *et al.*,[24] where it was found that a hydrolytic polymer of Fe^{3+} having the composition $[FeO_{0.75}(OH)(H_2O)_{0.4}](NO_3)_{0.5}$ has a room-temperature magnetic moment of 3.5 BM.

In summary, the nature of this oxidized complex cannot be determined with confidence, but the interpretation given here is at least consistent with the other stages in this reaction.

Reduced Complex.—If the oxidized complex is stirred in alcohol and hydrazine hydrate added, a light brown complex is obtained, which is similar in color to the unisomerized and half-isomerized complexes. By filtering under nitrogen and washing with ether, one can obtain a fairly dry sample for study. If the compound is left in air, it will slowly (over a period of about 30 min) turn green again, and the cycle may be repeated. If the sample has been dried of most of the ether, however, it will spontaneously ignite in air, giving once again the green compound, as is shown by the infrared spectrum. This reduced complex apparently corresponds to the true isomerization product of this system, *e.g.*, a complex which has Cr^{3+} in the nitrogen holes, Fe^{2+} in the carbon holes, and the original amount of Fe^{2+} in interstitial sites.

The infrared spectrum of the reduced complex is identical with that of the isomerized complex, as would be expected for a reduction which does not involve the lattice framework. The observed lattice constant for this compound is 10.19 A. This increase of 0.12 A from the oxidized complex is much less than would be expected for the reduction of iron in the nitrogen holes; however, it is somewhat greater than expected for reduction of Fe^{3+} in the interstitial sites. It is possible that there is a significant distribution of iron between the nitrogen holes and interstitial sites, but the Mössbauer data given below favor a single type, namely, interstitial Fe^{2+}.

Figure 4 shows the Mössbauer spectrum of the reduced complex, along with an attempted resolution. Although the spectrum could not be adequately resolved in the region near +0.5 mm/sec, some generalizations can still be made which are independent of the resolution in the low-velocity region. First, if an ionic Fe^{3+} is being reduced, then we expect a decrease in absorption near +1.0 mm/sec and a corresponding increase near +2.5 mm/sec, and this is found to be the case. Also, if the Fe^{3+} which is being reduced occupies an interstitial site, then the position of the high-velocity absorption should be near the velocity of the interstitial Fe^{2+} in the unisomerized complex and the ob-

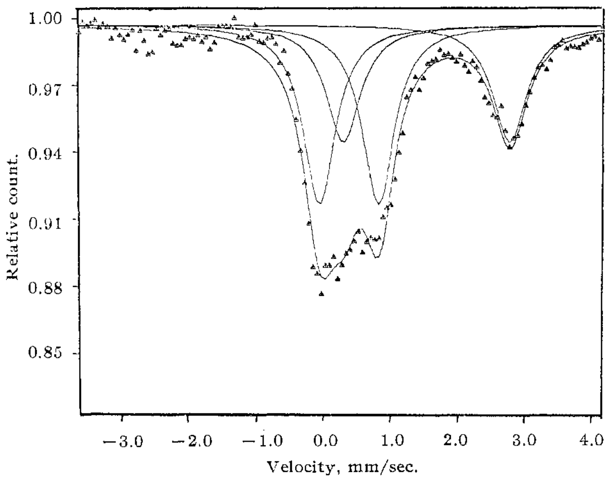

Figure 4.—Mössbauer spectrum of the reduced complex at −75°. Peaks 1 and 3 and peaks 2 and 4 were constrained to be equal in half-width and intensity.

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[23] K. Chandra, D. Raj, and S. P. Puri, *J. Chem. Phys.*, **46**, 1466 (1967).

[24] M. B. Robin, A. Terzis, and T. G. Spiro, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967, L47, and personal communication.

servation of a single high-velocity peak indicates that only one type of Fe^{2+} is present. The positions of the high-velocity peak for several samples at low temperature were found to be about 2.8–2.9 mm/sec, close to the position of the interstitial Fe^{2+} in the unisomerized complex. Intensity arguments are useful here. If all of the carbon holes contain Fe^{2+} and the remainder of the iron is being reduced, then the relative intensity of the high-velocity absorption is expected to be $^1/_2(0.38) = 0.19$. For two samples at −52 and −75° the relative intensities were found to be 0.22 and 0.20, in close agreement with the predicted value.

The gram-susceptibility for the reduced complex at 300°K is about 36×10^{-6} cgs, with $\theta = 11°$K. After the usual treatment and the assumption that all carbon holes contain Fe^{2+}, the effective magnetic moment per paramagnetic iron is found to be about 4.95 BM. This value appears somewhat low, but can perhaps be justified on two grounds. First, in order to perform the magnetic measurements, the sample must spend a significant amount of time exposed to the atmosphere. As a result, there is a possibility that the samples have been partially reoxidized. Also, since the symmetry of the interstitial sites is not octahedral, the magnetic moment is expected[16] to be reduced toward the spin-only value of 4.9 BM.

Details of the Isomerization.—An attempt was made to study the kinetics of the first reaction step by measuring the change in magnetic susceptibility as a function of time. Samples under a helium flow were heated by flowing warm air through the dewar surrounding the sample cell. The temperature was found to be constant to within ±0.5° by this method, and the sample deflection was measured over 1 or 2 half-lives. Plots of the log of the relative deflection change (*e.g.*, log $[(\Delta w_t - \Delta w_\infty)/(\Delta w_0 - \Delta w_\infty)]$) *vs.* time gave fairly good straight lines, indicating a reaction first order in total complex. Values of Δw_0 and Δw_∞ were obtained from the previously determined Curie–Weiss law equations. Therefore, the apparent rate law is

$$\frac{-\mathrm{d}[\text{unisomerized}]}{\mathrm{d}t} = k[\text{unisomerized}]$$

with $k = 1.0 \times 10^{-4}$ sec^{-1} at 50°. A plot of ln k *vs.* $1/T$ was close to being linear, yielding the approximate activation energy, E_a, equal to 17 kcal/mole for the displacement of Cr^{3+} from the carbon holes by Fe^{2+}.

Attempts to observe directly a fully isomerized but unoxidized compound (which should correspond in nearly all particulars to the reduced complex) have so far proved unsuccessful, although it is probable that this is what is present in samples which have been thoroughly heated while carefully isolated from the atmosphere. The transition from the unisomerized to the half-isomerized complex occurs within a matter of a few hours at 50°, as evidenced by a distinct leveling off in the magnetic susceptibility. If the temperature is raised to about 100° while a helium stream is maintained over the sample, the magnetic susceptibility drops very slowly and does not level off completely even after 3 days at this temperature. A sample removed from the Faraday balance at this point was dark brown, almost green, and an infrared spectrum indicated that, although the sample was predominantly a ferrocyanide, there was still some chromicyanide remaining. Apparently some oxidation had taken place, and the important point here is that the isomerization and oxidation processes for the half-isomerized complex must be somehow intimately connected. A sample heated to 100° in the atmosphere would be completely isomerized within a few hours, but this sample, heated out of contact with the atmosphere, was not fully isomerized after 3 days.

The bulk of the data, then, shows that there are four distinct complexes in this system and that the system does indeed exhibit linkage isomerism, although this apparently does not occur by so simple a process as a cyanide "flip."

Acknowledgment.—This research was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center. We are grateful to Dr. P. Loach, who designed the Faraday balance. We also thank Dr. Harris P. Marcus for assistance with the Mössbauer equipment and computer programs.