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Structures and Solid-State Reactions of Prussian Blue Analogs Containing Chromium, Manganese, Iron, and Cobalt[1a]

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For the series of cubic metal cyanide polymers studied here a knowledge of starting materials, coupled with measurement of cyanide stretching frequencies, X-ray powder patterns, magnetic susceptibilities, optical spectra, and ^{57}Fe Mössbauer spectra, has permitted structural assignments. Two systems appear to undergo solid-state reactions. One of these, $Fe_3[Mn(CN)_6]_2$, initially contains Fe–N and Mn–C bonds, which rearrange to give a material containing Fe–C bonds. A second compound of approximate composition $Co_3[Cr(CN)_6]_2$ appears to undergo isomerization on heating in an inert atmosphere to a product containing Co(II)–C bonds. Air oxidation then leads to a material containing Cr^{3+}–N and Co(III)–C linkages.

Introduction

Although Prussian blue has been known for over 260 years, its structure has only recently been elucidated.[2] Studies of infrared,[3] visible–ultraviolet,[4] and Mössbauer spectra,[4–6] in conjunction with earlier X-ray powder diffraction data,[7] show that the framework of Prussian blue is adequately described as shown in Figure 1.[4] Furthermore, X-ray powder diffraction data indicate that the face-centered-cubic lattice of Prussian blue is characteristic of many other transition metal cyanide compounds.[2] This structure incorporates metal ions in three types of sites: carbon "holes," in which a metal is octahedrally coordinated by the carbon end of cyanide, nitrogen holes in which a metal is octahedrally coordinated by the nitrogen end of cyanide, and large interstitial sites.[8] These interstitial sites will accommodate a variety of ions which are required to maintain electroneutrality. When more than one type of metal is present, the problem in characterizing these complexes is to determine the identity of metal ions in each of the three types of sites, and the oxidation state of the metal in a given site. With the exception of recent studies,[4,9,10] most literature reports present a single measurement (*e.g.*, infrared spectrum, powder pattern, or magnetic susceptibility) for a series of complexes. Unfortunately, such limited data usually do not afford an unambiguous determination of the sites occupied by the metal ions.

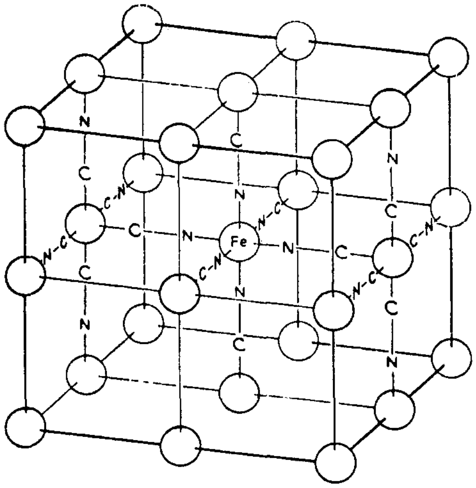

Figure 1.—The unit cell of Prussian blue. Four potassium ions and a number of CN groups have been omitted for clarity.

When a Prussian blue analog is generated by the reaction of a *substitution-inert* hexacyanometalate with a labile hexaaquo transition metal ion, it is reasonable to assume that the initial product will retain the metal–carbon bonding of the original hexacyanometalate.[11] Neglecting interstitial ions, we may represent this by[12]

$$M(aq)^{n+} + M'(CN)_6(aq)^{m-} \longrightarrow M(NC)_6M'(s)^{n-m}$$

However, with certain combinations of M and M′, this initial product may be metastable with respect to an interchange of metal ions between the various sites.[9,11] For example, interchange may occur between the carbon and nitrogen sites

$$M(NC)_6M'(s) \longrightarrow M'(NC)_6M(s)$$

(Alternatively, this type of reaction may be described formally as linkage isomerism of the CN group.) Metal ion interchange with the interstitial sites is also possible.[9]

Previously we have studied the interchange reactions

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[2] For a review of compounds containing bridging CN^- see D. F. Shriver, *Struct. Bonding* (Berlin), **1**, 32 (1966).

[3] G. Emshwiller, *Compt. Rend.*, **238**, 1414 (1954).

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[8] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **46**, 99 (1942).

[9] D. B. Brown, D. F. Shriver, and L. H. Schwartz, *Inorg. Chem.*, **7**, 77 (1968).

[10] K. Maer, Jr., M. L. Beasley, R. C. Collins, and W. O. Milligan, *J. Am. Chem. Soc.*, **90**, 3201 (1968).

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

[12] Two types of formulas are employed in the text. A conventional one like $Fe_3[Cr(CN)_6]_2$ is often used to indicate the empirical composition. To place emphasis on the nitrogen-coordinated (Fe^{2+}) and carbon-coordinated (Cr^{3+}) metals, these structural aspects are often indicated by formulas like $Fe^{2+}(NC)_6Cr^{III}$. This notation also stresses the high-spin "ionic" nature of the metal–nitrogen interaction by means of the plus charge, while the Roman numeral oxidation state implies the more covalent nature of metal–carbon bonds. (These descriptive formulas were originally suggested to us by C. K. Jørgensen.)

of $Fe_3[Cr(CN)_6]_2$.[9] The present work was designed to find new examples of site-interchange reactions in Prussian blue analogs and to characterize these reactions by the use of several physical measurements.

Experimental Section

All complexes were prepared by the slow addition of the potassium hexacyanometalate to a solution containing an excess of the appropriate metal salt. $K_3Cr(CN)_6$, purchased from A. D. McKay, Inc., was recrystallized once from water and ethanol; $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were the commercial salts; $K_3Co(CN)_6$ was prepared by the method of Bigelow,[13] and $K_3Mn(CN)_6$ was prepared following the method of Lower and Fernelius.[14] Since Cr^{3+} is substitution inert, chromium complexes were made by the addition of the appropriate hexacyanometalate to a solution of Cr^{2+} (prepared by Deyrup's method[15]), followed by air oxidation. All other metal salts used were the commercial products.

Depending upon their ease of filtration, complexes were collected by either filtration or centrifugation. The complexes were washed with water, alcohol, and ether and then dried under vacuum at room temperature for approximately 12 hr. This drying procedure eliminated most of the organic solvents, but the materials retained significant quantities of absorbed water.

Carbon, hydrogen, and nitrogen analyses were performed by Miss Hilda Beck of this department for all complexes. Owing to the variable degrees of hydration, as well as the possibility of different polymer compositions, the absolute values of these analytical results are not significant unless combined with metal analyses. The relative carbon and nitrogen values, which should have a ratio of 1:1, are significant. This ratio was always close to 1:1. Metal analyses, performed by Schwarzkopf Microanalytical Laboratory and/or Alfred Bernhardt Mikroanalytisches Laboratorium, were obtained for several complexes where this information was judged essential and these results will be presented in the discussion.

Reduction with hydrazine and oxidation with both hydrogen peroxide and nitrogen dioxide were attempted on alcohol slurries of several of the complexes. As noted previously,[9] there was, in some cases, a marked instability of the reduction products.

Infrared spectra of the samples were measured on Nujol mulls in the region 800–4000 cm^{-1} using a Beckman IR-10 and in the cyanide stretching frequency region using the more accurate Beckman IR-9. Spectra of Nujol mulls of some of these materials in the visible region were obtained using a Cary 14 spectrometer. Magnetic susceptibilities were measured by the Faraday method.[9] Standard diamagnetic corrections were applied for $C\equiv N$ and water. X-Ray powder patterns were obtained using a 57.3-mm Debye–Scherrer camera and vanadium-filtered Cr radiation. In most cases, reflections assignable to both Cr $K\alpha$ (λ 2.2909 Å) and Cr $K\beta$ (λ 2.0848 Å) were observed, and the lattice parameters were obtained using both sets of lines. No correction was made for film shrinkage. Iron-57 Mössbauer spectra were obtained using an NSEC constant-acceleration instrument with approximately 1-mCi ^{57}Co in Pd as the source. The instrument was calibrated using $Na_2Fe(CN)_5NO\cdot 2H_2O$, which is also the reference ($\delta = 0$) for isomer shifts reported in this work. All values taken from the literature have also been corrected to this standard. All parameters were estimated visually from recorded tracings of the 512 channel analyzer memory.

Results and Discussion

Lattice Parameters and Radii of Hexacyanometalates.—Systematics of the lattice parameters for the Prussian blue analogs have been discussed previously.[2] However, a more detailed survey is given here to provide the basis for an interpretation of lattice parameters determined in this work.

From the magnetic and spectral properties of metal ions in the N-coordinated sites it is known that the metal is generally in its high-spin state (Co(III) may be an exception), and therefore it is reasonable to utilize conventional ionic radii for these ions. Half of the lattice parameter, which represents the sum of the M–NCM′ bond lengths, minus the ionic radius of M yields the effective radius of $M'(CN)_6{}^{n-}$ in the crystal. Considerable scatter is observed for M^{3+} salts of ferrocyanide. This is demonstrated by the $Fe(CN)_6{}^{4-}$ radii obtained from the following M^{3+} salts: Fe^{3+}, 4.57 Å;[7] Cr^{3+}, 4.48 Å;[9] Al^{3+}, 4.44 Å.[16] The method appears to be much more reliable for the M^{2+} salts, and they will be used here.

In the case of the M^{2+} ferrocyanides, there are in general several different complexes available with the same M^{2+} (*e.g.*, $Cu_2Fe(CN)_6$, $K_2CuFe(CN)_6$, $K_2Cu_3[Fe(CN)_6]_2$, etc.). The variations for a given M^{2+} are small; we report here the average values obtained from all available complexes. The combination of the M^{2+} Goldschmidt ionic radii[17,18] and the published[7,16,19] lattice parameters for the complexes give the following values for the effective radius of $Fe(CN)_6{}^{4-}$ derived from the corresponding M^{2+} salts: Cu^{2+}, 4.34 Å; Co^{2+}, 4.36 Å; Fe^{2+}, 4.34 Å; Ni^{2+}, 4.32 Å; Zn^{2+}, 4.31 Å.[20] The average value is 4.33 ± 0.02 Å. In the case of the M^{2+} ferricyanides of general formula $M_3[Fe(CN)_6]_2$ combination of the M^{2+} ionic radii and the measured lattice parameters for the complexes[21] gives the following values for the effective radius of $Fe(CN)_6{}^{3-}$: Cu^{2+}, 4.40 Å; Ni^{2+}, 4.44 Å; Co^{2+}, 4.47 Å; Zn^{2+}, 4.51 Å; Mn^{2+}, 4.44 Å; Cd^{2+}, 4.42 Å. The average value is 4.45 ± 0.04 Å. It thus appears that the effective radius of ferrocyanide is smaller than that of ferricyanide by about 0.12 Å.

For a series of M^{2+} hexacyanocobaltate(III) salts[22] the effective $Co(CN)_6{}^{3-}$ radius is calculated to be 4.44 ± 0.02 Å. From the lattice parameter of $Co_2[Co(CN)_6]$—*i.e.*, $Co(CN)_2$[23]—an effective radius of 4.38 Å is calculated for $Co(CN)_6{}^{4-}$. However, it is possible that the measurement was taken on an oxidized product and other complications associated with this type of compound are mentioned later. For the manganese, zinc, and nickel hexacyanochromate(III) salts[24] a radius of 4.56 ± 0.05 Å is calculated. For hexacyanochromate(II) a single lattice parameter of 10.24 Å is available for the Cu^{2+} salt,[19] and this yields an effective radius of 4.45 Å for $Cr(CN)_6{}^{4-}$. Finally, six M^{2+} hexacyanomanganates(III) yield a radius of 4.52 ±

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[13] J. H. Bigelow, *Inorg. Syn.*, **2**, 225 (1946).

[14] J. A. Lower and W. C. Fernelius, *ibid.*, **2**, 213 (1946).

[15] A. J. Deyrup, *Inorg. Chem.*, **3**, 1645 (1964).

[16] R. Rigamonti, *Gazz. Chim. Ital.*, **68**, 803 (1938).

[17] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 43.

[18] K. Knox, *Acta Cryst.*, **14**, 583 (1961).

[19] R. Rigamonti, *Gazz. Chim. Ital.*, **67**, 137 (1937).

[20] P. A. Rock and R. E. Powell, *Inorg. Chem.*, **3**, 1593 (1964), have shown that the zinc system is not cubic.

[21] A. K. van Bever, *Rec. Trav. Chim.*, **57**, 1259 (1938).

[22] A. Ferrari, M. E. Tani, and G. Magnano, *Gazz. Chim. Ital.*, **89**, 2512 (1959).

[23] A. Weiss and W. Rotherstein, *Angew. Chem. Intern. Ed. Engl.*, **2**, 396 (1963).

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

TABLE I

EXPERIMENTAL DATA AND PROBABLE FRAMEWORK STRUCTURES FOR SOME PRUSSIAN BLUE ANALOGS

Complex no.	Prepn	Color	ν_{CN}, cm^{-1}	Lattice parameter, Å	Probable structure
I-1	$Cr^{2+} + K_3Mn(CN)_6$ + air	Light brown	2163	10.63	$Cr^{3+}(NC)_6Mn^{III}$
I-2	I-1 + N_2H_4	Dark brown	2067	10.61	$Cr^{3+}(NC)_6Mn^{II}$
I-3	I-1 + heat	Brown			Decomposed
I-4	$Mn(OAc)_2 + K_3Cr(CN)_6$	Light green	2163	10.71	$Mn^{2+}(NC)_6Cr^{III}$
			2159[a]	10.84[b]	
I-5	I-4 + heat	Brown	2167	10.72	$Mn^{2+}(NC)_6Cr^{III}$(?)
I-6	I-5 + N_2H_4	Brown	2167		$Mn^{2+}(NC)_6Cr^{III}$
II-1	$Mn(OAc)_2 + K_3Mn(CN)_6$	Tan	2151	10.63	$Mn^{2+}(NC)_6Mn^{III}$
II-2	II-1 + N_2H_4	Brown	2071	Not cubic	$Mn^{2+}(NC)_6Mn^{II}$(?)
III-1	$CoSO_4 + K_3Mn(CN)_6$	Light brown	2173	10.30	$Co^{2+}(NC)_6Mn^{III}$
				10.23[c]	
III-2	III-1 + heat	Brown			Decomposed
III-3	III-1 + N_2H_4	Dull blue	Ignited upon drying		$Co^{2+}(NC)_6Mn^{II}$(?)
III-4	$MnSO_4 + K_3Co(CN)_6$	White	2171	10.39	$Mn^{2+}(NC)_6Co^{III}$
			2168[a]	10.41[d]	
IV-1	$CoSO_4 + K_3Fe(CN)_6$	Dark red	2161	10.22	$Co^{2+}(NC)_6Fe^{III}$ [g]
			2160[e]	10.23[f]	
IV-2	IV-1 + heat	Brown	2126, 2085		Decomposed
IV-3	IV-1 + N_2H_4	Tan	2096		$Co^{2+}(NC)_6Fe^{II}$
IV-4	IV-3 + air	Green	2097		$Co^{2+}(NC)_6Fe^{II}$
IV-5	$CoSO_4 + K_4Fe(CN)_6$	Green	2091	10.10	$Co^{2+}(NC)_6Fe^{II}$ [i]
			2082[c]	10.12, 10.08[h]	
IV-6	IV-5 + NO_2	Purple	2100	10.04	$Co^{3+}(NC)_6Fe^{II}$(?)
IV-7	IV-5 + H_2O_2	Blue	2090	10.09	$Co^{2+}(NC)_6Fe^{II}$(?)
IV-8	$FeSO_4 + K_3Co(CN)_6$	Yellow	2170	10.25	$Fe^{2+}(NC)_6Co^{III}$ [j]
			2175[a]	10.30[d]	
IV-9	$CoSO_4 + K_3Co(CN)_6$	Pink (moist)	2177	10.17	$Co^{2+}(NC)_6Co^{III}$
		Blue (dry)		10.20[k]	

[a] Reference 11. [b] Reference 24. [c] Reference 25. [d] Reference 22. [e] Reference 3. [f] Reference 21. [g] Mössbauer parameters determined in this work were $\delta = 0.09$ mm/sec and $\Delta E = 0.47$ mm/sec. Reference 29 reported $\delta = 0.05$ mm/sec and $\Delta E = 0.45$ mm/sec for this complex. [h] References 16 and 19. [i] Reference 29 reported an isomer shift of $\delta = 0.15$ mm/sec, with no quadrupole splitting. J. Richardson and N. Elliott, *J. Am. Chem. Soc.*, **62**, 3182 (1940), reported a magnetic moment of 4.90 BM for $K_2CoFe(CN)_6$. [j] A Mössbauer spectrum of very poor quality, obtained in these laboratories, indicated $\delta = 1.36$ mm/sec and $\Delta E = 1.75$ mm/sec for this material, indicative of high-spin Fe^{2+}. P. G. Salvadeo, *Gazz. Chim. Ital.*, **89**, 2184 (1959), reported a magnetic moment of 5.33 BM for $Fe_3[Co(CN)_6]_2 \cdot 12H_2O$. [k] Reference 22; A. Vaciago and A. Mugnoli, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, **25**, 531 (1958); *Chem. Abstr.*, **55**, 5080g (1961).

0.08 Å for this anion.[25] This can be compared to a radius of 4.41 Å for $Mn(CN)_6^{4-}$, calculated from the lattice parameter for $Cu_2[Mn(CN)_6]$.[26]

Some of the data used above are not of high quality. However, it will be noted that a consistent result is found; that is, $M^{II}(CN)_6^{4-}$ ions have *smaller* effective radii than their $M^{III}(CN)_6^{3-}$ counterparts. This observation and the specific hexacyanometalate radii deduced here are used to infer structures from lattice parameters.

The origin of the unusual order for the effective radii, $M^{II}(CN)_6^{4-} < M^{III}(CN)_6^{3-}$, probably resides in metal–carbon or metal–nitrogen distances because $C\equiv N$ bond distances are quite insensitive to variations in the chemical environment.[27] It is possible that the $M^{II}—C$ linkages are shorter than $M^{III}—C$ owing to back-π-bonding.[2] However, a definitive answer must await complete X-ray structure determinations.

Infrared Spectra.—The infrared stretching frequency of a bridging cyanide ion is indicative of the oxidation state of the metal to which the carbon end of cyanide is bonded.[3,11,28] In the case of Prussian blue analogs, compounds with M(II)–C bonds should absorb around 2100 cm^{-1}, while those with M(III)–C bonds absorb near 2170 cm^{-1}. However, it is difficult if not impossible to identify further the metal by means of the CN stretching frequencies.

Stable Prussian Blue Analogs.—Of the ten possible combinations for the metal ions under consideration, two, the Fe–Cr and Fe–Fe systems, have been treated adequately in the past and will not be discussed here.[2-9] In addition, the Cr–Cr system was omitted; this leaves seven combinations which were investigated. Infrared spectra and lattice constants along with lack of change upon standing indicate that most of these compounds are directly related to the starting materials and do not involve ion-interchange reactions. Table I may be consulted for experimental results and probable structures. By contrast, two systems (Mn–Fe and Co–Cr) exhibit site-interchange reactions and will be discussed in detail.

Mn–Fe. Addition of a $K_3Fe(CN)_6$ solution to an excess of Mn^{2+} gives a brown precipitate of approximate composition $Mn_3[Fe(CN)_6]_2$. The analytical ratio of Mn to Fe is 1.6 (calcd for $Mn_3[Fe(CN)_6]_2$, 1.5). The infrared spectrum contains an intense band at 2168 cm^{-1} and the lattice parameter is 10.48 Å (van Bever[21]

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(25) A. Ferrari, E. Morisi, and M. E. Tani, *Acta Cryst.*, **17**, 311 (1964).

(26) M. A. Rollier and G. Cesoni, *Gazz. Chim. Ital.*, **69**, 674 (1939).

(27) D. Britton, *Perspectives Struct. Chem.*, **1**, 109 (1967).

(28) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

reports 10.48). All of these observations are consistent with an $Mn^{2+}(NC)_6Fe^{III}$ framework. The sample is unaffected by heating for 1 hr at 100° in air. This brown solid can be reduced by N_2H_4 to give an off-white solid which appears to have the $Mn^{2+}(NC)_6Fe^{II}$ framework, since the color, infrared spectrum (ν_{CN} 2060 cm^{-1}), and lattice parameter (10.02 Å) are similar to those of a sample prepared from Mn^{2+} and $Fe(CN)_6^{4-}$. Previously Chandra and coworkers have shown from Mössbauer spectra that this compound contains Fe(II) in the carbon sites.[29]

The reaction of $FeSO_4$ and $K_3Mn(CN)_6$ gives a deep blue precipitate similar in color to Prussian blue. Analyses show iron to manganese ratios of 1.95 (Bernhardt) and 1.89 (Schwarzkopf) and an average nitrogen to manganese ratio of 6.02. Thus, the composition, exclusive of water, is $Fe_2Mn(CN)_6$. An infrared spectrum of the fresh product exhibited a band at 2149 cm^{-1} and a weaker band at 2079 cm^{-1}. The presence of these two bands indicates a mixture of M(II) and M(III) metals in carbon holes. The relative intensities of these bands change with time, until the low-frequency absorption predominates. Upon heating the sample in air, a very dark green material is obtained which has a strong absorption at 2082 cm^{-1}, indicating M(II)—C coordination, while the presence of some M(III)—C bonding is indicated by a shoulder at *ca.* 2140 cm^{-1}.

If the blue material is treated with N_2H_4, a second dark green complex results which has a single C≡N stretch at 2077 cm^{-1}, indicating M(II)—C coordination exclusively. The Mössbauer spectrum (Figure 2) contains two symmetric bands at 0.17 and 0.92 mm/sec. A reasonable assignment is $Fe^{II}(CN)_6$ at 0.17 mm/sec and high-spin Fe^{3+} at 0.92 mm/sec. These data and the lattice parameter, 10.16 Å, are consistent with a structure containing Fe(II) in carbon holes and Mn^{2+} and Fe^{3+} in interstitial and nitrogen holes.

The Mössbauer spectrum of the original blue material (Figure 3) is similar to that of the green reduction product but may be distinguished from it by two properties. First, the low-velocity absorption is not symmetrical, so that it appears that low-spin iron in this complex exists as a mixture of $Fe^{II}(CN)_6$ and $Fe^{III}(CN)_6$. This agrees with the infrared data which showed that even after heating some M(III) remains in carbon holes. Apparently some of the iron which goes into carbon holes is oxidized by the Mn^{3+} which is expelled from these sites. Also, there is a small absorption in the region of 2–3 mm/sec indicative of a small quantity of high-spin Fe^{2+}. This low intensity is in keeping with the infrared data which indicated isomerization should be fairly complete in the time it took to mount the sample and run its Mössbauer spectrum. The lattice parameter, measured shortly after preparation, 10.41 Å, is smaller than the predicted value, 10.56 Å. The smaller value may be due to partial isomerism which will produce a dramatic decrease in the lattice parameter.

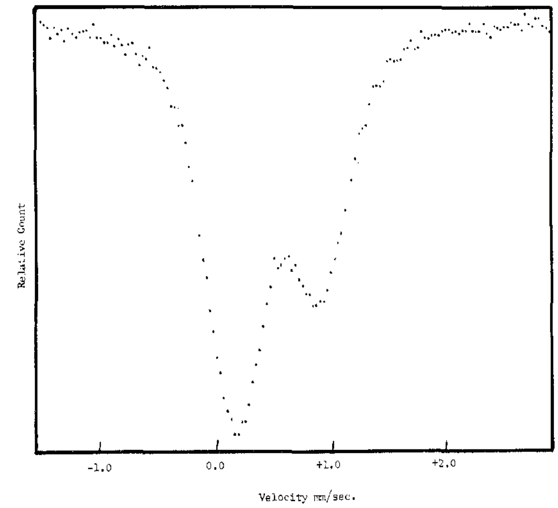

Figure 2.—Mössbauer spectrum of the complex formed by the reaction of $FeSO_4 + K_3Mn(CN)_6$ in air, followed by reaction with hydrazine.

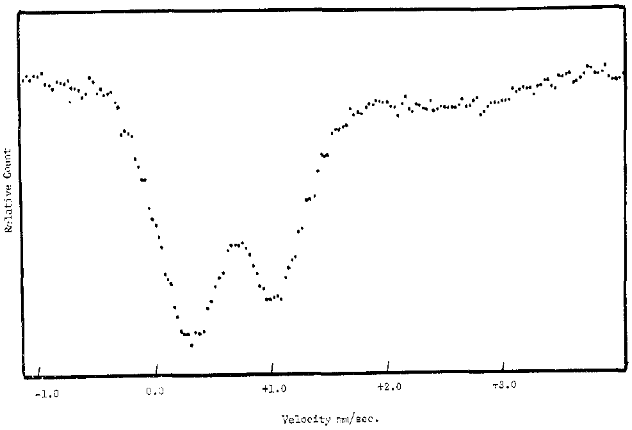

Figure 3.—Mössbauer spectrum of the complex formed by the reaction of $FeSO_4$ with $K_3Mn(CN)_6$.

In summary, the results for the Fe^{2+}–$Mn(CN)_6^{3-}$ system indicate that the principal reactions are

$$Fe(aq)^{2+} + Mn(CN)_6(aq)^{3-} \longrightarrow Fe^{2+}(NC)_6Mn^{III} \longrightarrow Mn^{2+} \text{ or } Fe^{3+}(NC)_6Fe^{II}$$

Co–Cr.—The cobalt–chromium system appears to involve a clear case of linkage isomerism. The reaction of Cr^{2+} with $K_3(Co(CN)_6)$ gave an aqua-colored precipitate which rapidly became gray upon exposure to air, presumably owing to oxidation of Cr^{2+} to Cr^{3+}. Analytical data (Schwarzkopf) for this complex indicated 18.33% Cr, 15.10% Co, and 18.05% N. The observed ratios are N:Cr = 5.6, N:Co = 7.7, and Cr:Co = 1.37. These results do not fit a simple formula. For example, $Cr[Co(CN)_6]$ requires N:Cr = 6, N:Co = 6, and Cr:Co = 1.0. The infrared spectrum of this compounds exhibits a sharp absorption at 2207 cm^{-1}, unique in that it lies about 25 cm^{-1} higher than the cyanide stretching frequency of any other complex observed in this work but in agreement with M(III)–C bonding. The basic structure is undoubtedly $Cr^{3+}(NC)_6Co^{III}$. The lattice parameter of 10.05 Å is reasonable for this structure. This complex is inert to hydrazine and is unaffected by extensive heating.

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

The reaction of $CoSO_4$ and $K_3Cr(CN)_6$ gives a peach-colored precipitate which is light purple when dry. This color change is very similar to that observed in the Co–Co system, and this complex is then presumably $Co_3[Cr(CN)_6]_2$. The analytical data in general support this formulation. Results obtained were 18.32% N (average of three values), 20.81% Co, and 10.60% Cr (Schwarzkopf); X-ray fluorescence analyses indicate 18.1% Co and 11.8% Cr. The averages of these two analytical data sets lead to a Co:Cr ratio of 1.53:1, which indicates the formula $Co_3[Cr(CN)_6]_2$. The infrared spectrum exhibits a band at 2175 cm^{-1}, indicative of M(III)–C coordination. The lattice parameters of two separate samples were 10.51 and 10.40 Å. Ferrari and coworkers[24] reported 10.36 Å for $Co_3[Cr(CN)_6]_2 \cdot 6H_2O$. As will become clear later, it is likely that some isomerization has taken place in all of these samples, so that the actual lattice parameter for $Co^{2+}(NC)_6Cr^{III}$ is probably greater than or equal to 10.51 Å. The lattice parameter predicted from Co^{2+} and $Cr(CN)_6{}^{3-}$ radii is 10.50 Å.

If this peach (or purple) complex is heated while exposed to air, it becomes gray, changing to tan upon cooling in atmospheric moisture. The infrared spectrum of the resulting material contains a band at 2206 cm^{-1}, coincident with that found for $Cr^{3+}(NC)_6Co^{III}$. Apparently, linkage isomerization has taken place, followed by (or accompanied by) oxidation of cobalt in the carbon holes to Co^{3+}. As further verification of this formulation, the lattice parameter of the material which was heated in air is 10.08 Å, nearly identical with that reported above for $Cr^{3+}(NC)_6Co^{III}$. This ion interchange plus oxidation apparently was observed by Cruser and Miller,[30] although they did not recognize it as such. These authors stated that $Co_3[Cr(CN)_6]_2$ is a light rose-colored precipitate which is yellowish brown when dried.

The magnetic susceptibilities for this system substantiate the conclusion that linkage isomerization is taking place, and allow the suggestion of a possible reaction sequence. The susceptibility for a freshly prepared, unisomerized sample was found to be $\chi_g = 13.72 \times 10^{-3}/(T - 8)$ cgsu. In order to draw structural conclusions, the susceptibility expected for the various possible structures has to be compared with this experimental value by a method which has been described previously[9] and is summarized below.

It is established that the magnetic moment of Cr(III) in a wide variety of octahedral complexes is very close to 3.8 BM. Using this value and a 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. Subtracting this value from the observed susceptibility (at 300°K) gives the susceptibility due to cobalt. Some assumption is then made about the distribution of different cobalt species in the system and, using the analytical data for cobalt, the magnetic moment is calculated. This moment can be compared to the expected moments for various possible structures. This treatment leads to a contribution due to cobalt of 34.45×10^{-6} cgsu. Coupling this value with the percentage of cobalt and treating all cobalt as equivalent yields a magnetic moment of 5.00 BM which is the value expected for high-spin octahedral Co^{2+} complexes. Thus, the initial product appears to contain Co^{2+} in interstitial and nitrogen-coordinated sites.

If this unisomerized complex is heated for several hours in an *inert atmosphere*, the susceptibility drops. After it has completely leveled off, the susceptibility has the temperature dependence $\chi_g = 9.07 \times 10^{-3}/(T + 32)$. In view of our previous work on the iron–chromium–cyanide system[9] it was reasonable to postulate a structure for this new complex generated by an interchange of Co^{2+} and Cr^{3+} between the interstitial sites and carbon holes. If this is the case, then two-thirds of the cobalt should be unchanged and have the same susceptibility as it did in the unisomerized complex. However, this structure is untenable, since the remaining one-third of the cobalt, presumably in carbon holes, would have to possess a large negative susceptibility to account for the observed susceptibility. Assuming that complete isomerization has occurred, cobalt will occupy all carbon holes and the remaining Co (one-third of the total cobalt) will occupy interstitial sites and thus its moment will be unchanged from the value in the unisomerized complex. With this assumed structure the magnetic moment for the cobalt in the carbon holes is found to be 1.82 BM. This value is very close to that expected for low-spin Co^{2+} and substantiates the contention that in the absence of air a complete linkage isomerism occurs, as illustrated by

$$Co^{2+}(NC)_6Cr^{III} \xrightarrow{\Delta} Cr^{3+}(NC)_6Co^{II}$$

or possibly[31,32]

$$Co^{2+}(NC)_6Cr^{III} \xrightarrow{\Delta} Cr^{3+}(CN)(NC)_5Co^{II}$$

It is interesting that upon heating in the absence of air this linkage isomerization reaction goes to completion. In our previous work on $Fe_3[Cr(CN)_6]_2$ similar treatment led to interchange of interstitial Fe^{2+} with C-coordinated Cr^{3+}, rather than interchange of the N- and C-coordinated metal ions.

If, at this point in the reaction, the sample is exposed to the atmosphere, it very rapidly changes color from a dull blue to tan, and this is undoubtedly due to oxidation. The susceptibility measured for this oxidized form is $\chi_g = 7.69 \times 10^{-3}/(T + 23)$ cgsu. The logical assumption that the cobalt in carbon holes is oxidized results in two-thirds of the cobalt being low-spin Co^{3+} and therefore diamagnetic. On this basis, the remain-

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(31) One problem with structures containing $Co^{II}(CN)_6{}^{4-}$ groups is the lack of evidence for this ion in aqueous solution along with the theoretical reasons for its instability. However, a pentacyanoisocyanide complex, $Co^{II}(CN)_5(NC)^{4-}$, would be expected to be more stable than the hexacyano complex.

(32) The magnetic data also allow some occupation of nitrogen holes by Co^{2+} and interstitial sites by Cr^{3+}. However, stoichiometric considerations make it clear that at least 50% of the nitrogen holes will be filled by Cr^{3+} and the observed structure for the oxidized product, $Cr^{3+}(NC)_6Co^{III}$, makes it likely that all of the nitrogen holes are occupied by Cr^{3+}.

ing one-third of the cobalt (either in interstitial sites or nitrogen holes) has a calculated magnetic moment of 4.90 BM. This is close to the value calculated for the high-spin cobalt in the unisomerized material, as it should be. Accordingly, we write

$$\mathrm{Co^{2+}(NC)_6Cr^{III}} \xrightarrow{\Delta,\ \mathrm{O_2}} \mathrm{Cr^{3+}(NC)_6Co^{III}}$$

for the over-all reaction.

In previous work on the site-interchange reactions of $\mathrm{Fe[Cr(CN)_6]_2}$,[9] it was found that the reaction proceeded in a stepwise fashion, and it may be inferred that the isomerization mechanism involves a movement of metal ions between carbon-coordinated, interstitial, and nitrogen-coordinated sites. In the present study no evidence for intermediates was found. This leaves open the question of the mechanism; however, one simple explanation of the present results is that this reaction occurs by an end-for-end flip of the $\mathrm{C{\equiv}N}$ groups.

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The Environment of Interstitial Ions in a Prussian Blue Analog, $\mathrm{Co_3[Co(CN)_6]_2}$

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Magnetic data indicate that interstitial $\mathrm{Co^{2+}}$ is present as a high-spin octahedral complex in the pink solid $\mathrm{Co_3[Co(CN)_6]_2 \cdot }$ $x\mathrm{H_2O}$. Visible and infrared spectra of this pink hydrate, along with changes in these spectra and of magnetic moments upon dehydration, indicate the octahedral interstitial complex is $\mathrm{Co(H_2O)_6^{2+}}$. Previous pressure–composition studies on similar Prussian blue analogs are discussed. Contrary to an earlier interpretation, a smooth decrease in pressure with decreasing water content does not imply the absence of discrete species such as $\mathrm{M(H_2O)_6^{2+}}$. Since $\mathrm{NH_3}$ should form a stronger complex than water and adsorb less readily, a study was carried out on the system $\mathrm{NH_3}$–$\mathrm{Co_3[Co(CN)_6]_2}$. The absorption isotherms demonstrate the existence of $\mathrm{Co_3[Co(CN)_6]_2 \cdot 6NH_3}$, for which stoichiometry and infrared data indicate the presence of $\mathrm{Co(NH_3)_6^{2+}}$ interstitial complexes.

Introduction

In Prussian blue and its numerous analogs, nitrogen-coordinated and carbon-coordinated metal ions occur in a 1:1 ratio. X-Ray powder diffraction and, to some extent, spectroscopic data show that the nitrogen- and carbon-coordinated metals are in regular octahedral environments.[3-10]

A third type of metal ion (which we call interstitial) is generally present to maintain electroneutrality of the Prussian blue analog. For example, the compound $\mathrm{Co_3[Co(CN)_6]_2}$ contains two nitrogen-coordinated, two carbon-coordinated, and one interstitial cobalt atoms. By contrast to the N- and C-coordinated metal ions, the first coordination sphere for interstitial ions is quite uncertain.

From the X-ray powder diffraction studies of Weiser, Milligan, and Bates[5] and of subsequent workers, it appears that the interstitial ions are distributed in a random fashion over the eight sites of $\bar{4}3m$ (T_d) symmetry in the unit cell (space group Fm3m). This site is illustrated in Figure 1 where it may be seen that there are no groups within bonding distance of the interstitial metal ion. The shortest distance is *ca.* 3.5 Å from the ion to one edge of the octant, that is, to the axis of the $\mathrm{C{\equiv}N}$ group. Individual C and N atoms are even further removed. Actually, this energetically unfavorable situation may not exist because water which is generally present in these compounds conceivably may be coordinated to the metal ions. Indeed, coordination by water was proposed in a number of early reports.[3,11] However, somewhat more recent studies of the partial pressure of water *vs.* composition were interpreted in terms of adsorption with no specific chemical interaction.[12]

The present detailed investigation of $\mathrm{Co_3[Co(CN)_6]_2}$ was designed to clarify the nature of the interstitial species in a typical Prussian blue analog. This par-

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(2) NASA Trainee, 1965–1966; NSF Predoctoral Fellow, 1966–1968.

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