decomposition under vacuum. The prior work on the samples of Figures 4 and 5 could only indicate that substantial quantities of divalent europium were formed with increasing temperature but the X-ray patterns and Mössbauer spectra did not correlate with any known carbide, nitride, or cyanide of europium. Figures 1 and 2, however, clearly show that the decomposition in a nonoxidizing atmosphere is hydrolytic in nature whereby the trivalent europium ion reacts with the water of crystallization during the decomposition of the complex in the overall manner

$$2EuFe(CN)_6\cdot 5H_2O \longrightarrow 2EuOOH + 2Fe(CN)_2 + (CN)_2 + 6H_2O + 6HCN \quad (1)$$

$$NH_4EuFe(CN)_6\cdot 4H_2O \longrightarrow EuOOH + Fe(CN)_2 + NH_3 + 2H_2O + 4HCN \quad (2)$$

The $Fe(CN)_2$ decomposes at higher temperatures to finally yield iron, carbon, and nitrogen as described previously. The EuOOH loses water over a fairly prolonged temperature range and the resulting oxide reacts with the carbon produced as indicated above to form the lower oxide of europium and carbon monoxide. The lines of EuO are clearly discernible in the X-ray patterns shown in Figures 6 and 7 of the earlier work.[2]

The infrared spectra in Figures 4 and 5 of this work also indicate the hydrolytic nature of the decomposition. The hydroxyl bands persist to around 650° consistent with the decomposition of EuOOH.[3]

Conclusions

The decomposition of $EuFe(CN)_6\cdot 5H_2O$ and $NH_4EuFe(CN)_6\cdot 4H_2O$ under vacuum has been shown to be hydrolytic in nature with respect to europium. The iron intermediates during the decomposition are $Fe(CN)_6 \rightarrow Fe_3C \rightarrow Fe$. Cyanogen is liberated during the reduction of hexacyanoferrate(III). The europium ion reacts with the water of hydration to form EuOOH and evolve HCN. This EuOOH then loses water and the resulting oxide reacts with the carbon present at elevated temperature under vacuum to form EuO.

(3) R. C. Rau and W. J. Glover, Jr., *J. Amer. Ceram. Soc.*, **47**, 382 (1964).

Contribution from the Departments of Chemistry and Physics,
Texas Tech University, Lubbock, Texas 79409

The Prussian Blues[1]

By R. E. WILDE,*[2a] SURENDRA NATH GHOSH,[2b] and B. J. MARSHALL[2c]

Received March 20, 1970

Soluble and insoluble Prussian blues have been prepared and characterized by elemental analyses, magnetic susceptibility, infrared, and X-ray investigations. The magnetic susceptibility studies show that the Prussian blues obey a Curie–Weiss law with $\mu_{eff} = 6.29$ and 5.97 BM per Fe(III) for soluble and insoluble Prussian blue, respectively. Infrared spectra of the Prussian blues and Turnbull's blue were obtained in the region 70–4000 cm^{-1}. Analysis of the infrared spectra supports the cubic supercomplex structure and indicates that insoluble Prussian blue contains interstitial hydrated Fe(III). The infrared spectra of Turnbull's blue are identical with those of Prussian blue.

Introduction

There is gradually being acquired a large body of information on the "iron blues," as they were called by Holtzman.[3] The iron blues consist of "soluble" and "insoluble" Prussian blues[4] (ferric ferrocyanides) and Turnbull's blue (ferrous ferricyanide). Recent Mössbauer studies[5-9] have conclusviely shown that Prussian blue and Turnbull's blue are identical—namely, ferric ferrocyanides. In spite of a large number of powerful physical methods such as X-ray analysis,[10-12] visible–ultraviolet transmission and reflectance spectroscopy,[13,14] magnetic susceptibility studies,[15-16] and Mössbauer spectroscopy having been brought to bear on the structural problem of Prussian blue, there is still uncertainty as to the actual constitution of Prussian blue and the large number of Prussian blue analogs.

The accepted chemical formulas for the two Prussian blues date back to work by Muller and coworkers.[17] These formulas were arrived at indirectly, and all papers concerning the Prussian blues published since have been devoid of quantitative analytical data. With this in mind, we decided that it was necessary to establish

---

(1) (a) This research was supported by a grant from the Robert A. Welch Foundation. (b) Presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 27, 1970.

(2) (a) Department of Chemistry; to whom correspondence should be addressed. (b) Department of Chemistry. (c) Department of Physics.

(3) H. Holtzman, *Ind. Eng. Chem.*, **37**, 855 (1945).

(4) "Soluble" and "insoluble" refer to the ease with which the Prussian blues are peptized. The Prussian blues are insoluble in water, but they do form sols.

(5) L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

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

(7) J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963).

(8) K. Maer, Jr., M. L. Beasley, R. L. Collins, and W. O. Milligan, *J. Amer. Chem. Soc.*, **90**, 3201 (1968).

(9) A. Ito, M. Suenaga, and K. Ono, *J. Chem. Phys.*, **48**, 3597 (1968).

(10) J. F. Keggin and F. D. Miles, *Nature (London)*, **137**, 577 (1936).

(11) A. K. Van Bever, *Recl. Trav. Chim. Pays-Bas*, **57**, 1259 (1938).

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

(13) M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

(14) P. S. Braterman, *J. Chem. Soc. A*, 1471 (1966).

(15) D. Davidson and L. A. Welo, *J. Phys. Chem.*, **32**, 1191 (1928).

(16) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

(17) See the references and historic discussion in ref 3.

whether or not two Prussian blues actually do exist and, if they do, to make physical measurements which would show the difference and thus would provide a criterion by which the two blues could be identified.

Experimental Section

Two different methods of preparation of Prussian blue and Turnbull's blue were employed. To prepare soluble Prussian blue, 0.05 mol of reagent grade $K_4Fe(CN)_6$ was mixed, by shaking, with 0.0125 mol of reagent grade anhydrous $FeCl_3$ until the mixture was homogeneous. The mixture was then slowly sprinkled into 400 ml of rapidly stirred water; the Prussian blue sol formed immediately. The Prussian blue sol was allowed to settle for 12 hr. The solution above the sol was then removed with a pipet, and the sol was centrifuged. The Prussian blue centrifugate was then repeatedly washed with 50% ethanol by means of the centrifuge, the decantate changing color with each washing from yellow to yellow-green to green to blue-green to turbid blue. These color changes represent removal of the ferrocyanide and ferric ion impurities. It was assumed that a turbid blue wash solution indicates that the washing is complete. The sample was then washed with pure ethanol, air dried, ground into a fine powder, and then dried under vacuum for 24 hr. The soluble Turnbull's blue was prepared in the same manner except for the use of $FeCl_2$ and excess $K_3Fe(CN)_6$.

The preparation of insoluble Prussian blue was the same as that of the soluble except for use of a fourfold molar excess of $FeCl_3$. The washing procedure was slightly different, the centrifugate being washed alternately with 50% ethanol and with pure ethanol until the ethanol decantate was blue. The insoluble Turnbull's blue was prepared in the same manner except for the use of $K_3Fe(CN)_6$ and excess $FeCl_2$.

Samples of Prussian blue and Turnbull's blue were also prepared by the standard methods of mixing 0.1 *M* solutions of the reactants.[8] Once the samples were prepared, they were washed as above.

Infrared spectra were obtained with Beckman IR-9 and IR-11 spectrophotometers. All wave numbers were measured with an estimated probable error of ± 2 cm^{-1}. At wave numbers less than 700 cm^{-1}, all spectra were obtained with the samples dispersed in Nujol on 2-mil high-density polyethylene. At wave numbers greater than 700 cm^{-1}, the spectra were of samples brushed directly onto a slightly roughened KBr window. Some spectra of the samples incorporated into KBr or CsI pellets were obtained, but these spectra were inferior to the Nujol mull spectra.

The infrared spectra (400–4000 cm^{-1}) of Prussian blue and Turnbull's blue brushed onto a KBr window and incorporated in KBr pellets were studied from room temperature to 4°K. The optical cryostat used in these studies was an Andonian modular dewar.[18]

The magnetic susceptibilities were measured using the Faraday method,[19] which consists of measuring the force exerted on a hypothetical point source of the magnetic material placed in a magnetic field gradient. The gradient field was produced by a Varian V-3700 15-cm electromagnet, V-FR2902 Fieldial regulated power supply, and a set of constant $(H)\mathrm{d}H/\mathrm{d}z$ pole faces. The sample was contained in a 2-mm diameter Suprasil holder which in turn was suspended in the gradient field by a thin glass fiber which was connected to the lever arm of a Cahn RM automatic electrobalance. The electrobalance combined with a Hewlett-Packard 3400A digital voltmeter allowed a visual readout to the nearest 0.001 mg of mass change. The gradient field was calibrated, for all Fieldial settings, with Mohr's salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The temperatures were monitored with a copper–constantan thermocouple, placed in the proximity of the sample, and a Leeds and Northrup six-dial guarded potentiometer facility. The values of χ_g at 300, 195, and 78°K were measured for stable temperatures maintained sufficiently long for the sample and thermocouple to reach an equilibrium temperature.

The mass of the Suprasil holder and the sample were initially measured with a Mettler semimicrobalance. The sample, in the Suprasil container, was then placed in a vacuum jar and evacuated to a pressure of 1 μ. One end of the Suprasil holder was open so that water could leave the sample. The sample remained at this pressure for at least 1 week before the vacuum jar was filled with dry helium gas. It was then removed and its mass was remeasured in order to determine the water loss. The soluble Prussian blue sample lost 4% water, and the insoluble Prussian blue sample lost 10% water. The sample was then placed in the magnetic susceptibility cryostat, which was evacuated to a pressure of approximately 1 μ. Susceptibility studies were begun after it had remained under vacuum for 1 week.

Standard susceptibility corrections were made for the Suprasil holder.[20]

X-Ray powder patterns were obtained with a Norelco wide-range goniometer and proportional counter using Cu Kα radiation with a Ni filter. The samples were mounted in a flat rotating specimen holder.

The soluble and insoluble Prussian blue samples were analyzed in duplicate (Schwarzkopf Microanalytical Laboratory). The results of these analyses are given in Tables I and II and discussed in the next section.

Results and Discussion

Preparation of Prussian Blue.—The preparative procedure outlined above, whereby the dry, powdered reactants are premixed before addition to water, was considered the best way to prepare the completely soluble and insoluble Prussian blues. The washings were repeated as described above until considerable Prussian blue remained in the wash solution as determined by the color of the solution.

TABLE I

ANALYTICAL RESULTS FOR SOLUBLE PRUSSIAN BLUE

Element	Prussian blue wt % KFe[Fe(CN)$_6$]	Impurities wt %				Wt %	
		$K_4Fe(CN)_6$	Fe_2O_3	KCl	H_2O	Total	Found
C	15.31	3.38				18.69	19.26
H					1.13	1.13	1.13
N	17.86	3.94				21.80	21.81
Fe	23.74	2.62	2.18			28.54	28.54
K	8.31	7.89		1.70		17.90	17.90
Cl				1.55		1.55	1.55
O			0.94		8.95	9.89	9.89
Total	65.22	17.89	3.12	3.25	10.08	99.50	100.08

The analyses shown in Tables I and II were aided by X-ray powder patterns[21] which showed a 5–15% impurity of α-Fe_2O_3 in the insoluble Prussian blue. The quantitative analysis of the impurities from the elemental analyses presupposes a knowledge of the impurities present. We believe that our interpretation is reasonable in view of the method of preparation. The carbon percentage in both cases was found to be slightly higher than calculated, probably because of residual ethanol. The effects of these impurities on the physical

---

(18) Andonian Associates, Inc., Waltham, Mass.

(19) P. W. Selwood, "Magnetochemistry," Interscience, New York, N. Y., 1961, p 11.

(20) B. J. Marshall, R. Johnson, D. Follstaedt, and J. Randorff, *Rev. Sci. Instrum.*, **40**, 375 (1969).

(21) These patterns were made available to us by Dr. W. O. Milligan.

Table II

Analytical Results for Insoluble Prussian Blue

Element	Prussian blue wt % $Fe_4[Fe(CN)_6]_3$	Impurities wt % Fe_2O_3	KCl	HCl	H_2O	Wt % Total	Found
C	16.28					16.28	16.76
H				0.14	2.38	2.52	2.79
N	19.00					19.00	19.00
Fe	29.45	3.68				33.13	33.13
K			1.52			1.52	1.52
Cl			1.37	5.07		6.44	6.44
O		1.58			18.86	20.44	20.44
Total	64.73	5.26	2.89	5.21	21.24	39.33	100.08

measurements will be discussed in the appropriate paragraphs below.

Magnetic Susceptibility Measurements.—The magnetic susceptibility studies of Davidson and Welo[15] and of Cambi[22] indicate that the Fe(III) ions are all high-spin species in both soluble and insoluble Prussian blue.

After correcting for the diamagnetism[23] of the sample and impurities and for the antiferromagnetism of the α-Fe_2O_3,[24,25] $1/\chi_m$ (χ_m is the molar susceptibility) was plotted against temperature for the three points at which very careful measurements were made. This plot, shown in Figure 1, obeys a Curie–Weiss law, $\chi_m = C/(T + \Theta)$, where $C = 4.88$, $\Theta = 2°$, and $\mu_{eff} = 6.29$ BM per Fe(III) for soluble Prussian blue and where $C = 17.6$, $\Theta = 0°$, and $\mu_{eff} = 5.97$ BM per Fe(III) for insoluble Prussian blue. In making these calculations, it was assumed that the soluble Prussian blue contained no water and that the insoluble Prussian blue had lost 10% of its water with respect to the values reported in Table II. Keeping 6% of the water in the soluble Prussian blue calculation does not change the interpretation of high-spin Fe(III), but it does give an exceptionally high value of $\mu_{eff} = 6.50$ BM per Fe(III). Before doing the magnetic susceptibility studies, the samples were ground to a very fine powder in a mortar. This grinding may have removed about 6% of the water from the soluble Prussian blue, since all indications are that the soluble Prussian blue has less tendency to retain water than does the insoluble Prussian blue. All magnetic susceptibility measurements were repeated on different preparations of soluble and insoluble Prussian blue with essentially the same results.

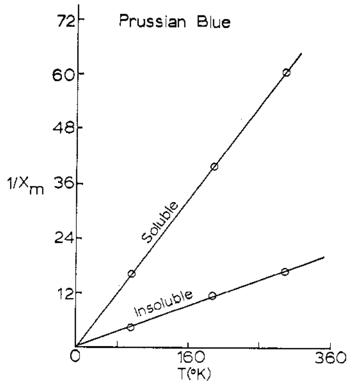

Figure 1.—Temperature dependence of molar magnetic susceptibility for soluble and insoluble Prussian blues.

Our magnetic susceptibility studies are in general agreement with those of Davidson and Welo[15] in that both studies have shown that the Fe(III) are all high-spin species. However, we have extended our studies to lower temperatures and have made measurements for samples whose impurity content is known. Our effective magnetic moments per Fe(III) are higher than the 5.71 and 5.62 BM obtained by Davidson and Welo[15] for soluble and insoluble Prussian blue, respectively.

Infrared Measurements.—The far-infrared spectra of the Prussian blues are shown in Figure 2. The samples whose spectra are shown in Figure 2 are the ones whose analyses are reported in Tables I and II and which were used for the effective magnetic moments reported above. These spectra differ significantly in many respects. The most striking difference occurs in the 600-cm^{-1} band, which is a strong band in the spectrum of the soluble Prussian blue and a weak band in the spectrum of the insoluble compound.

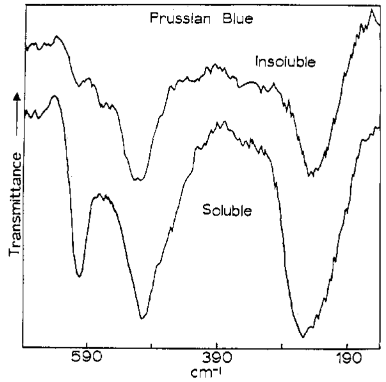

Figure 2.—Far-infrared spectra of Prussian blue.

A band of medium intensity occurs at 562 cm^{-1} in the spectrum of the insoluble compound but does not appear in the soluble Prussian blue spectrum.

Another difference occurs in the region of 500 cm^{-1}, the 500- and 515-cm^{-1} bands forming a strong doublet in the insoluble Prussian blue spectrum, whereas the 514-cm^{-1} band occurs only as a shoulder in the spectrum of the soluble compound. The preparation of the soluble Prussian blue in 1 *M* HCl by conventional methods gives a much sharper spectrum (Figure 3) and shows distinctly the band at 514 cm^{-1}, which is also evident as a shoulder in the spectra of our second preparation of the Prussian blues in Figure 3. The bands at 562 and 471 cm^{-1} in the spectrum of insoluble Prussian blue might be the α-Fe_2O_3 impurity (Figure 4). The band at 363 cm^{-1} might also arise from an α-Fe_2O_3 band.

---

[22] L. Cambi, *Gazz. Chim. Ital.*, **77**, 575 (1947).

[23] L. N. Mulay, "Magnetic Susceptibility," Reprint, Interscience, New York, N. Y., 1963.

[24] S. T. Lin, *Phys. Rev.*, **116**, 1447 (1959).

[25] A. K. Mukerjee, *Indian J. Phys.*, **43**, 465 (1967).

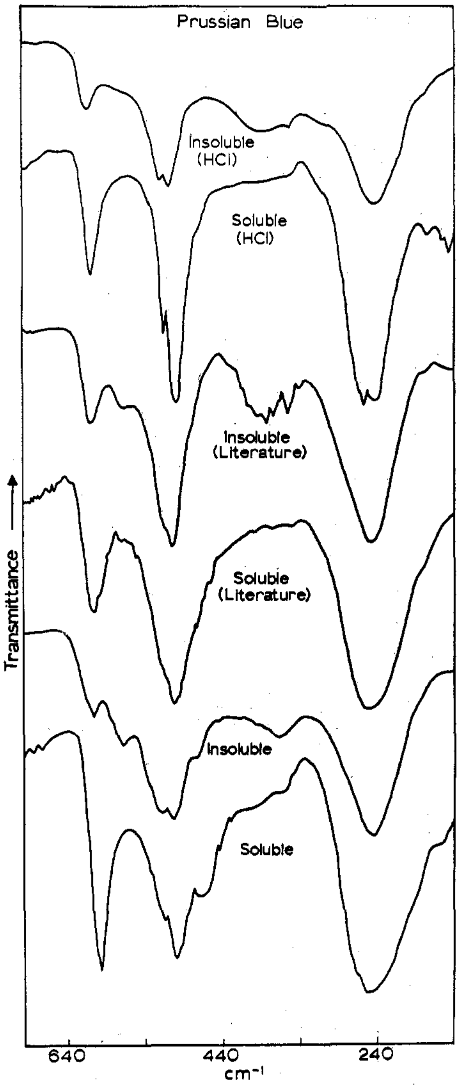

Figure 3.—Far-infrared spectra of a second Prussian blue preparation, a preparation by the conventional method (Literature), and a preparation in 1 *M* HCl (HCl).

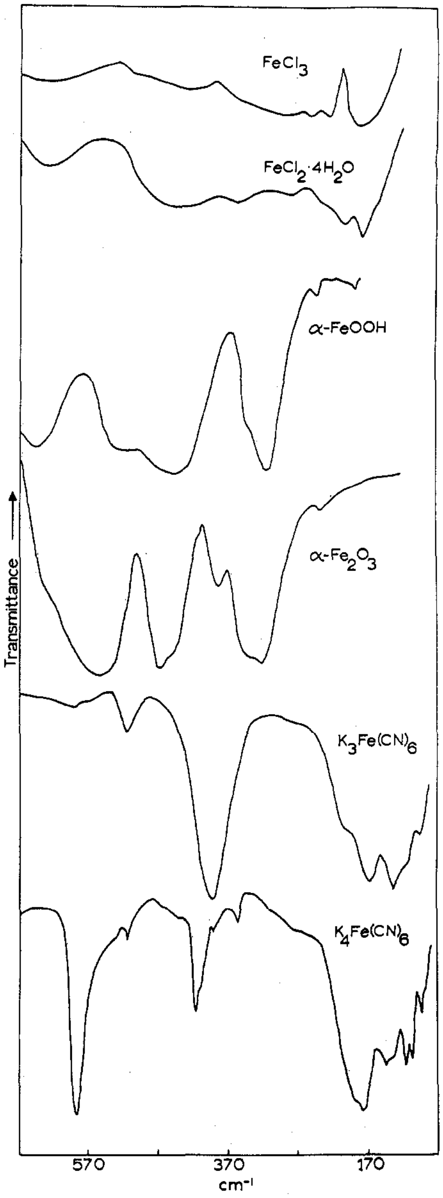

Figure 4.—Far-infrared spectra of the possible impurities present in Prussian blue.

There is apparently a very broad band in the region of 300–450 cm^{-1} in the spectrum of insoluble Prussian blue, which does not appear in the soluble compound, since the spectrum of the soluble compound shows nearly 100% transmittance in this region. This cannot be attributed to any known impurity. Nakagawa and Shimanouchi[26] have done force constant calculations on a number of aquo complexes of the first-row transition metals. They have assigned metal–oxygen stretching vibrational frequencies to broad bands observed in the 300-500-cm^{-1} region of the spectra of these complexes.

The number of bands observed in the low-frequency region of the spectra of the Prussian blues and the differences between the spectra of the soluble and insoluble blues indicate that the crystals are not ionic but that they are supercomplexes in which the ferrocyanide groups strongly interact with the Fe(III). Thus, the bands in the region 450–650 cm^{-1} can be associated with the Fe—C≡N—Fe bending modes, while the broad band at 250 cm^{-1} is to be associated with the stretching vibrations. The replacement of interstitial K$^+$ with hydrated Fe(III) affects the bending modes more than the stretching modes, since the differences between the soluble and insoluble Prussian blue spectra are more pronounced in the bending region.

Figure 5 shows the spectra of Turnbull's blue prepared by premixing the dry reactants and adding them to water. The spectra indicate that the Turnbull's blue converts to either soluble or insoluble Prussian blue depending upon whether $K_3Fe(CN)_6$ or $FeCl_2$, respectively, is in excess. Comparison of the soluble Turnbull's blue and soluble Prussian blue spectra with the spectra of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ reveals that not enough crystalline $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ are present to appear in the spectra. Since $K_4Fe(CN)_6$ is present in the soluble Prussian blue to the extent of 23 mol % of the soluble Prussian blue, adsorbed ferro-

---

[26] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

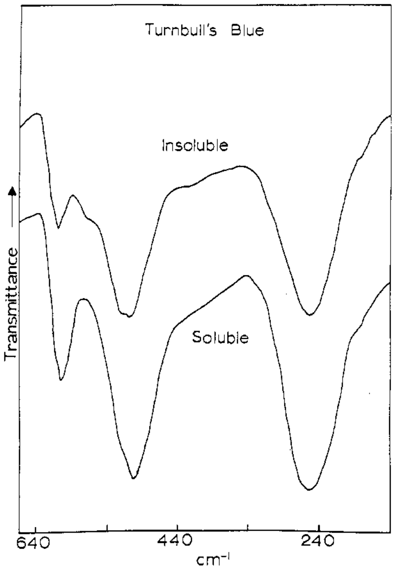

Figure 5.—Far-infrared spectra of Turnbull's blue.

cyanide ion could make some contribution to the 596-cm^{-1} band, but it is doubtful that it could account for all of the intensity observed in the 596-cm^{-1} band of the soluble Prussian blue spectrum. It should not be present in the soluble Turnbull's blue spectrum unless the adsorbed ferricyanide ion is reduced to ferrocyanide.

Shown in Figure 3 are spectra of the Prussian blues made by the conventional method and also by the conventional method in a 1 *M* HCl solution. Comparison of these spectra with those of soluble and insoluble Prussian blue shows that preparation by the conventional literature method leads to a product which is primarily the desired Prussian blue but with some of the undesired Prussian blue present—perhaps as much as 25%.

The spectra of soluble Prussian blue prepared in 1 *M* HCl showed much narrower bands, indicating more homogeneity and longer range order. This is in agreement with the results of Weiser, *et al.*,[12] who obtained sharper X-ray patterns for Prussian blue samples prepared in 12 *M* HCl.

Spectra of Prussian blue and Turnbull's blue were obtained at temperatures from room temperature to 4°K. The spectra remained unchanged except for a sharpening of the bands at low temperatures.

X-Ray Studies.—X-Ray powder patterns of both the soluble and insoluble Prussian blues were obtained. Careful detailed studies were not attempted because of the unavailability of an iron source and the high background present with the Cu source. Our results agree with those of Weiser, *et al.*,[12] for the insoluble Prussian blue. The soluble Prussian blue pattern differs from the insoluble in that the line associated with the 400 reflection is stronger than the line associated with the 200 reflection. The reflection positions are the same for both blues, however.

The X-ray and magnetic susceptibility studies have indicated that Prussian blue forms a face-centered-cubic structure with either potassium ions or ferric ions occupying the interstices in the lattice. However, there are other possible structures which might also be compatible with the X-ray and magnetic susceptibility data. Some of these have been discussed by Davidson.[27]

If Fe(III) is four-coordinate, it is possible to build up rings composed of eight $Fe[Fe(CN)_6]$ groups wherein octahedral and tetrahedral edges are shared. It is then possible for octahedral Fe(III) to bridge three rings, giving rise to a maximum Fe(III) to Fe(II) ratio of 4:3. This structure, which would possess only short-range order, should lead to two distinct $C\equiv N$ stretching frequencies, especially in the case of the soluble Prussian blue. Alternatively, helices can be formed. However, the overlap is poor and does not favor Fe—N bonding.

Structures involving octahedral coordination to both cyanide and water have not been considered, although Ludi and Güdel[28] have recently advanced this structure to explain the X-ray powder patterns of $Co_3[Co(CN)_6]_2$ and $Cd_3[Co(CN)_6]_2$.

The observation of only one $C\equiv N$ stretching band at 2081 cm^{-1} in the infrared spectra (resolution $\sim$1 cm^{-1}) of the Prussian blues and the interpretation of the X-ray powder patterns as being diagnostic of a face-centered-cubic structure probably eliminate any structure involving Fe(III) in tetrahedral coordination. We believe that the correct structure is the one proposed by Keggin and Miles[10] involving octahedral coordination at the octrahedral corners.

Acknowledgments.—The authors are very grateful to Dr. W. O. Milligan, who suggested this study and who has provided advice and encouragement throughout this work. The assistance of Mr. D. L. Cox is also gratefully acknowledged.

---

(27) D. Davidson, *J. Chem. Educ.*, **14**, 277 (1937).

(28) A. Ludi and H. U. Güdel, *Helv. Chim. Acta*, **51**, 2006 (1968).