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The Color and Electronic Configurations of Prussian Blue[1]

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An interpretation of the electronic spectrum of Prussian blue based on ligand field theory is presented which is consistent with the dye having the constitutional formula $KFe^{III}[Fe^{II}(CN)_6]$. The blue color of the dye arises from a charge transfer transition between the $Fe^{II}(CN)_6{}^{4-}$ and Fe^{III} ions; the measured intensity of the transition indicates that the optical electrons are in very large part (99%) localized on the $Fe^{II}(CN)_6{}^{4-}$ ions in the ground state. The interpretation of the shift of the high frequency charge transfer bands of $Fe^{II}(CN)_6{}^{4-}$ on substituting the Fe^{II} with Ru^{II} or Os^{II} then can be used to predict the shifts of the low frequency charge transfer bands of Prussian blue on substituting $Fe^{II}(CN)_6{}^{4-}$ with $Ru^{II}(CN)_6{}^{4-}$ or $Os^{II}(CN)_6{}^{4-}$.

Introduction

It long has been known that the presence in a crystal of two ions of the same or similar metal atoms in different oxidation states can lead to a deep color which apparently is unrelated to the colors of either of the ions taken separately.[2] The most famous example of this startling phenomenon is the formation of the intensely blue dye Prussian blue, $[K,Fe^{II},Fe^{III}](CN)_6$, made by mixing the colorless solutions of $Fe^{III}(ClO_4)_3$ and $K_4Fe^{II}(CN)_6$. Not only is the deep color of Prussian blue at first sight perplexing, but its chemical constitution is left ambiguous by the fact that a substance having an electronic spectrum and powder pattern identical to those of Prussian blue also can be formed by mixing solutions of $Fe^{II}(ClO_4)_2$ and $K_3Fe^{III}(CN)_6$. It will be shown that the ambiguous formulation of Prussian blue as either the ferric salt of hydroferrocyanic acid or as the ferrous salt of hydroferricyanic acid can be resolved by the application of simple orbital theory to the explanation of the Prussian blue electronic spectrum.

Since Prussian blue can be synthesized only as a microcrystalline powder which then may be readily peptized to form a colloidal dispersion, the work herein reported was done on dispersions of this type. The unit cell of the dispersed crystalline material is face centered cubic[3a] with cyanide ions joining each of the iron ions to its six octahedral nearest neighbor iron ions (Fig. 1). The potassium ions in the structure surround the iron ions tetrahedrally. If one assumes that the Fe–C and C–N distances of 1.85 and 1.18 Å., respectively, taken from the structure determination[3b] of the octahedral ion $Fe^{II}(CNCH_3)_6{}^{2+}$ can be used in the Prussian blue crystal, then the cell constant of 10.20 Å. yields an Fe–N distance of 2.07 Å. It also is relevant that on formation of Prussian blue and subsequent basic hydrolysis, the cyanide ligands remain firmly attached to the iron ion with which they are associated in the starting material and do not turn about within the Prussian blue crystal.[4] Thus there are two

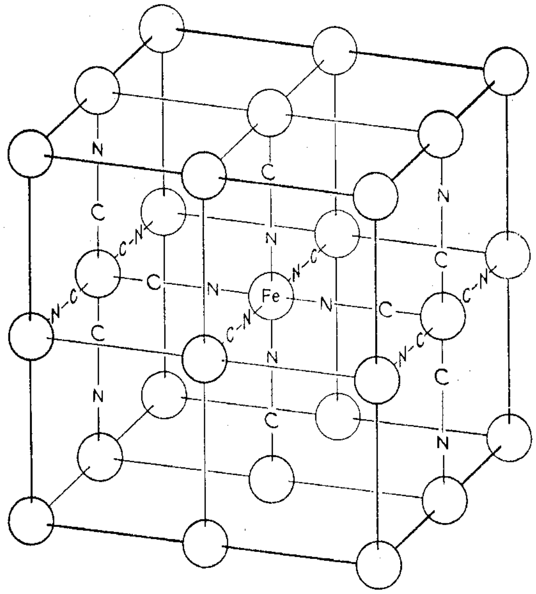

Fig. 1.—The unit cell of Prussian blue. Four potassium ions which surround the body centered iron ion tetrahedrally have been omitted for clarity.

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[1] Presented in part at the Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June 14, 1961, and at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 5, 1961.

[2] W. Biltz, *Z. anorg. u. allgem. Chem.*, **127**, 169 (1923); H. L. Wells, *Am. J. Sci.*, [5] **3**, 417 (1922).

[3] (a) J. F. Keggin and F. D. Miles, *Nature*, **137**, 577 (1936); (b) H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc.*, 799 (1945).

[4] I. A. Korshunov and Z. M. Lebedeva, *Zhur. Neorg. Khim.*, **1**, 1912 (1956).

distinct kinds of iron ions in the crystal, those in octahedral holes formed by the carbon ends of the cyanide ligands and those in octahedral holes formed by the nitrogen ends of the cyanide ligands.

Static susceptibility measurements by Davidson and Welo[5] show that Prussian blue is paramagnetic, having a moment of 5.72 B.M. per molecule of $KFe_2(CN)_6$, and obeys the Curie law over the region 200–300°K. The measured moment would correspond to five unpaired spins per two iron ions if orbital contributions were small or nonexistent.

Experimental

Aqueous dispersions of Prussian blue were prepared by adding a stoichiometric amount of $K_4Fe^{II}(CN)_6$ solution to a $Fe^{III}(ClO_4)_3$ solution prepared by dissolving a weighed amount of standard iron wire (99.99%) in a small volume of hot concentrated $HClO_4$ and diluting with a large volume of water. Dispersions of related dyes were prepared in the same manner, substituting solutions of $K_4Ru^{II}(CN)_6$ or $K_4Os^{II}(CN)_6$ for the $K_4Fe^{II}(CN)_6$ solution. The spectra recorded on a Cary Model 14 spectrophotometer using 1-cm. cells are shown in Fig. 2.

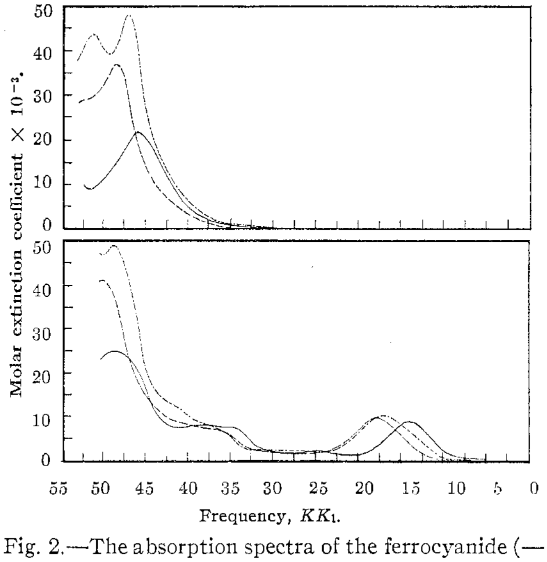

Fig. 2.—The absorption spectra of the ferrocyanide (—), ruthenocyanide (— — — —), and osmocyanide (— · —) ions in water (*upper*) and the spectra of dispersions of the dyes formed from them on adding $Fe^{III}(ClO_4)_3$ (*lower*).

The Electronic Configuration

Let us now look at the molecular orbital diagrams to be expected for iron ions in the carbon holes and in the nitrogen holes of Prussian blue. The molecular orbitals for the cyanide ion are shown in the center of Fig. 3, the ordering of the levels being derived from the previously assigned bands of the cyanide radical.[6] Depending upon whether the nitrogen or carbon ends of the CN^- ligands coördinate with the metal ions, metal–ligand orbitals may be assumed to form, as shown on either the left or the right hand side of Fig. 3. The metal ion in the carbon hole invariably has the low spin, strong field configuration indicative of a large splitting of the metal ion d orbitals. However, the observed susceptibility of 5 spins/2 Fe then demands that the splitting of the metal ion orbitals in the nitrogen hole be small so as to give a high spin, low field configuration in this hole. Each iron ion then has at least five d electrons and an eleventh is in either the carbon hole giving the configuration $(t_{2g})^6{}_C({}^1S)(t_{2g})^3{}_N(e_g)^2{}_N({}^6S)$ or in the nitrogen hole giving the configuration $(t_{2g})^5{}_C({}^2I)(t_{2g})^4{}_N(e_g)^2{}_N({}^5D)$. Thus the ambiguity in constitution.

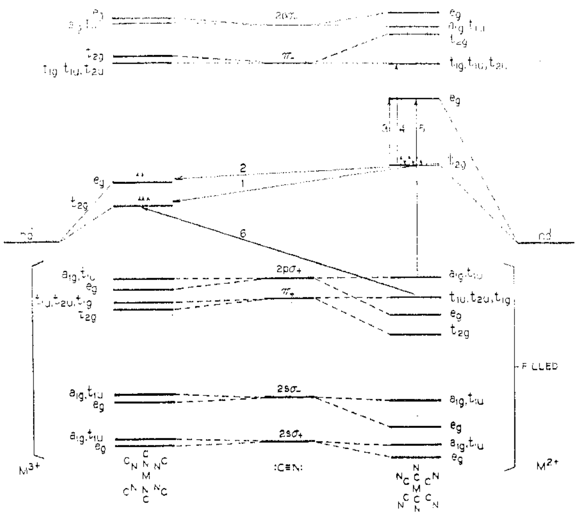

Fig. 3.—A molecular orbital scheme for Prussian blue. The symmetry labels on any column of levels are appropriate only to the molecule listed at the foot of that column. The pertinent level and state symmetries of a collection of the ions, arranged as is found in a crystal of Prussian blue, are presented in the text. Thus, for example, in the case of an Fe^{II} ion surrounded octahedrally by six Fe^{III} ions, the appropriate Fe^{III} orbitals will not be the t_{2g} or e_g orbitals shown above, but linear combinations of these orbitals taken over all six Fe^{III} centers.

According to Fig. 3, the lowest available orbital for the eleventh electron in the nitrogen hole is less antibonding than the corresponding orbital in the carbon hole. Though the eleventh electron would be thought to favor the nitrogen hole in the ground state, the interelectronic repulsion and exchange effects in the strong field and weak field iron ions[7] consort to place the electron in the carbon hole, the intra-atomic electrostatic energy

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

[6] A. E. Douglas and P. M. Routly, *Astrophys. J.* (Suppl. ,295 (1955); P. K. Carroll, *Can. J. Phys.*, **34**, 85 (1956).

[7] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954).

of the $(t_{2g})^6_{\mathrm{C}}(^1S)(t_{2g})^3_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^6S)$ configuration being $14B_{\mathrm{N}} - 4B_{\mathrm{C}} + 2C_{\mathrm{C}} \approx 13{,}400$ cm.$^{-1}$ lower than that of $(t_{2g})^5_{\mathrm{C}}(^2I)(t_{2g})^4_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^5D)$. Thus the one and two electron energies act in opposition as regards the ground state configuration of Prussian blue and at this point it cannot be said which predominates.

If we first suppose that the ground state configuration of Prussian blue is $(t_{2g})^6_{\mathrm{C}}(^1S)(t_{2g})^3_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^6S)$, then the 14,100 cm.$^{-1}$ transition observed in Prussian blue (Fig. 2) is assigned as that labeled 1 in Fig. 3. Though we represent the transition as one between an iron ion in a carbon hole and one in a nitrogen hole, in the actual crystal all six iron ions in the nitrogen holes surrounding the carbon hole would be involved in the excited state. The inclusion of the other five nitrogen holes surrounding the carbon hole has no effect on the energy because of the large distances between holes, but we must consider all six holes when problems of symmetry arise. A second transition labeled 2 also is expected in Prussian blue, its excited state differing from that of transition 1 by the excitation of an electron from t_{2g} to e_g in the weak field *ferrous* ion. The t_{2g} to e_g separation corresponds exactly to the $^5T \rightarrow {}^5E$ band of aqueous ferrous ion, observed at 10,150 cm.$^{-1}$. Moreover, while transition 1 is symmetry allowed from the A_{1g} ground state to the two T_{1u} excited states, all six components of which are approximately degenerate, transition 2 is forbidden due to local orthogonality of the atomic 3d orbitals. Thus if the transition is from a carbon hole to a nitrogen hole, two bands are predicted, $(t_{2g})^6_{\mathrm{C}}(^1S)(t_{2g})^3_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^6S) \rightarrow (t_{2g})^5_{\mathrm{C}}(^2I)(t_{2g})^4_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^5D)$ and $(t_{2g})^6_{\mathrm{C}}(^1S)(t_{2g})^3_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^6S) \rightarrow (t_{2g})^5_{\mathrm{C}}(^2I)(t_{2g})^3_{\mathrm{N}}(e_g)^3_{\mathrm{N}}(^5D)$, the first being of high intensity and the second of low intensity and situated about 10,000 cm.$^{-1}$ to the high frequency side of the first band.

On the other hand, if the color of Prussian blue involves the transfer of an electron from the $(t_{2g})^4(e_g)^2$ nitrogen hole iron ion to the $(t_{2g})^5$ carbon hole iron ion, two bands again are predicted, one allowed and one forbidden. The two bands would arise from the transitions $(t_{2g})^5_{\mathrm{C}}(^2I)(t_{2g})^4_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^5D) \rightarrow (t_{2g})^6_{\mathrm{C}}(^1S)(t_{2g})^3_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^6S)$ and $(t_{2g})^5_{\mathrm{C}}(^2I)(t_{2g})^4_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^5D) \rightarrow (t_{2g})^5_{\mathrm{C}}(e_g)^1_{\mathrm{C}}(^1I)(t_{2g})^3_{\mathrm{N}}(e_g)^2_{\mathrm{N}}(^6S)$ and would be expected to be split by $10Dq_{\mathrm{C}} - C_{\mathrm{C}} \approx 29{,}500$ cm.$^{-1}$. Looking now at the spectrum of Prussian blue given in Fig. 2, it is seen that the weak second band occurs at 10,000 cm.$^{-1}$ higher frequency, exactly as predicted for a crystal of ferric ferrocyanide. That Prussian blue is indeed a ferric ferrocyanide is born out by the Mössbauer resonance spectrum of this substance which shows two lines with "isomeric shifts" characteristic of ferric ion and ferrocyanide ion.[8] Before attempting to interpret the remainder of the Prussian blue spectrum and the spectra of the Ru and Os homologs, let us move to a discussion of the spectra of the $n\mathrm{d}^6$ hexacyanide ions.

The two weak crystal field bands of $\mathrm{Fe^{II}(CN)_6^{4-}}$ ion found at 31,000 and 37,000 cm.$^{-1}$ previously have been assigned by Jorgensen[9] as transition 3 of Fig. 3. One component of this pair is found at 31,000 cm.$^{-1}$ in the $\mathrm{Ru^{II}(CN)_6^{4-}}$ ion while neither could be located in the $\mathrm{Os^{II}(CN)_6^{4-}}$ ion. The very much stronger charge transfer bands centered at about 50,000 cm.$^{-1}$ are assigned as metal $t_{2g} \rightarrow$ CN-π-antibonding t_{1u} and metal $t_{2g} \rightarrow$ CN-π-antibonding t_{2u}, both of which are allowed with equal intensity. In the molecular orbital scheme, the estimated overlap of 0.008 between adjacent $\mathrm{CN^-}$ groups will lead to a splitting of the t_{1u} and t_{2u} orbitals of *ca.* 2,000 cm.$^{-1}$. The charge transfer bands of the d^6 hexacyanides indeed are doubled, being split by 4,000 cm.$^{-1}$ (in $\mathrm{Fe^{II}(CN)_6^{4-}}$ the second component occurs as a shoulder at 50,000 cm.$^{-1}$) while the intensities of the two components are approximately equal. The alternative assignment for the charge transfer would have the electron going in the opposite direction, *i.e.*, CN-π-bonding $t_{1u} \rightarrow$ metal e_g (transition 5 of Fig. 3) and suffers from the fact that only *one* band would be symmetry allowed.

Since the acceptor levels (CN-π-antibonding) in the charge transfer bands are the same in the three ions, $\mathrm{Fe^{II}(CN)_6^{4-}}$, $\mathrm{Ru^{II}(CN)_6^{4-}}$, and $\mathrm{Os^{II}(CN)_6^{4-}}$, the differences in the centers of gravity of the charge transfer bands of these ions reflect the ease with which an electron may be transferred from the $n\mathrm{d}^6$ metal ions to the common acceptor, $\mathrm{CN^-}$. Returning now to the dyes, the differences in the frequencies of the charge transfer bands in the three dyes $\mathrm{KFe^{III}Fe^{II}(CN)_6}$ (14,100 cm.$^{-1}$), $\mathrm{KFe^{III}Ru^{II}(CN)_6}$ (17,400 cm.$^{-1}$), and $\mathrm{KFe^{III}Os^{II}(CN)_6}$ (16,400 cm.$^{-1}$) also will reflect the relative ease with which an electron may be transferred from the $n\mathrm{d}^6$ metal

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(8) The Mössbauer experiment was performed by Dr. G. K. Wertheim, Bell Telephone Laboratories, Murray Hill, N. J.

(9) C. K. Jorgensen, quoted in J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961, p. 425.

ions to a common acceptor, in this case Fe^{III}. In fact, the shifts observed in the centers of gravity of the charge transfer bands of the hexacyanide ions on replacing $3d^6$ Fe^{II} with $4d^6$ Ru^{II} or $5d^6$ Os^{II} should equal the shifts observed in the low frequency charge transfer bands of the dyes on similar substitution. The difference between the centers of gravity of the charge transfer bands of $Fe^{II}(CN)_6^{4-}$ and $Ru^{II}(CN)_6^{4-}$ is found from Fig. 2 to be +4,000 cm.$^{-1}$, while the observed shift of the low frequency charge transfer bands in the corresponding dyes is +3,300 cm.$^{-1}$. Looking next at the effect of replacing the $4d^6$ Ru^{II} with the $5d^6$ Os^{II} ion, the center of gravity of the hexacyanide ion charge transfer band then is found to move 1,000 cm.$^{-1}$ to *lower* frequency, exactly as observed for the low frequency charge transfer bands in the Ru^{II} and Os^{II} dyes.

Moreover, the split between the first and second charge transfer bands in the dyes is governed by $10Dq$ of the nitrogen hole ion in the excited state (Fe^{II} in all cases), so that in the Ru^{II} and Os^{II} dyes a weak band also should be found 10,000 cm.$^{-1}$ to the high frequency side of the first strong band. Such a band indeed is found in the Os^{II} dye spectrum, however the band cannot be located in the Ru^{II} dye spectrum but presumably is present.

The strong absorptions in the dyes at 50,000 cm.$^{-1}$ are the metal $t_{2g} \rightarrow$ CN-π-antibonding t_{1u}, t_{2u} bands of the d^6 hexacyanide ions and by elimination one then should hope the 33,000–43,000 cm.$^{-1}$ absorptions correspond to the expected CN-π-bonding $\rightarrow Fe^{III}$ t_{2g} transitions (transition 6, Fig. 3). The ligand → metal charge transfer absorption should be split into two components of equal intensity, the two separate components occurring at the same frequencies in all three dyes. From Fig. 2 we see that the first two expectations are realized, the third only poorly and so sheds some doubt on this assignment.

The Energy

The energy of the low frequency charge transfer band in Prussian blue is written as the sum of three terms

$$h\nu\ (\text{cm.}^{-1}) = 13{,}400 - E_{\text{one}} + E_{\text{crystal}}$$

where the change in intra-atomic electrostatic energies is 13,400 cm.$^{-1}$, E_{one} is the difference in the one electron energies of a t_{2g} electron in an iron ion in a nitrogen hole and in a carbon hole, and E_{crystal} is the coulombic energy expended in transferring the electron from the carbon hole to the nitrogen hole in the electrostatic field of all the ions in the crystal. Assuming a point charge lattice, E_{crystal} then can be calculated using a cycle in which an Fe^{II} ion and an adjacent Fe^{III} ion are removed from the lattice to infinity, an electron transferred between them, and the ions returned to their original sites in the crystal. From such a cycle one calculates

$$E_{\text{crystal}} = \frac{e^2}{r_0}\left(\frac{1}{2}\alpha_2 - \frac{1}{3}\alpha_3 - 1\right)$$

The Madelung numbers α_2 and α_3 for the Fe^{II} and Fe^{III} ions in the lattice were calculated to be −14.23 and −26.57, respectively, under the assumption that the CN^- point charges are equidistant between the iron ions.[10] Each of the α's should be multiplied by 0.90 to correct for the neglect of non-coulombic repulsive terms in the crystal potential.[11] The value of 12,900 cm.$^{-1}$ so computed for E_{crystal} using r_0 = 5.10 Å. would appear to be an upper limit to this part of the energy since the only other factor of importance with regard to E_{crystal} is the polarizability of the crystal which, quite roughly, would introduce a factor of $1/\epsilon$, ϵ being the dielectric constant. All other reasonable choices for the position of the CN^- charge also give values of E_{crystal} smaller than 12,900 cm.$^{-1}$ using r_0 = 5.10 Å. Setting $h\nu$ = 14,100 cm.$^{-1}$ and $E_{\text{crystal}} \leq$ 12,900 cm.$^{-1}$ yields $E_{\text{one}} \leq$ 12,200 cm.$^{-1}$ which, in its crude way, demonstrates that in the ground state the two-electron stabilization (13,400 cm.$^{-1}$) is sufficient to overcome the one-electron promotion energy ($\leq$ 12,200 cm.$^{-1}$) required to place the eleventh electron in the carbon hole.

The Intensity and Delocalization

The transfer of an electron from the $(t_{2g})^6$ carbon hole of Prussian blue to the six surrounding nitrogen holes each with half-filled t_{2g} orbitals results in 54 excited states, the symmetry of each being contained in the direct product of the symmetry of the carbon hole function in the excited state, t_{2g}, and the nitrogen hole functions available to the electron in the excited state (a_{1g}, e_g, $2t_{1u}$, t_{1g}, t_{2g}, t_{2u}). The one excited state in this manifold with total symmetry A_{1g}, derived from the configuration $\psi_N(A_{1g})C^5(t_{2g})N^{31}(t_{2g})$, will mix with the ground state function $\psi_C(A_{1g})C^6(a_{1g})N^{30}(a_{1g})$ through interelectronic in-

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(10) The author is grateful to Dr. L. C. Snyder of the Bell Telephone Laboratories, Inc., who programmed our I.B.M. 7090 computer to carry out the calculation of the Madelung sums.

(11) C. Kittel, "Introduction to Solid State Physics," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 77.

teraction to produce the first-order wave function

$$\psi_0(\mathrm{A_{1g}}) = \psi_\mathrm{C}(\mathrm{A_{1g}})\mathrm{C}^6(\mathrm{a_{1g}})\mathrm{N}^{30}(\mathrm{a_{1g}}) + \gamma\psi_\mathrm{N}(\mathrm{A_{1g}})\mathrm{C}^5(\mathrm{t_{2g}})\mathrm{N}^{31}(\mathrm{t_{2g}})$$

In this discussion, γ will be taken as a parameter, though formally it is equal to

$$\frac{\int \psi_\mathrm{C}(\mathrm{A_{1g}})\mathrm{C}^6(\mathrm{a_{1g}})\mathrm{N}^{30}(\mathrm{a_{1g}}) \sum\limits_{i\neq j} \frac{e^2}{r_{ij}} \psi_\mathrm{N}(\mathrm{A_{1g}})\mathrm{C}^5(\mathrm{t_{2g}})\mathrm{N}^{31}(\mathrm{t_{2g}})\mathrm{d}\tau}{\Delta W}$$

ΔW being the energy difference between the configurations. A large value of γ can be interpreted as indicating an appreciable ground state delocalization of the optical electron among the carbon and adjacent nitrogen holes while a small value of γ indicates the electron is localized in the carbon hole. A rough estimate of the value of γ in Prussian blue can be obtained in the following manner.

The integrated intensity of an absorption band is related to the transition moment integral μ, by the relation

$$\mu^2 = 9.17 \times 10^{-4} \int kd \log \lambda$$

where k is the molar extinction coefficient at wave length λ and μ^2 is measured in cm.^{2}. Application of this equation to the 14,100 cm.$^{-1}$ charge transfer band of Prussian blue yields the result $\mu = 1.23$ Å. The experimentally determined μ involves the $\mathrm{A_{ig}}$ ground state and the $\mathrm{T_{1u}}$ excited state and is equal to

$$\sqrt{2} \int \{\psi_\mathrm{C}(\mathrm{A_{1g}})\mathrm{C}^6(\mathrm{a_{1g}})\mathrm{N}^{30}(\mathrm{a_{1g}}) + \gamma\psi_\mathrm{N}(\mathrm{A_{1g}})\mathrm{C}^5(\mathrm{t_{2g}})\mathrm{N}^{31}(\mathrm{t_{2g}})\} \times \sum_i er_i\psi_\mathrm{N}(\mathrm{T_{1u}})\mathrm{C}^5(\mathrm{t_{2g}})\mathrm{N}^{31}(\mathrm{t_{1u}})\mathrm{d}\tau$$

where the factor $\sqrt{2}$ is amended because there is a second $\mathrm{T_{1u}}$ excited state, derived from $\mathrm{C}^5(\mathrm{t_{2g}})$-$\mathrm{N}^{31}(\mathrm{t_{2u}})$ which also should be included in the moment expression but which gives a contribution to the intensity equal to that expressed above. Because of the small overlap of d orbitals in the carbon and nitrogen holes, the moment expression may be shortened to

$$\mu = \gamma \sqrt{2} \int \psi_\mathrm{N}(\mathrm{A_{1g}})\mathrm{C}^5(\mathrm{t_{2g}})\mathrm{N}^{31}(\mathrm{t_{2g}}) \times \sum_i er_i\psi_\mathrm{N}(\mathrm{T_{1u}})\mathrm{C}^5(\mathrm{t_{2g}})\mathrm{N}^{31}(\mathrm{t_{1u}})\mathrm{d}\tau$$

If we now define atomic d orbitals in accord with Fig. 4, the abbreviated moment integral reduces to

$$\mu = 6\gamma \int \frac{1}{2\sqrt{3}} \{xy_\mathrm{C}[z_2 + z_3 + z_4 + z_5]_\mathrm{N} + yz_\mathrm{C}[x_1 + x_6 + x_4 + x_2]_\mathrm{N} + xz_\mathrm{C}[y_1 + y_6 + y_3 + y_5]_\mathrm{N}\} \times \sum_i er_i \frac{1}{2\sqrt{2}} \{xy_\mathrm{C}[z_3 - z_5 + x_1 - x_6]_\mathrm{N} + xz_\mathrm{C}[x_2 - x_4 + y_3 - y_5]_\mathrm{N}\}\mathrm{d}\tau$$

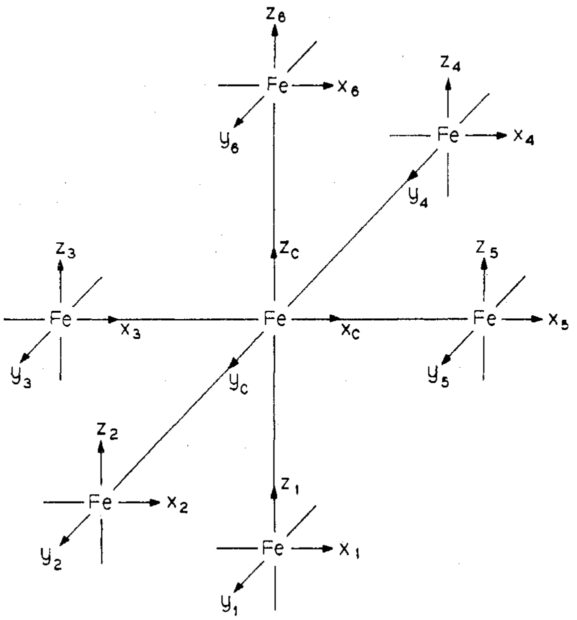

Fig. 4.—The coördinate axes used in defining the d orbitals encountered in a small piece of Prussian blue containing only one carbon hole iron ion and six iron ions in nitrogen holes octahedrally surrounding the carbon hole. The orbital y_5, for example, is an iron d orbital ($\mathrm{t_{2g}}$) centered in hole 5 with the line of intersection of its nodal planes parallel to the y axis.

where the factors $\sqrt{3}$ and $\sqrt{6}$ have been introduced to account for the fact that only one of the three $\mathrm{T_{1u}}$ components is present in the wave function in the integrand and that any one of six electrons can make the jump from a particular carbon hole to the adjacent nitrogen holes. Evaluation of the integral yields

$$\mu = \frac{(6\gamma)(2)(10.2)}{4\sqrt{6}} = 1.23\ \text{Å. or } \gamma = 0.10$$

This value of γ corresponds to the optical electrons being 99% localized in the carbon holes of Prussian blue in the ground state.

The earlier attempts to explain the color of Prussian blue as due to an "oscillation of valence" or resonance between the structures

$$\mathrm{Fe^{II}(CN)_6Fe^{III}} \longleftrightarrow \mathrm{Fe^{III}(CN)_6Fe^{II}}$$

thus are seen to be invalid.

As regards intensities in the Prussian blue dyes, it is curious that the intensities of the bands which involved transfer of an electron from $\mathrm{Fe^{II}}$, $\mathrm{Ru^{II}}$, or $\mathrm{Os^{II}}$ to the common acceptor $\mathrm{Fe^{III}}$ are quite nearly equal, while the intensities of the bands which involve transfer of an electron from $\mathrm{Fe^{II}}$, $\mathrm{Ru^{II}}$, or $\mathrm{Os^{II}}$ to the common acceptor $\mathrm{CN^{-1}}$ increase rapidly in the order $\mathrm{Fe^{II}}$, $\mathrm{Ru^{II}}$, $\mathrm{Os^{II}}$. These facts can be explained in part by assuming that in the hexacyanide ions, the strong perturbation of the metal ion by the ligands results in the mixing of the T_{1u} charge transfer configuration and the promoted configuration $nd^5(n + 1)p^1$. As a result of the mixing, the transition moment will depend in part on the integral

$$\int \psi(nd^6) \sum_i er_i \psi(nd^5(n + 1)p^1)d\tau$$

which integral increases with n. However, the predicted increase is only 20% of that observed, and it would appear that such a mechanism, if operative at all, is not the only one of importance. Nevertheless, as regards the above mechanism in the dyes, integrals of the above kind appear with only a very small weight since not only do the electrons involved in the mixing integral have a much smaller overlap, but ΔW is much larger.

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Chemistry of the Difluorides of Germanium and Tin

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BY E. L. MUETTERTIES

The difluorides of germanium and tin have been prepared in good yield by the reaction of the metals with hydrogen fluoride. Complexes of the difluorides with fluoride ion and with organic bases are described. The fluorocomplexes have the composition MF_3^-. The hydrolytic stability of GeF_3^- is greater than that of SnF_3^-; solutions of SnF_3^- slowly deposit crystalline SnO. All of the germanium and tin complexes, in solution, are oxidized by oxygen.

Germanium difluoride first was prepared by the reaction of Ge and GeF_4 above 100°.[1,2] Recently, we reported that germanium metal and hydrogen fluoride in a sealed vessel at 225° yield a mixture of GeF_2 and GeF_4.[3] By using stoichiometric amounts of reactants, this latter method serves as a simple, high-yield synthesis of GeF_2. In a similar fashion, stannous fluoride is quantitatively prepared at 200°; here excess hydrogen fluoride may be employed since this difluoride is not oxidized by hydrogen fluoride.

Germanium difluoride reacts exothermally with concentrated aqueous solutions of alkali metal fluorides, and crystalline trifluogermanites have been isolated from these solutions, *e.g.*, $CsGeF_3$ and $KGeF_3$. These complexes do not have the perovskite structure and this probably reflects the stereochemical significance of the non-bonding pair of electrons in GeF_3^-.[4]

Although GeF_3^- is hydrolytically stable, it does undergo very rapid exchange with fluoride ion. Aqueous solutions of $CsGeF_3$ and CsF show single F^{19} n.m.r. resonances which are between the GeF_3^- and the F^- resonances; the exact position is a function of the GeF_3^- and F^- concentrations. The fluostannite ion, described below, also was found to undergo fast exchange with fluoride ion.

Neutral aqueous solutions of $CsGeF_3$ absorb oxygen at a measurable rate at 25°, and in the presence of excess fluoride ion the final state of the germanium is the hexafluogermanate anion. Oxidation of the crystalline salt does not take place in the absence of moisture. In moist air or oxygen, oxygen absorption occurs and an orange color rapidly develops on the surfaces of the crystals. Oxidation of GeF_3^- takes a different course in strongly acid solutions in that hydrogen ion rather than oxygen is reduced. A solution of $CsGeF_3$ in 48% hydrofluoric acid rapidly evolves hydrogen and complete oxidation of GeF_3^- to $GeF_6^=$ takes only a few hours at 25°. Under acid conditions, oxidation may proceed through interaction of the proton with the non-bonding pair of electrons to give $HGeF_3$, which ultimately would yield hydrogen and $GeF_6^=$.

There have been several reports of fluoride

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(1) L. M. Dennis and A. W. Laubengayer, *Z. physik. Chem.*, **130**, 530 (1927).

(2) G. N. Bartlett and K. C. Yu, *Can. J. Chem.*, **39**, 80 (1961).

(3) E. L. Muetterties and J. E. Castle, *J. Inorg. & Nuclear Chem.*, **18**, 148 (1961).

(4) G. N. Bartlett and K. C. Yu, ref. 2, have shown that GeF_2 does not possess either of the two typical difluoride lattices (rutile and low quartz) but apparently is related to the SeO_2 structure. They suggest a pseudotetrahedral coördination for the germanium atom with three fluorine atoms and a non-bonding pair of electrons and a sharing of tetrahedra through fluorine atoms to give chains.