

The Synthesis and Properties of Binuclear Pentacyanoiron(III)- μ -Cyano-Amminetetrayanoiron(III) $[(C_6H_5)_4P]_4[(NC)_5Fe-NC-Fe(CN)_4NH_3] \cdot 6H_2O$

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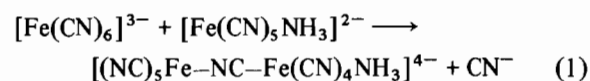
Abstract

The binuclear cyanoferrate, tetraphenylphosphonium pentacyanoiron(III)- μ -cyano-amminetetrayanoiron(III), $[(C_6H_5)_4P]_4[Fe_2(CN)_{10}NH_3]^{4-}$, was synthesized by air oxidation of aqueous solutions of $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$. Single crystal X-ray diffraction studies show the compound to contain the binuclear, cyano-bridged anion, $[(NC)_5Fe-NC-Fe(CN)_4NH_3]^{4-}$. This compound is structurally identical to the one prepared by A. Ludi *et al.*, [*Inorg. Chim. Acta*, 34, 113 (1979)], with the exception that $[Fe(CN)_6]^{3-}$ is not required for the synthesis of this compound. The Fe(III) atoms are antiferromagnetically coupled through the CN^- bridge, as shown by a maximum in the magnetic susceptibility at 50 K. The electronic and IR spectra of the complex in the solid state and in solution are discussed.

Introduction

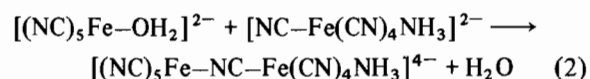
The nature of the cyano-bridged dimer that forms in solutions of a monosubstituted cyanoferrate, such as $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$, has been the subject of considerable investigation over the last two decades. Emschwiller and Legros postulated both single and double cyano-bridged dimers, on the evidence of elemental analysis of a lead precipitate of the dimer, and the absence of coordinated water in its IR spectrum [1]. Based on studies of the rate of substitution of pentacyanoferrates by uncharged ligands Asperger *et al.* ruled out the double-bridged dimer, and they proposed that the single-bridged dimer $[(NC)_5Fe-NC-Fe(CN)_4OH_2]^{6-}$, formed by two monosubstituted pentacyanoferrate ions, is present in solutions of $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ [2].

At about the same time Ludi *et al.* isolated and determined the structure of the binuclear cyanide-bridged complex (BCF), $[(NC)_5Fe-CN-Fe(CN)_4NH_3]^{4-}$, from solutions containing $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_5NH_3]^{2-}$ [3]. They proposed that the binuclear cyanoferrate complex came about by substitution of one cyanide ligand on the complex $[Fe(CN)_6]^{3-}$ by another cyanide group belonging to $[Fe(CN)_5NH_3]^{2-}$. The reaction they proposed:



rationalizes their X-ray structure, which shows five carbon atoms bonded to each iron center. However, the proposed reaction sequence requires the normally non-labile $[Fe(CN)_6]^{3-}$ to undergo a thermal substitution, while the normally labile $[Fe(CN)_5NH_3]^{2-}$ remains unaffected.

The formation of the BCF group can also be explained by less exotic cyanoferrate substitution reactions, the principal one being



That this pathway is reasonable is confirmed by our synthesis of the BCF group by air oxidation of aqueous solutions of $[Fe(CN)_5NH_3]^{3-}$ and isolation of the resulting BCF group (Fig. 1) as the tetraphenylphosphonium (TPP) salt. This compound is referred to as TPPBCF in this paper. Ferricyanide is *not* required for this synthesis, nor does its presence affect the nature of the product. At the beginning of our study, we believed it quite possible that the ammine ligand of TPPBCF might instead be water. To check this point we performed a single crystal X-ray structure of TPPBCF prepared in our laboratory.

In this paper, we provide a better understanding of the synthesis of TPPBCF and discuss its unusual

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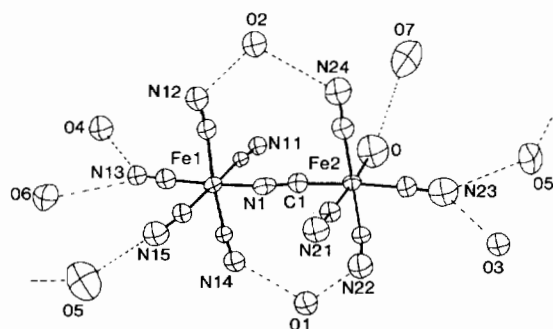


Fig. 1. ORTEP plot of $[\text{Fe}_2(\text{CN})_{10}\text{L}]^{4-}$ together with the oxygen atoms of hydrogen bonded water molecules. Unlabelled atoms are carbon. Dashed lines represent hydrogen bonds. The odd ligand ($\text{L} = \text{H}_2\text{O}$ or NH_3) is labelled O.

spectroscopic and magnetic properties. Variable temperature magnetic susceptibility studies show unequivocally that the bridging cyanide group mediates a moderate ($-J \sim 27 \text{ cm}^{-1}$) antiferromagnetic exchange interaction between the bridged Fe(III) atoms.

Experimental

The starting material for the synthesis of the cyanoferrate dimer was $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$, prepared according to a modification of Kenney *et al.* [4]. The resulting yellow powder was purified by washing the product with ethanol to remove unreacted nitroprusside and excess NaOH. It was then dried to constant mass over KOH, which absorbs alcohol but not NH_3 . A strong, sharp peak in the IR spectrum at 1247 cm^{-1} indicated that the NH_3 ligand was present [5].

Two mmol of aminopentacyanoferrate(II) were dissolved in 10 ml of distilled water. The oxidation of iron(II) to iron(III) was then effected by stirring air into the mixture for 15 minutes, resulting in a marked darkening of the solution. An excess (6 mmol) of $(\text{C}_6\text{H}_5)_4\text{PCl}$ in 20 ml of 2:1(v/v) water to ethanol was then added (the $(\text{C}_6\text{H}_5)_4\text{PCl}$ was obtained from the Alfa-Ventron Corp., and was used without further purification). Very slow evaporation of the solution over a period of a few days yielded dark green crystals of the compound tetraphenylphosphonium pentacyanoiron(II)- μ -cyanamminetetracyanoiron(III), (TPPBCF).

Elemental and Karl Fisher water analyses were done by Galbraith Laboratories, Knoxville, Tenn., U.S.A.

The infrared spectra of TPPBCF and tetraphenylphosphonium chloride, as 1% mixtures in KBr pellets,

Analytical Data

Element	Calcd. ^a	Found	Ludi <i>et al.</i> [3]
C	68.65%	69.82%	68.42%
Fe	6.02	6.31	6.02
P	6.68	6.99	6.78
H	5.16	5.15	5.12
N	8.31	8.33	8.31
H_2O	5.83	5.74	—

^aCalculated for $[(\text{C}_6\text{H}_5)_4]_4[\text{Fe}_2(\text{CN})_{10}\text{NH}_3] \cdot 6\text{H}_2\text{O}$. For an H_2O ligand instead of NH_3 , N = 7.55%, H_2O = 6.80%.

were recorded from 450 to 4000 cm^{-1} using a Perkin-Elmer 621 double-grating spectrophotometer, and a Perkin-Elmer 1500 Fourier-transform spectrometer.

Electronic absorption spectra of the cyanoferrate dimer were obtained from 360 to 750 nm using silica cells in a Cary 14 spectrophotometer. The electronic spectrum of the solid was obtained as a nujol mull on filter paper using nujol-saturated paper as a reference.

Magnetic susceptibility data were obtained using a Faraday balance over the temperature range 4.2–300 K. A correction was made for what is probably a small amount of paramagnetic impurity. The paramagnetic susceptibility at 4.2 K was assumed to be due only to the impurity, and it was further assumed that the susceptibility of the impurity could be fit by a C/T relation. The impurity is the equivalent of $\sim 3.5\%$ (mass) of $\text{K}_3[\text{Fe}(\text{CN})_6]$. The susceptibilities reported in this paper, χ_M , have been calculated as follows: $\chi_M = (\text{MW})(\chi_g) - \chi_{\text{DIA}} - \chi_{\text{IMP}}$, where MW is the molecular weight, χ_g is the gram susceptibility, χ_{DIA} is the diamagnetic susceptibility (-1000×10^{-6} cgsu/mol) and χ_{IMP} is the impurity susceptibility.

The Mössbauer spectrum of the binuclear cyanoferrate crystals was obtained using a constant acceleration drive with a 1.3 mCi Co-57 source, imbedded in a copper matrix, obtained from the New England Nuclear Co. The system was calibrated using enriched Fe-57. In order to obtain adequate resolution, a half-maximum velocity of 0.10 cm/sec was used which gave peak separations during runs of nearly 40 channels when data was stored in a Tektronix 400-channel analyzer.

A single crystal X-ray diffraction of TPPBCF gave the cell constants shown in Table I, indicating our compound was isomorphous with the compound prepared by Ludi *et al.* [3]. We hoped to resolve the ambiguity of whether the non-cyano ligand is water or ammonia by solving the structure. By means of an ENRAF-NONIUS CAD-4 diffractometer, 13,591 reflections were collected, of which 11,776 had an intensity greater than three standard

TABLE I. Comparison of the Crystal Parameters of Ludi *et al.* [3] and those of TPPBCF^a. Both are space group P1 with $Z = 1$.

Parameter	Ludi <i>et al.</i> ^b	TPPBCF ^{b, c}
a (Å)	12.828(5)	12.849(1)
b (Å)	14.214(8)	14.162(1)
c (Å)	14.148(5)	14.259(1)
α	92.66(4)°	92.77(1)°
β	103.72(3)°	104.72(1)°
γ	104.14(4)°	103.24(1)°
Density, g cm ⁻³	1.285(9)	1.299(3) ^d
Calculated density	1.282	1.275

^aCell constants obtained by automatic centering of 25 reflections. ^bThe uncertainty in the least significant figure is in parenthesis. ^cOur unit cell, arbitrarily chosen by the Enraf-Nonius CAD-4 program, differs from that of Ludi *et al.* ^dMeasured by neutral-bouyancy method.

deviations above background. These were used in the final least square refinement. The SHELX-76 Program Package was used for all crystallographic computations [6]. The positions of both iron atoms and many of the atoms in the inner coordination spheres were located by direct methods. All other atom positions except hydrogen were determined by difference Fourier syntheses. The final cycle of least squares refinement, using 11,776 reflections with unit weights, gave the conventional agreement factor $R = 12.2\%$. The atom positions agree with those of Ludi *et al.*, but our bond lengths are more precise, and there is greater uniformity in the length of equivalent bonds (Table II). Differences between our calculated and observed intensities show no trends.

TABLE II. Comparison of Bond Lengths of Equivalent Fe–C and C–N Bonds in our Refinement of the TPPBCF Structure with Those of Ludi *et al.* [3]. Uncertainties in the least significant figure are given in parentheses. All bond lengths are in Angstrom units.

Bond	This work	Ludi <i>et al.</i> ^a	Bond	This work	Ludi <i>et al.</i>
Fe1–C14	1.95(2)	C(51) 1.92(3)	C14–N14	1.14(2)	1.07(5)
Fe1–C12	1.96(2)	C(41) 1.93(4)	C12–N12	1.13(2)	1.19(5)
Fe2–C22	1.95(2)	C(42) 1.90(3)	C22–N22	1.20(2)	1.18(4)
Fe2–C24	1.94(2)	C(52) 1.88(4)	C24–N24	1.20(1)	1.28(7)
Fe1–C13	1.94(2)	C(31) 1.86(3)	C13–N13	1.16(2)	1.23(4)
Fe2–C23	1.90(2)	C(32) 1.91(4)	C23–N23	1.16(2)	1.11(5)
Fe1–C11	1.99(2)	C(21) 1.93(3)	C11–N11	1.10(2)	1.12(4)
Fe2–C21	1.79(2)	C(22) 1.85(6)	C21–N21	1.26(2)	1.20(7)
Fe1–C15	1.96(1)	C(11) 1.91(4)	C15–N15	1.17(2)	1.21(5)
Fe1–N1	1.96(2)	N(61) 1.90(2)	C1–N1	1.17(1)	1.16(2)
Fe2–C1	1.91(2)	C(62) 1.97(1)			
Fe2–O	1.96(2)	N(12) 2.08(4)			

^aThe orientation of the dimer and the numbering of atoms in Ludi *et al.*'s ORTEP plot differ from ours (Fig. 1). Ludi *et al.*'s designation of the equivalent C or N atom is given.

Complete structural details from our single-crystal X-ray analysis are not presented since they generally agree with those reported previously [3]. The main differences between our structure and the Ludi *et al.* structure are a few details of the hydrogen bonding scheme, including the occupancy factor of waters of crystallization, and the ambiguity that the ligand labelled O in Fig. 1 may be H₂O instead of NH₃, and the bond lengths of the cyano bridge. The latter will be discussed later. Details of the X-ray analysis results are available on request from the authors.

X-ray powder patterns of TPPBCF, prepared with and without K₃[Fe(CN)₆], were obtained using CuK α radiation with samples in 0.5-mm capillaries mounted in a Debye–Scherrer camera of 57.3-mm radius. Samples were exposed for four hours.

Table III lists the locations of the observed lines in the powder patterns of TPPBCF, and their probable assignments based on the measured intensities from the single crystal study. Where ambiguity occurs because of closely spaced calculated d -values, the assignment was made to the most intense calculated d -value of the region. No film lines were found that could not be attributed to at least one d -value of total relative intensity greater than 150.

Results and Discussion

No Role for Ferricyanide in TPPBCF Synthesis

The binuclear cyanoferrate(III), [(NC)₅Fe–NC–Fe(CN)₄NH₃]⁴⁻ (BCF), forms when a concentrated solution of pentacyanoferrate(II) is air-oxidized to Fe(III). One pentacyanoferrate(III)-ion replaces its non-cyano ligand with the nitrogen end of the cyano ligand of a second pentacyanoferrate-ion, forming

TABLE III. Observed Lines in the X-ray Powder Pattern of TPPBCF, the Most Intense Reflection with d -values Calculated from Single-crystal Analysis, and Its Observed Intensity Taken from the Single-crystal X-ray Determination.

Line	d -values		h	k	l	Intensity ^c
	obs. ^a	calc. ^b				
1	10.16	10.257	0	1	-1	151
2	9.07	8.955	1	-1	-1	167
3	7.87	7.820	-1	1	-1	121
4	6.81	6.726	1	0	-2	309
5	6.13	6.096	2	-1	-1	235
6	5.28	5.177	2	2	-1	276
7	4.67	4.589	0	2	2	402
8	4.42	4.378	-2	-1	-1	251
9	4.16	4.183	2	0	-3	245
10	3.95	3.982	-3	1	2	297
11	3.60	3.532	-1	0	4	358
12	3.42	3.419	0	3	-3	278
13	3.27	3.304	-3	2	3	243
14	3.05	3.065	4	-2	0	224
15	2.35	2.358	2	3	-5	312
16	2.26	2.262	4	-3	3	235
17	2.02	2.022	3	-3	5	207

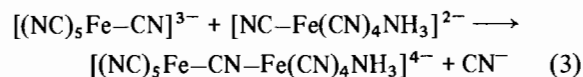
^aIn Angstrom units. The estimated uncertainty in the d -value varies from 0.17 Å for line 1 to 0.01 Å for line 17.

^bUsing the cell constants reported in this paper. ^cIn units of (electrons)² based on our single crystal work.

a cyanide bridge, as given in eqn. 2. The binuclear anion is then isolated from solution as a tetraphenylphosphonium salt. The structure of the BCF was first determined by Ludi *et al.*, who have shown that the CN-bridge has a preferred direction (Fig. 1) such that each iron atom is bound to five carbon atoms of cyano ligands and to one nitrogen atom [3]. For one iron atom this is the nitrogen atom of the bridging cyanide, and for the other it is ammonia (or water).

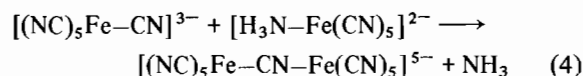
In the reported synthesis of BCF [3] where both $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_5\text{NH}_3]^{2-}$ were present in the starting solution, there are three conceivable paths by which both these ions become part of BCF through the breaking of one iron-to-ligand bond. According to Ludi *et al.*, normally stable ferricyanide has one of its cyano ligands replaced by the nitrogen-end of a cyano ligand from $[\text{Fe}(\text{CN})_5\text{NH}_3]^{2-}$, as shown in eqn. 1. This hypothetical reaction would account for the structure of BCF, with the CN-bridge in the direction required by the single crystal X-ray structure determination. However, Ludi *et al.*'s reaction sequence requires the unprecedented thermal substitution of a cyano ligand of ferricyanide.

Secondly, if a cyano ligand on the $[\text{Fe}(\text{CN})_5\text{NH}_3]^{2-}$ was replaced by the N-end of a cyano ligand of $[\text{Fe}(\text{CN})_6]^{3-}$ according to the reaction



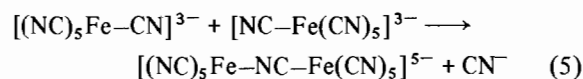
the direction of the CN-bridge would be opposite to that observed.

The third alternative is the reaction in which the pentacyanoferrate(III) loses the NH_3 ligand to give $[\text{Fe}_2(\text{CN})_{11}]^{5-}$ by the reaction

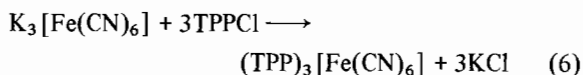


However, no isolatable solid containing the $[\text{Fe}_2(\text{CN})_{11}]^{5-}$ anion has yet been characterized.

If ferricyanide were sufficiently thermally labile to self-dimerize according to the reaction



a single CN-bridged complex (identical to that in eqn. 4) would result. But, addition of tetraphenylphosphonium chloride (TPPCL) to a solution of $[\text{Fe}(\text{CN})_6]^{3-}$ produces a yellow solid whose IR spectrum has the band of a terminal CN-stretching to Fe(III), but not that of a bridging CN band. Moreover, the existence of $(\text{TPP})_3[\text{Fe}(\text{CN})_6]$ has already been reported [7], and it seems to be formed when TPPCL is added to $[\text{Fe}(\text{CN})_6]^{3-}$, by the metathesis reaction



Thus, ferricyanide does not become part of a binuclear cyanoferrate by thermal substitution, and there is no evidence that it takes part in the synthesis of TPPBCF or is in any way necessary in the synthesis. Regardless of whether ferricyanide is in solution with $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$, the X-ray powder patterns and the IR spectra of the products are identical. Furthermore, synthesizing TPPBCF from 2 mmol of $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ and 6 mmol of TPPCL yields twice as much TPPBCF as does starting with 1 mmol each of $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.

The Reaction Sequence

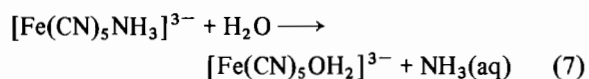
That pentacyanoferrate(II) forms dimers in solution has been assumed by several authors, most recently Asperger *et al.* [2]. The possibility of isolating a binuclear cyanoferrate dimer in the Fe(II) state was investigated by preventing oxidation of $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ in solution. After aminopenta-

cyanoferrate(II) was dissolved in N₂-saturated water, the reaction was carried out under nitrogen atmosphere, and the solution remained a light brown, probably indicating that only cyanoferrate(II) was present. Addition of TPPCl to this did not yield a precipitate, perhaps because of the high negative charge (-6), which would be required for a cyanoferrate(II) dimer. Having found that a solid dimer with Fe(II) could not be obtained, we purposely aerated the reaction solutions to oxidize the cyanoferrate to Fe(III).

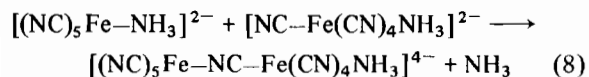
Since refinement of single crystal X-ray data has not shown conclusively whether the non-cyano ligand of TPPBCF is NH₃ or H₂O, there is a question whether [Fe(CN)₅OH₂]²⁻, or [Fe(CN)₅NH₃]²⁻, or both form the dimer in the reaction solution. Analytical data from nitrogen and Karl Fisher water analyses support NH₃ rather than H₂O as the odd ligand in BCF.

Starting with [Fe(CN)₅NH₃]³⁻, which is purported to undergo aquation to [Fe(CN)₅OH₂]³⁻, we tried unsuccessfully to remove NH₃ from our reaction mixture through degassing by aspiration. Not only is ammonia not removed quantitatively from solution by the procedure, but substitution of H₂O for NH₃ may be quite incomplete at the concentration in which the BCF synthesis is carried out. This is currently under investigation [8].

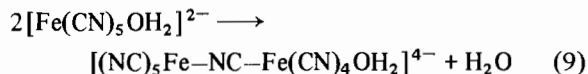
Most kinetic studies of the substitution reactions of pentacyanoferrates have started with millimolar concentrations of [Fe(CN)₅NH₃]³⁻. At a millimolar concentration the ammine-complex is presumed to convert readily to the aquo-complex, which is involved in the substitution reactions [2, 9, 10] although the NH₃ may remain in the solution. In the preparation of TPPBCF, however, the concentration of the ammine-complex is 0.2 M. If [Fe(CN)₅NH₃]³⁻ is only slightly labile, and the reaction



proceeds very slowly in concentrated solution, then solutions in this preparation contain a mixture of the aquo- and ammine-pentacyanoferrates. The aquo is assumed to be quite labile, and after air oxidation the reaction forming the dimer may be the one given by eqn. 2. This would account for NH₃ being the ligand O (in Fig. 1), and would also make use of the greater lability of the aquo-complex in bringing about the dimer formation. The possibility that the BCF is formed directly from [Fe(CN)₅NH₃]²⁻ according to the reaction

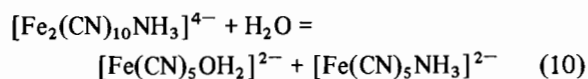


cannot be ruled out at this time [8]. Nor for that matter can we rule out that the dimer complex forms from aquopentacyanoiron(III) by the reaction



The Electronic Spectra

Crystals of TPPBCF are dark green, but when dissolved in water or ethanol the solution is purple. The dilute, purple solution probably results from a shift of equilibrium from the Fe(III) dimer to the Fe(III) monomer, according to the equation



The electronic spectra are shown in Fig. 2. The visible spectrum of the aqueous solution has three

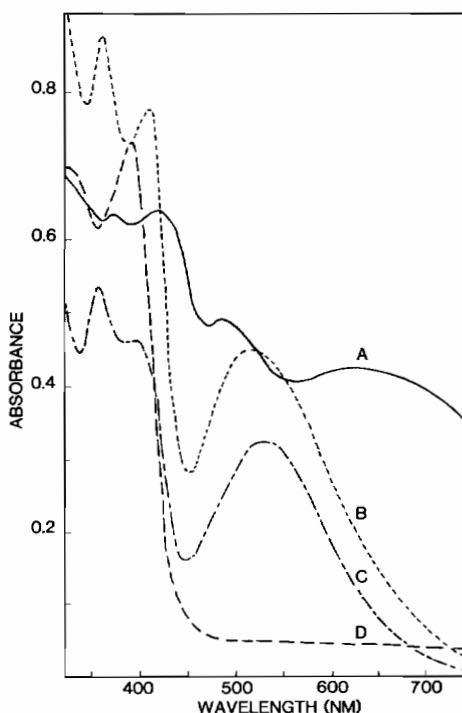


Fig. 2. Electronic spectra of TPPBCF (A), [Fe(III)(CN)₅OH₂]²⁻ in ethanol (B), [Fe(III)(CN)₅OH₂]²⁻ in water (C), [Fe(II)(CN)₅NH₃]³⁻ in water (D), (A, B, C) from this work, (D) from [9].

maxima, at 360, 395 and 530 nm. The low solubility of TPPBCF in water at room temperature (~1 × 10⁻⁴ M) made it difficult to obtain accurate extinction coefficients. The dimer dissolves more readily in ethanol, with the peaks shifted to 360 nm (ε = 3300 M⁻¹ cm⁻¹), 410 nm (ε = 2940 M⁻¹ cm⁻¹) and 515 nm (ε = 1700 M⁻¹ cm⁻¹), where the ex-

tion coefficient, ϵ , has been calculated per mol of Fe^{3+} . Gale and McCaffery report a spectrum of $[\text{Fe}(\text{CN})_5\text{OH}_2]^{2-}$ with peaks at 285, 360, 395 and 570 nm. Their extinction coefficients are about $3000 \text{ M}^{-1} \text{ cm}^{-1}$, and the absorbances have been assigned as $L(\pi) \rightarrow M(t_{2g})$ transitions [11].

Our spectrum of a freshly prepared solution of TPPBCF may be the sum of the spectra of these two pentacyanoferrate(III) monomers. The Gale and McCaffery spectrum of room temperature aqueous $[\text{Fe}(\text{CN})_5\text{NH}_3]^{2-}$ is quite different from that of $[\text{Fe}(\text{CN})_5\text{OH}_2]^{2-}$ in that there is no 4th lower energy transition given [11], and there does not appear to be a well-documented spectrum of $[\text{Fe}(\text{CN})_5\text{NH}_3]^{2-}$ in the literature.

The spectrum of the solution changes on standing overnight (D in Fig. 2). The resulting solution has its lowest energy peak around 390 nm, and its spectrum resembles that reported by Toma *et al.* for the amminepentacyanoferrate(II) [10]. However, the aquopentacyanoferrate(II) is expected to be formed under these conditions, and Toma *et al.* report the lowest energy absorption peak of $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$ to be at 440 nm [10]. This is a curious result.

The spectrum of the dark green crystals of TPPBCF consists of four overlapping peaks resulting in maxima at 370, 420, 485 and 625 nm (A in Fig. 2). The spectrum of BCF can be interpreted in terms of the two different chromophores in the dimer, $\text{FeC}_5(\text{NC})$ and $\text{FeC}_5(\text{NH}_3)$. The electronic absorption

spectra of various chromophores of $[\text{Fe}(\text{CN})_5\text{X}]^{n-}$ ($n = 2$ for $\text{X} = \text{H}_2\text{O}, \text{NH}_3$; $n = 3$ for $\text{X} = \text{N}_3, \text{NCS}, \text{NCSe}$) have been interpreted [11, 12]. There are three charge transfer bands $[\text{CN}(\sigma, \pi) \rightarrow M(t_{2g})]$ characteristic of $[\text{Fe}(\text{CN})_6]^{3-}$, the parent ion, that are usually observed as well as an additional lower-energy band $[\text{X}(\pi) \rightarrow M(t_{2g})]$, which are shown in Table IV.

In the case of BCF, at least the most energetic charge transfer band $[\text{CN}(\pi) \rightarrow \text{Fe}(t_{2g})]$ is probably below 340 nm, as it is for all this series, and was not recorded from our nujol sample. Corresponding ligand-to-metal charge transfer bands of each chromophore are not always of exactly the same energy (Table IV), thus making assignment of the TPPBCF bands plausible at best. The three remaining transitions $\pi(\text{CN}) \rightarrow t_{2g}(\text{Fe})$, $\sigma(\text{CN}) \rightarrow t_{2g}(\text{Fe})$, and $\pi(\text{NH}_3 \text{ or } \text{NC}) \rightarrow t_{2g}(\text{Fe})$ of each of the two chromophores, $\text{FeC}_5(\text{NH}_3)$ and $\text{FeC}_5(\text{NC})$, can be assigned to the four absorption peaks of TPPBCF, as shown in Table IV. By analogy with $\text{X} = \text{OH}_2$ it seems reasonable to assign the second transition of both chromophores to the 370 nm maximum. The filled $\pi(\text{NH}_3)$ -orbital is assumed to be lower in energy relative to $t_{2g}(\text{Fe})$ than $\pi(\text{NC})$. This is assuming that the $\pi(\text{NC})$ -orbital is similar in energy to the $\pi(\text{NCS})$ -orbital, as shown in Fig. 8 of reference 11[†].

The Binuclear Anion Structure

A few details of the bond lengths of BCF are noteworthy. In our structure determination of BCF we found the Fe–C bond length {1.907(20) Å} 0.05 Å shorter than the Fe–N bond length {1.957(17) Å}. However, these differences may not be statistically significant at the 3 σ level. Our result is in contrast to Ludi *et al.*'s {Fe–C 1.97(1) Å and Fe–N 1.90(2) Å} (Table II). In a structural determination of $[(\text{NH}_3)_5\text{Co–NC–Co}(\text{CN})_5]$, Schaefer *et al.* found the Co–C bond length (1.886 Å) 0.04 Å shorter than the Co–N bond length (1.921 Å) [15].

In our structure the Fe–C bond trans to the Fe–NH₃ is significantly shorter (0.06 Å) than the average Fe–C bond, 1.95(2) Å, to any other terminal cyanide. This effect, signifying a stronger Fe–C bond, is attributed to the greater availability of π -electrons in this Fe atom in the direction of back π -bonding to the cyano ligand, since no π -bonding on the opposite side of the bond to NH₃ is possible.

TABLE IV. The Wavelength Maxima of Ligand-to-metal (t_{2g}) Charge Transfer Bands of TPPBCF and of Several Cyanoferrates $[\text{Fe}(\text{CN})_5\text{X}]^{n-}$ as Assigned in refs. 11 and 12.

X^a	(1) λ^b nm	(2) λ^b nm	(3) λ^b nm	(4) λ^b nm	Source
CN	260	303	426	e	[12] ^d
NH ₃	289	371	393	e	[11]
NH ₃ ^f	g	370	420 ^h	485 ^h	this work
NCS	265	323	350	521	[12] ^d
N ₃	283 ⁱ	305 ⁱ	418	556	[12] ^d
OH ₂	287	361	406	570 ^j	[11]
OH ₂	g	360	395	530	this work
NCSe	323	353	397	598	[12] ^d
NC ^f	g	370	420	625	this work

^aLigand is bound to the metal by its first atom. ^b(1 and 2) $\pi(\text{CN}) \rightarrow t_{2g}$; (3) $\sigma(\text{CN}) \rightarrow t_{2g}$; (4) $\pi(\text{X}) \rightarrow t_{2g}$. ^cIn $[\text{Fe}(\text{CN})_6]^{3-}$ the highest filled ligand orbital is degenerate. ^dIn EPA. ^e4th transition not given. ^fFrom spectrum of TPPBCF. ^gSpectra here not recorded below 340 nm. ^hThe 420 nm peak may be the 4th transition of $\text{FeC}_5(\text{NH}_3)$, and the 485 nm peak the 3rd transition of $\text{FeC}_5(\text{NC})$. ⁱ λ_{max} given without assignment. ^jEstimated from Fig. 5 of ref. 11.

[†]H. B. Gray [13] suggested that the 625 nm peak could be σ or $\pi(\text{H}_2\text{O}) \rightarrow t_{2g}(\text{Fe})$ if the ligand is H₂O. But nitrogen and water analyses of TPPBCF do not fit the composition where the ligand O is water. A peak at 625 nm has been observed in a mixture of $[\text{Fe}(\text{CN})_5\text{OH}_2]^{2-}$ and its dimer [14].

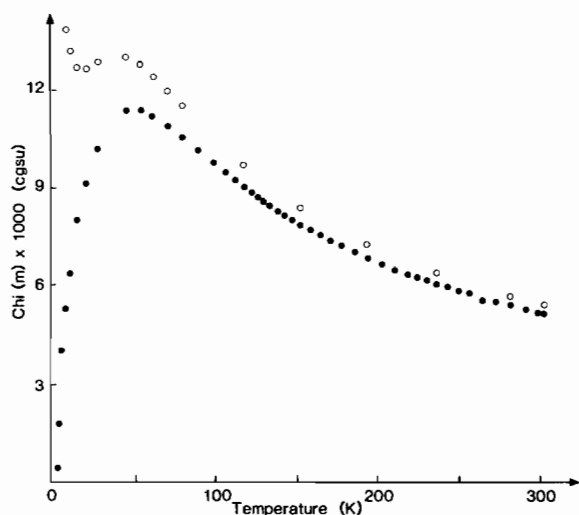


Fig. 3. Magnetic susceptibility per mol of dimer vs. absolute temperature for TPPBCF. Data corrected for paramagnetic impurity are shown as filled circles. A few data uncorrected for this impurity are shown as open circles.

Magnetic Properties

Figure 3 displays the results of magnetic susceptibility studies. The room temperature magnetic moment per mol of iron, $\mu = (4\chi_M T)^{1/2}$, is 2.48 B.M., a value typical of low spin Fe(III) compounds; for $K_3[Fe(CN)_6]$ $\mu = 2.24$ B.M. [16]. An excellent fit of the Curie-Weiss expression, $\chi_M = C(T - \theta)^{-1}$, to the data with $T \geq 100$ K is obtained with $C = 2.193$ and $\theta = -125$ K. Ludi *et al.* report values of $\mu(300 \text{ K}) = 2.50$ B.M. and $\theta = -104$ K in good agreement with our results [3].

The maximum in the susceptibility at 50 K suggests an intra-dimer antiferromagnetic exchange interaction between the iron atoms of TPPBCF*. Unfortunately, the ground state orbital degeneracy of the low-spin d^5 ions leads to significant spin-orbital coupling—as demonstrated by the considerable deviation of the magnetic moment from the spin-only value of 1.73 B.M.—and seriously complicates the analysis of the data [17, 18]. All attempts at fitting a simple, spin-only dimer susceptibility equation failed, and a mathematical model for the low-spin d^5 dimer does not appear in the literature. Still, a very rough estimate of the magnitude of the exchange interaction can be obtained from the location of the susceptibility maximum. For a spin-only dimer the coupling constant J is equal to $-0.55 T_{\max} (\text{cm}^{-1})$ where $-2J$ is the single-triplet state energy difference [19]. The value obtained in this manner for TPPBCF, $J \sim -27 \text{ cm}^{-1}$, indicates a moderately strong antiferromagnetic Fe-Fe interaction. Figure 5 of

*Ludi *et al.* [3] report "a possible phase transition ... at 40 K."

reference 19 suggests that the true coupling constant will be in the order of 25% larger (less negative) than the J calculated above, but a more quantitative conclusion awaits further analysis.

There is no doubt that the antiferromagnetic interaction in this compound is mediated by the bridging cyano group; the large Fe-Fe distance (5.03 Å) precludes any direct overlap of iron orbitals. As the iron atoms are low spin, the exchange pathway must involve the overlap of the iron t_{2g} orbitals with the π orbitals of the bridging cyano group. Coupling constants from -4 to -88 cm^{-1} have been reported for cyanide bridged Cu(II) dimers [20]. To our knowledge, no other magnetic susceptibility studies of cyanide-bridged metal dimers have been reported.

The IR Spectra

The IR spectrum of the product provides a relatively easy means of establishing the oxidation state of iron, as well as the presence of a cyano bridge.

The principal peaks of interest in the IR spectrum of TPPBCF are presented in Table V, and the spectrum is shown in Fig. 4. Only peaks arising from the structure of the anion are of concern here.

TABLE V. Selected Details of the Infrared Spectrum of TPPBCF as 1% Mixtures in KBr Disks.

Wavenumber (cm^{-1})	% Transmittance	Assignment
~ 3500	8.6	OH stretching
2159	64.7	CN bridging
2111	9.8	CN terminal
1247	66.1	NH_3 bending

The very broad water band in the 3500 cm^{-1} region is due to hydrogen bonding waters of crystallization. The terminal CN at 2111 cm^{-1} has the position and shape to confirm that Fe(III), but not Fe(II), is present. The smaller peak at 2159 cm^{-1} is due to the bridging ligand [21].

If the ligand O (Fig. 1) is NH_3 then the sharp bending peak of NH_3 at 1250 cm^{-1} , characteristic of ammine-pentacyanoferrate(II), might be expected in the IR spectrum of the dimer [5]. Instead a weak, broad peak is observed at 1247 cm^{-1} (Table V), a region where there is no TPPCl adsorption. The drastic change in intensity and shape of the NH_3 bending vibration may be due to the smaller ammonia-to-cyanide ratio in TPPBCF (1:10) than in $\text{Na}_3[Fe(CN)_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ (1:5). The hydrogen bonding of this O-ligand (Fig. 1) to water might account for the broadening of the NH_3 vibration.

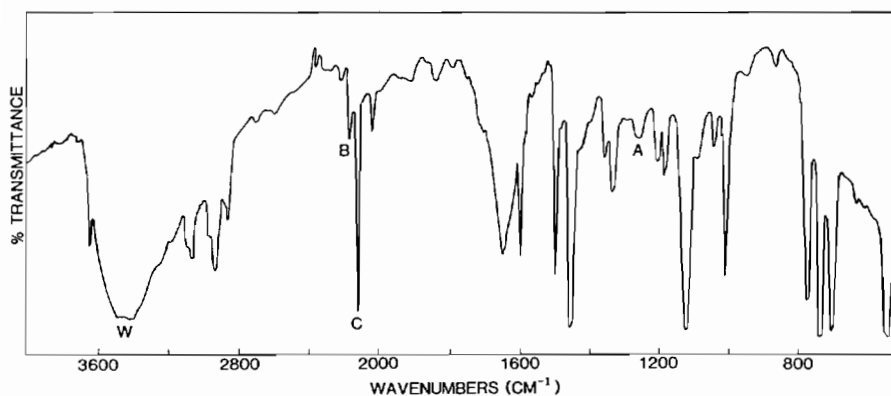


Fig. 4. The IR spectrum of TPPBCF recorded on an FTIR showing heavily hydrogen bonded waters of crystallization at 3500 cm^{-1} (W), the CN-bridging peak at 2159 cm^{-1} (B), the peak due to terminal cyanides at 2111 cm^{-1} (C), and the peak attributed to the NH_3 ligand (scissors vibration) at 1247 cm^{-1} (A). Unmarked peaks are those of the TPP cation.

The Mössbauer Effect

The Mössbauer spectrum we obtained for TPPBCF shows two distinct isomer shifts, thus supporting the hypothesis of two different iron centers. Each of these has quadrupole splitting because of the d^5 configuration of Fe(III). Roder and VanSteenwijk have described the Mössbauer spectrum of TPPBCF [22], and the ratio of two quadrupole splittings obtained in our study at room temperature is the same as theirs.

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