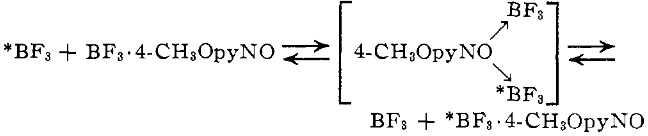
creases.[4,10] Again, the conclusion must be that $J_{^{11}\text{B}-^{19}\text{F}}$ is negative.

These discussions should not be misconstrued to suggest that the differences in hybridization and bond polarity are large, but, rather, the fact that such very small effects can result in such large relative differences in the coupling only reinforces the idea that two very large opposing mechanisms are operative.

Examination of the chemical shift data (Table II) for the 4-substituted pyridine 1-oxides shows that there is essentially no difference in the chemical shift arising from a difference in basicity. In going from 4-methoxy- to 4-nitropyridine 1-oxide there is only a 0.8-ppm change in chemical shift, whereas the change in pK_a is 3.8.[9] This same constancy in chemical shift is observable for 3,5-dimethylpyridine 1-oxide, as well as the series of 4-substituted quinoline 1-oxides. However, δ for the quinoline 1-oxides is about 1 ppm lower than the corresponding pyridine 1-oxides but is about the same as δ for the 2-substituted pyridine 1-oxides. This is not a surprising result, since quinoline 1-oxides are essentially "2-substituted" pyridine 1-oxides. Referring to Table II once more, δ for acridine 1-oxide is very nearly equal to δ for 2,6-dimethylpyridine 1-oxide; again the positions substituted are the same. Consequently, the chemical shift appears to be a reflection of the bulky nature of the ligand and its interaction with the fluorines.

The spectra represented in Figure 1 show a definite temperature dependence. Rapid exchange of fluorine among the boron atoms is occurring since there is a collapse of the quartet at high temperatures (Figure 1c, d). A possible mechanism for the fluorine exchange is a simple dissociation of the complex and, for discussion, is exemplified by use of the 4-CH$_3$OpyNO complex, $\text{BF}_3\cdot\text{4-CH}_3\text{OpyNO} \rightleftarrows \text{BF}_3 + \text{4-CH}_3\text{OpyNO}$. Addition of excess ligand causes the quartet structure to be maintained, even at high temperatures (Figure 1e, f). With added BF$_3$ the same result might be expected; however, the quartet is collapsed even at low temperatures. As a result, in addition to the above mechanism, it is suggested that the following mechanism is also operative



$$\text{*BF}_3 + \text{BF}_3\cdot\text{4-CH}_3\text{OpyNO} \rightleftarrows \left[\text{4-CH}_3\text{OpyNO}\begin{smallmatrix}\nearrow\text{BF}_3\\ \searrow\text{*BF}_3\end{smallmatrix}\right] \rightleftarrows \text{BF}_3 + \text{*BF}_3\cdot\text{4-CH}_3\text{OpyNO}$$

The proposed 1-oxide bridge intermediate is not without precedent. It has been demonstrated through X-ray studies that a bridging oxygen is involved in the copper complex of pyridine 1-oxide.[11]

Further support for the proposed exchange mechanisms can be gained from the following considerations. It was not possible to measure the boron–fluorine coupling constant directly for the aromatic amine 1-oxide–boron trifluoride adducts where the donor molecule had deactivating substituents such as the nitro or cyano groups. It was also necessary to estimate J for the adducts which involved the bulky ligands: 2,6-dimethylpyridine 1-oxide, the quinoline N-oxides, and acridine N-oxide. For the dissociation $\text{BF}_3\cdot\text{base} \rightleftarrows \text{BF}_3 + \text{base}$, the equilibrium constant would be larger for the weaker bases and the bulky donor molecules. A larger equilibrium constant would enhance the rate of exchange and would account for the loss of fine structure in the fluorine spectra of the above complexes.

In all the spectra recorded a small, broad singlet appeared (150.5–151.0 ppm). The magnitude of this peak is dependent on the strength of the base being used, the largest for the strongest base. A possible explanation for this observation is dehydrofluorination, resulting in a reduced fluorine-containing species.

Acknowledgment.—Support of this work by th Reesearch Corp. is gratefully acknowledged.

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[11] R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

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Isotopic Labeling for Mössbauer Studies. An Application to the Iron Cyanides[1]

BY A. K. BONNETTE, JR., AND JOE F. ALLEN*

Received September 29, 1970

The overlapping resonance absorption peaks in the Mössbauer spectra for iron atoms in the iron cyanides have been simplified by selective labeling with Mössbauer-inactive isotopes and with enriched, Mössbauer-active ^{57}Fe. The spectra for each of the three iron environments in Turnbull's and Prussian blues have been shown independently of each other, and in all cases the spectra for the two blues are the same. This isotopic labeling technique may be applied to any compounds containing a Mössbauer-active element in more than one chemical environment if suitable labeling techniques may be derived.

Mössbauer spectroscopy has been applied to the studies of solid compounds of iron, tin, etc., and has been a great aid in attaining a better understanding of the nature of the compounds studied. However, in compounds containing an element in more than one chemical environment, *e.g.*, mixed oxidation states, the interpretations of the Mössbauer spectra are not always clear-cut because of difficulties in interpreting the overlapping absorption peaks. Milligan, *et al.*,[2] have used selective isotope labeling with Mössbauer-active,

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[1] Presented in part to the South Carolina Academy of Sciences, Columbia, S. C., April 24, 1970.

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

enriched ^{57}Fe to distinguish between the spectra of the iron environments in Prussian and Turnbull's blues. The nature of the iron cyanides, especially those called Prussian blue and Turnbull's blue, has been studied extensively,[3–5] and a good review of much of this work is given by Robin and Day.[6]

The purpose of this paper is to demonstrate that the Mössbauer spectrum of a compound having one element in multiple environments can be simplified by labeling one or more of these environments with a Mössbauer-inactive isotope. Thereby, the spectrum for each of the individual environments can be observed. Enriched ^{56}Fe was chosen as the Mössbauer-inactive isotope because of its low price and ready availability, while natural iron (containing 2.19% ^{57}Fe) or enriched ^{57}Fe was used to label the Mössbauer-active positions. Specifically, this technique has been applied to the iron cyanides to show the spectra of the three possible environments in insoluble Prussian blue, $Fe^{3+}[Fe^{3+}Fe^{II}(CN)_6]_3$, to show some of the mutual interactions of these ions, and to supply additional evidence for the identity of Prussian blue ($Fe^{3+} + Fe^{II}(CN)_6^{4-}$) and Turnbull's blue ($Fe^{2+} + Fe^{III}(CN)_6^{3-}$).

Experimental Section

Preparation of Samples.—All samples were prepared at room temperature by the addition of 0.1 *M* ferric or ferrous chloride or sulfate solutions to a 0.1 *M* solution of potassium ferrocyanide or potassium ferricyanide. The solutions were kept slightly acidic to prevent formation of $Fe(OH)_3$. All samples, except for those in which the interstitial iron only was Mössbauer active, were allowed to stand in contact with their parent solutions for 3 days, after which they were washed five times with about 5 ml of H_2O and dried under vacuum. All reagents except the enriched iron isotopes were of reagent grade. The enriched iron isotopes were obtained from the Isotopes Development Center at the Oak Ridge National Laboratory.

Cation Environments Labeled with ^{56}Fe.—In order to see the peaks in the Mössbauer spectra corresponding to the two chemical environments in Berlin green and the three environments in Prussian blue and Turnbull's blue, selective labeling with Mössbauer-inactive ^{56}Fe was carried out. Samples of enriched $^{56}Fe_2O_3$ (99.93% ^{56}Fe) were dissolved in hot concentrated HCl and diluted to the desired volume with water. The resultant $^{56}Fe^{3+}$ solution was used to precipitate Prussian blue by addition to a freshly prepared solution of $K_4Fe(CN)_6$ and to precipitate Berlin green, $Fe^{3+}Fe^{III}(CN)_6$, by addition to a freshly prepared $K_3Fe(CN)_6$ solution. The Turnbull's blue preparation required reduction of $^{56}Fe^{3+}$ to $^{56}Fe^{2+}$ by SO_2. Excess SO_2 was expelled from the freshly prepared $^{56}Fe^{2+}$ solution with nitrogen gas. The $^{56}Fe^{2+}$ solution thus made was added to freshly prepared 0.1 *M* $K_3Fe(CN)_6$ to give the compound referred to as Turnbull's blue.

Anion Environments Labeled with ^{56}Fe.—In order to observe the Mössbauer spectrum of the cationic iron environments independent of the low-spin (carbon hole) environments, solutions of $K_4{}^{56}Fe(CN)_6$ and $K_3{}^{56}Fe(CN)_6$ were prepared. A solution of $^{56}Fe^{2+}$ was prepared as above under a nitrogen atmosphere and was added slowly with vigorous stirring to 100 ml of a saturated solution of KCN to produce $K_4{}^{56}Fe(CN)_6$. A second $^{56}Fe^{2+}$ solution was treated similarly, but the undried $K_3{}^{56}Fe(CN)_6$ was dissolved in water and treated with Cl_2 for 3–5 min to produce $K_3{}^{56}Fe(CN)_6$. If Cl_2 were too long in contact with $K_4Fe(CN)_6$ solution, a green solid was formed. The products were purified by repeated recrystallization from alcohol-water solutions. X-Ray diffraction patterns of the $K_4{}^{56}Fe(CN)_6$ and $K_3{}^{56}Fe(CN)_6$ were identical with those of spectra of the known compounds. Prussian blue, Turnbull's blue, and Berlin green were then prepared from these labeled compounds by the addition of solutions of Fe^{3+} or Fe^{2+} as described above.

Interstitial Environment Labeled with ^{57}Fe.—The interstitial iron environment was made Mössbauer active, independent of the other environments, by first preparing "soluble" Prussian blue by mixing equimolar quantities of $^{56}Fe^{3+}$ and $^{56}Fe(CN)_6{}^{4-}$. The blue precipitate was coagulated with acetone and then washed ten times with water. Then 5 ml of a 0.1 *M*, enriched, Mössbauer-active $^{57}Fe^{3+}$ (69.60% ^{57}Fe) solution was contacted with the blue precipitate for 3 days. The $^{57}Fe^{3+}$ solution was removed and the precipitate was washed five times with water and dried under vacuum. The ^{57}Fe-labeled interstitial position of Turnbull's blue was prepared in a similar manner, beginning with $^{56}Fe^{2+}$ and $K_3{}^{56}Fe(CN)_6$, followed by the addition of Mössbauer-active $^{57}Fe^{3+}$.

Mössbauer Spectra.—The Mössbauer spectra were obtained on an electromechanical constant-acceleration spectrometer built and operated at the USAEC Savannah River Laboratory, Aiken, S. C. The radiation source had the following characteristics (on Feb 24, 1969): 10 mCi of ^{57}Co in copper, electroplated onto 6-mm diameter, active area of 12.8-mm diameter, foil 25 μ thick, annealed at 1100° for 3 hr in hydrogen, and quenched. The source was obtained from the New England Nuclear Corp.

The transmission spectra were obtained using a Reuter-Stokes, RSG-30A krypton-methane filled proportional counter and associated components to limit detection to only the resonant 14.37-keV γ ray. The transmitted radiation was registered in a RIDL Model 34-12 B 400 channel analyzer operated in the multiscaler mode and in synchronization with the velocity-modulated radiation source.[7] The spectrometer was calibrated with Fe_2O_3, iron metal, and sodium nitroprusside. The average velocity increment was 0.128 mm/sec.

The samples to be studied were placed in brass disks and covered with 0.25-mil Mylar film. The sample thickness varied from 0.1 to 1 mm with a diameter of 10 mm. All samples were run at a room temperature of about 25°. The isomer shift is referred to an iron metal source with the center of an Fe_2O_3 standard used as the zero point. Both the isomer shift and the quadrupole splitting have a probable error of about 0.06 mm/sec.

Results and Discussion

The spectrum of Prussian blue samples prepared from natural iron has been described elsewhere,[2,6] and the Turnbull's blue spectrum has been shown to be essentially identical with that of Prussian blue. The Mössbauer spectra of the three iron environments (carbon hole, nitrogen hole, and interstitial) in Prussian blue are given in Figures 1–3. Table I contains the values for the isomer shifts and quadrupole splittings for the three environments in Prussian blue, Turnbull's blue, and Berlin green. For natural Prussian blue in which all of

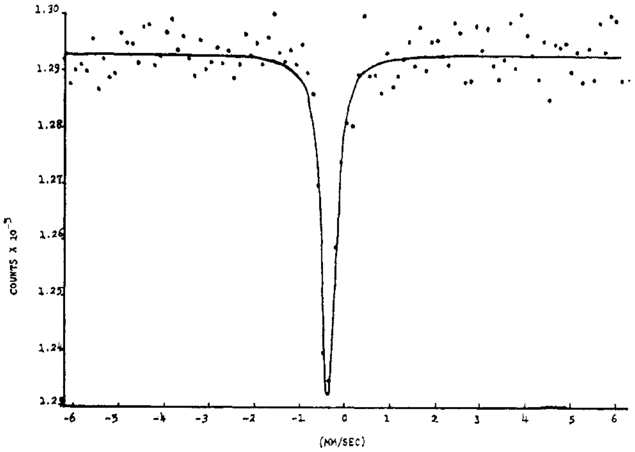

Figure 1.—Mössbauer spectrum at 298°K for $^{56}Fe^{3+}{}_4[Fe^{II}(CN)_6{}^{4-}]_3$, Prussian blue, obtained from $^{56}FeCl_3 + K_4Fe(CN_6)$.

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[3] (a) A, Ito, M. Suenaga, and M. Ono, *J. Chem. Phys.*, **48**, 3597 (1968); (b) A. H. I. Ben-Bassat, *Israel J. Chem.*, **6**, 91 (1968).

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

[5] M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

[6] M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

[7] J. A. Stone, personal communication.

TABLE I

MÖSSBAUER PARAMETERS[a]

	Carbon hole active			Nitrogen hole active			Interstitial hole ^{57}Fe		
Compound	δ	ΔE_Q	Half-width	δ	ΔE_Q	Half-width	δ	ΔE_Q	Half-width
Prussian blue	−0.40	...	0.36	+0.10	0.47	0.79	+0.10	0.46	1.00
Turnbull's blue	−0.40	...	0.36	+0.12	0.52	0.79	+0.10	0.47	1.00
Berlin green	−0.42	...	0.52	+0.10	0.57	1.09	...	...	...

[a] Isomer shifts (δ) and quadrupole splitting (ΔE_Q). The isomer shift is referred to an iron metal source with the center of an Fe_2O_3 standard used as the zero point. The half-width refers to the width of the absorption peak at half-maximum. The isomer shift, quadrupole splitting, and half-width, expressed in mm/sec, have a probable error of 0.06 mm/sec. All samples were examined at 25°.

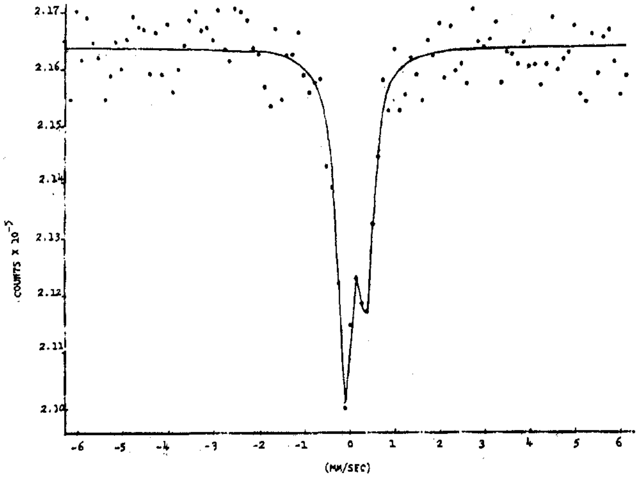

Figure 2.—Mössbauer spectrum at 298°K for $Fe^{3+}{}_4[{}^{56}Fe^{II}(CN)_6{}^{4-}]_3$, Prussian blue, obtained from $FeCl_3$ + $K_4{}^{56}Fe(CN)_6$.

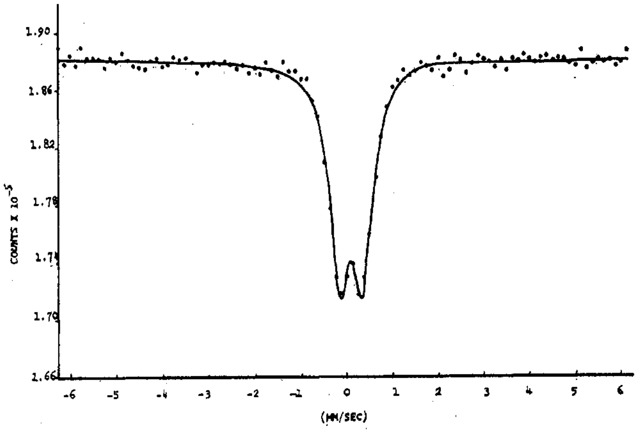

Figure 3.—Mössbauer spectrum at 298°K for $({}^{57}Fe^{3+}){}^{56}Fe^{3+}{}_3[{}^{56}Fe^{II}(CN)_6{}^{4-}]_3$, Prussian blue, obtained from $^{56}FeCl_3$ + $K_4{}^{56}Fe(CN)_6$ followed by addition of $^{57}FeCl_3$.

the iron environments are Mössbauer active, the large absorption peak at about −0.40 mm/sec has been assigned to carbon hole Fe(II) and the remainder of the spectrum has been attributed to nitrogen hole Fe^{3+} which has quadrupole splitting with one peak hidden in the Fe(II) absorption. The spectra for Prussian blue, Turnbull's blue, and Berlin green in which only the carbon hole iron is Mössbauer active show a single peak at −0.40 mm/sec. This peak in Prussian and Turnbull's blues verifies the earlier interpretations in assigning this peak to the low-spin Fe(II). The spectrum for Berlin green, however, is broader than in the other two compounds. This broadening of the low-spin Fe(III) peak was expected due to unresolved quadrupole splitting from the asymmetric arrangement of five electrons in the low-lying t_{2g} orbitals.

The same compounds were prepared with ^{56}Fe in the carbon hole and natural iron in both the nitrogen hole and the interstitial positions, except that Berlin green has no interstitial ions. The data in Table I for the nitrogen hole iron are in good agreement with the data of Milligan[2] when the difference in Fe_2O_3 and Fe standards are taken into consideration (our isomer shift is about 0.35 mm/sec less positive). The quadrupole-split Fe^{3+} peaks in Prussian and Turnbull's blues are asymmetric, apparently due to the effect of the interstitial ions upon the nitrogen hole Fe^{3+}. This is substantiated by the spectrum of Berlin green labeled with ^{56}Fe in the carbon hole, $Fe^{3+}[{}^{56}Fe^{III}(CN)_6{}^{3-}]$, in which the peaks for Fe^{3+} appear to be essentially symmetrical. The peaks for Berlin green again appear to be broader than for Prussian and Turnbull's blues and this broadness, too, may in some way be due to the presence of interstitial ions. The reason the structures containing interstitial ions should be sharper than those without is not clear at present.

In order to obtain the Mössbauer spectrum of the interstitial iron position, which is occupied to a lower degree than the lattice positions, it was necessary to establish that no exchange occurred between the interstitial ions and those in the lattice. Exchange of iron ions between the nitrogen hole and carbon hold and of these two positions with aqueous Fe^{3+} has been reported not to occur at any appreciable rate at room temperature.[8,9] However, no studies have been reported to show whether exchange occurs between solution and the interstitial position nor between interstitial ions and those in the nitrogen or carbon holes. The absence of exchange between interstitial iron and either of the lattice positions has now been verified by radioactive tracer studies for sodium Prussian blue, but aqueous Fe^{3+} has been shown to exchange slowly with interstitial iron ions, and "soluble" Prussian blue, *i.e.*, $KFe^{3+}Fe^{II}(CN)_6$, exchanges alkali metal ions for radioactive $^{59}Fe^{3+}$ in solution.[10] These data allow the preparation of an ^{57}Fe-labeled interstitial position free of interference from other Mössbauer-active iron ions by contacting $K^{56}Fe^{3+}[{}^{56}Fe^{II}(CN)_6{}^{4-}]$ with aqueous $^{57}Fe^{3+}$ for 3 days. The Mössbauer spectra of the interstitial $^{57}Fe^{3+}$ for Prussian blue and Turnbull's blue are virtually identical, again establishing that these two blues become identical by the high-spin iron ions being oxidized to the 3^+ state and the low-spin iron environments being reduced to Fe(II) whenever necessary to attain these more stable configurations.

It must be noted, however, that the method of preparing Turnbull's blue with interstitial ^{57}Fe ions was somewhat artificial and unlike the normal preparation of Turnbull's blue. Turnbull's blue is not normally

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(8) R. C. Thompson, *J. Amer. Chem. Soc.*, **70**, 1045 (1948).

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allowed to stand in contact with aqueous solution for 3 days, but this was necessary in order to get appreciable exchange into the solid blues previously prepared with ^{56}Fe in the lattice sites (carbon and nitrogen holes). Further verification of the fact that the interstitial iron is, indeed, Fe^{3+} for aged Turnbull's blue is demonstrated by the fact that no peak is found at or above +1.5 mm/sec. This peak is one of a pair of peaks centered at about +0.8 mm/sec and with quadruple splitting of about 1.7–3.0 mm/sec which are normally encountered for high-spin Fe^{2+}. The peak at about −0.3 mm/sec would be obscured by the nitrogen hole Fe^{3+} peak. The +1.5-mm/sec peak is also missing from the spectrum of Turnbull's blue shown in Figure 7 of Milligan's work,[2] in which the sample was prepared quickly and then frozen and in which there was a very large percentage absorption. Therefore we can clearly state that Prussian and Turnbull's blues are the same compound upon aging. There may be some low-oxidation preparation circumstances in which the Turnbull's blue could be kept with interstitial Fe^{2+} rather than Fe^{3+}, but for an aqueous preparation requiring more than 30 min, the high-spin field at this position causes the iron to be oxidized to the Fe^{3+} state. Either traces of some oxidizing agent such as dissolved oxygen or hydronium ions from the water itself must be the oxidizing agent since only the nitrogen hole Fe^{2+} would be oxidized by the $Fe^{III}(CN)_6^{3-}$ ion. Since the preparations reported here and those of Milligan, *et al.*,[2] were done under nitrogen, the hydronium ion is the most likely oxidizing agent.

Close study of the spectra show that the absorption peaks are somewhat broader and the quadrupole splitting is less for the interstitial Fe^{3+} than for the nitrogen hole Fe^{3+}. However, the isomer shift of +0.10 mm/sec and the quadrupole splitting of 0.47 mm/sec are close enough to those of the nitrogen hole Fe^{3+} that in a preparation with both these positions Mössbauer active the spectrum would appear to be a single pair of peaks. The less concentrated interstitial iron positions would be submerged under the more prominent nitrogen hole Fe^{3+} peaks. The absorption of these interstitial ions cannot be added to those of the nitrogen hole Fe^{3+} to give the asymmetry observed in insoluble Prussian blue. That asymmetry must be due to some other influences of the interstitial ions upon the nitrogen hole Fe^{3+}.

Acknowledgments.—The authors wish to thank Dr. John Stone for his advice and aid in performing these experiments and to thank the USAEC, the Savannah River Laboratory, and E. I. du Pont de Nemours and Co. for the use of the Mössbauer spectrometer through Contract AT(38-1)-555.

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Mössbauer and Electron Paramagnetic Resonance Studies of Some Iron Nitrosyl Complexes

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Fluorocarbon-bridged ligands react easily with $Fe(NO)_2(CO)_2$ to give the complexes $(L\text{-}L)Fe(NO)_2$ ($L\text{-}L = (CH_3)_2AsCCF_3{=}CCF_3As(CH_3)_2$, $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(C}F_2)_n$ ($n = 2, 3, 4$)). The mixed ligand $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ gives both chelate and monosubstituted derivatives. Mössbauer data for compounds of the sort $(L\text{-}L)Fe(NO)_2$, $LFe(NO)_2X$, $[Fe(NO)_2X]_2$, and $LFe(CO)(NO)_2$ are reported. The spectra of the compounds $LFe(CO)(NO)_2$ indicate that the π-acceptor strengths of L increase in the order $(C_6H_5)_3P < (C_6H_5)_2(CH_3)P \sim (C_6H_5)_3As < (C_6H_5O)_3P < CO < NO$. The π-acceptor strengths of the ditertiary phosphines in the compounds $(L\text{-}L)Fe(NO)_2$ are approximately equal to $(C_6H_5)_3P$ and it is predicted that the sign of V_{zz} is positive for the fluorocarbon-bridged derivatives. The epr spectra of the paramagnetic compounds $(C_6H_5)_3PFe(NO)_2Br$ and $(C_6H_5)_3AsFe(NO)_2Br$ show hyperfine interactions with the phosphorus (or arsenic) and the bromine atoms with a greater spin density on the iron atom in the case of the phosphorus compound. The dimer $[Fe(NO)_2Br]_2$ gives a weak epr signal in CCl_4 solution which intensifies and alters on the addition of complexing agents. The nitrosyl iodide dimer gives a signal in CCl_4 solution which can be attributed to $Fe(NO)_2I(CCl_4)$.

Introduction

In recent years increasing attention has been paid to the chemistry of transition metal–nitric oxide complexes. These compounds are of interest from the theoretical standpoint of the bonding involved as well as from their chemical and biochemical properties.[1-4]

Complexes between iron and nitric oxide have been known for a long time and have been subjected to a number of electron paramagnetic resonance (epr) studies.[5-9] These studies have indicated that in most cases the NO ligand is acting as NO^+ and that most of the spin density resides on the central iron atom. The

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