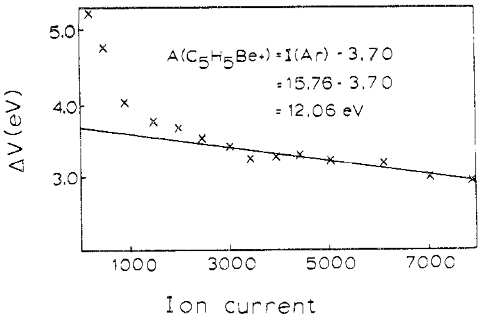

Figure 5. Appearance potential for $C_5H_5Be^+$.

from the parent ion, the dissociation energy of the Be–C bond in the parent ion can be determined using eq 2. The ionization

$$DE(C_5H_5Be\cdots CH_3) = AP(C_5H_5Be^+) - IP(C_5H_5BeCH_3) \qquad (2)$$

potential of $C_5H_5BeCH_3$ (Figure 3) is 9.83 eV. The appearance potential for $C_5H_5Be^+$ (Figures 4 and 5) is 12.06 eV. The calculated bond dissociation energy is 51 kcal/mol. The observed tailing in Figure 5 suggests that the dissociation process occurs with excess kinetic energy and the derived bond energy should be regarded as the upper limit. The bond energies (Be–C) in a series of dialkylberyllium monomers have been determined in an analogous manner.[31] For comparison the Be–C bond energy in dimethylberyllium is reported to be 46.1 kcal/mol.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. GP-8595. We thank Dr. David Nelson at the University of Wyoming for help in obtaining the mass spectral data.

Registry No. $C_5H_5BeCH_3$, 36351-95-8; C_5H_5BeCl, 36346-97-1; C_5H_5BeBr, 52140-35-9; C_5H_5BeI, 62571-44-2; $(CH_3)_2Be$, 506-63-8; $(C_5H_5)_2Be$, 12083-43-1.

References and Notes

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(2) G. F. Reynolds and S. R. Daniel, *Inorg. Chem.*, **6**, 480 (1967).
(3) M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).
(4) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).
(5) G. E. Parris and E. C. Ashby, *J. Organomet. Chem.*, **72**, 1 (1974).
(6) J. R. Sanders, Jr., E. C. Ashby, and J. H. Carter II, *J. Am. Chem. Soc.*, **90**, 6385 (1968).
(7) N. A. Bell, *J. Organomet. Chem.*, **13**, 513 (1968).
(8) E. L. Head, C. F. Holley, and S. W. Pabideau, *J. Am. Chem. Soc.*, **79**, 3687 (1957).
(9) G. E. Coates and P. D. Roberts, *J. Chem. Soc. A*, 2651 (1968).
(10) E. O. Fischer and S. Schreiner, *Chem. Ber.*, **92**, 938 (1959).
(11) D. A. Drew and A. Haaland, *Acta Crystallogr., Sect. B*, **28**, 3671 (1972).
(12) C. H. Wong, T. Y. Lee, K. J. Chao, and S. Lee, *Acta Crystallogr., Sect. B*, **28**, 1668 (1972).
(13) G. B. McVicker and G. L. Morgan, *Spectrochim. Acta, Part A*, **26a**, 23 (1970).
(14) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3079 (1972).
(15) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3351 (1972).
(16) A. Haaland and D. P. Novak, *Acta Chem. Scand., Ser. A*, **28**, 3 (1974).
(17) D. A. Drew, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **26**, 2147 (1972).
(18) A. Bjorseth, D. A. Drew, K. M. Marstokk, and H. Mollendal, *J. Mol. Struct.*, 13 (1972).
(19) P. A. Akishin, V. P. Spiridonov, and G. A. Sabolov, *Dokl. Akad. Nauk SSSR*, **118**, 1334 (1958).
(20) O. Y. Lopatko, N. M. Klimenko, and M. E. Dyatkina, *J. Struct. Chem. (Engl. Transl.)*, **13**, 1044 (1972).
(21) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **49**, 2904 (1927).
(22) G. L. Morgan and G. B. McVicker, *J. Am. Chem. Soc.*, **90**, 2789 (1968).
(23) R. A. Kovar and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 5067 (1970).
(24) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).
(25) T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 6487 (1970).
(26) A. Buchler and W. Klemperer, *J. Chem. Phys.*, **29**, 121 (1958).
(27) D. A. Coe, J. W. Nibler, T. H. Cook, D. Drew, and G. L. Morgan, *J. Chem. Phys.*, **63**, 4842 (1975).
(28) A. Snelson, *J. Phys. Chem.*, **72**, 250 (1968).
(29) P. A. Akishin and V. P. Spiridinov, *Kristallografiya*, **2**, 475 (1957).
(30) J. W. Warren, *Nature (London)*, **165**, 810 (1950).
(31) D. B. Chambers, G. E. Coates, and F. Glockling, *J. Chem. Soc. A*, 741 (1970).

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Magnetic Isomers of Iron(II). Bis(*C*-cyanotrihydroborate)bis(phenanthroline)iron—a Spin Triplet[1]

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Received November 23, 1976 AIC60850X

The synthesis of an unusual six-coordinated, spin triplet ($S = 1$) ferrous complex, $Fe(phen)_2(NCBH_3)_2$, with cis geometry is described. This complex is characterized by its magnetic moment and infrared, visible-region, and Mössbauer spectra. On the basis of these data and the angular overlap model of metal–ligand bonding, $^-NCBH_3$ is characterized as a ligand possessing moderate σ- and π-donor characteristics toward $Fe(phen)_2^{2+}$. How a proper balance of σ- and π-donor properties of $-NCBH_3$ and phen yields the spin-triplet state of the ferrous complex is discussed. Consideration of the CN stretching frequency data for the isomeric pairs of $Fe(phen)_2(NCBH_3)_2$ and $Fe(phen)_2(CNBH_3)_2$ and other bridged cyano species raises interesting questions about the effect of double coordination of cyanide on the CN σ bonding. Finally, thermal stability studies of the $Fe-CN-BH_3$ and $Fe-NC-BH_3$ linkages eliminate the possibility of isomerization by a facile CN flip mechanism within the Fe and B cage and suggest that $(phen)_2Fe(NCBH_3)_2$ is the thermodynamically favored isomer.

Since our initial suggestion[2a] that $NCBH_3^-$ possesses a significant degree of coordinating ability there have been several reports of such complexes.[3] Most of the latter have exhibited N-coordination but in the case of $[Cu(PPh_3)_2(NCBH_3)]_2$ coordination of Cu by N *and* H of $NCBH_3^-$ has been documented.[3d,e] Furthermore, different modes of synthesis affect the structure of at least one complex $[Cu(PPh_3)_3(NCBH_3)]$, for both N- and H-bound forms are claimed.[3c,d] Other examples of H-bound $NCBH_3^-$ have also been reported.[3c]

While we had a variety of reasons to attempt synthesis of $Fe(phen)_2(NCBH_3)_2$, two of the more important ones have been (i) a desire to prepare the isomer of $Fe(phen)_2(CNBH_3)_2$[4] (with the intent to investigate the interconversion of these bridged cyano species) and (ii) the promise that $Fe(phen)_2(NCBH_3)_2$ might have unusual magnetic properties. This latter prediction derives from the unusual magnetic properties[5] of $Fe(phen)_2(NCS)_2$ ($S = 2$ above 173 K, $S = 0$ below 170 K). The only examples, of which we are aware, of two molecular linkage isomers of bridging cyanide are $(H_3N)_5Co(CN,NC)Co(CN)_5$[6] and $H(Et_3P)_2Pt(CN,NC)BPh_3$;[7] the latter was reported as this work neared completion.

The subjects of this report are the synthesis of $Fe(phen)_2(NCBH_3)_2$, its electronic structure, the characterization

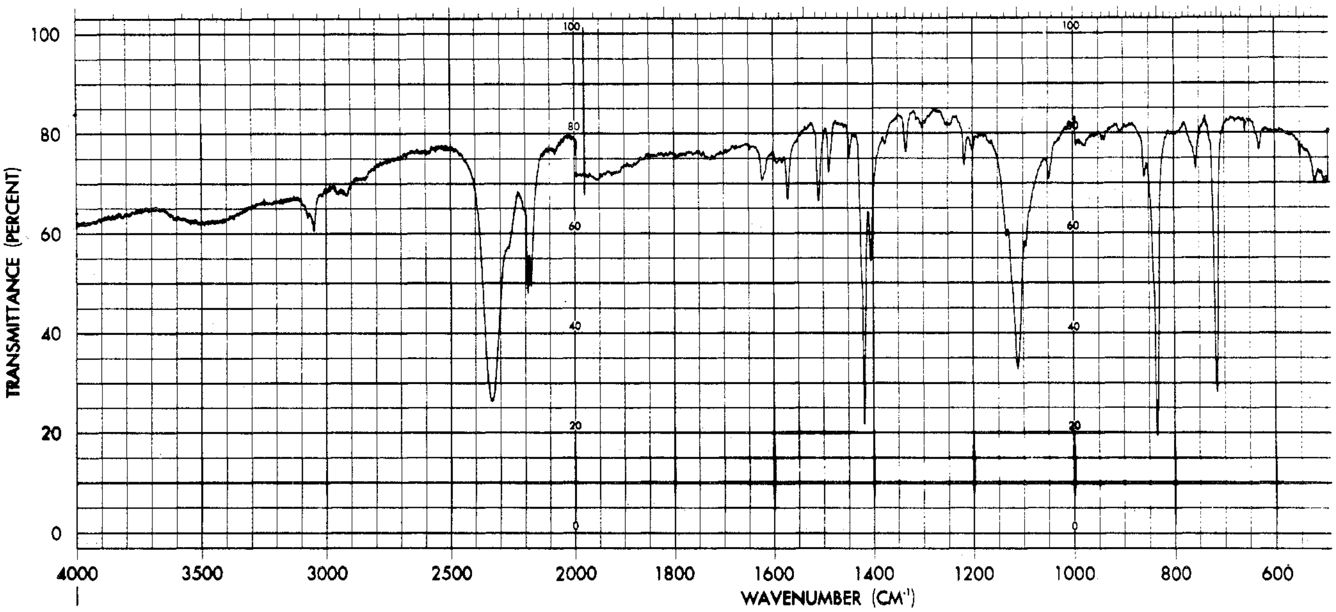


Figure 1. Infrared spectrum of $Fe(phen)_2(NCBH_3)_2$; KBr pellet.

of $NCBH_3^-$ as a ligand, and the thermal stability of the complexes in the solid state.

Experimental Section

Preparation of Compounds. All reactions were carried out under an atmosphere of dry N_2. The synthesis of $KNCBH_3$ has been reported previously by us.[2a]

$Fe(phen)_2(NCBH_3)_2$. $KNCBH_3$ (0.6567 g, 8.313 mmol) was dissolved in 100 mL of dry THF and the solution was filtered. The filtrate was added quickly to a 3-necked flask containing 1.15 g (2.363 mmol) of $Fe(phen)_2Cl_2$ (blue), prepared by Madeja's[5c] method, and the reaction flask was purged with N_2 gas again for about 15 min. After 3 days of refluxing (the mixture was protected from atmospheric moisture with a mercury bubbler), IR spectra of the solvent showed no further change in the intensities of absorption in the region of 2500–2000 cm^{-1} (for the reactant ratio given, the intensity of the CN absorption band of $KNCBH_3$ decreased to about half of its original value).

The purplish red solid was filtered off (after the slurry had cooled to room temperature) and washed with THF and a minimum amount of water to remove KCl. The residue was then washed with anhydrous ether and dried in an Abderhalden drying pistol overnight at 56 °C. The yield is 85%. Chemical analyses were carried out by Atlantic Microlab and Galbraith Laboratories. Anal. Calcd: C, 62.95; N, 16.95; H, 4.48; Fe, 11.26; B, 4.36. Found: C, 61.34; N, 15.86; H, 4.69; Fe, 11.41; B, 4.11.

$Fe(phen)_2(CNBH_3)_2$. $Fe(phen)_2(CN)_2$ (dark blue) was prepared using Schilt's[8] method. About 15 mL of 1 M BH_3/THF solution was diluted with 50 mL of dry THF and added to a reaction flask containing 0.8620 g (1.842 mmol) of $Fe(phen)_2(CN)_2$. After 10 h of reluxing and then cooling of the mixture to room temperature, a red solid was filtered from the reaction mixture, washed with THF and anhydrous ether, and dried on an air frit. A 0.9135-g amount of $Fe(phen)_2(CNBH_3)_2$ was collected. Anal. Calcd: C, 62.95; N, 16.95; H, 4.48; Fe, 11.26; B, 4.36. Found: C, 60.12; N, 15.50; H, 4.72; Fe, 11.33; B, 4.09.

The somewhat low carbon and nitrogen analyses stand in marked contrast to the *excellent H, Fe, and B results* and apparently are not unusual for iron–phenanthroline–cyano species.[4] Owing to the low volatilities and insolubilities of these compounds it has proven impossible to check purities by sublimation, chromatography, and crystallization techniques. The presence of unreacted starting materials, in both cases, is *not* consistent with correct H, Fe, and B analyses and low C and N analyses. In the case of $Fe(phen)_2(CNBH_3)_2$ we could detect, by IR, a trace of unreacted $Fe(phen)_2(CN)_2$, but this impurity obviously has little effect on the analyses since its presence would cause *high* C, N, and Fe percentages and *low* H and B percentages. But for carbon, the analytical results for the two linkage isomers are identical; given the greatly different synthetic routes, there is either inadequacy in the standard analytical methods applied to these compounds or a mysterious, common impurity which otherwise has escaped detection.

Thermal Stability Studies. Samples of the complexes $Fe(phen)_2(NCBH_3)_2$, $Fe(phen)_2(CNBH_3)_2$, $Fe(phen)_2(CN)_2$, and $Fe(phen)_2(NCS)_2$ were put separately into a sublimation tube and heated, under vacuum, with silicone oil to 170 °C for several days. The products, after cooling to room temperature, were collected and their IR spectra recorded in KBr pellets.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were obtained at room temperature by Gouy's method. The effective magnetic moments of the complexes were obtained from $\mu_{eff} = 2.83(T\chi)^{1/2}$. $HgCo(SCN)_4$ was used as the tube calibrant and diamagnetic corrections were made using values given by Figgis and Lewis.[9] For each complex, tube packings were repeated at least 3 times. The effective magnetic moments reported in Table I are estimated to be accurate to within 0.1.

Infrared Spectra. The infrared spectra of hand-pressed KBr pellets were recorded with a Perkin-Elmer Model 180 spectrometer. Polystyrene was used for calibration and the ν_{CN} frequencies recorded in Table II are accurate to ±2 cm^{-1}.

Mössbauer Spectra. Mössbauer spectra were recorded at room temperature using a standard speaker–drive system[10] operating in the constant-acceleration mode. Two spectra (+ and − drive acceleration) were accumulated simultaneously ($\sim 10^5$ per channel) in a 1024 channel analyzer running in the multiscaling mode. The spectra obtained using this apparatus for $Fe(phen)_2Cl_2$ and $Fe(phen)_2(CN)_2$, as reported in Table I, agree within experimental error (±0.05 mm/s) with previously published results.[11] The absorbers consisted of loosely packed polycrystalline disks suspended on 3M tape and the source was 10-mCi ^{57}Co in Pd. The velocity scale was calibrated with a ^{57}Fe (in Fe) absorber foil. The isomer shifts reported in Table I are relative to the centroid of the ^{57}Fe spectrum.

Electronic Spectra. KBr pellet spectra were recorded on Cary 11 and 14 spectrophotometers.

Results

The KBr pellet IR spectrum of $Fe(phen)_2(NCBH_3)_2$ is shown in Figure 1 and its Mössbauer spectrum is given in Figure 2. The magnetic moments, the CN stretching frequencies, and the isomer shifts and quadrupole splittings which form the basis of the characterization of $Fe(phen)_2(NCBH_3)_2$, $Fe(phen)_2(CNBH_3)_2$, and related complexes are collected in Table I. The visible spectrum of a KBr pellet of $Fe(phen)_2(NCBH_3)_2$ is presented later.

Our attempts to find a suitable solvent for $Fe(phen)_2(NCBH_3)_2$ have not been particularly fruitful. None of the following were found suitable for NMR spectra: nitromethane,

Table I. Data for $Fe(phen)_2X_2$ and Related Compounds

Compd ($M = Fe(phen)_2{}^{2+}$)	μ_{eff}[a]	IS[b]	QS[b]	ν_{CN}[e]	
MCl_2	5.19	1.00	3.00		
$M(NCS)_2$	5.15	1.01[c]	2.82[c]	2072	2060
$M(NCBH_3)_2$	2.9	0.40	0.18	2198	2186
$M(CNBH_3)_2$	0.41	0.15	0.61	2161	2146
$M(CN)_2$	0.76	0.16	0.62	2081	2064
Mphen[j]	0.79	0.43[d]	0.20[d]		
KCN				2080[f]	
$KNCBH_3$				2179[g]	
$KCNBH_3$				2070[h]	
KBH_3CNBH_3				2260[h]	
KSCN				2053[f]	
$NaSCNBH_3$				2075[i]	

[a] At 301 K. [b] Isomer shift, relative to iron foil, and quadrupole splitting, both in mm/s. [c] Reference 11. [d] Reference 12. [e] In cm^{-1}. [f] Reference 13. [g] Reference 14. [h] Reference 2. [i] Reference 15. [j] $Fe(phen)_3Cl_2 \cdot 7H_2O$.

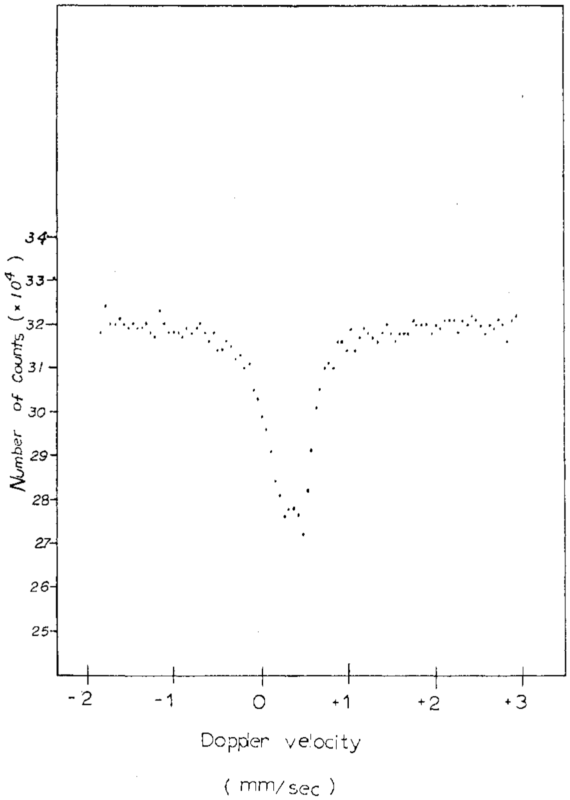


Figure 2. Mössbauer spectrum of $Fe(phen)_2(NCBH_3)_2$.

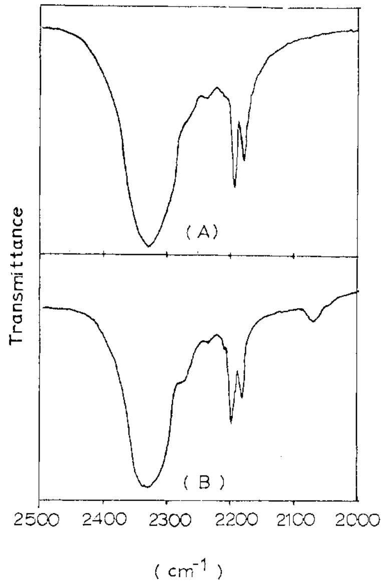


Figure 3. Infrared spectrum of $Fe(phen)_2(NCBH_3)_2$ (A) before heating and (B) after heating at 170 °C under vacuum for 5 days; KBr pellets.

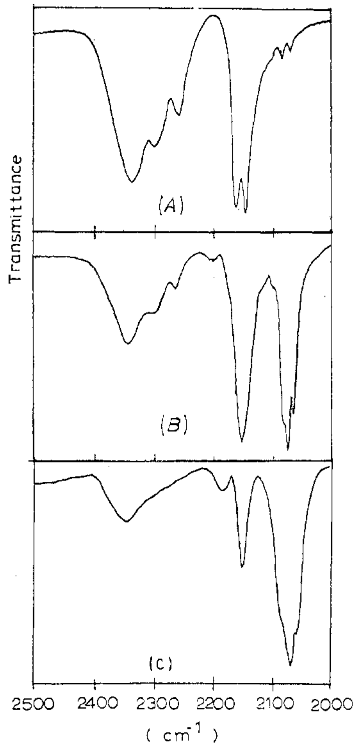


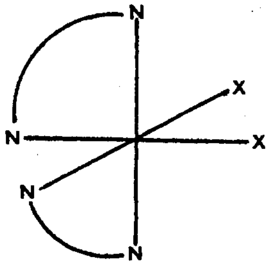
Figure 4. Infrared spectra of $Fe(phen)_2(CNBH_3)_2$ (A) before heating, (B) after heating at 170 °C under vacuum for 3 days, and (C) after heating at 170 °C for 10 days; KBr pellets.

acetonitrile, sulfolane, pyridine, dichloromethane, dichloroethane, acetone, acetic acid, and water. Anomalous X-band ESR spectra of solid samples of the Fe–NC–B isomer resulted, a situation not uncommon when zero-field splitting of the triplet gound state nearly matches the X-brand frequency.

$Fe(phen)_2(NCBH_3)_2$ and $Fe(phen)_2(CNBH_3)_2$ persist unchanged at room temperature. Heating $Fe(phen)_2(NCBH_3)_2$ under vacuum at 170 °C for several days results in small IR changes only (Figure 3). Heating $Fe(phen)_2(CNBH_3)_2$ under the same conditions results in more dramatic changes (Figure 4). On the other hand, the same treatment of $Fe(phen)_2(CN)_2$ and $Fe(phen)_2(NCS)_2$ yields no changes in their IR spectra.

Discussion

Magnetic Susceptibilities and Mössbauer Data. It is well-known that *octahedral* ferrous complexes, $Fe^{II}L_6$, display two kinds of magnetic properties, i.e., diamagnetic complexes with no unpaired electrons and paramagnetic complexes with four unpaired electrons, depending upon the position of the ligands in the spectrochemical series. Effective magnetic moments of ~0 and ~5 μ_B are usually observed for such low-spin and high-spin complexes, respectively. Mössbauer spectra are also characteristic of the electronic configurations of high- and low-spin ferrous ion complexes.[11,12,17] Thus, the low-spin d^6 complexes of general formula FeL_6 are characterized by minor quadrupole splitting and isomer shifts of a few tenths of 1 mm/s, relative to an Fe foil centroid; high-spin cases are distinguished by QS of 2–3 mm/s and IS on the order of 1 mm/s.



	$Fephen_3^{+2}$	$Fephen_2X_2$	
ϵ_{z^2}	$3e_{\sigma n}$	$5/2e_{\sigma n} + 1/2e_{\sigma x} = 3e_{\sigma n} - 1/2\delta e_{\sigma}$	diff = δe_{σ}
$\epsilon_{x^2-y^2}$	$3e_{\sigma n}$	$3/2e_{\sigma n} + 3/2e_{\sigma x} = 3e_{\sigma n} - 3/2\delta e_{\sigma}$	
ϵ_{xy}	$2e_{\pi n}$	$2e_{\pi n} + 2e_{\pi x}$	diff = $e_{\pi n} + e_{\pi x}$
$\epsilon_{xz} = \epsilon_{yz}$	$2e_{\pi n}$	$e_{\pi n} + e_{\pi x}$	

Figure 5. Relative d-orbital energy levels from the angular overlap model. e_σ and e_π are the unit antibonding energy shifts for σ and π overlap. Note that each X possesses two π-type orbitals while phen is presumed to have but one π orbital per nitrogen.

A few complexes of the type $Fe(phen)_2X_2$ (with cis geometry) have been studied by magnetic susceptibility measurements[5c,8] and Mössbauer spectroscopy.[11,12,17] With X = halide or ^-NCS, which appear early in the spectrochemical series, magnetic moments of $\sim 5.2\ \mu_B$ are observed and these complexes also have very large isomer shifts and very large quadrupole splittings (see Table I). For the complexes $Fe(phen)_2(CN)_2$ and $Fe(phen)_3^{2+}$, where CN^- and phen appear later in the spectrochemical series, the observed magnetic moments are nearly zero and isomer shifts and quadrupole splittings are all small.

The bis(*N*-cyanotrihydroborate)bis(phenanthroline)iron isomer behaves in a typical low-spin fashion. That the IS of $Fe(phen)_2(CNBH_3)_2$ is within experimental error of that of $Fe(phen)_2(CN)_2$ indicates little net change in electron density at the Fe nucleus is incurred by coordination of BH_3 to N. Increased 4s density leads to −IS while increased 3d density leads to +IS. The almost negligible change in IS for the conversion $(phen)_2Fe(CN)_2 \rightarrow (phen)_2Fe(CNBH_3)_2$ implies offsetting changes in 4s and 3d populations. According to Shriver and Posner's[4] CNDO calculations, coordination to nitrogen of cyanide by some acid should decrease $NC^- \rightarrow Fe$ σ transfer and increase the π-acceptor nature of NC^- (decreased $^-NC \rightarrow Fe$ π transfer). The former decreases the 4s density and the $3d_\sigma$ density while the latter decreases the $3d_\pi$ density. Thus, both the 4s (σ) and 3d ($\sigma + \pi$) densities are expected to decrease and to have offsetting effects on the IS. Experience indicates that the 4s (σ) changes dominate the 3d (σ) changes; later, in discussing the charge-transfer spectra of $Fe(phen)_2X_2$, it will be seen that the bridged cyano species fit this generalization. Thus, in agreement with recent calculations,[18] BH_3 hyperconjugation (which would reduce the π-acceptor nature of ^-CN) appears relatively unimportant.

That the IS values of $Fe(phen)_2(CNBH_3)_2$ and $Fe(phen)_2(CN)_2$ are smaller than that of $Fe(phen)_3^{2+}$ indicates the ^-CN and $^-CNBH_3$ complexes have higher electron density at the ferrous nucleus. This is reasonably attributed to greater Fe ← C than Fe ← N σ interaction and perhaps greater Fe → C than Fe → N π interaction. Accordingly the QS values of $Fe(phen)_2(CNBH_3)_2$ and $Fe(phen)_2(CN)_2$ are larger than those of $Fe(phen)_3^{2+}$ and $Fe(phen)_2(NCBH_3)_2$, indicating that the replacement of nitrogen by carbon at the ligating points leads to a significant alteration of the electric field gradient at the Fe nucleus. Most interesting here is that the Mössbauer parameters (both IS and QS) suggest that the Fe nucleus in $(phen)_2Fe^{2+}$ does not distinguish 2 $^-NCBH_3$ from 1 phen.

In marked contrast with "normal" six-coordinate Fe(II) complexes, the bis(*C*-cyanotrihydroborate)bis(phenanthroline)iron isomer exhibits a μ_{eff} corresponding to an $S = 1$ state but IS and QS parameters diagnostic of $S = 0$.[19] This apparent conflict has been treated by the crystal field model[20b] and is readily resolved (see later) by the realization that a certain 3d orbital ordering for $S = 1$ yields IS and QS parameters much like those for an $S = 0$ state. An important finding is that low IS and QS Mössbauer parameters are necessary but not sufficient conditions for the occurrence of low-spin Fe(II). In addition to failure of the high- and low-spin FeL_6 models to account for these results for $Fe(phen)_2(NCBH_3)_2$, a trans geometry also does not explain the Mössbauer/magnetic susceptibility data. Were such a structure correct in this case, it would be possible to realize $S = 1$ for weakly bonding ligands in the trans positions, but a larger QS would appear in the Mössbauer spectrum. Given the steric problems for coplanar phenanthroline ligands and that two CN vibrations are found in its IR spectrum, $Fe(phen)_2(NCBH_3)_2$ must have a cis topology.

A simple accounting for these IR, magnetic, and Mössbauer characteristics of $^-NCBH_3$ complex comes from the angular overlap model of complex ion electronic structure. Using this model one can estimate, in terms of the σ and π interactions between d orbitals of a metal ion and σ and π orbitals of ligands, the relative d-orbital energy levels in complexes. Application of this model to $Fe(phen)_3^{2+}$ and $Fe(phen)_2X_2$ is shown in Figure 5 (here we have assumed idealized 90° interligand bond angles).[22]

The ordering of d* molecular orbital energies can be safely assumed, for X_2 = phen, Cl_2, $(NCS)_2$, $(CN)_2$, $(CNBH_3)_2$, and $(NCBH_3)_2$, to follow $(\epsilon_{d_{z^2}}, \epsilon_{d_{x^2-y^2}}) > (\epsilon_{d_{xy}}, \epsilon_{d_{xz}} = \epsilon_{d_{yz}})$. In general,

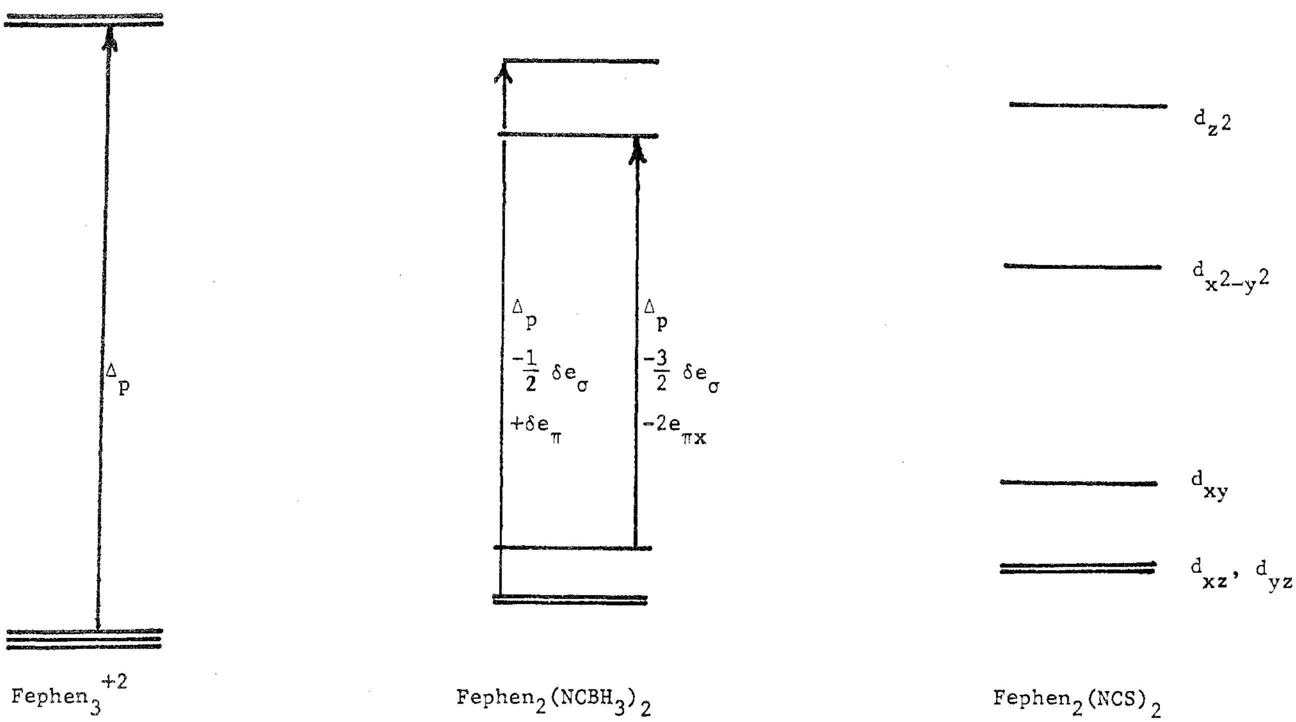


Figure 6. Relative orbital energy levels for $Fe(phen)_3^{2+}$, $Fe(phen)_2(NCBH_3)_2$, and $Fe(phen)_2(NCS)_2$, using the angular overlap model.

however, the relative d^*_σ, molecular orbital energies and relative d^*_π molecular orbital energies are not so readily apparent. The two possibilities for each of d^*_σ and d^*_π give rise to four general cases (see Table II).

In all cases the Fe valence electron (d^*) contribution to q_z is given by[23]

$$q_z = K_d[-N_{d_{z^2}} + (N_{d_{x^2-y^2}} + N_{d_{xy}}) - \frac{1}{2}(N_{d_{xz}} + N_{d_{yz}})]$$

where $K_d = {}^4/_7\langle n^{-3}\rangle_d$ and $N_{d_{z^2}}$ is the $d^*_{z^2}$ electron population, etc.

For the low-spin complexes [$X_2 = (CN)_2, (CNBH_3)_2$] the individual molecular orbital patterns in the above sequence cannot be distinguished on the basis of the electric field gradient at Fe, although intuition strongly suggests that both δe_σ and $(e_{\pi n} + e_{\pi x})$ should be <0.

Of the high-spin ($S = 2$) cases ($q_z \propto -{}^1/_2, 1, 1, -{}^1/_2$) for the orbital level sequence given above, determination of the sign of q_z could distinguish the sign of $(e_{\pi n} + e_{\pi x})$, while no information can be obtained from q_z as to the sign of δe_σ. The intermediate spin ($S = 1$) cases are more readily distinguished by $q_z \propto 0, {}^3/_2, -{}^1/_2, -2$ for the orbital sequences in Table II. Clearly,[24] that $q_z \approx 0$ for $Fe(phen)_2(NCBH_3)_2$ signifies $\delta e\sigma$ and $(e_{\pi n} + e_{\pi x})$ both >0. Thus $NCBH_3^-$ is poorer at σ interaction with Fe(II) than phen; this requirement agrees with the expected difference in donor properties of "sp" (NC) and "sp^2" (phen) nitrogen. If it is assumed the $e_{\pi n} < 0$ (that is, phen acts primarily in a π-acceptor rather than π-donor capacity), it follows that $e_{\pi x} > 0$ and $e_{\pi x} > |e_{\pi n}|$. In other words, $NCBH_3^-$ should be considered a π donor. Only if phen could be claimed to be a π donor would it be possible to claim $NCBH_3^-$ to be a π-acceptor type ligand. In summary, the orbital sequence $z^{2}* > x^2 - y^{2}* > xy* > xz*, yz*$ uniquely determines that $q_z \approx 0$ for the triplet state.

A most interesting question is: Why does replacement of BH_3 in $NCBH_3^-$ by S in NCS^- lead to a quintet ground state for $Fe(phen)_2X_2$? It is most likely correct that the difference in "sp" vs. "sp^2" donor hybrid character still requires $\delta e_\sigma > 0$ for NCS^-; further, one could argue that NCS^- should be a poorer σ donor than $NCBH_3^-$ on the basis of the inductive difference between "sp^3" boron and "sp" sulfur. Accordingly, $\delta e_\sigma(NCS) > \delta e_\sigma(NCBH_3) > 0$. On the other hand, NCS^- should be a much stronger π donor than $NCBH_3^-$ because BH_3 shows[18] little hyperconjugation with NC^-, whereas S is known to strongly conjugate:

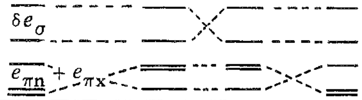
$$:N{\equiv}C{-}B{\equiv}H_3 \leftrightarrow :\ddot{N}{=}C{=}B{=}H_3$$

$$N{\equiv}C{-}\underset{..}{\ddot{S}}: \leftrightarrow :\ddot{N}{=}C{=}\ddot{S}:$$

Consequently, δe_σ and $(e_{\pi n} + e_{\pi x})$ are both >0 for NCS^- as well as $NCBH_3^-$. In terms of AOM d* molecular orbital energies of $Fe(phen)_3^{2+}$, $Fe(phen)_2(NCBH_3)_2$, and $Fe(phen)_2(NCS)_2$ we expect the diagram in Figure 6 to apply.

Defining $\Delta_P = 3e_{\sigma n} - 2e_{\pi n}$ and the d* -electron pairing energy as P, the transformation $Fe(phen)_3^{2+} \rightarrow Fe(phen)_2(NCBH_3)_2$ occasions a change from $P < \Delta_P$ to $P > (\Delta_P - {}^3/_2\delta e_\sigma - 2e_{\pi x})$, where, as seen earlier, δe_σ and $e_{\pi x}$ are both >0 for $NCBH_3^-$. Note, however that P remains $<(\Delta_P - {}^1/_2\delta e_\sigma + \delta e_\pi)$. The transformation $Fe(phen)_2(NCBH_3)_2 \rightarrow Fe(phen)_2(NCS)_2$ causes this last inequality to reverse sense to $P > (\Delta_P - {}^1/_2\delta e_\sigma + \delta e_\pi)$ for NCS^-. The differential σ- and π-donor properties of $NCBH_3^-$ (relative to phen) have struck a particularly fine balance so as to produce the unusual intermediate spin state for six-coordinate $Fe(phen)_2(NCBH_3)_2$. At the extremes we find Cl^-, NCS^- ("poor" σ donors, "good" π donors) and phen,

Table II. Ordering of the d Orbitals and the Electric Field Gradient for Low-, Intermediate-, and High-Spin States of the Octahedral Ferrous Complexes

δe_σ	+	+	−	−
$e_{\pi n} + e_{\pi x}$	+	−	−	+
d_{z^2} $d_{x^2-y^2}$ d_{xy} d_{xz}, d_{yz}				
Spin state	Electric field gradient (in units of K_d)[a]			
$S = 0$	0	0	0	0
$S = 1$	0	${}^3/_2$	$-{}^1/_2$	−2
$S = 2$	$-{}^1/_2$	1	1	$-{}^1/_2$

[a] See text for definition of K_d. These values are nominal for net integral d AO occupation numbers appropriate, strictly speaking, for no covalency in the Fe–Ligand σ and π interactions. Covalency corrections are typically unimportant in relation to the effects of changing spin state.

CN^-, $CNBH_3^-$ ("good" σ donors, "poor" π donors).

Spin-State Equilibration. In spite of the consistency of the Mössbauer parameters and magnetic moment in depicting a true triplet ground state for *cis*-$Fe(phen)_2(NCBH_3)_2$, the possibility of a rapid or slow spin-state equilibration (singlet $\rightleftarrows$ quintet) must be dealt with. Were there to be a slow equilibration (specific rate $<10^7$ s^{-1}), the equal amounts of singlet and quintet species required to explain the μ_{eff} value would be easily detected in the Mössbauer spectrum and in the ν_{CN} IR region. For intermediate to rapid interconversion, the Mössbauer spectrum would appear as a doublet with IS > 0.5 mm s^{-1} and QS ≈ 1.5 mm s^{-1}, while the IR experiment (time scale $\sim 10^{12}$ s^{-1}) would still reveal the presence of two kinds of complex through the appearance of four CN stretching modes. For example, slow-exchange behavior has been found[25] with $Fe(phen)_2(NCS)_2$. There the $S = 2$ state has a ν_{CN} doublet *fully* 40 cm^{-1} lower than the $S = 0$ doublet. The loss, on going from $S = 2$ to $S = 0$, of the $(x^2 - y^2)^*$ electron is responsible for the dramatic shift. In addition, the IR spectra in the 1600-cm^{-1} region (a doublet of very weak bands at 1620 and 1570 cm^{-1}) and the absence of a band at $\sim$640 cm^{-1} (strong in all high-spin $Fe(phen)_2X_2$ complexes) further support the conclusion that a quintet species is absent.[25] We are initiating high- and low-temperature Mössbauer, IR, and susceptibility studies to explore the possibilities for $S = 2 \rightleftarrows S = 1$ and $S = 1 \rightleftarrows S = 0$ interconversion at other temperatures.[26]

Thermal Stability. Thermal stability studies undertaken to identify the more stable form of the $Fe(phen)_2[(NC,CN)BH_3]_2$ linkage indicate Fe–NC–B to be the more stable linkage isomer but that isomerization of Fe–CN–B poorly competes with BH_3 loss. Heating a sample of the Fe–CN–BH_3 isomer at 170 °C for 3 days under vacuum resulted in important changes. Most significant is the collapse of the CN doublet of the Fe–C-N–BH_3 isomer to a broad singlet at the average of the doublet frequencies. By itself, this change suggests the formation of *trans*-$Fe(phen)_2(CNBH_3)_2$ or the loss of 1 equivalent of BH_3 to produce $Fe(phen)_2(CN)(CNBH_3)$. At lower frequency there appear two bands at the frequencies found for $Fe(phen)_2(CN)_2$ and a rather intense third band between these last two, as shown in Figure 4. On the basis of this low-frequency CN region spectral change it seems safe to conclude that thermolysis leads to a mixture of $Fe(phen)_2(CN)(CNBH_3)$ and $Fe(phen)_2(CN)_2$. Note that the change in relative CN/BH_3 band envelopes also suggests BH_3 loss. In addition, it appears that loss of the first BH_3 is much faster than loss of the second. Continued heating of $Fe(phen)_2(CNBH_3)_2$ (for up to 10 days) resulted in further decreases of the intensity of the BH_3 band envelope and of the sharp singlet at 2154 cm^{-1}; such prolonged heating also resulted in growth of the bands at 2064 and 2081 cm^{-1}. This confirms the formation of $Fe(phen)_2(CN)(CNBH_3)$ in the initial pyrolysis stages and that the second BH_3, after the first BH_3 is lost, is more tightly bound. The poor resolution in 2070-cm^{-1} region is believed to be due to the overlap of the doublet of $Fe(phen)_2(CN)_2$ with the terminal CN stretching band of $Fe(phen)_2(CN)(CNBH_3)$.

Of some importance is the weak, broad band just below 2200 cm^{-1} in Figure 4. This weak absorption is in the region found for the CN stretching frequencies in $Fe(phen)_2(NCBH_3)_2$ and appears to have gained intensity in Figure 4. We feel this band is due to $Fe(phen)_2(NCBH_3)_2$; the implication of this is that $Fe(phen)_2(NCBH_3)_2$ is thermodynamically favored over $Fe(phen)_2(CNBH_3)_2$.

$$\mathrm{Fe(phen)_2(CNBH_3)_2 \xrightarrow[-BH_3]{} Fe(phen)_2(CN)(CNBH_3) \xrightarrow[-BH_3]{} Fe(phen)_2(CN)_2}$$

$$\mathrm{Fe(phen)_2(CNBH_3)_2 \rightarrow Fe(phen)_2(NCBH_3)_2}$$

Table III. Shifts of the Charge-Transfer Envelope and Isomer Shift for $Fe(phen)_2X_2$ As X Is Varied

	ΔIS, mm s^{-1}	$\Delta\nu_{CT}$
$X = CN^- \rightarrow {}^-CNBH_3$	−0.01	Large blue
$X = {}^-NCBH_3 \rightarrow {}^-CNBH_3$	−0.25	Small blue
$X = {}^-NCBH_3 \rightarrow {}^-NCS$	+0.6	Small red

Similar treatment of the Fe–NC–BH_3 isomer (Figure 3) does not lead to the collapse of the original doublet but does incur the appearance of a very weak, broad band in the CN region of *cis*-$Fe(phen)_2(CN)_2$. Lack of band resolution is perhaps due to the weakness of the absorption. The spectra are such as to make it difficult to say whether there is formation of $Fe(phen)_2(CN)(NCBH_3)$. The broadness of the low-frequency band as well as the peak:valley ratio of the CN doublet at high frequency is not inconsistent with the presence of a small amount of both terminal and bridged CN. Loss of BH_3 from the Fe–NC–BH_3 isomer is much less pronounced, at 170 °C, than from the Fe–CN–BH_3 isomer. Loss of BH_3 from Fe–NC–BH_3 also seems to result in linkage isomerization of $Fe(phen)_2(NC)_2 \rightarrow Fe(phen)_2(CN)_2$. Finally, the fact that heating $Fe(phen)_2(NCBH_3)_2$ does not lead to the formation of $Fe(phen)_2(CNBH_3)_2$ is at least consistent with the idea that $Fe(phen)_2(NCBH_3)_2$ is the thermodynamically more stable isomer.

These studies lead us to conclude that there is no *facile* means of interconversion of the isomers, such as a simple CN flip within the Fe and B cage. The behavior of the Fe–N-C–BH_3 isomer stands in marked contrast with that[27] of $(H_3N)_5Ru(NCH)^{2+}$ which isomerizes by an unknown mechanism to $(H_3N)_5Ru(CNH)^{2+}$ in the solid state with subsequent polymerization of the latter to $[Ru(NH_3)_4CN]_x^{x+}$. Other such isomerizations have been reported for cyanide bridging metal ions.[28]

Charge-Transfer Spectra and Mössbauer IS. The room-temperature KBr pellet spectra of the $Fe(phen)_2X_2$ compounds obtained in this study do not exhibit sufficient resolution to permit detailed assignments, yet the metal → phen charge-transfer envelopes[4,8,22,29,30] ($d^* \rightarrow \pi^*$) in the 400–700-nm region exhibit interpretable general shifts to the red or blue as X is varied. Typical comparisons which we wish to emphasize are given in Figure 7. To interpret these shifts we rely on one simple concept: electron donation (σ and π) to the metal from X in the ground state tends to red shift the charge-transfer band envelope by means of elevation of the metal d-orbital energies. In the case of σ donation of electrons this elevation occurs through increased electron repulsion at the metal; with π donation of electrons to the metal, not only is there this general electron repulsion based d-orbital elevation but also a specific elevation arises through greater π^* character for the d_π orbitals. Table III summarizes the direction of changes of the charge-transfer energies and the Mössbauer isomer shifts.

The first transformation ($Fe(phen)_2(CN)_2 \rightarrow Fe(phen)_2(CNBH_3)_2$) is occasioned by reduced σ- and π-donor character of X. This means reinforcing blue shift effects on ν_{CT} and opposing effects on the iron IS from 4s (σ) and 3d (π) orbital population changes as discussed earlier. The second transformation (isomerization of $Fe(phen)_2(NCBH_3)_2$) finds greater σ donation and poorer π donation of the X ligand; these have compensating effects on the CT bands but reinforcing effects in a negative direction on the isomer shift, as expected. The final transformation (replacement of BH_3 by S) should, as noted in an earlier section, effect decreased σ donation to Fe but enhanced π donation. Again, the σ/π effects compete with respect to the charge-transfer shift but reinforce in a positive direction in the Mössbauer experiment, causing a large +IS change.

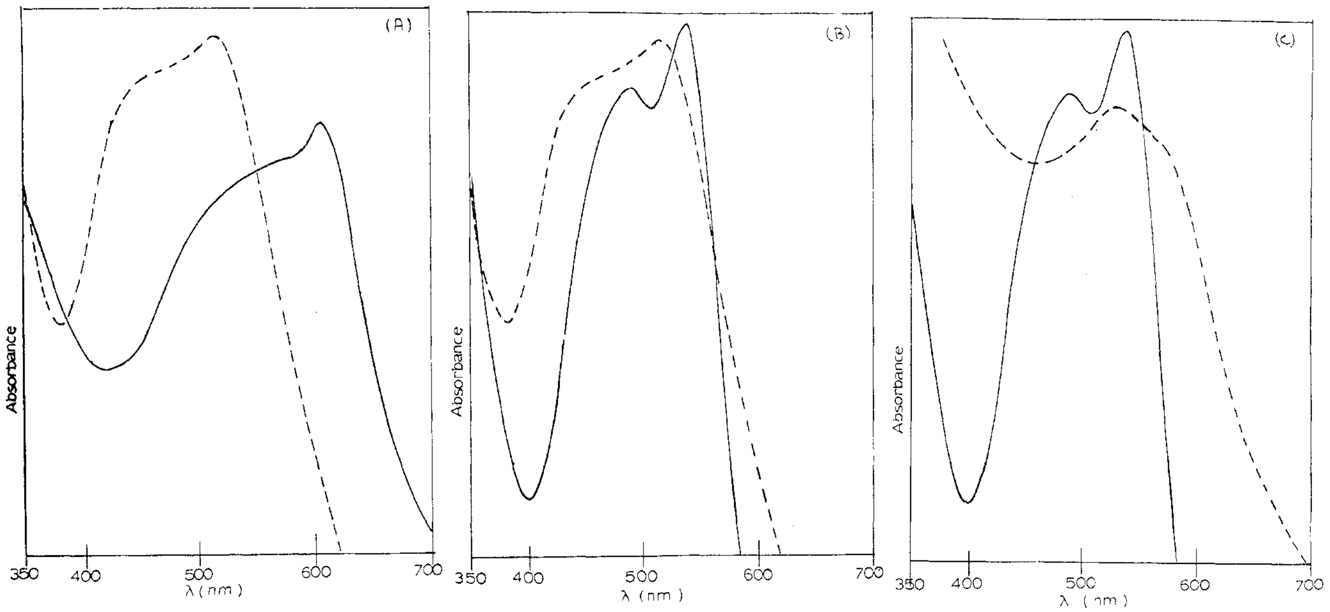


Figure 7. Visible spectra (KBr pellets): (A) $Fe(phen)_2(CN)_2$ (—) and $Fe(phen)_2(CNBH_3)_2$ (---); (B) $Fe(phen)_2(NCBH_3)_2$ (—) and $Fe(phen)_2(CNBH_3)_2$ (---); (C) $Fe(phen)_2(NCBH_3)_2$ (—) and $Fe(phen)_2(NCS)_2$ (---).

These interpretations of IS change are implicitly based on the supposition that Fe 4s population changes are more important than the $3d_\sigma$ changes. It seems that such an approximation may be generally appropriate to both weak and strong donor ligands. It is interesting (but perhaps generally dangerous) to note that the direction of the IS and the ν_{CT} changes could be predicted from consideration of the change in ligand π-donor nature alone. The magnitudes of the shifts, however, obviously require consideration of ligand σ-donor nature as well.

Vibrational Spectra in the CN Region. The CN vibrational data (Table I) are valuable for three reasons. First of all, the appearance of CN doublets for $Fe(phen)_2(NCBH_3)_2$ and $Fe(phen)_2(CNBH_3)_2$, together with the Mössbauer spectra, establishes their structures as cis (C_2) rather than trans (D_{2h}). Second, the presence of only two CN bonds for $Fe(phen)_2(NCBH_3)_2$ precludes a spin equilibrium. Finally, the data may be analyzed for chemical valency characterization of bridging CN^-. For example, the following adduct "reactions" characterize BH_3 as primarily a σ-acceptor acid while $Fe(phen)_2^{2+}$ and, to a greater extent, sulfur reveal considerable π-donor nature as well (the cm^{-1} changes in ν_{CN} are given above the arrows)

$$A\left\{\begin{array}{lll} (1) & CN^- & \xrightarrow{+99} H_3BCN^- \\ (2) & & \xrightarrow{-8} Fe(phen)_2(CN)_2 \\ (3) & & \xrightarrow{-27} SCN^- \end{array}\right.$$

$$B\left\{\begin{array}{lll} (4) & H_3BNC^- & \xrightarrow{+190} H_3BNCBH_3^- \\ (5) & & \xrightarrow{+84} (H_3BNC)_2Fe(phen)_2 \\ (6) & & \xrightarrow{+5} H_3BNCS^- \end{array}\right.$$

$$C\left\{\begin{array}{lll} (7) & H_3BCN^- & \xrightarrow{+81} H_3BCNBH_3^- \\ (8) & & \xrightarrow{+13} (H_3BCN)_2Fe(phen)_2 \\ (9) & (H_3BCN)_2Fe(phen)_2 & \xrightarrow{-38} (H_3BNC)_2Fe(phen)_2 \end{array}\right.$$

The breakdown of ν_{CN} from valency effects is as follows: (i) kinematic coupling of the CN and A–CN or A–NC coordinates (after CN coordinates A) will slightly increase ν_{CN}; (ii) rehybridization of the carbon or nitrogen digonal hybrids (to use a localized orbital view of σ-orbital changes) will stiffen the CN bond through enhanced C/N hybrid atomic orbital overlap;[31] this effect should be of greater importance for the more polarizable C hybrids; (iii) further polarization of the CN σ- and π-bond pairs in the direction of prior polarization would decrease the bond order[32] and thus depress ν_{CN} (note that increased hybrid s character implies greater polarization in the direction of that hybrid); this factor tends to enhance (ii) for C-coordination because the prior polarization of the CN σ and π pairs toward nitrogen is reduced; (iv) retrobonding via π electrons from the acid into the CN π^* orbitals depresses ν_{CN}. Items (i) and (ii) should always be operative and tend to make $\Delta\nu_{CN} > 0$. The sense of operation and magnitude of the item (iii) varies as C or N is the Lewis donor atom; for C-coordination $\Delta\nu_{CN} > 0$, for N-coordination $\Delta\nu_{CN} < 0$. Item (iv) will cause $\Delta\nu_{CN} < 0$ and be of greater importance for C- than N-coordination because the CN^- π^* molecular orbitals have greater concentration on carbon. The importance of (iv) in (2) and (3) relative to (1), in (5) and (6) relative to (4), and in (9) is readily seen.

In contrasting analogous reactions from sets B and C with those of set A, a prior coordination effect is easily discerned. Prior coordination of the cyanide nitrogen seems to stimulate greater enhancement than prior coordination of carbon of the CN frequency, upon bridge formation. This is strikingly revealed by the following comparisons

$$\begin{tikzcd}
& H_3BCN^- \arrow[dr, "+81\ cm^{-1}"] & \\
{}^-CN \arrow[ur, "+99\ cm^{-1}"] \arrow[dr, "-10\ cm^{-1}"'] & & H_3BCNBH_3^- \\
& H_3BNC^- \arrow[ur, "+190\ cm^{-1}"'] &
\end{tikzcd}$$

Particularly interesting is that the π-retrobonding effect which dominates (3) is subordinate to σ effects in (6). This prior coordination effect needs theoretical examination.

To conclude, we wish to make a brief comparison of the isomers $Fe(phen)_2(CNBH_3)_2/Fe(phen)_2(NCBH_3)_2$ with Manzer's[7] isomeric pair $HPt(PEt_3)_2(CNBPh_3)/HPt$-

$(PEt_3)_2(NCBPh_3)$. A curious feature of this latter pair is the common CN stretching frequency

$$Fe(phen)_2(NCBH_3)_2 \xrightarrow{-38\ cm^{-1}} Fe(phen)_2(CNBH_3)_2$$

$$H(Et_3P)_2Pt(NCBPh_3) \overset{0}{\to} H(Et_3P)_2Pt(CNBPh_3)$$

Assuming the kinematic change in each isomerization is negligible permits one to draw some interesting conclusions. Regarding the differential effects of BR_3 and metal complex fragments on ν_{CN}, the CN frequency should be depressed on isomerization through the retrobonding factor (iv). If the metal fragment exhibits less σ-inductive effect than BR_3, factors (ii) and (iii) would not greatly oppose the depression of ν_{CN} in these reactions (note carbon is more polarizable than nitrogen), while greater σ-acid character of the metal fragment should enhance ν_{CN} through factors (ii) and (iii). In the case of $HPt(PPh_3)_2^+$, the Pt fragment appears to have a greater σ-inductive effect than BPh_3, for the σ and π factors appear to be in opposition and largely canceling. For the iron fragment the conclusions are less firm; either the iron exhibits less σ-inductive effect on the CN than does BH_3 ((ii) and (iii) augment (iv) in the depression of ν_{CN}) or if the iron fragment does show greater σ induction than boron, then the σ perturbation must be less pronounced than the π-retrobonding. Given that the thermal isomerization studies suggest $(phen)_2Fe(NCBH_3)_2$ to be the more stable CN arrangement and that this arrangement is dictated by σ-, not π-, bonding preferences, it is logical to conclude that $Fe(phen)_2^{2+}$ exerts less σ-inductive effect than BH_3.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. Additional partial support by the U.S. Energy Research and Development Administration under Contract No. E(11-1)-2130 is acknowledged.

Registry No. $Fe(phen)_2(NCBH_3)_2$, 62561-27-7; $Fe(phen)_2(CNBH_3)_2$, 62562-23-6; $Fe(phen)_2Cl_2$, 15553-84-1; $Fe(phen)_2(CN)_2$, 15362-08-0; $Fe(phen)_2(NCS)_2$, 15319-93-4; $Fe(phen)_3Cl_2$, 14586-53-9.

References and Notes

(1) S. M. Yeh, M.S. Thesis, Kansas State University, 1975; paper presented at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., 1976.

(2) (a) J. R. Bershied, Jr., and K. F. Purcell, *Inorg. Chem.*, **9**, 624 (1970); (b) R. C. Wade, E. A. Sullivan, J. R. Bershied, and K. F. Purcell, *ibid.*, **9**, 2146 (1970).

(3) (a) P. C. Ford, *J. Chem. Soc., Chem. Commun.*, 7 (1971); (b) L. Vaska, W. V. Miller, and B. R. Flynn, *ibid.*, 1615 (1971); (c) D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Inorg. Nucl. Chem. Lett.*, **9**, 835 (1970); *Can. J. Chem.*, **42**, 2990 (1974); (d) S. J. Lippard and P. S. Welcker, *J. Chem. Soc., Chem. Commun.*, 515 (1970); *Inorg. Chem.*, **11**, 6 (1972); (e) K. M. Melmed, T. Li, J. J. Mayerle, and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 69 (1974); (f) S. J. Lippard and B. G. Segal, *Inorg. Chem.*, **13**, 822 (1974).

(4) D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963); D. F. Shriver and J. Posner, *ibid.*, **88**, 1672 (1966).

(5) (a) W. A. Baker, Jr., and H. M. Bobonich, *Inorg. Chem.*, **2**, 1071 (1963); (b) K. Madeja and E. Konig, *J. Inorg. Nucl. Chem.*, **25**, 377 (1963); (c) K. Madeja, W. Wilke, and S. Schmidt, *Z. Anorg. Allg. Chem.*, **346**, 306 (1966); (d) W. A. Baker and H. M. Bobonich, *Inorg. Chem.*, **3**, 1184 (1964); (e) E. Konig and K. Madeja, *ibid.*, **6**, 48 (1967); (f) L. Dezsi, B. Molnar, T. Tarnoczi, and K. Tompa, *J. Inorg. Nucl. Chem.*, **29**, 2486 (1967); (g) A. T. Casey and F. Isaac, *Aust. J. Chem.*, **20**, 2765 (1967).

(6) F. R. Fronczek and W. P. Schaefer, *Inorg. Chem.*, **13**, 727 (1974).

(7) L. E. Manzer and W. C. Seidel, *J. Am. Chem. Soc.*, **97**, 1956 (1975).

(8) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(9) B. N. Figgis and J. Lewis, *Mod. Coord. Chem.*, 403 (1960).

(10) R. L. Cohen, P. G. McMullin, and G. K. Wertheim, *Rev. Sci. Instrum.*, **34**, 671 (1963).

(11) R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966).

(12) J. F. Duncan and K. F. Mok, *J. Chem. Soc.*, 1493 (1966).

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley, New York, N.Y., 1970.

(14) J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, **11**, 930 (1972).

(15) J. R. Bershied, Jr., Ph.D. Thesis, Kansas State University, 1970.

(16) J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1121 (1963).

(17) E. Konig et al., *Chem. Phys. Lett.*, **27**, 23 (1974), and references therein.

(18) K. F. Purcell and R. L. Martin, *Theor. Chim. Acta*, **35**, 141 (1974).

(19) This seems to be true for other spin-triplet complexes of Fe^{2+} as well: Konig's[20] $Fe(diimine)_2X_2$ ($X = F_2$, oxalate, malonate) and, more recently, Busch's[21] $[Fe(tetraamine)O_2N]^+$.

(20) (a) E. Konig and K. Madeja, *Inorg. Chem.*, **7**, 1848 (1969); (b) E. Konig, G. Ritter, and B. Kanellakopulos, *J. Chem. Phys.*, **58**, 3001 (1973).

(21) D. D. Watkins, Jr., D. P. Riley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, **15**, 387 (1976).

(22) K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", W. B. Saunders, Philadelpha, Pa., 1977. According to the AOM, the shift in d AO energy is proportional to $\sum S_i^2$, where S_i is the overlap integral for the ith ligand σ or π orbital with the metal orbital. With the overlap for d_{z^2} with a ligand σ-donor orbital along the $+z$ axis taken as reference, the d_{z^2} shift is e_σ. A similar definition applies to the d_{xz}–ligand p_π interaction $\equiv e_\pi$. Ligand σ orbitals have S^2 with the d_{z^2} collar only one-fourth that of the reference overlap; six equivalent ligands along the $\pm x$, $\pm y$, $\pm z$ axes give a d_{z^2} shift of $2e_\sigma + 4(e_\sigma/4) = 3e_\sigma$. The S^2 for $d_{x^2-y^2}$/ligand σ overlap is three-fourths that of the reference; therefore, the $d_{x^2-y^2}$ energy shift is $4(3e_\sigma/4) = 3e_\sigma$. Similar arguments for six ligands, each with two p_π orbitals for overlap, give, for example, the d_{xz} shift as $4e_\pi$, from the four p_π ligand AO's in the xz plane.

(23) G. B. Bancroft, "Mössbauer Spectroscopy", Wiley, New York, N.Y., 1973.

(24) Konig has successfully argued that both $^3A_2$ and ^31E ground terms (components of $^3T_{1g}(O_h)$) in tetragonal symmetry could give $q_{zz} = 0$; nevertheless he also noted that ^31E mixing with ^32E (from $^3T_{2g}(O_h)$) by both spin–orbit and low-symmetry effects creates a sizable q_{zz} for ^31E. Upon transformation of the CFT parameters (Dq, Ds, Dt) to the AOM equivalents we find that a $^3A_2$ state is to be expected whenever $\delta e_\sigma/(e_{\pi n} + e_{\pi x}) > -0.17$. The combination δe_σ, $(e_{\pi n} + e_{\pi x})$ both >0 most easily satisfies this relationship and is consistent with intuition; while it is mathematically *possible* to have $\delta e_\sigma > 0$, $(e_{\pi x} + e_{\pi n}) < 0$ and still obtain $^3A_2$, it is necessary that δe_σ be much smaller than $(e_{\pi n} + e_{\pi x})$. Such a circumstance is unlikely for the ligand combination here and further requires that a combination of spin–orbit and interelectronic repulsion factors stabilize the $^3A_2$ configuration $(xy)^1(xz, yz)^4(x^2 - y^2)^1$ below the ^3E configuration $(xy)^2(xz, yz)^3(x^2 - y^2)^a(z^2)^b$, where $a + b = 1$.

(25) E. Konig and K. Madeja, *Spectrochim. Acta, Part A*, **23a**, 45 (1967); *Chem. Commun.*, 61 (1966).

(26) The fact that μ_{eff} for $Fe(phen)_2(NCBH_2)_2$ is very close to the spin-only value of 2.8 μ_B is a little surprising in view of the results of others. Either there is an unusually small orbital contribution here or population of ^1A to a small extent (<15%) at room temperature is indicated.

(27) S. S. Isied and H. Taube, *Inorg. Chem.*, **14**, 2561 (1975).

(28) D. F. Shriver, *Struct. Bonding* (*Berlin*), **1**, 32 (1966).

(29) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(30) L. E. Orgel and N. K. Hamer, *Nature* (*London*), **190**, 439 (1961).

(31) K. F. Purcell, *J. Am. Chem. Soc.*, **89**, 6139 (1967); **91**, 3487 (1969); K. F. Purcell and R. S. Drago, *ibid.*, **88**, 919 (1966).

(32) The bond order due to two AO's (hybrid or Schrodinger) is maximum when the AO coefficients in the MO are the same (that is when both are $1/2^{1/2}$).