

BRIDGING CYANIDE IN $\text{Fephen}_2(\text{NCBH}_3)_2$ - A SPIN TRIPLET

by

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TABLE OF CONTENTS

	PAGE
LIST OF TABLES.....	iv
LIST OF FIGURES.....	v
I. Introduction.....	1
A. General Introduction to NCBH_3	1
B. NCBH_3 as a Ligand.....	2
C. Review of $\text{Fephen}_2(\text{NCS})_2$	6
II. Statement of Purpose.....	9
III. Experimental.....	11
A. Preparation of Compounds.....	11
B. Thermal Stability Study.....	14
C. Reactions of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$ with Nucleophiles.....	14
D. Physical Measurements.....	17
E. Unsuccessful Measurements.....	19
F. Purification of Solvents.....	19
IV. Results.....	21
V. Discussion	60
A. Magnetic Susceptibilities and Mössbauer data..	60

	PAGE
B. Charge Transfer Spectra.....	78
C. Vibrational Spectra in the CN Region.....	88
D. Solvolysis of $\text{Fephen}_2(\text{CNBH}_3)_2$ & $\text{Fephen}_2(\text{NCBH}_3)_2$	94
E. Thermal Stability.....	119
 VI. Further Development.....	 128
 VII. References.....	 129
 VIII. Appendix.....	 132

LIST OF TABLES

TABLE	PAGE
I. Reactions of $\text{Fephen}_2(\text{CNBH}_3)_2$ & $\text{Fephen}_2(\text{NCBH}_3)_2$ with Nucleophiles and the Solvolysis of the Complexes.....	15
II. Data for $\text{Fephen}_2\text{X}_2$ and Related Compounds.....	58
III. Relative d Orbital Energy Levels, Using the Angular Overlap Model.....	65
IV. Ordering of the d Orbitals and the Electric Field Gradient for Low, Intermediate and High Spin States of the Octahedral Ferrous Complexes.....	68
V. Relative d Orbital Energy Levels for Fephen_3^{++} , $\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{NCS})_2$	71
VI. Limits and Balance between σ and π Donating Ability of phen and X for a Spin-triplet $\text{Fephen}_2\text{X}_2$	74
VII. Shift of the Charge Transfer Bands and Change of the Isomer Shifts for $\text{Fephen}_2\text{X}_2$ as X Is Varied.	79

LIST OF FIGURES

FIGURE	PAGE
1. pmr spectrum of KNCBH_3 in D_2O	24
2. Infrared spectrum of KNCBH_3 ; KBr pellet.....	26
3. Infrared spectrum of $\text{Fephen}_2(\text{NCBH}_3)_2$; KBr pellet.	28
4. Infrared spectrum of $\text{Fephen}_2(\text{CNBH}_3)_2$; KBr pellet.	30
5. Infrared spectrum of $\text{Fephen}_2(\text{CN})_2$; KBr pellet....	32
6. Infrared spectrum of $\text{Fephen}_2(\text{NCS})_2$; KBr pellet...	34
7. Infrared spectrum of $\text{Fephen}_2\text{Cl}_2$; KBr pellet.....	36
8. Mössbauer spectrum of $\text{Fephen}_2(\text{NCBH}_3)_2$	38
9. Mössbauer spectrum of $\text{Fephen}_2(\text{CNBH}_3)_2$	40
10. Mössbauer spectrum of $\text{Fephen}_2(\text{CN})_2$	42
11. Mössbauer spectrum of $\text{Fephen}_2\text{Cl}_2$	44
12. Visible spectrum of $\text{Fephen}_2(\text{NCBH}_3)_2$; KBr pellet..	46
13. Visible spectrum of $\text{Fephen}_2(\text{CNBH}_3)_2$; KBr pellet..	48
14. Visible spectrum of $\text{Fephen}_2(\text{CN})_2$; KBr pellet.....	50
15. Visible spectrum of $\text{Fephen}_2(\text{NCS})_2$; KBr pellet....	52
16. Visible spectrum of $\text{Fephen}_2\text{Cl}_2$; KBr pellet.....	54
17. Visible spectrum of $\text{Fephen}_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$; KBr pellet..	56
18. Visible spectra of $\text{Fephen}_2(\text{CN})_2$ and $\text{Fephen}_2(\text{CNBH}_3)_2$; KBr pellets.....	81
19. Visible spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{CNBH}_3)_2$; KBr pellets.....	83
20. Visible spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{NCS})_2$; KBr pellets.....	85

21. Visible spectra of sulfolane solutions of Fephen ₂ (CN) ₂ and Fephen ₂ (NCBH ₃) ₂	95
22. Visible spectra of pyridine solutions of Fephen ₂ (CN) ₂ and Fephen ₂ (NCBH ₃) ₂	97
23. Visible spectra of methanol solutions of Fephen ₂ (CN) ₂ and Fephen ₂ (NCBH ₃) ₂	99
24. Visible spectra of aqueous solutions of Fephen ₂ X ₂ X ₂ = (NCBH ₃ ⁻) ₂ , (NCS ⁻) ₂ , (Cl ⁻) ₂ , phen.....	102
25. Visible spectra of nitromethane solutions of Fephen ₂ X ₂ ; X ₂ = (NCS ⁻) ₂ , phen, (Cl ⁻) ₂ , (NCBH ₃ ⁻) ₂ ..	104
26. Visible spectra of acetonitrile solutions of Fephen ₃ ⁺² and Fephen ₂ (NCBH ₃) ₂	106
27. Visible spectra of methanol solutions of Fephen ₃ ⁺² and Fephen ₂ (NCBH ₃) ₂	108
28. Visible spectra of acetic acid solutions of Fephen ₃ ⁺² and Fephen ₂ (NCBH ₃) ₂	110
29. Visible spectra of sulfolane solutions of Fephen ₃ ⁺² and Fephen ₂ (NCBH ₃) ₂	112
30. Visible spectra of pyridine solutions of Fephen ₃ ⁺² and Fephen ₂ (NCBH ₃) ₂	114
31. Visible spectra of Fephen ₂ (NCBH ₃) ₂ in dichlorome- thane, dichloroethane and acetone.....	116
32. ir spectra of Fephen ₂ (NCBH ₃) ₂ before and after heating at 170°C under roto-vacuo.....	120
33. ir spectra of Fephen ₂ (NCBH ₃) ₂ after prolong heating at 170°C under roto-vacu	122
34. ir spectra of Fephen ₂ (NCBH ₃) ₂ before and after heating at 170°C under roto-vacuo.....	124
35. Arrangement of the devices for the Mössbauer spectrometer.....	133

I. Introduction

A. General Introduction to NCBH_3^-

Wittig and Raff^{1,2} first reported the synthesis of LiNCBH_3 in 1951 by allowing LiBH_4 to react with excess HCN in diethyl ether at 100°C under pressure. Little attention was given to this compound in the next 15 years; only Drefahl³ indicated a limited applicability of NCBH_3^- as a reducing agent. In the past few years, however, there has been a renewed interest in the NCBH_3^- anion. In 1967, Wade and Purcell⁴ reported the synthesis of NaNCBH_3 and its isomer NaCNBH_3 . Borch⁵ has since shown that NCBH_3^- has a much broader utility in organic chemistry as a selective reducing agent than was previously reported; Kreevoy⁶ has published preliminary kinetic data for the acid hydrolysis of NCBH_3^- and observed hydrogen isotope exchange in D_2O at low pD . Also, Purcell^{7,8} has modified the synthesis procedure and prepared the corresponding sodium and potassium salts in good yield and purity. Wittig, Wade and Purcell have determined the solubility of NCBH_3^- salts in a number of solvents.

Complete spectral data for NCBH_3^- have been given by Berschied and Purcell,⁷ who recorded the Raman spectra and the i r spectra of the normal and deuterated compounds and assigned the fundamental vibrational bands and some overtone and combination bands. The p m r spectrum of NCBH_3^- is

characterized by its quartet and much weaker sextet due to the coupling of the protons with ^{11}B ($I = 3/2$) and ^{10}B ($I = 3$), respectively.

Purcell also reported the synthesis conditions under which $^-\text{CNBH}_3$ may be prepared.⁸ These two isomer ($^-\text{NCBH}_3$ and $^-\text{CNBH}_3$) are distinguished by their i.r. and p.m.r. spectra. The isocyanoborohydride, $^-\text{CNBH}_3$, is less stable to hydrolysis and can be isomerized to its normal form by H^+ and CN^- catalysis. The reducing action of $^-\text{NCBH}_3$ toward some metals was proposed to be through the inner-coordination mechanism.

B. $^-\text{NCBH}_3$ as a Ligand

The potential coordination ability to transition metals through the nitrogen of $^-\text{NCBH}_3$ is obvious since there is a lone pair on the nitrogen atom and the carbon, which has a very powerful coordination ability, is already bound to the Lewis acid BH_3 . After this ability was initially suggested by Purcell⁷ there have been several reports concerning $^-\text{NCBH}_3$ functioning as a ligand in transition metal complexes.

In 1963, Shriver⁹ synthesized the complex $\text{Fephen}_2(\text{CNBH}_3)_2$ by the reaction:



Although he initially considered the possibility of Fe-N-C bonding in this compound, his later studies¹⁰ of the charge transfer bands (visible region) of this complex and the related compounds $\text{Fephen}_2(\text{CNBX}_3)_2$ (where $\text{X} = \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$) and of the oxidation potentials of these complexes confirmed Fe-C-N bonding in $\text{Fephen}_2(\text{CNBH}_3)_2$.

Lippard,^{11,12} in 1970, synthesized several transition metal complexes containing cyanoborohydride and tertiary group V donor ligands with a general formula of $\text{L}_3\text{M}(\text{NCBH}_3)$, where $\text{M} = \text{Ag}^+, \text{Cu}^+, \text{Ni}^{++}$; $\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{Ph}_3\text{Sb}$. The occurrence of M-N bonding was suggested by their ir spectra and the following facts that:

- 1) there is no absorption corresponding to $\delta_{\text{M-H-B}}$;
- 2) when the hydrogen atoms of NCBH_3^- are replaced by phenyl groups the complexes still display similar i.r. spectra in the CN region;
- 3) ν_{CN} of complexed NCBH_3^- is relatively higher than that of free NCBH_3^- ;
- 4) the C_{3v} symmetry of the anion NCBH_3^- is closely retained in the complexes.

From the conductivity measurements in acetonitrile, they also noted that $(\text{Ph}_3\text{P})_3\text{Ag}(\text{NCBH}_3)$ is a much stronger electrolyte than $(\text{Ph}_3\text{P})_3\text{Cu}(\text{NCBH}_3)$. This implies weaker Ag-N binding than Cu-N binding, a result compatible with the small increase of ν_{CN} in $(\text{Ph}_3\text{P})_3\text{Ag}(\text{NCBH}_3)$.

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Since tetrahydroborate is well known to coordinate transition metals by forming multicenter, hydrogen-bridged bonds, the possibility that NCBH_3^- might act as a H-bridging ligand was also investigated. Lippard¹³ let NCBH_3^- react with a chloroform solution containing chloro bis (triphenylphosphine) -Cu in a 1 : 1 (NCBH_3^- : copper complex) ratio and formed $(\phi_3\text{P})_2\text{Cu}(\text{NCBH}_3)$. An X-ray study indicated that this compound exists as a dimer where each quasitetrahedral copper atom is bonded to two $\phi_3\text{P}$ and to a H and N atom from the different NCBH_3^- . There is an ir band at 2200 cm^{-1} corresponding to a Cu-H-M bending frequency and there are two ν_{CN} which are due to the distinctly different local site symmetries at the boron atoms of the two NCBH_3^- ligands.

In addition, Lippard synthesized the 5-coordinated $(\text{Me}_3\text{dien})\text{Cu}(\text{NCBH}_3)_2$ ¹⁴ and 6-coordinated $\text{Ni}(\text{en})_2(\text{NCBH}_3)_2$.¹¹ Both have proved to exhibit M-N bonding.

It's interesting to note that different experimental procedures may lead to different coordinating modes for NCBH_3^- . Wright^{15,16} synthesized the complex, $(\phi_3\text{P})_3\text{Cu}(\text{NCBH}_3)$, by reducing the dihydrated cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, with tertiary phosphine in ethanol solution followed by addition of NaNCBH_3 to the reaction mixture. This product shows $\delta_{\text{Cu-H-B}}$ absorptions and a melting point and a solubility different from Lippard's complex, which was synthesized by replacing Cl^- of $(\phi_3\text{P})_3\text{CuCl}$ by NCBH_3^- in ethanol-chloroform solvents. Wright

proposed in his complex the NCBH_3^- coordinates to Cu through the hydrogen, but no exact reason was given to explain this different coordination mode. After preparing a series of divalent Co^{2+} , Ni^{2+} and Cu^+ complexes containing NCBH_3^- and tertiary phosphine as ligands, he found in some cases as $\text{Cu}(\text{NCBH}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_3$, $\text{Cu}(\text{NCBH}_3)(\text{DBP})_3$ and $\text{NiCl}(\text{NCBH}_3)(\text{Dipos})$. The complexes were M-N bonding, whereas in $\text{Cu}(\text{NCBH}_3)(\text{Dipos})_{1.5}$, $\text{Ni}(\text{NCBH}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_2$, $\text{Ni}(\text{NCBH}_3)\text{H}(\text{P}(\text{C}_6\text{H}_5)_3)_2$, $\text{Co}(\text{NCBH}_3)(\text{DBP})_4$, $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{NCBH}_3)$, $\text{Ni}(\text{NCBH}_3)\text{H}(\text{DBP})$ and $\text{Co}(\text{NCBH}_3)(\text{Dipos})_2$ M-H binding was observed, Wright¹⁶ suggested that, although M-H bonding is always possible, strongly basic ligands other than NCBH_3^- in the complex would incur effective back-donating of metal electron density to NCBH_3^- and favor M- NCBH_3^- bonding, because nitrogen coordination allows NCBH_3^- to function as a π -accepting ligand (although its ability may be small). On the other hand, the steric effect of the other ligands tends to hinder the M-N bonding, and the rigid and flattened DBP favors the M-N bonding as all attempts to form Cu-H-B bonded $\text{Cu}(\text{NCBH}_3)(\text{DBP})_3$ failed.

The π -accepting ability of nitrogen of NCBH_3^- , in comparison with BH_4^- , was also claimed by Vaska¹⁷ in his complexes $\text{M}(\text{NCBH}_3)_2(\text{CO})(\text{PR}_3)$ and the corresponding $\text{M}(\text{BH}_4)_2(\text{CO})(\text{PR}_3)$, where M = Ir(I) or Rh(I), R = Ph or C_6H_{11} . The NCBH_3^- complexes are M-N bonding; the higher ν_{CO} of the NCBH_3^- complexes than that of the corresponding BH_4^- complexes indicates less electron back-donating into the π^*_{CO} orbitals. However, this

result is also expected from the more basic σ donor nature of H.

While ν_{CN} of NCBH_3 is generally shifted higher when nitrogen acts as the Lewis donor atom, a decrease of ν_{CN} in $(\text{H}_3\text{N})_5\text{Ru(II)(NCBH}_3)$ has been noted by Ford.^{18,19} The same depression was found for the monodentate organonitriles coordinating to penta-ammine Ru(II) species. This is interpreted by the unusually strong back-donating ability of the penta-ammine ruthenium(II) species. The corresponding Ru(III) complexes, on the other hand, do show the increase in the CN stretching frequencies typical for coordinated nitrile. The difference between Ru(II) and Ru(III) is probably due to greater σ acidity and less π basicity of Ru(III).

To date, the only isomeric pairs of bridging cyano complexes which have been reported are Schaefer's²⁰ $(\text{H}_3\text{N})_5\text{Co-CNCo(CN)}_5$ and $(\text{H}_3\text{N})_5\text{CoNCCo(CN)}_5$ and Manzer's²¹ $\text{H(Et}_3\text{P)}_2\text{Pt-(NCB}\phi_3)$ and $\text{H(Et}_3\text{P)}_2\text{Pt(CNB}\phi_3)$. They were reported in 1974 and earlier this year, separately, as our work neared completion.

C. A Review of $\text{Fephen}_2(\text{NCS})_2$

$\text{Fephen}_2(\text{NCS})_2$ with cis-geometry was first prepared by Baker²² and Madeja,^{23,24} independently, in 1963. Both groups^{25,26} observed the high-spin character of this complex at room tem-

perature and the remarkable temperature dependency of its magnetic susceptibility: when the temperature is lowered, there is a sudden, sharp decrease of the magnetic moment at the critical temperature (174°K). The X-ray studies by both groups at high and low temperature reveal no crystal phase change of the complex that might cause the spin-state change. Baker²⁵ first recorded the Mössbauer spectra of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ above and below 170°K but failed to observe any change of the spectrum, which would have indicated the occurrence of a high spin - low spin transformation. This turned out to be erroneous because König²⁶ did observe Mössbauer parameter changes. The room temperature spectrum has a large isomer shift and large quadrupole splitting while the spectrum at 77°K gives small i.s. and small q.s.; these differences are typical for high-spin and low spin, respectively, 6-coordinated ferrous complexes. The infrared spectrum at 77°K also reveals the low-spin character for $\text{Fe}(\text{phen})_2(\text{NCS})_2$; there is a shift to higher frequency for two CN stretching bands at low temperature because of greater electron back-donation from the ferrous ion to π^* of phen and stronger metal-ligand σ bonding as the σ^* molecular orbitals are depopulated.

The temperature-dependent Mössbauer spectra study by Tompa²⁷ fully maps the very interesting change of the electronic configuration of $\text{Fe}(\text{phen})_2(\text{NCS})_2$. At room temperature there are only two absorptions corresponding to the high-

spin $\text{Fephen}_2(\text{NCS})_2$. As the temperature is decreased to -100°C . There is an appearance of two new absorptions corresponding to the low-spin $\text{Fephen}_2(\text{NCS})_2$. When the temperature is lowered further, one can observe a decrease in the intensity of the absorptions for the high-spin complex and the increase of that for the low-spin $\text{Fephen}_2(\text{NCS})_2$. Furthermore, Casey and Issac,²⁸ noticed that the transition of $\text{Fephen}_2(\text{NCS})_2$ from high-spin state to low-spin state, at 173°K , fits a first-order rate law quite well. They also claimed, as König and Madeja did, that different methods of preparation, and even different samples prepared by the same method, give a variety of values for the effective magnetic moment, but the quantitative behavior is identical.

The room temperature Mössbauer spectrum of $\text{Fephen}_2(\text{NCS})_2$ was also confirmed by Duncan²⁹ and Collins.³⁰

II. Statement of Purpose

Since NCBH_3^- acts as a ligand, one would naturally ask "how strong is its ligand field" and "how strong are its σ bonding and π bonding abilities". 6-coordinated Fe(II) (d^6) complexes like $\text{Fephen}_2(\text{NCBH}_3)_2$, and $\text{Fephen}_2(\text{CNBH}_3)_2$ would offer a distinguished opportunity for such a study. Using data collected from infrared, visible, and Mössbauer spectroscopy and magnetic susceptibility measurements, we hoped to be able to characterize NCBH_3^- and CNBH_3^- with regard to their σ and π bonding abilities. We hoped further to obtain information, from a comparison of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$, on the effect of the double coordination on the cyano group. A third goal has been to determine which isomer of the pair is more stable and whether these isomers can be interconverted thermally.

Given the remarkable, sharp temperature dependence of the magnetic susceptibility of $\text{Fephen}_2(\text{NCS})_2$, we felt it worth the effort to synthesize the highly analogous $\text{Fephen}_2(\text{NCBH}_3)_2$ compound. Not only did we hope to find another example of the unusual high - low spin phenomenon for Fe(II) but also we planned to explore the effect of replacing S with BH_3 on such phenomena.

A long-term goal of interest to us is the synthesis of isocyanide compounds. $\text{Fephen}_2(\text{NCBH}_3)_2$ was prepared as a

precursor to $\text{Fephen}_2(\text{NC})_2$, whereas $\text{Fephen}_2(\text{CNBH}_3)_2$ could be used as a precursor to $^-\text{CNEH}_3$.

III. Experimental

A. Preparation of Compounds: all reactions were carried out under an atmosphere of dry N_2 .

$KNCBH_3$: in a typical preparation of $KNCBH_3$, 0.1 mole KCN, predried overnight in an Abderhalden drying pistol at $100^\circ C$, was added to a 3-neck flask containing 80 ml BH_3/THF solution (Apache Chem. Co. ~1 molar). The mixture was refluxed for 48 hours. After cooling to room temperature, the reaction flask was moved into a dry-box continuously purged with dry air and the excess KCN was filtered off. The volume of the THF solution was reduced to 30 ml with a rotary evaporator at room temperature and 250 ml of dry CH_2Cl_2 was added to precipitate $KNCBH_3$. The product was recrystallized from THF, washed with anhydrous ether and left to dry in the dry box for an hour. The yield is 80 %. This compound was stored in a capped vial in the dry-box until used.

$Fephen_2(NCBH_3)_2$: $KNCBH_3$ (0.6567 g, 8.313 mmole) was dissolved in 100 ml dry THF and the solution was filtered. The filtrate was added quickly to a 3-necked flask containing 1.15 g (2.363 mmole) of $Fephen_2Cl_2$ (blue), prepared by Madeja's²⁴ method, and the reaction flask was purged with N_2 gas again for about 15 minutes. After refluxing for 3 days (the mixture was protected from atmospheric moisture with a mercury bubbler), infrared spectra of the solvent showed no further change in the inten-

sities of absorptions 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 $\frac{1}{2}$ 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.

Calculated	C: 62.95	N: 16.95	H: 4.48	Fe: 11.26	B: 4.36
Found [#]	C: 57.72	N: 15.25	H: 4.35	Fe: 11.41	B: 4.11
Found [*]	C: 57.56	N: 15.51	H: 4.19		

$\text{Fephen}_2(\text{CNBH}_3)_2$: $\text{Fephen}_2(\text{CN})_2$ (dark-blue) was prepared using Schilt's^{3/} method. About 15 ml of one molar BH_3/THF solution was diluted with 50 ml dry THF and added to a reaction flask containing 0.8620 g (1.842 mmole) $\text{Fephen}_2(\text{CN})_2$. After refluxing for about 10 hours, and then cooling to room temperature, a red solid was filtered from the reaction mixture and washed with THF and anhydrous ether and dried on an air frit. 0.9135 g $\text{Fephen}_2(\text{CNBH}_3)_2$ was collected.

[#]The results obtained from Galbraith Laboratories

^{*}The results obtained from Atlantic Microlab

Calculated	C: 62.95	N: 16.95	H: 4.48	Fe: 11.26	B: 4.36
Found [#]	C: 60.16	N: 15.29	H: 4.72	Fe: 11.33	B: 4.09
Found [*]	C: 60.08	N: 15.70	H: 4.71		

Difficulty (low result) was encountered with the carbon and nitrogen analyses for both the complexes $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$, as reported by Shriver^{9,10} for similar compounds. Of the possible impurities in $\text{Fephen}_2(\text{NCBH}_3)_2$ ($\text{Fephen}_3\text{X}_2$, $\text{X} = \text{Cl}^-$, $^-\text{NCBH}_3$ and $\text{Fephen}_2\text{X}_2$, $\text{X} = \text{Cl}^-$, CN^-), the first three would be removed by the water treatment and the presence of the last one would be indicated by additional bands in the CN stretching region. In the case of $\text{Fephen}_2(\text{CNBH}_3)_2$, i.r. spectra in the CN region do show the presence of a trace of unreacted $\text{Fephen}_2(\text{CN})_2$, but this cannot account for the low C, N analyses obtained for a sample of $\text{Fephen}_2(\text{CNBH}_3)_2$.

That complete analysis for a sample of $\text{Fephen}_2(\text{NCS})_2$ (synthesized by Madeja's²⁴ method,) yields results differing from the calculated values by $<0.3\%$ for all elements suggests that B interferes with the C, N analyses. For $\text{Fephen}_2(\text{NCS})_2$

Calculated	C: 58.65	N: 15.79	H: 3.04	Fe: 10.49	B: 12.04
Found [#]	C: 58.45	N: 15.52	H: 2.90	Fe: 10.69	B: 11.79

[#]The results obtained from Galbraith Laboratories

^{*}The results obtained from Atlantic Microlab

B. Thermal Stability Studies:

Samples of complexes $\text{Fephen}_2(\text{NCBH}_3)_2$, $\text{Fephen}_2(\text{CNBH}_3)_2$, $\text{Fephen}_2(\text{CN})_2$ and $\text{Fephen}_2(\text{NCS})_2$ 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 checked by their i r spectrum (see Discussion C).

C. Reaction of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$ with Nucleophiles

$\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$ were added to solutions containing strongly basic donors and gently heated. The nucleophile/solvent combinations in Table I were tried:

Table I

Reactions of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$ with nucleophiles and the solvolyses of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$.

- x not soluble
- xx no reaction occurred
- 0 readily dissolved
- $\triangle$ slowly dissolved
- + impractical solubility of complex in solvents

	Fephen ₂ (NCBH ₃) ₂	Fephen ₂ (CNBH ₃) ₂
KCN/H ₂ O	XX	XX
Φ ₃ P/THF	XX	XX
Et ₃ N/Et ₃ N	XX	XX
Pyridine	△	0
Sulfolane	△	0
Methanol	0	0
Acetonitrile	0	0
Nitromethane	0	0
Acetic acid	+	X
Water	+	X
Acetone	+	X
Dichloromethane	+	X
Dichloroethane	+	X

D. Physical Measurements

1) Magnetic Measurements:

Magnetic susceptibilities were obtained at room temperature by Gouy's method. The effective magnetic moments of the complexes were obtained from $\mu_{\text{eff}} = 2.83 (\chi T)^{\frac{1}{2}}$. $\text{HgCo}(\text{SCN})_4$ was used as the tube calibrant and the diamagnetic corrections were made using values given by Figgis and Lewis.³² In preparing samples for measurement, the solid complex was put into the tube in small portions and the tube was tapped lightly against the desk to pack the crystals firmly. For each complex, at least 3 tube-packings were carried out. The effective magnetic moments reported in Table II are estimated to be accurate to within ± 0.05 for the low values and to within ± 0.10 for the high values.

2) 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 $\pm 2 \text{ cm}^{-1}$. Spectra of solutions were recorded with the same spectrometer, using a cavity cell of 0.1 mm length.

3) Mössbauer Spectra:

Mössbauer spectra were recorded using a standard speaker drive system³³ operating in the constant acceleration mode.

The design of the Mössbauer spectrometer and its operation is described in Appendix A. Two spectra were accumulated simultaneously in a 1024 channel analyzer running in the multiscaling mode. The spectra obtained using this apparatus for $\text{Fe}(\text{phen})_2\text{Cl}_2$ and $\text{Fe}(\text{phen})_2(\text{CN})_2$ as reported in Table II agree within experimental error (± 0.05 mm/sec) with previously published results.³⁰ The absorbers consisted of loosely packed polycrystalline disks suspended on 3 M tape. The source was 10 mCi ^{57}Co in Pd. The velocity scale was calibrated using the ^{57}Co (in Pd) source v.s. an ^{57}Fe (in Fe) absorber spectrum. The isomer shifts are relative to the centroid of the ^{57}Fe spectrum.

5) n.m.r. Spectra

The ^1H n.m.r. spectrum of KNCBH_3 in D_2O was recorded with a Varian T-60 spectrometer using the impurity H_2O in D_2O as internal standard.

The proton decoupled ^{13}C n.m.r. spectra of $\text{Fe}(\text{phen})_2(\text{CNBH}_3)_2$ in sulfolane, KNCBH_3 in THF and $\text{NaBH}_3\text{CNBH}_3$ in THF were recorded with an HA-100 spectrometer. Acetone was used as an external standard. The chemical shifts of these spectra were converted to values relative to external TMS.

E. Unsuccessful Measurements

Attempts at n.m.r. and e.s.r. solution measurements of $\text{Fephen}_2(\text{NCBH}_3)_2$ failed because no suitable solvent was found for this complex. Room temperature e.s.r. spectra of polycrystalline samples were also uninformative.

F. Purification of Solvents

The purification of solvents generally followed the procedures described by Jolly.³⁴

Dichloromethane, dichloroethane and pyridine (Mallinckrodt Inc., Analytical reagent grade), acetonitrile (Baker Chem. Co., A.C.S. certified) and nitromethane (Fisher Scientific Co., A.C.S. certified) were refluxed with BaO first for about an hour, followed by distillation. The initial distillates were discarded. The main distillates were stored in oven-dried screwcapped bottles.

Acetic acid (Baker Chem. Co., A.C.S. certified) was first treated by triacetylborate and then distilled. Acetone was dried over Drierite, followed by distillation. Sulfolane (Shell Co.) was dried over Type 4A molecular sieves.

Methanol (Fisher Scientific Co., A.C.S. certified) was first distilled, then treated with Drierite, and finally stored over molecular sieves.

Tetrahydrofuran (Mallinckrodt Inc., Analytical reagent grade) was first dried over pieces of fresh-cut sodium metal and stored in bottles stoppered with a drying tube containing Drierite.

IV. Results

KNCBH_3 was identified by its i.r. and ^1H n.m.r. spectra (Figures 1 and 2 respectively), which have been previously reported by this group. The i.r. spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ and related compounds are presented in Figures 3-7. Mössbauer spectra of the complexes are shown in Figures 8-11. The magnetic moments, the CN stretching frequencies, and the isomer shifts and quadrupole splittings which form the basis of the characterization of $\text{Fephen}_2(\text{NCBH}_3)_2$, $\text{Fephen}_2(\text{CNBH}_3)_2$ and related complexes are given in Table II. Visible spectra of KBr pellets of solid samples are presented in Figures 12-17.

$\text{Fephen}_2(\text{CNBH}_3)_2$ is soluble and stable in sulfolane; its i.r. spectrum gives two CN stretching frequencies at 2156 cm^{-1} and 2164 cm^{-1} and its visible region spectrum is shown in Figure 21. The sulfolane solution of $\text{Fephen}_2(\text{CN})_2$, on the other hand, gives two CN stretching bands at 2063 cm^{-1} and 2077 cm^{-1} and its visible spectrum is also shown in Figure 21. $\text{Fephen}_2(\text{CNBH}_3)_2$ is also soluble in nitromethane and acetonitrile.

Heating a pyridine solution of $\text{Fephen}_2(\text{CNBH}_3)_2$ resulted in a color change from red to deep blue; the visible spectra of the freshly prepared and heated solutions, together with that of a pyridine solution of $\text{Fephen}_2(\text{CN})_2$, are shown in Figure 22. The heated pyridine solution of $\text{Fephen}_2(\text{CNBH}_3)_2$ displays two CN stretching frequencies at 2063 cm^{-1} and 2079 cm^{-1} , corresponding to $\text{Fephen}_2(\text{CN})_2$. Heating $\text{Fephen}_2(\text{CNBH}_3)_2$

in methanol leads to the same result; its visible spectrum is shown in Figure 23.

Our attempts to find a suitable solvent for $\text{Fephen}_2(\text{NCBH}_3)_2$ have not been particularly fruitful. The complex does dissolve readily in nitromethane, methanol and acetonitrile and slowly dissolves in sulfolane and pyridine and has an impractically low solubility in dichloromethane, dichloroethane, acetone, acetic acid and water. The charge transfer region spectra of all these solutions (Figures 24-31) are all highly similar in appearance and reveal only a slight change from that of solid state $\text{Fephen}_2(\text{NCBH}_3)_2$ (Figure 12).

$\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{CNBH}_3)_2$ are stable at room temperature. Heating $\text{Fephen}_2(\text{NCBH}_3)_2$ under vacuum at 170°C for several days results in small changes only (Figure 34). Heating $\text{Fephen}_2(\text{CNBH}_3)_2$ under the same conditions results in an interesting change as shown by its i.r. spectrum (Figures 32-33). On the other hand, the same treatment of $\text{Fephen}_2(\text{CN})_2$ and $\text{Fephen}_2(\text{NCS})_2$ yields no change at all.

The ^{13}C n.m.r. spectrum of $\text{Fephen}_2(\text{CNBH}_3)_2$ (in sulfolane) gives one absorption at 146.11 ppm, down-field relative to TMS, whereas those of KNCBH_3 and $\text{NaBH}_3\text{CNBH}_3$ (both in THF) give very similar results, i.e., 146.01 ppm & 146.037 ppm, down-field relative to external TMS respectively. This suggests the electron densities at the carbon nuclei are amazingly similar,

(but no correction has been applied for the bulk susceptibility difference between sulfolane and THF).

Our attempts to strip " BH_3 " from $\text{Fe}(\text{phen})_2(\text{CNBH}_3)_2$ and $\text{Fe}(\text{phen})_2(\text{NCBH}_3)_2$ using strong nucleophiles ($\text{P}(\text{C}_6\text{H}_5)_3$, KCN , and Et_3N) were not successful, as the ir spectra of the products showed no change from the initial spectra at all.

Figure 1

p.m.r. spectrum of KNCBH_3 in D_2O .

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

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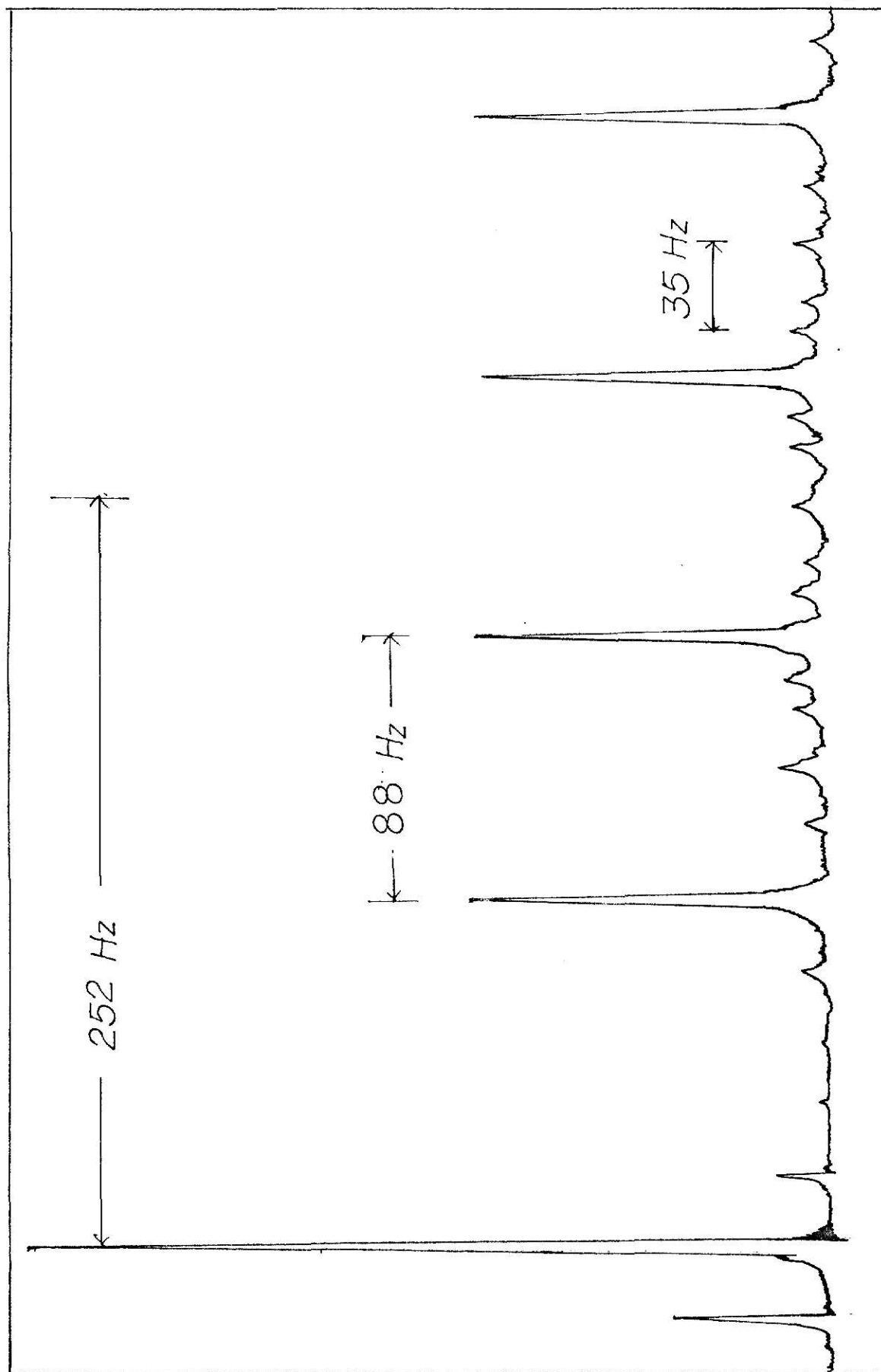


Figure 2

Infrared spectrum of KNCBH_3 ; KBr pellet.

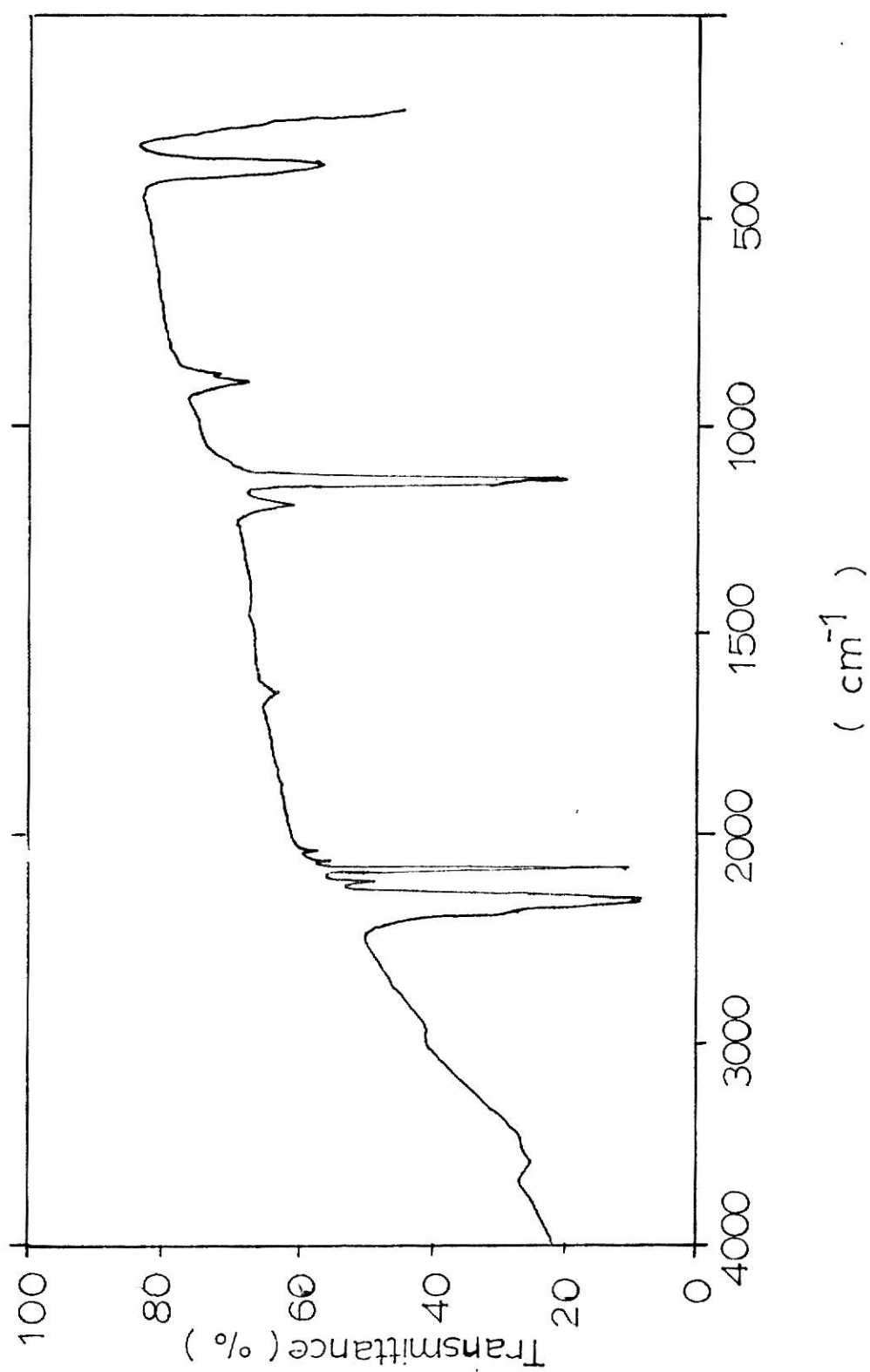


Figure 3

Infrared spectrum of $\text{Fe}(\text{phen})_2(\text{NCBH}_3)_2$; KBr pellet.

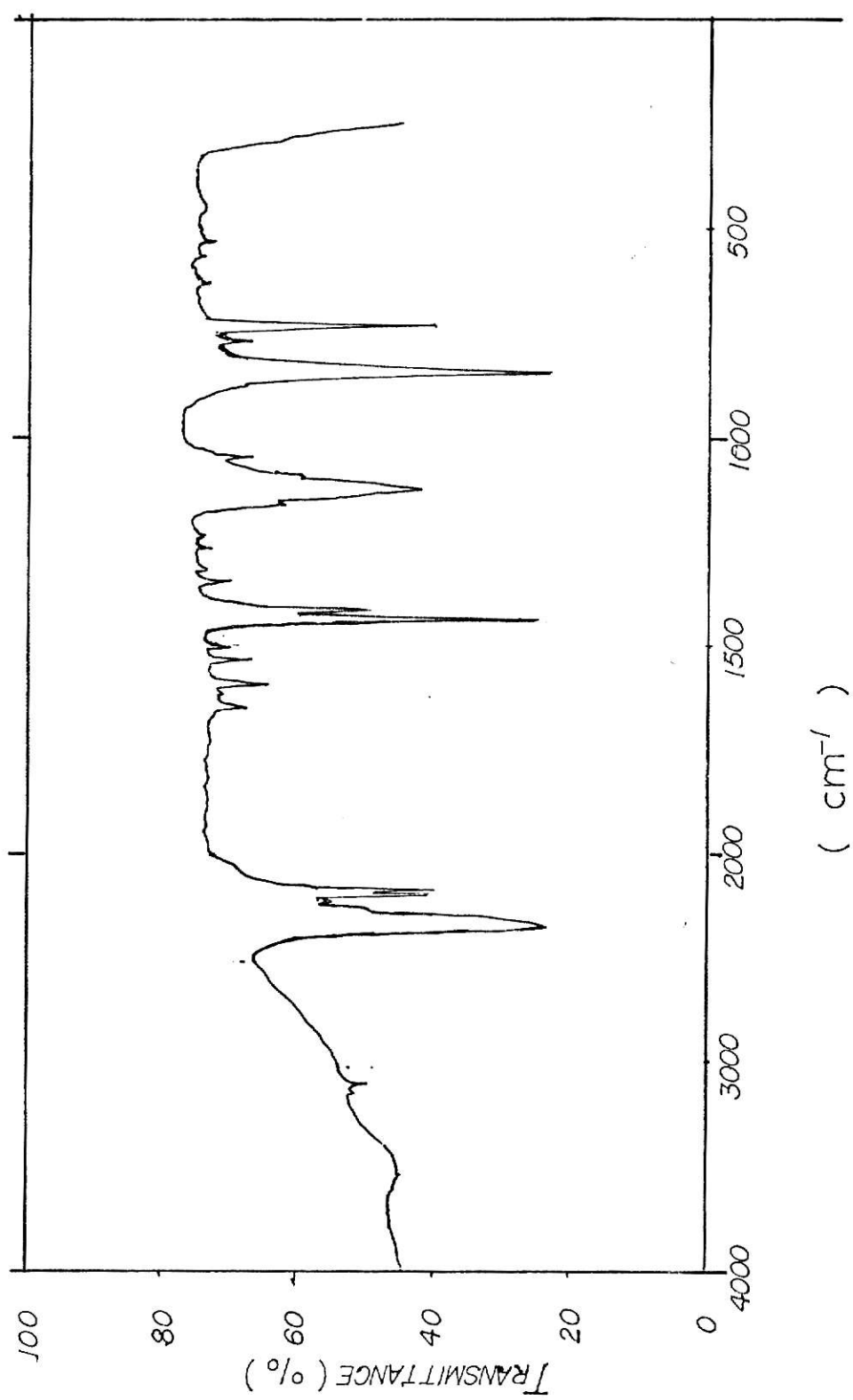


Figure 4

Infrared spectrum of $\text{Fe}(\text{phen})_2(\text{CNBH}_3)_2$; KBr pellet.

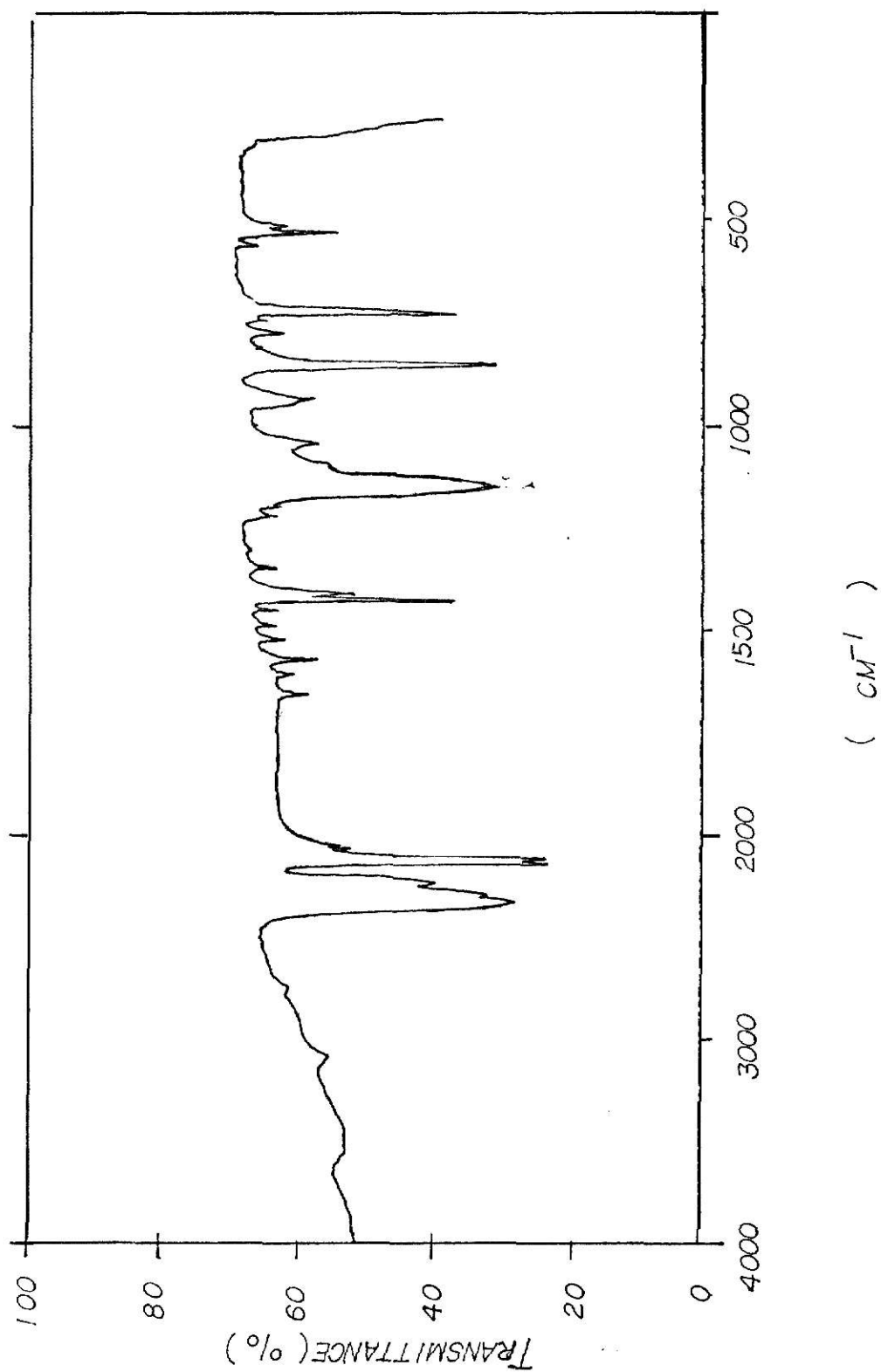


Figure 5

Infrared spectrum of $\text{Fephen}_2(\text{CN})_2$; KBr pellet.

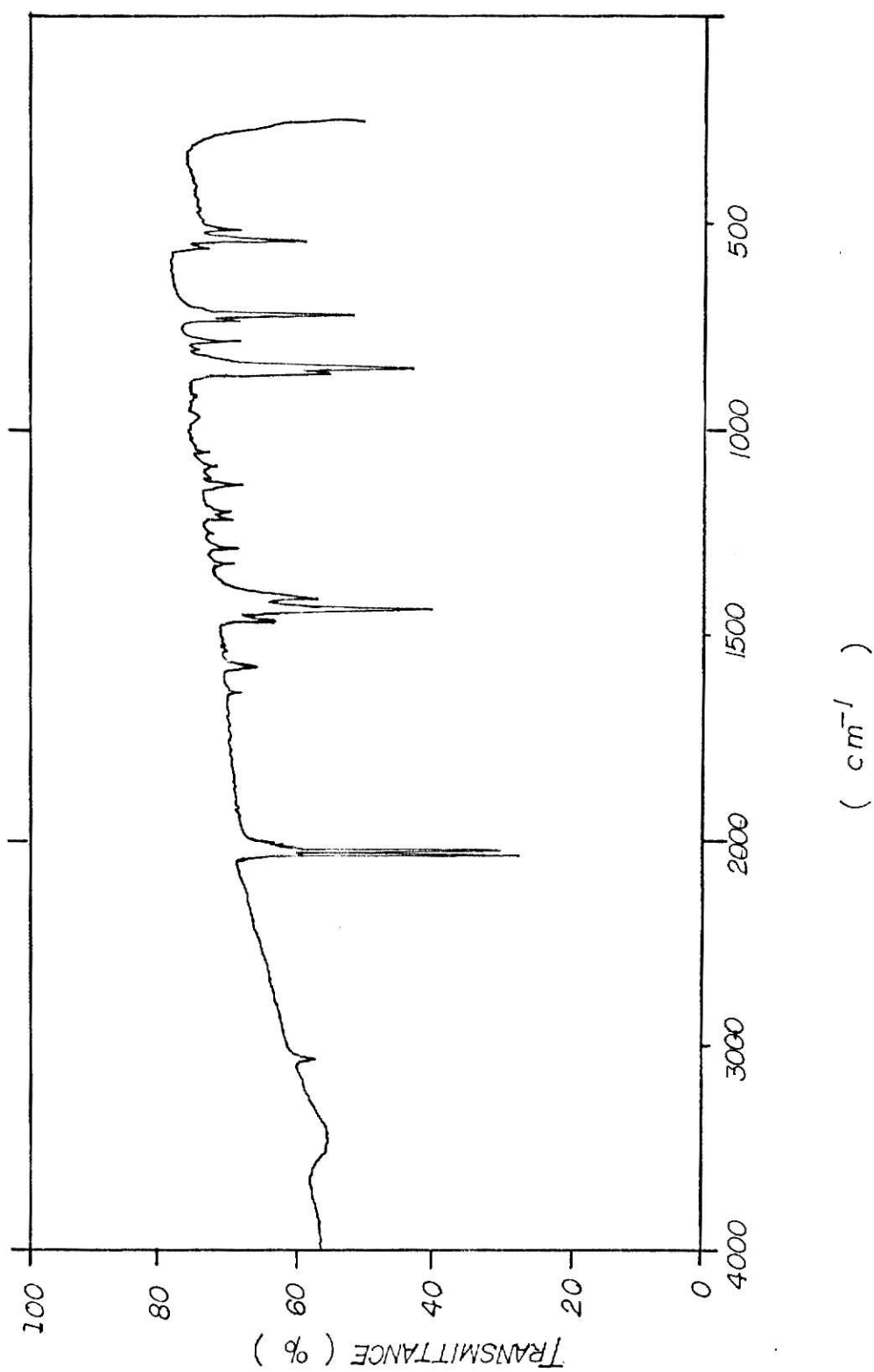


Figure 6

Infrared spectrum of $\text{Fephen}_2(\text{NCS})_2$; KBr pellet.

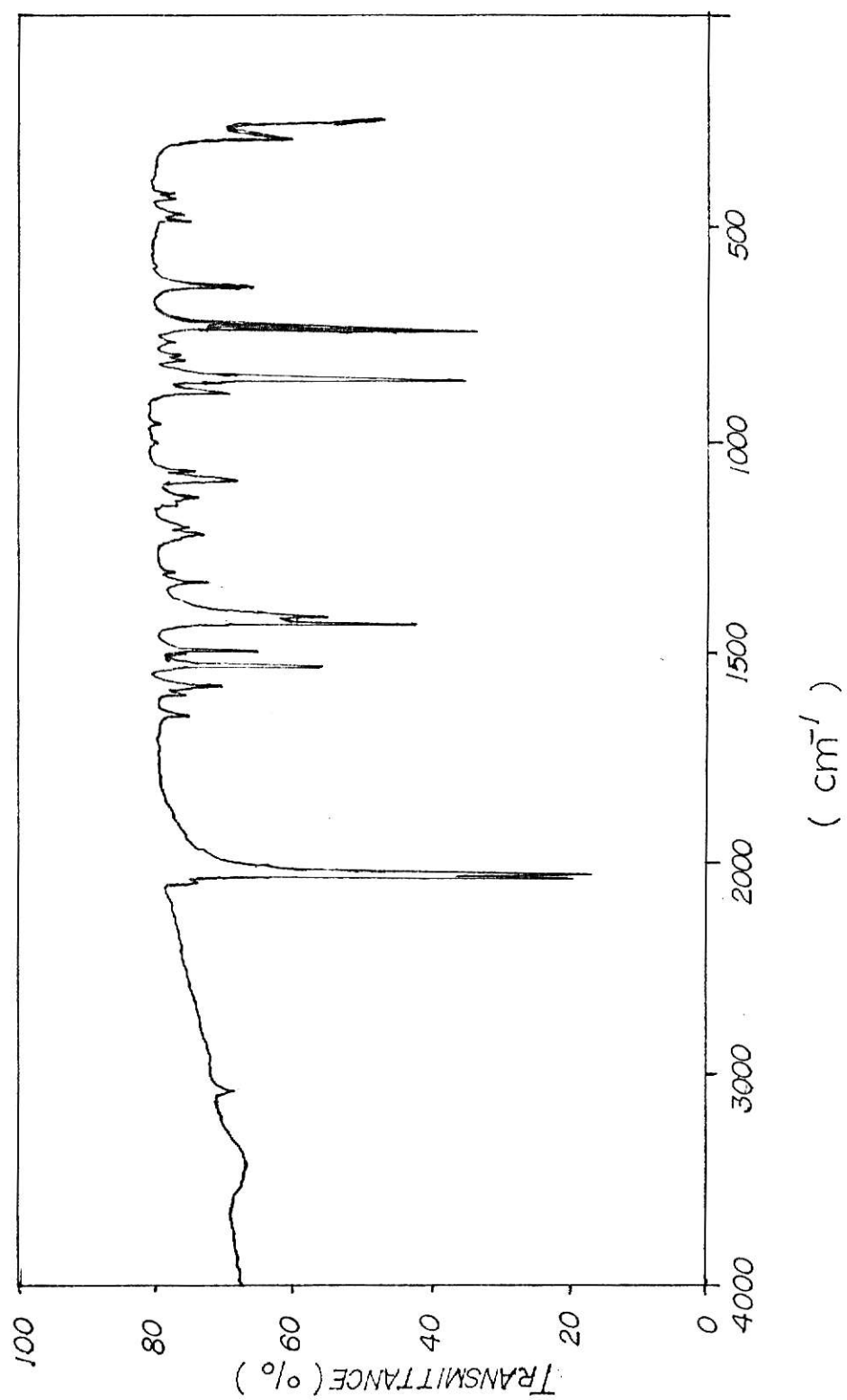


Figure 7

Infrared spectrum of $\text{Fe}(\text{phen})_2\text{Cl}_2$; KBr pellet.

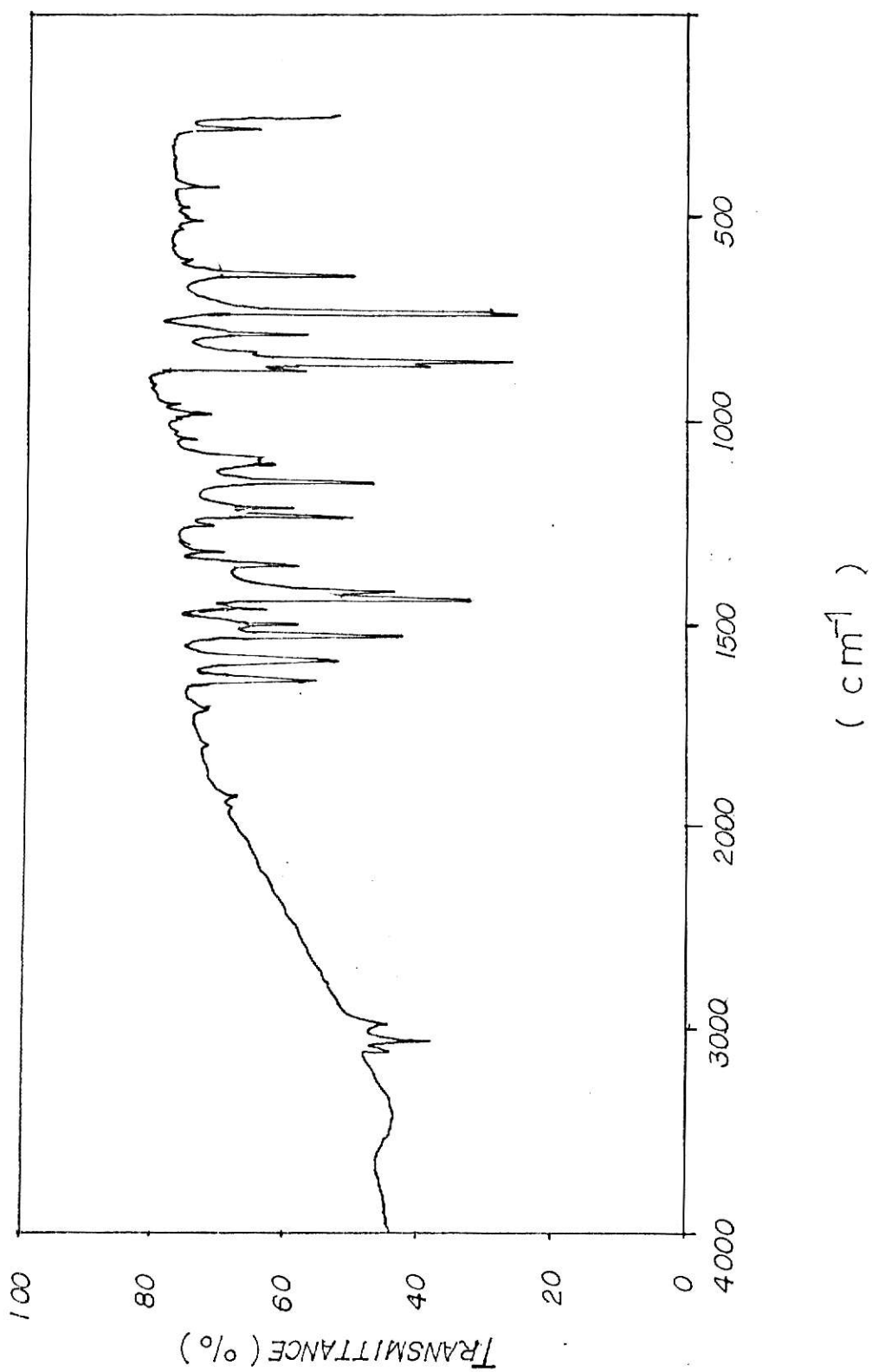


Figure 8

Mössbauer spectrum of $\text{Fephen}_2(\text{NCBH}_3)_2$.

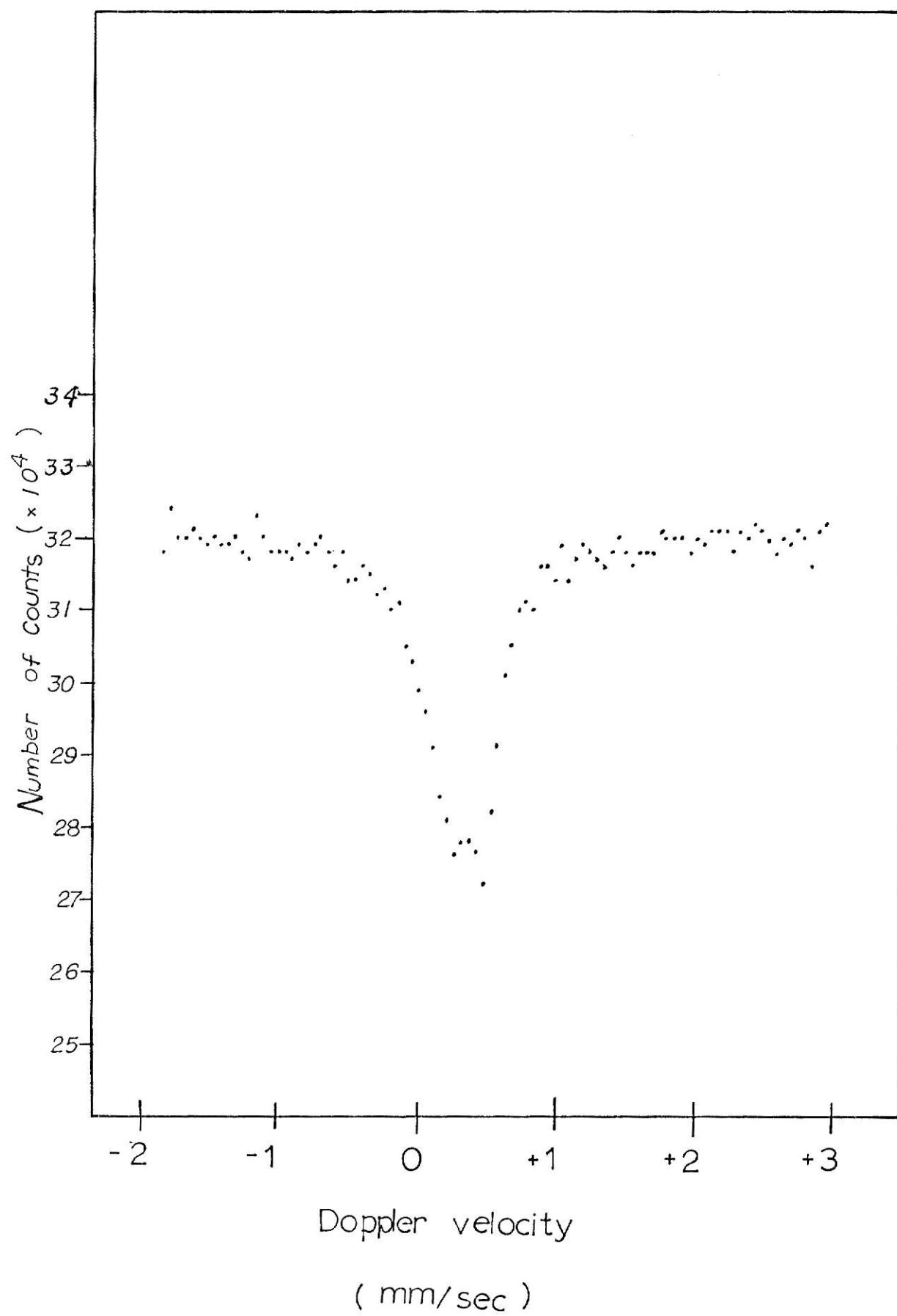


Figure 9

Mössbauer spectrum of $\text{Fephen}_2(\text{CNBH}_3)_2$.

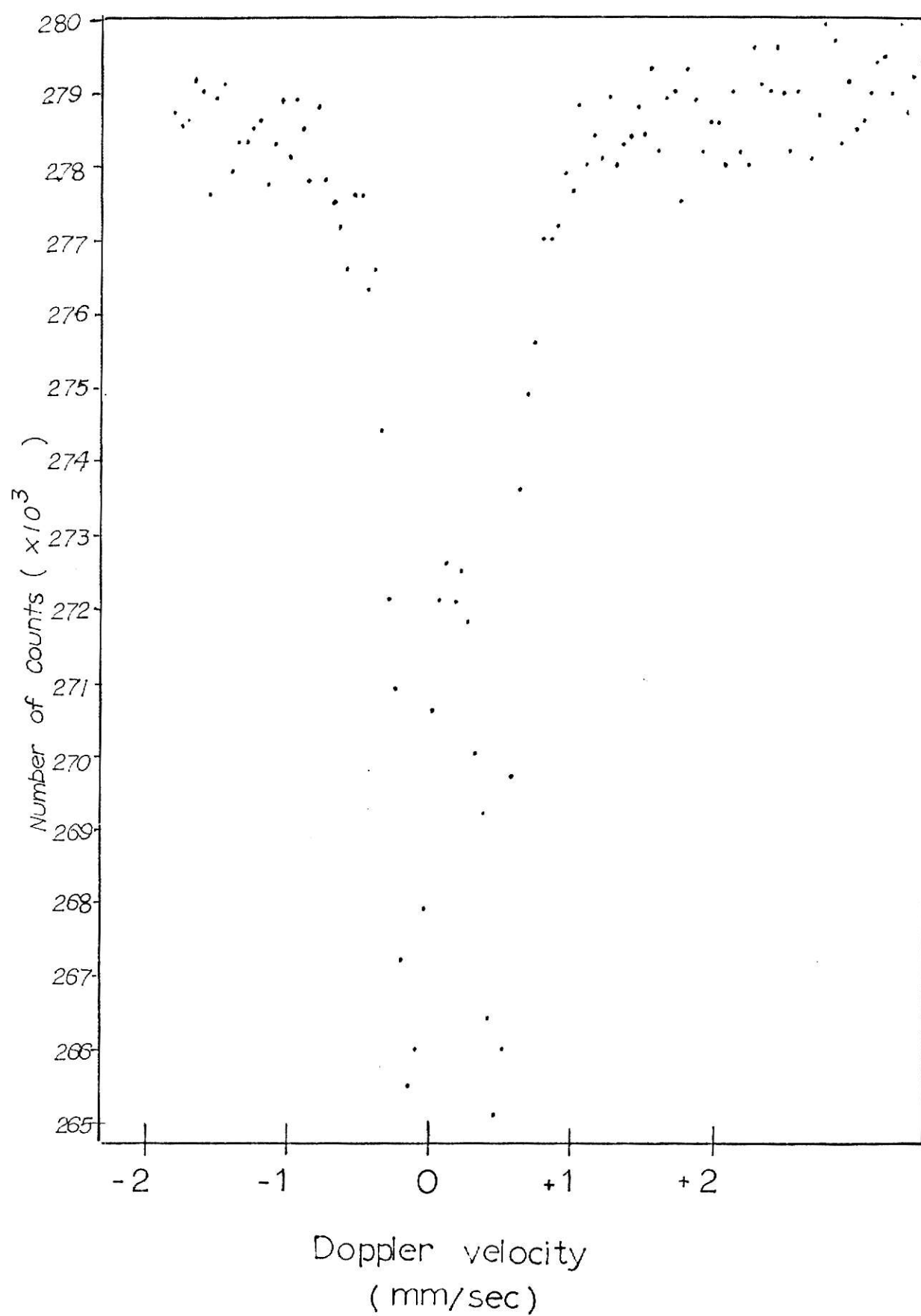


Figure 10

Mössbauer spectrum of $\text{Fephen}_2(\text{CN})_2$.

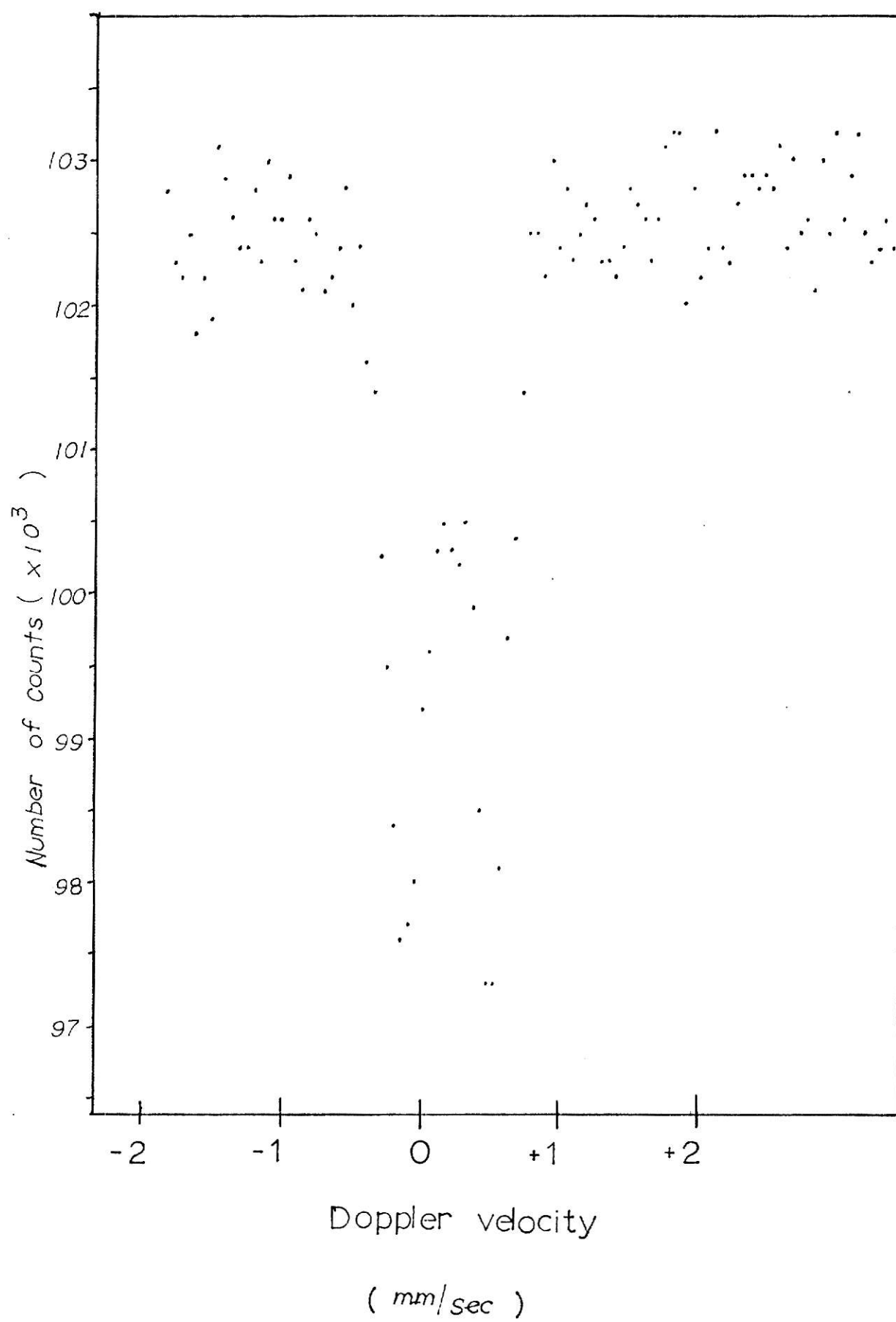


Figure 11

Mössbauer spectrum of $\text{Fe}(\text{phen})_2\text{Cl}_2$.

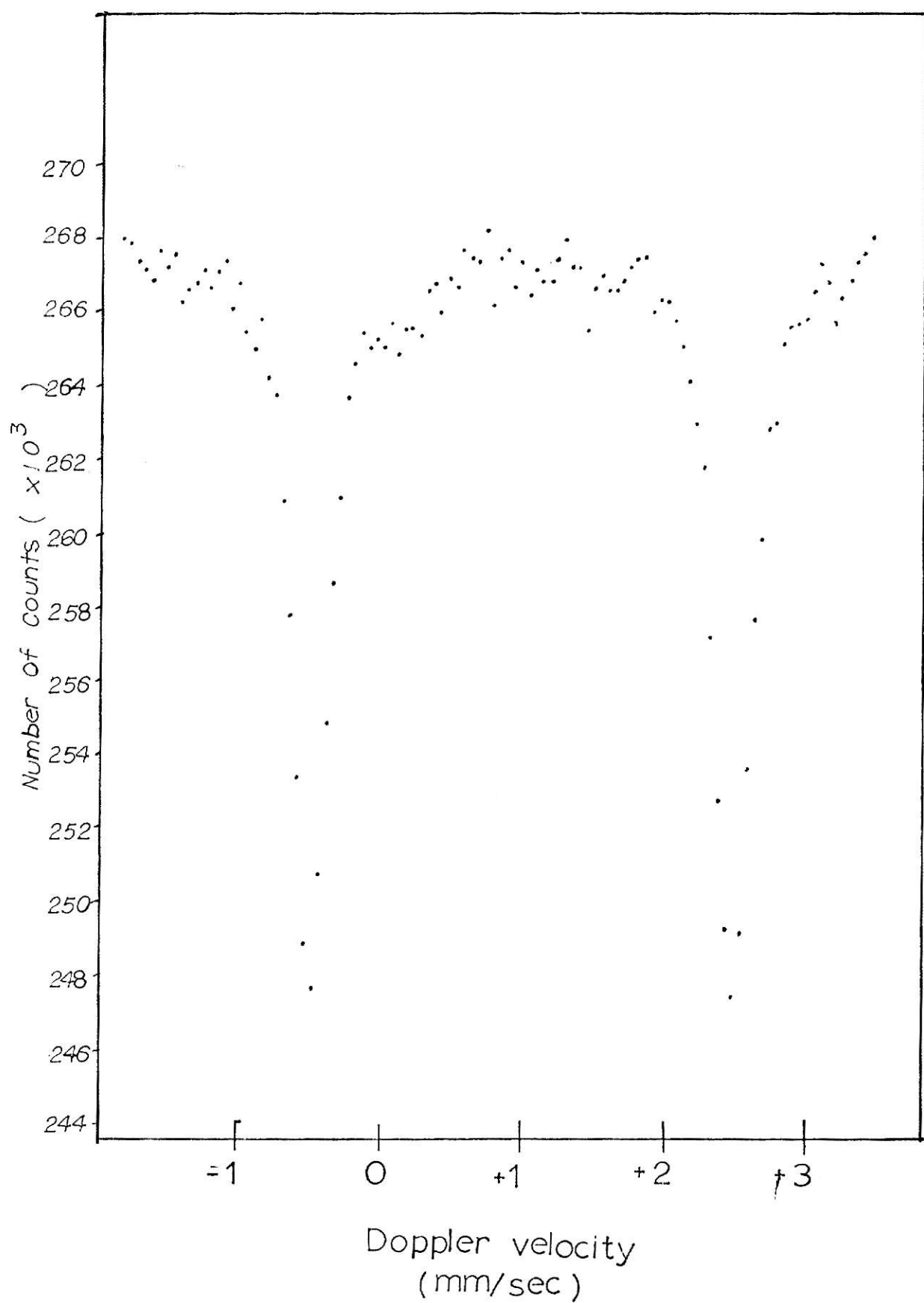


Figure 12

Visible spectrum of $\text{Fe}(\text{phen})_2(\text{NCBH}_3)_2$; KBr pellets.

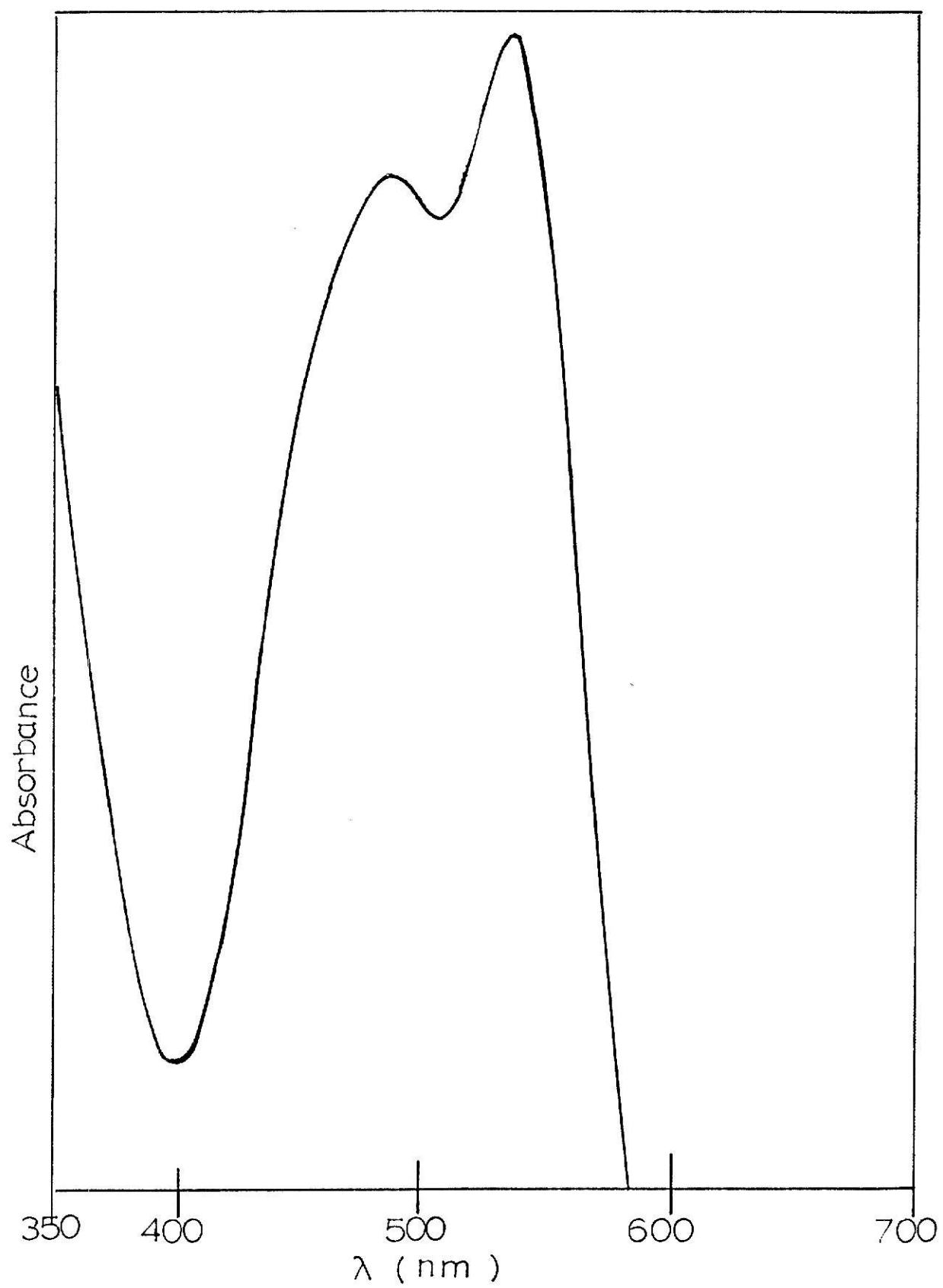


Figure 13

Visible spectrum of $\text{Fe}(\text{phen})_2(\text{CNBH}_3)_2$; KBr pellet.

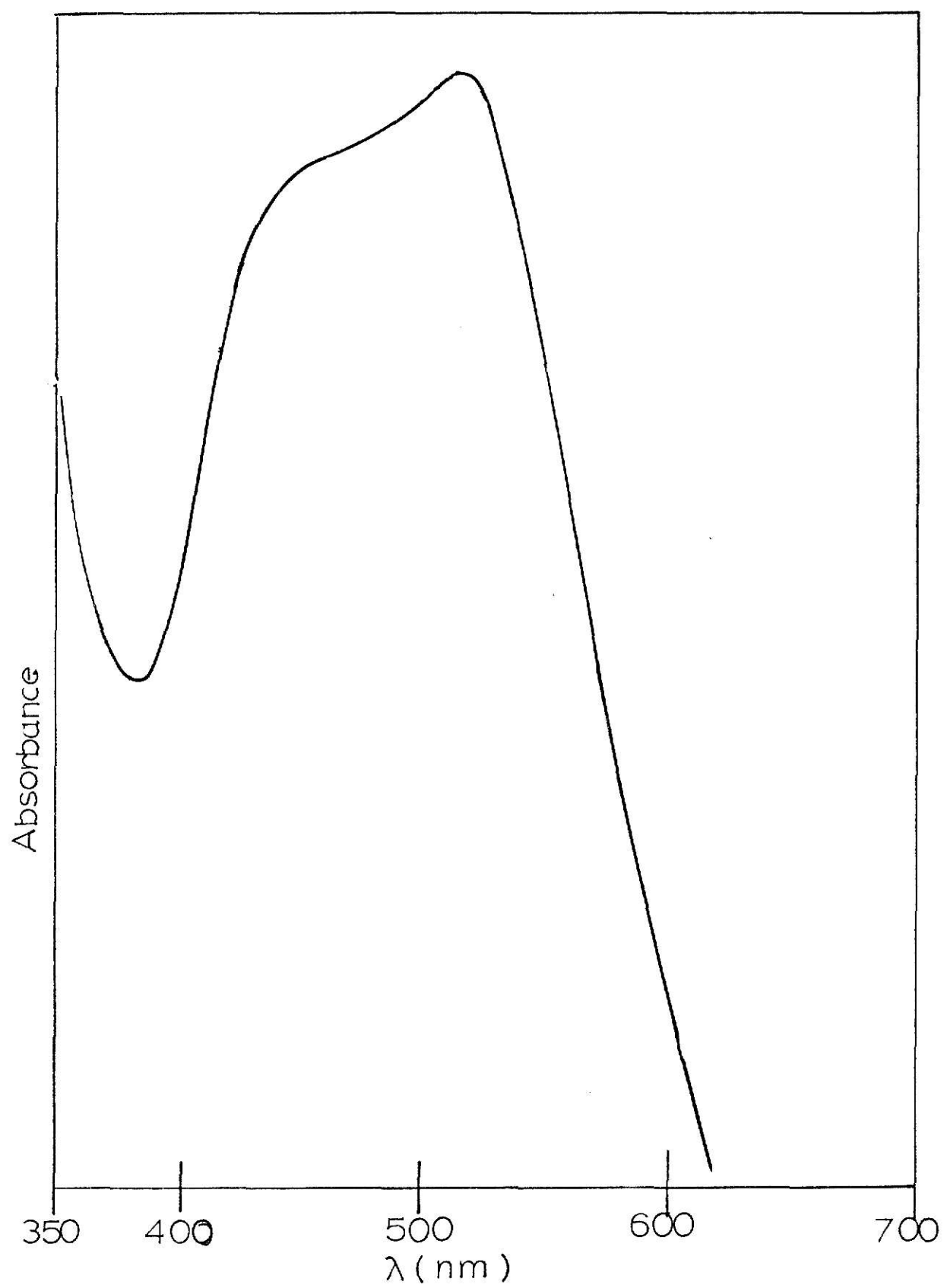


Figure 14

Visible spectrum of $\text{Fe}(\text{phen})_2(\text{CN})_2$; KBr pellet.

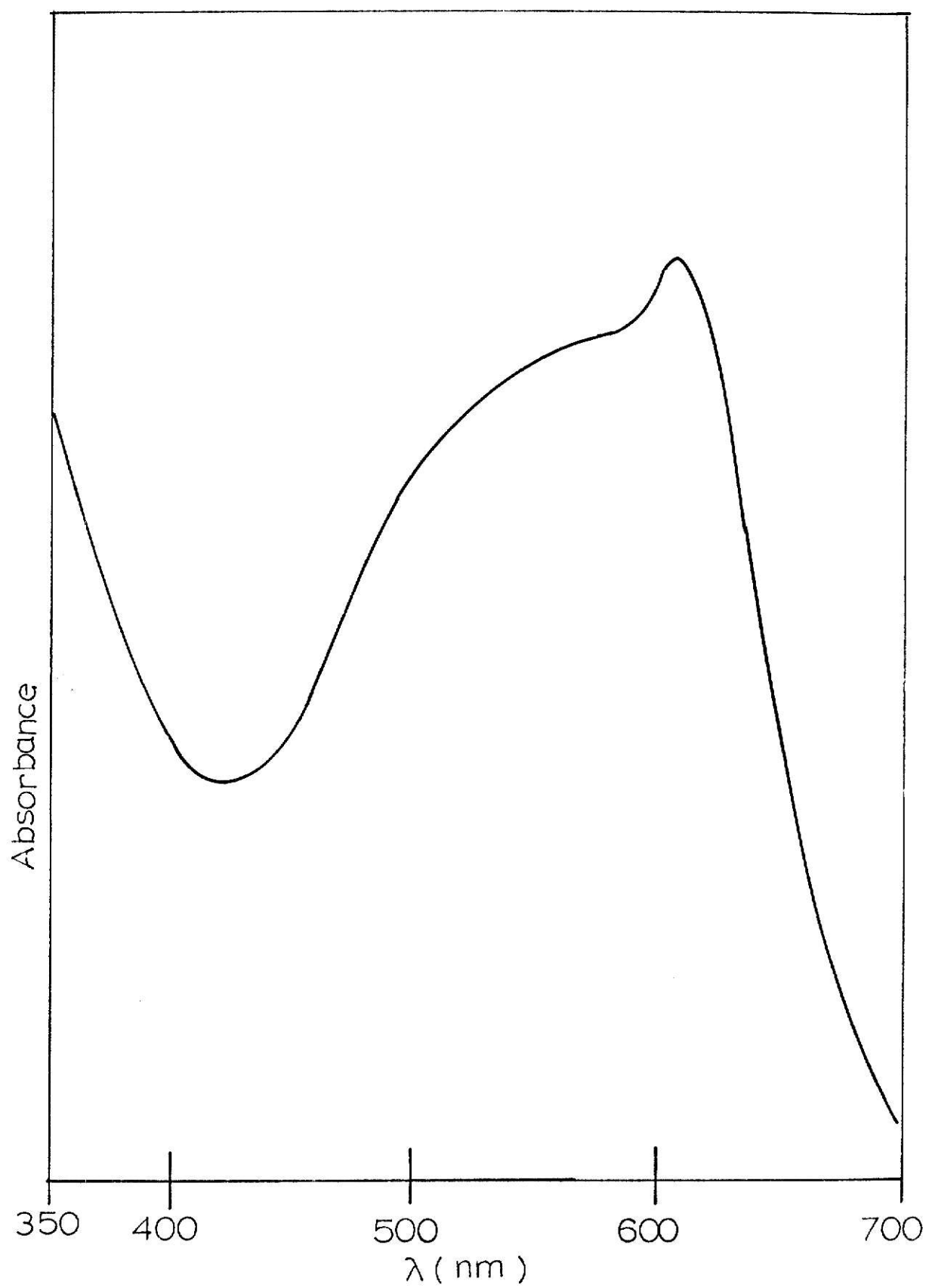


Figure 15

Visible spectrum of $\text{Fephen}_2(\text{NCS})_2$; KBr pellet.

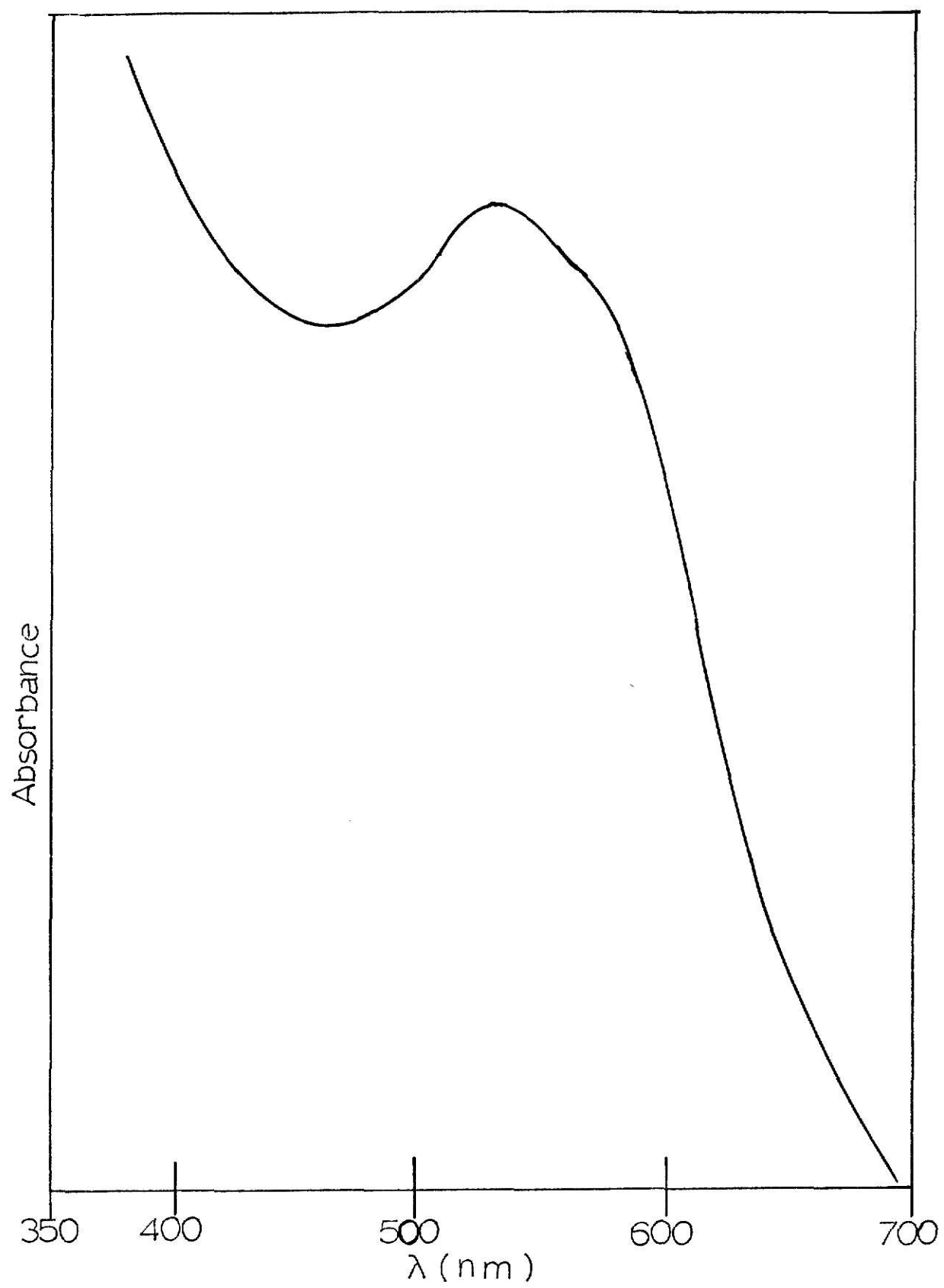


Figure 16

Visible spectrum of $\text{Fe}(\text{phen})_2\text{Cl}_2$; KBr pellet.



Figure 17

Visible spectrum of $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$; KBr pellet.

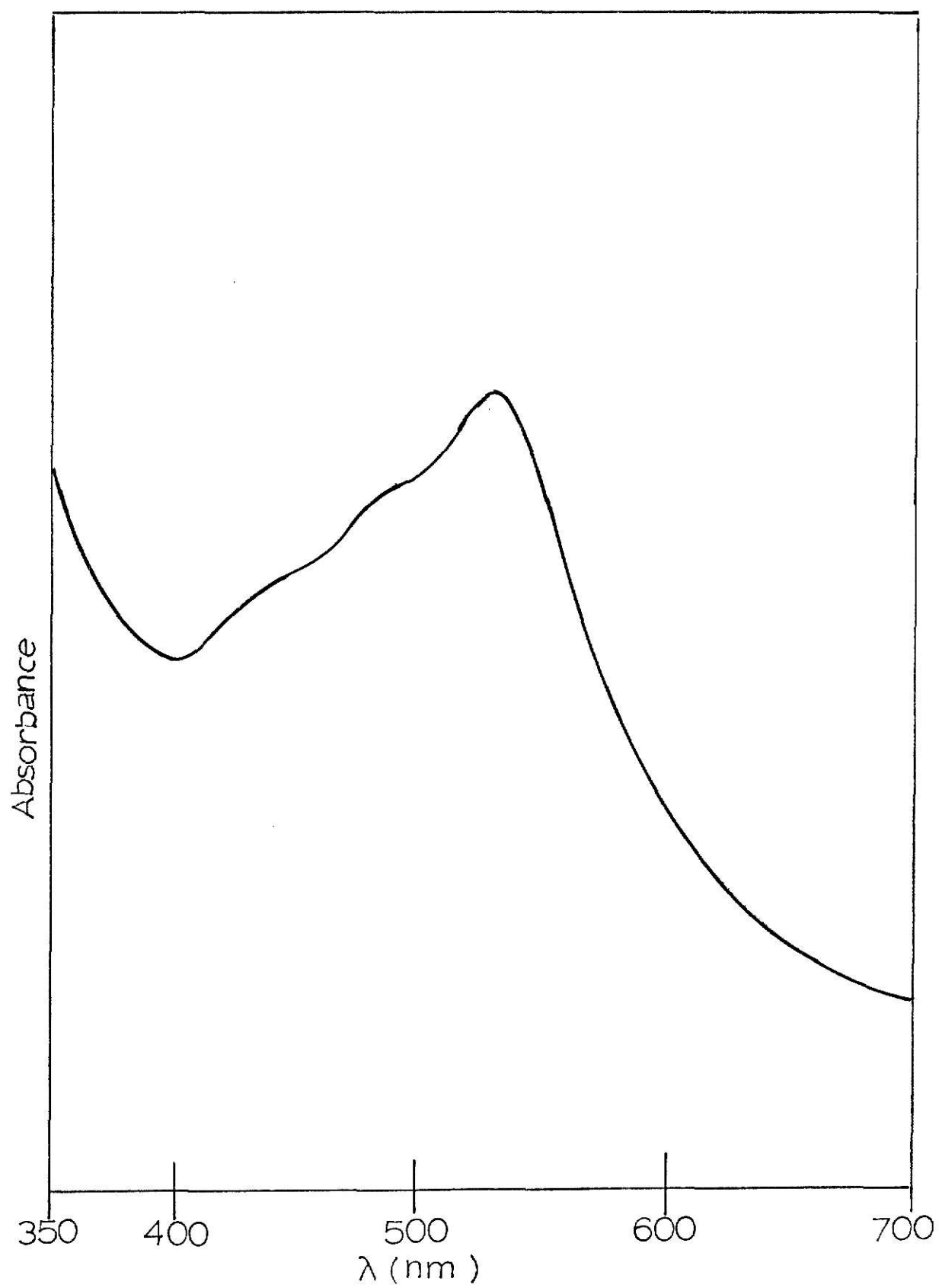


Table II

Data for $\text{Fephen}_2\text{X}_2$ and related compounds

- a 301°K
- b isomer shift relative to iron foil and quadrupole splitting, both in mm/sec.
- c reference 30
- d reference 29
- e cm^{-1}
- f reference 35
- g reference 4
- h reference 36
- i $\text{Fephen}_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$

<u>M = Fephen₂⁺²</u>	<u>μ_{eff}^a</u>	<u>i.s.</u> ^b	<u>q.s.</u> ^b	<u>ν_{CN}^e</u>	
M Cl 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	2162	2146
M (CN) ₂	0.76	0.16	0.62	2081	2064
M phen ¹	0.79	0.43 ^d	0.20 ^d	-	-
KCN	-	-	-	2080	^f
KNCBH ₃	-	-	-	2179	
KCNBH ₃	-	-	-	2070	^g
KBH ₃ CNBH ₃	-	-	-	2260	^g
KSCN	-	-	-	2053	^f
NaSCNBH ₃	-	-	-	2075	^h

V. Discussion

A. 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 4 unpaired electrons, depending upon the position of the ligands in the spectrochemical series. Effective magnetic moments of ~ 0 and ~ 5 are usually observed for such low-spin and high-spin complexes, respectively. Mössbauer spectroscopy also provides diagnostic data on the electronic configurations of high and low spin ferrous ion complexes.³⁷ The isomer shift reflects the electron density at the iron nucleus and can be employed, through the screening effect by electrons in the 3d orbitals, to study the electron population in 3d orbitals. In short, the greater the electron population in 3d orbitals, the more radially diffuse the Fe s atomic orbitals and the more positive the isomer shift. Furthermore, quadrupole splitting of the Mössbauer level reflects the distortion, from perfect octahedral symmetry, of the arrangement of the ligands. The quadrupole splitting is, to first order, due to a nonspherical distribution of valence-shell-electrons about the nucleus and secondarily from an asymmetric charge distribution from the nearest neighbor atoms. Thus, low-spin d^6 complexes of general formula FeL_6

are characterized by minor quadrupole splitting and isomer shifts less than a few tenths mm/sec, relative to an Fe foil; high spin cases are distinguished by q.s. of 2-3 mm/sec and i.s. on the order of 1 mm/sec.

A few complexes of the type $\text{Fephen}_2\text{X}_2$ (with cis-geometry) have been studied by magnetic susceptibility measurements^{24,31,38} and Mössbauer spectroscopy.^{29,30,38} With X = halide or NCS^- , which appear early in the spectrochemical series, magnetic moments of ~ 5.2 Bohr magnetons are observed (see Table II). These complexes also have very large isomer shifts and very large quadrupole splittings (see Table II). For the complexes $\text{Fephen}_2(\text{CN})_2$ and Fephen_3^{++} , 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 bisphenanthrolinebis(N-cyanotrihydroborate) iron isomer behaves in a typical low spin fashion. That the i.s. of $\text{Fephen}_2(\text{CNBH}_3)_2$ is within experimental error of that of $\text{Fephen}_2(\text{CN})_2$ indicates little net change in electron density at the Fe nucleus is incurred by coordination of BH_3 to N. There are two ways in which one can break-down an observed i.s. change: (i) a change in Fe 4s population vs a change in Fe 3d population and (ii) a change in ligand $\rightarrow$ Fe σ charge transfer vs a change in ligand $\rightarrow$ Fe π charge transfer. For (i), increased 4s density leads to -i.s. while increased 3d density leads to +i.s. The almost negligible

change in i.s. for the conversion $\text{phen}_2\text{Fe}(\text{CN})_2 \rightarrow \text{phen}_2\text{Fe}(\text{CNBE}_3)_2$ implies off-setting changes in 4s and 3d populations. According to Shriver and Posner's ¹⁰CNDO calculations, coordination to nitrogen of cyanide by some acid should decrease $\text{NC}^- \rightarrow \text{Fe } \sigma$ transfer and increase the π acceptor nature of CN^- (decreased $\text{NC}^- \rightarrow \text{Fe } \pi$ 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 decrease and have off-setting effects on the i.s. The second view of an i.s. change (ii) is less clear-cut. While the decrease in $3d_\pi$ density affords a -i.s., the 4s and $3d_\sigma$ density decreases are off-setting: the 4s change causes a +i.s. while the $3d_\sigma$ change incurs a -i.s. That is, the change in NC-Fe π bonding should cause a -i.s., while the change in NC-Fe σ bonding could cause a + or - i.s. as the 4s or $3d_\sigma$ change dominates the other. If the $3d_\sigma$ change is more important than the 4s change, it must be only barely so and the $3d_\pi$ change must be very small indeed. On the other hand if the 4s change is more important than the $3d_\sigma$ change, the $3d_\pi$ density loss has a compensating effect on the i.s. Later, in discussing the charge transfer spectra of $\text{Fe}(\text{phen})_2\text{X}_2$, we will encounter again the idea that changes in metal-ligand σ bonding seem to alter the i.s. principally through the 4s population change.

We also note, in agreement with recent calculations by Purcell & Martin,³⁹ that BH_3 hyperconjugation, which would

reduce the π acceptor nature of CN^- , is relatively unimportant.

The i.s. of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{CN})_2$ are smaller than that of Fephen_3^{+2} , indicating the CN^- and CNBH_3^- complexes have higher electron density at the ferrous nucleus. This finding translates into the chemical valency argument that the combined effect of ligand electron delocalization into the Fe 4s atomic orbital (-i.s.) and/or retrodelocalization of Fe 3d π electron density onto the ligands (-i.s.) is relatively more important than ligand electron transfer into the Fe 3d σ atomic orbitals (+i.s.) when CN^- and CNBH_3^- replace phen. Thus, CNBH_3^- should lie very high in the spectrochemical series. From the μ_{eff} and i.s. values one might argue that CNBH_3^- exceeds CN^- in that series. This substantiates Shriver's^{9,10} interpretation of the blue shifts in d-d bands for $\text{K}_4\text{Fe}(\text{CN})_6 \rightarrow \text{K}_4\text{Fe}(\text{CNBH}_3)_6$.

Finally, we note in passing that the q.s. of $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{CN})_2$ are larger than that of Fephen_3^{+2} and $\text{Fephen}_2(\text{NCBH}_3)_2$, indicating that the replacement of nitrogen by carbon at the ligating points leads to a significant alternation in the more remote contribution to the electric field gradient at the Fe nucleus. In fact, the Mössbauer parameters suggest that the Fe nucleus does not distinguish 2 NCBH_3^- from 1 phen.

In marked contrast with "normal" six coordinate Fe(II) complexes, the bisphenantholinebis(C-cyanotrihydroborate) iron isomer exhibits a μ_{eff} corresponding to an S = 1 state but i.s.

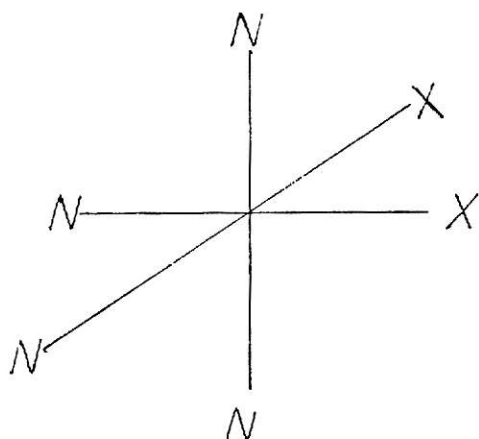
and q.s. parameters diagnostic of $S = 0$. This apparent conflict is readily resolved (see later) by the realization that a certain 3d orbital ordering for $S = 1$ yields i.s. and q.s. parameters much like those for a $S = 0$ state. An important finding here is that low i.s. and q.s. Mössbauer parameters 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 $\text{Fephen}_2(\text{NCBH}_3)_2$, neither does a trans-geometry 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-($\pm z$ axis) positions, but a larger q.s. would appear in the Mössbauer spectrum. Given that two CN vibrations are found in its i.r. spectrum (Table II), $\text{Fephen}_2(\text{NCBH}_3)_2$ must have a cis-topology.

To account for these i.r., magnetic, and Mössbauer characteristics of the NCBH_3 complex, this investigator has turned to "the angular overlap model"⁴⁰ 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 Fephen_3^{+2} and $\text{Fephen}_2\text{X}_2$ is shown in Table III (here we have assumed idealized 90° bond angles).

Table III

Relative d orbital energy levels^a from the angular overlap model.

^a e_{σ} and e_{π} are the unit anti-bonding energy shifts for σ and π overlap. Note that each X possesses 2 π type orbitals while phen is presumed to have but one π orbital per nitrogen.


 Fephen_3^{+2}
 $\text{Fephen}_2\text{X}_2$
 ϵ_{z^2}
 $3e_{\sigma n}$

$$5/2 e_{\sigma n} + 1/2 e_{\sigma x} = 3 e_{\sigma n} - 1/2 \delta e_{\sigma}$$

 $\epsilon_{x^2-y^2}$
 $3e_{\sigma n}$

$$3/2 e_{\sigma n} + 3/2 e_{\sigma x} = 3 e_{\sigma n} - 3/2 \delta e_{\sigma}$$

 ϵ_{xy}
 $2e_{\pi n}$

$$2 e_{\pi n} + 2 e_{\pi x}$$

 $\epsilon_{xz} = \epsilon_{yz}$
 $2e_{\pi n}$

$$e_{\pi n} + e_{\pi x} = 2 e_{\pi n} - \delta e_{\pi}$$

The ordering of d^* molecular orbital energies can be safely assumed, for $X_2 = \text{phen}, \text{Cl}_2, (\text{NCS})_2, (\text{CN})_2, (\text{CNBH}_3)_2$, and $(\text{NCBH}_3)_2$, to follow $(\epsilon_{d_{z^2}}, \epsilon_{d_{x^2-y^2}}) > (\epsilon_{d_{xy}}, \epsilon_{d_{xz}} = \epsilon_{d_{yz}})$. In general, 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^* mean four general cases may occur: (see Table IV)

For the low spin complexes $[X_2 = (\text{CN})_2, (\text{CNBH}_3)_2]$ 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 . In all cases the Fe valence electron (d^*) contribution to q_z is given by ^{4/}

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

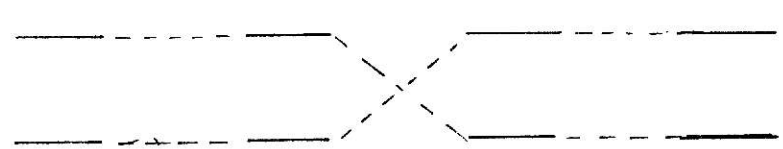
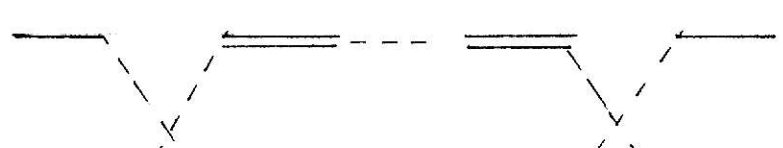
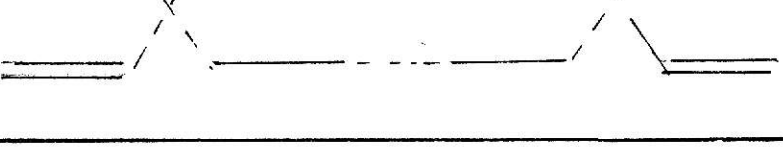
where $K_d = \frac{4}{7} \langle r^{-3} \rangle_d$

and $N_{d_{z^2}}$ = the $d_{z^2}^*$ electron population, etc.

All the low spin cases have $q_z = 0$, ignoring higher ordered effects due to ligand non-equivalence. Of the high spin ($S = 2$) cases, $q_z \propto -\frac{1}{2}, 1, 1, -\frac{1}{2}$ 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 inter-mediate spin ($S = 1$) cases are more readily distinguished by $q_z \propto 0, \frac{3}{2}, -\frac{1}{2}, -2$ for the orbital sequence above. Clearly, the Mössbauer data for $\text{Fephen}_2(\text{NCBH}_3)_2$ signify $\delta e_\sigma > 0$ and $(e_{\pi n} + e_{\pi x}) > 0$. Thus NCBH_3^- is poorer at σ interaction with Fe(II) than phen;

Table IV

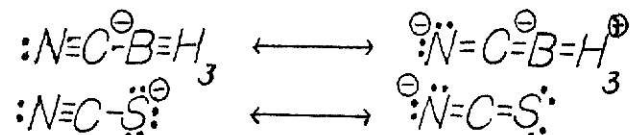
Ordering of the d orbitals and the electric field gradient for low, intermediate and high spin states of the octahedral ferrous complexes.

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 (K_d)			
$S = 0$	0	0	0	0
$S = 1$	0	$\frac{3}{2}$	$-\frac{1}{2}$	-2
$S = 2$	$-\frac{1}{2}$	1	1	$-\frac{1}{2}$

this requirement confirms the expected difference in donor properties of "sp" and "sp²" nitrogen. If it is assumed that $e_{\pi n} < 0$ (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.

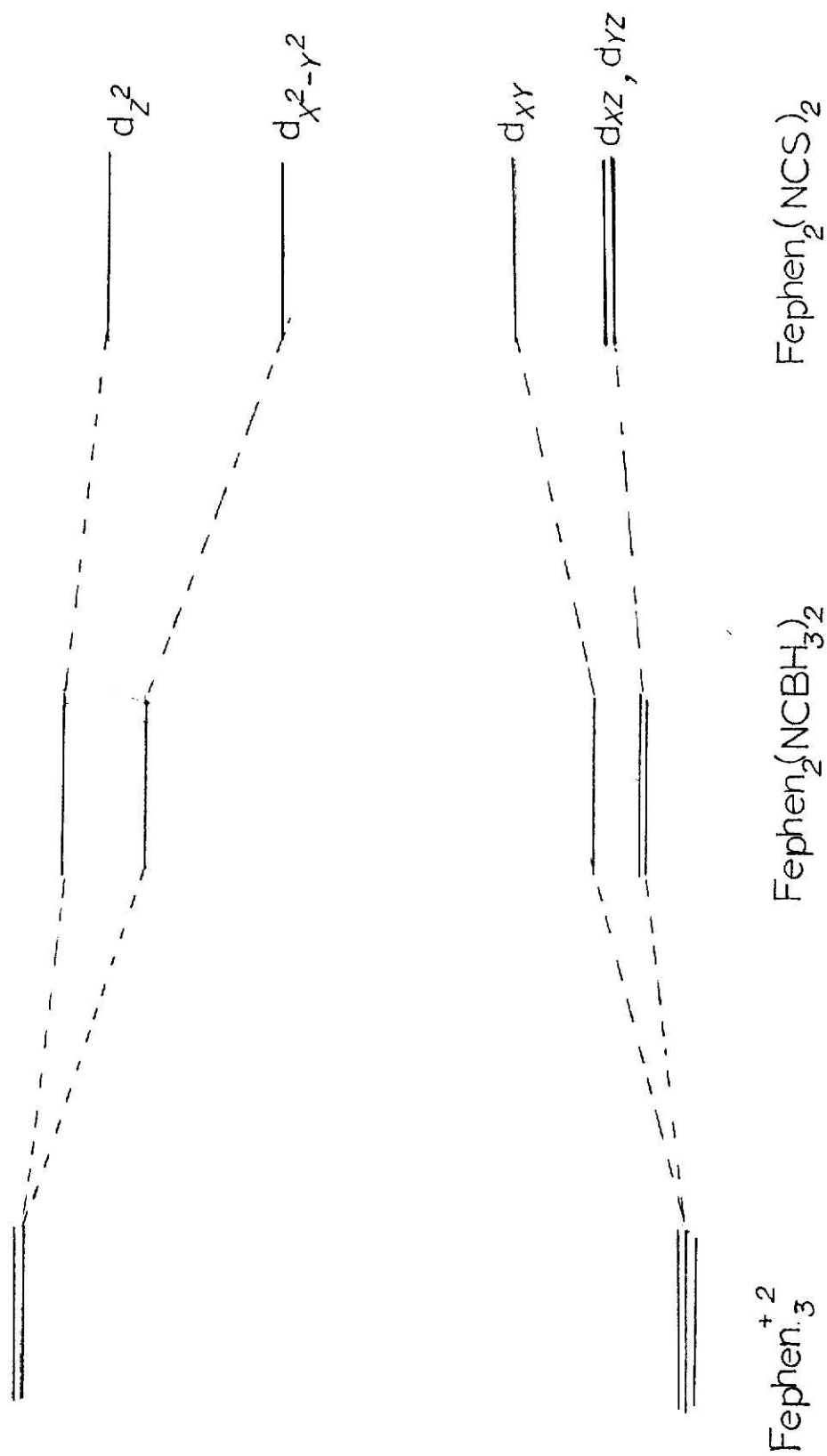
A most interesting question is "why does replacement of BH_3 in NCBH_3^- by S lead to a quintet ground state?" It is most likely correct that the difference in "sp" versus "sp²" donor hybrid character still requires $\delta e_\sigma > 0$ for NCS^- ; alternately one could argue that NCS^- should be a poorer σ donor than NCBH_3^- on the basis of the inductive difference between "sp³" boron and "sp" sulfur. Accordingly, $\delta e_\sigma(\text{NCS}) > \delta e_\sigma(\text{NCBH}_3) > 0$. On the other hand, NCS^- should be a much stronger π donor than NCBH_3^- because BH_3 shows little conjugation with NC^- , whereas S is known to strongly conjugate:



Consequently, δe_σ and $(e_{\pi n} + e_{\pi x})$ are both > 0 for NCS^- as well as NCBH_3^- . In terms of the AOM d* molecular orbital energies of Fephen_3^{2+} , $\text{Fephen}_2(\text{NCBH}_3)_2$, $\text{Fephen}_2(\text{NCS})_2$ we expect the following diagram to apply: (see Table V).

Table V

Relative orbital energy levels for Fephen_3^{++} ,
 $\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{NCS})_2$, using angular
overlap model.

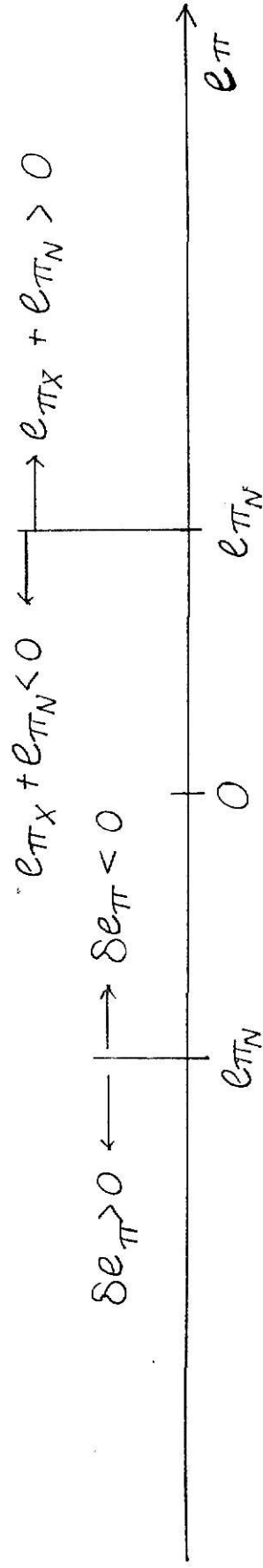


Defining $\Delta_P = (3e_{\sigma_N} - 2e_{\pi_N})$ and the d^* electron pairing energy as P , the transformation $\text{Fephen}_3^{2+} \rightarrow \text{Fephen}_2(\text{NCBH}_3)_2$ occasions a change from $P < \Delta_P \rightarrow P > (\Delta_P - \frac{3}{2}\delta e_{\sigma} - 2e_{\pi_X})$, where, as seen earlier, δe_{σ} and e_{π_X} are both > 0 for NCBH_3^- . Note, however, that P remains $< (\Delta_P - \frac{1}{2}\delta e_{\sigma} + \delta e_{\pi})$. The transformation $\text{Fephen}_2(\text{NCBH}_3)_2 \rightarrow \text{Fephen}_2(\text{NCS})_2$ causes this last inequality to reverse sense to $P > (\Delta_P - \frac{1}{2}\delta e_{\sigma} + \delta e_{\pi})$ 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(II) . At the extremes we find Cl^- , NCS^- ("poor" σ donors, "good" π donors) and phen, CN^- , CNBH_3^- ("good" σ donors, "poor" π donors).

Starting with Fephen_3^{++} (singlet) and substituting one phen with two ligands X , one should be able to synthesize Fephen_2X_2 with triplet spin state, subject to some semi-quantitative limits shown in Table VI. If X is a poorer π donor ($\delta e_{\pi} = e_{\pi_N} - e_{\pi_X} > 0$), X must also be a poorer σ donor than phen ($\delta e_{\sigma} > 0$) within the limits of $2(\delta e_{\pi} + K) > \delta e_{\sigma} > \frac{2}{3}(\delta e_{\pi} + K)$. This is the case for the extreme left side of Table VI. $\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{NCS})_2$ fall into the extreme right-hand-side region of Table VI, where $e_{\pi_N} + e_{\pi_X} > 0$, $\delta e_{\sigma} > 0$. A suitable balance between the σ and π characters of phen and NCBH_3^- satisfies the condition $2(K + \delta e_{\pi}) > \delta e_{\sigma} > \frac{2}{3}(K - 2e_{\pi_X})$, whereas in $\text{Fephen}_2(\text{NCS})_2$, δe_{π} is too negative and/or δe_{σ} is too positive, so that $\delta e_{\sigma} > 2(K + \delta e_{\pi})$ and $\text{Fephen}_2(\text{NCS})_2$ is a spin-quintet.

Table VI

Limits and balance between σ and π donating ability
of phen and X for a spin-triplet $\text{Fephen}_2\text{X}_2$.



$$\delta e_{\sigma} \text{ MUST } > 0$$

$$\text{IF } \delta e_{\sigma} > 0$$

$$\text{IF } \delta e_{\sigma} > 0$$

AND

$$2(K + \delta e_{\pi}) > \delta e_{\sigma} > \frac{2}{3}(K + \delta e_{\pi})$$

$$2(K + \delta e_{\pi}) > \delta e_{\sigma} > \frac{2}{3}(K - e_{\pi_X})$$

$$2(K + \delta e_{\pi}) > \delta e_{\sigma} > \frac{2}{3}(K + \delta e_{\pi})$$

$$\text{IF } \delta e_{\sigma} < 0$$

$$\text{IF } \delta e_{\sigma} < 0$$

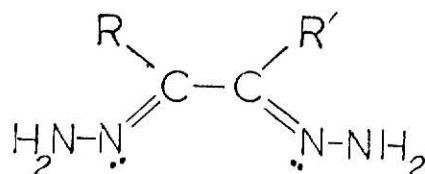
$$\frac{2}{3}(K + \delta e_{\pi}) > \delta e_{\sigma} > 2(K + \delta e_{\pi})$$

$$\frac{2}{3}(K + \delta e_{\pi}) > \delta e_{\sigma} > 2(K - e_{\pi_X})$$

In general, then, it should be possible to make some substitution on the ring of phen and on carbon or boron of N^-NCBH_3 in $\text{Fephen}_2(\text{NCBH}_3)_2$ to change its spin state. Replacing BH_3 with S is such an example. A more strongly π accepting and/or more strongly σ donating phen may tip the balance in favor of the singlet state while a less strongly π accepting and/or less strongly σ donating phen might favor the quintet state. Similarly, a better π donating and/or poorer σ donating X will favor the quintet state (e.g., $\text{Fephen}_2(\text{NCS})_2$) and a better π accepting and/or σ donating X could produce a singlet state (e.g., $\text{Fephen}_2(\text{CN})_2$). In this way, one can envision an entire class of $\text{Fephen}_2\text{X}_2$ compounds covering the range of spin state; the borderline cases among these would be expected to show interesting temperature dependent properties like $\text{Fephen}_2(\text{NCS})_2$.

The only other reports about the intermediate spin 6-coordinated ferrous complexes come from Stoufer's⁴² and König's⁴³ works. Stoufer suggested a trans geometry for his complexes, $\text{Fe}(\text{GdH})_2\text{Cl}_2$ and $\text{Fe}(\text{PvdH})_2\text{Cl}_2$ where GdH and PvdH are some α -dihydrazones.* In these cases a significant

* α -dihydrazones



GdH $\text{R} = \text{R}' = \text{H}$

PvdH $\text{R} = \text{CH}_3, \text{R}' = \text{H}$

tetragonal distortion may result and yield a triplet state, but no Mössbauer data are available for these complexes and the i.r. spectra do not strongly confirm the trans-geometry. König's complexes with the general formula $\text{Fe(II)} (\text{diim})_2 \text{X}_2$ with cis-geometries (where X_2 stands for bidentate oxalate, malonate, or two F^- ligands) give small i.s. and q.s. Magnetic moments of ~ 4 B.M. are observed for the tris-bidentate complexes, but for $\text{X}_2 = \text{F}_2$, the complex has a magnetic moment of 4.8 B.M. almost that for a high spin Fe(II) complex. These moments are considerably greater than that of $\text{Fe}(\text{phen})_2(\text{NCBH}_3)_2$ which gives essentially a spin-only value. The large magnetic moments of König's complexes are believed due to a second order Zeeman effect.

B) Charge Transfer Spectra

The room temperature KBr pellet spectra of the $\text{Fephen}_2\text{X}_2$ compounds obtained in this study are of the quality to be expected—not sufficiently good to bear quantitative interpretation. The author feels justified only in describing the broad envelopes in the 400-700 nm region as metal $\rightarrow$ phen charge transfer in origin^{10,31,43,44,45} and in noting general shifts to the red or blue as X is varied. Typical comparisons on which the author wishes to comment are given in Figures 18-20. To interpret these shifts we rely on one simple concept: charge transfer (σ and π) to the metal from X 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, there is not only this general electron repulsion based d orbital elevation but also a specific elevation arises through greater π^* character for the d_π orbitals. Table IV summarizes the direction of changes of the charge transfer energies and the Mössbauer isomer shifts.

The first transformation 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 i.s. from 4s (σ) and 3d (π) orbital population changes. The second transformation finds greater σ donation and poorer π donation of the ligand;

Table VII

Shift of the charge transfer bands and change of the isomer shifts for $\text{Fephen}_2\text{X}_2$ as X is varied.

			$\Delta i.s.$	$\Delta \tilde{\nu}_{C.T.}$
$X = CN^-$	$\longrightarrow$	$^-CNBH_3$	-0.01	large blue
$^-NCBH_3$	$\longrightarrow$	$^-CNBH_3$	-0.25	small blue
$^-NCBH_3$	$\longrightarrow$	^-NCS	+0.6	small red

Figure 18

Visible spectra of $\text{Fephen}_2(\text{CN})_2$ (————) and
 $\text{Fephen}_2(\text{CNBH}_3)_2$ (-----); KBr pellets.

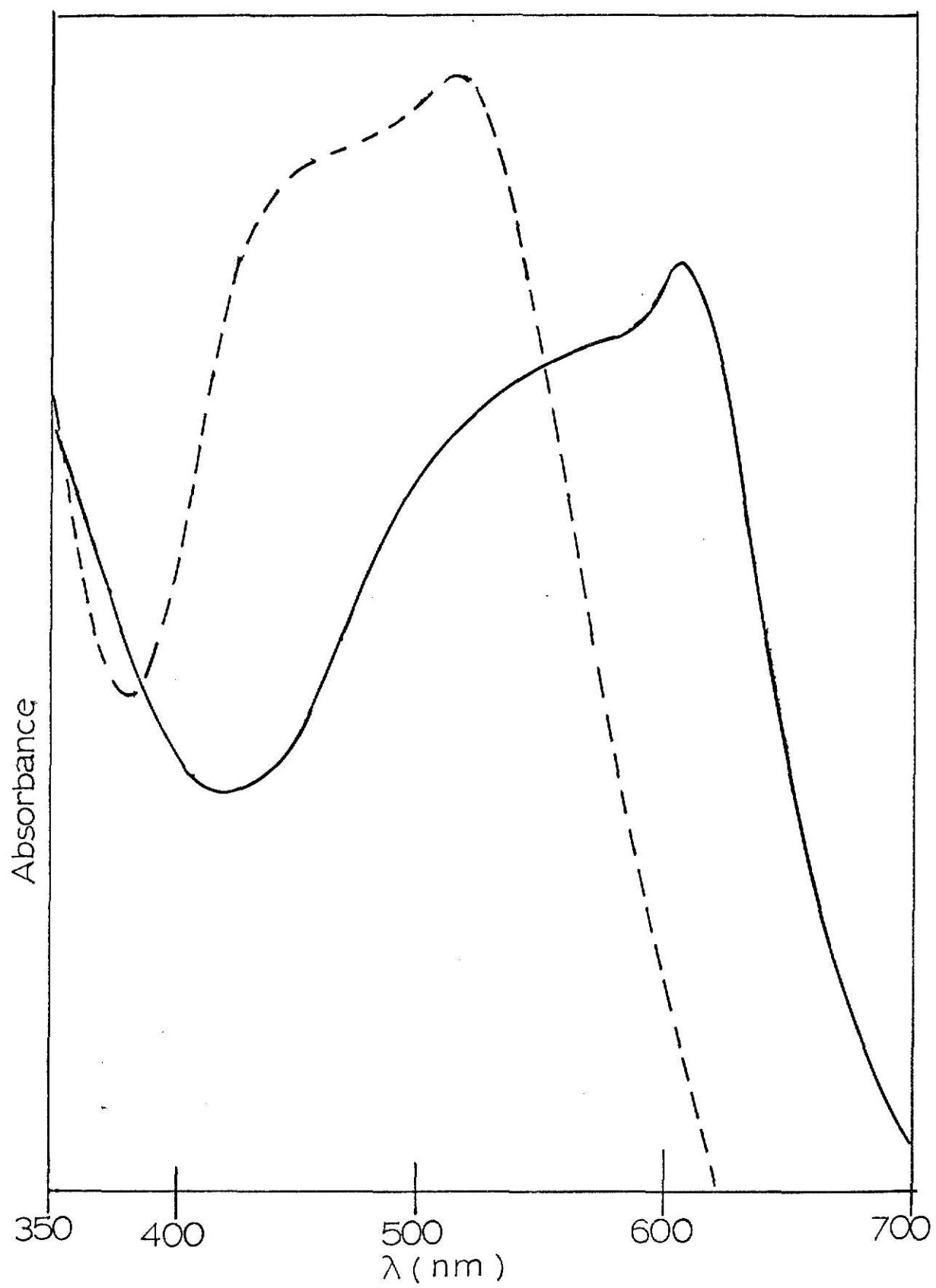


Figure 19

Visible spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ (————) and
 $\text{Fephen}_2(\text{CNBH}_3)_2$ (-----); KBr pellets.

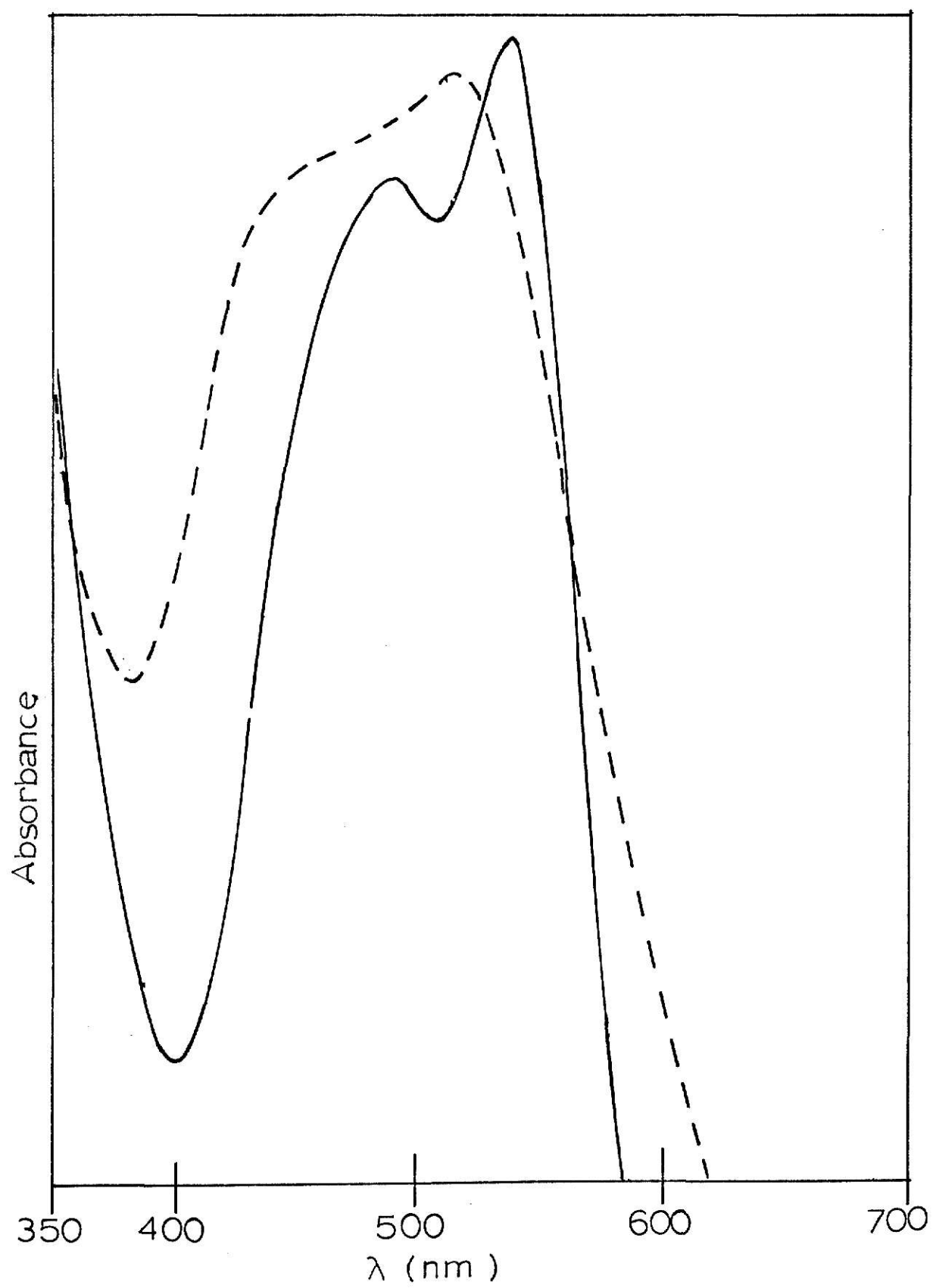
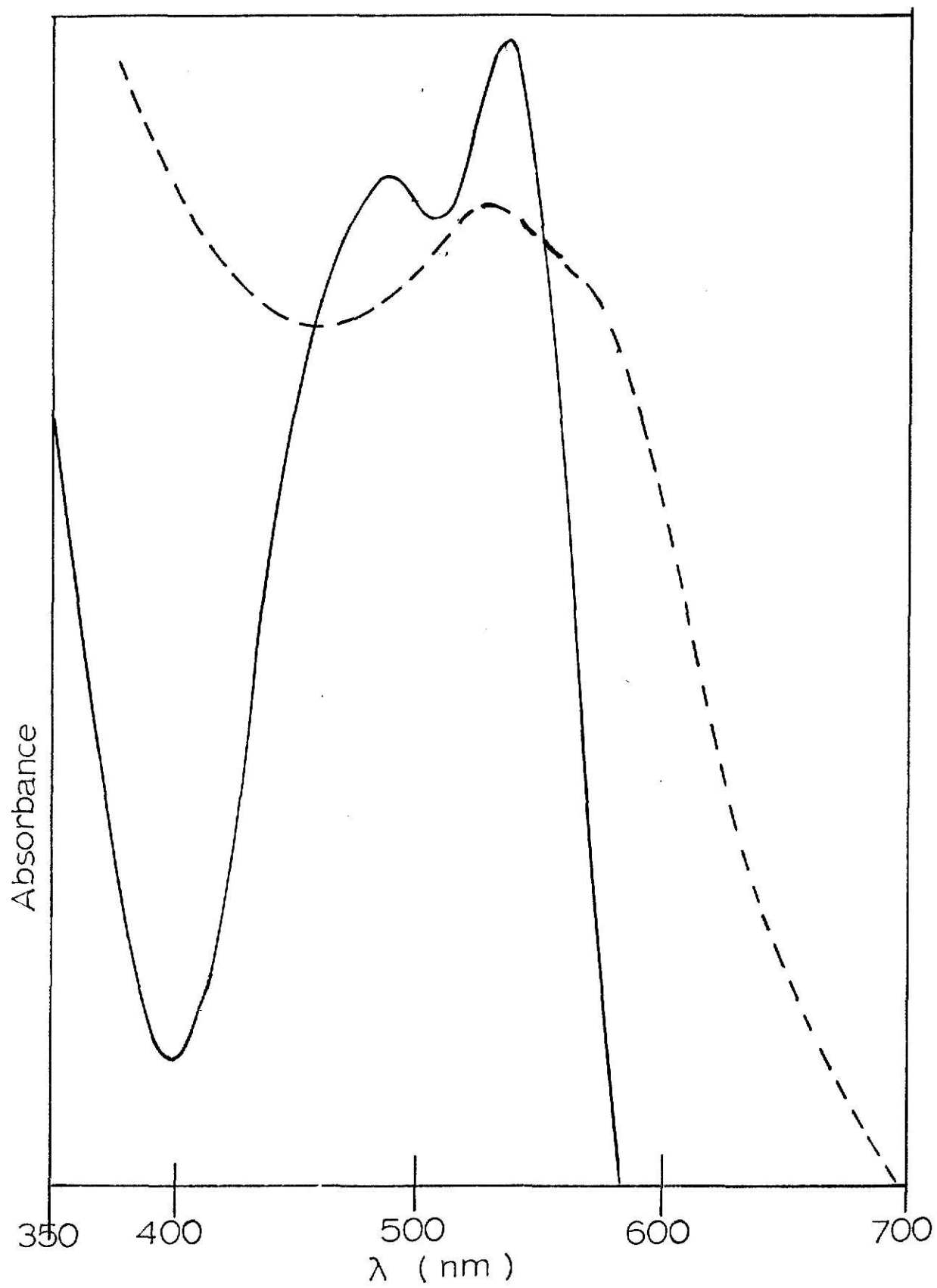


Figure 20

Visible spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ (——) and
 $\text{Fephen}_2(\text{NCS})_2$ (-----); KBr pellets.

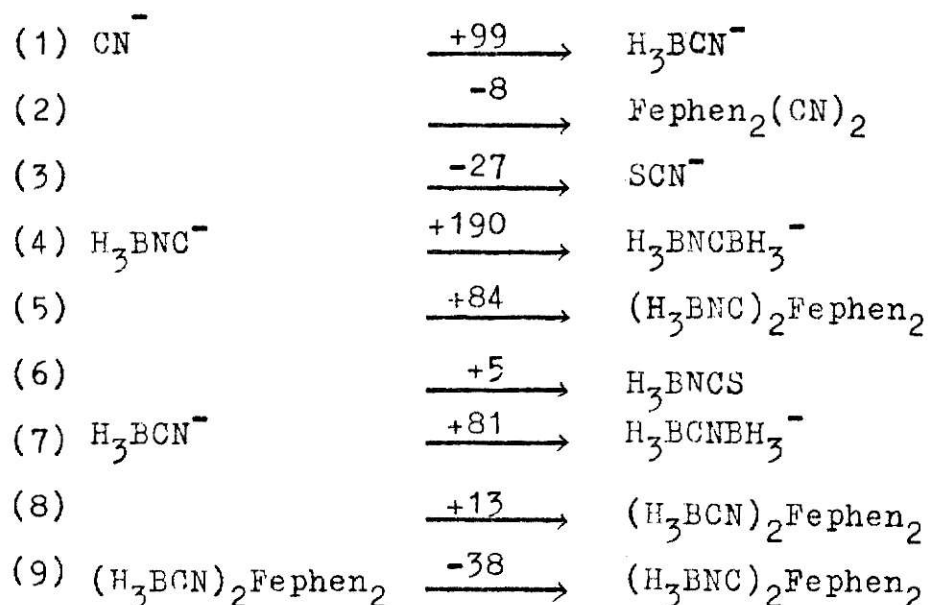


these have compensating effects on the CT bands but reinforcing effects on the isomer shift. The final transformation should, as noted in the earlier section, affect decreased σ donation to Fe but enhanced π donation. Again, the σ/π effects compete with respect to the charge transfer shift but reinforce in the Mössbauer experiment, causing a large +i.s. change.

These interpretations of i.s. change are implicitly based on the supposition that Fe 4s population changes are more important than the $3d_{\sigma}$ changes. Recalling the discussion in the former section (p.62) it seems that such an approximation may be generally appropriate. It is interesting (but perhaps generally dangerous) to note that the direction of the i.s. 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.

C. Vibrational Spectra in the CN Region

The CN vibrational data (Table II) are valuable for two reasons. First of all, the appearance of CN doublets for $\text{Fephen}_2(\text{NCBH}_3)_2$, and $\text{Fephen}_2(\text{CNBH}_3)_2$, together with the Mössbauer spectra, establishes their structures as cis-(C_2) rather than trans-(D_{2h}). Secondly, 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 Fephen_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):



These conclusions follow from the breakdown of $\tilde{\nu}_{\text{CN}}$ as follows:

- (i) kinematic coupling of the CN coordinate, after the $\leftarrow\text{CN}$ and/or $\text{CN}\rightarrow$ coordinates, will slightly increase $\tilde{\nu}_{\text{CN}}$;

- (ii) re-hybridization 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;^{46,47} this effect should be of greater importance for the more polarizable C hybrid:
- (iii) further polarization of the CN σ or π bond pairs in the direction of prior polarization would decrease the bond order and thus depress $\nu_{\text{CN}}^{\#}$ (note that increased hybrid s character implies greater polarization in the direction of the hybrid); this factor tends to enhance (ii) for C-coordination because the prior polarization of the CN σ bond toward nitrogen is reduced;
- (iv) retro-bonding via π electrons from the acid into the CN π^* orbitals depresses ν_{CN} .

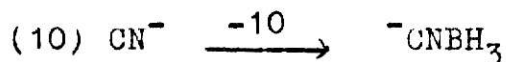
Item (i) & (ii) should always be operative and tend to make $\Delta\tilde{\nu}_{\text{CN}} > 0$. The sense of operation and magnitude of the item (iii) varies as C or N is the Lewis donor atom; for C-coordination $\Delta\tilde{\nu}_{\text{CN}} > 0$ for N-coordination $\Delta\tilde{\nu}_{\text{CN}} < 0$. Item (iv) will cause

[#]The bond order between two hybrid atomic orbitals is largest when there is equal mixing of them (polarization = 0).

$\Delta\tilde{\nu}_{\text{CN}} < 0$ and be of greater importance for NC^- than CN^- coordination because the $\text{CN}^- \pi^*$ 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), in (8) relative to (7) and in (9) is readily seen.

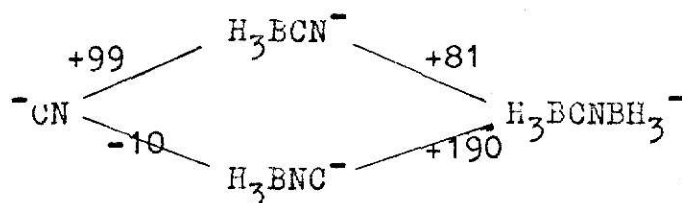
To analyze $\Delta\tilde{\nu}_{\text{CN}}$ between corresponding "reactions" of different sets, one must acknowledge the effect of the prior coordination of BH_3 to CN^- . It is true that such prior coordination does not appear to effect the trend that (iv) is of increasing importance relative to (i), (ii), (iii), in the series of BH_3 , FePhen_2^{+2} and S. On the other hand, when C-coordination occurs, (i), (ii) and (iii) appear to be of greater importance after the prior coordination of BH_3 to nitrogen than for bare CN^- . It is unlikely that the kinetic coupling effect (i) varies significantly in a comparison of (1) with (4), of (2) with (5), and of (3) with (6). That is, if, as expected, the prior BH_3 coordination to nitrogen enhances retro-bonding (iv), then (ii) and (iii) experience even greater enhancement.

The situation with the "nitrogen coordination" is less well defined because there are fewer examples. Comparing with (7) to (10)

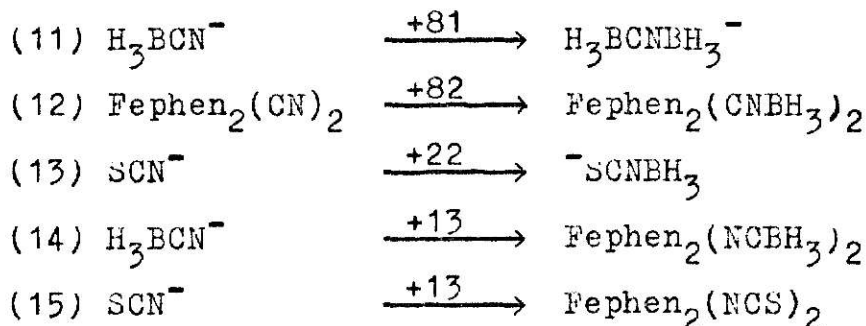


One finds the prior coordination of BH_3 to carbon effects a large enhancement of (ii) relative to (iii). (10) is the

only example of which we are aware for which factor (iii) dominates (ii). Apparently, prior formation of the B-C bond reverses their order of importance for subsequent nitrogen coordination, otherwise, prior coordination of BH_3 to C is similar to prior coordination of BH_3 to nitrogen — both sensitize the CN bond to the σ effects from other-donor atom coordination — with the former less sensitizing than the latter.



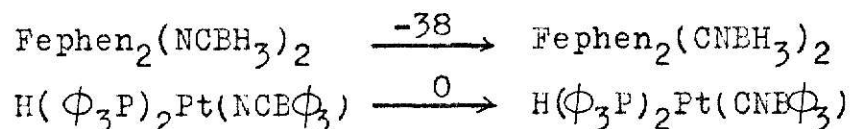
There are also other comparisons one can make regarding the effect of prior coordination



For the series of (11)-(13), kinematic coupling (i) and rehybridization at nitrogen (ii) effects are seen to dominate the polarization (iii) effects and, in (12) & (13), retrobonding (iv) from FePhen_2^{+2} and S to ^-CN . The last factor appears to be of considerable importance for SCN^- , where the sulfur has 2 lone pairs for retrobonding, while in $\text{FePhen}_2(\text{CN})_2$ the analogous pairs number only 3/2 per CN and are likely involved in π retrobonding into π^* of phen and so are less available for retrobonding to ^-CN .

From the similarity of $\Delta\tilde{\nu}_{\text{CN}}$ of (13) & (15), one is impressed with what appears to be the ready electron "give-and-take" action of the sulfur. The difference of 9 cm^{-1} is within the range of kinematic differences and is dangerous to interpret further in terms of chemical valency concepts. In comparing (11) with (13), where BH_3 is a "sigma-only" acid, the π donor role of sulfur is quite apparent. The analogous comparison of (14) with (15), where Fephen_2^{2+} is a sigma acid/ π donor, shows a greatly damped π donor role for sulfur.

In closing this section, we would like to make a brief comparison of the isomers of $\text{Fephen}_2(\text{CNBH}_3)_2$, $\text{Fephen}_2(\text{NCBH}_3)_2$ with Manzer's²¹ isomeric pair $\text{HPt}(\text{P}\phi_3)_2(\text{CNB}\phi_3)$ and $\text{HPt}(\text{P}\phi_3)_2(\text{NCB}\phi_3)$. A curious feature of Manzer's data is that his isomeric pair displays the same CN stretching frequency, not found in this study.



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 $\tilde{\nu}_{\text{CN}}$, the CN frequency should be depressed in isomerization through the retrobonding factor (iv). If the metal fragment exhibits less σ inductive effect than BR_3 , factor (ii) & (iii) would support the depression of $\tilde{\nu}_{\text{CN}}$ in these reactions (note C is more polarizable), while greater acid character of the metal fragment should enhance $\tilde{\nu}_{\text{CN}}$ through

factors (ii) & (iii). In the case of $\text{HPt}(\text{PPh}_3)_2^+$, 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 cancelling. For the iron fragment the conclusions are less firm; either the iron exhibits less σ inductive effect on the CN than does BH_3 , (augmenting the depression of $\tilde{\nu}_{\text{CN}}$) or if the iron fragment does show greater σ acidity than boron, then the σ perturbation must be less pronounced than the π -retro-bonding.

Unfortunately, it is not possible at this point to compare the relative importance of these effects in the iron and platinum complexes. Only were it possible to independently state that the platinum complex exhibits a greater π retro-bonding than the iron complex would we be able to make a useful statement: namely, that the σ acidities fall in the order of $\text{Pt} > (\text{B}, \text{Fe})$. Similarly, it is not possible on the basis of $\Delta\tilde{\nu}_{\text{CN}}$ alone to rank BH_3 and $\text{Fe}(\text{phen})_2^{+2}$ with regard to σ perturbation of CN^- .

D. Solvolysis of $\text{Fephen}_2(\text{CNBH}_3)_2$ & $\text{Fephen}_2(\text{NCBH}_3)_2$

1) $\text{Fephen}_2(\text{CNBH}_3)_2$

$\text{Fephen}_2(\text{CNBH}_3)_2$ is quite stable in sulfolane solution, as evidenced with its visible spectra (Figure 21, 13, 14). When $\text{Fephen}_2(\text{CNBH}_3)_2$ dissolves into pyridine, pyridine slowly displaces BH_3 from $\text{Fephen}_2(\text{CNBH}_3)_2$, while heating accelerates this reaction, and forms $\text{Fephen}_2(\text{CN})_2$, as shown by the visible region spectra (Figure 22, 13, & 14). The CN region i.r. spectrum of the solution also give two CN bands found for $\text{Fephen}_2(\text{CN})_2$. Heating the methanol solution of $\text{Fephen}_2(\text{CNBH}_3)_2$ also leads to the formation of $\text{Fephen}_2(\text{CN})_2$ as shown by its visible spectrm (Figure 23, 13, 14).

Although the nucleophiles like H_2O , $\phi_3\text{P}$, Et_3N and CN^- failed to remove BH_3 from $\text{Fephen}_2(\text{CNBH}_3)_2$ and $\text{Fephen}_2(\text{NCBH}_3)_2$ under the heterogeneous conditions, loss of BH_3 from $\text{Fephen}_2(\text{CNBH}_3)_2$ in pyridine and methanol solution suggests that we could chemically strip BH_3 from $\text{Fephen}_2(\text{CNBH}_3)_2$, and possibly from $\text{Fephen}_2(\text{NCBH}_3)_2$ also, perhaps through a homogeneous mode of reaction.

Figure 21

Visible spectra of sulfolane solutions of
 $\text{Fephen}_2(\text{CN})_2$ (————) and $\text{Fephen}_2(\text{CNBH}_3)_2$ (-----).

The concentrations are different.

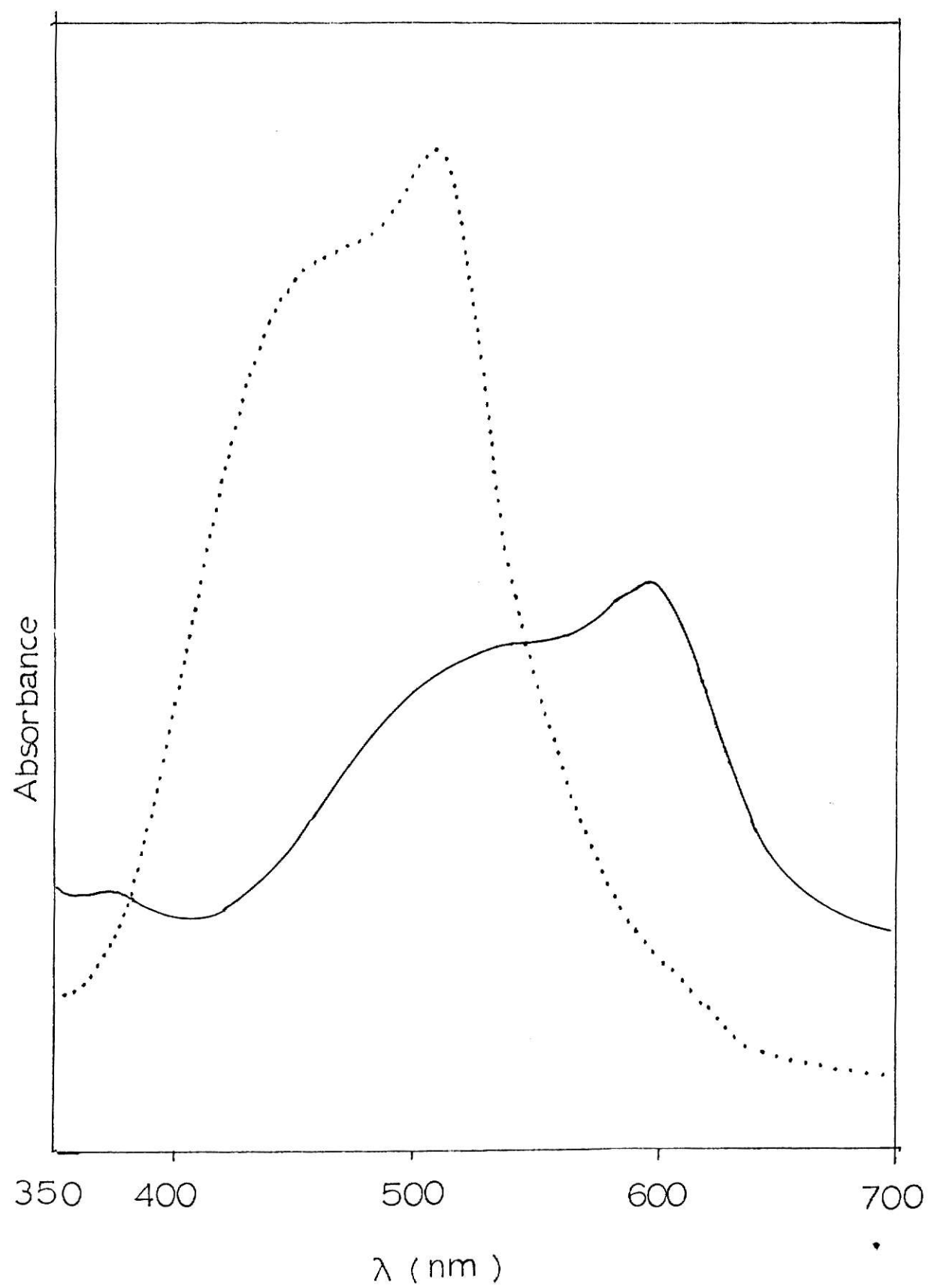


Figure 22

Visible spectra of pyridine solutions of $\text{Fephen}_2(\text{CN})_2$ (————), freshly prepared $\text{Fephen}_2(\text{CNBH}_3)_2$ (······) and $\text{Fephen}_2(\text{CNBH}_3)_2$, after heating (-----).

The room temperature aging of a pyridine solution of $\text{Fephen}_2(\text{CNBH}_3)_2$ for days gives the same spectrum as that of the heated pyridine solution of $\text{Fephen}_2(\text{CNBH}_3)_2$.

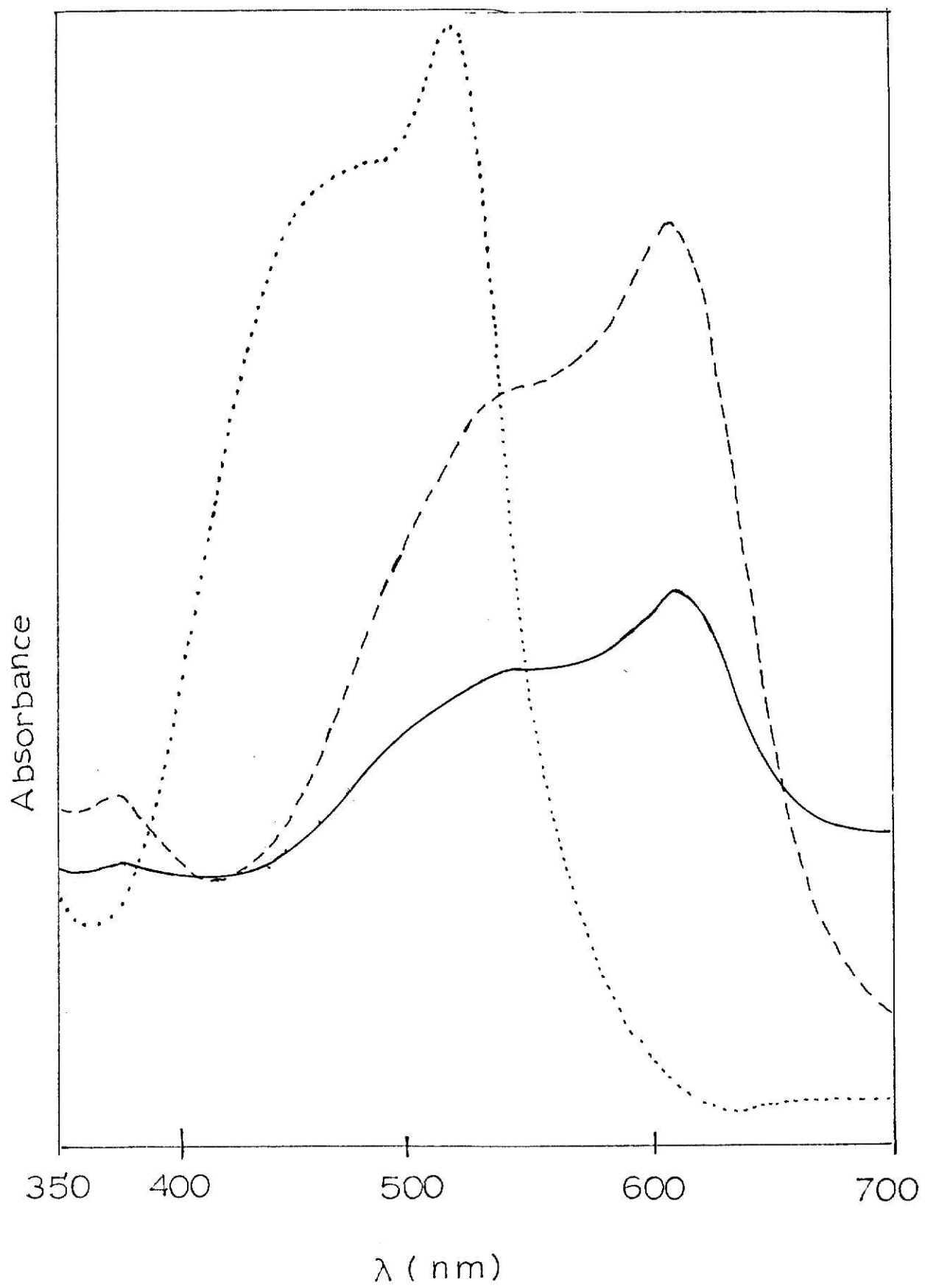
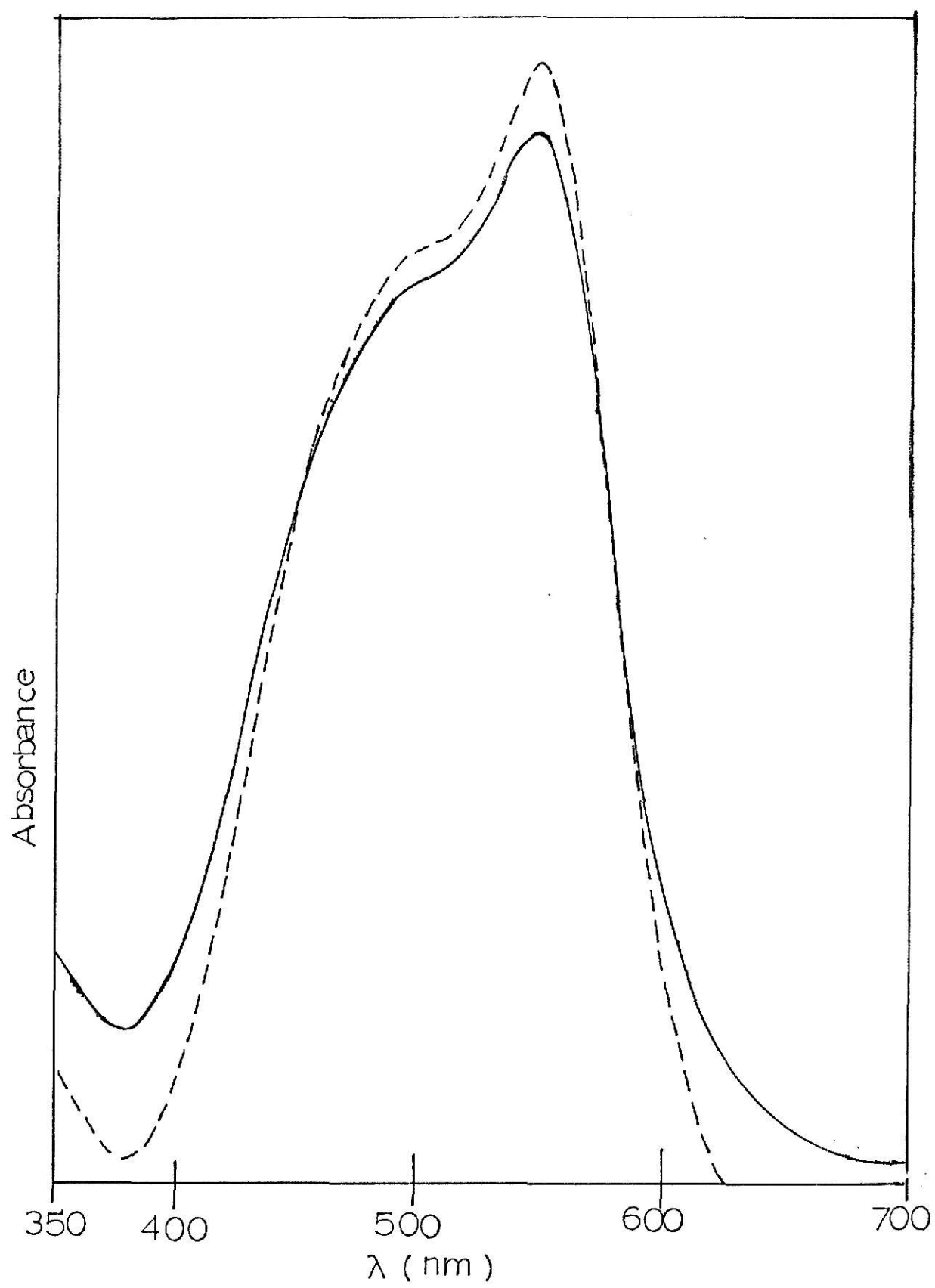


Figure 23

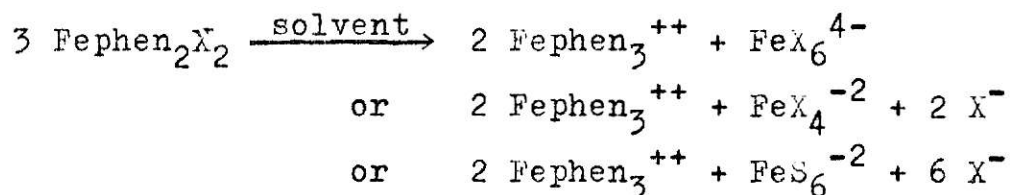
Visible spectra of $\text{Fephen}_2(\text{CN})_2$ in methanol (-----)
and of a heated methanol solution of $\text{Fephen}_2(\text{CNBH}_3)_2$
(———).

The concentrations are different.



2) $\text{Fephen}_2(\text{NCBH}_3)_2$

$\text{Fephen}_2\text{Cl}_2$ and $\text{Fephen}_2(\text{NCS})_2$, when dissolved in water (Figure 24) or nitromethane (Figure 25), experience solvolysis (comparing with the solid state spectra in Figures 15 & 16). In both solvents it appears that Fephen_3^{++} is the only phen containing species present, as suggested by Madeja.²⁴ Any of the following equilibria could be involved to account for the decomposition.



where FeX_6^{4-} , FeX_4^{-2} and FeS_6^{++} do not have appreciable absorption in the charge transfer region of Fephen_3^{++} .

The effect of solvents on the spectrum of $\text{Fephen}_2(\text{NCBH}_3)_2$ is much more difficult to discern than in the $\text{Fephen}_2\text{Cl}_2$ & $\text{Fephen}_2(\text{NCS})_2$ cases. Reference to Figures 12 & 17 reveals a much closer resemblance of $\text{Fephen}_2(\text{NCBH}_3)_2$ to Fephen_3^{++} than in the cases of $\text{Fephen}_2\text{Cl}_2$ & $\text{Fephen}_2(\text{NCS})_2$. Spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ in CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$ solutions (Figure 31) suggest that in non-basic/non-ionizing solvents, $\text{Fephen}_2(\text{NCBH}_3)_2$ has a spectrum very much like that of Fephen_3^{++} in the solid state (Figure 17) and in various other solvents (Figure 24 - 30). This is not greatly surprising since NCBH_3 approaches phen in the net effect of σ and π donor character on the CT transitions. Were $\text{Fephen}_2(\text{NCBH}_3)_2$ to lose BH_3 in solution it would

Figure 24

Visible spectra of aqueous solutions of $\text{Fephen}_2(\text{NCBH}_3)_2$ (— — — —), $\text{Fephen}_2(\text{NCS})_2$ (-----), $\text{Fephen}_2\text{Cl}_2$ (.....) and $\text{Fephen}_3 \cdot 7\text{H}_2\text{O}$ (————).

The concentrations are different.

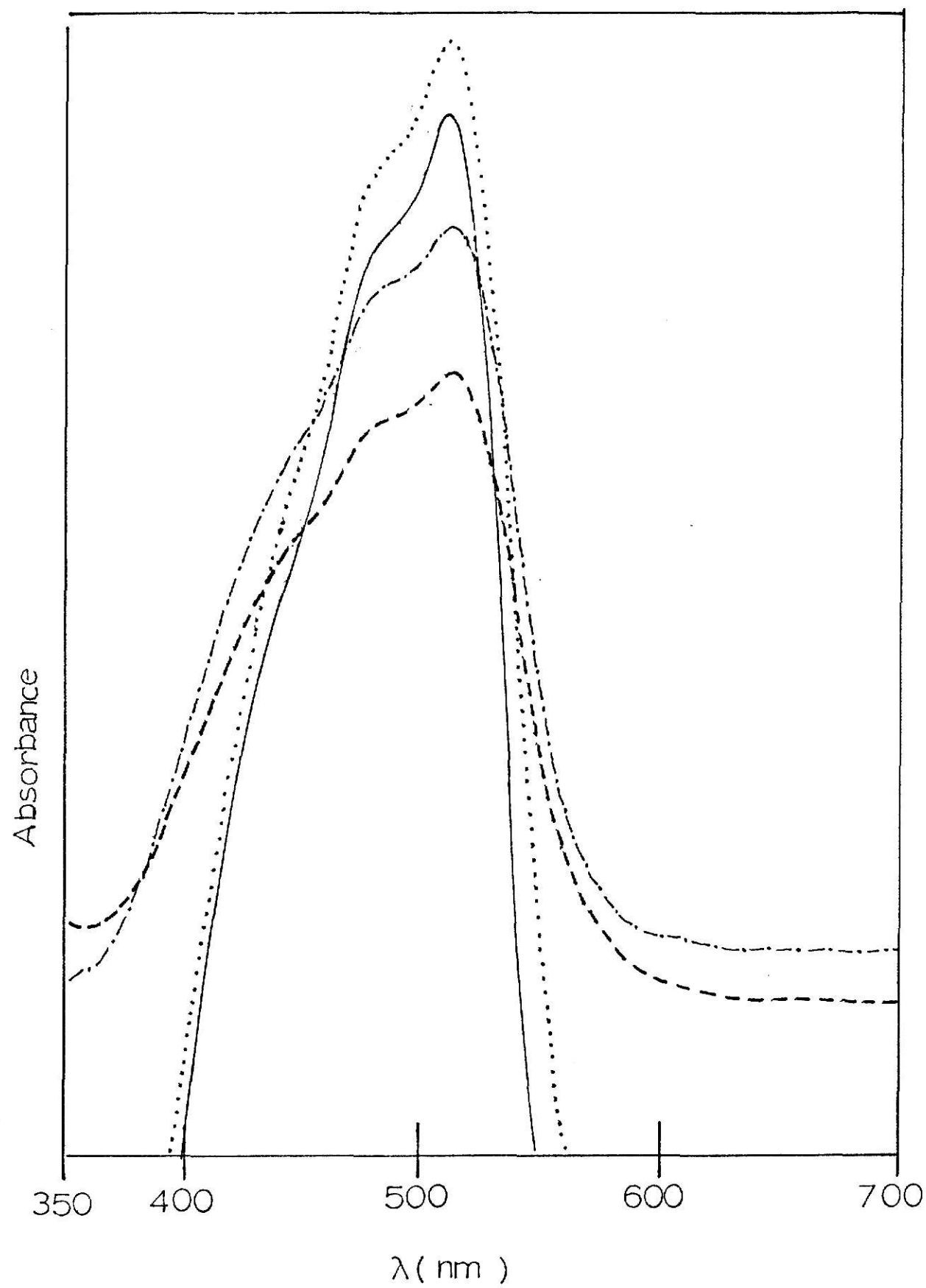


Figure 25

Visible spectra of CH_3NO_2 solutions of $\text{Fephen}_2(\text{NCS})_2$ (— · — · — · — · —), $\text{Fephen}_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ (————), $\text{Fephen}_2\text{Cl}_2$ (······) and $\text{Fephen}_2(\text{NCBH}_3)_2$ (-----). The concentrations are different.

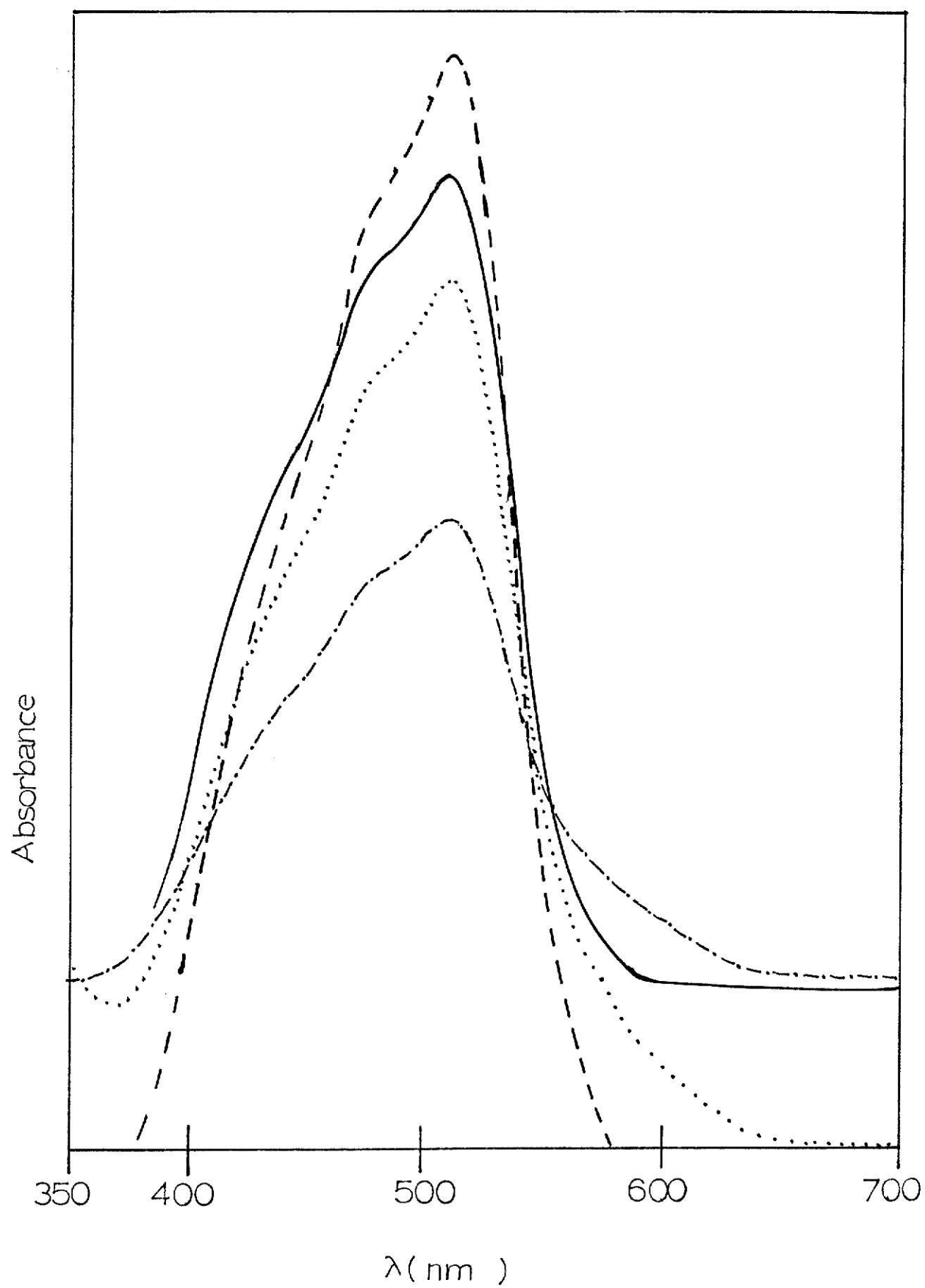


Figure 26

Visible spectra of CH_3CN solutions of Fephen_3^{++}
(——) and of $\text{Fephen}_2(\text{NCBH}_3)_2$ (.....).

The concentrations are different.

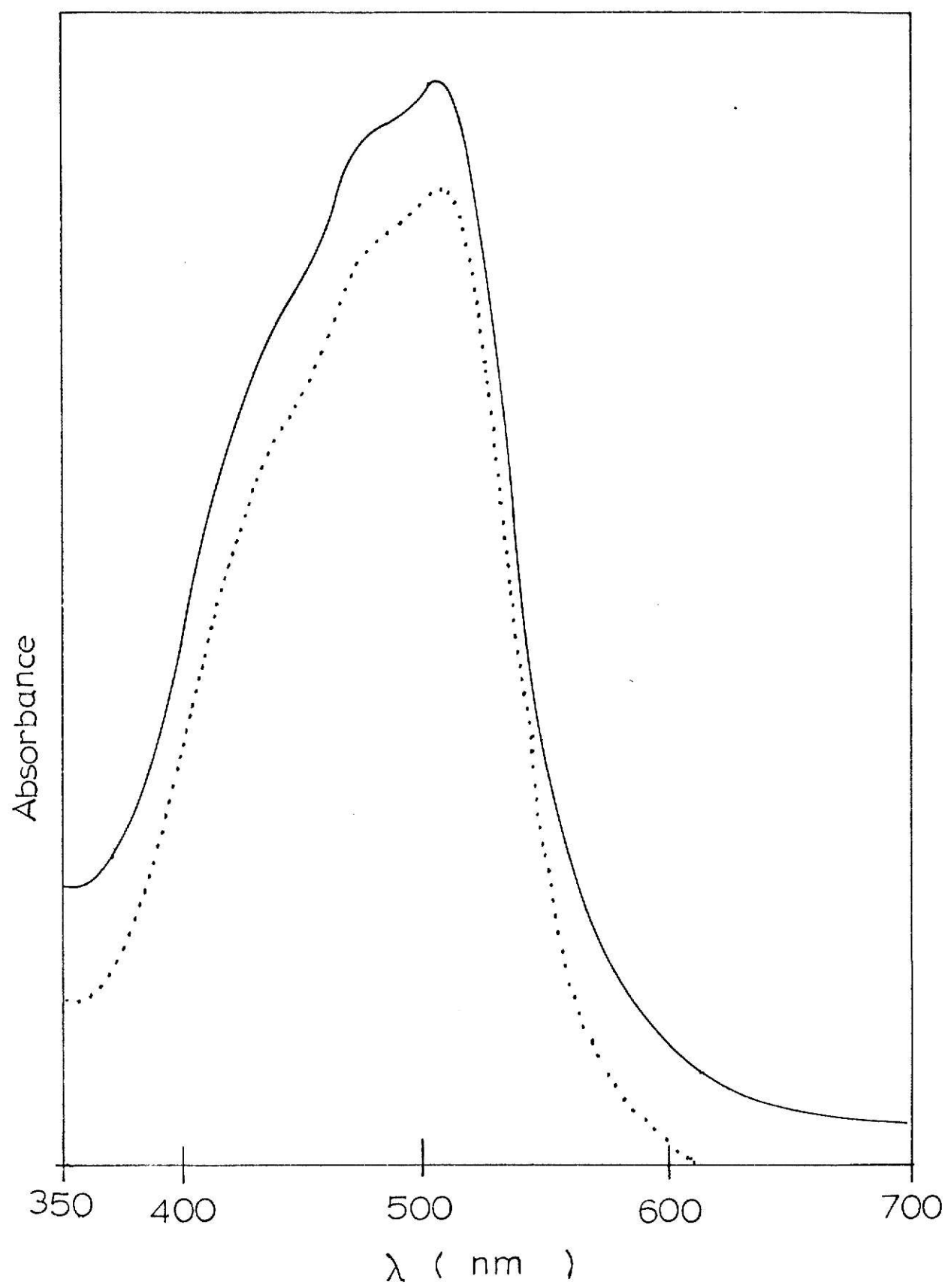


Figure 27

Visible spectra of CH_3OH solutions of Fephen_3^{++}
(——) and of $\text{Fephen}_2(\text{NCBH}_3)_2$ (·····).

The concentrations are different.

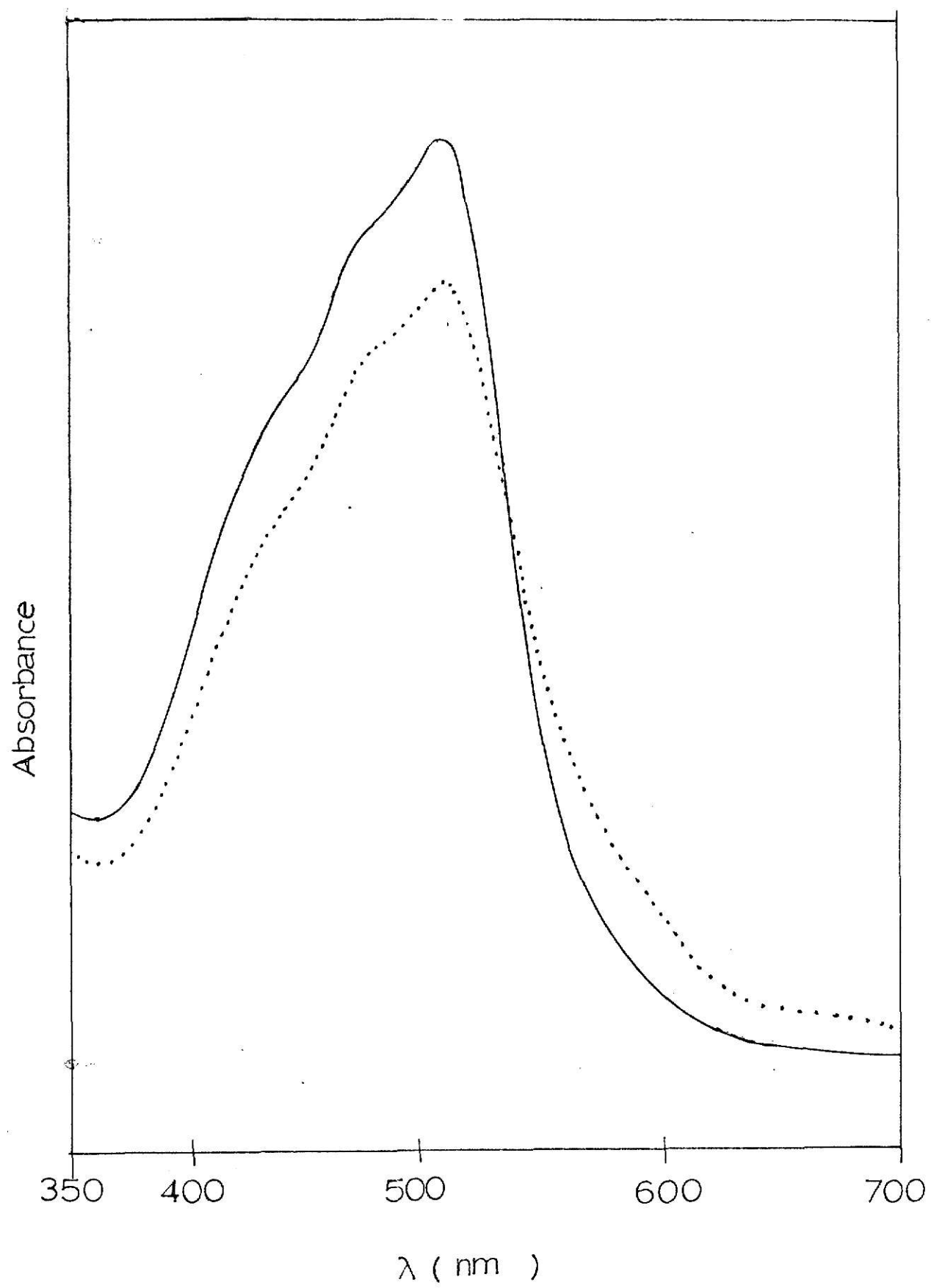


Figure 28

Visible spectra of CH_3COOH solutions of Fephen_3^{++}
(——) and of $\text{Fephen}_2(\text{NCBH}_3)_2$ (.....).

The concentrations are different.

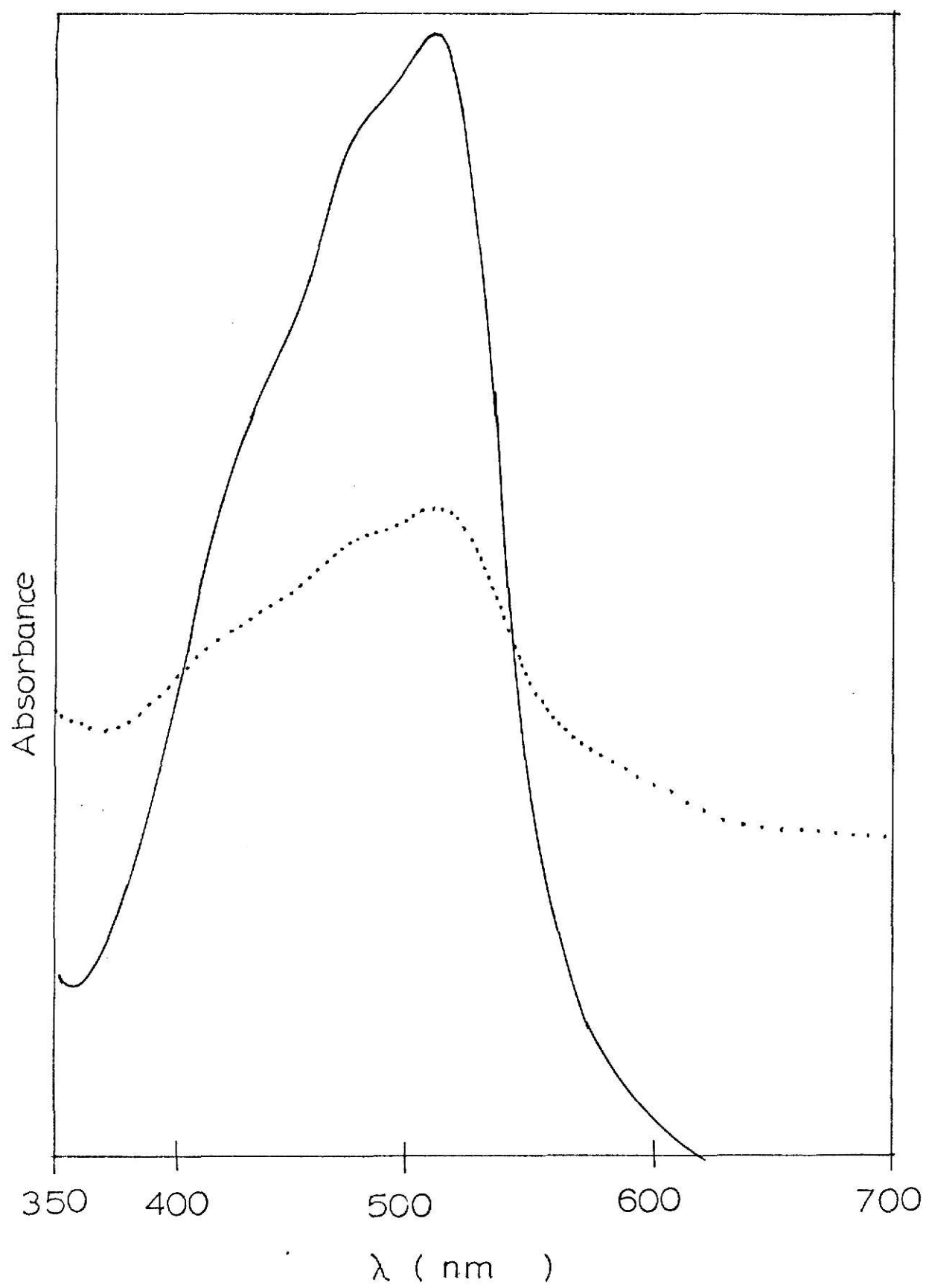


Figure 29

Visible spectra of sulfolane solutions of Fephen_3^{++}
(——) and of $\text{Fephen}_2(\text{NCBH}_3)_2$ (.....).

The concentrations are different.

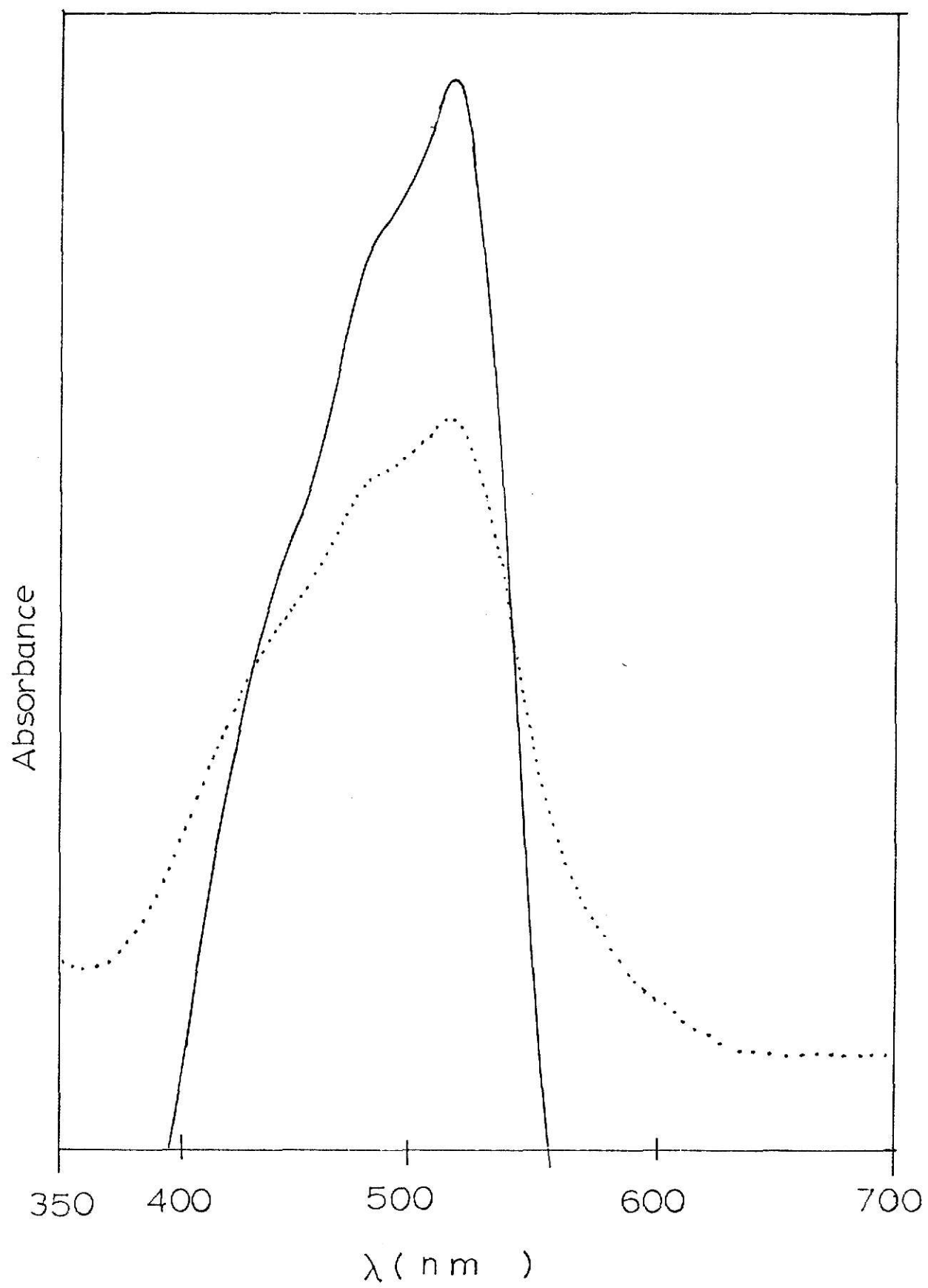


Figure 30

Visible spectra of pyridine solutions of Fephen_3^{++}
(——) and of $\text{Fephen}_2(\text{NCBH}_3)_2$ (.....).

The concentrations are different.

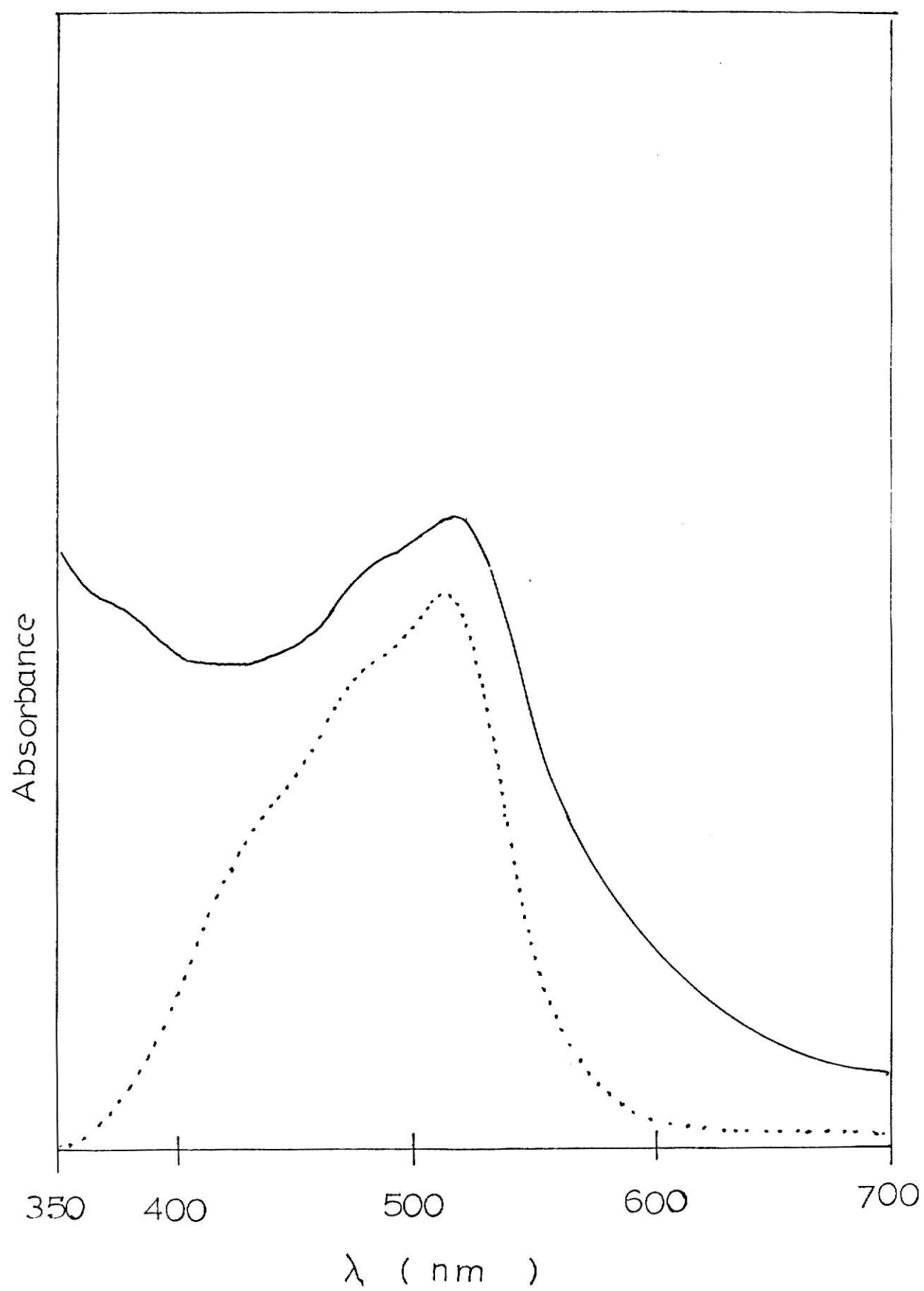
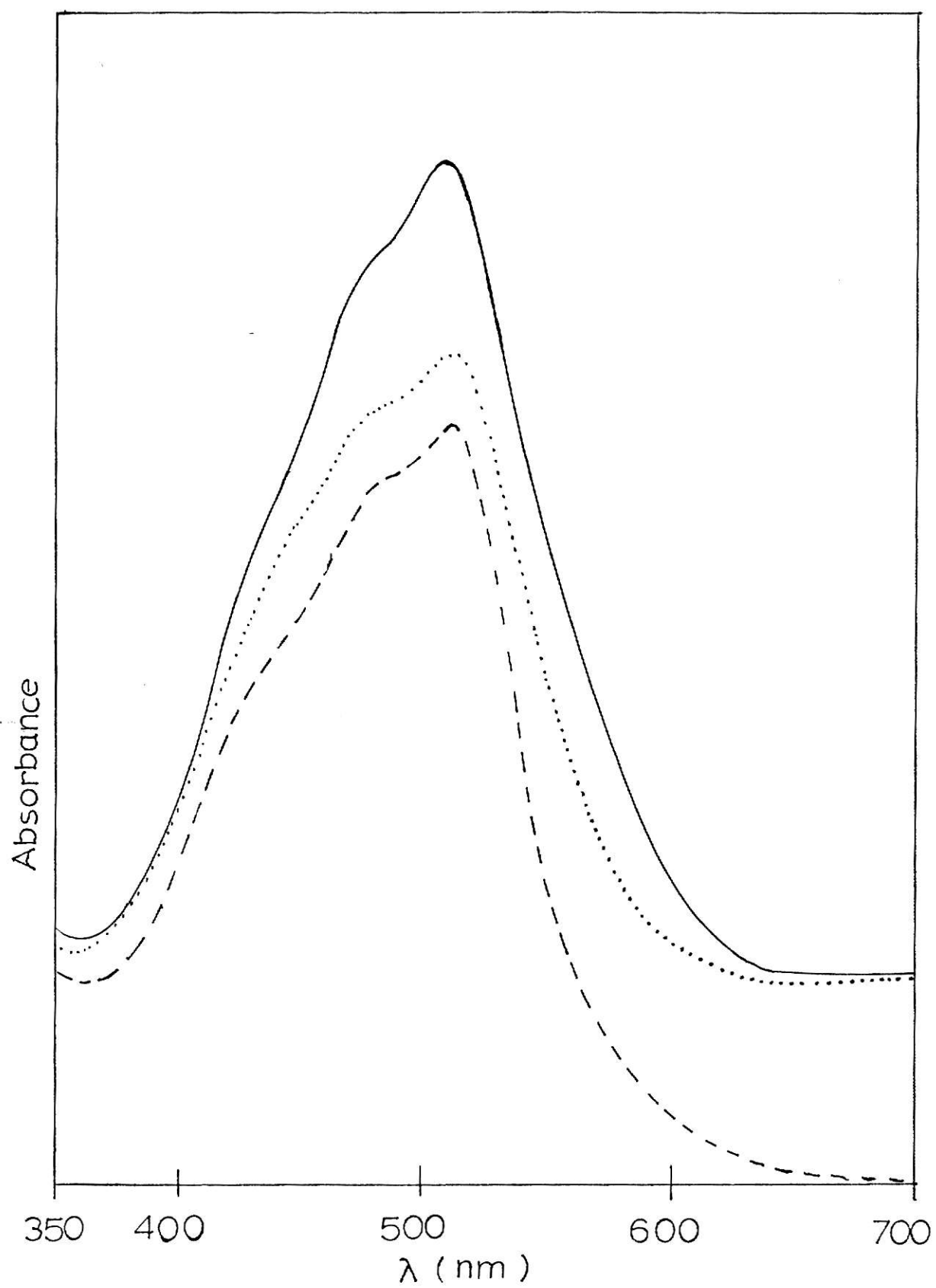


Figure 31

Visible spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ in CH_2Cl_2 (————),
in $\text{C}_2\text{H}_4\text{Cl}_2$ (······) and in $(\text{CH}_3)_2\text{CO}$ (-----).

The concentrations are different.



be generally possible to detect $\text{Fephen}_2(\text{CN})_2$, but distinguishing $\text{Fephen}_2(\text{NC})_2$ from Fephen_3^{++} and $\text{Fephen}_2(\text{NCBH}_3)_2$, on the basis of the visible spectra only, would be very difficult. In fact all the Figures 24 - 31 show qualitatively the same spectra of $\text{Fephen}_2(\text{NCBH}_3)_2$ and all are very close to that of Fephen_3^{++} in those same solvents (except for the chlorohydrocarbon and acetone solvents in which Fephen_3^{++} would not dissolve). Indeed, the i.r. spectra of the sulfolane and the nitromethane solutions do give a single band in the CN stretching region, (2168 cm^{-1}) and suggest the formation of NCBH_3^- anion in these two solutions (KNCBH_3 displays ν_{CN} in sulfolane and nitromethane at 2164 cm^{-1} and 2168 cm^{-1} , respectively). Consequently, we feel unjustified on the basis of these electronic spectra alone to draw any firm conclusions as to the fate of $\text{Fephen}_2(\text{NCBH}_3)_2$ in the other solvents.

E. Thermal Stability

Thermal stability studies undertaken to identify the more stable form of the $\text{Fephen}_2[(\text{NC}, \text{CN})\text{BH}_3]_2$ linkage have failed to reveal simple interconversion. Heating a sample of the Fe-CN-BH_3 isomer at 170°C for three days in vacuum resulted in important changes. Most significant is the collapse of the CN doublet of the Fe-CN-BH_3 isomer to a broad singlet at the average of the doublet frequencies. By itself, this change suggests the (unlikely) formation of trans- $\text{Fephen}_2(\text{CNBH}_3)_2$, or the loss of one equivalent of BH_3 to produce $\text{Fephen}_2(\text{CN})(\text{CNBH}_3)$. At lower frequency we find two bands at the frequencies found for $\text{Fephen}_2(\text{CN})_2$, and a rather intense third band between these last two, as shown in Figure 32. Based on this low frequency spectral change it seems safe to conclude that thermolysis leads to a mixture of $\text{Fephen}_2(\text{CN})(\text{CNBH}_3)$, and $\text{Fephen}_2(\text{CN})_2$. Note that the change in relative CN/ BH_3 band envelopes suggests BH_3 loss too. In addition, it appears that loss of the first BH_3 is much faster than loss of the second.

Heating $\text{Fephen}_2(\text{CNBH}_3)_2$, under the same conditions as before, for 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 cm^{-1} and 2081 cm^{-1} (Figure 33). This confirms the formation of $\text{Fephen}_2(\text{CN})(\text{CNBH}_3)$ in the initial pyrolysis stages and that the second BH_3 , after the first BH_3 is lost,

Figure 32

Infrared spectra of $\text{Fephen}_2(\text{CNBH}_3)_2$: (A) before heating and (B) after heating at 170°C under vacuum for 3 days; KBr pellets.

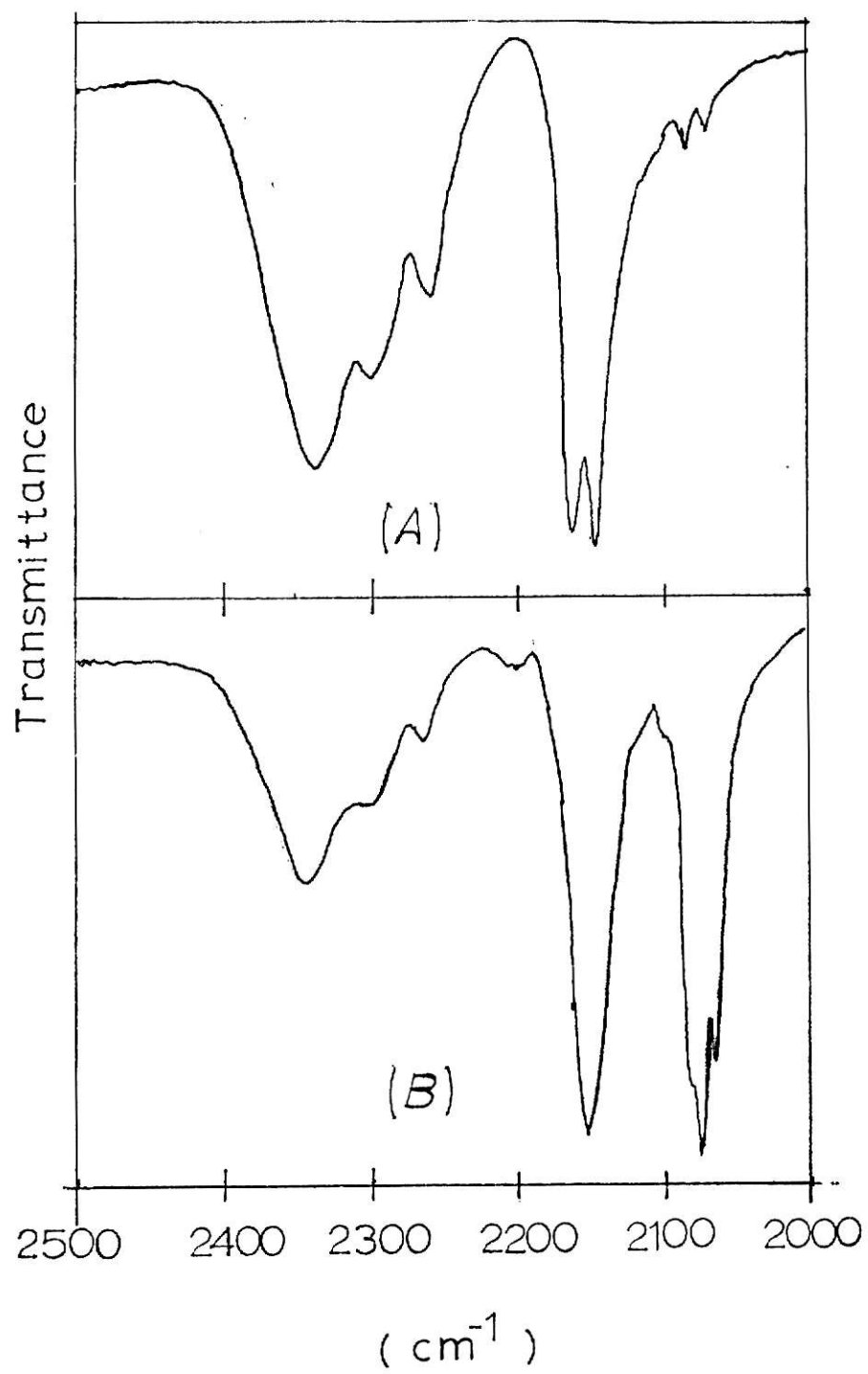


Figure 33

Infrared spectra of $\text{Fe}(\text{phen})_2(\text{CNBH}_3)_2$ after heating at 170°C under vacuum for 10 days; KBr pellet.

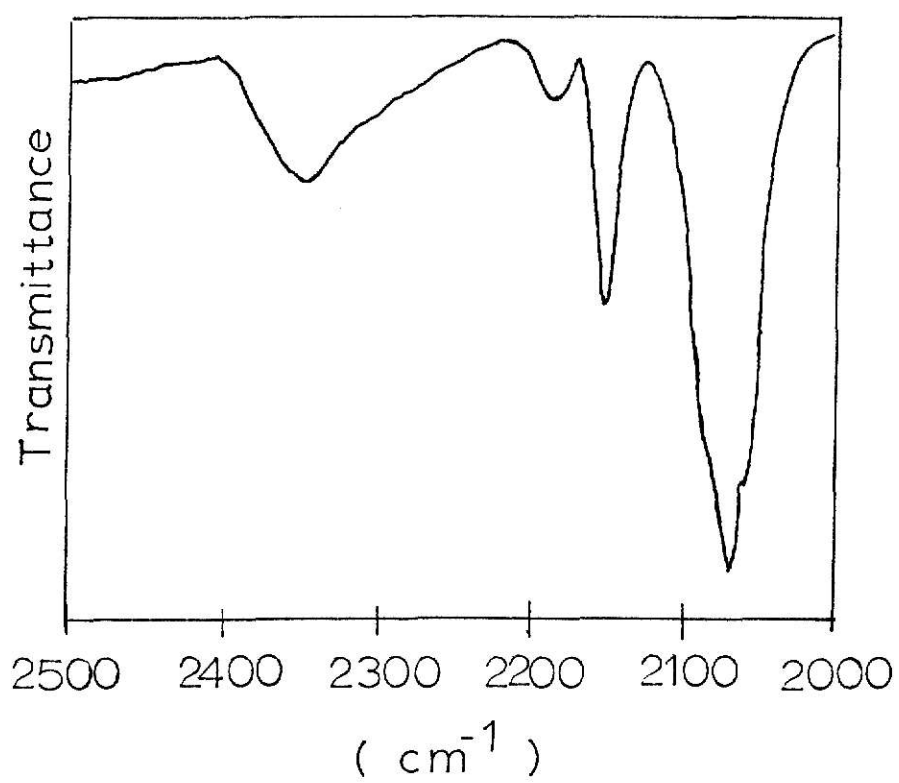
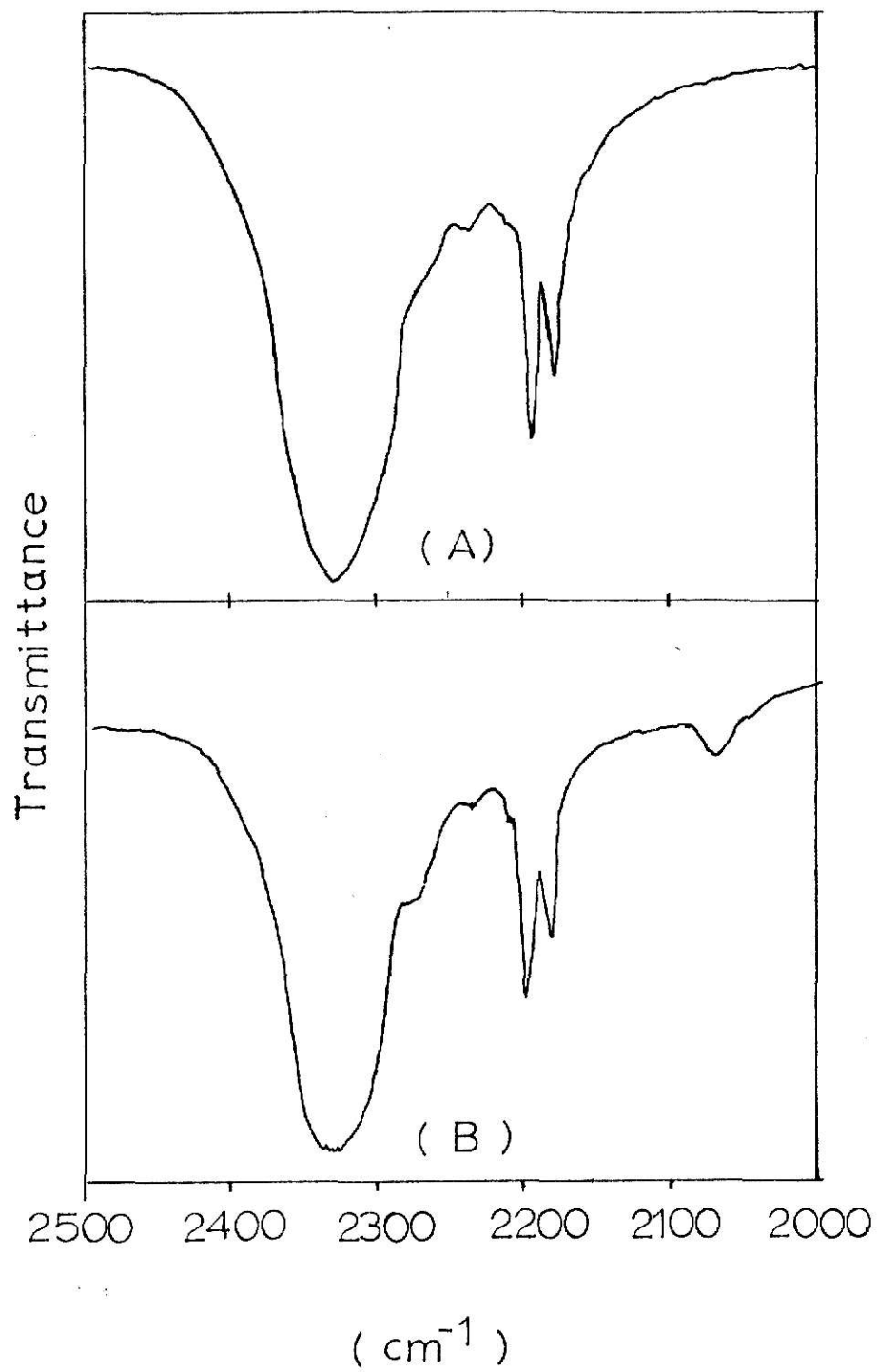


Figure 34

Infrared spectra of $\text{Fe}(\text{phen})_2(\text{NCBH}_3)_2$: (A) before heating and (B) after heating at 170°C under vacuum for 5 days; KBr pellets.



is more tightly bound. The poor resolution in 2070 cm^{-1} region is believed to be due to the overlap of the doublet of $\text{Fephen}_2(\text{CN})_2$ with the terminal CN stretching band of $\text{Fephen}_2(\text{CN})(\text{CNBH}_3)$.

Of great importance is the weak, broad band just below 2200 cm^{-1} in Figures 32,33. This weak absorption is in the region found for the CN stretching frequencies in $\text{Fephen}_2(\text{NCBH}_3)_2$ and appears to have gained intensity in Figure 33. We feel this band is due to $\text{Fephen}_2(\text{NCBH}_3)_2$; the implication of this is that $\text{Fephen}_2(\text{NCBH}_3)_2$ is thermodynamically more stable than $\text{Fephen}_2(\text{CNBH}_3)_2$.

Similar treatment of the Fe-NC-BH_3 isomer 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- $\text{Fephen}_2(\text{CN})_2$ (Figure 34). 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 $\text{Fephen}_2(\text{CN})(\text{NCBH}_3)$. The broadness of the low frequency band as well as the peak: valley ratio of the CN doublet at high frequency are not inconsistent with the presence of a small amount of terminal and bridged CN. Loss of BH_3 from the Fe-CN-BH_3 isomer is much less pronounced, at this temperature, than from the Fe-NC-BH_3 isomer. Loss of BH_3 from Fe-NC-BH_3 also seems to result in linkage isomerization of $\text{Fephen}_2(\text{NC})_2 \rightarrow \text{Fephen}_2(\text{CN})_2$. Finally, the fact that heating $\text{Fephen}_2(\text{NCBH}_3)_2$ does not lead to the formation of $\text{Fephen}_2(\text{CNBH}_3)_2$

is at least consistent with the idea that $\text{Fephen}_2(\text{NCBH}_3)_2$ is thermodynamically more stable.

Thermolyses of $\text{Fephen}_2(\text{NCS})_2$ and $\text{Fephen}_2(\text{CN})_2$ resulted in no change of the ir spectra.

These studies lead us to conclude that there is no facile means of interconversion of the isomers, such as a simple "flip" within the Fe and B "cage". The behavior of the Fe-NC-BH_3 isomer stands in marked contrast with that of $(\text{H}_3\text{N})_5\text{Ru-(NCH)}^{+2}$ which isomerizes by an unknown mechanism to $(\text{H}_3\text{N})_5\text{Ru-(CNH)}^{+2}$ in the solid state with subsequent polymerization of the latter to $[\text{Ru}(\text{NH}_3)_4(\text{CN})_x]^{x-}$.⁴⁸ Other such isomerization have been reported for cyanide bridging metal ions.⁴⁹

VI. Further Development

There are still questions about the isomeric pair of $\text{Fephen}_2(\text{NCBH}_3)_2$ and $\text{Fephen}_2(\text{CNBH}_3)_2$ which have not been answered at this point. We don't know which isomer is thermodynamically more stable. Perhaps more gentle heating in an environment of BH_3 will reveal the answer. Neither do we know whether it is possible to thermally induce a transition of $\text{Fephen}_2(\text{NCBH}_3)_2$ from the spin-triplet state to the quintet state or to the singlet state. If these transitions are possible, will they be abrupt as with the complex $\text{Fephen}_2(\text{NCS})_2$? Studies of the temperature dependences of the magnetic susceptibility and Mössbauer spectrum of $\text{Fephen}_2(\text{NCBH}_3)_2$ are definitely called for and may give a better understanding of the behavior of $\text{Fephen}_2(\text{NCS})_2$ in the vicinity of 170°K. In addition, more thorough study of the $\text{Fephen}_2(\text{NCBH}_3)_2$ electronic spectrum in the red and nearinfrared region is in order, for the studies reported here failed to locate d-d transitions.

A suitable solvent or mixed solvent is needed to allow the characterization of the complex $\text{Fephen}_2(\text{NCBH}_3)_2$ by n.m.r. and e.s.r. spectroscopies. Dissolution of the complex may also be approached by using appropriately substituted phen ligands. The synthesis of soluble forms of $\text{Fephen}_2(\text{NCBR}_3)_2$ and $\text{Fephen}_2(\text{CNBR}_3)_2$, where $\text{R} = \text{H}, \text{Ph}, \text{Me}, \text{etc.}$, is also important to our long term goal of synthesizing $\text{Fephen}_2(\text{NC})_2$ and of finding a method to form CNBH_3^- in good yield.

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VII. Appendix A

Operation of the Mössbauer Spectrometer

The Mössbauer spectrometer used in this study was locally constructed in the Chemistry and Physics Departments of Kansas State University. It consists of four main parts: (1) the driving system, (2) the detecting system and (4) the output devices. The Figure 35 illustrates the arrangement of these devices.

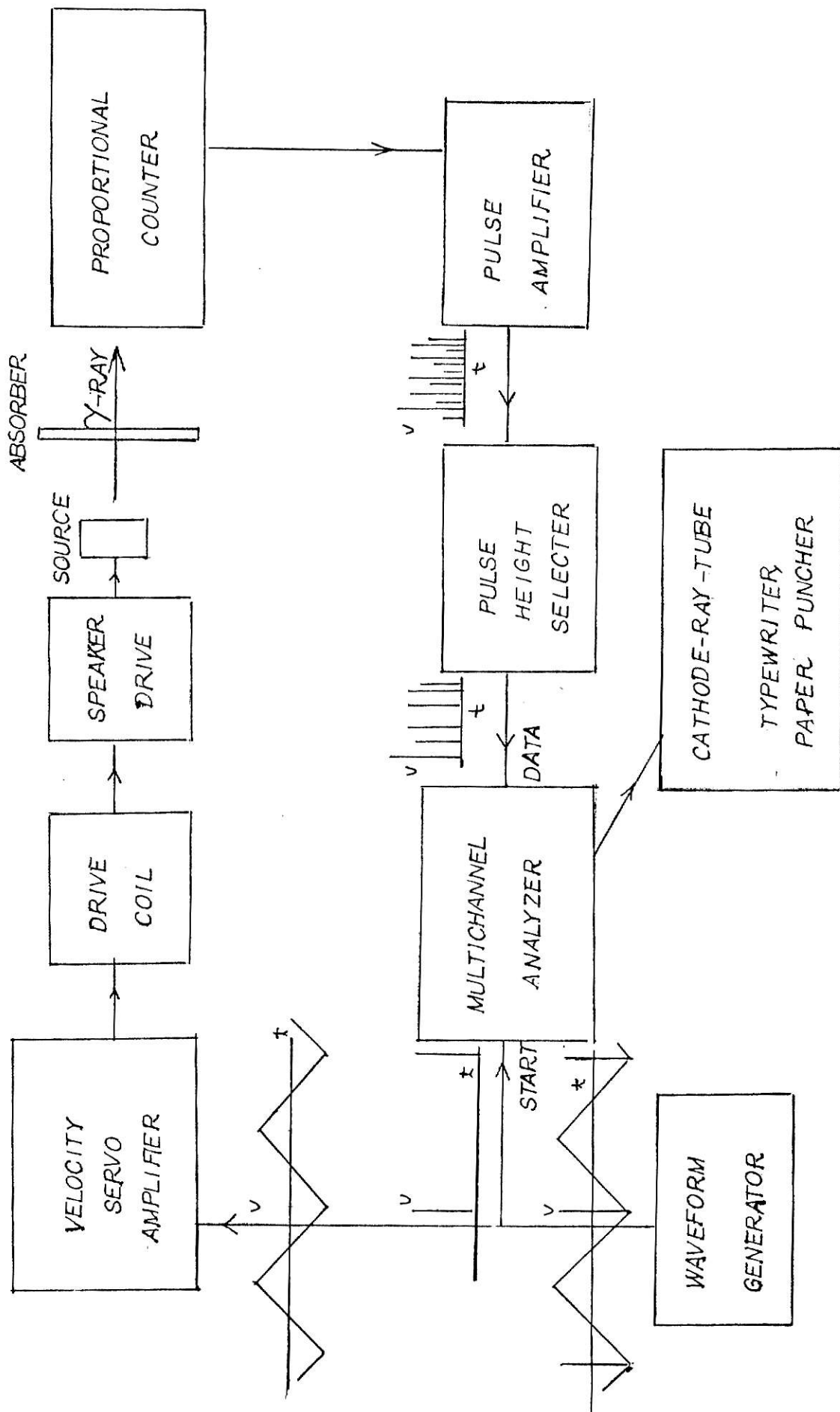
1) The Driving System

A standard speaker driving system is used. The symmetrical, double-ramp driver signal causes the spectrum to be scanned with constant acceleration in alternately opposite directions. This produces a double (mirror-image) spectrum which can be folded to give an additional check on the drive system linearity.

The triangular waveform generated by a waveform generator provides the source Doppler motion and is controlled by a servo-amplifier. The linearity of the waveform was checked using a monitor scope, which shows the actual velocity waveform from the transducer, before running the spectrum. The monitor scope had as input the output from a magnetic transducer mounted opposite the source on the same driver rod.

Figure 35

Arrangement of the devices for the Mössbauer spectrometer.



2) Source and Absorber

A source of ^{57}Co in Pd with a radioactivity of 10 mCi was purchased from Isotope Products Laboratories. The source is attached to the standard speaker drive which provides the Doppler motion.

Adequate absorber were easily made by sandwiching the polycrystalline sample between layers of 3 M tape. This disk was then held with a suitable holder positioned at the axis of the Doppler motion of the source. The absorber must have a finite thickness for the absorption to be observed, but an increase in absorber thickness will tend to decrease the resolution and the precision with which a single line can be located. In this study about 0.5 gm of complex is needed to prepare a adequate absorber disk.

3) The Detecting System

A gas-filled (Ar-CH_4) proportional counter was used as a detector. Two lead bricks were used to shield the detector from spuriously scattered γ -rays. To lower the radiation background, aluminum foils were inserted behind the absorber to filter the 6.4 K e.v. X-ray emitted from the source as it decays. To remove the pulse generated by the 20 K e.v. γ -ray, a pulseheight selector was used; a "window" was electronically

defined so as to pass only the voltage generated by the 14.4 K e.v. γ -ray of interest and remove all pulses generated by the remaining 20 K e.v. γ -ray and other spurious radiation.

The multichannel analyzer (MCA) is operated in a multiscaling mode. In this mode of operation, a sweep through 1024 channels is initiated by a trigger pulse which is also provided from the waveform generator. This pulse is synchronized with the start of the triangular velocity waveform. The multichannel analyzer starting with channel 1 steps from one channel to the next remaining a fixed time in each channel. All data pulses which are accumulated while the MCA is in a given channel are stored in that channel.

Many pulses are detected and stored during each cycle of motion and successive cycles over a long period of time allow the spectrum to build up as a whole. At velocities where the resonance absorption occurs, the accumulation rate of γ -counts in those channels will be slower.

The MCA also has a Cathode-ray-tube (CRT) display, in which a voltage proportional to the accumulated counts of a channel is used as the vertical deflection and a voltage proportional to the channel address number is used as a horizontal deflection and this gives a continuous visual display of all channels. The operator can inspect the spectrum at any time during the course of a run.

4) Out-put Devices

The data stored in the MCA were transferred to output devices such as a typewriter or paper-punch. The data displayed from these out-put devices were the number of γ -ray counts registered in the corresponding channel of MCA. In the experiment, 1024 channels were used for the entire spectrum (two mirror-image halves). The spectrum was then hand-plotted and the two halves were folded over in order to improve the counting statistics.

5) Velocity Calibration

The velocity scale was calibrated with the spectrum of an enriched ^{57}Fe metal foil. After every few runs, the spectrum of ^{57}Fe (in Fe) vs ^{57}Co (in Pd) was run to check the velocity scale. Such calibrations showed our driving system to be very stable and its reproducibility good. The isomer shifts of the complexes are also measured relative to the centroid of the ^{57}Fe spectrum.

It takes about one day to run a typical spectrum with a natural abundance ^{57}Fe absorber. The statistical behavior of the γ -emission results in a standard deviation of $\sqrt{N}$ for a total number of N registered γ -counts. Usually, the longer

the counting time, the better the definition of the resonance line, within the limit of the long term stability or reproducibility of the apparatus.

Since the γ -photon travelling to the detector at an angle θ to its axis will have a effective Doppler velocity $v \cos \theta$, a large solid angle in the counting geometry will cause a distortion in the shape of the Mössbauer absorption lines. This difficulty was overcome in our study by maintaining an adequate separation (~ 1 foot) between the source and detector.

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BRIDGING CYANIDE IN $\text{Fe}(\text{phen})_2(\text{NCBH}_3)_2$ - A SPIN TRIPLET

BY

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B. S., Fu-Jen University, 1971

AN ABSTRACT OF A MASTER'S THESIS

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1976

Abstract

The synthesis of an unusual 6-coordinated, spin triplet ($S=1$) ferrous complex $\text{Fephen}_2(\text{NCBH}_3)_2$ with cis-geometry is described. This complex is characterized by its magnetic moment and infrared, visible region and Mossbauer spectra. Based on these data and the "angular overlap model" of metal ligand bonding, NCBH_3 is characterized as a ligand possessing moderate σ and π donor nature. Comparison of $\text{Fephen}_2(\text{NCBH}_3)_2$ with the low spin Fephen_3^{+2} and the spin quintet $\text{Fephen}_2(\text{NCS})_2$ facilitates this characterization. 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.

In contrast, $\text{Fephen}_2(\text{CNBH}_3)_2$ displays typical low spin (singlet) properties. The magnetic moment and the Mössbauer and visible region spectra of this complex reveal the good σ donor and good π acceptor nature of CNBH_3 with the former likely weaker than CN but the latter possibly exceeding that of cyanide.

Consideration of the CN stretching frequency data for the isomeric pairs of $\text{Fephen}_2(\text{NCNH}_3)_2$ and $\text{Fephen}_2(\text{CNBH}_3)_2$ and other bridged cyano species raises interesting questions

about the effect of double coordination of cyanide on the CN sigma bonding.

Finally, the thermal stability studies of the Fe-CN-BH₃ and Fe-NC-BH₃ linkages eliminate the possibility of isomerization by a simple CN flip mechanism within the Fe and B cage.