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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

TERESA BYERS

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COMPLEXES IN FROZEN SOLUTION

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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An Electron Paramagnetic Resonance Study of Copper (II) Complexes in Frozen Solution

By

Teresa Byers

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Introduction

Copper (II) beta-diketonates and copper(II) chelates of Schiff bases have been the focus of many investigations by electron paramagnetic resonance. In the frozen solution EPR spectra of these complexes, multiple sets of lines often appear, indicating the presence of multiple species, which may be isomers or adducts with Lewis base solvents or solvent impurities. The ability of such complexes to form adducts in non-aqueous solution has been the subject of several studies by both UV-VIS and EPR spectroscopy.[1,2,3,4] Frozen solution EPR is an especially valuable technique since it is frequently the only means for obtaining full anisotropic information about the solvent adducts of these complexes. Also, even in the rare instances where the adducts prove stable enough to be isolated as single crystals or polycrystalline powders, such a conformation may be a distortion of the actual structure present in solution. Studies in frozen solution are therefore necessary in order to make measurements on these complex adducts in their true state.

The purpose of the study presented here is the investigation of the equilibrium of Cu(II) complexes with Lewis bases by frozen solution EPR spectroscopy. The study is divided into two parts. In chapter one, a qualitative investigation of the frozen solution spectra of several Cu(II) complexes is presented, and the problems involved in the acquisition of useful spectra are discussed. In chapter two, selected Cu(II) complexes from

chapter one are the focus of a quantitative equilibrium study with pyridine, a heterocyclic Lewis base.

Chapter 1. Frozen Solution EPR Spectra of Cu(II) Complexes

A major obstacle in obtaining useful frozen solution EPR spectra of Cu(II) complexes is the selection of an appropriate solvent system, for which there are several limiting factors:

1) The solvent system must form a glass upon freezing for the spectrum to be sharp and well resolved. A good glass is characterized by the absence of local paramagnetic aggregates, which will broaden spectral lines.[5]

2) The solvent system must solubilise the copper complex to an adequate degree for a strong EPR signal to be seen. It is frequently difficult to find a solvent system which will provide the required degree of solubility and at the same time form a good glass upon freezing.

3) The solvent system must not form unexpected adducts with the complex or contain impurities which form unexpected adducts, since this will confuse interpretation of spectra containing multiple sets of lines.

With these limitations in mind, several complexes were examined in various solvent systems to determine which would give sharp, well-resolved spectra containing only one species. These complexes, and the solvents the spectra were obtained in, are listed in Table 1.

TABLE 1.

Complex	[Complex] (mM)	Solvent
$^{63}Cu(dtc)_2$	10	20% $CHCl_3$/80% toluene
$Cu(dtc)_2$	< 1	ethanol
	10	50% $CHCl_3$/50% toluene
	10	ethanolamine
$Cu(salim)_2$	10	dimethylformamide (DMF)
$Cu(mesalim)_2$	10	50% acetone/50% toluene
	10	50% acetonitrile/50% toluene
	10	50% $CHCl_3$/50% toluene
	10	50% DMF/50% toluene
$^{63}Cu(acac_2en)$	10	50% $CHCl_3$/50% toluene
$Cu(benzac)_2$	1	50% pyridine/50% toluene
	10	50% $CHCl_3$/50% toluene
$Cu(acac)_2$	10	50% $CHCl_3$/50% toluene
	1	50% pyridine/50% toluene
		5% hexane/95% toluene

I. Experimental

Preparation of complexes

1. Cu(II) dithiocarbamate: ($Cu(dtc)_2$) was prepared by dissolving stoichiometric amounts of $CuCl_2$ and sodiumdiethyldithiocarbamate in deionized H_2O. Concentrated HCl was added to the aqueous $CuCl_2$ solution to prevent $Cu(OH)_2$ formation. The solutions were combined, and the precipitated product was filtered, washed with H_2O, and dried.

Anal. calc. for $C_{10}H_{20}N_2S_4Cu$: C=33.44%, H=5.48%, N=7.5%, Cu=17.45%

Found: C=32.55%, H=5.48%, N=7.64%,
Cu=18.09%

2. Cu(II) bis-salicylaldimine: $Cu(salim)_2$ was prepared according to a published method.[6]

Anal. calc. for $C_{14}H_{12}O_2N_2Cu$: C=55.24%, H=3.95%, N=9.2%,
Cu=20.9%

Found: C=51.22%, H=3.76%, N=8.21%,
Cu=23.78%

3. Cu(II) bis-(N-methyl salicylaldimine): $Cu(mesalim)_2$ was also prepared according to a published method.[6]

Anal. calc. for $C_{16}H_{16}O_2N_2Cu$: C=57.8%, H=4.85%, N=8.44%,
Cu=19.1%

Found: C=57.57%, H=4.96%, N=8.52%,
Cu=19.17%

4. Bis-acetylacetoneethylenediamine: $Acac_2en$ ligand was prepared by adding a stoichiometric amount of ethylenediamine to 2,4-pentanedione in ethanol. The crude orange product precipitated from solution upon concentration by heating, and was recrystallized twice from CCl_4. The resulting pure product was found to be an off-white color.

Anal. calc. for $C_{12}H_{20}O_2N_2$: C=64.29%, H=8.56%, N=12.5%

Found: C=63.76%, H=8.86%, N=12.47%

Cu(II) bis-acetylacetoneethylenediamine: $Cu(acac_2en)$ was prepared by an adaptation of the method of McCarthy, et. al.[7] An acetone

solution of $acac_2en$ ligand was refluxed for 4 hours with an excess of $Cu(OH)_2$. An excess of $Cu(OH)_2$ was used since separation of $acac_2en$ ligand and $Cu(acac_2en)$ was found to be difficult. The soluble $Cu(acac_2en)$ product was hot filtered to remove the unreacted $Cu(OH)_2$, and the isolated product was recrystallized once from methylcyclohexane to give dark purple, needle-like crystals.

$Cu(OH)_2$ was prepared as follows: cupric oxide was dissolved in deionized H_2O plus concentrated HCl with the addition of heat. The solution was cooled to 0 C, and 6M NaOH was added dropwise until a slightly basic pH was reached. The precipitated $Cu(OH)_2$ was filtered and washed with H_2O.

Anal. calc. for $C_{12}H_{18}O_2N_2Cu$: C=50.4%, H=6.3%, N=9.8%

Found: C=50.27%, H=6.51%, N=9.92%

5.6 6. Cu(II) bis-acetylacetonate and Cu(II) bis-benzoylacetonate: Sufficiently pure $Cu(acac)_2$ and $Cu(benzac)_2$ were available in lab.

II. Spectra

All spectra were recorded on a Varian E-109 X-band spectrometer with a working frequency of about 9.1 GHz. Variable temperature equipment was used to attain a temperature of approximately 110K. The spectra obtained are in Appendix 1.

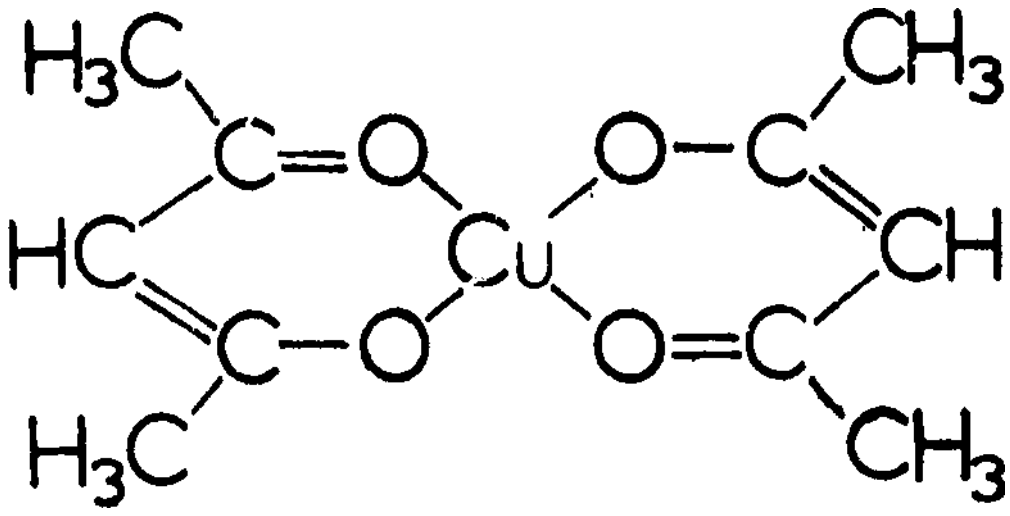
III. Discussion

The spectra obtained are those for which the solvent system appeared to glass well and provide adequate solubility. As can be seen, the frozen spectra are in many cases broad. The sharpest, best resolved spectra are of $Cu(acac)_2$, $Cu(benzac)_2$, $Cu(acac_2en)$, and $Cu(dtc)_2$ in a mixture of chloroform and toluene. These spectra contain one set of lines, indicating the presence of only one species; thus, adduct formation with the chloroform/toluene solvent system does not occur.

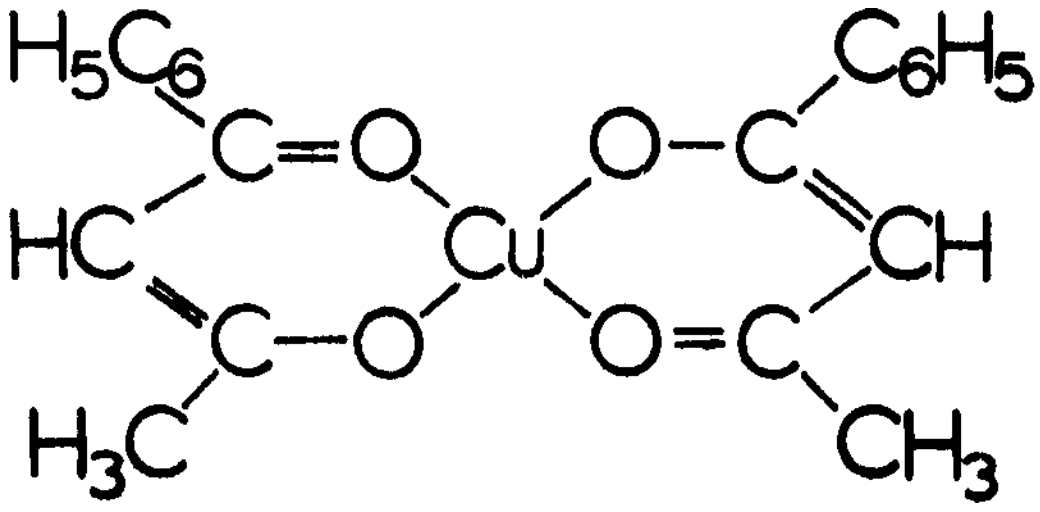
CHAPTER 2. Equilibrium Study of $Cu(acac)_2$, $Cu(benzac)_2$, and $Cu(acac_2en)$

1. Introduction

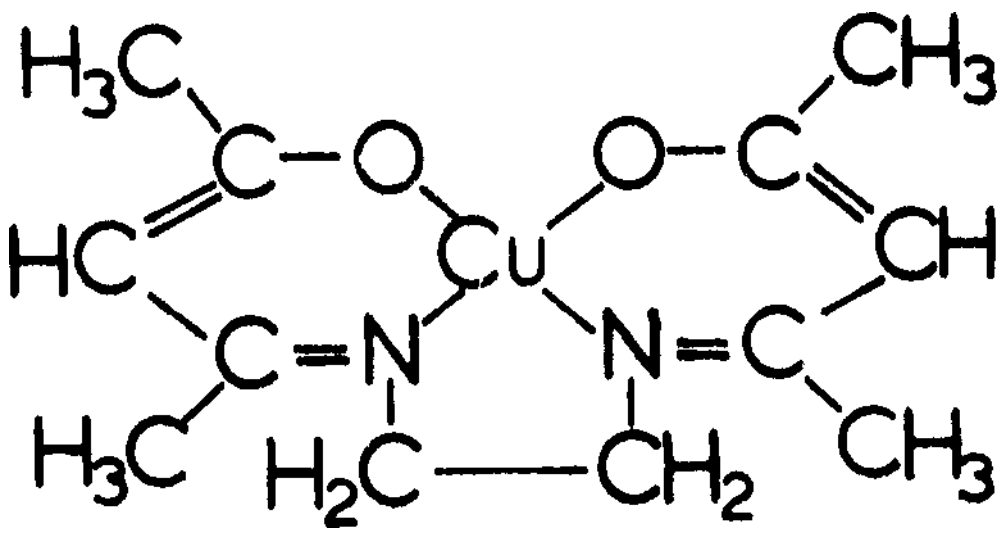
After the initial examination of the frozen solution spectra of the complexes of chapter 1, further study of $Cu(acac)_2$, $Cu(benzac)_2$, and $Cu(acac_2en)$ was decided upon. These three compounds were chosen for several reasons: [1] A convenient solvent system for frozen EPR study was common to all of them, namely a 1:1 mixture of chloroform and toluene. This system formed a good glass and provided adequate solubility. [2] The spectra of these complexes contain only one species, and the presence of multiple sets of lines can be positively attributed to adduct formation with an added base. [3] The three complexes function as Lewis acids and have the ability to bind with pyridine, a heterocyclic Lewis base, to form five coordinated 1:1 adducts[1,8,9]. In addition, $Cu(acac)_2$ and $Cu(benzac)_2$ show the ability to form six coordinated 1:2 adducts at high concentrations of pyridine[9]. The pyridines have been determined to coordinate in the axial positions[10]. [4] The complexes are similar in structure; all are approximately planar, four coordinated cupric chelates. Thus, differences in adduct stability can be predicted by the electron withdrawing and donating effects of the differing ligands on the electron density at the copper center[1,2]. [5] Previous studies of the equilibrium of $Cu(acac)_2$ and $Cu(benzac)_2$ with pyridine in non-aqueous



Cu(acac)$_2$



Cu(benzac)$_2$



Cu(acac$_2$en)

solution at room temperature have been done by both UV-VIS and EPR spectroscopy[1,2,10], and the results of these studies can be used as an indication of the accuracy of the results obtained by frozen solution EPR.

I. Experimental

Preparation of Samples

Ten and twenty millimolar stock solutions of $Cu(acac)_2$ and $Cu(acac_2en)$ and ten millimolar stock solutions of $Cu(benzac)_2$ were prepared by addition of the appropriate amount of complex to a 1:1 mixture of chloroform and toluene. Chloroform was distilled from phosphorus pentoxide to remove the ethanol stabilizer, which was found to form a 1:1 adduct with the complexes. Pyridine and/or solvent was added to aliquots of stock solution to produce samples of the following concentrations:

TABLE 2: $Cu(acac)_2$ + pyridine

Sample	$[Cu(acac)_2]_i$(mM)	$[PYD]_i$
1	10	3 mM
2	10	5 mM
3	10	8 mM
4	10	10 mM
5	10	99 mM
6	8	2.5 M
7	6	4.9 M
8	5	6.2 M
9	4	7.4 M
10	3	8.7 M
11	5	6.2 M
12	5	7.4 M
13	5	9.3 M

TABLE 3: $Cu(benzac)_2$ + pyridine

Sample	$[Cu(benzac)_2]_i$ (mM)	$[PYD]_i$
1	10	3 mM
2	10	5 mM
3	10	8 mM
4	10	10 mM
5	10	99 mM
6	8	2.5 M
7	6	4.9 M
8	5	6.2 M
9	4	7.4 M

TABLE 4: $Cu(acac_2en)$ + pyridine

Sample	$[Cu(acac_2en)]_i$ (mM)	$[PYD]_i$
1	10	10 mM
2	10	99 mM
3	9.3	93 mM
4	5	7.4 M
5	5	9.3 M

II. Data

$Cu(acac)_2$, $Cu(benzac)_2$, and $Cu(acac_2en)$ data was collected using a Bruker ER 220D X-band spectrometer interfaced to either a Zenith or IBM personal computer for data acquisition and storage. Because of almost complete overlap between the $Cu(acac_2en)$ and $Cu(acac_2enPYD)$ spectral features, additional $Cu(acac_2en)$ data was collected using a Varian E-115 Q-band spectrometer interfaced to a Zenith PC. In both cases, variable temperature equipment was used to attain a temperature of approximately 110K. Example spectra containing 1:1 and 1:2 adducts for $Cu(acac)_2$ and $Cu(benzac)_2$ are in appendix 2. $Cu(acac_2en)$ spectra are in

appendix 3.

III. Data Analysis

A. K_1

The equilibrium expression for the formation of the 1:1 and 1:2 adducts is

$$CuL_2 + PYD \rightleftharpoons CuL_2PYD + PYD \rightleftharpoons CuL_2PYD_2$$

Therefore, $K_1=[CuL_2PYD]_f/([CuL_2]_f[PYD]_f)$. If x moles of CuL_2PYD are formed, then $K_1= x/(([CuL_2]_i-x)([PYD]_i-x))$. The quantity $[CuL_2PYD]_f/[CuL_2]_f$ can be determined from the EPR spectrum, since the area under the absorption spectrum (or the double integral of the derivative spectrum) is proportional to the concentration of species giving rise to the signal. In order to determine this ratio, spectra of pure CuL_2 and pure CuL_2PYD were first normalized to the same total double integral so as to represent the same concentration of species. This was done by scaling the larger data set using the program SCAL2 (Appendix 4). The spectra were then scaled again to match the corresponding peaks of an experimental spectrum containing both species, and added together. The scaling factors were used to determine $[CuL_2PYD]_f/[CuL_2]_f$ (=scaling factor for CuL_2PYD spectrum/scaling factor for CuL_2 spectrum). Thus the value of x could be solved for and K_1 determined.

All data manipulation was done on an IBM PC using the program DATAPG.[9] DATAPG is capable of comparing experimental and

calculated EPR spectra and performing various manipulations, including spectral addition and subtraction, single and double integration, and horizontal and vertical expansion.

B. K_2

The expression for K_2 is

$$K_2=[CuL_2PYD_2]_f/([CuL_2PYD]_f[PYD]_f)$$
$$= Y/\{([CuL_2]_i-Y)([PYD]_i-[CuL_2]_i-Y)\}$$
$$=Y/\{([CuL_2]_i-Y)([PYD]_i-Y)\} \quad (\text{since } [PYD]_i>>[CuL_2])$$

The ratio $[CuL_2PYD_2]_f/[CuL_2PYD]_f$ could not be determined by the method of spectral addition, as was done for $[CuL_2PYD]/[CuL_2]$ discussed in the previous section. At the concentrations of pyridine required to see a signal due to the 1:2 adduct, significant shifts in the spectral parameters with change in concentration of pyridine was observed. Consequently, it proved impossible to obtain a spectrum of pure 1:2 adduct by subtraction of a pure 1:1 spectrum from one containing both adducts, and to re-add the pure species spectra to reproduce the experimental spectra. Instead, the ratio of the adducts was determined by single integration of the $m_I=+1/2$ and $m_I=-1/2$ parallel features of the spectrum using DATAPG.

IV. Results

A. K_1

1) $Cu(acac)_2$ and $Cu(benzac)_2$:

For all $Cu(acac)_2$ and $Cu(benzac)_2$ samples, the ratio of 1:1 adduct to complex were such that all of the added pyridine was found to be coordinated. Thus, the equilibrium lies essentially to the right and the equilibrium constant is immeasurably large. Appendix 5 contains a comparison of the experimental and added spectra, and the ratios of CuL_2PYD to CuL_2 used to produce the added spectra.

2) $Cu(acac_2en)$:

The Q-band spectra obtained are noisy and contain broad, unresolved structure. Because of this, it was not attempted to obtain the spectra necessary to complete the equilibrium analysis. Comparison of the X-band spectra of $Cu(acac_2en)$ to those for $Cu(acac)_2$ and $Cu(benzac)_2$ of the same initial concentrations of complex and pyridine qualitatively shows $Cu(acac_2en)$ to coordinate less strongly to pyridine than $Cu(acac)_2$ and $Cu(benzac)_2$.

B. K_2

From section IIB.,

$$K_2 = Y/(([CuL_2]-Y)([PYD]_i-Y))$$

$$= \{[CuL_2PYD_2]/[CuL_2PYD]\}/([PYD]_i-Y)$$

$$=\{[CuL_2PYD_2]/[CuL_2PYD]\}/[PYD]_i \quad (\text{Since } [PYD]_i >> Y).$$

TABLE 5: K_2

	$[CuL_2PYD_2]/[CuL_2PYD]$		K_2 (M^{-1})	
Sample	$m_I=+1/2$	$m_I=-1/2$	$m_I=+1/2$	$m_I=-1/2$
L=acac				
8	0.243	0.240	0.04	0.04
9A	0.488	0.453	0.07	0.06
9B	0.779	0.778	0.09	0.09
10	0.438	0.466	0.06	0.06
11	0.206	0.263	0.03	0.04
12	0.408	0.418	0.05	0.06
13	0.858	0.465	0.09	0.09
L=benzac				
7	0.602	0.616	0.12	0.13
8	1.02	0.954	0.17	0.15
9	1.46	1.34	0.20	0.18

TABLE 6: K_2 (M^{-1})(avg.)

	K_2 ($m_I=+1/2$)	K_2 ($m_I=-1/2$)	K_2 (avg.)
$Cu(acac)_2$	0.06	0.06	0.06
$Cu(benzac)_2$	0.16	0.15	0.16

V. Discussion

A: K_1

Analysis of the equilibrium data collected at 110K for $Cu(acac)_2$ and $Cu(benzac)_2$ resulted in an immeasurably large equilibrium constant with pyridine. Literature values for similar systems at room temperature have reported the following:

Complex	Solvent	Method	Temp.	K_1	Ref.
$Cu(acac)_2$	$CHCl_3$	UV-VIS	298K	2.0 $mole^{-1}$	1
$Cu(acac)_2$	toluene	EPR	298K	5.8 M^{-1}	3
$Cu(benzac)_2$	$CHCl_3$	UV-VIS	293K	2.8 $mole^{-1}$	1

Thus it appears that the equilibrium is shifting to the right with decrease in temperature. This is supported by a thermodynamic study of $Cu(acac)_2$ and related Cu(II) chelates with pyridine in 40% chloroform/60% toluene by Marov, et. al.[4]. The thermodynamic parameters ΔH and ΔS were found to be -5.4 kcal/mole and -14.5 cal/mole, respectively. Consideration of the thermodynamic relation $-RTlnK = \Delta H - T\Delta S$ using these values shows that at low temperatures K_1 becomes very large.

In attaining the low temperatures necessary for frozen solution EPR study, the samples were flash frozen in liquid nitrogen. At the onset of this study it was assumed that the equilibrium would not be largely affected in the finite amount of time required for the solution to freeze. This assumption was not valid, as it appears that the kinetics of the coordination is fast enough to drastically affect the equilibrium while the solution is freezing.

B. K_2

In the calculation of K_2, it was assumed that the height of the $m_I=1/2$ and $m_I=-1/2$ parallel absorption spectra features were proportional to the concentration of species. Since the concentration of species is proportional to the total area under

the absorption curve, this assumption is not necessarily valid.

However, there is some evidence in support of this assumption. In the previously cited thermodynamic study by Marov, et.al.[4], it was also assumed that the area under a single parallel region feature is proportional to species concentration. This assumption was checked by measuring the total area under the absorption spectra for each species. They found their values of $[CuL_2PYD]/[CuL_2]$ determined by the two methods to agree within 20%. The $Cu(acac)_2$ and $Cu(benzac)_2$ K_1 data in this study was tested in a similar fashion. The single integration method described in section III was used to determine $[CuL_2PYD]/[CuL_2]$ for several samples. Listed below is a comparison of $[CuL_2PYD]/[CuL_2]$ found by single integration of individual features, and the ratio as predicted from the spectral addition method result of very large K_1:

TABLE 7: $[CuL_2PYD]/[CuL_2]$

	Sample*	Spectral Addition	Single Integration
L=acac	1	.4	.3
	2	1.0	.9
	3	4.0	4.0
L=benzac	1	.4	.3
	2	1.0	.9
	3	4.0	2.8

It is difficult to assess whether the discrepancy between the two methods is due to a falseness of the assumption, or experimental and/or data analysis error. Sources of experimental error include errors in the weighing, pipeting and syringing involved

in sample preparation. An effort was made to eliminate these by using many concentrations of pyridine and multiple stock solutions. As for data analysis errors, there is some question as to the accuracy of the numbers obtained for the height of the absorption curve due to overlap between the CuL_2 and CuL_2PYD features and sloping baselines.

Caution must be exercised in the interpretation of the numbers for K_2 for $Cu(acac)_2$ and $Cu(benzac)_2$. While the samples used in the analysis were run at approximately 110K, it is unclear as to what temperature the equilibrium constants are actually a measure for. If it is reasonable that the equilibrium rearrangement stops or is significantly slowed once the solution is frozen, then the K_2 measured could be at approximately the freezing point of the system.

C. Trend in equilibrium constants

As mentioned in the introduction to this chapter, differences in the adduct stability for the three complexes can be understood by the differences in the electron density at the copper center. The presence of electron withdrawing groups on the ligand will increase the strength of the complex as a Lewis acid, and result in more stable adducts[1,2]. Consider $Cu(acac)_2$ as the reference compound (see page 9). The electron withdrawing phenyl rings on $Cu(benzac)_2$ should increase its strength as a Lewis acid relative to $Cu(acac)_2$. In $Cu(acac_2en)$, the copper is coordinated through two nitrogens and two oxygens, as opposed to

the four oxygens in $Cu(acac)_2$. Because nitrogen is less electronegative than oxygen, $Cu(acac_2en)$ should exhibit decreased strength as a Lewis acid relative to $Cu(acac)_2$. Thus, the expected trend in adduct stability is $Cu(benzac)_2$ > $Cu(acac)_2$ > $Cu(acac_2en)$.

The results of this study support the expected trend. Comparison of K_2 for $Cu(acac)_2$ and $Cu(benzac)_2$ shows $Cu(benzac)_2$ > $Cu(acac)_2$ As discussed in the results, qualitative consideration of the $Cu(acac_2en)$ data shows that the 1:1 adduct is coordinated less strongly than for $Cu(acac)_2$ and $Cu(benzac)_2$.

VI. Conclusion

In summary, the following information has been found from the equilibrium study of $Cu(acac)_2$, $Cu(benzac)_2$, and $Cu(acac_2en)$ with pyridine by frozen solution EPR spectroscopy at 110K:

1) The equilibrium constants for the formation of the 1:1 adducts of $Cu(acac)_2$ and $Cu(benzac)_2$ with pyridine in 50% toluene/50% chloroform have been determined to be immeasurably large.

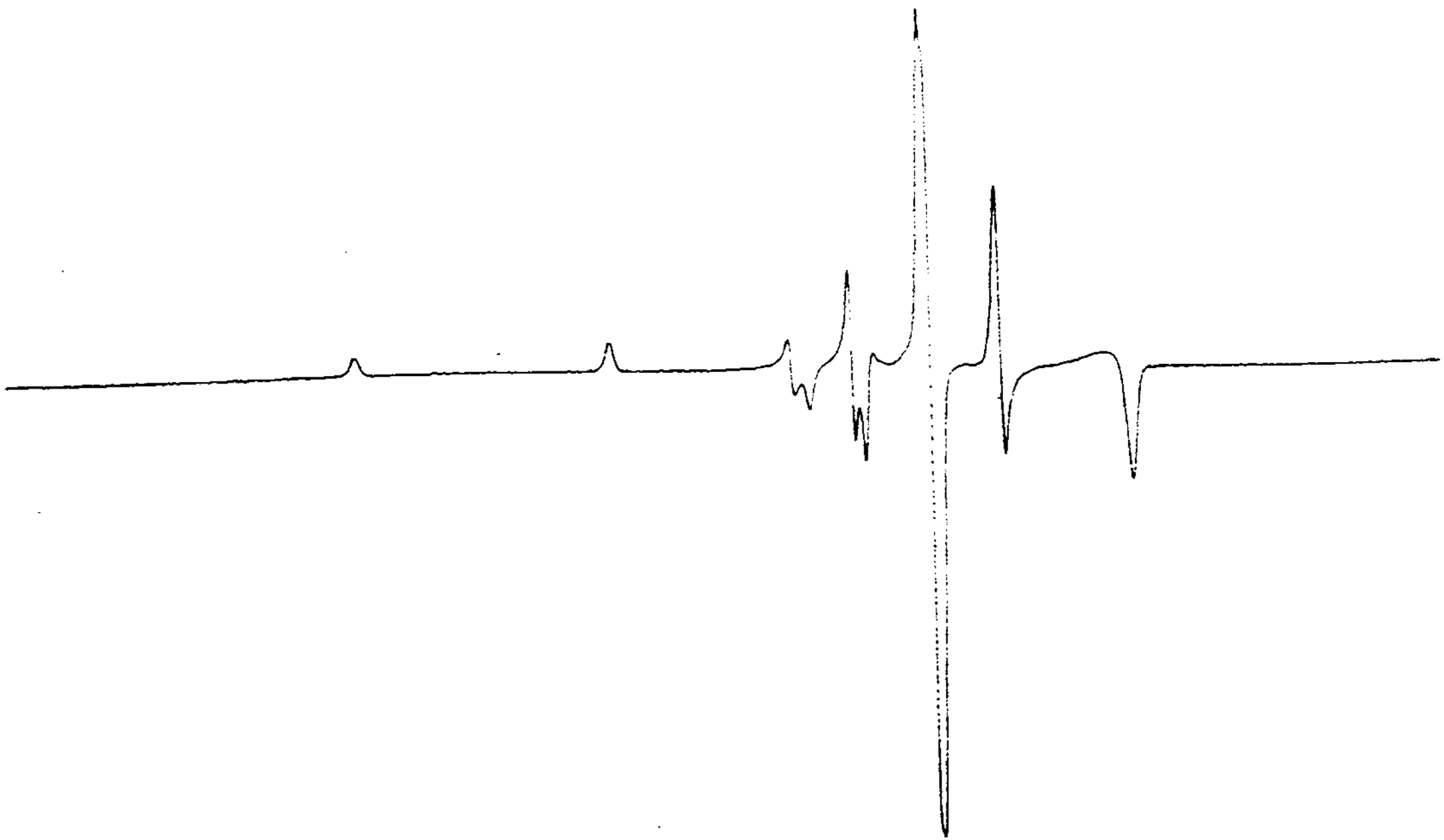
2) The equilibrium constants for the 1:2 adducts of $Cu(acac)_2$ and $Cu(benzac)_2$ with pyridine are finite and have been determined.

3) Adduct stability was found to follow the expected rend, $Cu(benzac)_2PYD$ > $Cu(acac)_2PYD$ > $Cu(acac_2en)PYD$. Thus, the relative adduct stability can be predicted by consideration of the electron withdrawing or donating effect of the ligand.

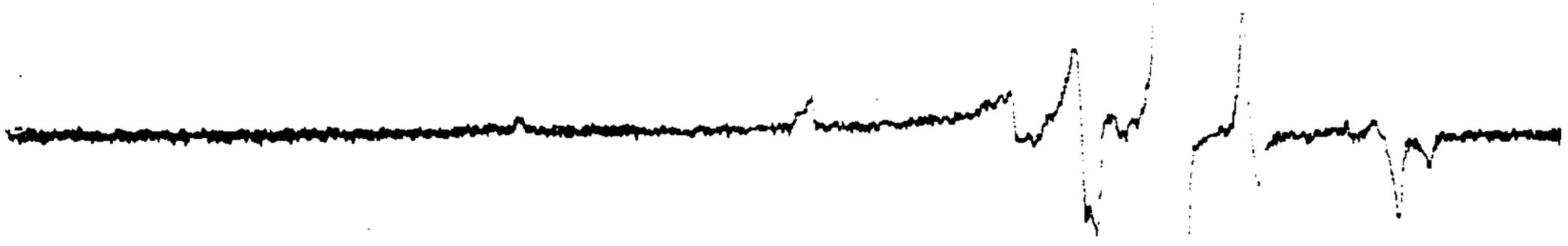
4) The kinetics of the adduct formation for $Cu(acac)_2$ and $Cu(benzac)_2$ was found to be fast enough to drastically effect the equilibrium while the samples were being frozen for study. Thus, frozen solution EPR is not the method of choice for a room temperature equilibrium study of these systems.

5) There is considerable question as to what temperature the K_2 values obtained are a measure for; it is conjectured that they are a measure for a temperature at approximately the freezing point of the solvent system. Further experiments might be done around this temperature and compared to the results obtained here.

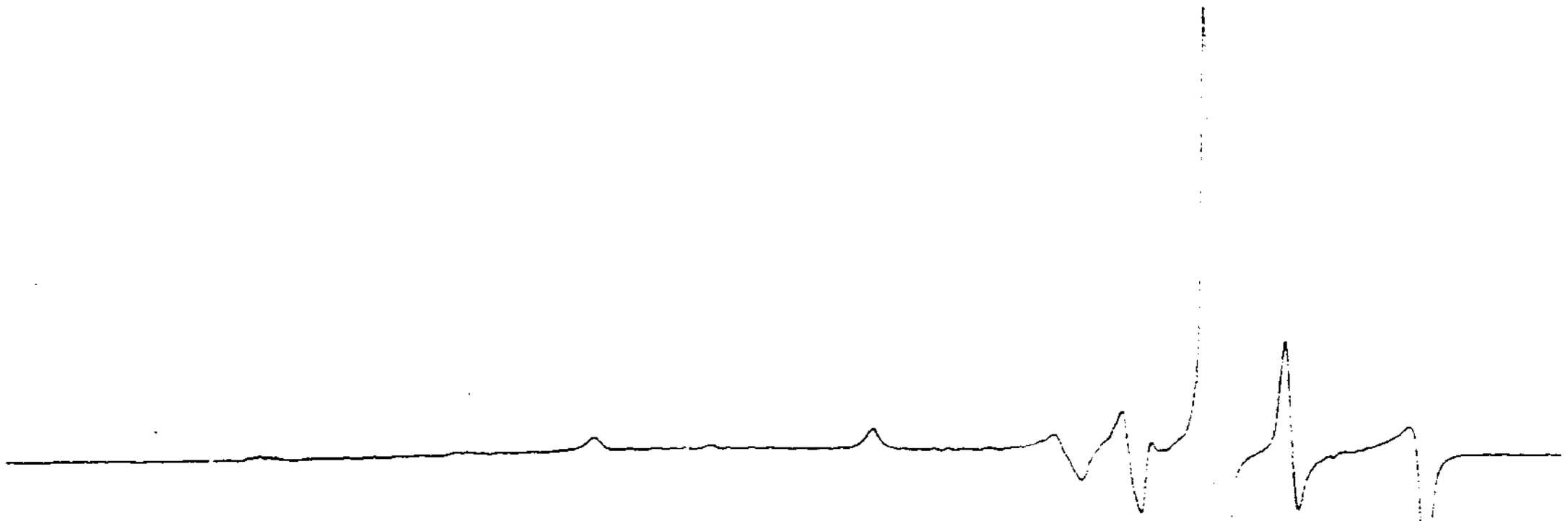
Appendix 1. Spectra From Table 1, Chapter 1.



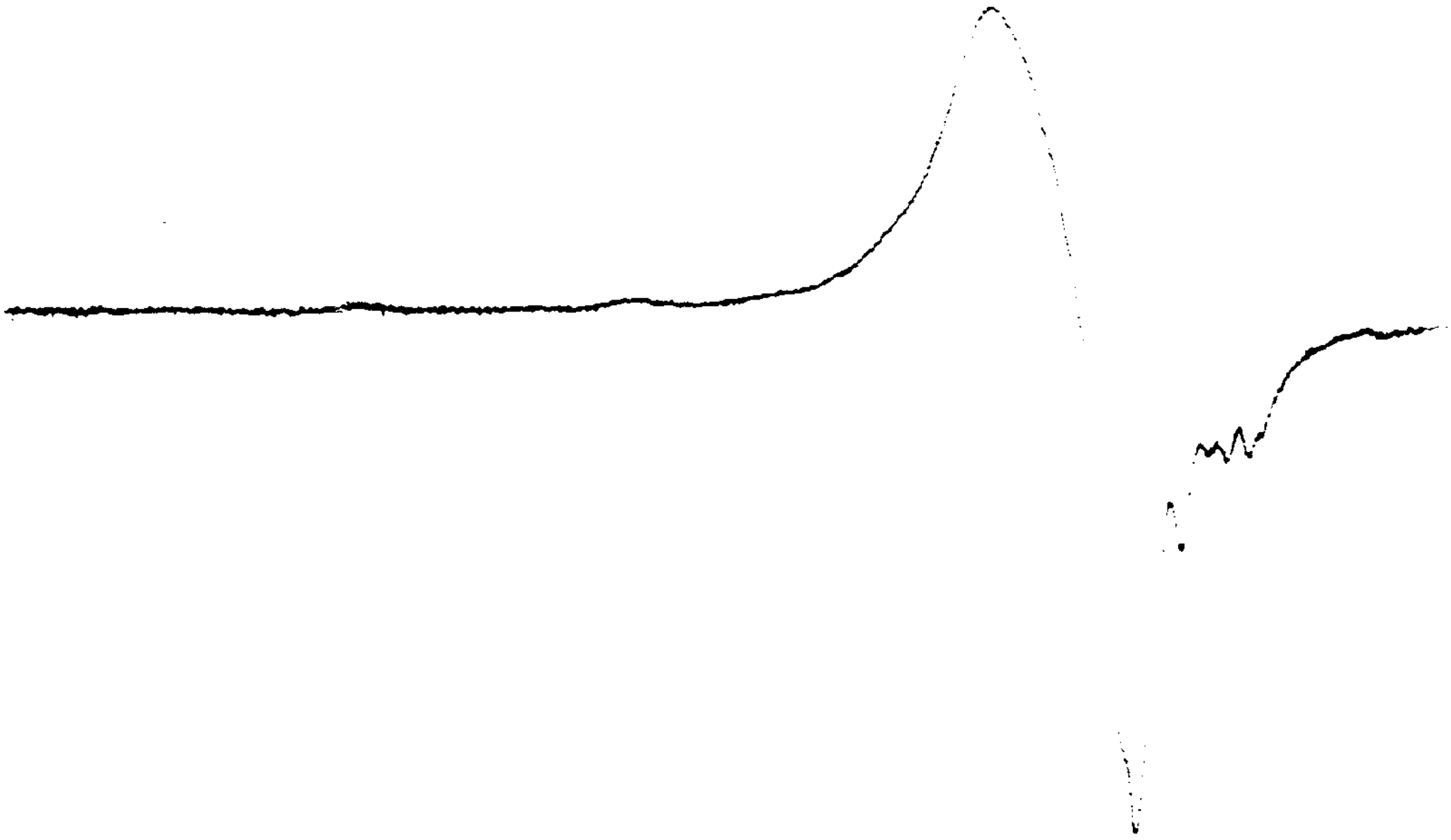
$^{63}Cu(dtc)_2$ in 20% $CHCl_3$/80% toluene



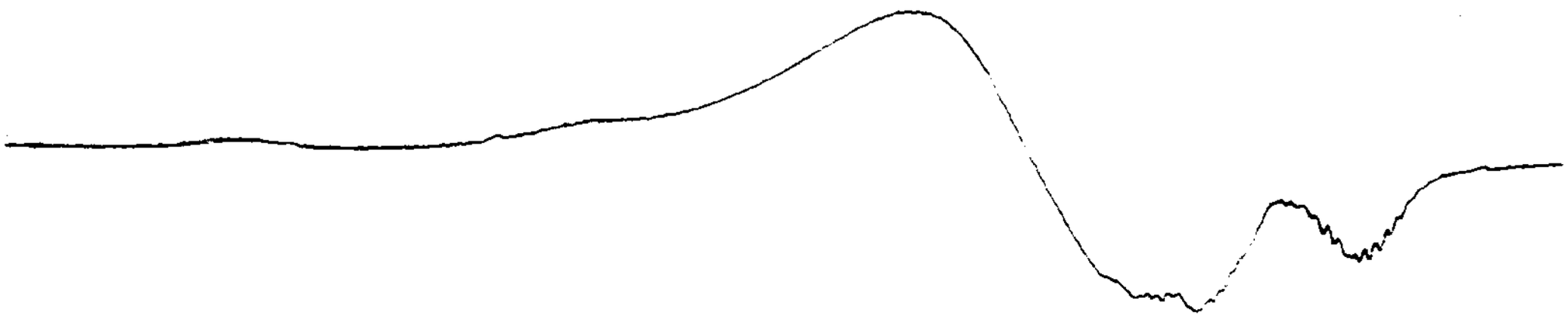
$Cu(dtc)_2$ in ethanol



$Cu(dtc)_2$ in 50% $CHCl_3$/50% toluene



$Cu(dtc)_2$ in ethanolamine



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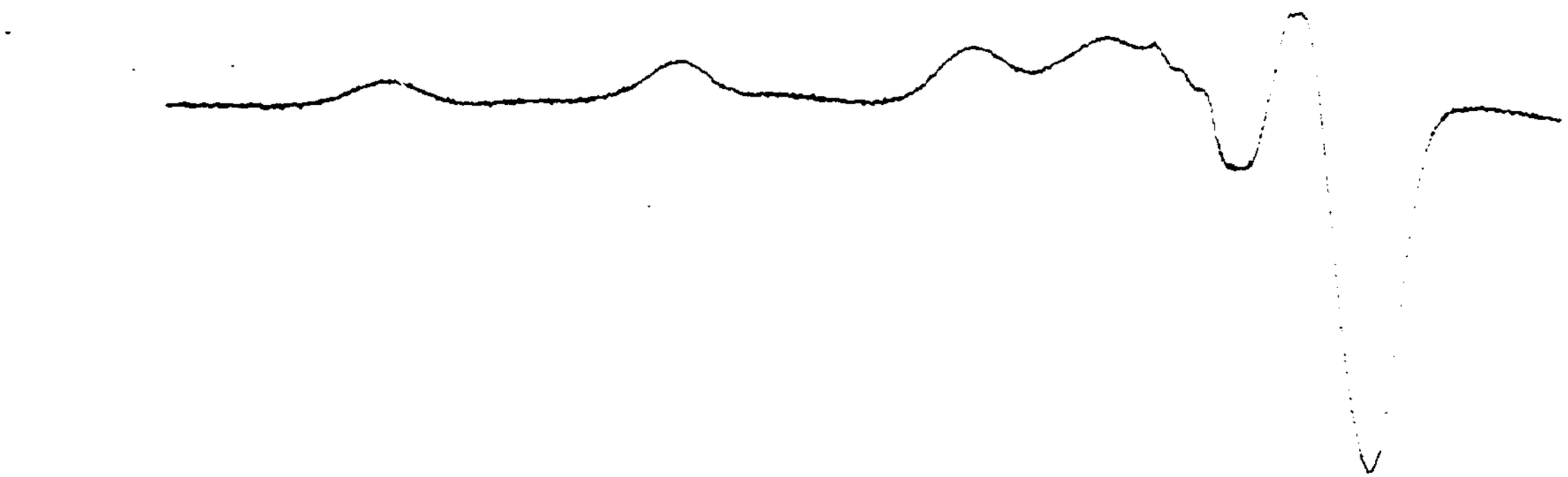
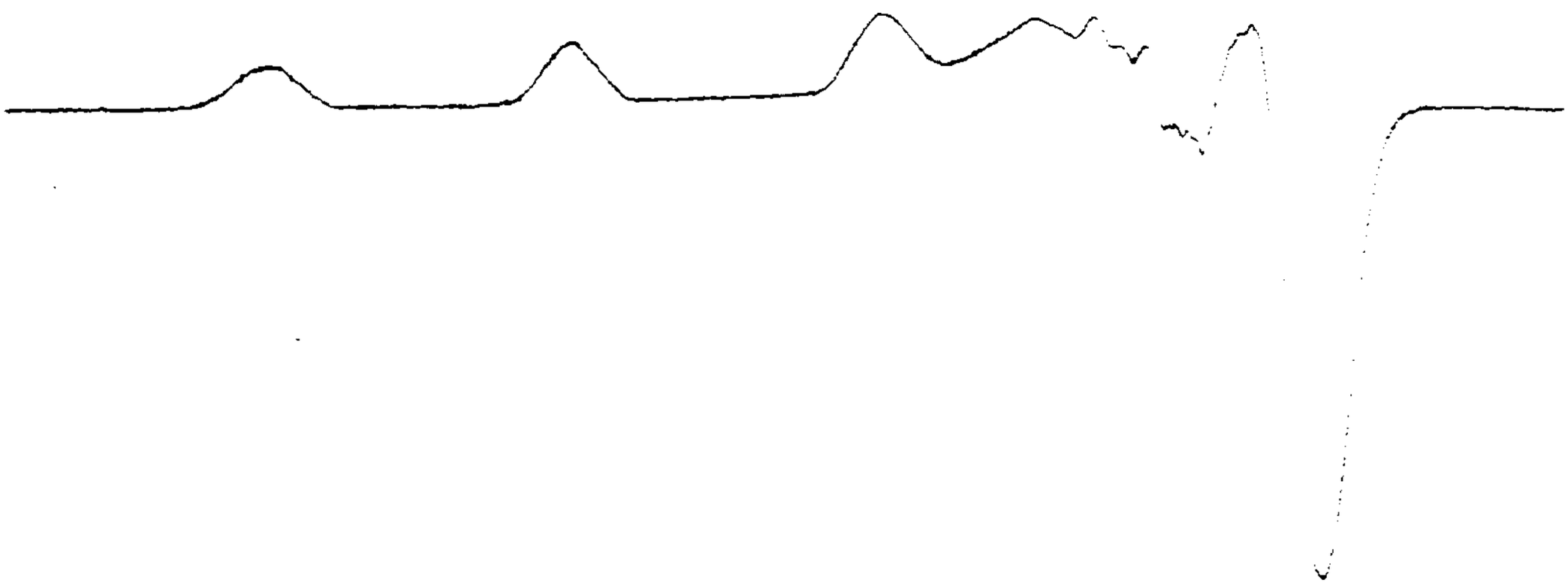
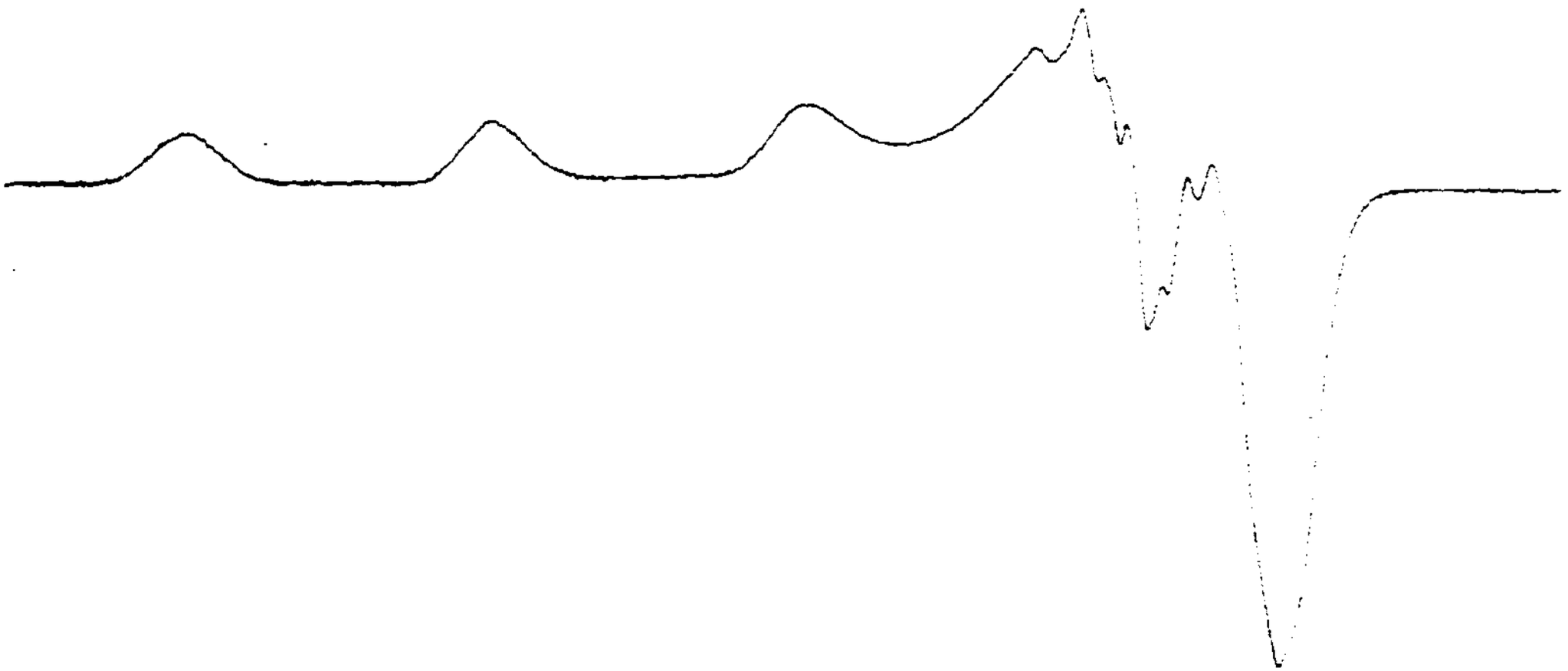


$Cu(mesalim)_2$ in 50% acetone/50% toluene

$Cu(mesalim)_2$ in 50% acetonitrile/50% toluene

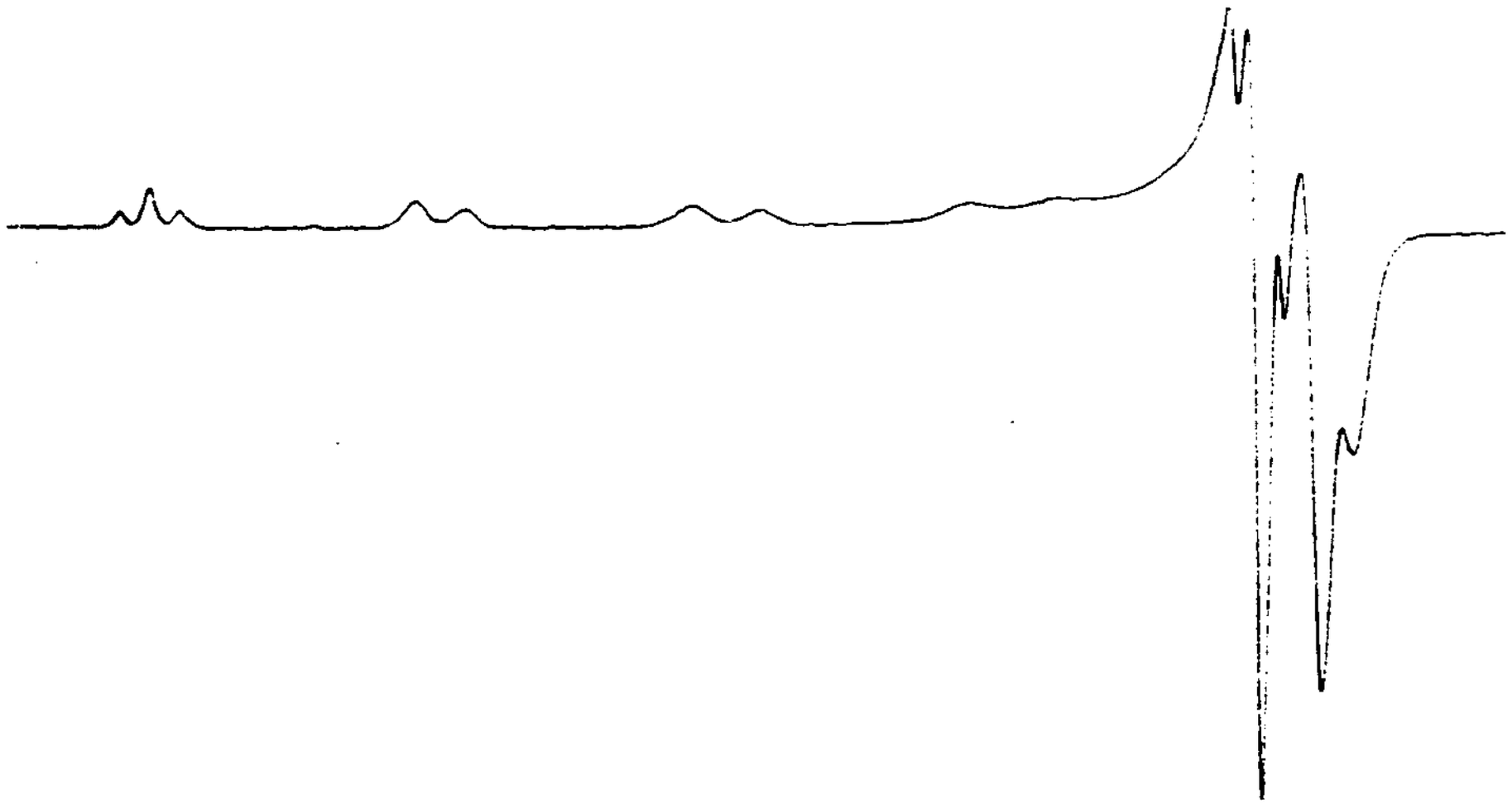


Cu(mesalim)$_2$ in 50% $CHCl_3$/50% toluene

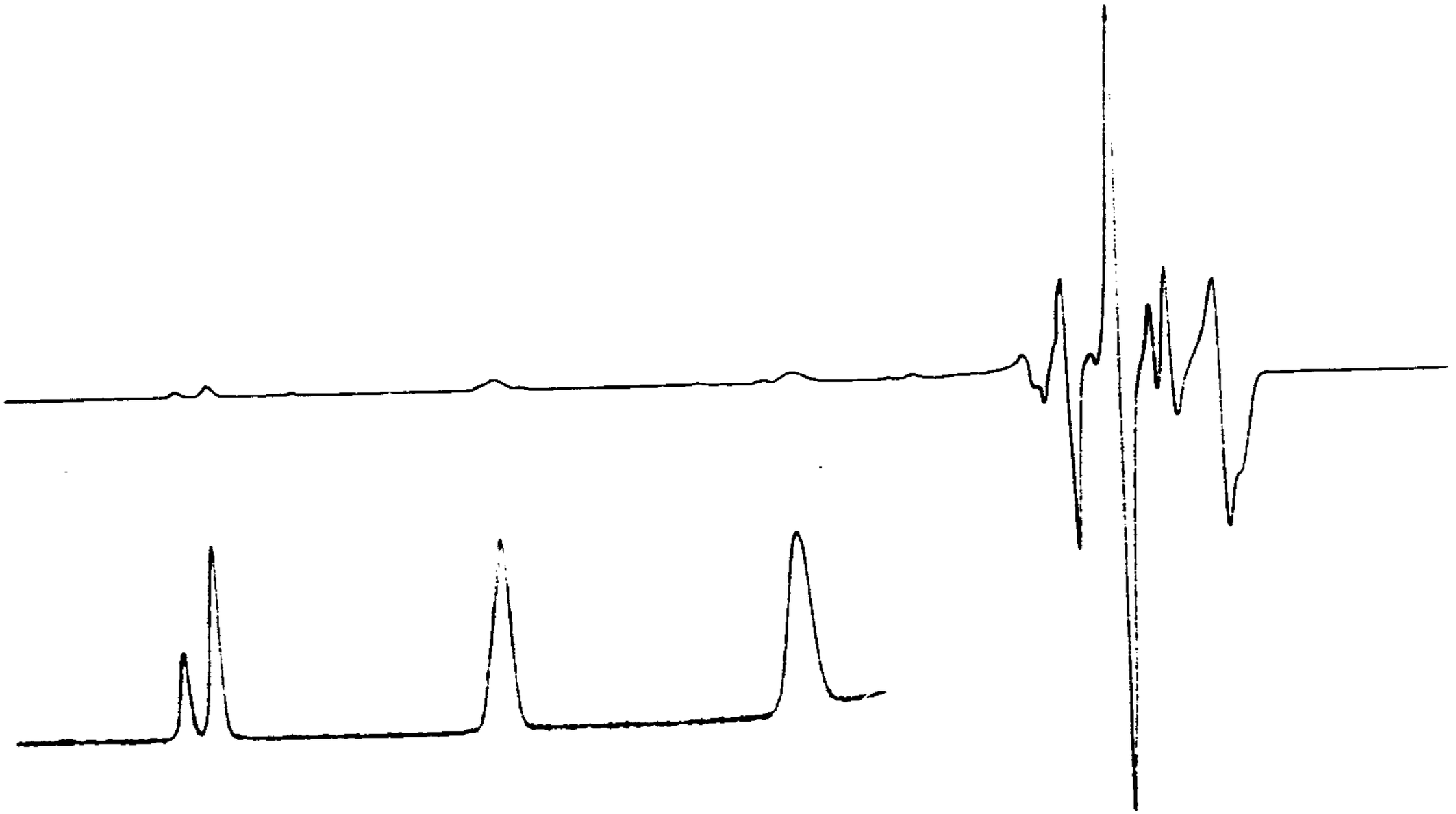


$Cu(mesalim)_2$ in 50% DMF/50% toluene

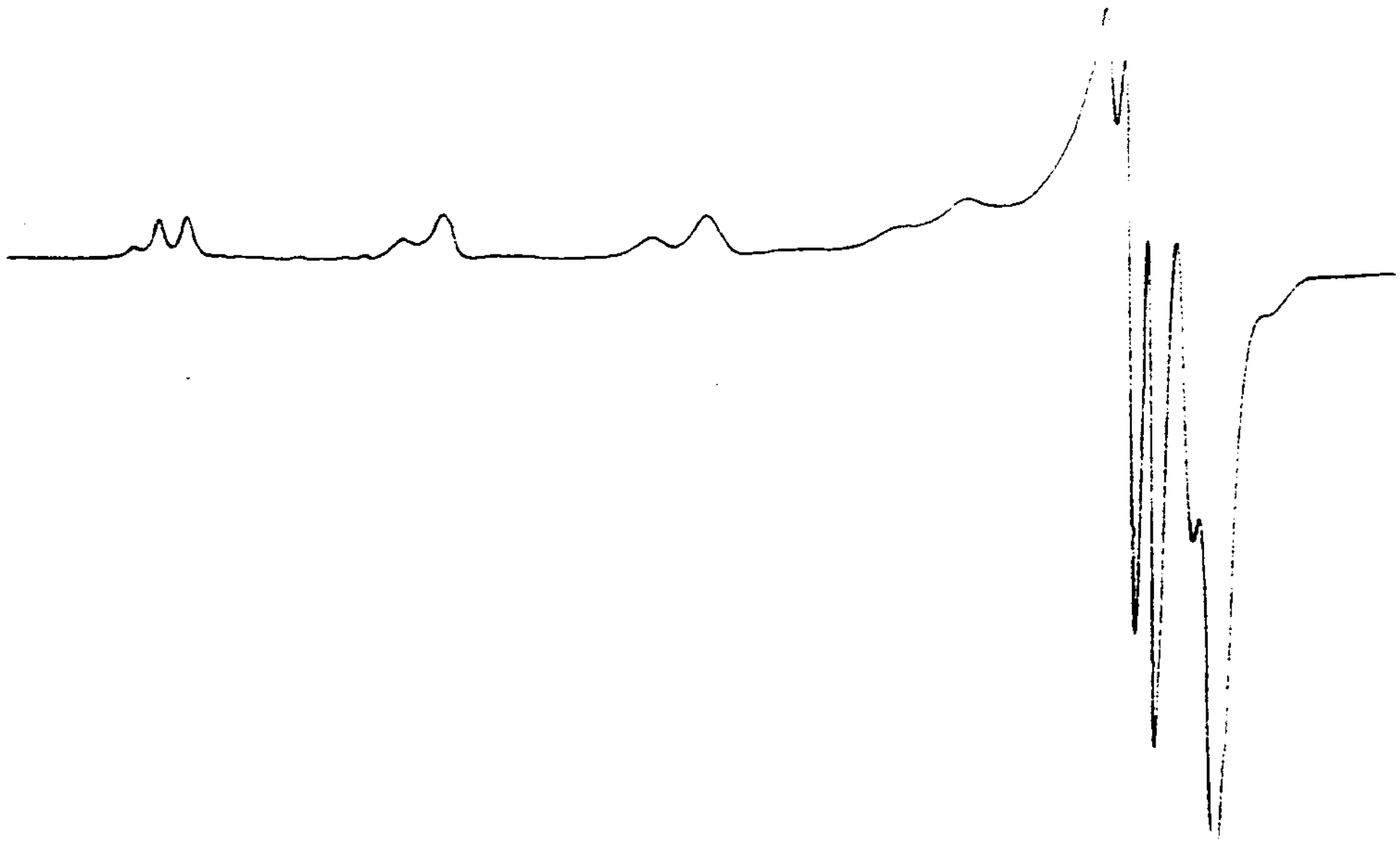
^{63}Cu(acac$_2$en) in 50% CHCl$_3$/50% toluene



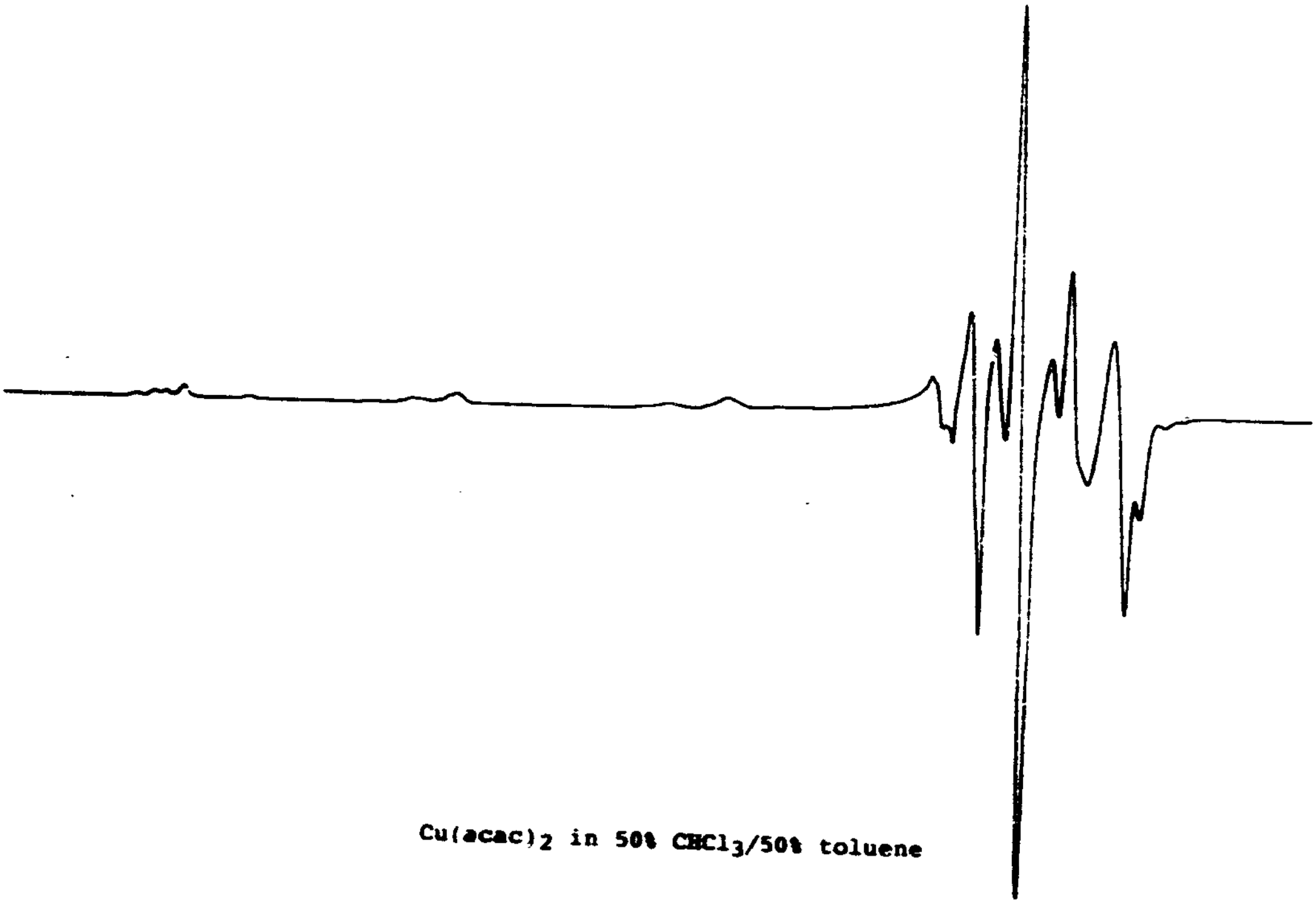
Cu(benzac)$_2$ in 50% pyridine/50% toluene



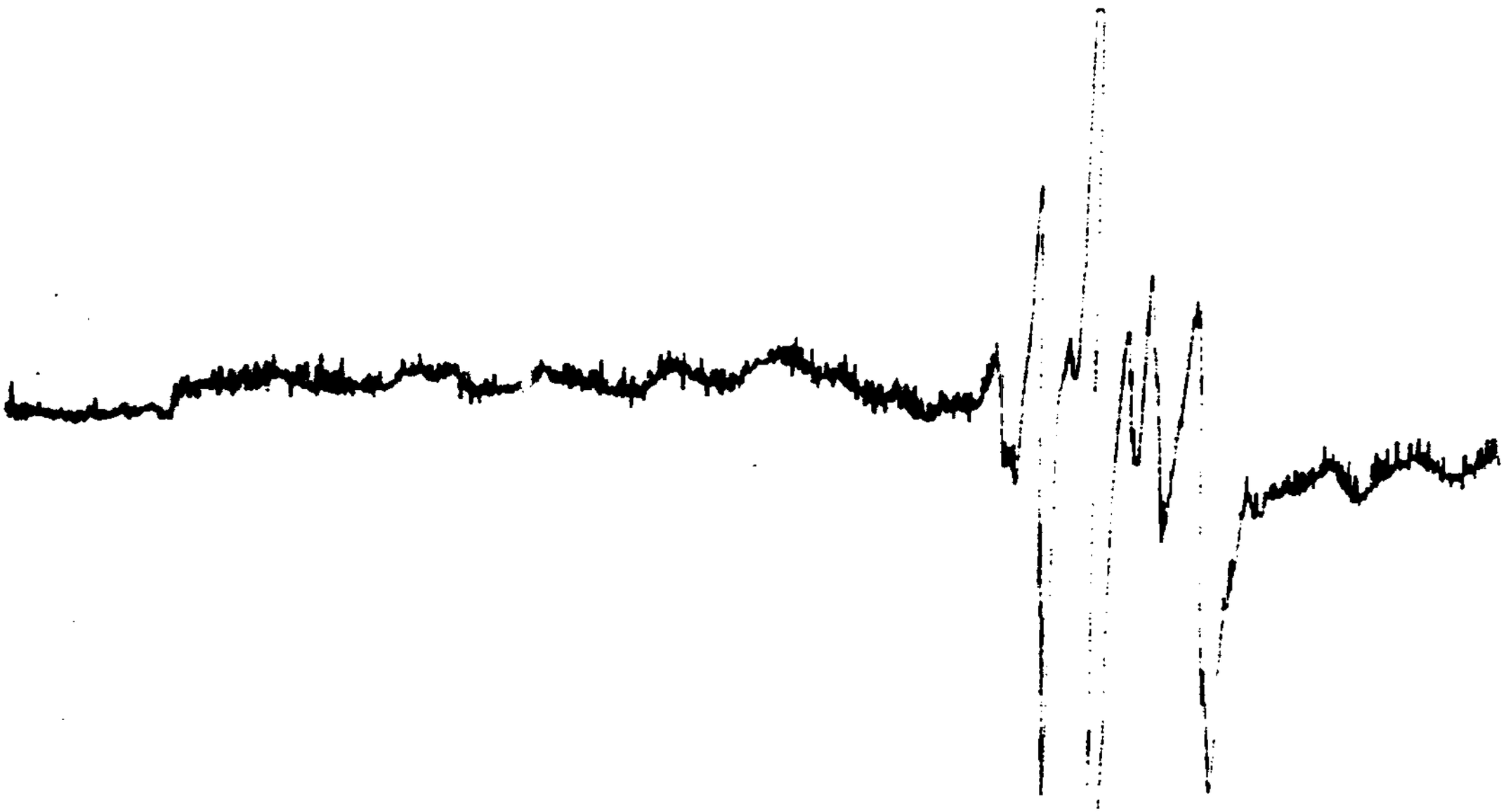
$Cu(benzac)_2$ in 50% $CHCl_3$/50% toluene



$Cu(acac)_2$ in 50% pyridine/50% toluene

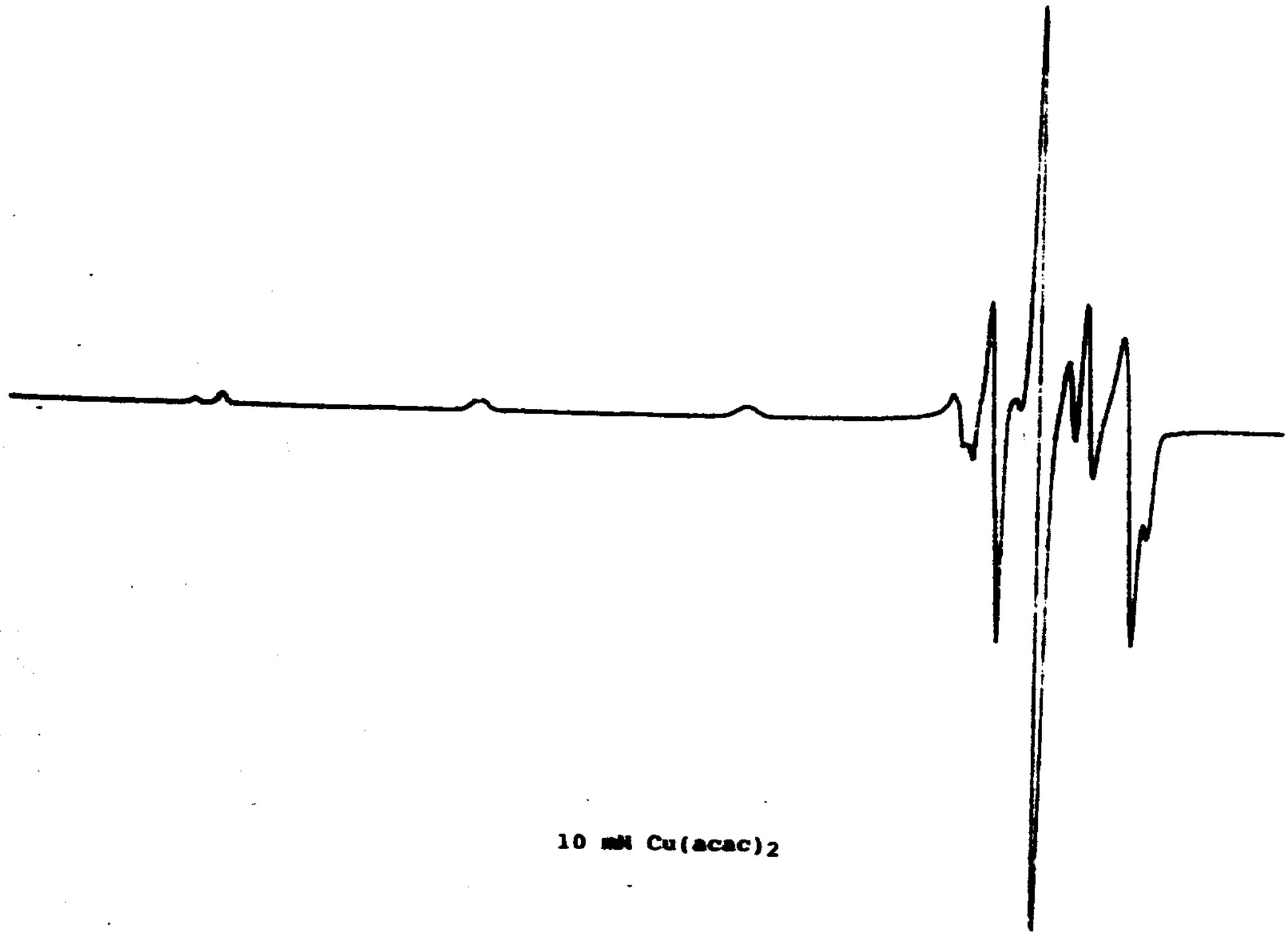


$Cu(acac)_2$ in 50% $CHCl_3$/50% toluene

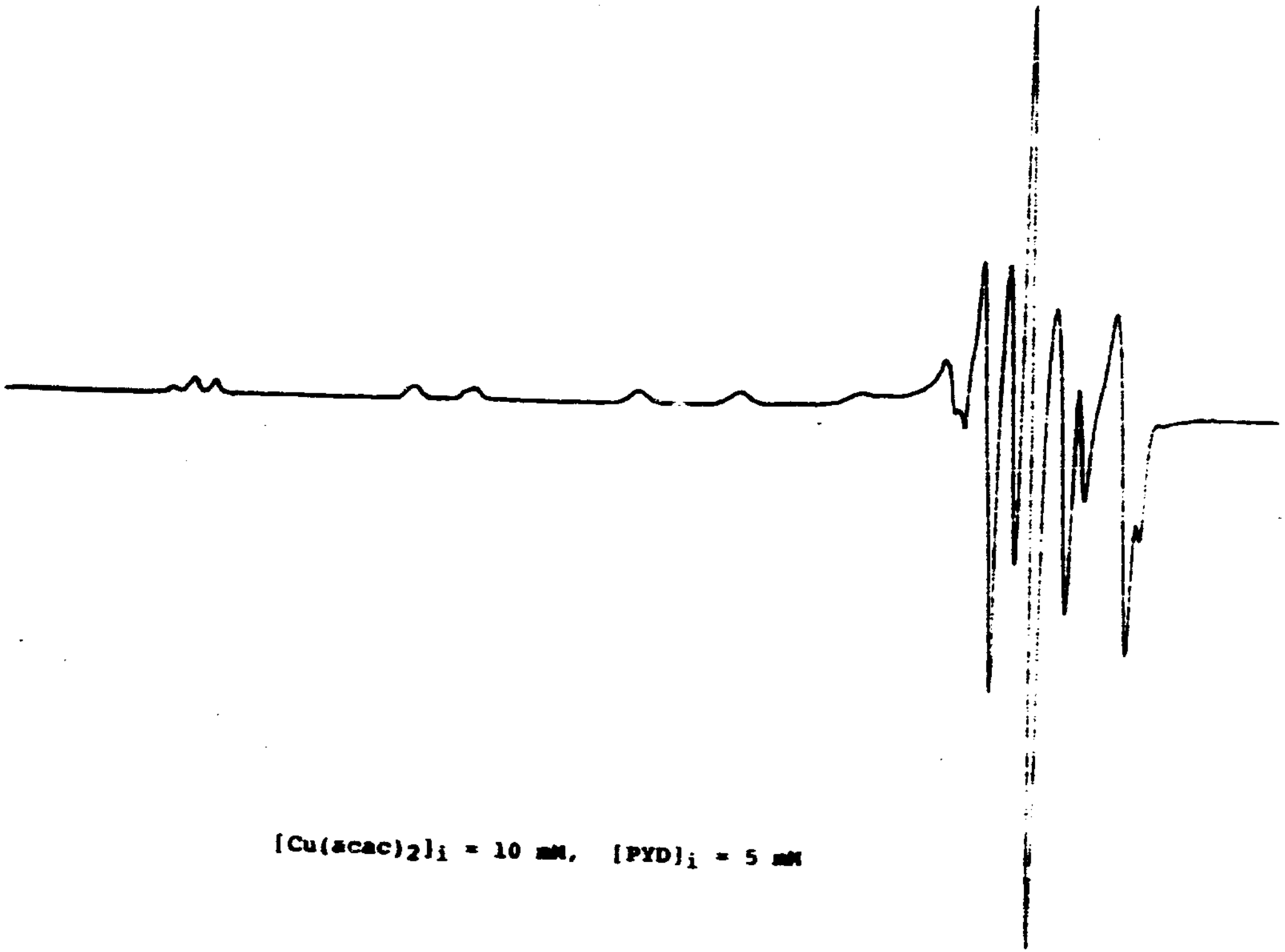


$Cu(acac)_2$ in 5% hexane/95% toluene

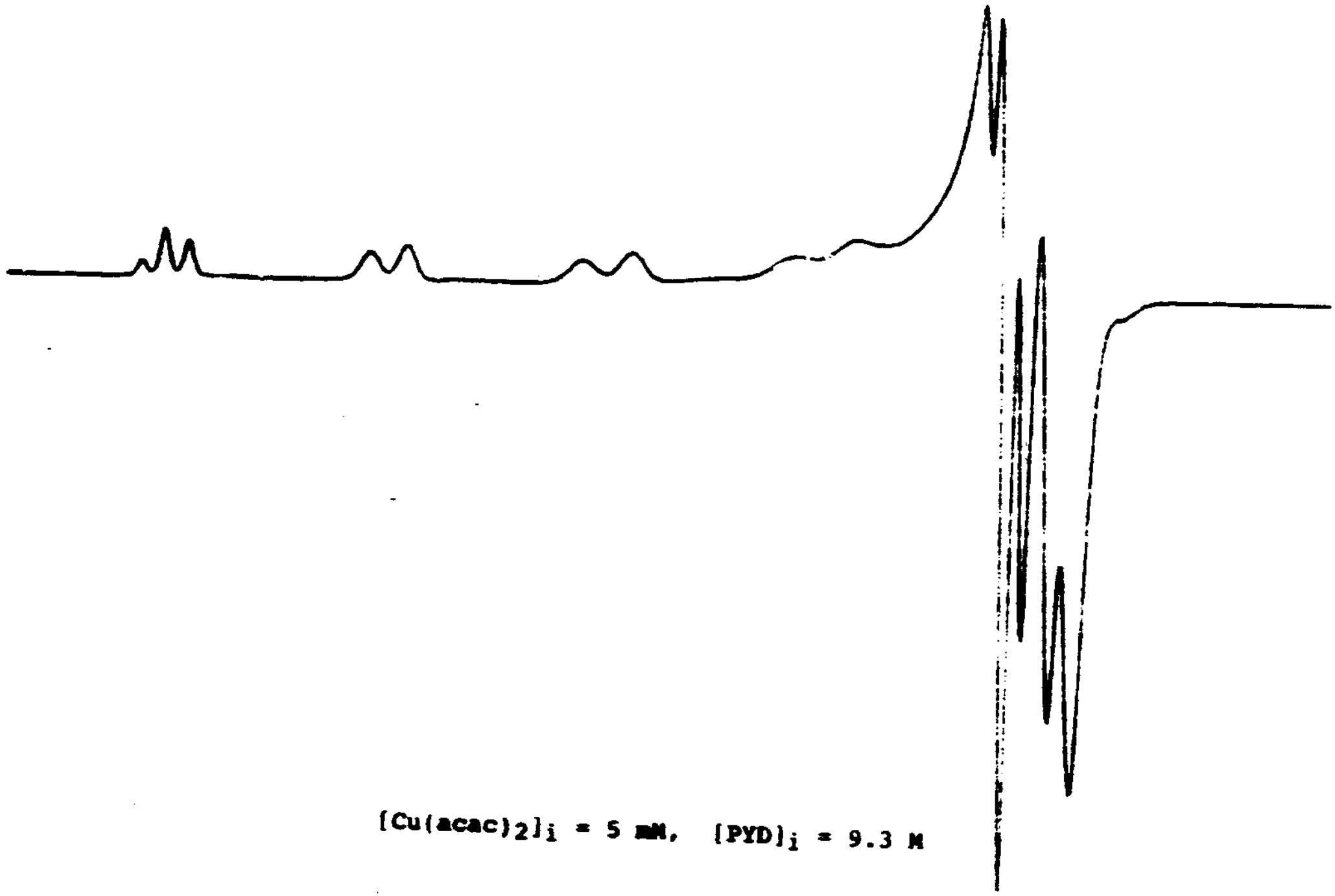
Appendix 2. $Cu(acac)_2$ and $Cu(benzac)_2$ Spectra.



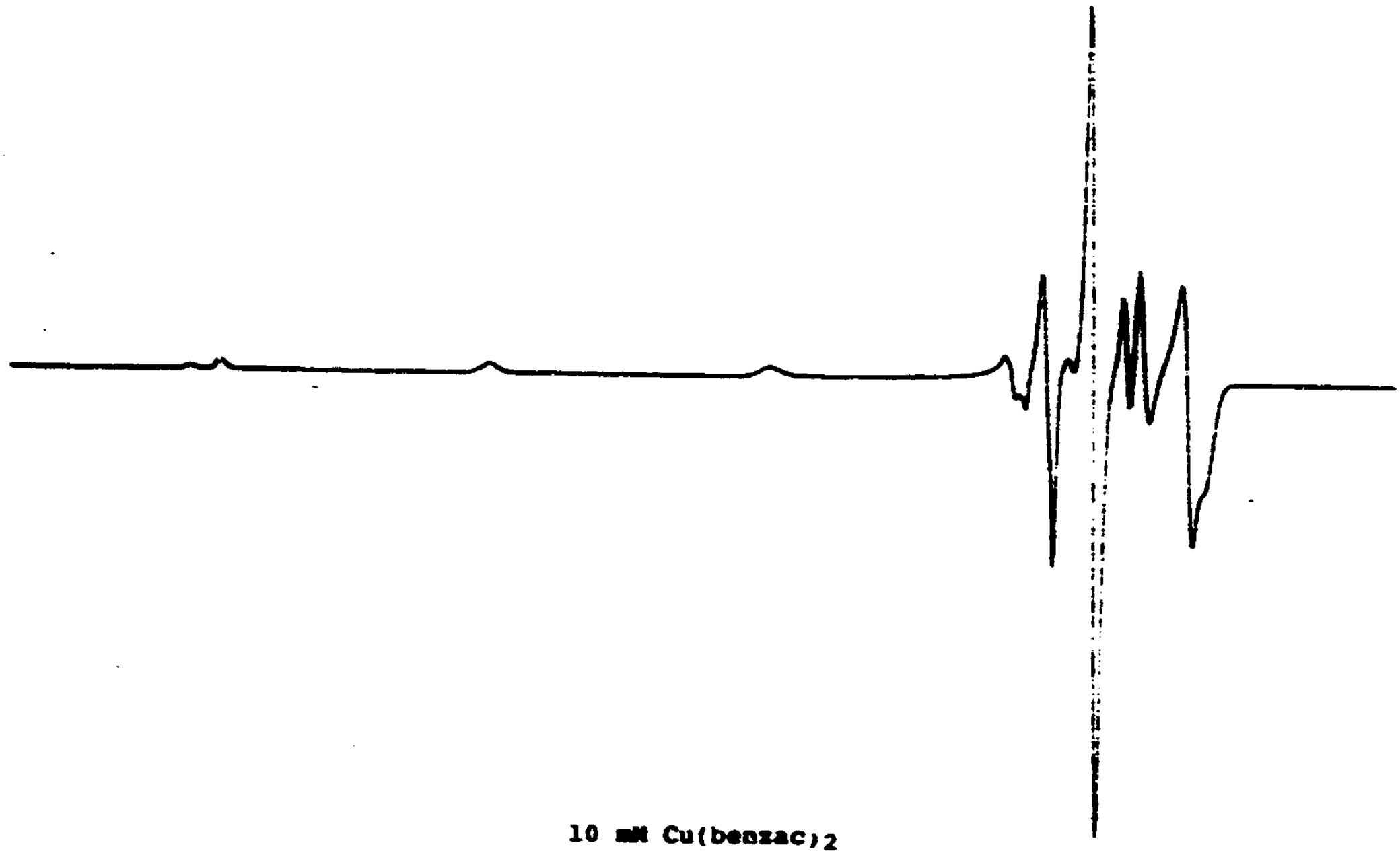
10 mM $Cu(acac)_2$



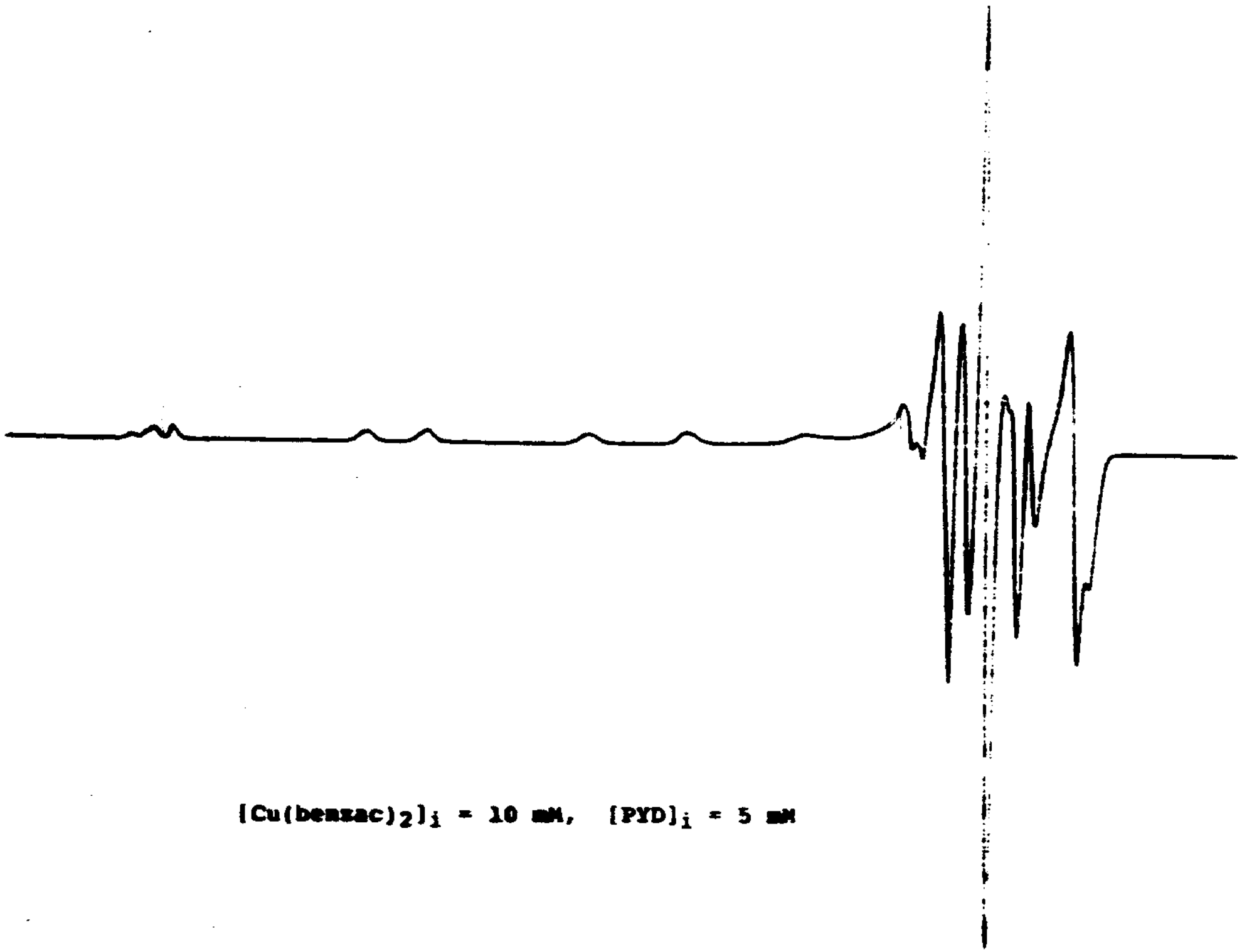
$[Cu(acac)_2]_i$ = 10 mM, $[PYD]_i$ = 5 mM



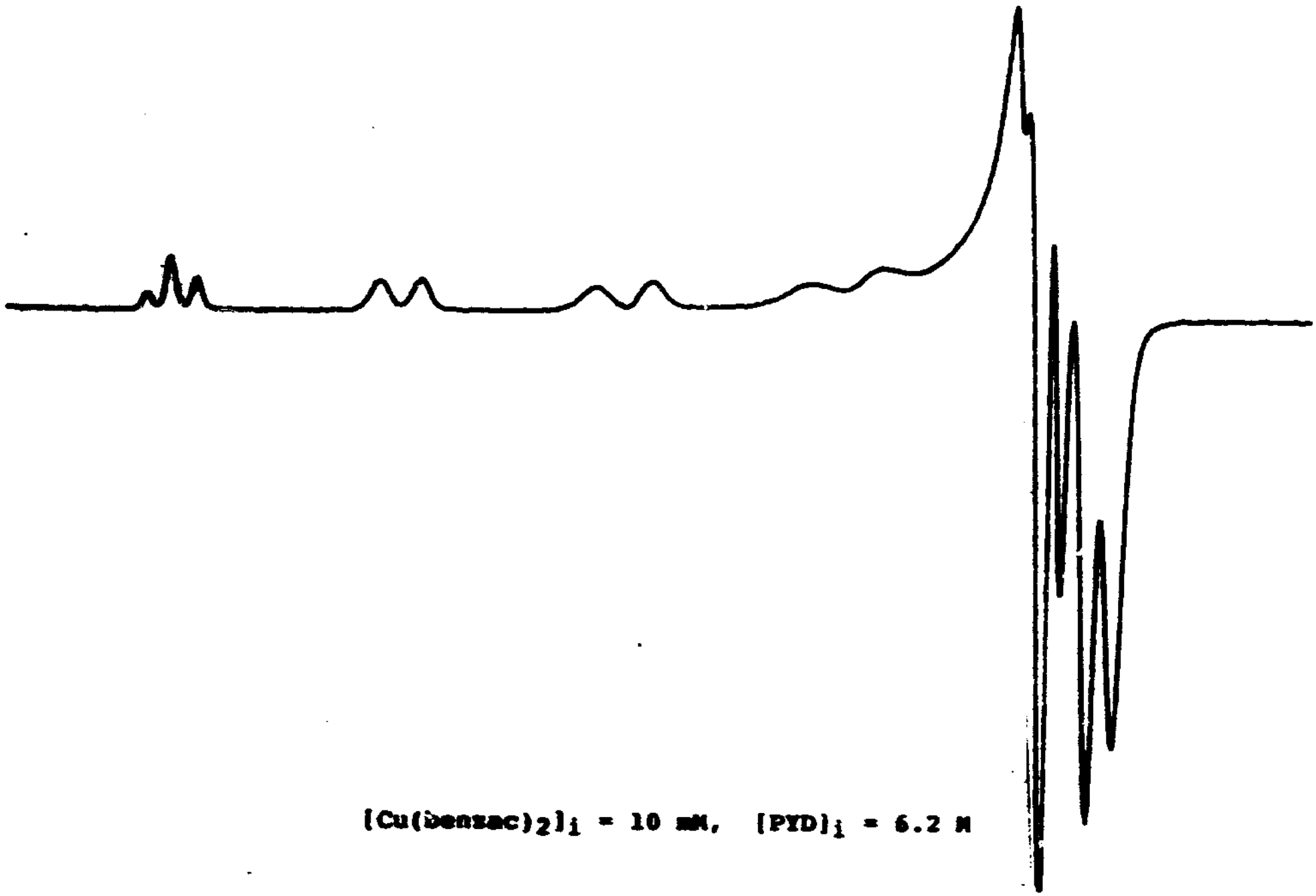
$[Cu(acac)_2]_i$ = 5 mM, $[PYD]_i$ = 9.3 M



10 mM $Cu(benzac)_2$

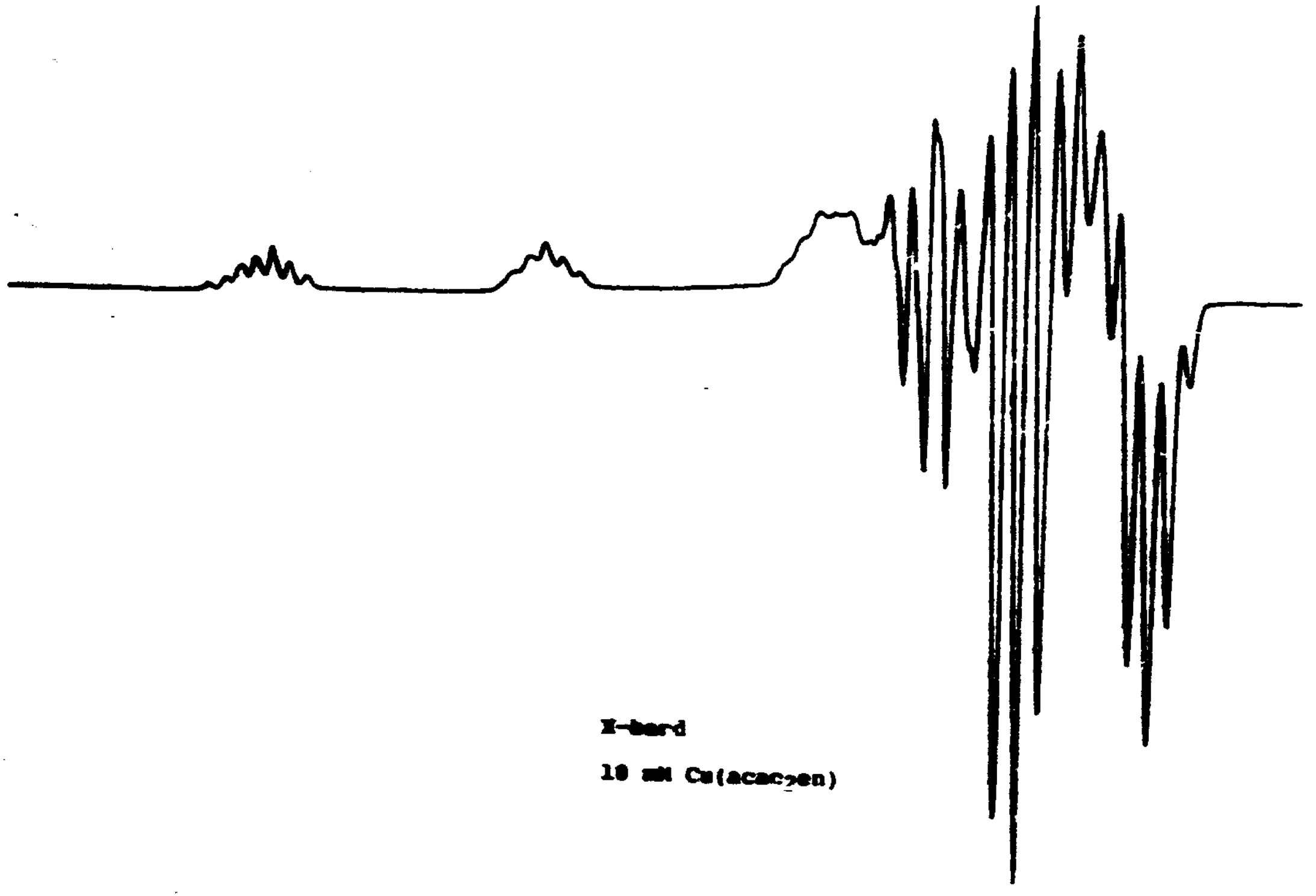


$[Cu(benzac)_2]_i$ = 10 mM, $[PYD]_i$ = 5 mM



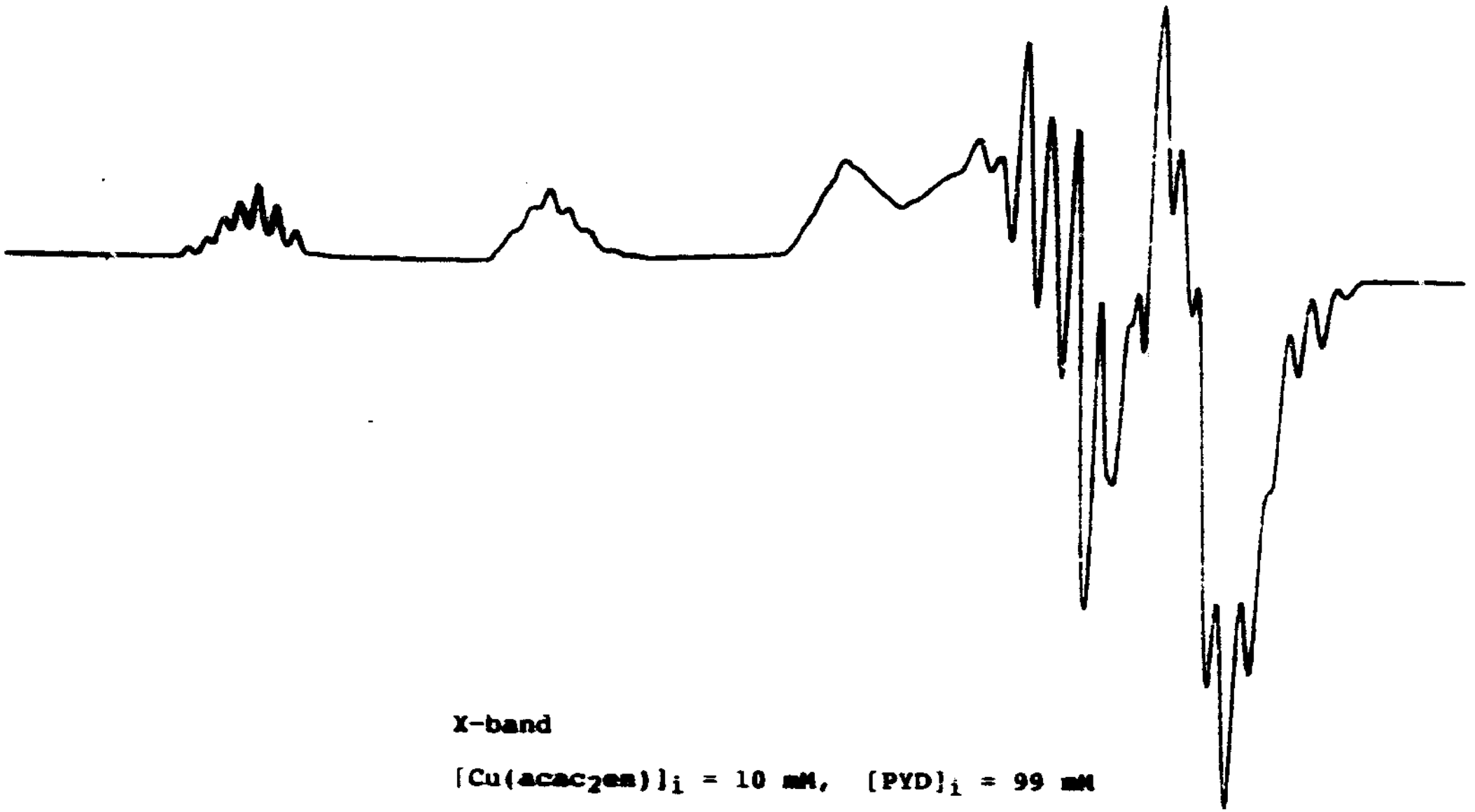
$[Cu(benzac)_2]_i$ = 10 mM, $[PYD]_i$ = 6.2 M

Appendix 3. $Cu(acac_2en)$ Spectra.



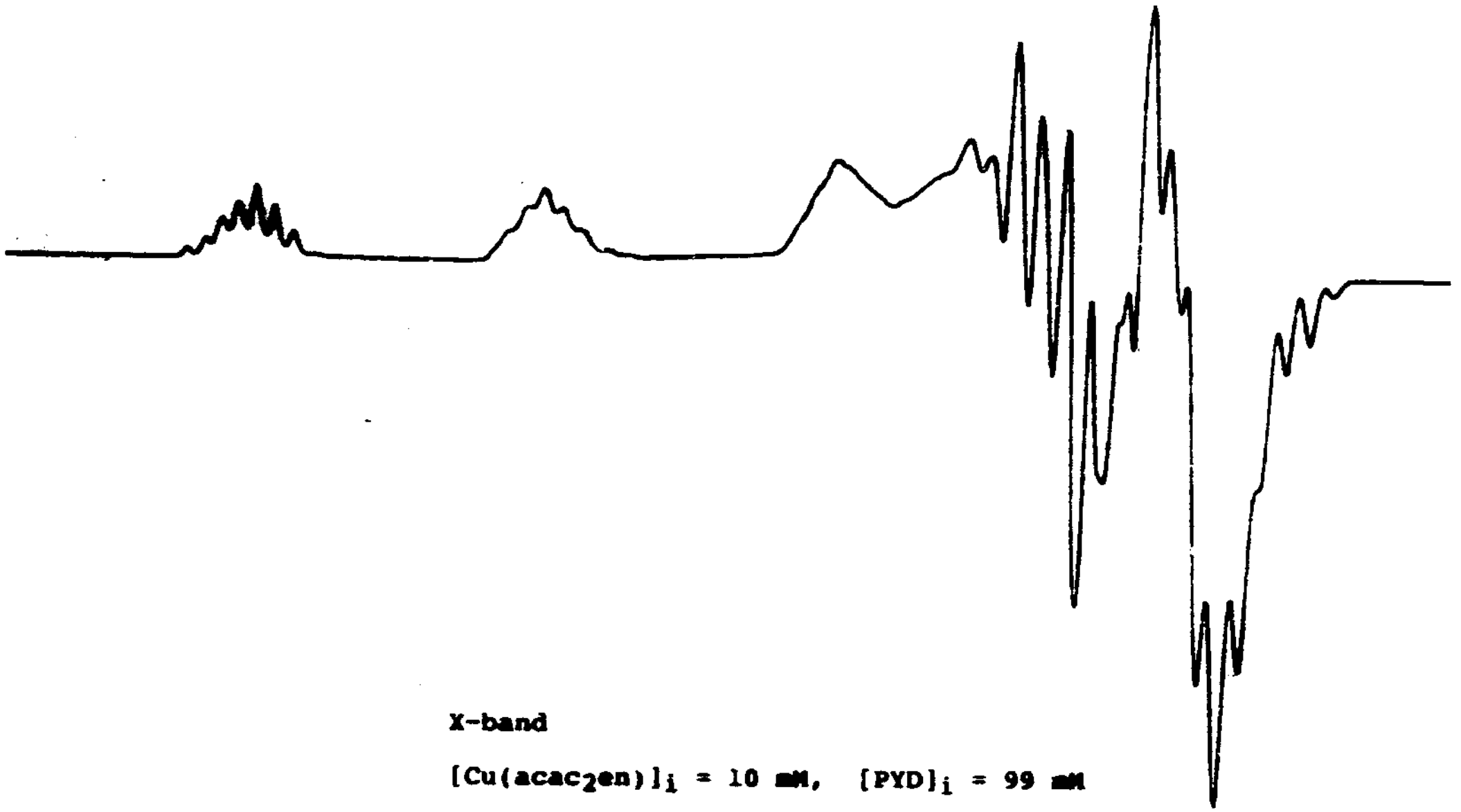
X-band

10 mM Cu(acac$_2$en)



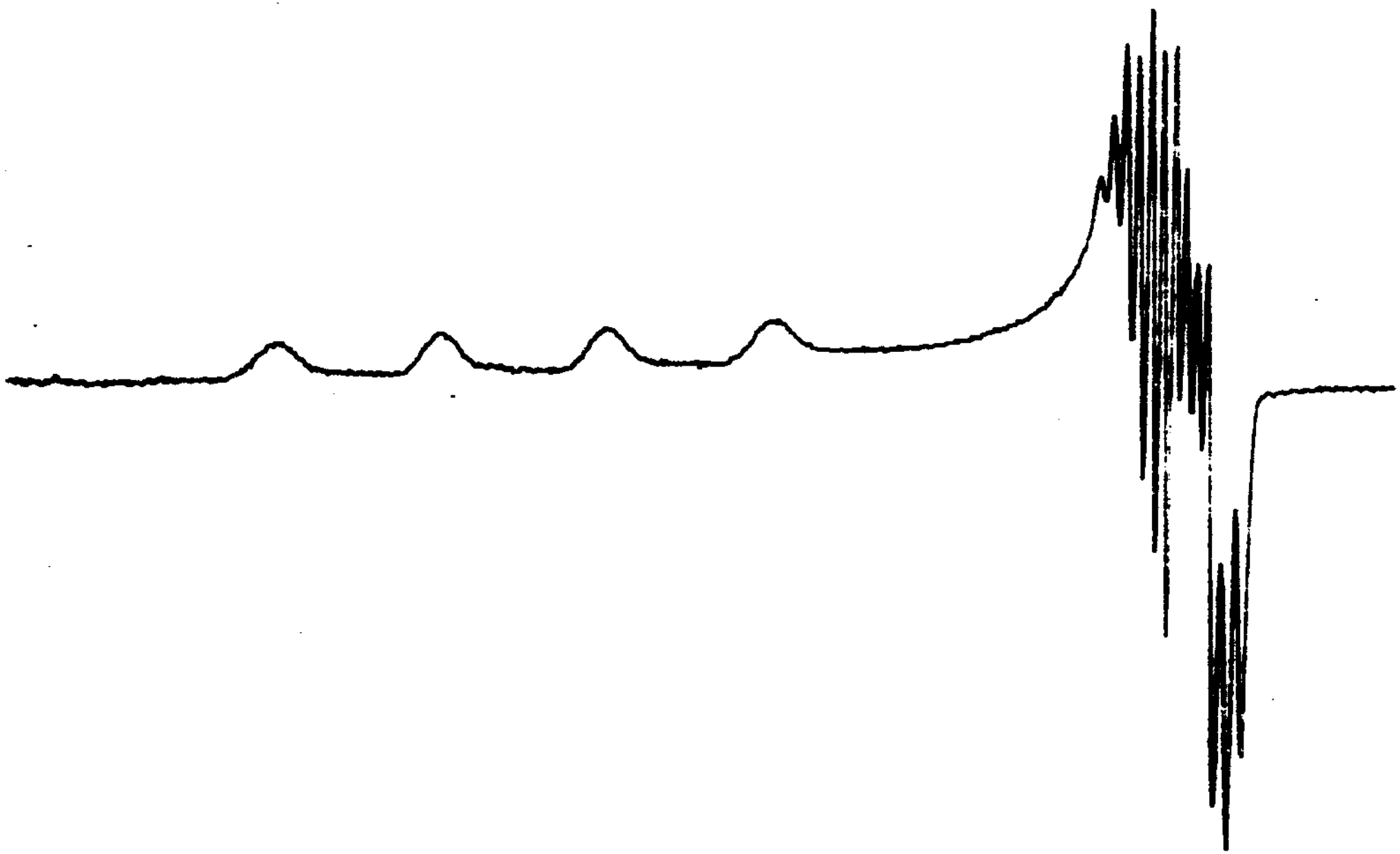
X-band

$[Cu(acac_2en)]_i$ = 10 mM, $[PYD]_i$ = 99 mM



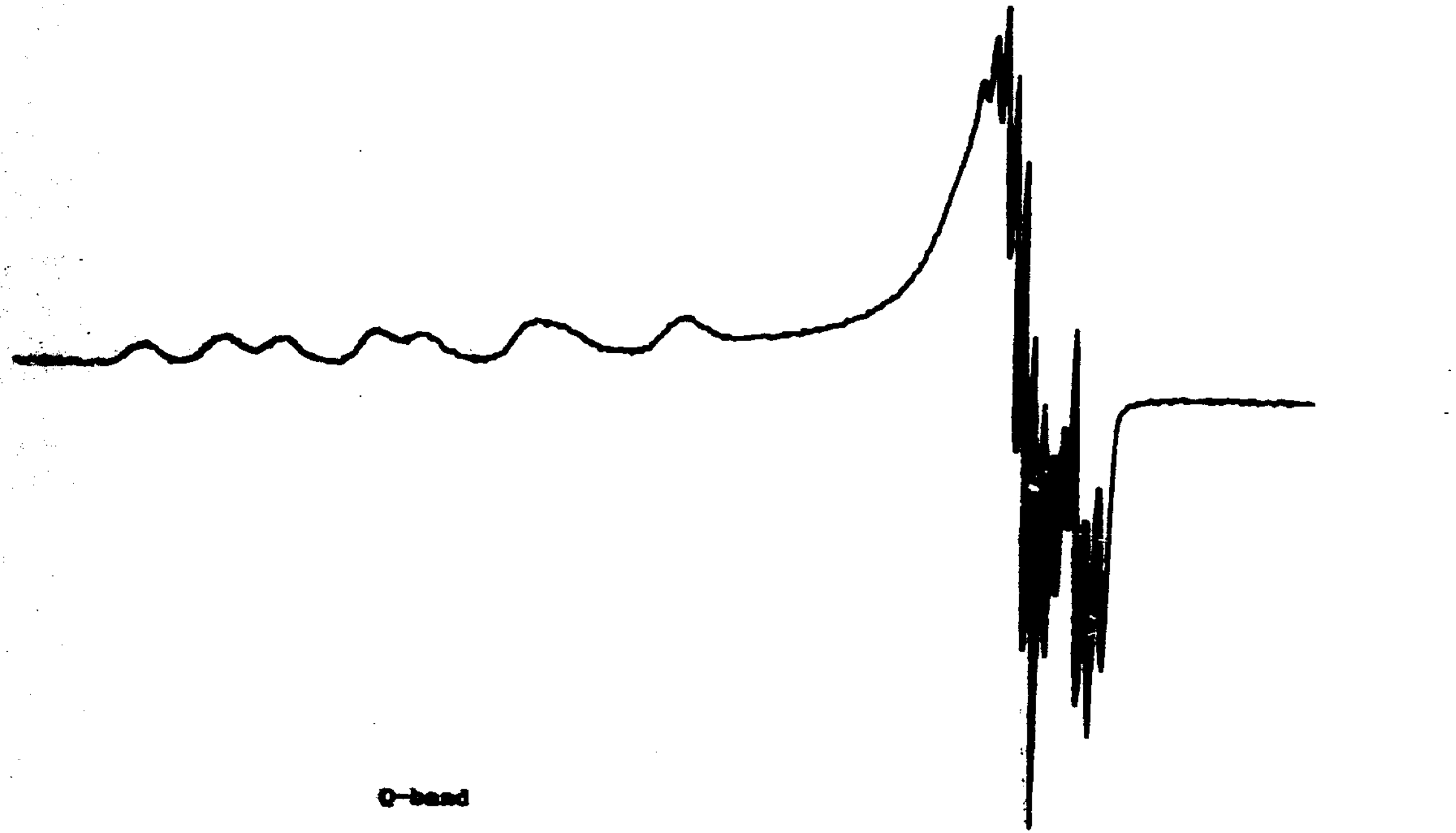
X-band

$[Cu(acac_2en)]_i$ = 10 mM, $[PYD]_i$ = 99 mM



Q-band

10 mM $Cu(acac_2en)$



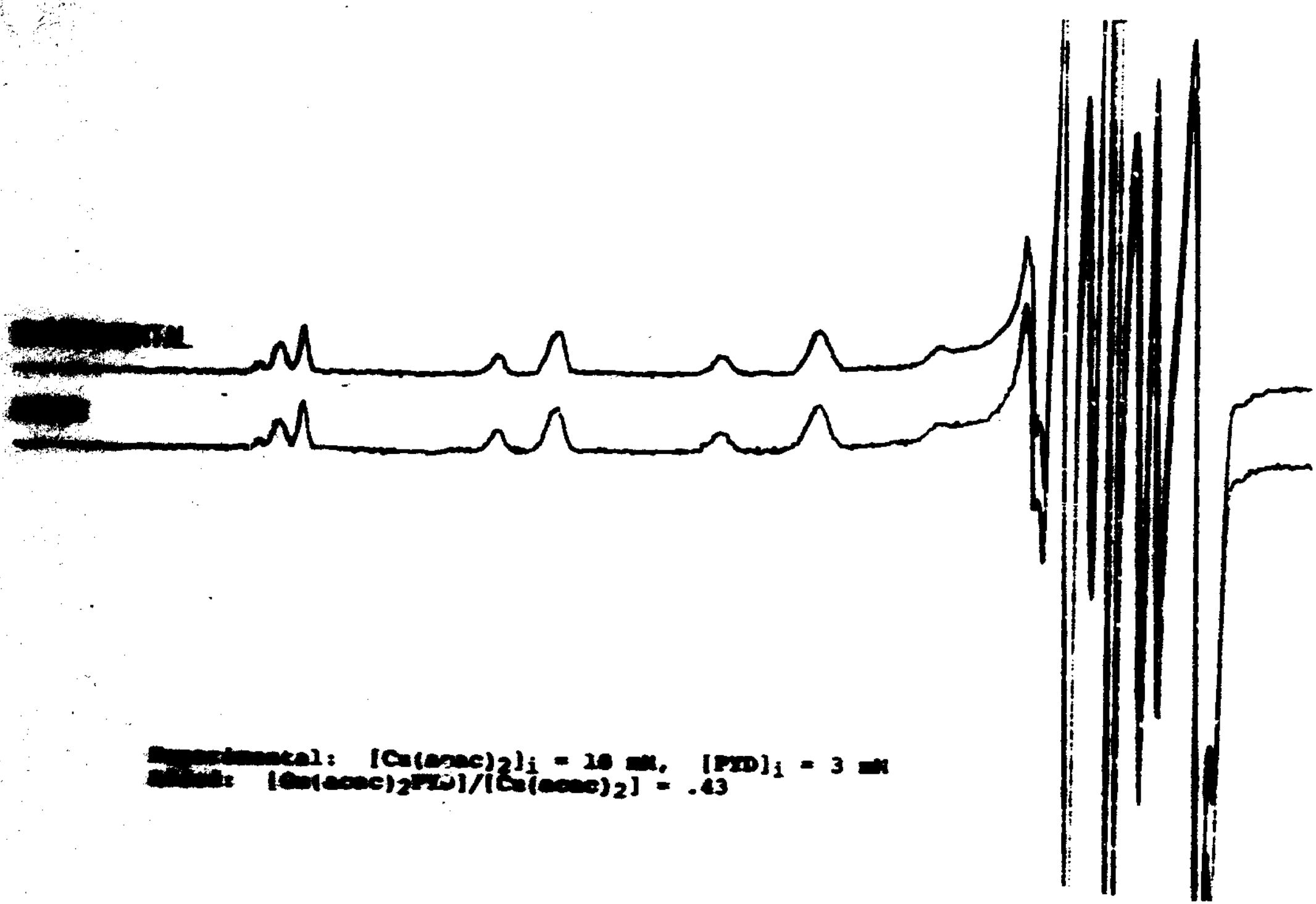
O-band

$[Cu(acac_2en)]_i$ = 10 mM, $[PYD]_i$ = 99 mM

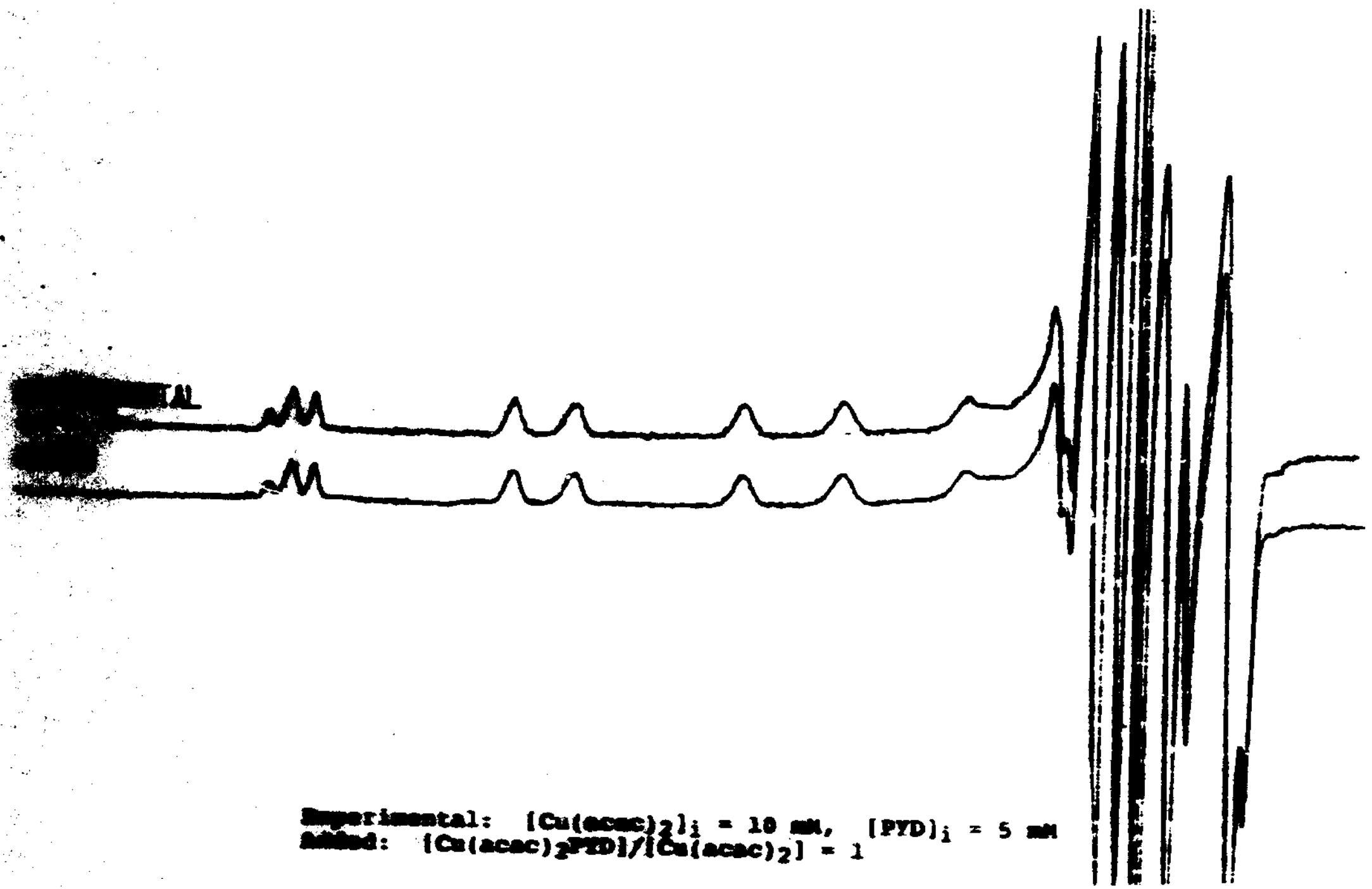
Appendix 4 : SCAL2

```
C
C  READ IN DATA SET ACQUIRED WITH ZENITH DATA ACQUISITION PROGRAM
C  AND SCALES THE POINTS BY A USER INPUT FACTOR
C
      DIMENSION DATA(1024), IDATA(1024)
      CHARACTER*14 INFILE,OUTFILE
      CHARACTER*127 SKIP
      INTEGER MIN,MAX
      WRITE(*,*) ' ENTER INPUT FILENAME '
      READ(*,'(A)') INFILE
      OPEN(UNIT=7,FILE=INFILE)
      READ(7,'(A)') SKIP
      WRITE(*,'(A)')SKIP
      READ(7,9) MAX,MIN
    9 FORMAT(I4,10X,I5)
      WRITE(*,9)MAX,MIN
      DO 10 I=1,1024
      READ(7,*) DATA(I)
10    CONTINUE
      WRITE(*,*) ' ENTER SCALING FACTOR '
      READ(*,*) SCALE
      MAX=NINT(MAX*SCALE)
      MIN=NINT(MIN*SCALE)
      DO 20 I=1,1024
      DATA(I)=DATA(I)*SCALE
      IDATA(I)=NINT(DATA(I))
20    CONTINUE
      WRITE(*,*) ' ENTER OUTPUT FILENAME '
      READ(*,'(A)') OUTFILE
      OPEN(UNIT=8,FILE=OUTFILE)
      WRITE(8,'(A)')SKIP
      WRITE(8,9)MAX,MIN
      DO 30 I=1,1024
      WRITE(8,*) IDATA(I)
30    CONTINUE
      END
```

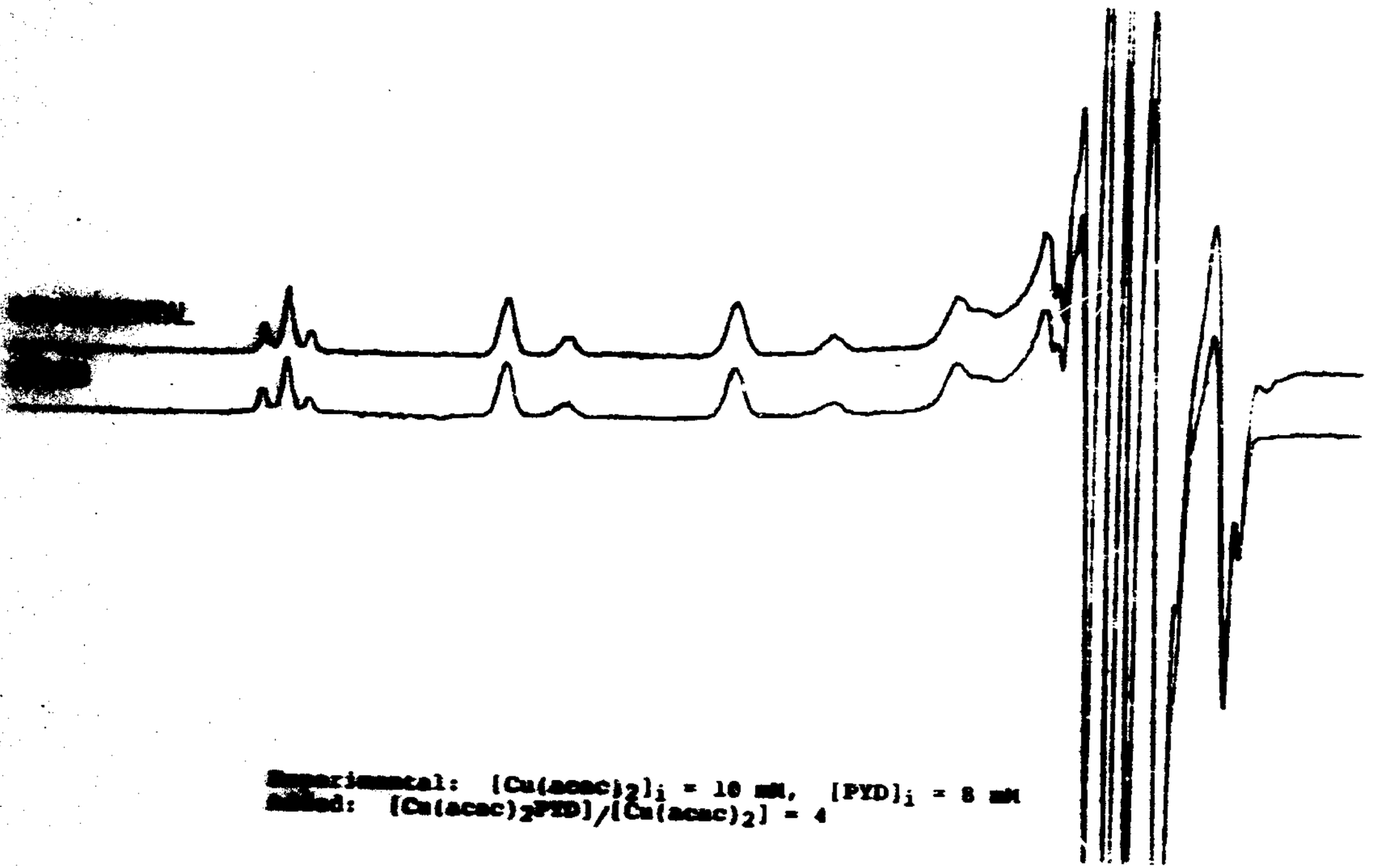
Appendix 5. Comparison of Experimental and Added $Cu(acac)_2$ and $Cu(benzac)_2$ Spectra.



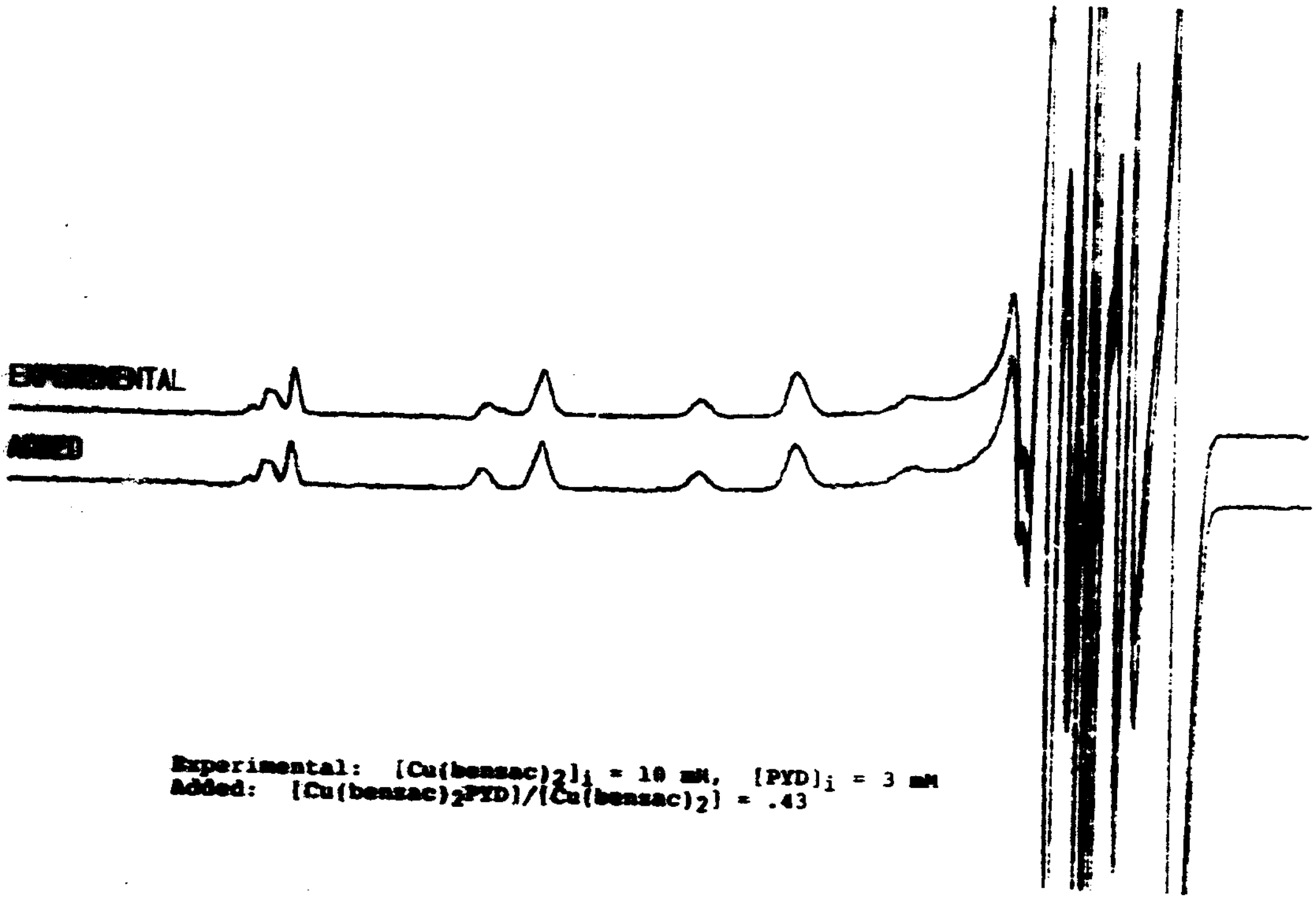
[illegible]: $[Cu(acac)_2]_i$ = 10 mM, $[PZD]_i$ = 3 mM
[illegible]: $[Cu(acac)_2PZD]/[Cu(acac)_2]$ = .43



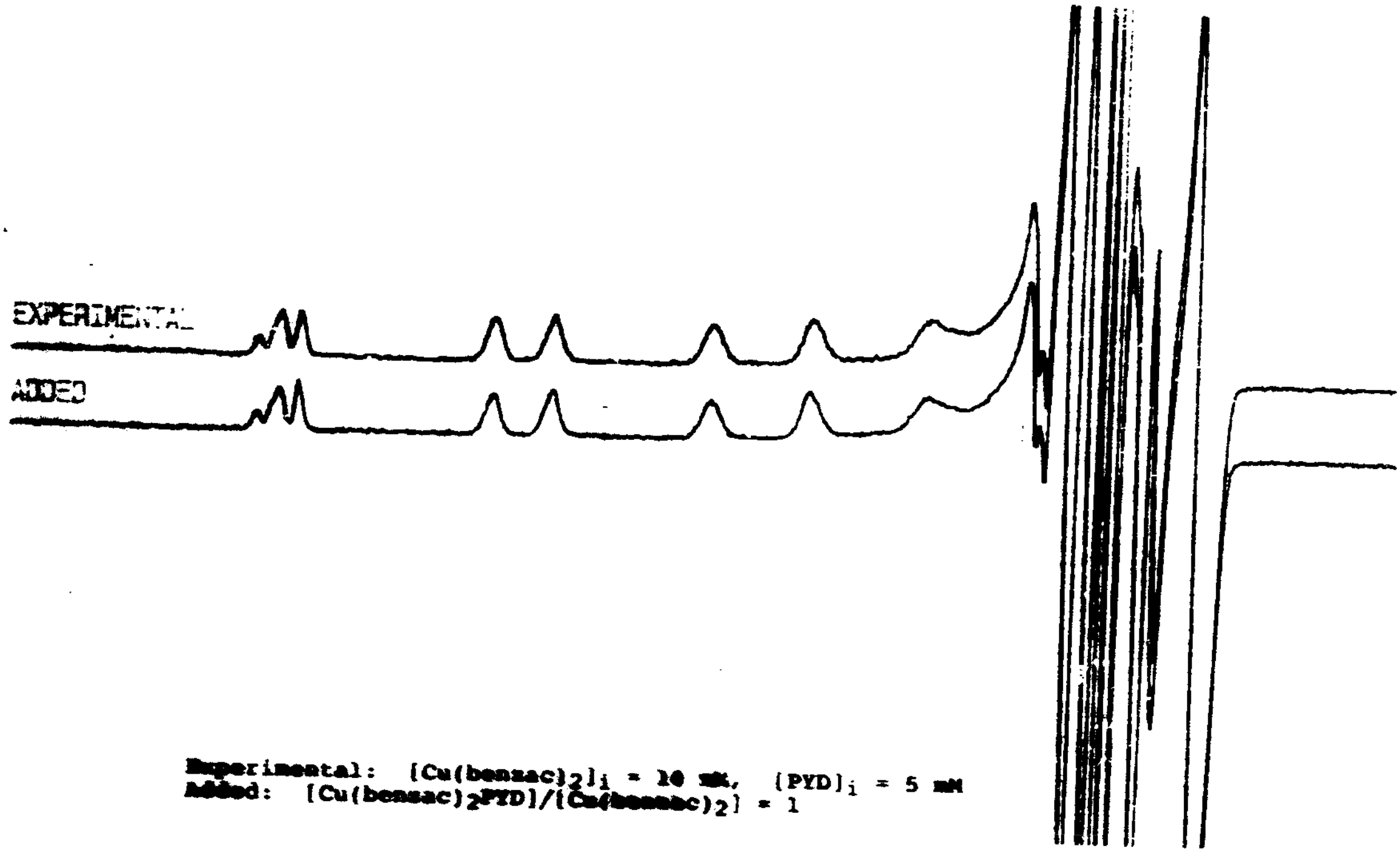
Experimental: $[Cu(acac)_2]_i$ = 10 mM, $[PYD]_i$ = 5 mM
Added: $[Cu(acac)_2PYD]/[Cu(acac)_2]$ = 1



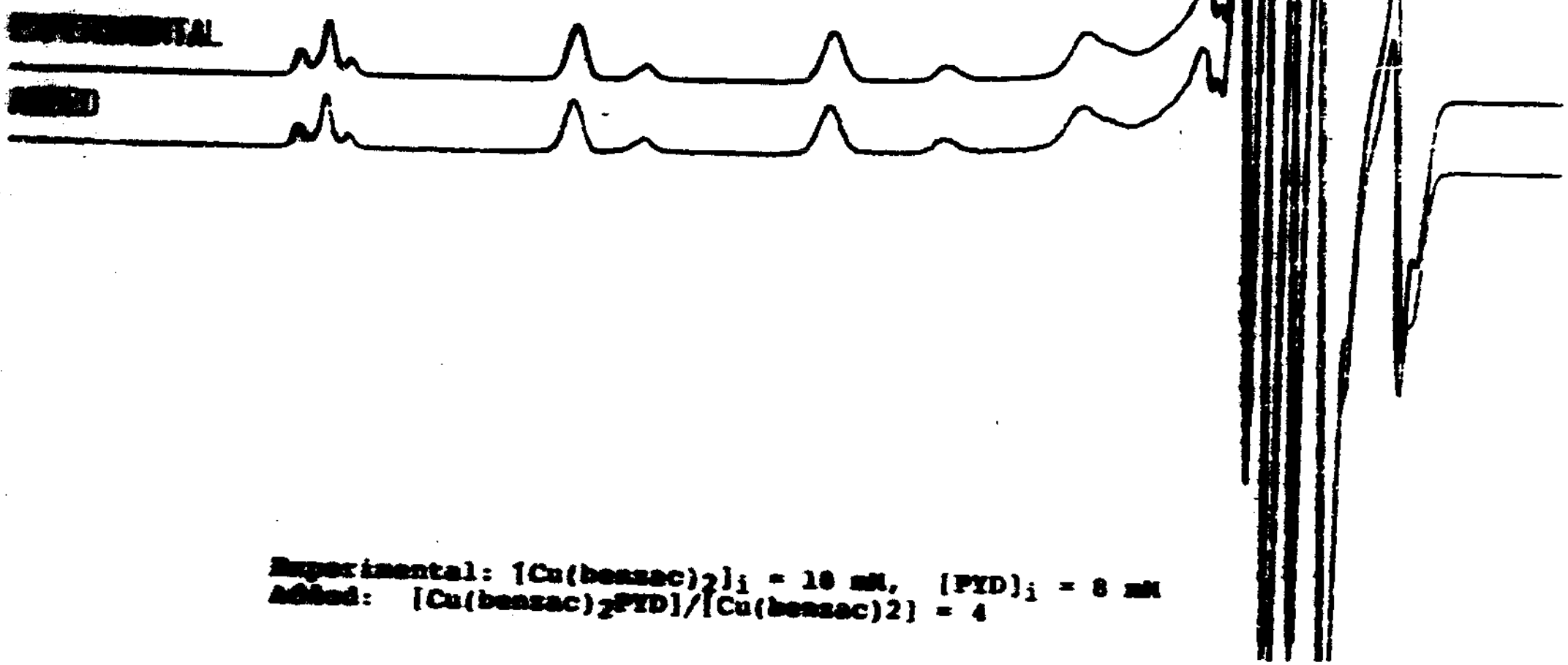
Experimental: $[Cu(acac)_2]_i$ = 10 mM, $[PYD]_i$ = 8 mM
Calculated: $[Cu(acac)_2PYD]/[Cu(acac)_2]$ = 4



Experimental: $[Cu(benzac)_2]_i$ = 10 mM, $[PYD]_i$ = 3 mM
Added: $[Cu(benzac)_2PYD]/[Cu(benzac)_2]$ = .43



Experimental: $[Cu(benzac)_2]_i$ = 10 mM, $[PYD]_i$ = 5 mM
Added: $[Cu(benzac)_2PYD]/[Cu(benzac)_2]$ = 1



Experimental: $[Cu(benzac)_2]_i$ = 10 mM, $[PYD]_i$ = 8 mM
Added: $[Cu(benzac)_2PYD]/[Cu(benzac)2]$ = 4

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