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The complexes of palladium (II) and nickel (II) with cycloalkanecarboxylic acid

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The Complexes of Palladium (II) and Nickel (II)
with Cycloalkanecarboxylic Acid

A Thesis
Presented to
the Faculty of the Graduate School
University of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Thaimos E.T. Yeh
December, 1973

This thesis, written and submitted by

Thaimos E.T. Yeh

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Dated August 26, 1973

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TABLE OF CONTENTS

CHAPTER	PAGE
I. Introduction	1
II. Theory	5
1. Background of Coordination Chemistry	5
A. The Valence bond method	6
B. The Molecular Orbital theory	6
C. The Crystal field theory	7
D. The ligand field theory	9
2. Charge transfer Spectra	9
3. The infrared spectra of metal-carboxylic acid complexes	9
4. pH dependence of the reaction	11
III. Experimental	12
1. The preparation of intermediates	12
A. Hydrous palladium Oxide (HPdO)	12
B. The Hydrous Nickelous Oxide (HNiO)	13
2. Synthesis of the Chelates	14
I. Palladium complex preparation	14
a. Biscyclopropanecarboxylatopalladium(II)	14
b. Bicyclobutanecarboxylatopalladium(II)	15
c. Bicyclopentanecarboxylatopalladium(II)	16
d. Biscyclohexanecarboxylatopalladium(II)	16
e. Biscycloheptanecarboxylatopalladium(II)	17
II. Preparation of the Nickel Complexes	18
a. Preparation of Biscyclopropanecarboxylatonickel (II)	18
b. Preparation of Bicyclobutanecarboxylatonickel (II)	19
c. Preparation of Bicyclopentanecarboxylatonickel (II)	20
d. Preparation of Biscyclohexanecarboxylatonickel (II)	20
e. Preparation of Biscycloheptanecarboxylatonickel (II)	21

CHAPTER

PAGE

IV. Spectra 23

V. Discussion 27

VI. Summary 30

BIBLIOGRAPHY 32

APPENDIX I 34

LIST OF FIGURES

FIGURE	PAGE
1. Splitting of the d orbitals in square-planar complexes of palladium(II) and nickel(II)	8
2. Cyclopropanecarboxylic acid in Dimethylformamide	36
3. Cyclobutanecarboxylic acid in Dimethylformamide	37
4. Cyclopentanecarboxylic acid in Dimethylformamide	38
5. Cyclohexanecarboxylic acid in Dimethylformamide	39
6. Cycloheptanecarboxylic acid in Dimethylformamide	40
7. Biscyclopropanecarboxylatopalladium(II) in Dimethylformamide.	41
8. Biscyclobutanecarboxylatopalladium(II) in Dimethylformamide .	42
9. Biscyclopentanecarboxylatopalladium(II) in Dimethylformamide.	43
10. Biscyclohexanecarboxylatopalladium(II) in Dimethylformamide .	44
11. Biscycloheptanecarboxylatopalladium(II) in Dimethylformamide.	45
12. Cyclopropanecarboxylic acid in Methanol	46
13. Cyclobutanecarboxylic acid in Methanol	47
14. Cyclopentanecarboxylic acid in Methanol	48
15. Cyclohexanecarboxylic acid in Methanol	49
16. Cycloheptanecarboxylic acid in Methanol	50
17. Biscyclopropanecarboxylatonickel(II) in Methanol	51
18. Biscyclobutanecarboxylatonickel(II) in Methanol	52
19. Biscyclopentanecarboxylatonickel(II) in Methanol	53
20. Biscyclohexanecarboxylatonickel(II) in Methanol	54
21. Biscycloheptanecarboxylatonickel(II) in Methanol	55
22. Hydrous Palladium Oxide	56
23. Hydrous Nickelous Oxide	57
24. Cyclopropanecarboxylic Acid	58
25. Cyclobutanecarboxylic Acid	59
26. Cyclopentanecarboxylic Acid	60
27. Cyclohexanecarboxylic Acid	61
28. Cycloheptanecarboxylic Acid	62
29. Biscyclopropanecarboxylatonickel(II)	63
30. Biscyclobutanecarboxylatonickel(II)	64
31. Biscyclopentanecarboxylatonickel(II)	65

FIGURE

PAGE

32.	Biscyclohexanecarboxylatonickel(II)	66
33.	Biscycloheptanecarboxylatonickel(II)	67
34.	Biscyclopropanecarboxylatopalladium(II)	68
35.	Biscyclobutanecarboxylatopalladium(II)	69
36.	Biscyclopentanecarboxylatopalladium(II)	70
36A.	Biscyclopentanecarboxylatopalladium(II)	71
37.	Biscyclohexanecarboxylatopalladium(II)	72
38.	Biscycloheptanecarboxylatopalladium(II)	73

LIST OF TABLES

TABLE	PAGE
I. The stretching frequencies of acetato and oxylato complexes of nickel(II)	11
II. Ultraviolet Absorption Sepctra of Palladium(II) complexes in Dimethylformamide and Nickel(II) complexes in Methanol . .	25
III. Infrared Absorption Spectra of Palladium(II) and Nickel(II) complexes (cm^{-1})	26

Chapter I

Introduction

Although some organic hydroxy acid complexes of palladium(II) and nickel(II) have been described (1-9), crystalline palladium(II) and nickel(II) dicycloalkanecarboxylates have not been reported.

The interaction of a palladium salt such as Na_2PdCl_4 or a nickel salt such as $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with cycloalkanecarboxylic acids which contain 3, 4, 5, 6, and 7 carbons produces deep green carboxylates with palladium(II) and yellowish green carboxylates with nickel(II).

A suitable hydrous palladium oxide (referred to hereafter as HPdO.) and hydrous nickel oxide (referred to hereafter as HNiO.) for conversion to crystalline palladium and nickel dicycloalkane-carboxylates is first prepared by treatment of aqueous solutions of a soluble palladium(II) salt or nickel(II) salt with an alkaline reagent such as NaOH to precipitate HPdO and HNiO; these form rapidly at room temperature. If HPdO and HNiO are precipitated hot or slowly, they will in part be converted to polymeric hydrous palladium(II) oxide and polymeric hydrous nickel(II) oxide respectively, which on treatment with acid yield polymeric palladium hydroxycycloalkane-carboxylate $\text{Pd}(\text{OH})(\text{OOCR}^*)$ and polymeric nickel hydroxycycloalkane-carboxylate $\text{Ni}(\text{OH})(\text{OOCR}^*)$ (3).

In preparing suitable HPdO readily available soluble palladium salts can be employed; e.g. disodium tetrachloropalladate(II) (Na_2PdCl_4), the corresponding dipotassium tetrachloropalladate(II) (K_2PdCl_4) and the like. Of these, the chloro-compounds are preferred by reason of

their availability and lower cost. The sodium salt is preferred because it is less expensive and HPdO can be precipitated with lower heat of reaction (3); thus the precipitation temperature can be readily controlled and maintained.

In preparing suitable HNiO , nickelous(II) chloride is employed; the precipitation takes place very rapidly at room temperature. The chloride ion can be completely removed.

Conventional bases can be employed as the alkaline reagent for treatment of palladium and nickel salt solutions. Sodium hydroxide, potassium hydroxide, sodium carbonate, and the like are added as solids or preferably as aqueous solutions to the salt solution. The concentration of aqueous alkaline reagent is not critical; generally HPdO and HNiO precipitation is complete at a pH of 9-10 but excess alkali may be employed without harmful effect. The base used in this study was 10% aqueous sodium hydroxide.

If the filter cake of HPdO and HNiO is completely dried by heating for prolonged periods of time, the HPdO and HNiO will partially polymerize and will not dissolve in acid to yield high purity crystalline palladium(II) and nickel(II) cycloalkanecarboxylates. Preferably a cake content of at least 20% water should be maintained (3). If a very large excess of acid is employed, crystallization will not occur since the desired salt is quite soluble in acids.

The complex of palladium recovered from various solvents is dried at a temperature below 50°C preferably under nitrogen; when

heated in air, the complex decomposes to yield the metal and combustion products at temperatures of 164°C-198°C. This complex is deep green in color and generally crystallizes in short plates.

The complex of nickel recovered from ether or petroleum ether (30°C-60°C) is dried at a temperature below 75°C; if heated in air, the complex decomposes to give the metal and combustion products at a temperature of 305°C-324°C. The complex is yellowish green in color and crystallizes as fine powder.

Other than the introduction of the $\text{PdO} \cdot x\text{H}_2\text{O}$ and $\text{HNiO} \cdot x\text{H}_2\text{O}$ technique, this study involved the preparation of the coordination compounds of palladium(II) and nickel(II) with cycloalkanecarboxylic acids which contain 3, 4, 5, 6, and 7 carbons. A first analysis of the problem would seem to indicate that the preparation would be straightforward. Stephenson, Morehouse, and Wilkinson (2) stress the great coordination tendency of the carboxylates for palladium(II); Johnson (5), Ellis (7), and the others (9, 18) have synthesized a number of nickel(II) complexes of carboxylates apparently with a minimum of difficulty. Closer analysis of the problem, however, reveals many inherent difficulties. From the structure of each cycloalkanecarboxylic acid under study, instability of its complex can be predicted because chloride ion can be attached to cycloalkanecarboxylic acids at high temperature and very low pH if the chloride is not completely removed. Secondly, the preparation of complexes required the solid product in order that carbon-hydrogen analyses could be used to establish compositions. In a large majority of the

preparations cited in the literature, the complexes prepared were characterized in solution. Further, mention was generally made of their instability.

Steps in the various syntheses will be outlined in the following sections pointing out the difficulties encountered. Characterization-- based on carbon-hydrogen analyses, infra-red spectra, and UV-Vis spectra-- will also be described.

Chapter II

Theory

I. Background of Coordination Chemistry

The field of coordination chemistry has grown in little more than a half-century from a readily defined and limited area into what is now perhaps the most active field of research in inorganic chemistry. In recent years it has received not only much experimental study, but also extensive theoretical treatment. Early theories offered by Graham (1837), Blomstrand (1869) and Jorgensen (1878) are of little more than historical interest now since the coordination theory proposed by Alfred Werner in 1893 has proved to be all-encompassing in scope. This theory, which has been extended via wave mechanics and substantiated experimentally, has been largely responsible for the rapid growth of inorganic chemistry since the turn of the century.

The basic postulate of Werner's coordination theory, in his own words (11) is as follows: "Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages, the possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principle valences, still other bonds on the atoms, called auxiliary valences, may be called into action."

During the past ten years a number of carboxylic acid complexes of palladium(II) and nickel(II) have been prepared and characterized (1-9). In choosing the preparations to be cited, consideration was primarily given to those which differed as much as possible, and secondly, an attempt was made to include as many different cycloalkane-carboxylic complexes with palladium(II) and nickel(II) as possible. After due consideration of the literature one can predict that theoretically one can have two cycloalkanecarboxylate ions chelated to palladium(II) or nickel(II).

It is well at this point to consider the various methods of bonding applied to the coordination of metal complexes as follows:

A. The valence bond method:

The valence bond method predicts two possible tetravalent configurations-tetrahedral and square planar. Elements having no d-electrons of suitable energy available use sp^3 hybridization and must therefore be tetrahedral in structure when coordinating. If d-electrons are available, then the four coordinate chelate may be either tetrahedral or square planar with the latter preferred. Since both palladium and nickel have d orbital available, the dsp^2 configuration involving the hybridization of the $d_{x^2-z^2}$, s, p_x and p_y atomic orbitals, would most likely occur.

B. The molecular orbital theory:

The molecular orbital method uses the same orbitals as the valence bond approach, but compounds them with ligand orbitals

to give molecular orbitals. The orbitals symmetries are such that the d_{x-y} and s orbital of palladium and nickel combine with the electrons from cycloalkanecarboxylic acid, but the p_x and p_y orbital can only overlap with the bidentate along the x and y axis. (10)

C. The crystal field theory:

The crystal field theory is essentially an electrostatic theory of bonding. It considers the complex as a positively charged central ion symmetrically surrounded by anions or by the negative ends of dipolar ligands. In a simple electrostatic theory of bonding the total binding energy will be made up of the sum of the energy of attraction between central ion and ligand and the repulsive energy due to ligand repulsion. The greater the attractive energy as compared to the repulsive energy, the more stable will be the bond. These simple calculations give excellent agreement with experimental bond energies, but this method does not give any information about the magnetic properties. Crystal field theory supplies this information by considering the effect of the ligand on the energy of the d electrons in central ion. The five d orbitals of the free metal ion are all of the same energy and are said to be fivefold degenerate. In addition, these orbitals have maximum electron densities directed in space, which are different for each of the five orbitals. The d_z^2 orbital has maximum electron density directed along the z axis, while the $d_{x^2-y^2}$ orbital has maximum density along the x and y axis. The d_{xy} , d_{xz} and d_{yz} have maximum density directed between the ligands approach to form the complex, electrostatic repulsion between the

ligand and d orbitals arises which destroys the equality of the five d orbital energies, that is, destroys the degeneracy of the d orbitals that was present in the free metal ion. Those orbitals that lie along the direction of ligand approach are raised in energy because of repulsion, and the orbitals that lie furthest away from the approaching ligand are lowered in energy. The net result is a splitting of the five d orbitals into groups of orbitals of different energy.

Figure 1 taken from Day and Selbin (11) shows the d orbital splittings for the square planar complexes of palladium(II) and nickel(II).

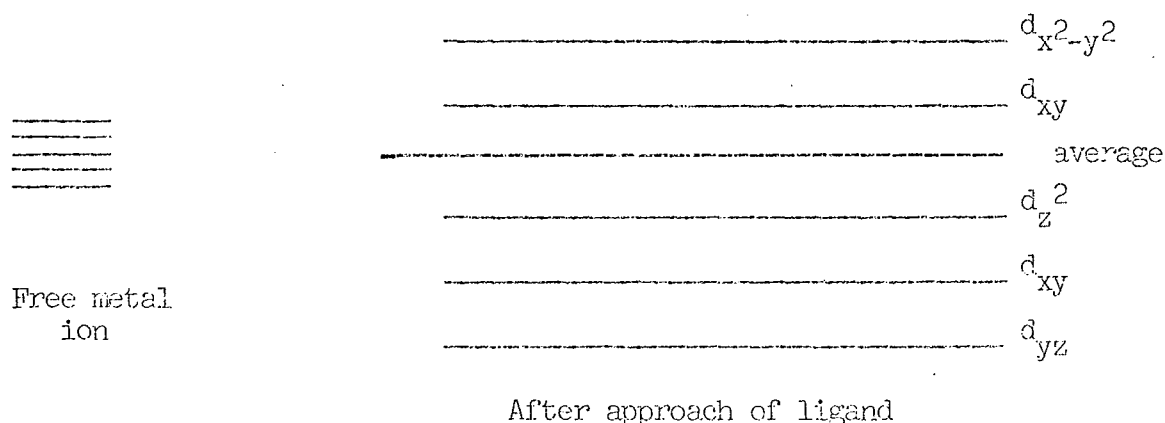


Figure 1. Splitting of the d orbitals in square-planar complexes of palladium(II) and nickel(II).

The arrangement of the ligand molecules causes the $d_{x^2-y^2}$ level to have the highest energy since the axis of its lobes lies in the plane of the ligands. Basolo and Pearson (12) indicate that the d_z^2 orbital has a slightly higher energy than the d_{xy} and d_{yz} orbitals; this is justified by the collar of charge in the xy plane which gives a greater repulsion to the ligand field. The d_{xy} and d_{yz} are affected similarly and become degenerate.

D. The ligand field theory:

Because of the apparent inadequacy of the crystal field theory, the ligand field theory must be introduced. The electrons which are not concerned in the transitions supply the perturbation potential and are then ignored, but the symmetry of this potential decides the symmetry of the molecular orbitals, which can form the ligand and the metal ion orbitals. The occupation of these molecular orbitals, which were in the crystal field model purely t_{2g} and e_g electrons localized on the central ion, allows a discussion of the spectra on a fully molecular basis.

2. Charge transfer Spectra.

Examination of the UV and Vis spectra of many of the complexes of the second and third row transition elements shows that the charge transfer bands swamp out any bands which might be crystal field type. The intensity of the charge transfer bands indicates only whether a transition is electronically allowed or forbidden and that the electron transfers from one center to the other. It is immaterial whether the electron arises from the metal orbitals and transfers to the ligands, or vice versa. On the whole this presents some complications in spectrum interpretation. Also the complications of spin-orbit coupling are likely to be much greater and this requires many of the theoretical approaches be of the intermediate Domain type; these are often difficult to interpret (14).

3. The infra-red spectra of metal-carboxylic acid complexes.

Lewis and Wilkins (14) state that certain general facts have been established which form a basis for the interpretation of the spectra

of complexes of ligands containing carboxyl groups or amino acids. Monomeric carboxylic acids have a strong carbonyl (C=O) absorption near $1770-1720\text{ cm}^{-1}$, whereas the dimers formed by hydrogen bonding absorb at somewhat lower frequencies ($1740-1690\text{ cm}^{-1}$). Salts of carboxylic acids have no strong bands in this region, but rather have strong bands around $1620-1550\text{ cm}^{-1}$ because the C=O bond orders become equal in RCO_2^- by resonance, and the strong band in the region $1620-1550\text{ cm}^{-1}$ is assigned to the asymmetric stretching mode of the CO_2^- group. There is evidence that the symmetric stretching mode absorbs between $1400-1300\text{ cm}^{-1}$. Similarly, there are strong bands near 2980 and 2860 cm^{-1} instead of bands at 2650 cm^{-1} from -CH- stretching. For example, Nakamoto, et al (19-20), and Paulsen (21) state that the free acetate ion of acetate complexes has 15 infra-red active fundamentals; among those, the vibrations due to the most characteristic COO^- group are assym. C-O stretching (1576 cm^{-1}). A characteristic but less useful band from C-O group stretching (1425 cm^{-1}) and four additional absorptions bands which may be due to CO_2 bending, CO_2 out-of-plane bending and CO_2 rocking modes are $1250-1290\text{ cm}^{-1}$; $1000-1050\text{ cm}^{-1}$; $900-990\text{ cm}^{-1}$; $810-885\text{ cm}^{-1}$ are present also. Table 1 gives the frequencies of CO stretching modes which can be assigned with certainty. The separation of asymmetric C=O and symmetric C=O stretching in the complex is smaller than in the free carboxylate ions.

Table 1. The stretching frequencies of acetato and oxylato complexes of nickel(II)

	Assym. (C=O)	Sym. (C=O)	Separation
Free CH_3COO^- ion	1578	1425	153
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	1530	1418	112
Free OX^{2-} ion	1664	1335	329
K_2NiOX_2	1620	1316	304

This fact is expected, however; as the two C-O bands become less equal the separation of the two C-O stretching increases whereas the bands between free ion and complex will shift to lower frequencies.

4. pH dependence of the reactions.

It was shown by Hausman, Grasso, and Pond (3) in their investigation of palladium(II) diacetate that coordinating capacity is greatly reduced in strongly acid solutions, that is below a pH of 3.0 for cycloalkanecarboxylic acid. Above a pH of 6.5 $\text{Pd}(\text{OH})(\text{OOCR}^*)$ and $\text{Ni}(\text{OH})(\text{OOCR}^*)$ are formed. Optimum conditions are thus at a pH of about 3.5 to 4. Since the chelating agents attack in the anion form, it is evident that chelation is favored over hydroxyl ions for the coordination positions about the metal ion.

Chapter III

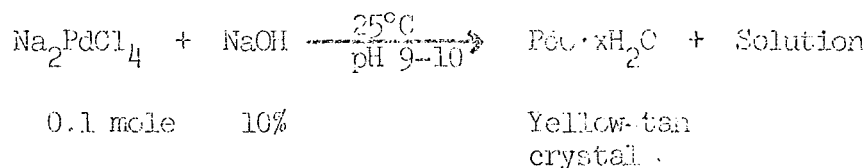
Experimental

Microanalyses were made by the SCHWARZKOPF MICROANALYTICAL LABORATORY, Woodside, NY; melting points of the complexes were determined in a Thomas-Hoover capillary melting point apparatus. Infra-red spectra were obtained on a Perkin-Elmer model 337 using KBr tablets, and UV spectra were prepared using a Perkin-Elmer model 202 spectrophotometer and stoppered silica cells of path length 1.00 ± 0.01 cm at room temperature (approximately 25°C). Reagents were obtained as follows: sodium tetrachloropallate from ALFA Inorganics, Beverly, Mass., nickelous chloride from Allied General Chemical Company, New York, NY, cycloalkanecarboxylic acids containing 3,4, 5, 6, and 7 carbons from Pfaltz and Bauer Inc., Flushing, NY, dimethylformamide and methanol from J.T. Baker Chemical Co., Phillipsburg, NJ. All were of reagent grade quality.

1. The preparation of intermediates.

A. Hydrous palladium Oxide (HPdO):

The hydrous palladium oxide was prepared according to the method of Hausman, Grasso, and Pond (3).



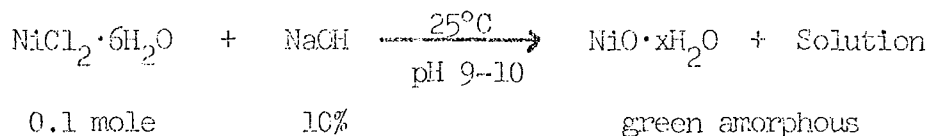
0.1 mole (0.147 grams) of disodium tetrachloropalladate(II) was dissolved in 3 ml of distilled water and placed in a 25 ml vial.

To the solution 0.45 ml of 10% aqueous sodium hydroxide was added at room temperature causing complete precipitation of HPdO. The precipitate was washed by decanting 5 times with 25 ml of water, filtered and dried at 70°C. The cake weighed approx. 0.1275 grams. Characterization of the yellow-tan crystals of $\text{PdO} \cdot x\text{H}_2\text{O}$ was partially accomplished by hydrogen and oxygen analysis:

	<u>$\text{PdO} \cdot x\text{H}_2\text{O}$</u>	
	Theoretical	Reported
1. Oxygen	22.5%	21.12%
2. Hydrogen	2.82%	2.09%

Data are poor for oxygen and hydrogen because $\text{PdO} \cdot x\text{H}_2\text{O}$ is sensitive to air, time, and temperature as indicated by Pond et al (3). The $\text{PdO} \cdot x\text{H}_2\text{O}$ decomposes to PdO and H_2O which evaporates gradually on standing. The IR spectrum shows there is no strong COO^- band near $1550\text{--}1620 \text{ cm}^{-1}$ (14)(19). Instead, the O-H stretching band of $3000\text{--}3700 \text{ cm}^{-1}$ is broadened.

B. Hydrus nickel oxide (modification of the above).



0.1 mole (0.475 grams) of nickel chloride was dissolved in 2 ml of distilled water in a 25 ml beaker. To the solution 0.60 ml of 10% sodium hydroxide solution was added at room temperature causing complete precipitation of NiO . The precipitate was washed by decanting 5 times with 25 ml of water, filtered, and dried at 70°C;

the cake weighed 0.1168 grams. Characterization of the green amorphous $\text{NiO} \cdot 2\text{H}_2\text{O}$ was partially accomplished by hydrogen and oxygen analysis:

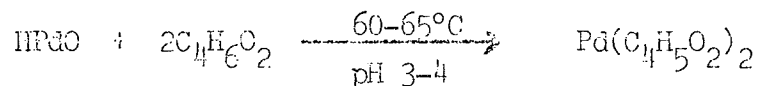
	$\text{NiO} \cdot 2\text{H}_2\text{O}$	
	Theoretical	Reported
1. Oxygen	50.5%	49.98%
2. Hydrogen	3.10%	3.02%

The IR spectrum presented later in this study showed a broadened band in $3000\text{-}3700\text{ cm}^{-1}$ for -OH- stretching and no strong band of C=O around $1500\text{-}1700\text{ cm}^{-1}$ (14, 19).

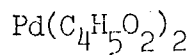
2. Synthesis of the Chelates.

I. Palladium complex preparation

a. Biscyclopropanecarboxylatopalladium(II)



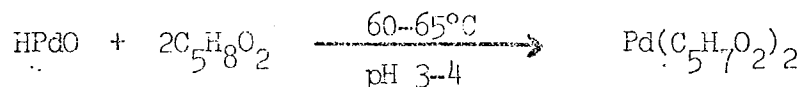
0.1275 grams of hydrous palladium oxide were placed in a 25 ml standard taper Florence flask fitted with a reflux condenser. Two moles (or 1.8 ml 100%) of cyclopropanecarboxylic acid was added and nitrogen was passed through the flask, ($60\text{-}65^\circ\text{C}$). The mixture was refluxed for one hour; during this period the solution color changed slowly from yellow-tan to deep green. Green solid was obtained by using water and a micro-porous filter to remove any unreacted cyclopropanecarboxylic acid; it was dried at room temperature under a nitrogen stream. The yield is approximately 0.19962 grams; characterization of the green product was partially accomplished by carbon-hydrogen analysis:



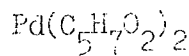
	Theoretical	Reported
1. Carbon	34.33%	33.95%
2. Hydrogen	3.61%	3.66%

The decomposition point was 164°C; the IR spectrum indicated the C=O band had been shifted from 1720 to 1620 cm^{-1} , (14, 19, 20, and 23), and the -CH- bands from 2650 cm^{-1} to 2860 and 2980 cm^{-1} . The UV spectrum showed a maximum at 278 nm and a minimum at 275 nm in DMF; the ligand has a maximum at 272 nm.

b. Biscyclobutanecarboxylatopalladium(II)



This complex was obtained in virtually quantitative yield in a similar way by refluxing 1.98 ml (or 2.0 moles) of cyclobutanecarboxylic acid and 0.1274 hydrous palladium oxide under nitrogen for 1.5 hours. After completion of the reaction and cooling, the precipitate was washed with 10 ml 2-Bromobutane. The yield is approximately 0.02495 grams; product had a decomposition temperature of 178°C. The IR spectrum shows the C=O band shifted from 1720 to 1580 cm^{-1} and -CH- bands from 2650 to 2950 and 2850 cm^{-1} . The UV maximum was 277 nm in DMF; the ligand has a UV maxima at 274 nm. Carbon-hydrogen data are as follows:



	Theoretical	Reported
1. Carbon	39.42%	38.95%
2. Hydrogen	4.59%	4.51%

c. Biscyclopentanecarboxylatopalladium(II)

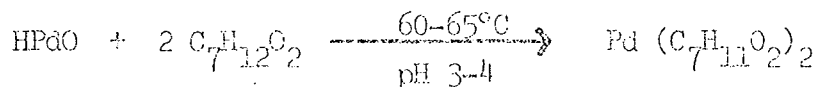


This complex was obtained in a similar manner by reacting 0.1285 grams of HPdO and 2.0 moles (or 2.3 ml) of cyclopentanecarboxylic acid under nitrogen gas for 45 minutes at 60-65°C. After cooling the product was washed with petroleum ether (30-60°C range) and dried at room temperature under nitrogen for 5 minutes; decomposition temperature was 192°C and yield was 0.05218 grams. The IR spectrum indicated the C=O band shifted from 1720 to 1620 cm^{-1} (14, 19, 20, and 23), and the -CH- stretching bands from 2650 to 2950 and 2860 cm^{-1} . The UV spectrum shows a maximum at 304 nm in DMF, the ligand has a maximum at 275 nm. Carbon-hydrogen data are as follows:

	<u>Pd (C₆H₉O₂)₂</u>	
	Theoretical	Reported
1. Carbon	43.3 %	43.71%
2. Hydrogen	5.4%	6.03%

The percentages of hydrogen and carbon were rather higher than the theoretical values indicating that there were small amounts of impurities in the sample.

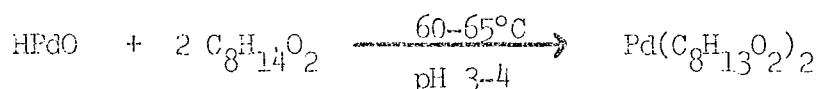
d. Biscyclohexanecarboxylatopalladium(II)



This complex was obtained in virtually quantitative yield in a similar way by reacting 2.0 moles (or 1.28 gram) of cyclohexanecarboxylic acid with 0.1272 grams of HPdO under nitrogen for 3 hours at pH 3-4. After the completion of the reaction, the product was cooled and washed with 10 ml ether. The yield was approximately 0.05012 grams; the deep green crystals decomposed at 196°C. The IR spectrum showed the C=O band shifted from 1720 to 1600 cm^{-1} , and the -CH- band shifted from 2680 cm^{-1} to 2950 and 2860 cm^{-1} . The UV spectrum showed a maximum at 281 nm and a minimum at 277 nm; the ligand itself has a maximum at 280 nm and a minimum at 275 nm in DMF. Carbon-hydrogen data are as follows:

	<u>Pd (C₇H₁₁O₂)₂</u>	
	Theoretical	Reported
1. Carbon	46.6 %	46.62%
2. Hydrogen	6.1 %	6.04%

e. Biscycloheptanecarboxylatopalladium(II)



This complex was obtained in virtually quantitative yield under conditions specified in (d). 1.42 grams (or 2.0 moles) of cycloheptanecarboxylic acid and 0.1269 grams of HPdO were reacted under nitrogen at pH 3-4. After 3 hours, the reaction was complete; product was cooled and washed with 10 ml 2-Bromobutane and dried at 50°C; yield was 0.02554 grams. The decomposition temperature was 191°C. The IR spectrum indicated the C=O band had been shifted from 1720 to 1600 cm^{-1} ;

the -CH- stretch band was shifted from 2680 to 2925 and 2860 cm^{-1} . The UV spectrum showed a maximum at 278 nm in DMF; the ligand had a maximum at 282 nm and a minimum at 257 nm. Characterization by carbon-hydrogen analysis is as follows:

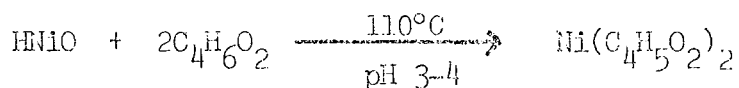
	<u>$\text{Pd}(\text{C}_8\text{H}_{13}\text{O}_2)_2$</u>	
	Theoretical	Reported
1. Carbon	49.5 %	49.53%
2. Hydrogen	6.7 %	7.32%

The percentage of hydrogen was rather higher than the theoretical value because the sample could not be completely dried without some decomposition.

II. Preparation of the Nickel Complexes

The method of preparation of the nickel(II) complexes of cycloalkancarboxylic acids which contain 3, 4, 5, 6, and 7 carbons employed here was similar to that used by Hausman, Grassom and Pond (3) in preparing palladium(II) acetic acids.

a. Preparation of Biscyclopropanecarboxylatonickel(II)



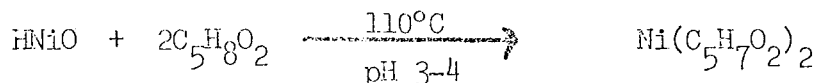
0.1168 grams of hydrous nickel oxide was placed in a 25 ml standard taper Florence flask. This was fitted with a reflux condenser and 0.4 moles (or 0.70 ml) of cyclopropanecarboxylic acid was added; the mixture was refluxed for 4 hours at a temperature of 110°C. During this period the solution color changed slowly from green to yellowish green. After the flask had cooled to room temperature,

30 ml of diethyl ether was added and the whole was put into the refrigerator overnight. The pale yellowish green solution was filtered and recovered crystals were dried at 70°C; yield was 0.1491 grams.

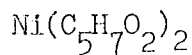
Decomposition temperature of this compound was 324°C. The IR spectrum showed maxima at 2980 and 2950 cm^{-1} for the -CH- stretch instead of 2650 cm^{-1} ; the C=O band had shifted from 1720 to 1580 cm^{-1} . The UV spectrum showed a maximum at 204 nm in methanol, whereas the ligand had a maximum at 222 nm. Carbon-hydrogen data are as follows:

	$\text{Ni}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 1/2 \text{H}_2\text{O}$	
	Theoretical	Reported
1. Carbon	40.38%	40.47%
2. Hydrogen	4.62%	4.70%

b. Preparation of Discyclobutanecarboxylatonickel(II)

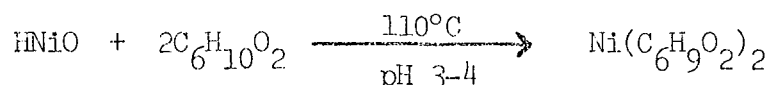


This complex was prepared in the same way as (a), but with an excess of cyclobutanecarboxylic acid (1.21 grams) and more than 1 hour of reaction. Yellowish green crystals with a m.p. at 320°C (decomposition) were obtained; yield was 0.06629 grams. The IR spectrum indicated -CH- stretching bands at 2980 and 2860 cm^{-1} instead of 2650 cm^{-1} , and the C=O band had shifted from 1720 to 1550 cm^{-1} . The UV spectrum showed a maximum at 205 nm instead of 219 nm for the ligand in methanol. Characterization by carbon-hydrogen is as follows:

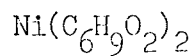


	Theoretical	Reported
1. Carbon	46.7 %	46.09%
2. Hydrogen	5.4 %	5.54%

c. Preparation of Biscyclopentanecarboxylatonickel(II)

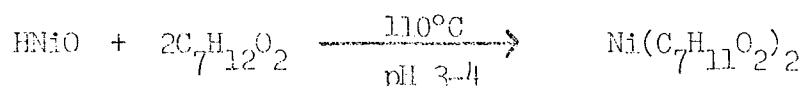


1.4 ml (or 0.4 moles) of cyclopentanecarboxylic acid was added to 0.1178 grams of HNiO at 110°C (pH 3-4) and refluxed for 4 hours. The yellowish green precipitate formed immediately. The product was filtered off after adding 30 ml ether at room temperature and storage in refrigerator overnight. The yield was 0.0526 grams. The melting point (decomposition) was 311°C. The IR spectrum showed 2950 and 2850 cm^{-1} for -CH- stretching instead of 2650 cm^{-1} , and the C=O band shifted from 1720 to 1550 cm^{-1} . The UV spectrum showed maximum at 203 nm instead of 221 nm for the ligand in methanol. Carbon-hydrogen data are as follows:



	Theoretical	Reported
1. Carbon	50.5 %	49.81%
2. Hydrogen	6.3 %	6.27%

d. Preparation of Biscyclohexanecarboxylatonickel(II)

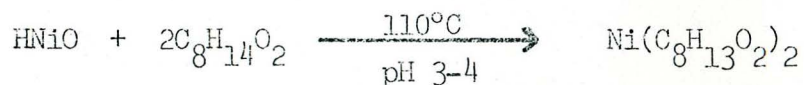


1.5 grams (or 0.4 moles) of cyclohexanecarboxylic acid was pre-heated until it was melted, and was then added to 0.1175 grams of

HNiO in a reaction flask at 110°C and pH 3-4 and refluxed for 6 hours. The yellowish green precipitate was filtered off by adding ether at room temperature and allowing the mixture to stand in the refrigerator overnight. Yield was 0.16325 grams; m.p. was 325°C (decomposition). The IR spectrum indicated that the stretching -CH- band shifted from 2650 to 2925 and 2850 cm^{-1} , and the C=O band shifted from 1720 to 1550 cm^{-1} . The UV spectrum exhibited maximum at 207 nm instead of at 223 nm for the ligand in methanol. Carbon-hydrogen are as follows:

	$\text{Ni}(\text{C}_7\text{H}_{11}\text{O}_2)_2$	
	Theoretical	Reported
1. Carbon	53.7 %	53.12%
2. Hydrogen	7.03%	7.06%

e. Preparation of Biscycloheptanecarboxylatonickel(II)



1.6 ml (or 0.4 moles) of cycloheptanecarboxylic acid was added to 0.1167 grams of HNiO and reacted for 4 hours. The yellowish green precipitate was filtered off by adding 30 ml ether (or Petroleum ether; 30-60°C) at room temperature and allowing the mixture to stand in the refrigerator overnight. The crystals were dried at 70°C in an oven for 5-10 mins. Yield is approximately 0.05732 grams; m.p. was 305°C (decomposition). The IR spectrum indicated that the -CH- stretching band had shifted from 2650 to 2920 and 2850 cm^{-1} , and the C=O band shifted from 1720 to 1550 cm^{-1} . The UV spectrum showed a maximum at 205 nm instead of at 221 nm for the ligand in methanol.

Carbon-hydrogen data are as follows:

	<u>Ni(C₈H₁₃O₂)₂</u>	
	Theoretical	Reported
1. Carbon	56.4 %	55.95%
2. Hydrogen	7.62%	7.79%

Chapter IV

Spectra

Use of molecular spectra is a great aid in characterizing chelates and studying their configurations. Molecules can absorb radiation by making a transition from one energy state to another of higher energy. A molecular absorption spectrum can be obtained by passing radiation of a continuous spectrum, such as ultraviolet, visible, or infrared through the substance. The transitions may involve changes in electronic, vibrational and rotational energies.

The electrons in molecules may be in one of a number of possible energy states or levels. These energy levels are of very different energies and transitions from one level to an excited state of higher energy produce absorption in the UV region of the spectrum. The much smaller energy changes associated with the quantized vibrations of the nuclei about equilibrium positions in the molecule produce absorption in the infrared regions of wavelengths from approximately 1 to 25 microns. The energy associated with the rotation of the molecule about its center of gravity (or mass) is also quantized, but the quanta are very small, and the absorption produced by changes in rotations appears in the far infrared and radiomicrowave regions of very long wavelength.

A detailed analysis of the UV absorption spectra in Table II of molecules presents many difficulties and in this case very little can actually be ascertained from them except that the spectra of the

palladium(II) and nickel(II) complexes are sufficiently dissimilar from those of the ligands to indicate that coordination has taken place. Because of the slight solubility of inorganic salts in most nonaqueous solvents, relatively little attention has been paid in the past to the study of such solutions (24). Since the complexes of palladium(II) and nickel(II) in this study did not dissolve in most common solvents such as water, cyclohexane, chloroform, ether, esters, dioxane, acetonitrile, dichloromethane, alcohols (except methanol), benzene, heptane, xylene, CS_2 , CCl_4 , DMSO, glycerol, etc., the UV spectra presented here can't successfully be used in identifying the complexes because the complexes dissolve in methanol and dimethylformamide only in the concentration range to 2.0×10^{-4} M. Spectra are included in Figures 1-20 in Appendix III.

Even though these compounds do not have characteristic absorption spectra in the UV region, they have very detailed spectra in the infrared. This can be extremely useful as an identifying characteristic. Fortunately studies have been made which have led to cataloging of the IR Spectra of many compounds. Functional groups have been assigned characteristic absorption bands and one is able to determine the principal functional groups within the compound of interest and thereby identify it. However, while IR spectra are extremely useful in identification, they are not always conclusive evidence. Details of IR spectra of palladium and nickel complexes are summarized in Table III.

Table II

Ultraviolet Absorption Spectra of Palladium(II) complexes in
Dimethylformamide and Nickel(II) complexes in Methanol

	<u>Solvent</u>	<u>Maximum</u> (nm)	<u>Minimum</u> (nm)
Cyclopropanecarboxylic acid	DMF	272	----
Cyclobutanecarboxylic acid	DMF	274	----
Cyclopentanecarboxylic acid	DMF	276	----
Cyclohexanecarboxylic acid	DMF	280	275
Cycloheptanecarboxylic acid	DMF	282	257
Biscyclopropanecarboxylatopalladium(II)	DMF	278	275
Biscyclobutanecarboxylatopalladium(II)	DMF	277	----
Biscyclopentanecarboxylatopalladium(II)	DMF	304	278
Biscyclohexanecarboxylatopalladium(II)	DMF	281	277
Biscycloheptanecarboxylatopalladium(II)	DMF	278	----
Cyclopropanecarboxylic acid	MeOH	222	----
Cyclobutanecarboxylic acid	MeOH	219	----
Cyclopentanecarboxylic acid	MeOH	265	222
Cyclohexanecarboxylic acid	MeOH	224	201
Cycloheptanecarboxylic acid	MeOH	221	----
Biscyclopropanecarboxylatonickel(II)	MeOH	203	----
Biscyclobutanecarboxylatonickel(II)	MeOH	205	----
Biscyclopentanecarboxylatonickel(II)	MeOH	202	----
Biscyclohexanecarboxylatonickel(II)	MeOH	208	----
Biscycloheptanecarboxylatonickel(II)	MeOH	205	----

Table III

Infrared Absorption Spectra of Palladium(II) and Nickel(II) Complexes (cm⁻¹)

	-CH-	-CH-	RCCO- Assym.	-COO- Symm.	-COO- Deformation	-COO- Deformation	-CH- Cyclizing
C ₄ H ₆ O ₂	3500-2700	2580, 2650	1720	1450	1350	935	820
C ₅ H ₈ O ₂	3500-2720	2650	1720	1420	1350	930	920
C ₆ H ₁₀ O ₂	3500-2700	2650	1720	1425	1320	940	740
C ₇ H ₁₂ O ₂	3500-2700	2650	1720	1450	1300	950	890
C ₈ H ₁₄ O ₂	3500-2700	2650	1720	1450	1280	940	880
Pd(C ₄ H ₅ O ₂) ₂	3700-3100	3100, 3030	1620	1435	1320	952	750
Pd(C ₅ H ₇ O ₂) ₂	3700-3100	2950, 2850	1600	1385	1285	920	810
Pd(C ₆ H ₉ O ₂) ₂	3700-3100	2950, 2860	1600	1390	1310	945	770
Pd(C ₇ H ₁₁ O ₂) ₂	3700-3100	2940, 2860	1600	1400	1340	938	895
Pd(C ₈ H ₁₃ O ₂) ₂	3700-3100	2940, 2860	1600	1400	1340	960	890
Ni(C ₄ H ₅ O ₂) ₂	3700-3100	2950, 2850	1550	1420	1300	950	760
Ni(C ₅ H ₇ O ₂) ₂	3700-3100	2950, 2850	1550	1400	1300	928	910
Ni(C ₆ H ₉ O ₂) ₂	3700-3100	2950, 2850	1550	1405	1325	920	760
Ni(C ₇ H ₁₁ O ₂) ₂	3700-3100	2940, 2850	1550	1410	1350	925	900
Ni(C ₈ H ₁₃ O ₂) ₂	3700-3100	2940, 2850	1550	1420	1350	900	875
NiO·xH ₂ O	3700-5000	---	---	---	---	---	---
PdO·xH ₂ O	3700-5000	---	---	---	---	---	---

Chapter V Discussion

In this study, several things should be noted. Firstly, the percent of water contained in the HPdO intermediate is critical; it should be as low as possible, because the ligands have a tendency toward increased oiliness as the number of carbons increases. According to present research, 15-20% water content results in the desired products.

Secondly, the relative amount of $\text{PdO} \cdot x\text{H}_2\text{O}$ per millimole of individual ligand is also important; if a very large excess of cycloalkanecarboxylic acid is employed, crystallization will not occur because the desired salt is quite soluble in the acid. Generally, the HPdO containing 15-20% water is treated with from 10-20 millimoles cycloalkanecarboxylic acid per millimole of cake (HPdO) in the manner described. HNiO cake containing 10-20% water reacts best with 2-5 millimoles cycloalkanecarboxylic acid per millimole of cake (HNiO).

Thirdly, the reaction times of different compounds are quite variable among the five ligands. The completion of reaction was determined by the visual color change. The structure of cyclohexanecarboxylic acid and cyclobutanecarboxylic acid are quite stable, and more time is needed to complete the reaction at the same conditions of temperature and pH. These experiments show that complexes of palladium with cyclopentanecarboxylic acid change color in 25 minutes, cyclopropanecarboxylic acid in 30 minutes, cycloheptanecarboxylic acid in 45 minutes, cyclobutanecarboxylic acid in 1.5 hours, and cyclo-

hexanecarboxylic acid in 3 hours. Similarly with the complexes of nickel(II) and cycloalkanecarboxylic acids, the acids which contains 3, 5, and 7 carbons complete reaction in 4 hours, but cyclobutanecarboxylic acid requires 5 hours and cyclohexanecarboxylic acid, 6 hours.

Fourthly, the temperature of reaction between HNiO and ligands is critical; at temperature above 110°C (pH 3-4) HNiO will decompose to a polymeric black residue. Below 110°C , the reaction proceeds, but yellowish-orange crystals (Appendix II) are obtained instead of yellowish green crystals. (Results of carbon-hydrogen analyses indicate crystals have the formula $\text{Ni(OH)(cycloalkanecarboxylate ion)}$.) In a word, temperature and pH are the main factors determining whether reaction takes place or not.

Fifthly, the test for chloride ion in the intermediate HPdO and HNiO is important. Solutions of HPdO or HNiO treated with aqueous silver nitrate give no precipitate indicating the absence of chloride ion. This eliminates the possibility of a positive complex ion having been formed in place of the proposed neutral complex later in the synthesized of acid with HPdO and HNiO .

Sixthly, the most characteristic absorption frequencies in the infrared spectra of carboxylic acids and their salt are those due to the C=O stretch of the carboxyl group or the asymmetric C=O stretch of the carboxylate anion, these bands usually occur at $1750\text{-}1550\text{ cm}^{-1}$ (22-23).

In this study, the free cycloalkanecarboxylic acid spectra showed

the band at 1750-1720 cm^{-1} assigned to the asymmetric carboxylic group, the band at 1450 and 1328-1350 cm^{-1} assigned to symmetric C=O stretching (19-21), the broad bands between 2500-3500 cm^{-1} due to -O-H stretching (17), the bands at 940 cm^{-1} and 680 cm^{-1} were assigned to -COO- bending and rocking modes, and the weak bands at 2650 and 2580 cm^{-1} were attributed to -CH- stretching in the molecule.

When the carboxyl group was bonded to a metal ion, the absorptions were shifted to low frequencies. The metal-oxygen bond and the shift of bending and rocking frequencies are not simple to explain (19-20). In addition, Ballamy (24) stated that the C=O stretching modes at 1300-960 cm^{-1} are often difficult to recognize as this is a region of the spectrum where many other kinds of strong bands commonly occur; it is also very sensitive to changes in the mass and nature of the attached group.

The spectra of palladium(II) and nickel(II) complexes presented in this study indicate the following changes: the band at 1720 cm^{-1} has been shifted to 1620 cm^{-1} or 1550 cm^{-1} , the band at 1450 cm^{-1} and 1350 cm^{-1} shifted to 1420 and 1320 cm^{-1} or lower, the weak bands at 2650 cm^{-1} and 2580 cm^{-1} disappeared instead of showing two bands at 2850 and 2950 cm^{-1} indicating strong stretching of -CH- (17), and the band attributed to the hydroxyl group has been shifted from 3500-2700 cm^{-1} to 3700-3100 cm^{-1} . This latter is due to lattice water attached on the complexes. Thus, it is concluded that the carboxyl group was bonded to palladium(II) and nickel(II) to form the complexes.

Chapter VI

Summary

Palladium(II) and nickel(II) complexes of cycloalkanecarboxylic acid have been successfully synthesized, although considerable difficulty was encountered in the preparation of the palladium(II) complexes. The difficulty of preparation of each was correctly predicted by using structural data and the experience gained from previous similar preparations. No record was found in the literature of any of the preparations having been successfully attempted.

Sensitive pH adjustment was required to assure removal of chloride ion in the preparations of HPdO and HNiO; Optimum values were 9-10. The pH values should be maintained at 3-4 during reaction with ligand to avoid the formation of $\text{Pd}(\text{OH})(\text{OOCR}^*)$ or $\text{Ni}(\text{OH})(\text{OOCR}^*)$ in the preparation of complexes of palladium and nickel from HPdO and HNiO with cycloalkanecarboxylic acids which contain 3, 4, 5, 6, and 7 carbons.

The percentage of water contained in the cakes of HPdO and HNiO is critical. To avoid undesired products, it should not contain over 20% of water in the cake.

The temperature in the reaction flask containing metal salt and ligand should be kept constant; variable temperature will lead to black residues of palladium and nickel.

The complexes were characterized by correlating the theoretical and reported carbon and hydrogen elemental analyses, infrared spectra and ultraviolet spectra. These also aided in determining the structures which had already been theoretically predicted for the various chelates.

It is suggested by the writer that the ligands behave as bidentates in the case of the tetravalent species palladium(II) and nickel(II). Therefore, the structures of complexes are square planar rather than tetrahedral (1-9)

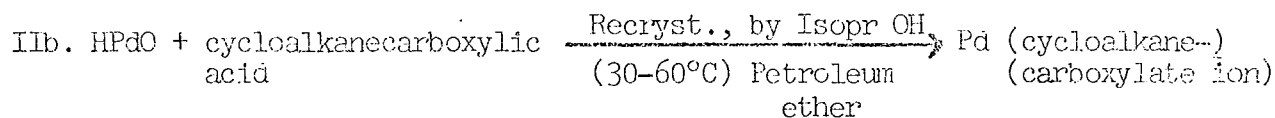
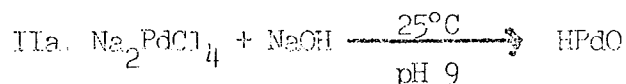
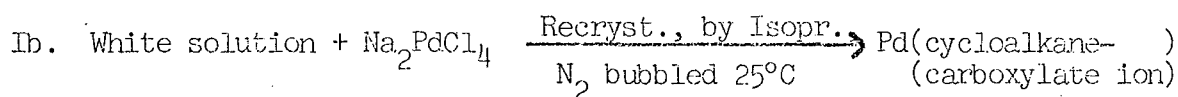
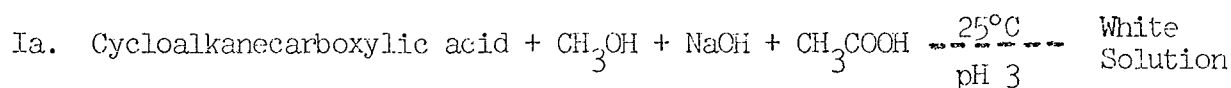
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Appendix I

Attempts to synthesize palladium(II) complexes of cycloalkane-carboxylic acid using the following methods were unsuccessful. The methods used in the attempted preparation weren't identical to those employed in the preparation of the other complexes. Although a reaction did occur, all attempts to recover complexes, if they did form, were unsuccessful.



Characterization by carbon-hydrogen analyses of the product indicated as follows:

For example, cyclopropanecarboxylic acid with Na_2PdCl_4

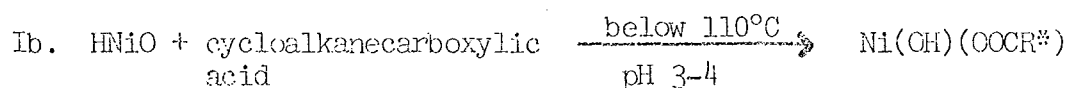
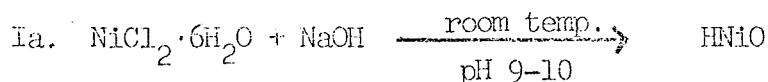
	I		II	
	Theoretical	Reported	Theoretical	Reported
1. Carbon	34.33%	4.42%	34.33%	11.05%
2. Hydrogen	3.61%	0.64%	3.61%	1.25%

The IR spectra show that there was a weak band at 1620 cm^{-1} and broadening of the band at $3500\text{-}3100 \text{ cm}^{-1}$. This is evidence that the

produced palladium(II) complexes depend not only on the temperature but also on the pH value. If temperature was raised, care was taken throughout the preparations to maintain a nitrogen atmosphere, otherwise it is easy to form polymeric black residue PdO_2 . The successful reaction will take place at the proper temperature of 60-65°C and time one to three hours.

Difficulties were encountered in the synthesis of nickel(II) complexes of cycloalkanecarboxylic acid. The reaction of metal ion and ligands in methyl alcohol at 64°C was impossible. Regardless the C=O peak in 1550 cm^{-1} of IR spectrum was still obtained, but they were not the desired salts because the results of carbon-hydrogen analyses were far from theoretical value.

The yellowish orange crystals were obtained, because the temperature was below 110°C in the processing.



For instance, cyclopentanecarboxylic acid with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, carbon-hydrogen data are as follows:

	Theoretical	Reported
1. carbon	38.4 %	38.09%
2. hydrogen	5.32%	4.21%

Although there was the C=O peak in 1550 cm^{-1} of IR spectrum, they were not the desired salts.

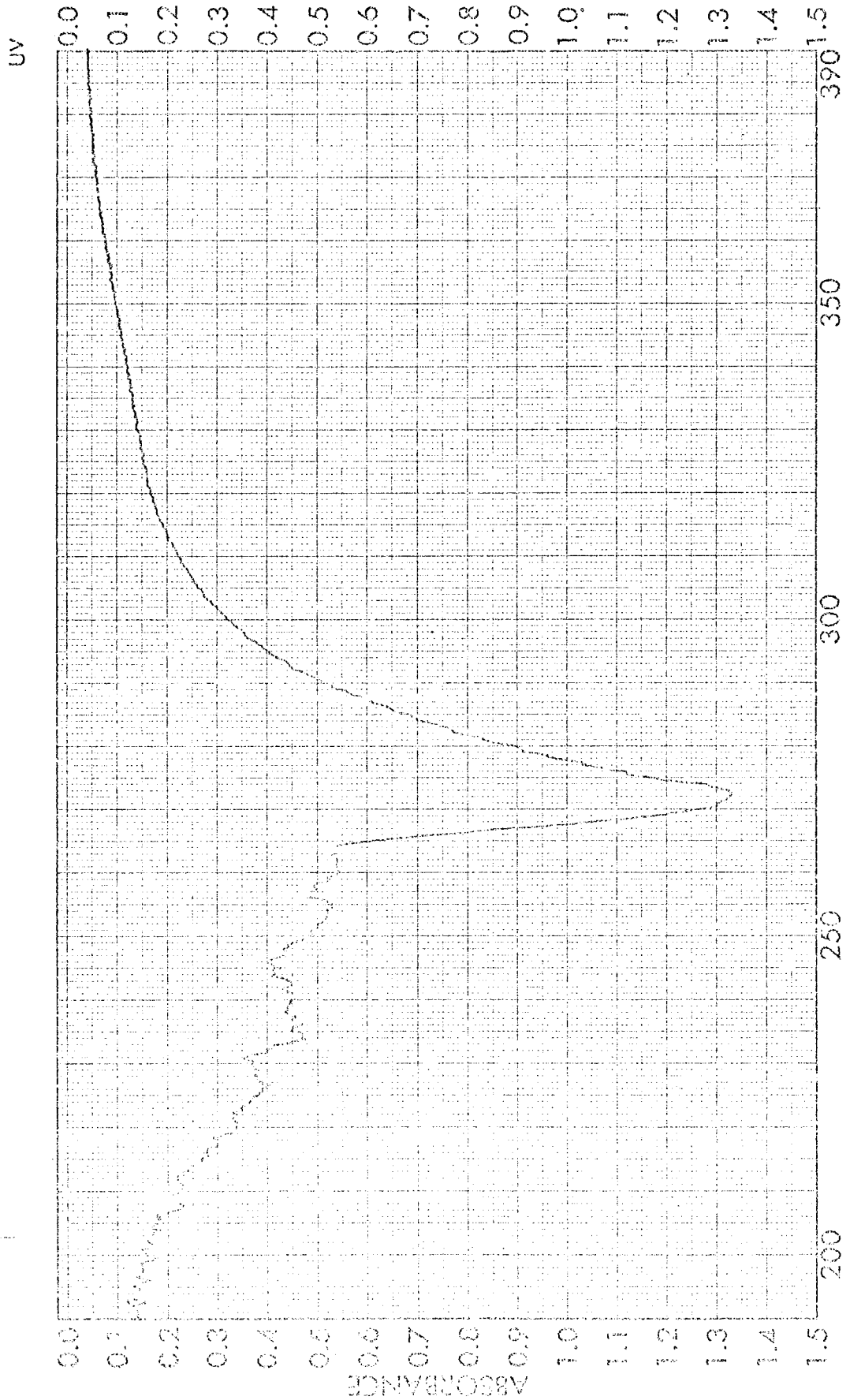
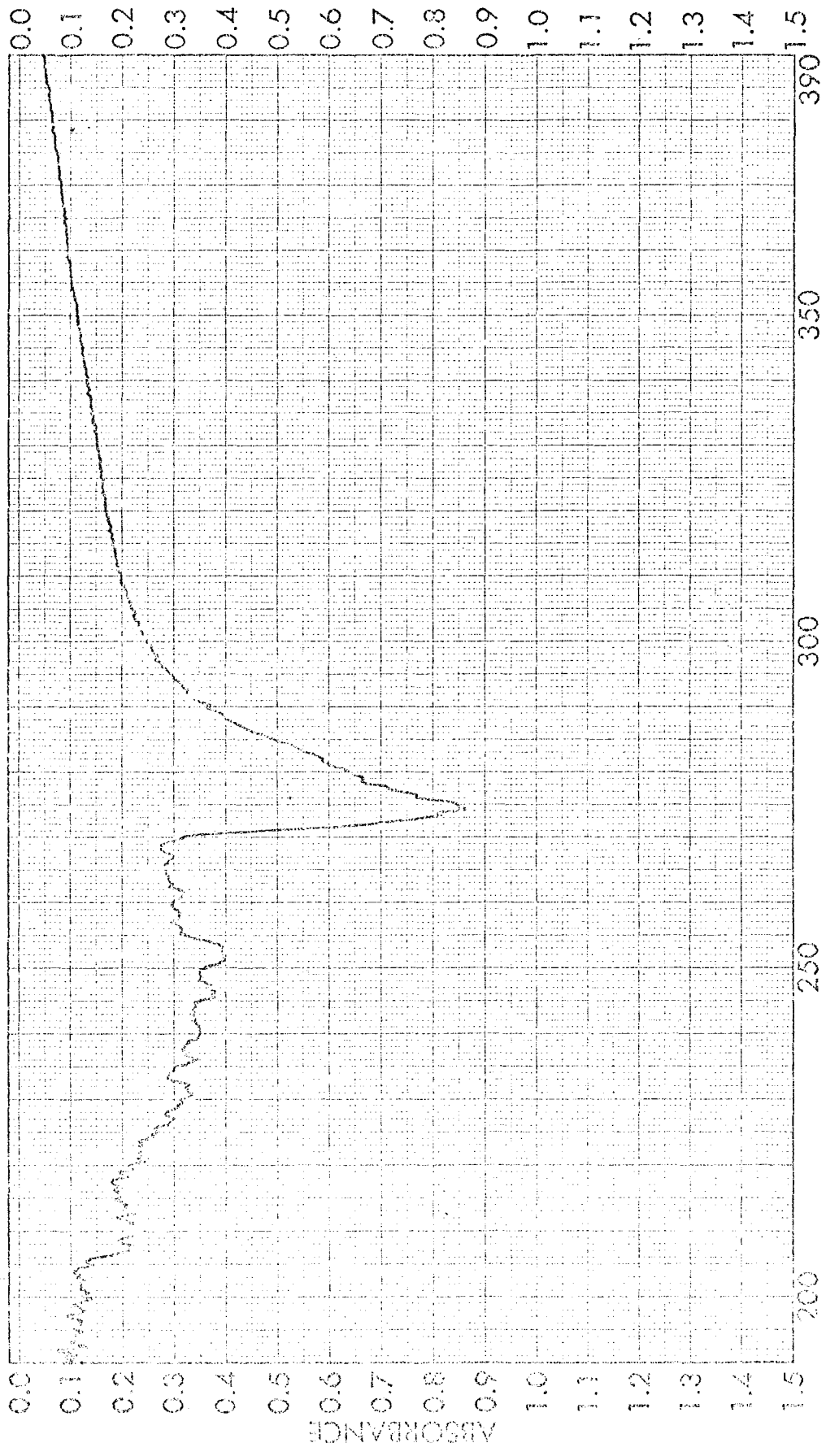


Figure 2. Cyclopropanecarboxylic acid in Dimethylformamide

UV



WAVELENGTH (MILLIMICRONS)

Figure 3. Cyclobutanecarboxylic acid in Dimethylformamide

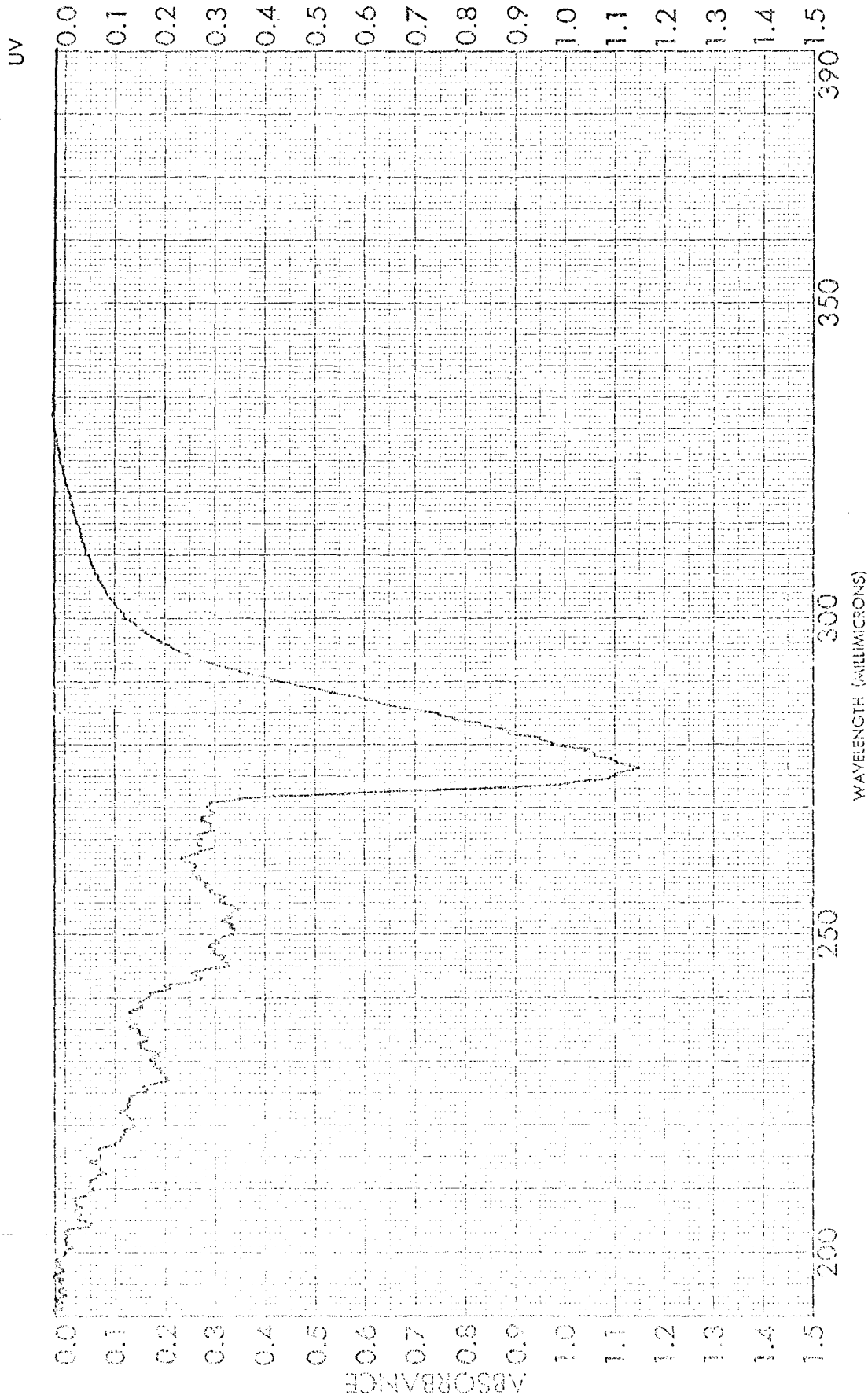


Figure. 4. Cyclopentanecarboxylic acid in Dimethylformamide

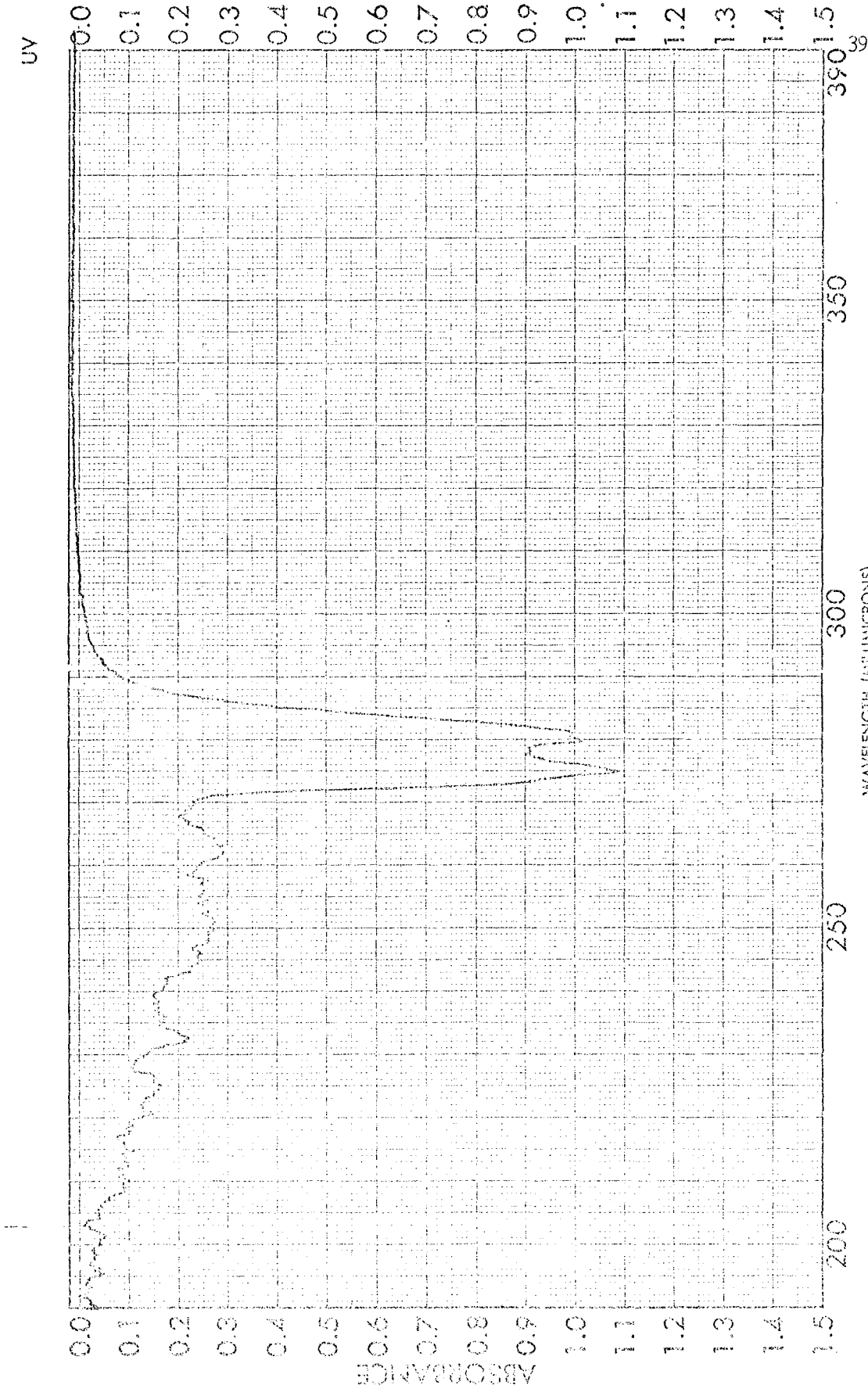


Figure 5. Cyclohexanecarboxylic acid in Dimethylformamide

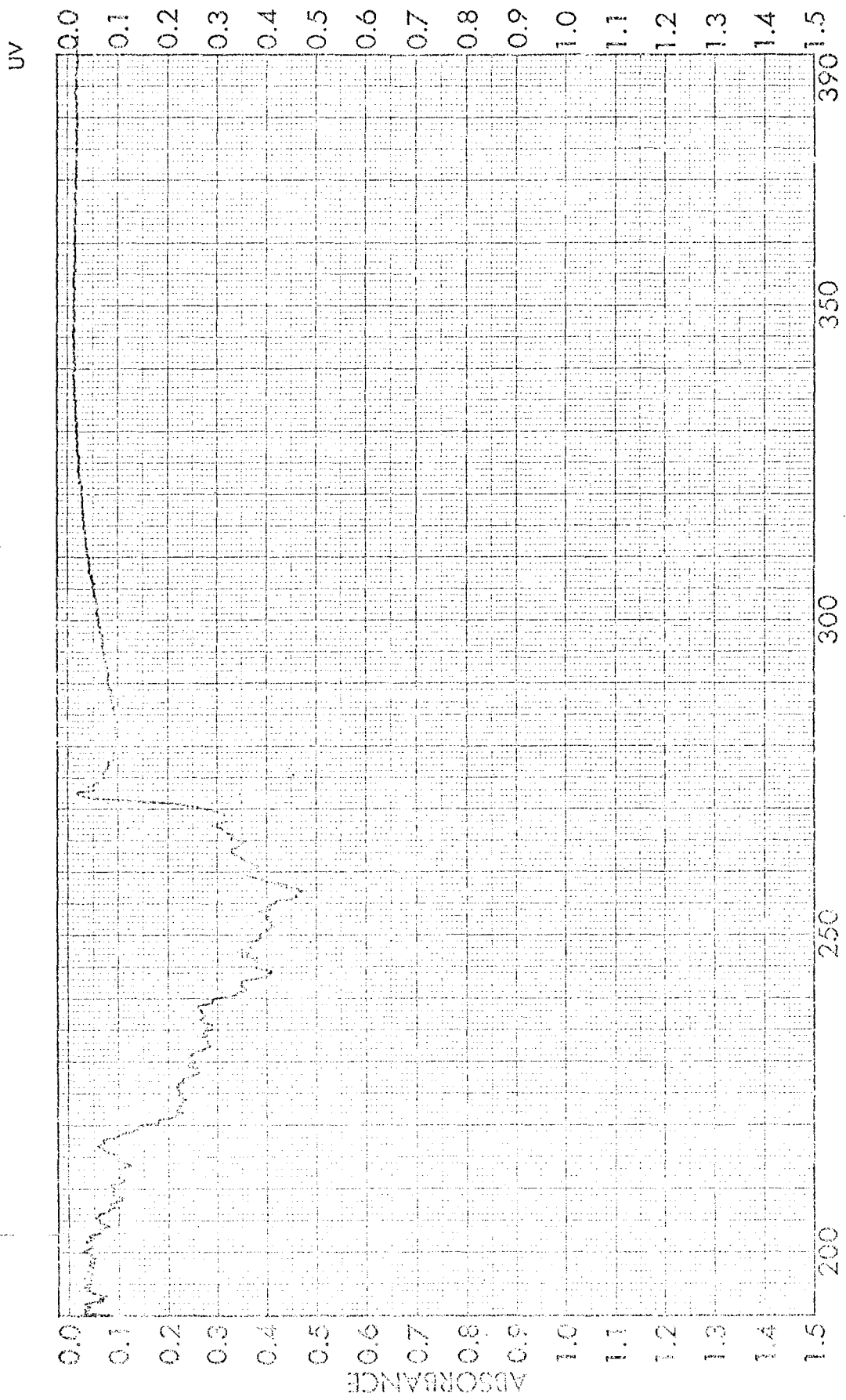


Figure 6. Cycloheptenecarboxylic acid in Dimethylformamide

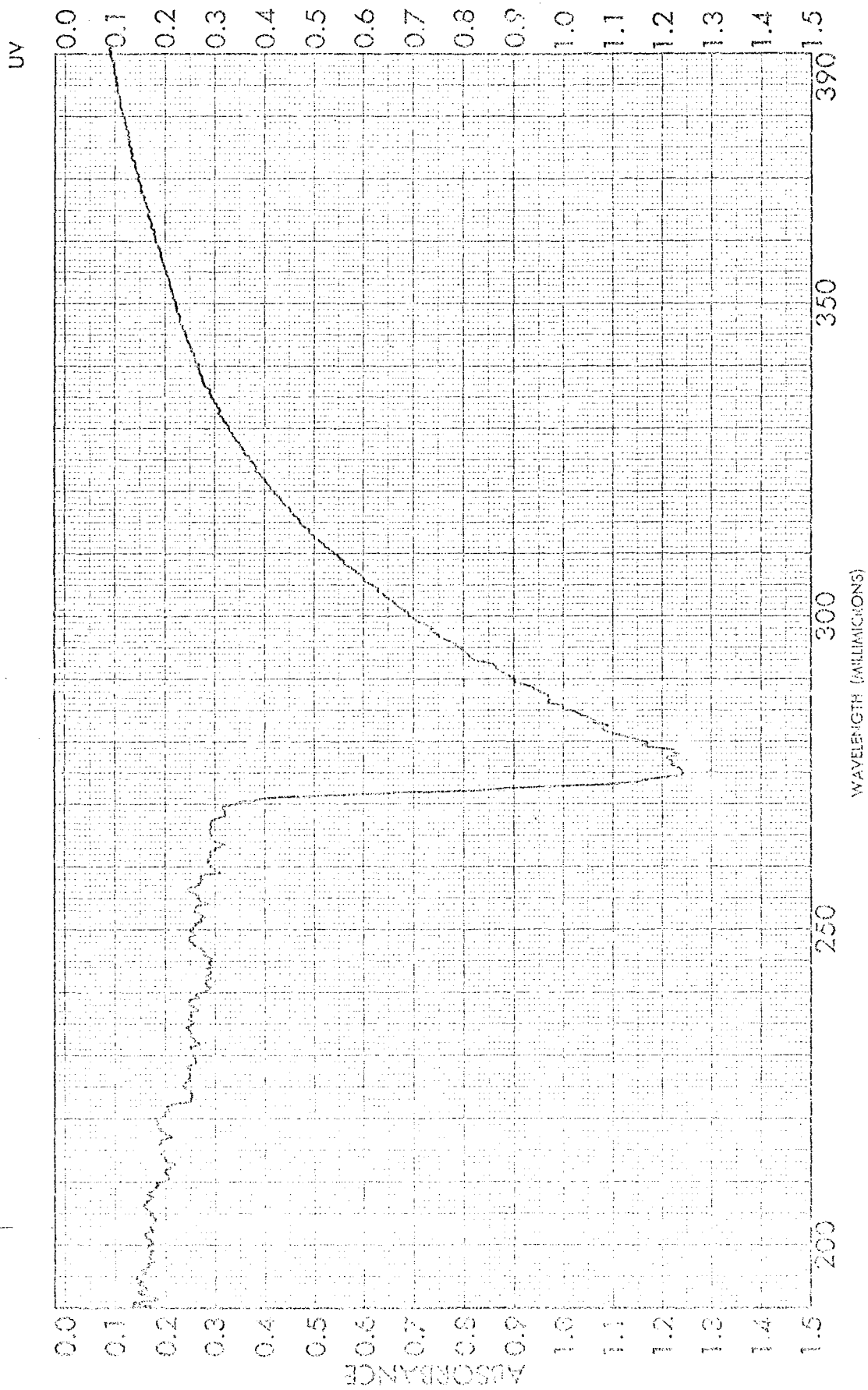


Figure 7. Biscyclopropanecarboxylatopalladium (II) in Dimethylformamide

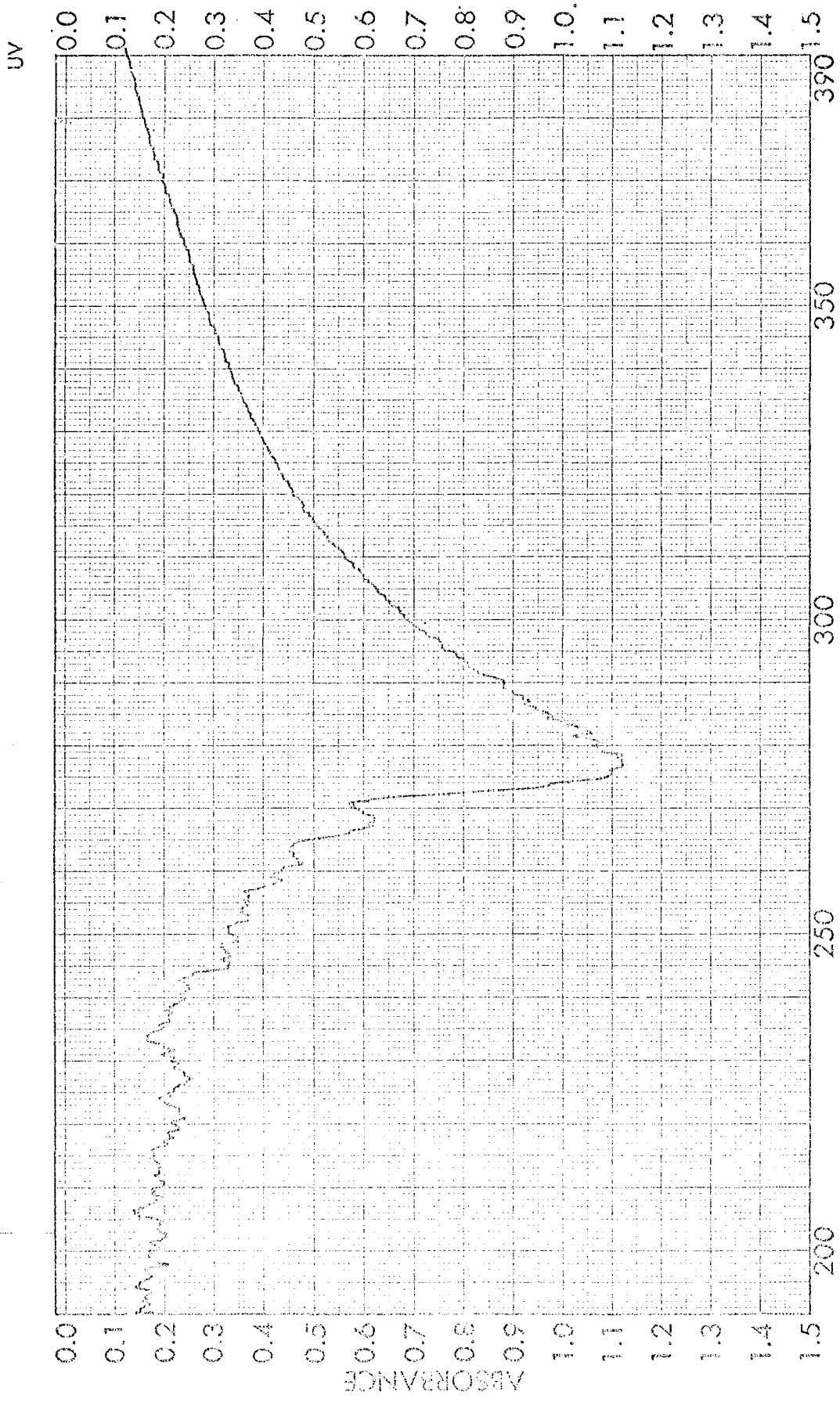


Figure 8. Bis(cyclobutanecarboxyleteopalladium (II)) in Dimethylformamide

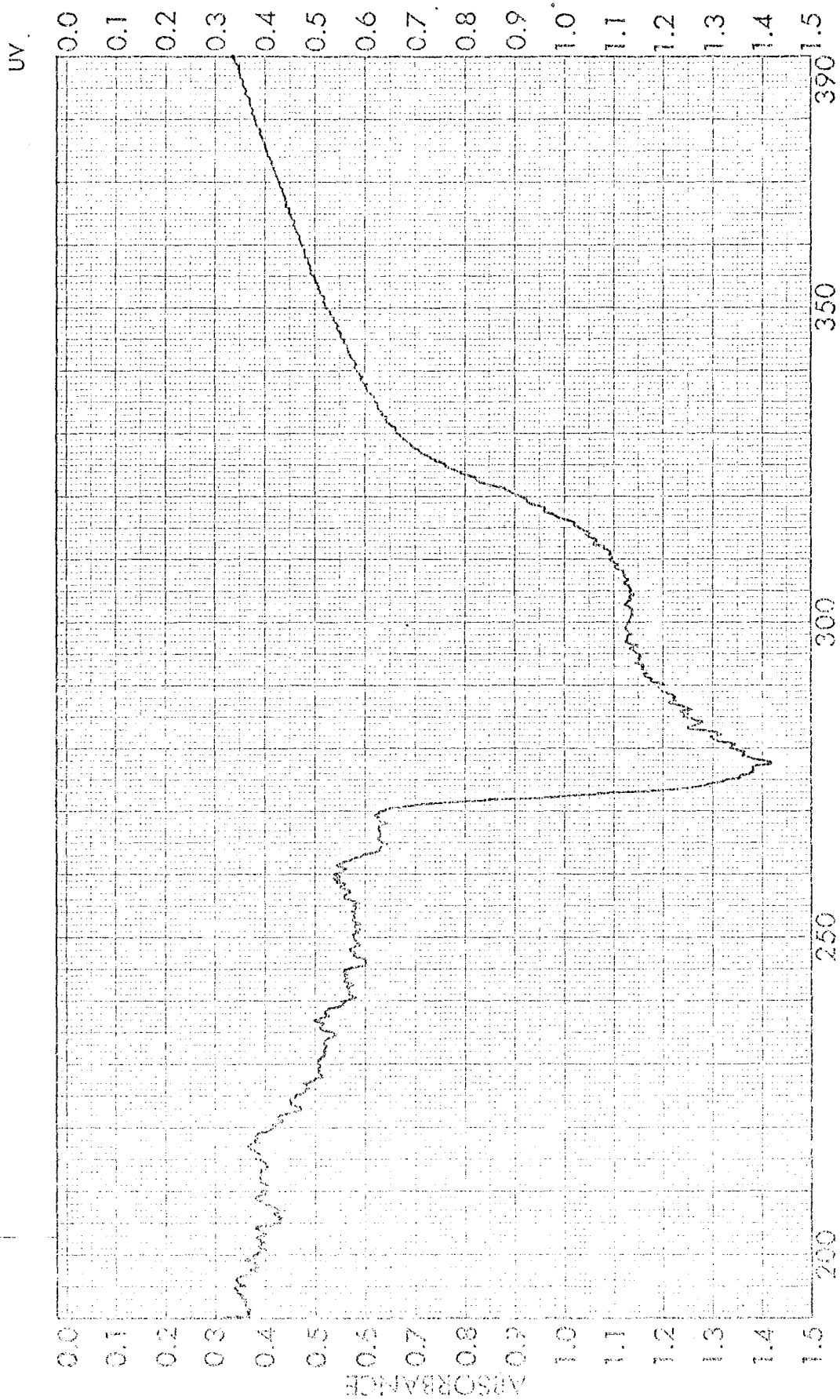


Figure 9. Biscyclorentenecarboxylatopalladium (II) in Dimethylformamide

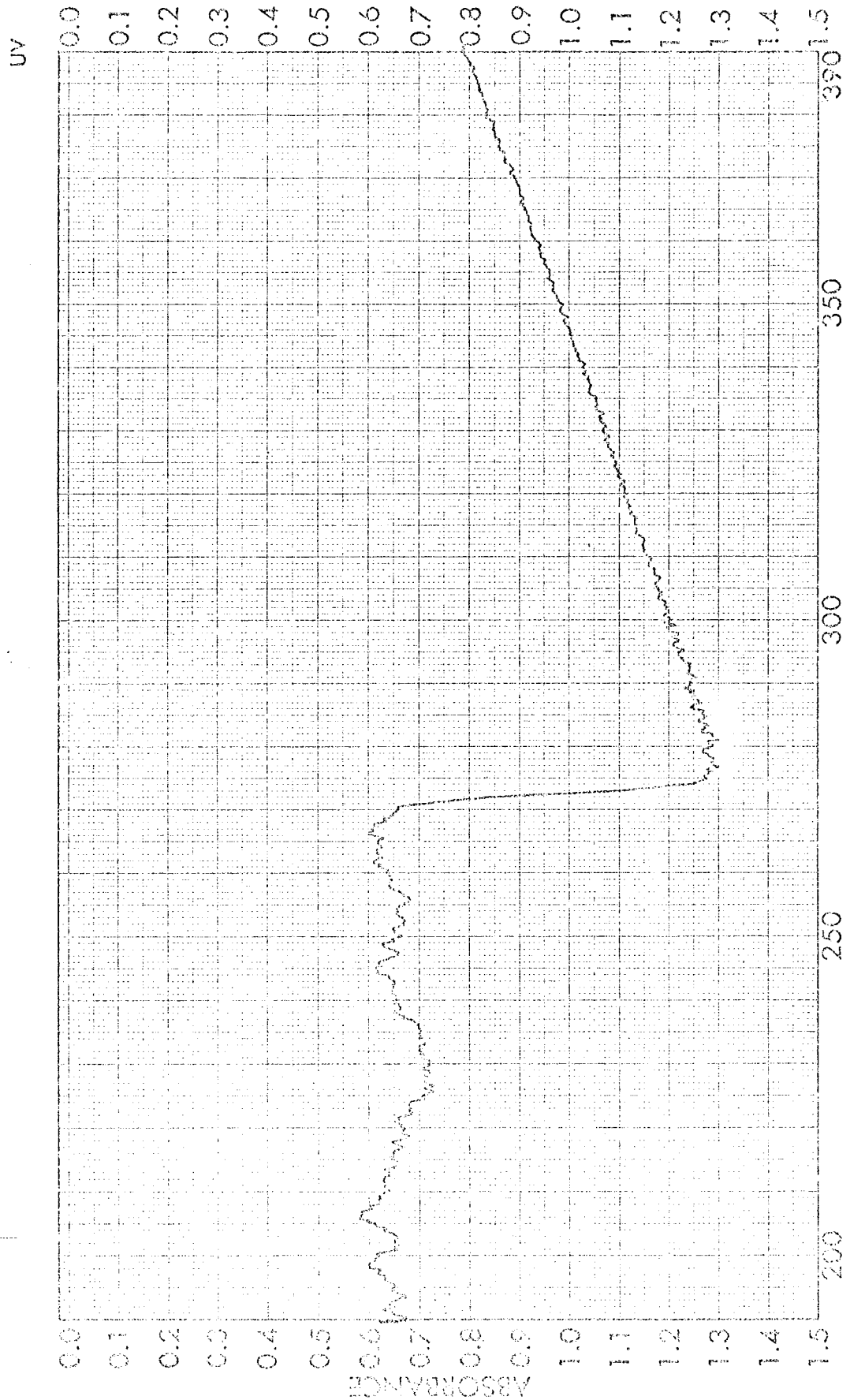


Figure 10. Biscyclohexanecarboxylatopelladium (II) in Dimethylformamide

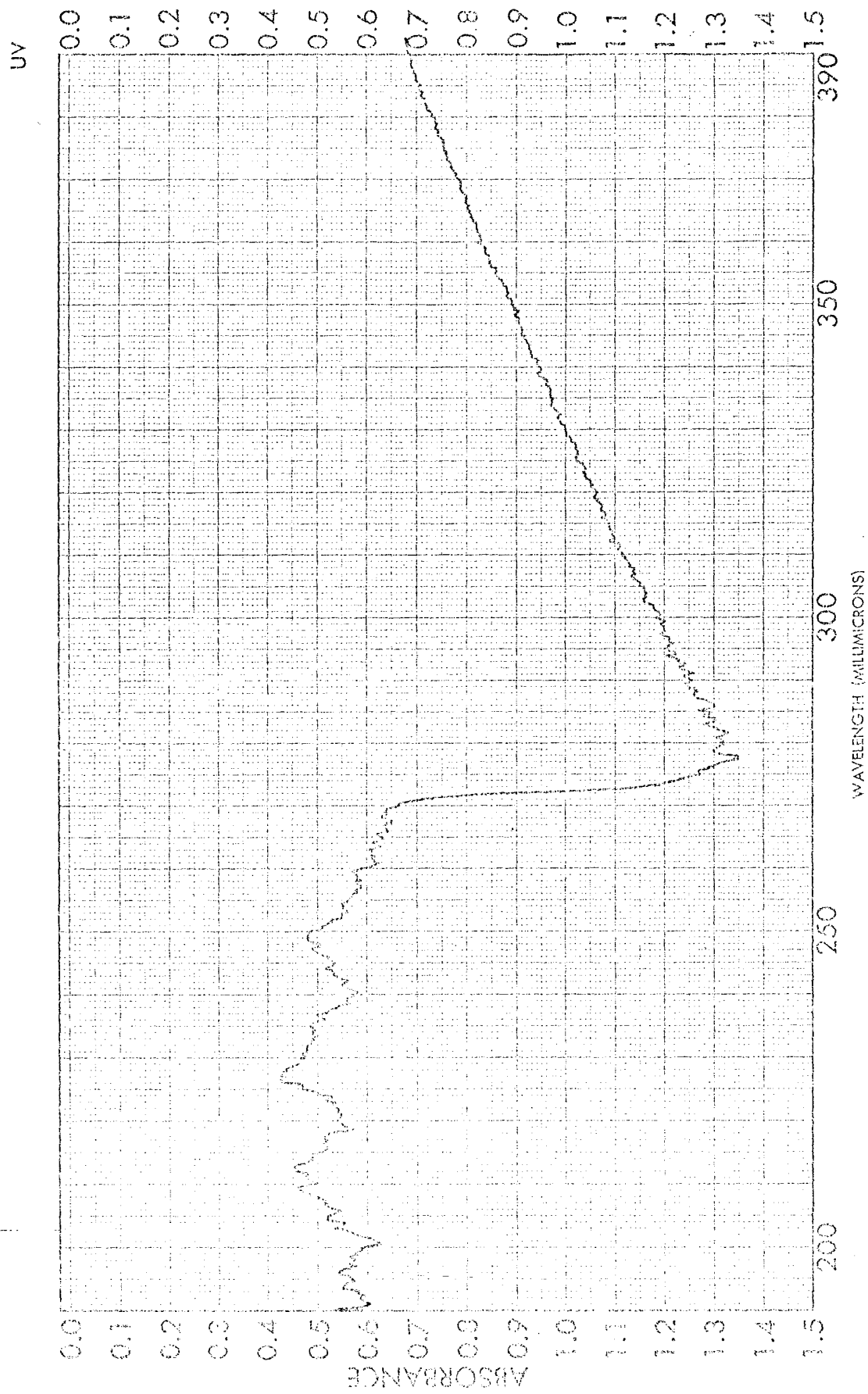


Figure 11. Biscycloheptanecarboxylatopalladium (II) in Dimethylformamide

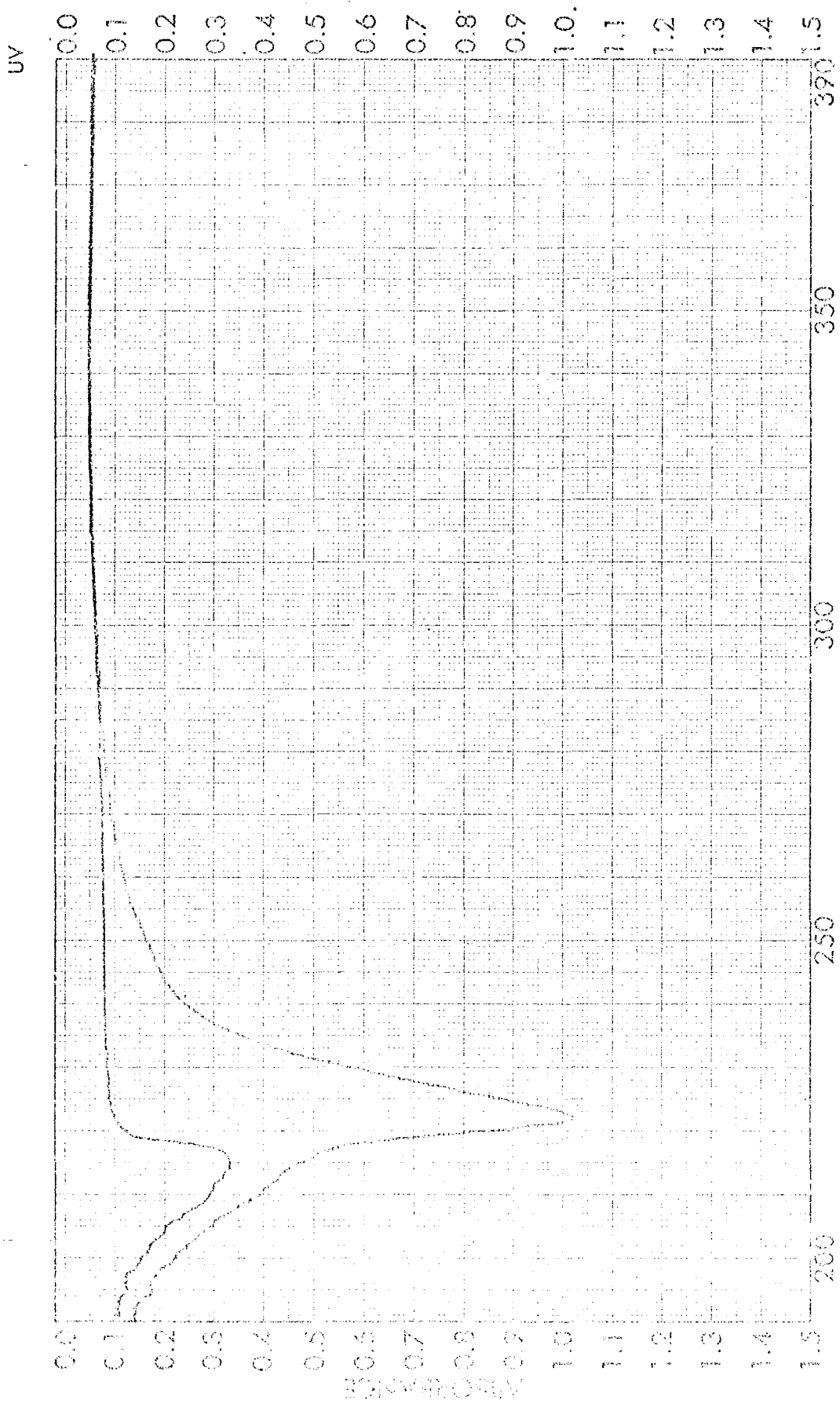


Figure 12. Cyclopropenecarboxylic acid in Methanol

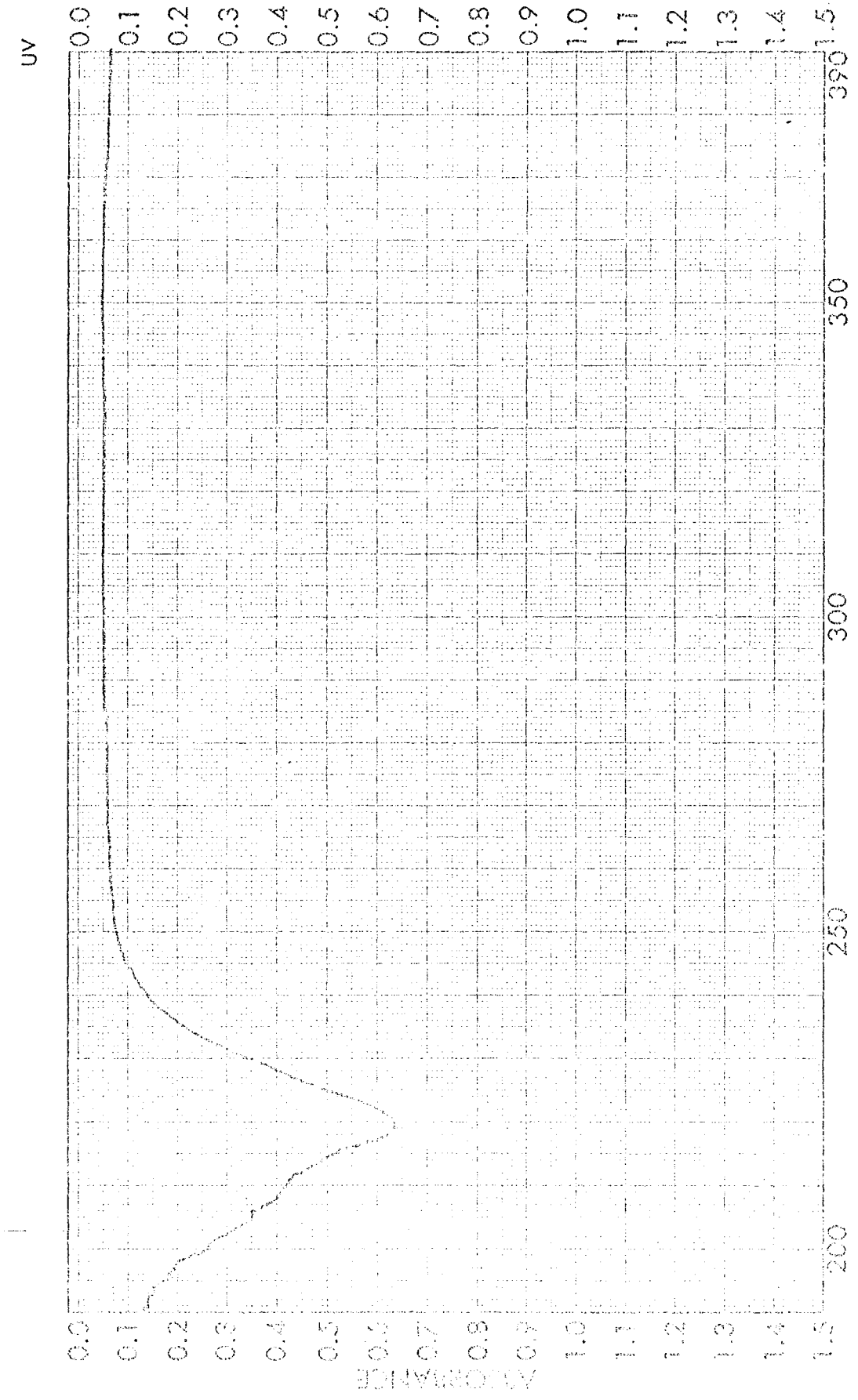


Figure 13. Cyclobutanecarboxylic acid in Methanol

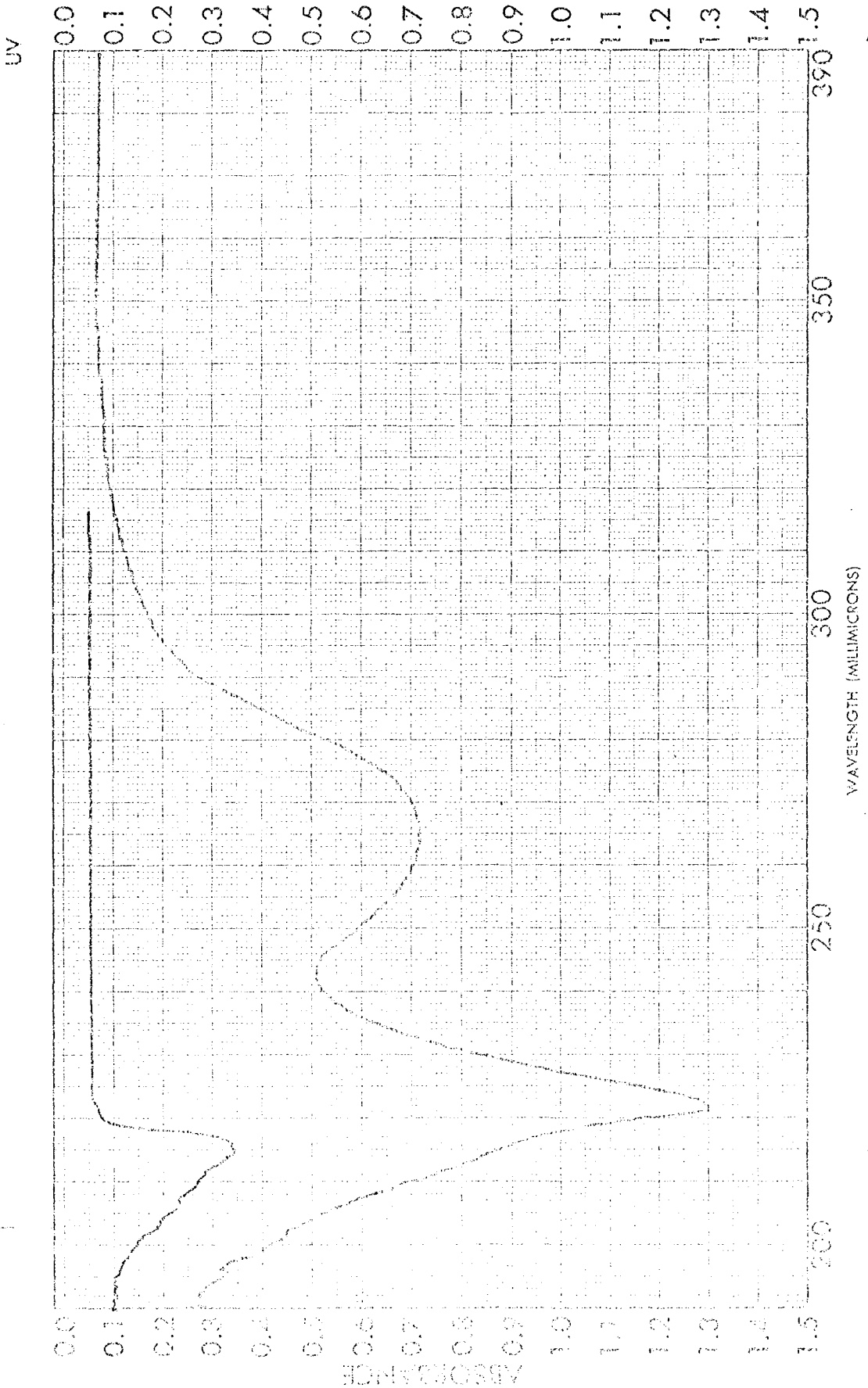


Figure 14. Cyclopentanecarboxylic acid in Methanol

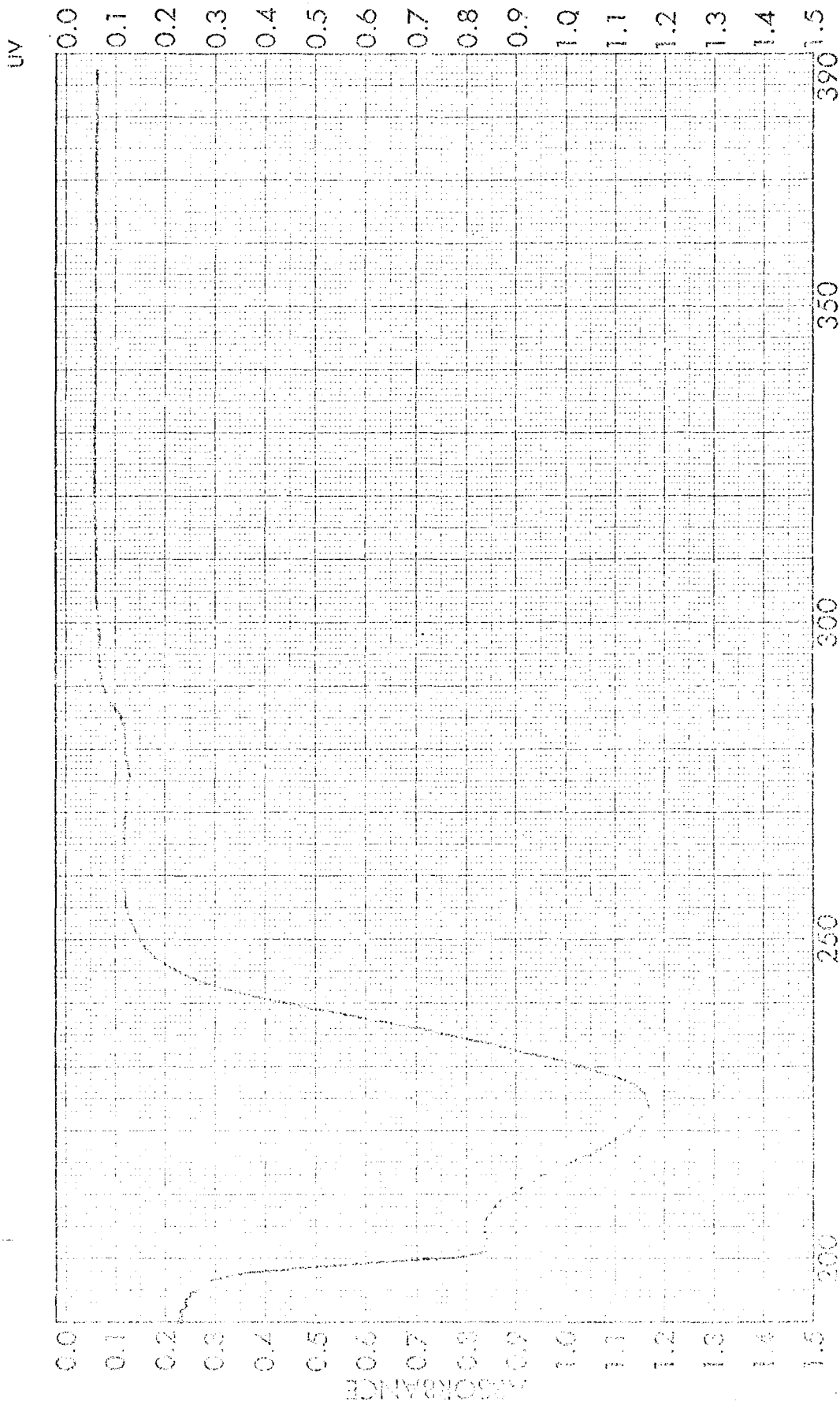


Figure 15. Cyclohexanecarboxylic acid in Methanol

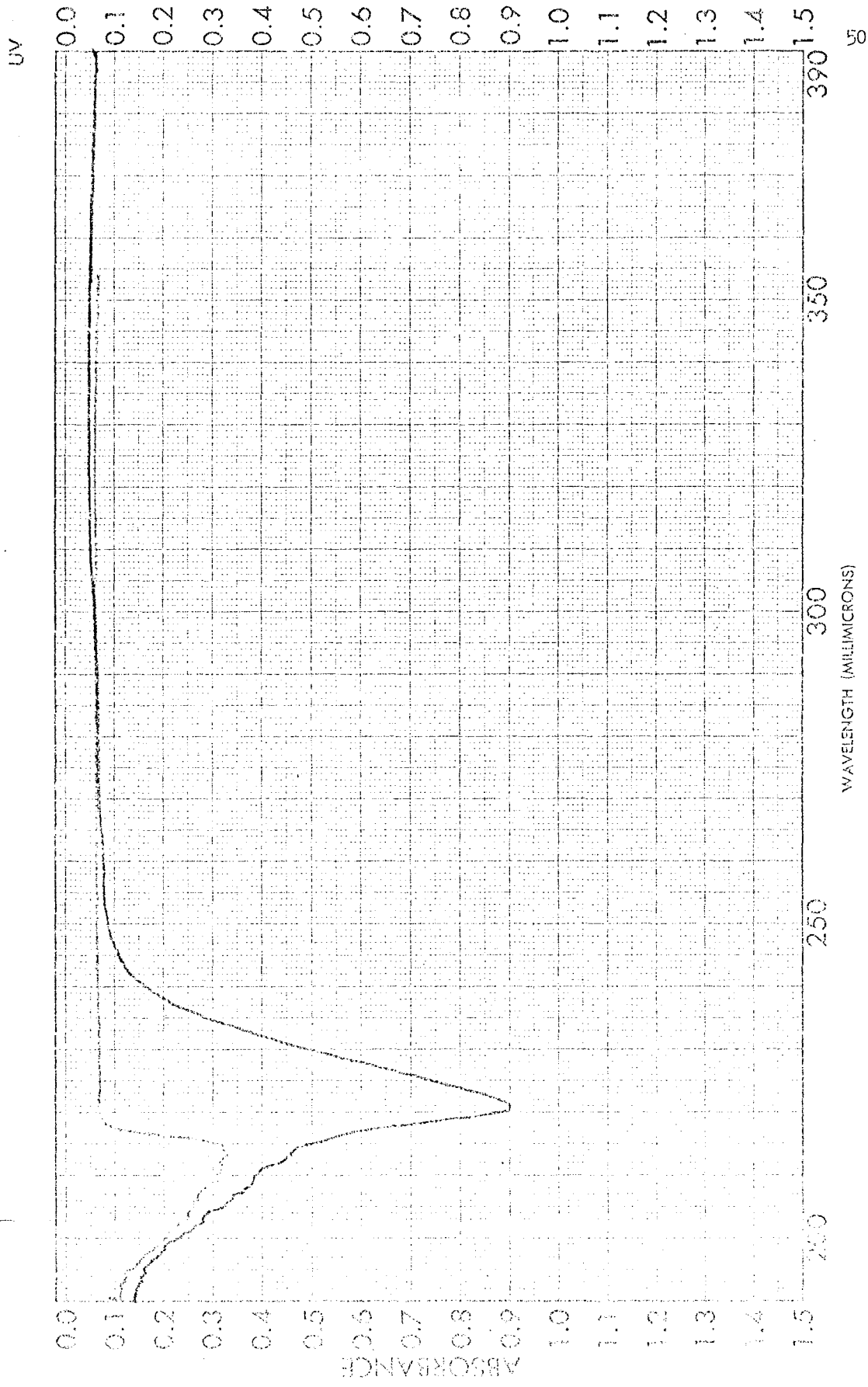


Figure 16. Cycloheptanecarboxylic acid in Methanol

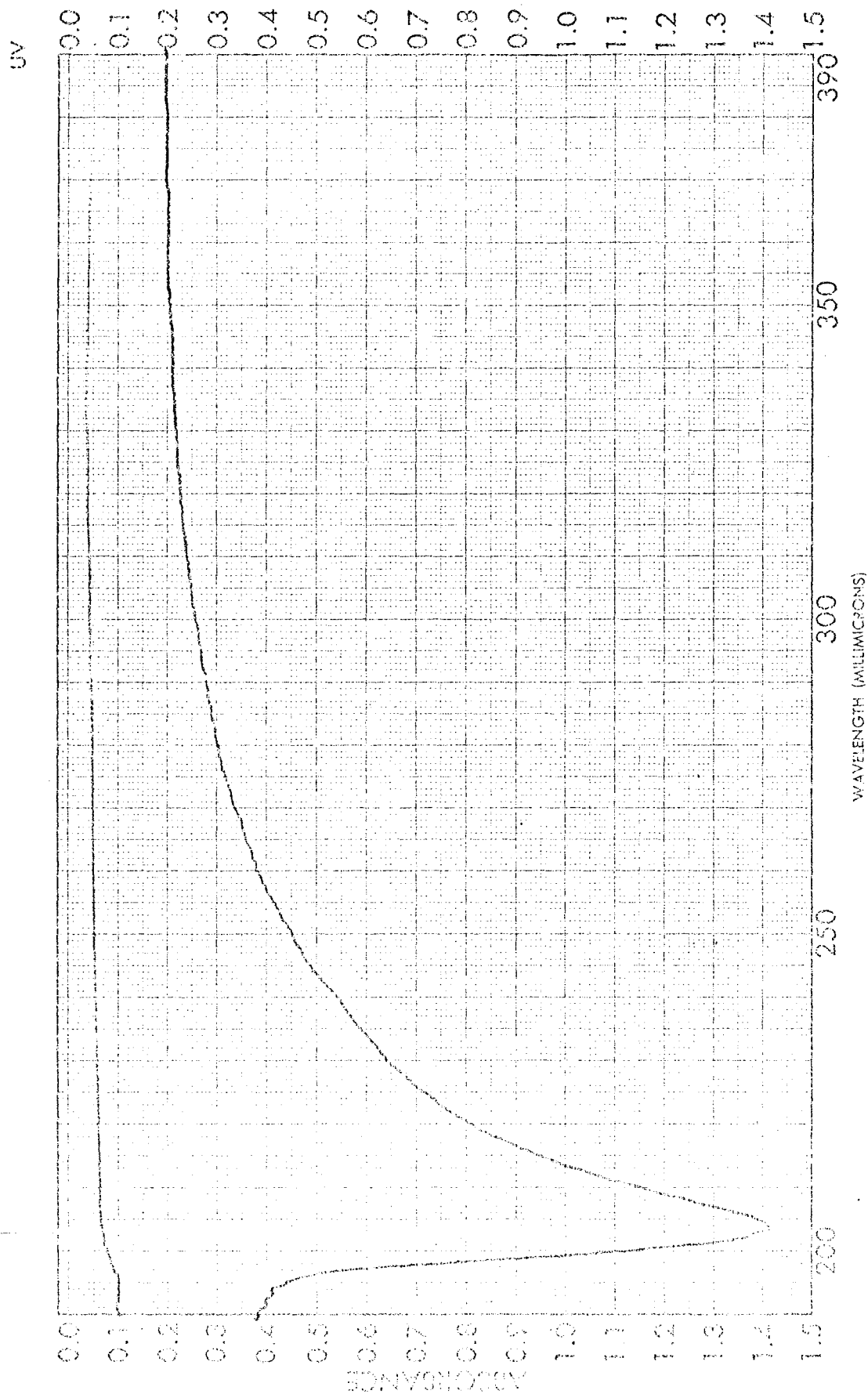


Figure 17. Biscyclopropanecarboxylatonicel (II) in Methanol

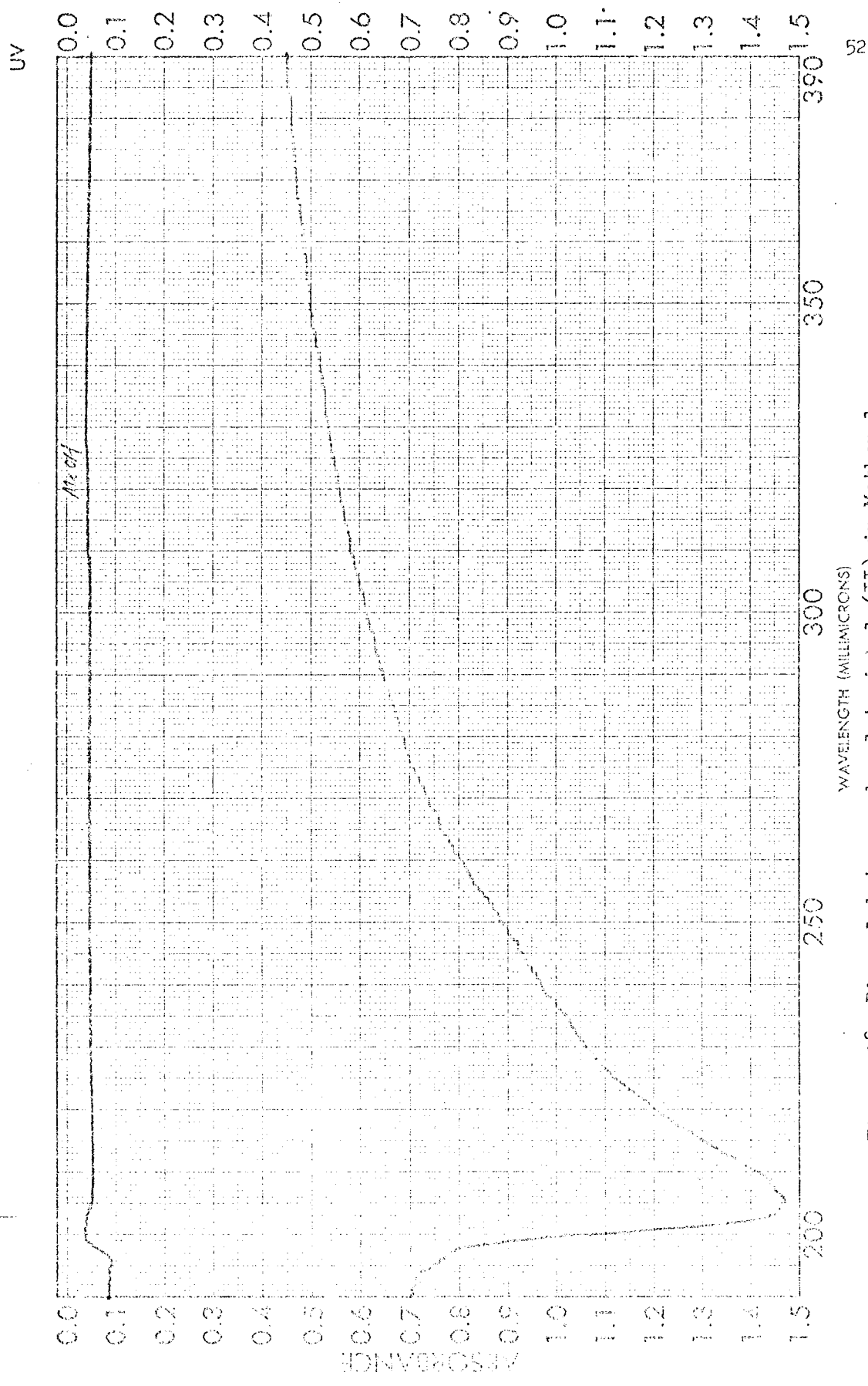


Figure 18. Biscyclobutenecarboxylatonickel (II) in Methanol

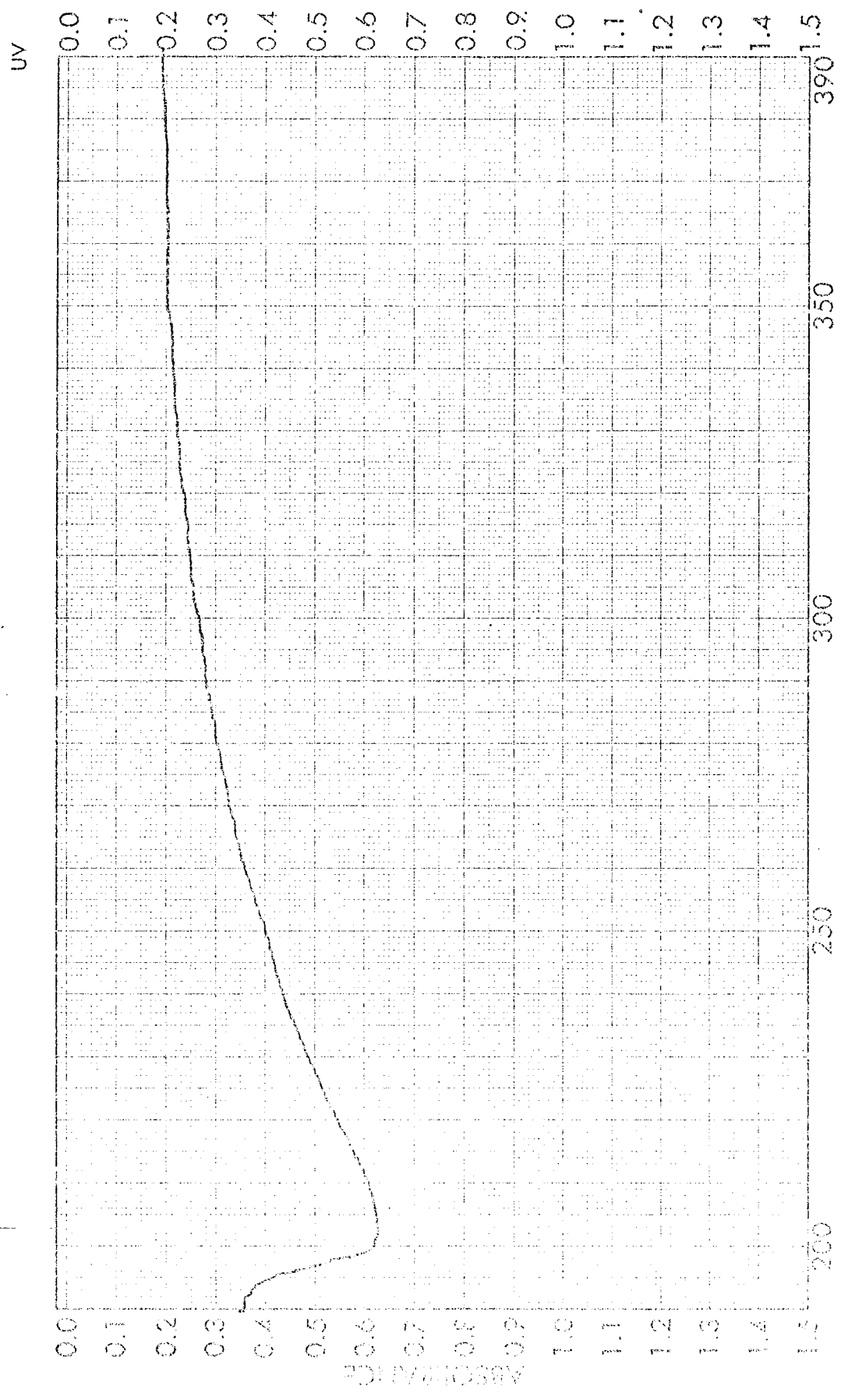


Figure 19. Biscyclopentanecarboxylatonicel (II) in Methanol

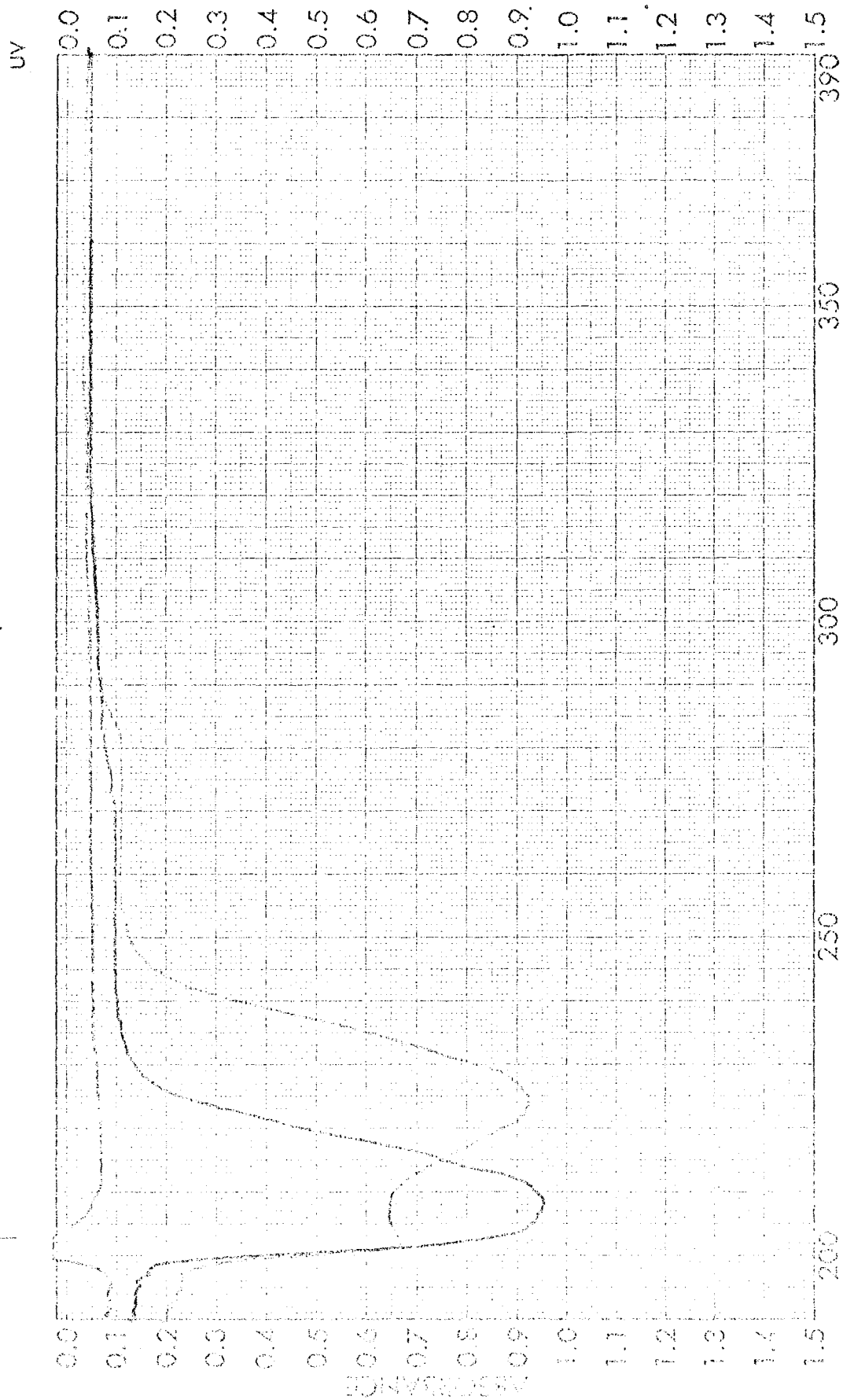


Figure 20. Biscyclhexanecarboxylatonickel (II) in Methanol

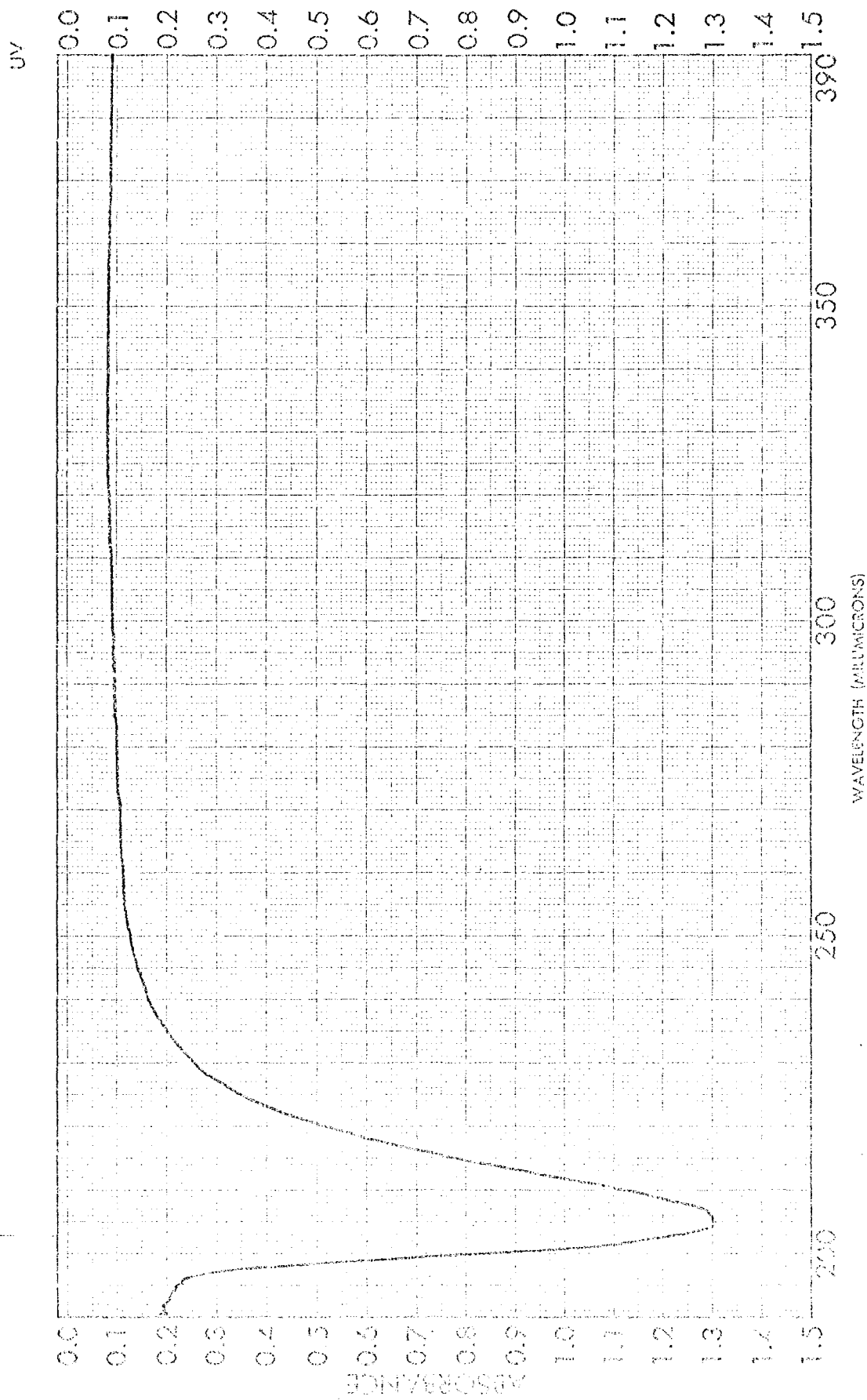


Figure 21. Biscyclopentanecarboxylatonicel (II) in Methanol

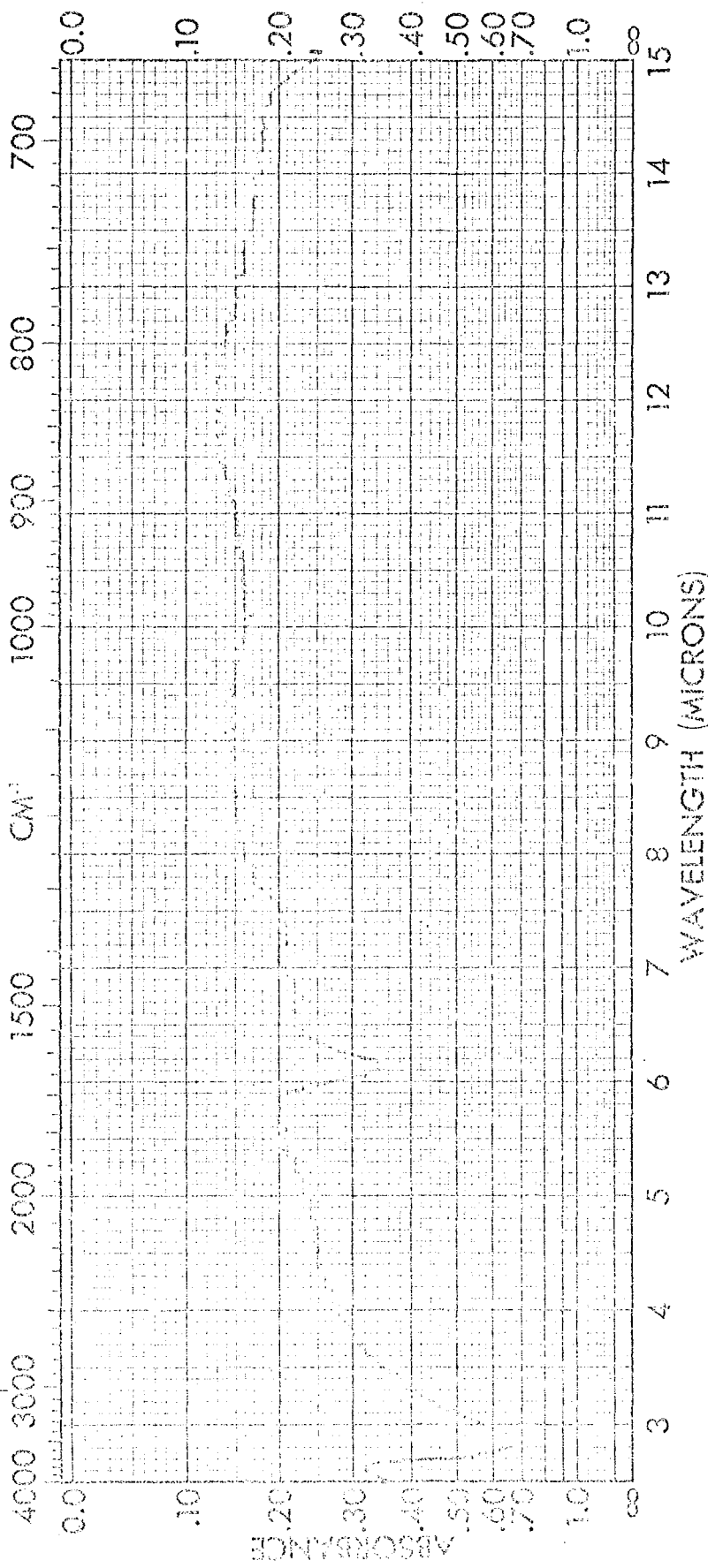


Figure 22. Hydrrous Palladium Oxide

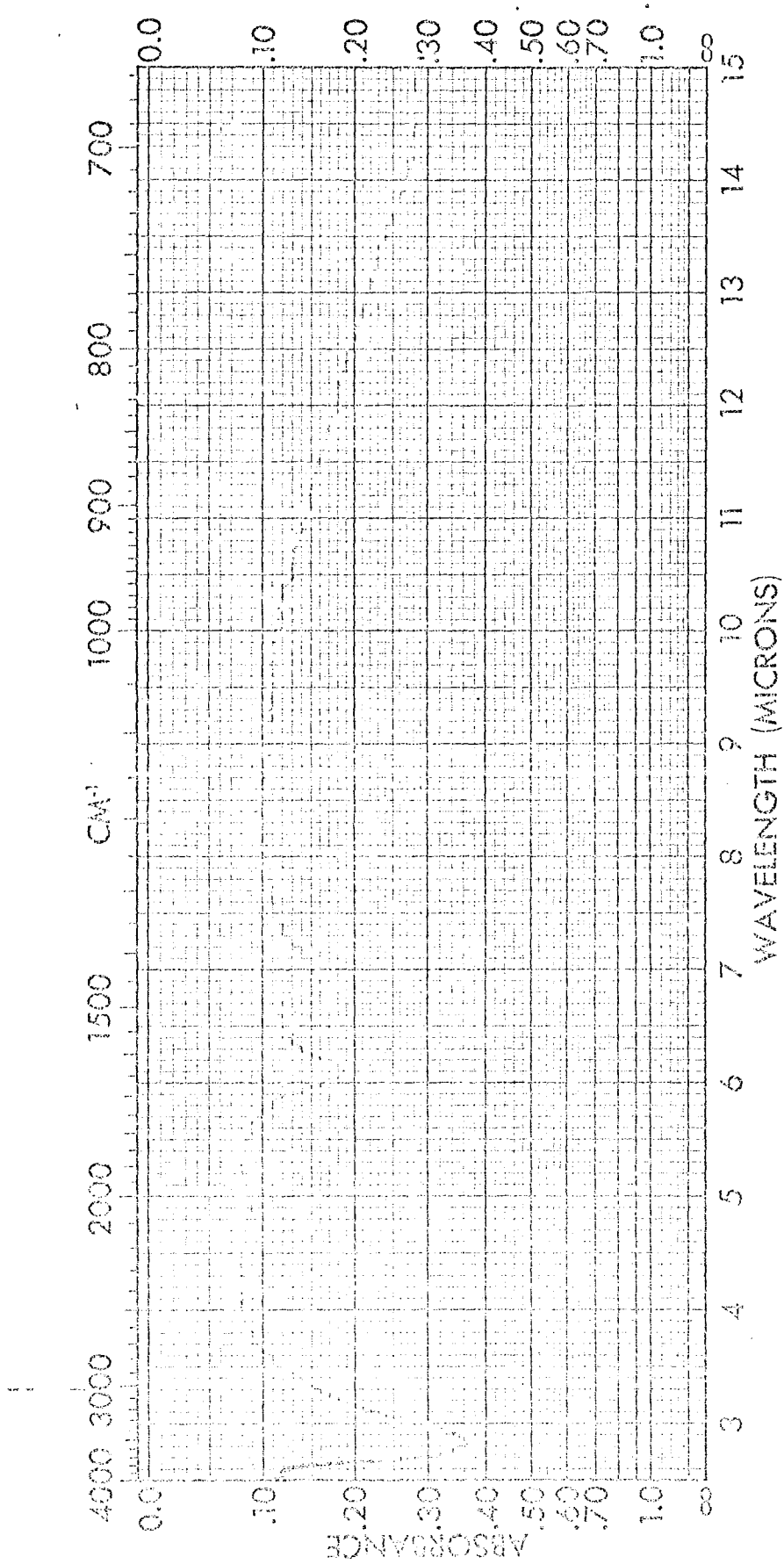


Figure 23. Hydrrous Nickelous Oxide

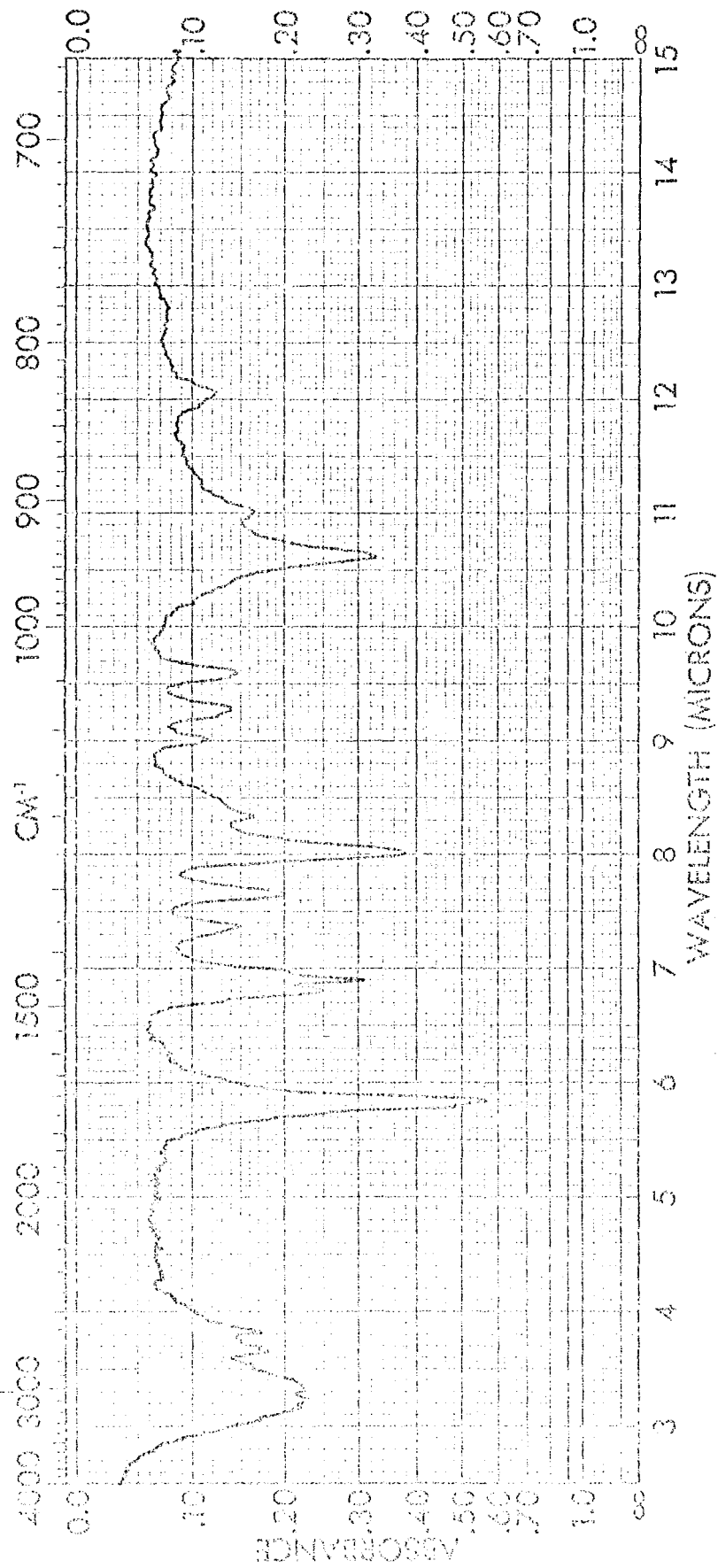


Figure 24. Cyclopropanecarboxylic acid

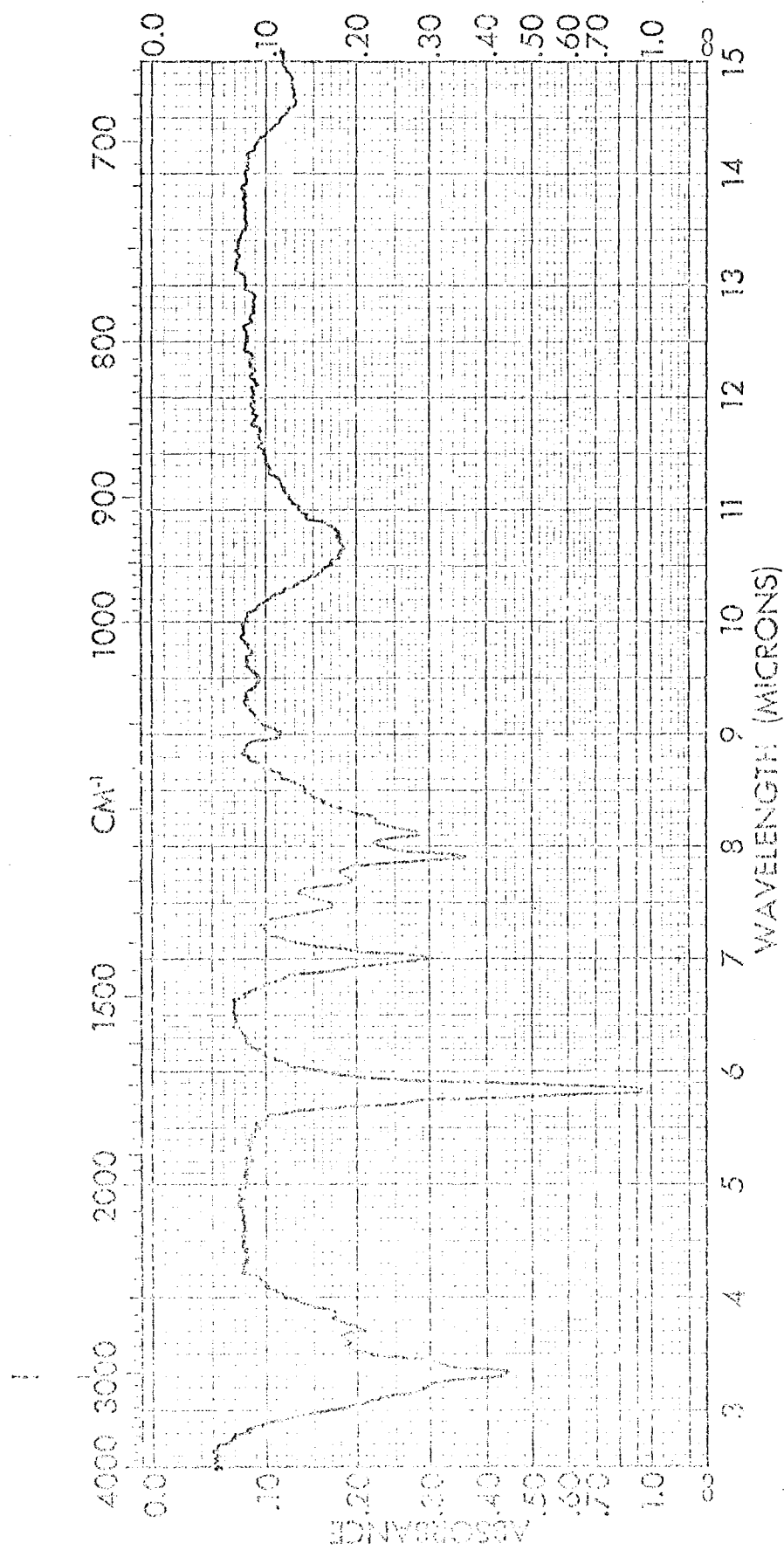


Figure 25. Cyclobutanecarboxylic acid

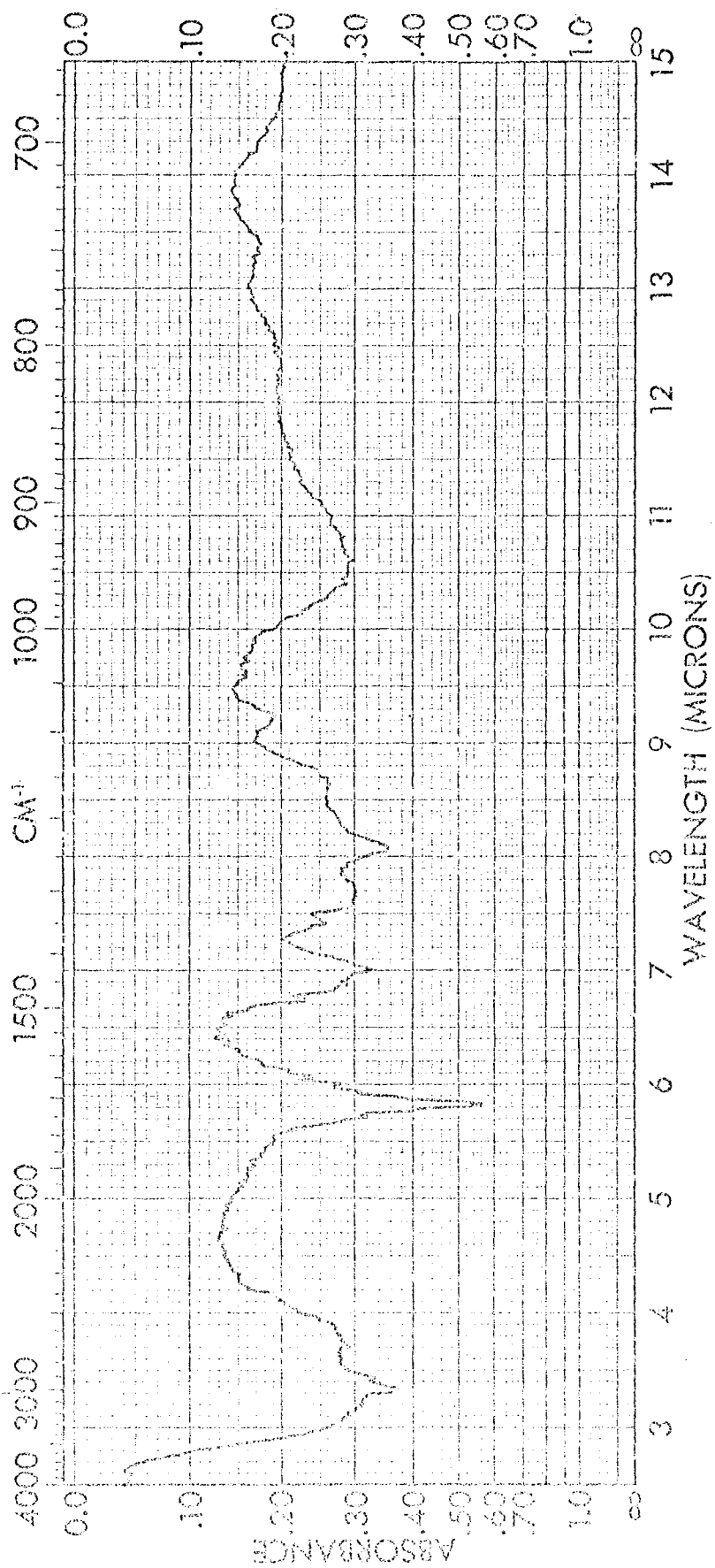


Figure 26. Cyclopentanecarboxylic acid

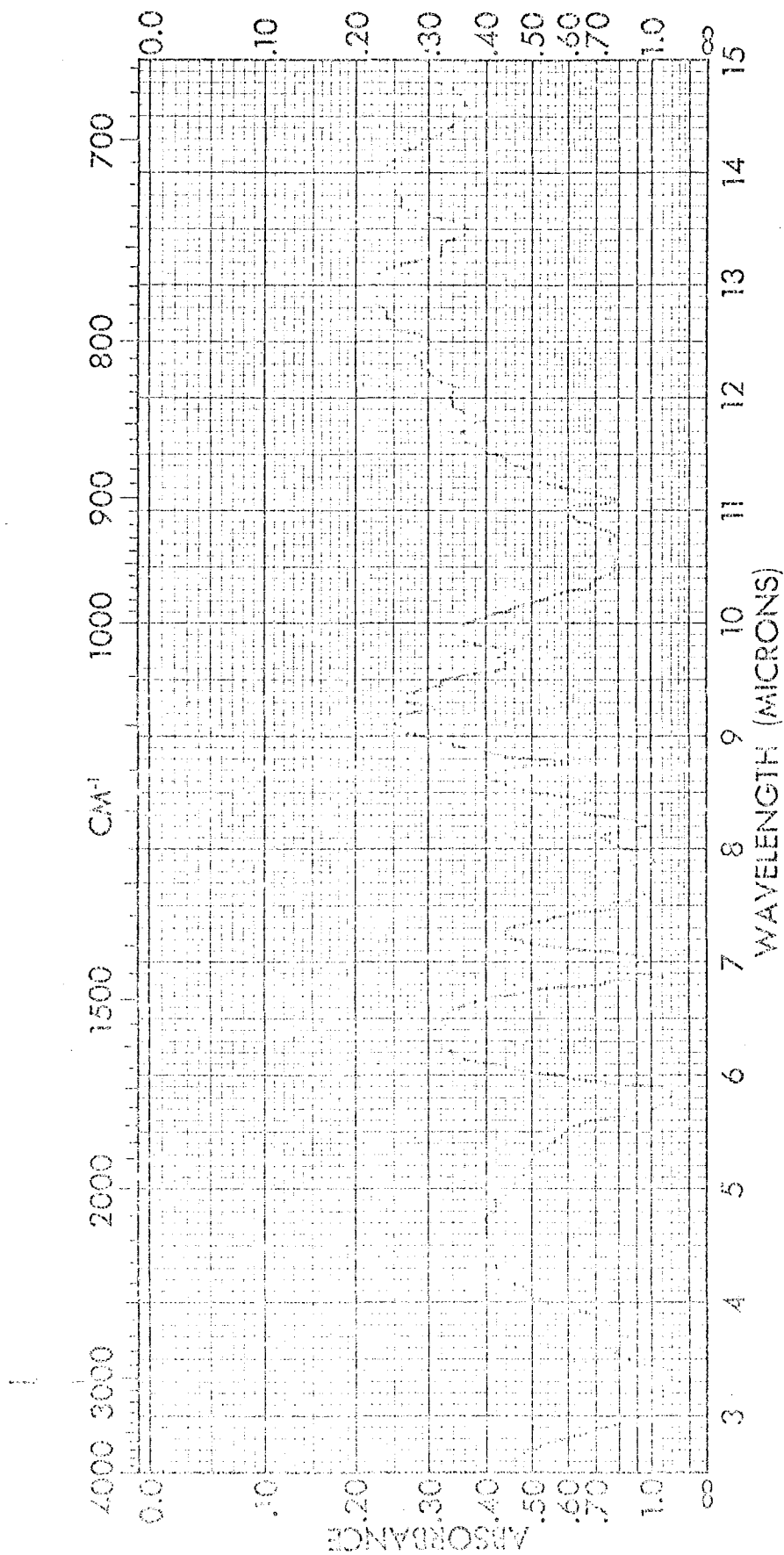


Figure 27. Cyclohexanecarboxylic acid

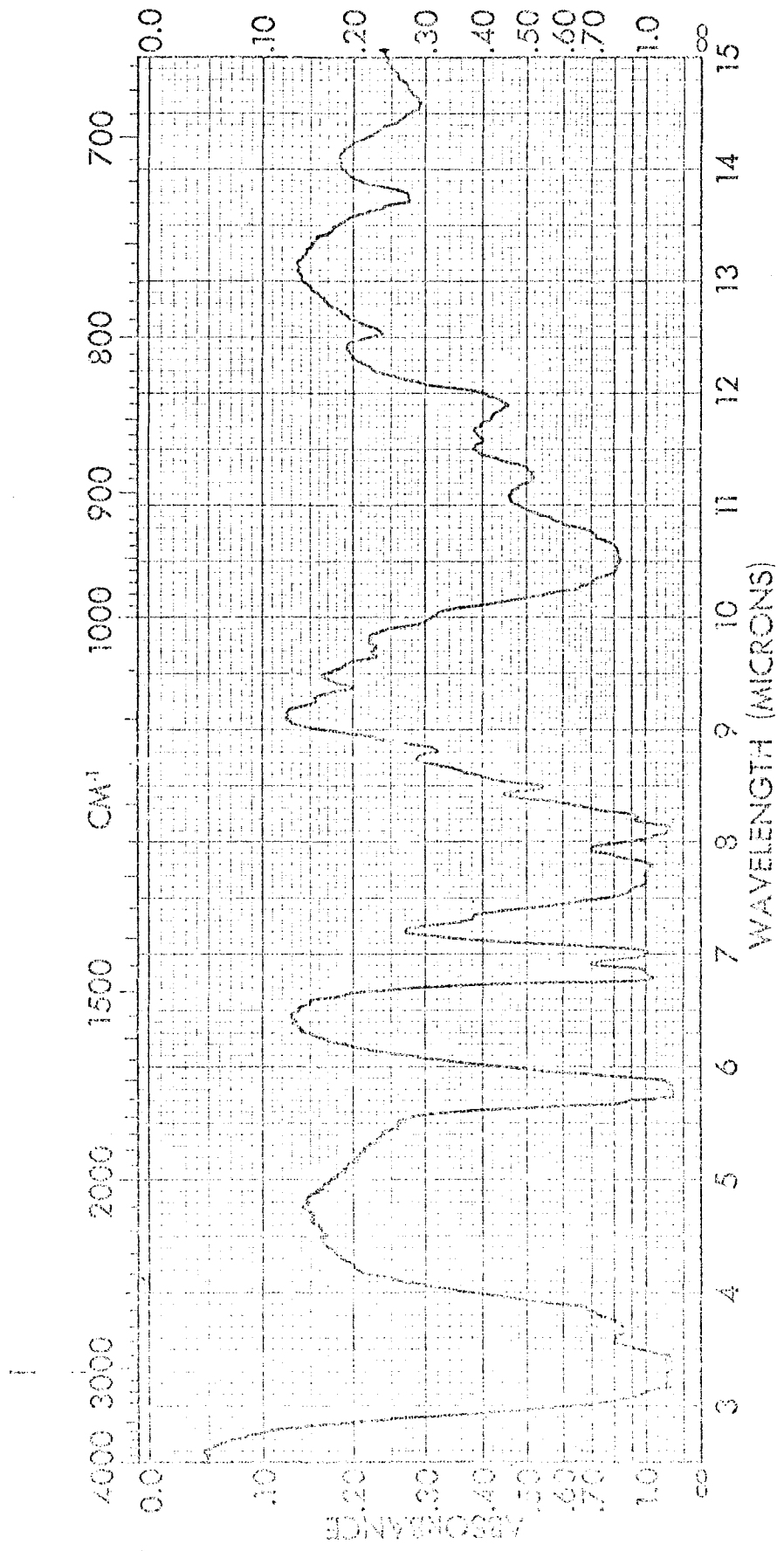


Figure 28. Cycloheptanecarboxylic acid

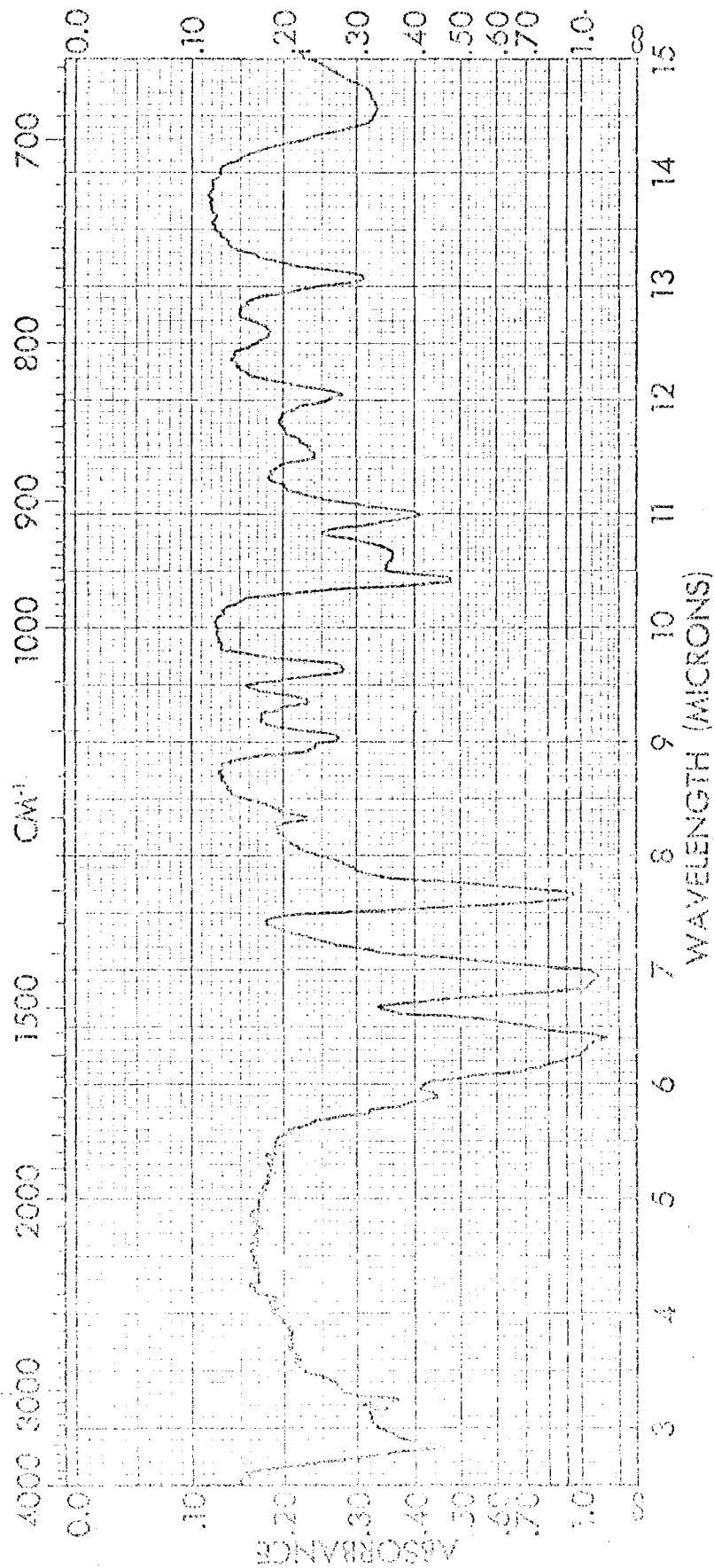


Figure 29. Biscyclopropanecarboxylatonicikel (II)

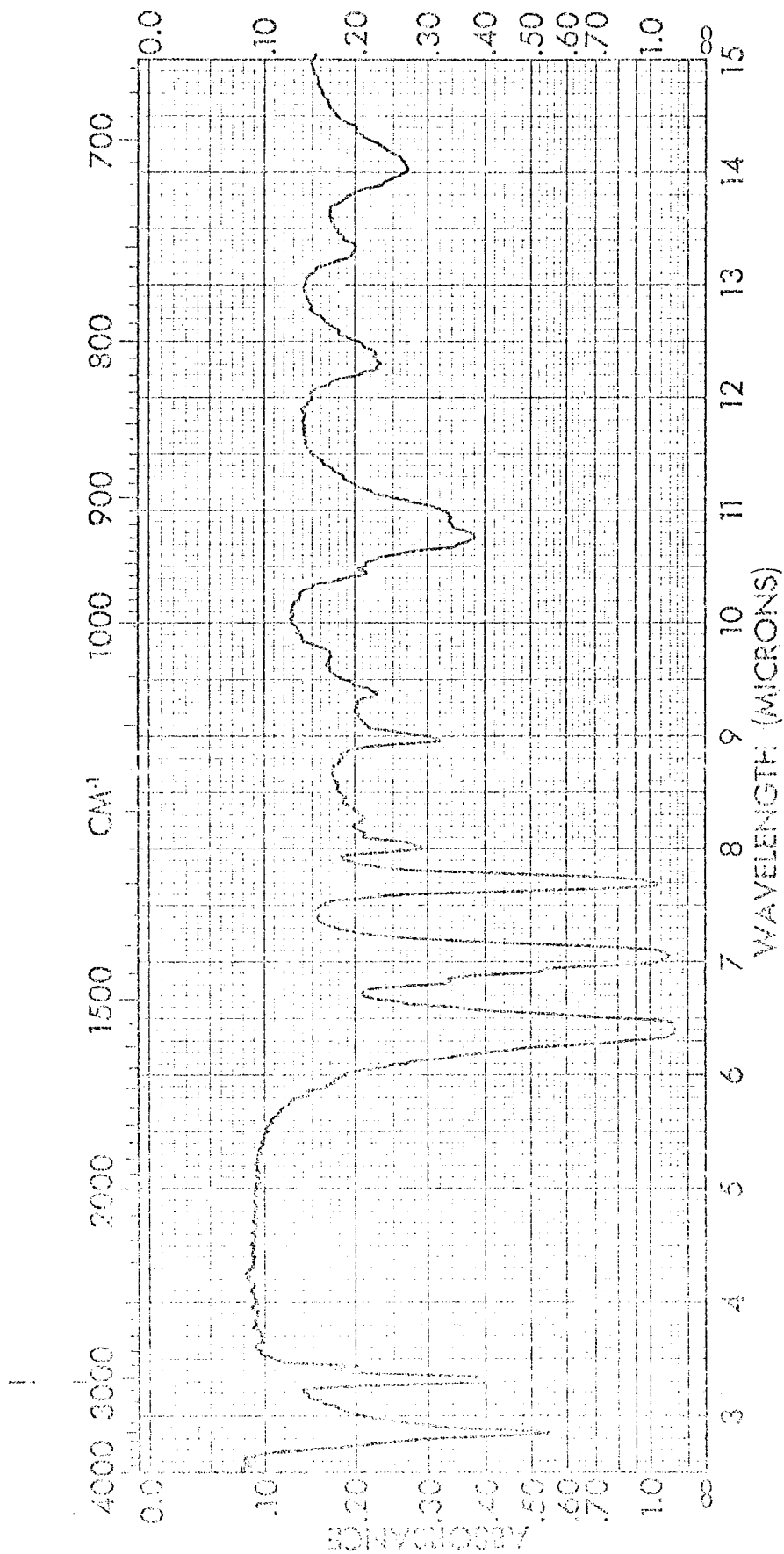


Figure 30. Biscyclobutenecarboxylatnickel (II)

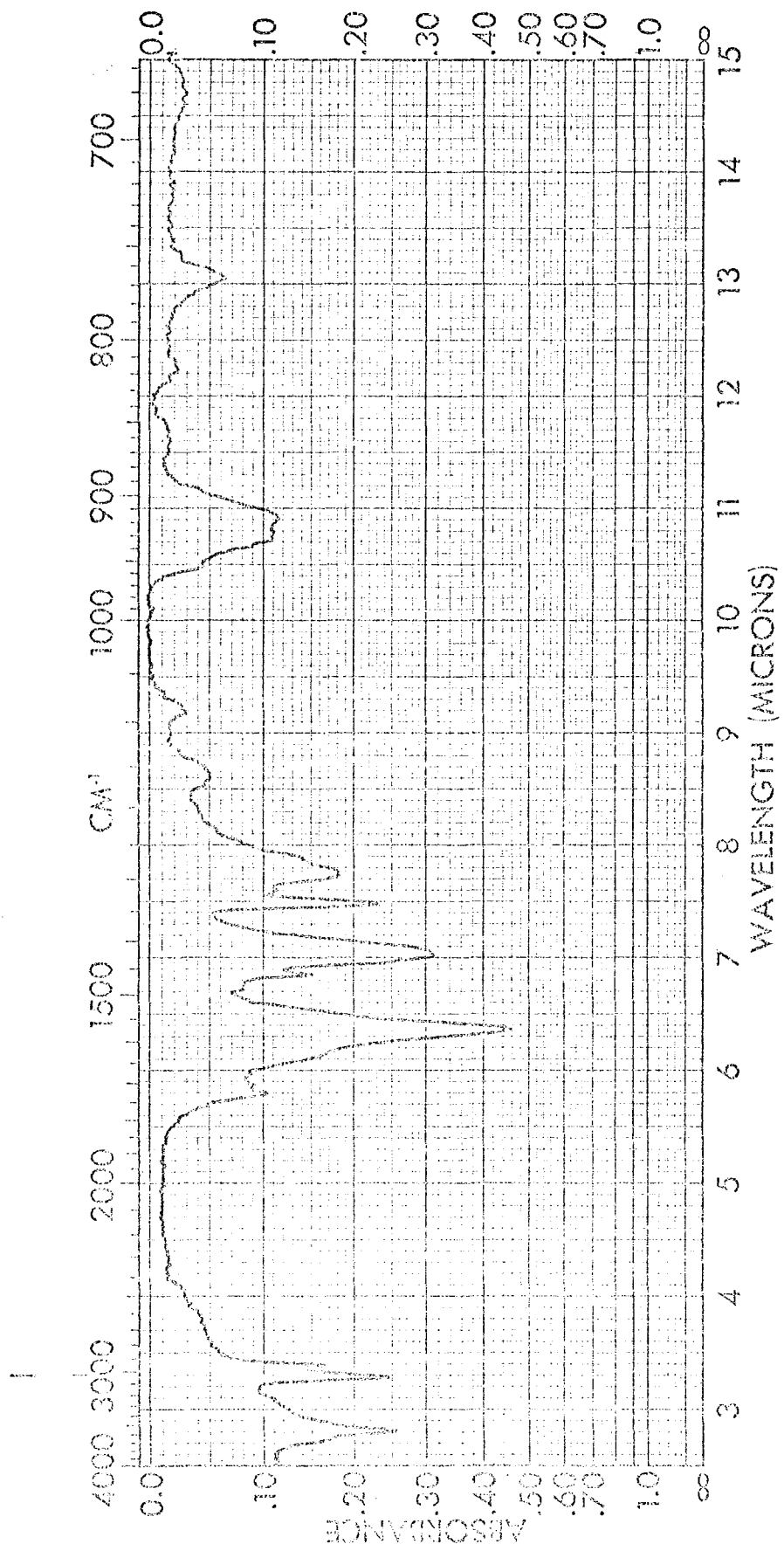


Figure 31. Biscyclopentene carboxylatonickel (II)

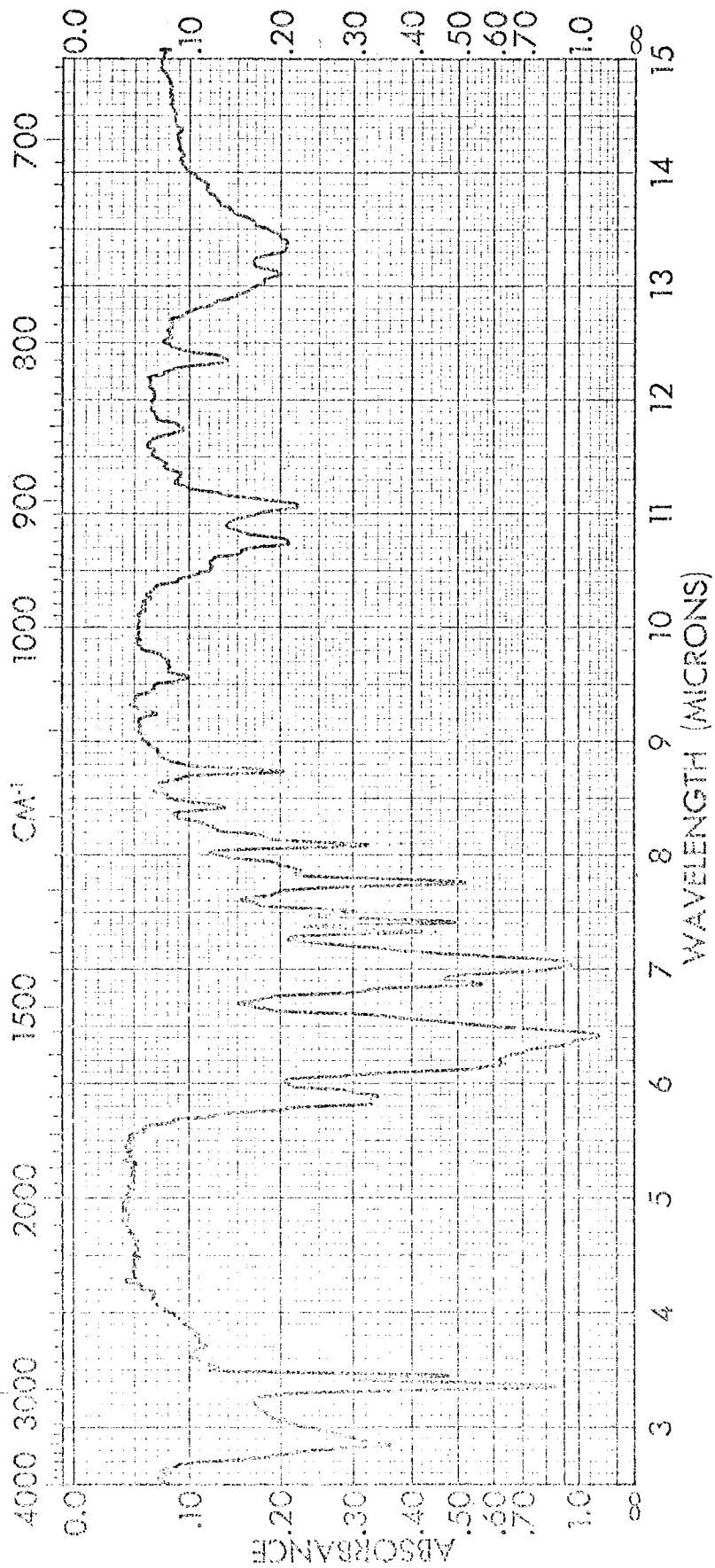


Figure 32. Biscyclohexanecarboxylatonicikel (II)

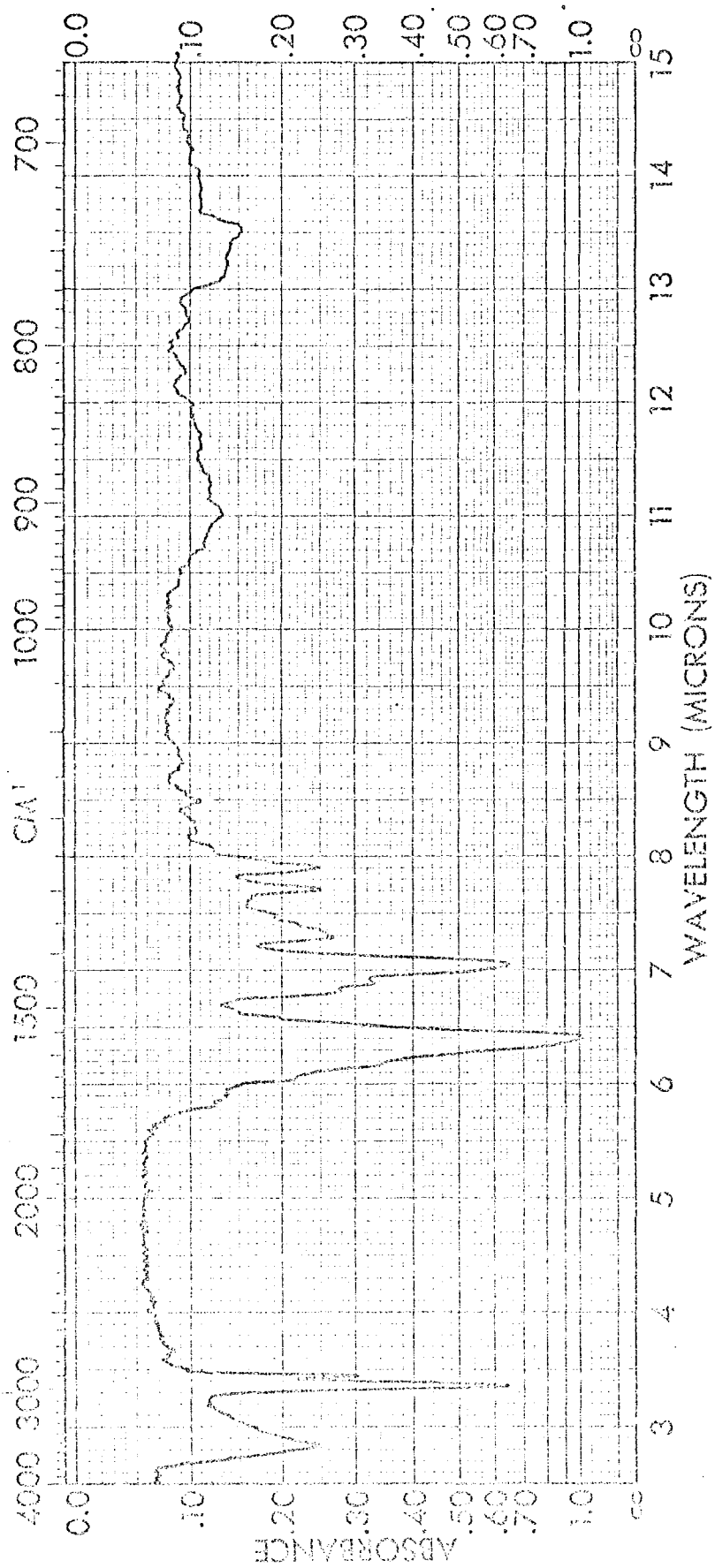


Figure 33. Biscycloheptanecarboxylatonickel (II)

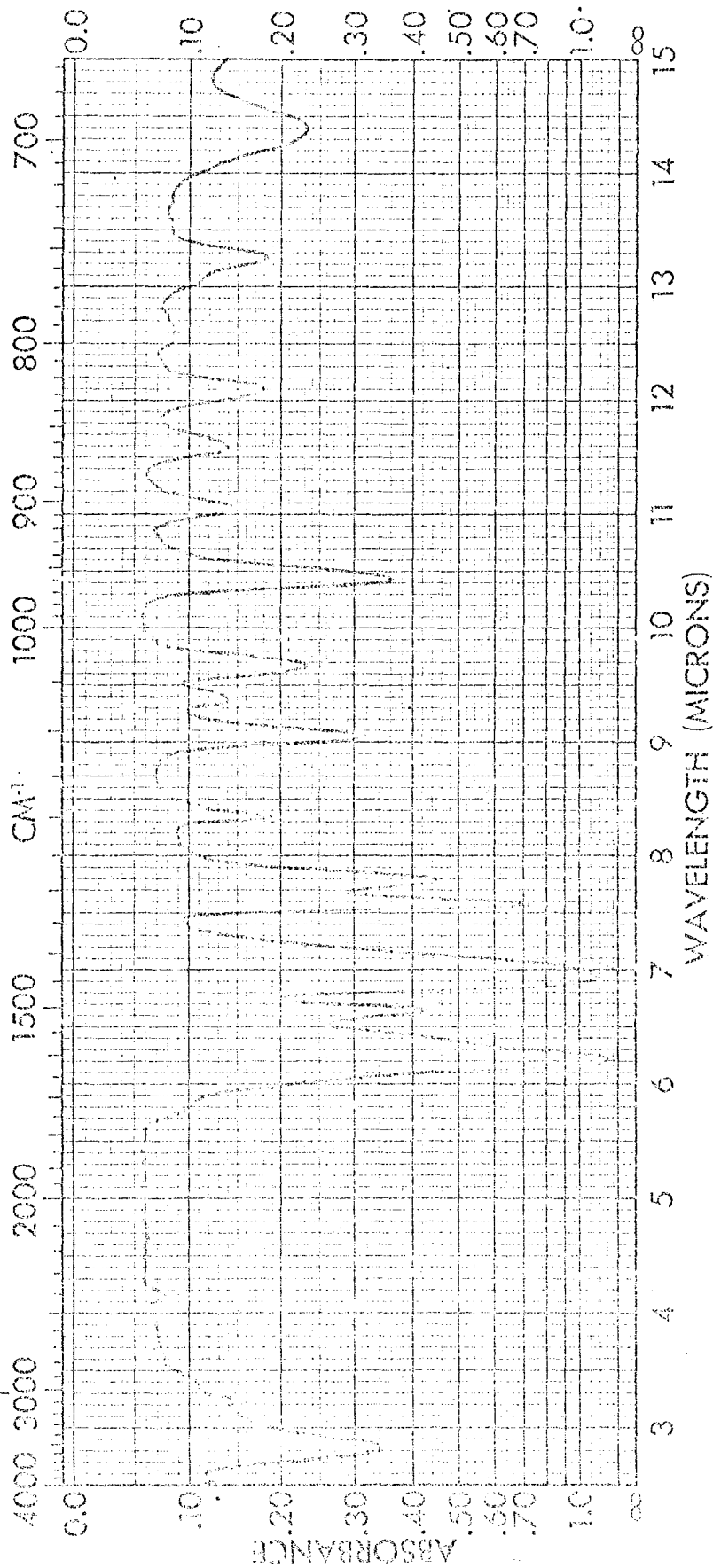


Figure 34. Biscyclopropenecarboxylatopaladium (II)

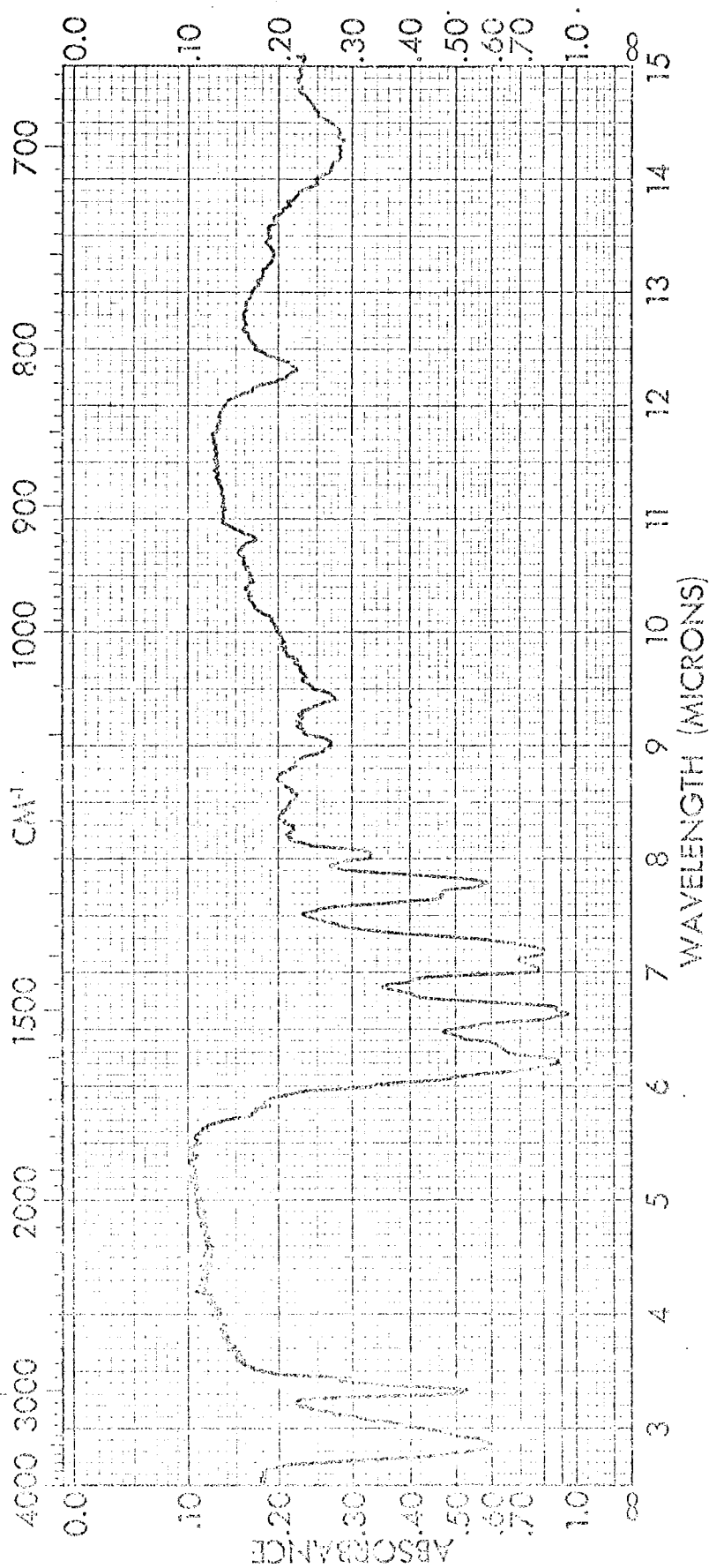


Figure 35. Biscyclobutenecarboxylatopalladium (II)

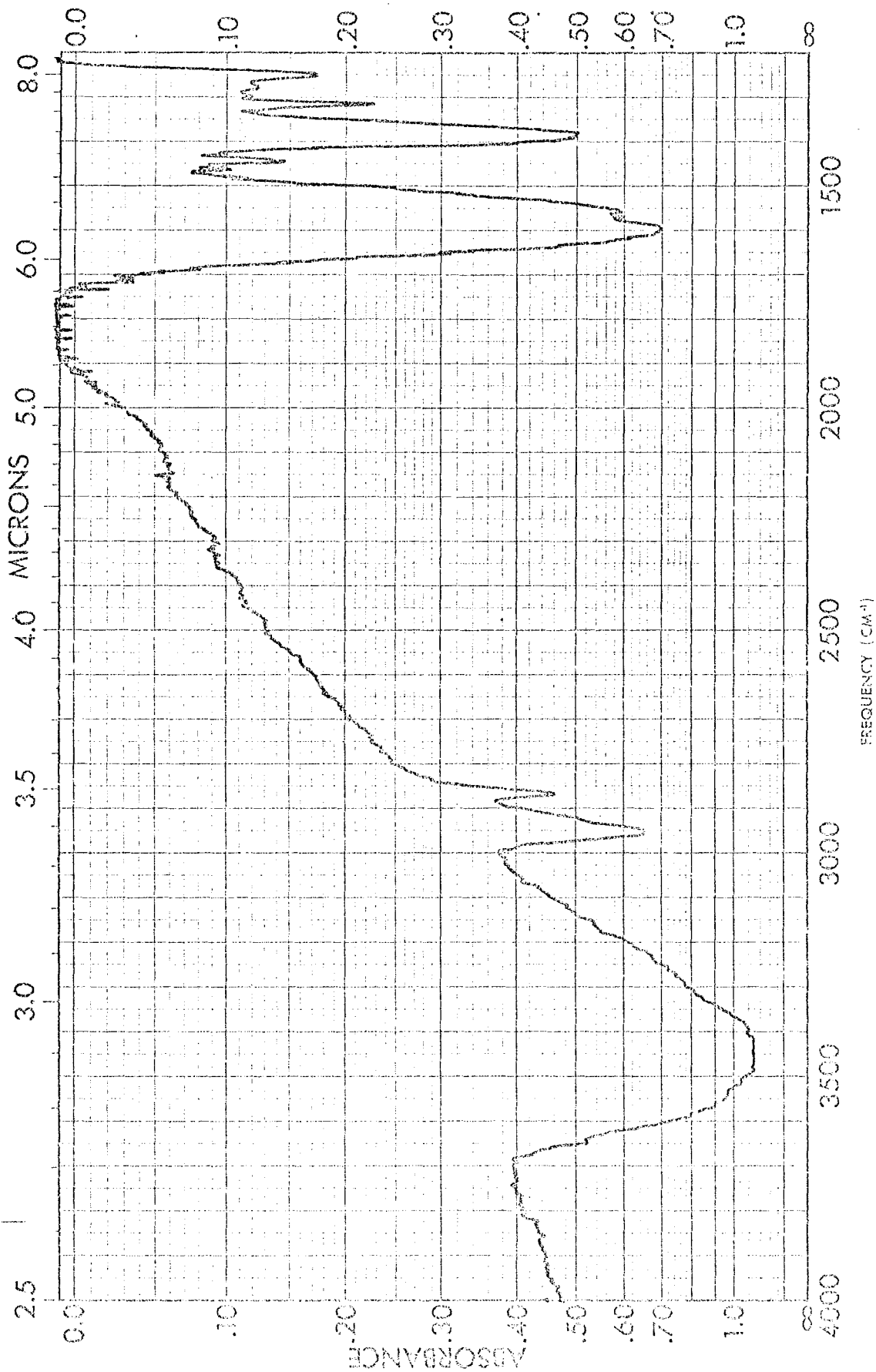


Figure 36. Biscyclopentanecarboxylatopalladium (II)

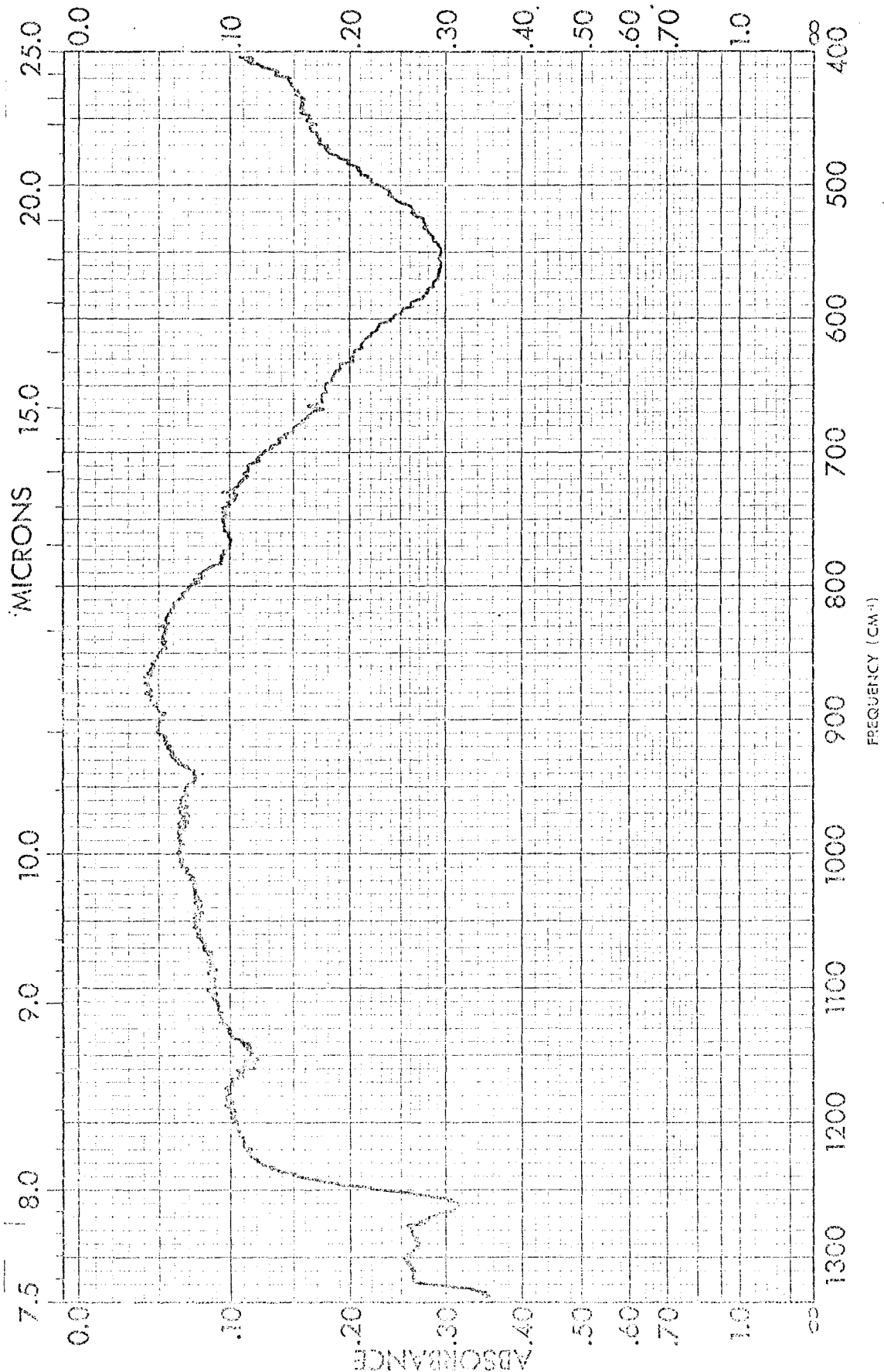


Figure 26 A. Biscyclopentanecarboxylatopalladium (II)

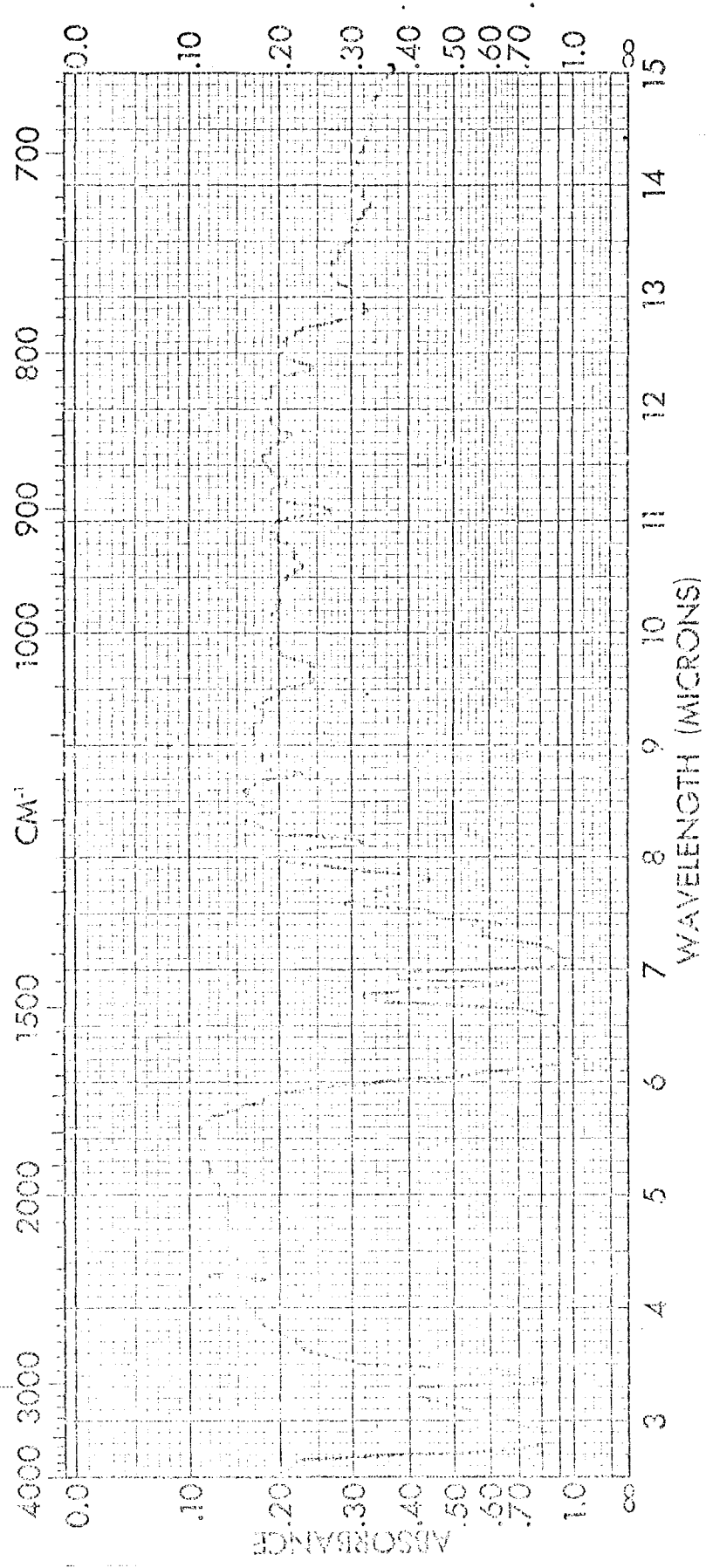


Figure 37. Biscyclohexanecarboxylatepalladium (II)

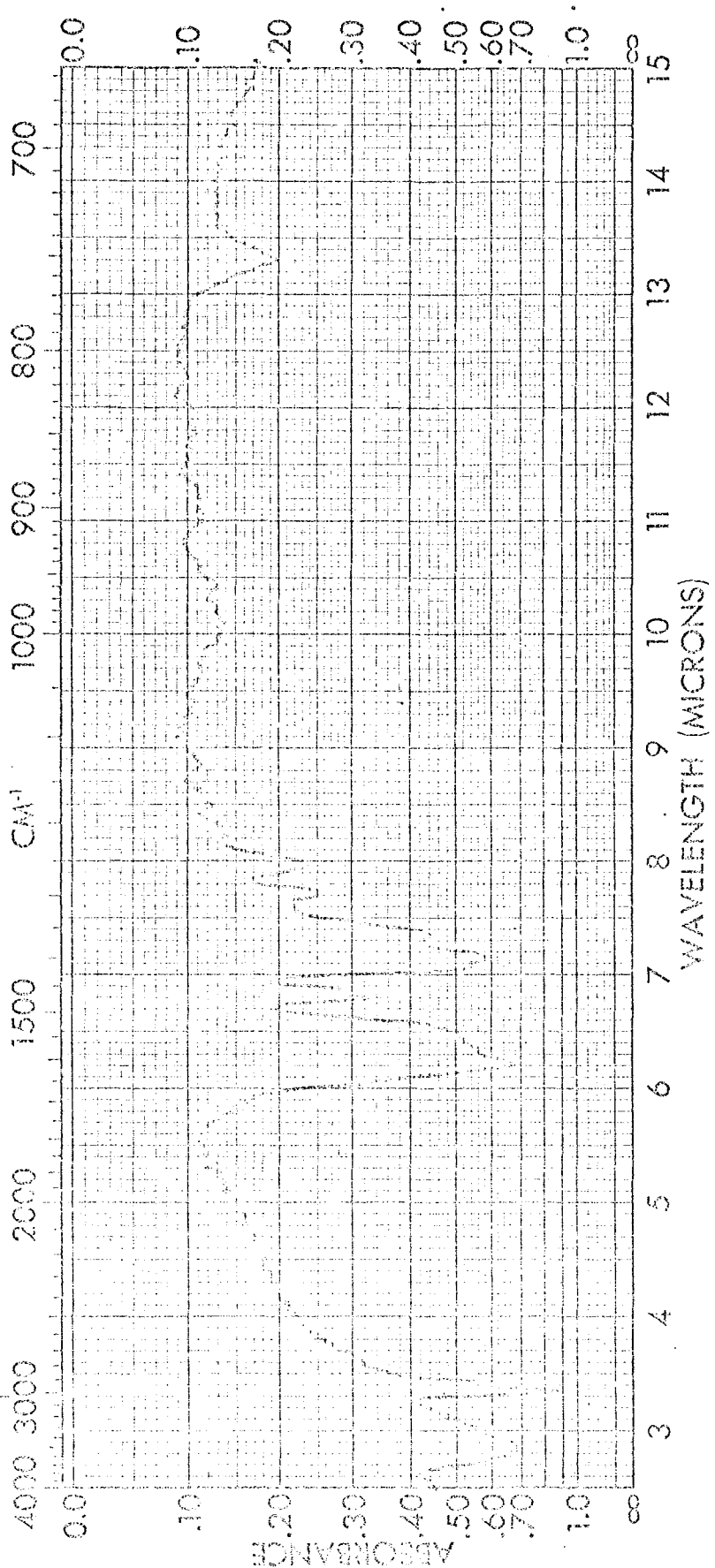


Figure 38. Piscycloheptanecarboxylatonelladium (II)