COMPLEXATION OF ALIZARIN BLUE SKY AND DISPERSE BLUE WITH Zn(II), Cd(II),Hg(II), Ti(IV), Zr(IV) AND Pd(II) AND THEIR ANALYTICAL APPLICATION.

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN
PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER
OF SCIENCE IN CHEMISTRY.

BY

ADAM MOALIM YAGOUB

June, 1994.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks and gratitude to my advisors, prof. A. k. Abd-elkader and Dr. Negussie Retta for identifying the problem and for guidance, advice, encouragement and support throughout this work.

I am very much grateful to the members of Chemistry department, Addis Ababa university, for the various supports and friendly assistance.

I would like to thank and acknowledge Dr. Fikru Tafesse, Dr.Berhanu Abegas and Dr. Ermias Dagne and their assistants for the valuable and useful comments and recommendations I received.

I wish to acknowledge and thank the Deutscher Akademischer Autauschdienst (DAAD) and the Natural Product Research Network for Eastern and Central Africa (NAPRECA) for the scholarship.

Dedicated to my father who passed away when I was away from home as I undertook my studies in Addis Ababa University.

ABSTRACT

Complexation of Zn(II), Cd(II), Hg(II), Ti(IV), Zr(IV) and Pd(II) with two anthraquinone derivatives, alizarin blue sky (ABS) and disperse blue (DB), was studied spectrophotometrically. The spectral behaviour of the ligands were investigated. The suitable conditions for complexation were selected and the stoichiometry of the complexes in solution were determined. The solid complexes were isolated and characterized by elemental analysis and IR data. The mode of ligands binding were investigated. Analytical procedure for quantitative determination of Ti(IV) in TiO_2 using ABS as an analytical reagent was developed.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS I

DEDICATION II

ABSTRACT III

LIST OF TABLES VI

LIST OF FIGURES VII

1 INTRODUCTION 1

- 1.1 The coordination compounds and the coordinate bond 1
- 1.2 Dyes and Pigments 1
- 1.3 Metal Complexes of Organic Dyestuffs 2
- 1.4 General Nature and Uses of Complexes 4

2 LITERATURE SURVEY 5

3 OBJECTIVES 11

4 EXPERIMENTAL 12

- 4.1 INSTRUMENTS AND EQUIPMENT 12
- 4.2 CHEMICALS, REAGENTS AND SOLUTIONS 12
- 4.3 SPECTROPHOTOMETRIC STUDIES 13
  - 4.3.1 The spectral behaviour of the ligands 13
    - 4.3.1.1 Beer's Law 13
    - 4.3.1.2 Effect of pH 19
  - 4.3.2 THE STOICHIOMETRY OF COMPLEXES 22
  - 4.3.3 THE EFFECT OF pH ON COMPLEXES 22
- 4.4 ISOLATION OF THE SOLID COMPLEXES 37
  - 4.4.1 PREPARATION OF ZnABS COMPLEX 39
  - 4.4.2 PREPARATION OF CdABS COMPLEX 39
  - 4.4.3 PREPARATION OF HgABS COMPLEX 40
  - 4.4.4 PREPARATION OF TiABS COMPLEX 40

4.4.5 PREPARATION OF ZrABS COMPLEX 41
4.4.6 PREPARATION OF PdABS COMPLEX 41
4.4.7 PREPARATION OF ZnDB COMPLEX 42
4.4.8 PREPARATION OF CdDB COMPLEX 42
4.4.9 PREPARATION OF HgDB COMPLEX 43
4.4.10 PREPARATION OF TiDB COMPLEX 43
4.4.11 PREPARATION OF ZrDB COMPLEX 43
4.4.12 PREPARATION OF PdDB COMPLEX 44
5 RESULTS AND DISCUSSION 45
5.1 IR SPECTRA 45
5.2 NATURE OF BONDING BETWEEN THE LIGANDS AND THE METAL IONS 68
5.3 ANALYTICAL APPLICATION 74
5.4 CONCLUSION 76
6 REFERENCES 77

LIST OF TABLES

Table 1 Some anthraquinone derivatives 7

Table 2 3.6 x 10^{-5}M ABS, A vs pH at λ_{max} 630 nm 20

Table 3 5.22 x $^{-4}$M DB, A vs pH at λ_{max} 56 21

Table 4 Variation of A with pH for ABS metal ion complexes at λ_{max}630 nm 35

Table 5 Variation of A with pH for DB metal ion complexes atλ_{max} 567 nm 36

Table 6 Analytical data for ABS and DB metal complexes 38

Table 7 FT-IR data for ABS and it's metal complexes 62

Table 8 FT-IR data for DB and it's metal complexes 63

Table 9 The thermal analysis data for DB and CdDB complex 67

Table 10 Blank absorbance (ABS) 75

LIST OF FIGURES

Fig. 1 5.22 x 10^{-4}M ABS 14

Fig. 2 5.22 x 10^{-4}M DB 15

Fig. 3 ABS, A vs C at λ_{max} 584 nm 16

Fig. 4 ABS, A vs C at λ_{max} 630 nm 17

Fig. 5 DB, A vs C at λ_{max} 567 nm 18

Fig. 6 Molar ratio curve for ZnABS complex 23

Fig. 7 Molar ratio curve for CdABS complex 24

Fig. 8 Molar ratio curve for HgABS complex 25

Fig. 9 Molar ratio curve for TiABS complex 26

Fig. 10 Molar ratio curve for ZrABS complex 27

Fig. 11 Molar ratio curve for PdABS complex 28

Fig. 12 Molar ratio curve for ZnDB complex 29

Fig. 13 Molar ratio curve for CdDB complex 30

Fig. 14 Molar ratio curve for HgDB complex 31

Fig. 15 Molar ratio curve for TiDB complex 32

Fig. 16 Molar ratio curve for ZrDB complex 33

Fig. 17 Molar ratio curve for PdDB complex 34

Fig. 18 FT-IR, ABS 48

Fig. 19 FT-IR, ZnABS complex 49

Fig. 20 FT-IR, CdABS complex 50

Fig. 21 FT-IR, HgABS complex 51

Fig. 22 FT-IR, TiABS complex 52

Fig. 23 FT-IR, ZrABS complex 53

Fig. 24 FT-IR, PdABS complex 54

Fig. 25 FT-IR DB 55

Fig. 26 FT-IR ZnDB complex 56

Fig. 27 FT-IR CdDB complex 57

Fig. 28 FT-IR HgDB complex 58
Fig. 29 FT-IR TiDB complex 59
Fig. 30 FT-IR ZrDB complex 60
Fig. 31 FT-IR PdDB complex 61
Fig. 32 Thermal analysis curve for DB 65
Fig. 33 Thermal analysis curve for CdDB complex 66

1 INTRODUCTION

1.1 The coordination compounds and the coordinate bond [1,2]

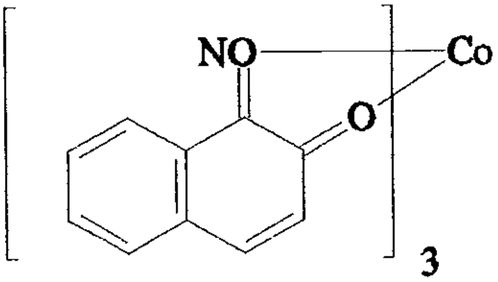
According to the theory of Sidgwick and Lowry [1,2] a coordinate bond can be formed between any atom, molecule or ion which accepts a pair of electrons (the acceptor) from another atom, molecule or ion which is able to donate a pair of electrons (the donor). The donor atom is usually non-metallic and is often a part of a molecule capable of independent existence. This may be neutral, a negative ion or occasionally a positive ion. The donor molecule or ion is called the ligand, examples of which are NH_3, H_2O, CO, Cl^-, NO_3^-, $(N_2H_5)^+$. The resulting complex may be either a positive or negative ion or neutral molecule depending on the balance of the metal and the ligand ionic charges.

1.2 Dyes and Pigments [3]

Purely inorganic coordination compounds comprise only a small fraction of the pigments and dyes being used. Most dyestuffs are synthetic organic compounds and of these, the large class of metal dye compounds (dye lakes) are of greater importance. These are of two types: coordination compounds and metal salts.

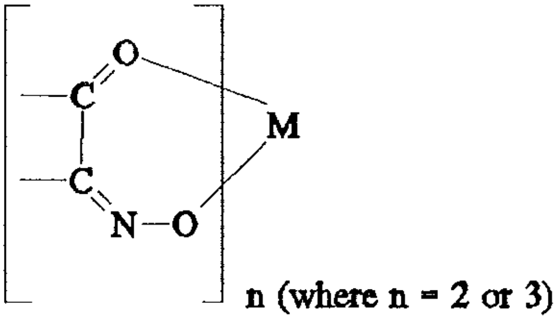
1.3 Metal Complexes of Organic Dyestuffs [4]

Any organic compound containing intramolecular hydrogen bonds will, in general, reacts with metal ions to form coordinate covalent bonds. Coordination can occur with any class of dyes which has derivatives containing the necessary donor groups in the proper positions. The most characteristic groupings found in commercial dyes are -OH, COOH, C=O, NOH and $-NH_2$. Naphthol Green B was the first commercially available soluble acid dye combining a coordinated metal ion. The -NO, -OH groups characteristics of this dyestuffs occur in many metallized dyes. When Gambine Y (1,2-naphthoquinone-1-Oxime) [4] was allowed to react with $[CO(NH_3)_6Cl_3]$ at room temperature a simple salt was formed. Upon warming the salt, six molecules of ammonia were evolved and the following chelate compound was isolated.



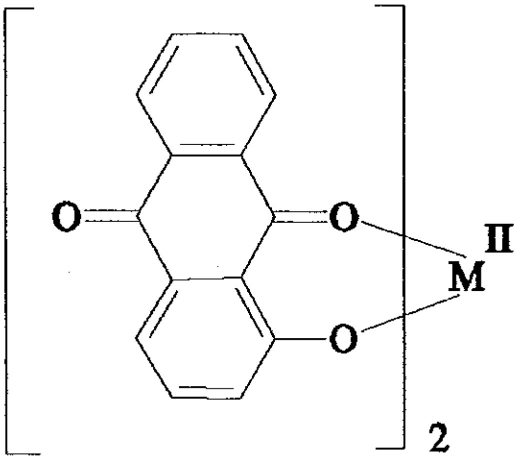
2-nitroso-1-naphthol and the related Nitroso-R- salts have been suggested as analytical reagents for cobalt [4] and for the colorimetric and photometric determination of iron [4].

The α-oximinoketones form metal complexes of the type



These have been patented for use on photo-images [4].

Complexes of 1-hydroxy anthraquinone with several transition metal ions have been investigated and formulated as



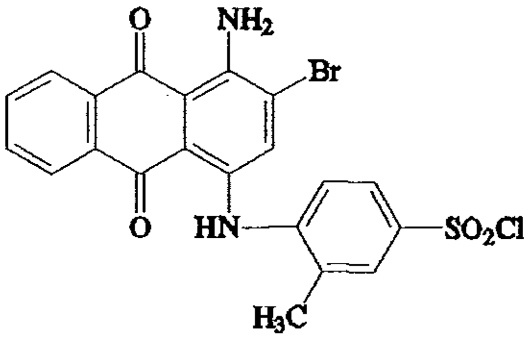
Many compounds related to alizarin are of commercial importance as dyes and most of them are applied in conjunction with metal salts. Typical examples are anthragallol, alizarin cyanine NS, anthracene blue WR, bordeaux B and alizarin Red S.

1.4 General Nature and Uses of Complexes [4]

An understanding of the mechanisms of even a simple inorganic reaction requires at the minimum a quantitative knowledge about the constitution and environment of the reactants and products. Thus one of the major aspects of coordination Chemistry is to study reaction mechanisms of inorganic compounds. In analytical Chemistry increasing use is being made of organic precipitating and complexing agents such as EDTA. The organic chemists often use coordination compounds in preparative reactions. Examples are Friedel-Crafts and Grignard reactions. In physical Chemistry complexes have provided suitable compounds for testing and expanding the theories in the area of bonding, electrolytic behaviour of ions, magnetic behaviour, solution thermodynamic and kinetic behaviour. In biochemistry the effect of metal ions in the form of complexes on biological processes is of prime interest. The haem and chlorophyll-a contain co-ordinated Fe[II] and Mg[II], respectively, while vitamin B_{12} contains cobalt ion at its center. Many enzymes are active only if trace amount of metal ions are present and in many cases the active site of the enzyme is at a co-ordination position of the metal.

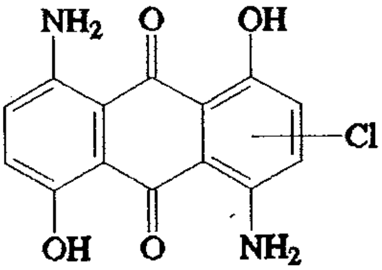
2 LITERATURE SURVEY

While the unsulphonated arylamino-anthraquinones were prepared as early as 1929 [5], alizarin blue sky [6] (1-amino-2-bromo-4-(-2 methyl-4-sulphonylchloride) anthraquinone (I), [$C_{21}H_{14}BrClN_2O_4S$, dark Blue Crystals, Mw = 505.5, m.p. 245-247 °C, soluble in water, ethanol, acetone, and dimethylsulphoxide (DMSO) but insoluble in chloroform and n-hexane]



I

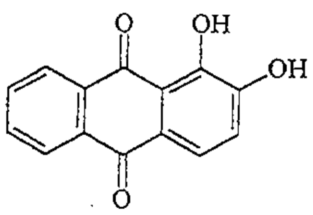
was first prepared in 1973 and is being used since then as a dye. Disperse blue (1,5-dihydroxy-4,8diaminochloroanthraquinone (II)) has the structural formula shown below (Black crystals, $C_{14}H_9ClN_2O_4$, Mw = 304.5, m.p. 285°C, soluble in water, acetone, and DMSO, slightly soluble in ethanol and chloroform but insoluble in n-hexane). It was first prepared in 1971 [4], and since then, it is being used as a dye.



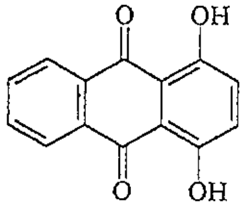
II

The literature of hydroxy-anthraquinone and their derivatives (Table 1) in complex formation with metal ions is rich. However, little is known about the complex formation of amino-anthraquinone and their derivatives with metal ions. The first report [8] on the colour reactions of sodium dioxide with 1,2-di and 1,2,3-tri-hydroxy-anthraquinone, was followed by a great deal of work. The product obtained by reacting $SnCl_4$ with alizarin and quinizarin were found to be $C_6H_4(CO)_2C_6H_2(OH)SnCl_3$[9] and $C_6H_4(CO)_2C_6H_2(O)_2SnCl_2$ respectively. The Na, K, and Ca salts of alizarin ferric acid [10], R = $C_6H_4(CO)_2C_6H_2(O^-)_2$, $[FeR_3]K_3.8H_2O$, $[FeR_3]$ $Na_3.12H_2O$ and $[FeR_3]Ca_3.6H_2O$ were prepared. The Bi-alizarin complex $C_{14}H_7O_5Bi$ was isolated and applied to chemotherapeutic study [11]. Alizarin was used as a complexing reagent for the colorimetric determination of Al and Fe [12,13]. The structure of Al-Ca-alizarin complex was given as,

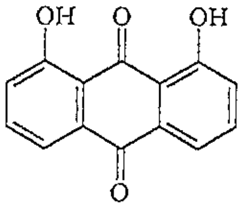
Table 1. Some anthraquinone derivatives



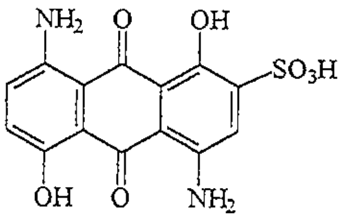
Alizarin



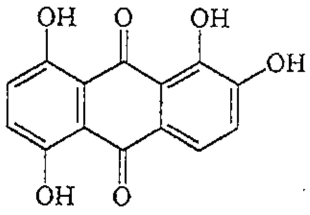
Quinizarin



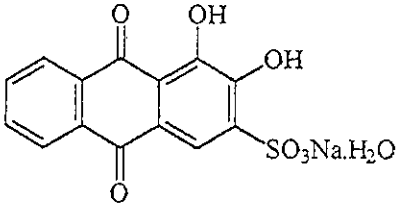
Chrysazin



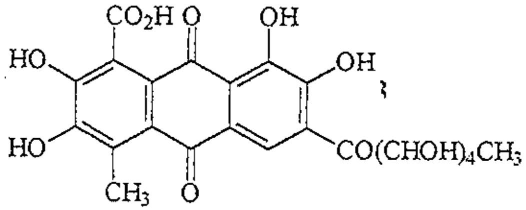
Alizarin Safirol SE



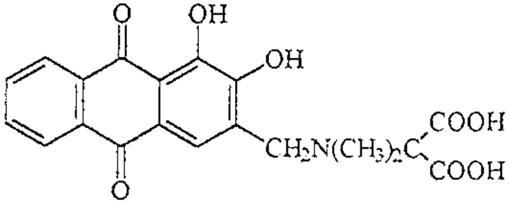
Quinalizarin



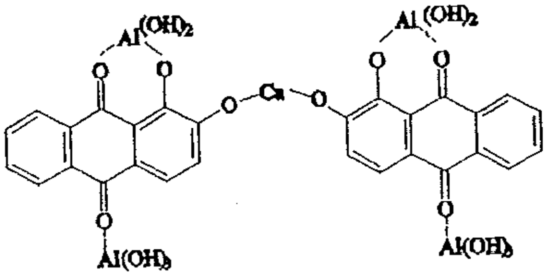
Alizarin Red S



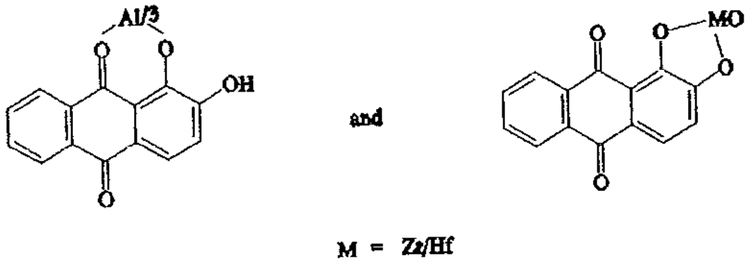
Carminic acid



Alizarin complexone



An attempt was made to explain the mechanism of formation [14]. Alizarin-Al, Fe, Co, Cr, Cu, Zn, Ca, Ga complexes were reported [15-17]. Alizarin was used as a complexing agent for spectrophotometric determination of Zr, Hf and Al, and the structures [18-22] were given as



1-amino-4-hydroxyanthraquinone was recommended as an analytical reagent for determination of Ti [23]. Complexes of Zr, Th, Ce and La with alizarin were used as colorimetric reagents for the determination of fluoride and sulphate ions in food, natural water and agricultural products [24-32]. Alizarin complexone was used for the determination of Nb in Nb_2O_5 (Nb-L 1:3) [33]. Complexes of alizarin complexone with Cu, Ce, Al, Fe, Ni, Y, Yb, Ti, V, Pb, Zn in molar ratio 1:1, 1:2 with Bi and La were reported [34,35]. Microcolour spot test for Be^{2+}, VO^{2+} and UO^{2+} with alizarin red S was reported [36]. Pd[II], Pt[II], Cu[II] alizarin complexes in molar ratio 1:2 were

3 OBJECTIVES

Literature survey reveals that complexes of alizarin blue sky and disperse blue have not been prepared or characterized, and their application in analytical Chemistry has not been tried. Our objective is to prepare and characterize the complexes of alizarin blue sky and disperse blue with Zn(II), Cd(II), Hg(II), Ti(IV), Zr(IV) and Pd(II) and find out their application in analytical chemistry.

4 EXPERIMENTAL

4.1 INSTRUMENTS AND EQUIPMENT

The electronic spectra were recorded using a Beckmann Du 65 UV/V spectrophotometer in quartz cuvette of 1 cm path length. A Beckmann FT-IR 1600 spectrophotometer was used for recording the IR spectra in KBr discs and nujol mull. All pH values were measured with a Beckmann Chem-Mate pH meter (calibrated against standard buffer solutions of pH 4 and 7). The melting points were determined using Thomas Hoover capillary melting point apparatus. The thermal analysis charts were recorded by Shimadzu apparatus. The elemental analysis for C, H and N were done in Cairo University, Egypt.

4.2 CHEMICALS, REAGENTS AND SOLUTIONS

The following metal salts which are of BDH grade were used: $Zn(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$, $Hg(NO_3)_2.H_2O$, TiO_2, $ZrOCl.8H_2O$ and $PdCl_2$. Alizarin blue sky (ABS) and disperse blue (DB), were provided by Mehalla Elkobra company (Egypt) and were used without further purification. Stock solutions (5×10^{-3} M) were prepared by dissolving an accurate weight of each substance in the appropriate volume of distilled water. A universal buffer solution covering the pH range 1.8 to 12 was prepared from a mixture of 0.04 M acids (phosphoric, acetic and boric) and 0.2 N sodium hydroxide [66], to keep the ionic strength constant.

4.3 SPECTROPHOTOMETRIC STUDIES

4.3.1 The spectral behaviour of the ligands

4.3.1.1 Beer's Law

The spectra of ABS and DB, each at a concentration of 5.22 x 10^{-4} M, were recorded in the range 210-890 nm (Figs. 1 and 2). The spectra showed that, ABS absorbs at wave lengths 244 nm (ϵ = 5 x 10^3 LM^{-1} cm^{-1}), 284 nm (ϵ=4.8 x 10^3 LM^{-1} cm^{-1}), 584 nm (ϵ = 5.4 x 10^3 LM^{-1} cm^{-1}) and 630 nm (ϵ = 5.4 x 10^3 LM^{-1} cm^{-1}). Also two shoulders appear at 309-322 nm (ϵ = 1.9 x 10^3 LM^{-1} cm^{-1}) and 366-394 nm (ϵ = 1.1 x 10^3 LM^{-1} cm^{-1}). DB absorbs at 244 nm, 284 nm and 567 nm with molar absorptivities, ϵ, of 5 x 10^3, 4.8 x 10^3 and 2.8 x 10^3 LM^{-1} cm^{-1} respectively.

Beer's law is applicable up to concentration ranges 5.5 x 10^{-4}M and 1 x 10^{-3}M for ABS and DB respectively(Figs. 3, 4 and 5).

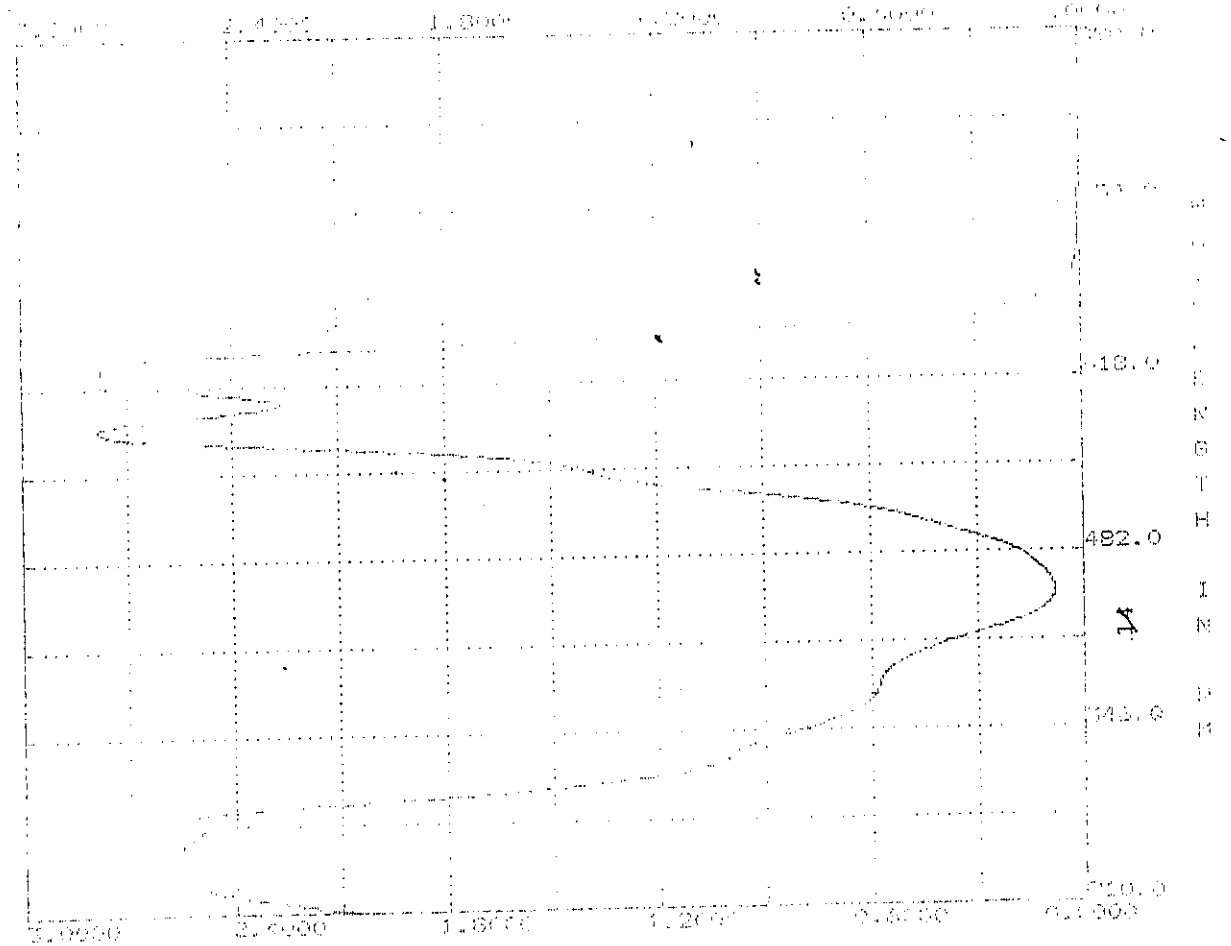


Fig.1 Electronic spectra of 5.22 X 10^{-4} M ABS

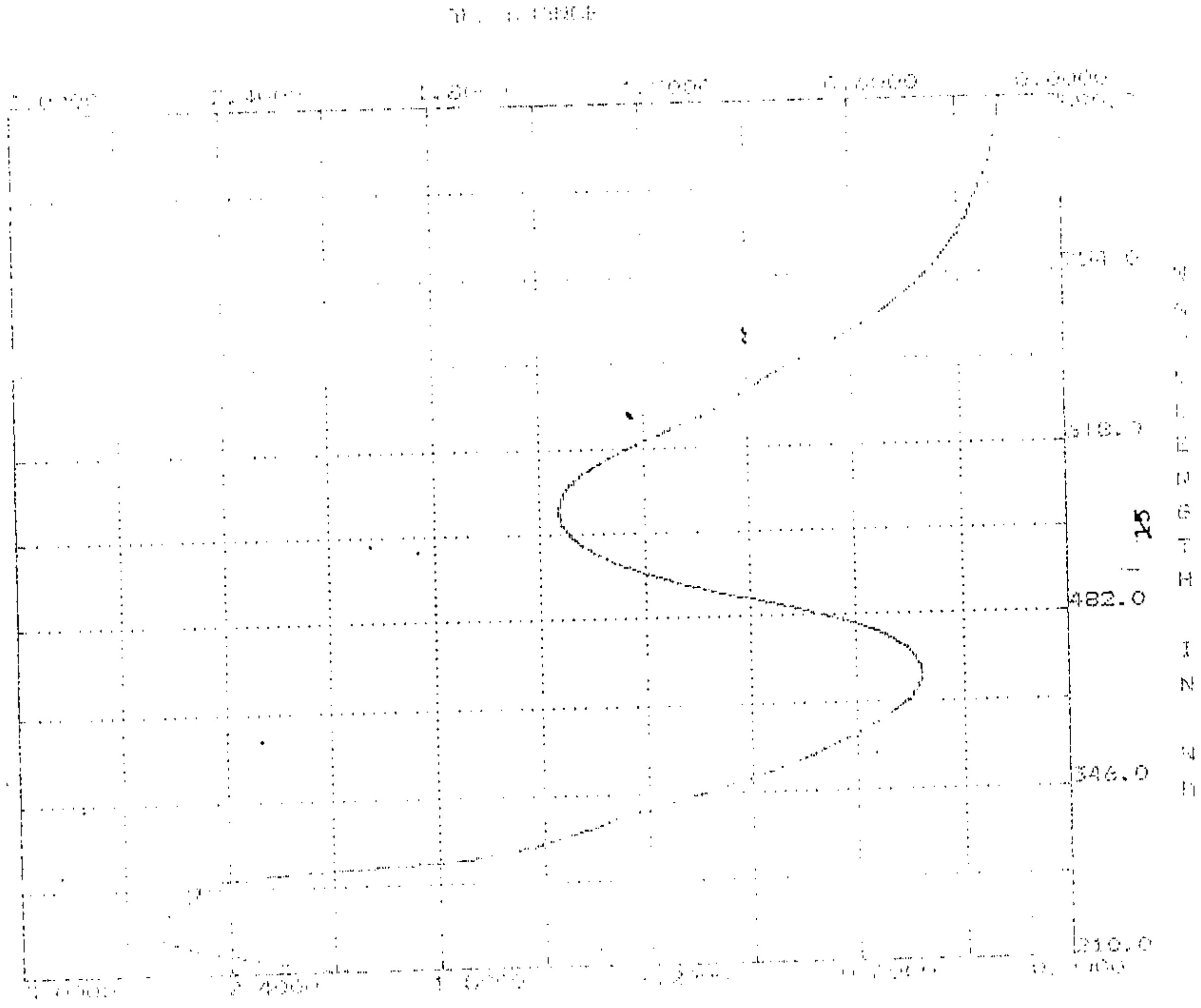


Fig.2 Electronic spectra of 5.22 X 10^{-4} M DB

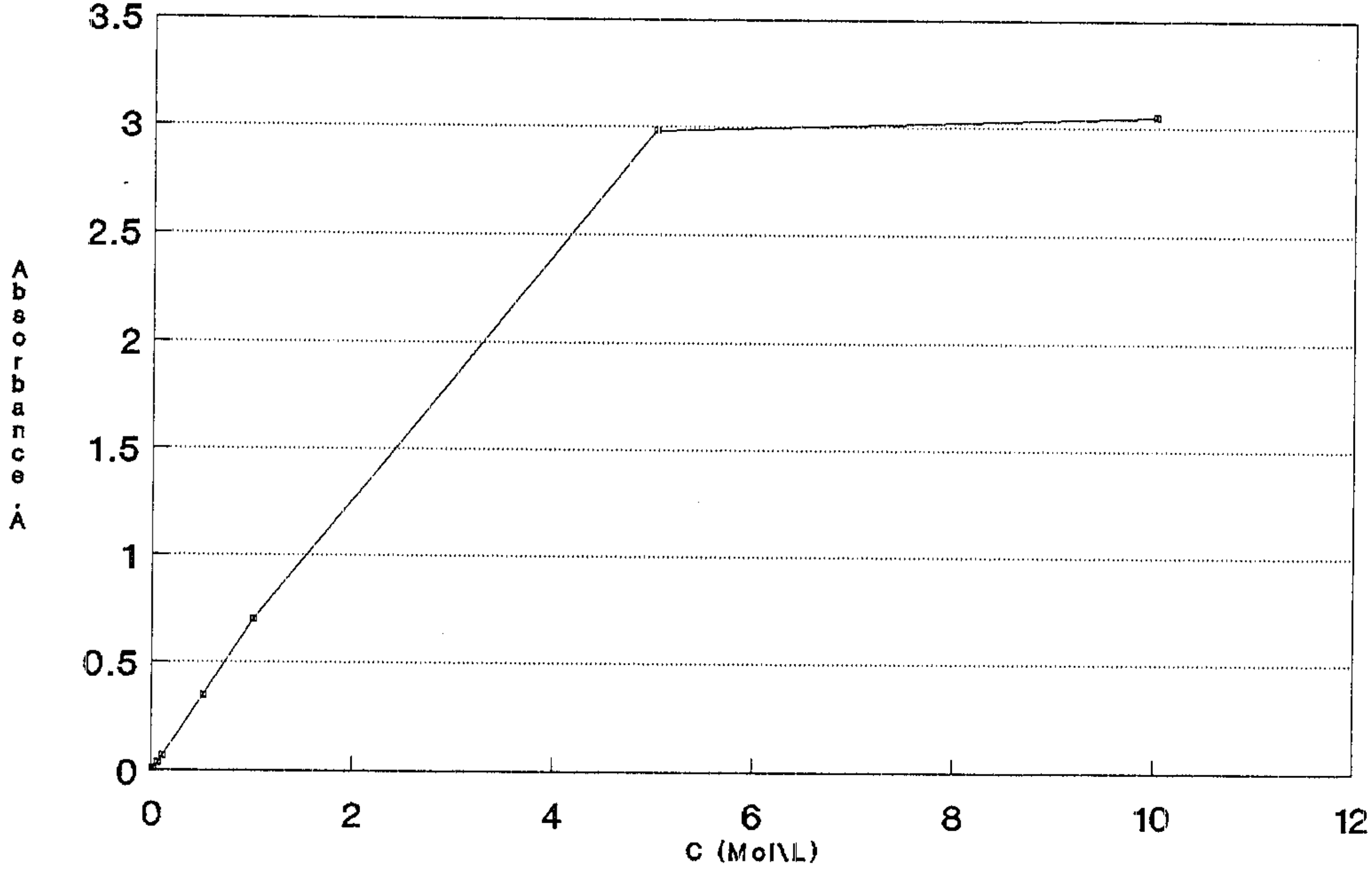


Fig.4 ABS A vs Concn.C,(Mol.\L)
at 630 nm.

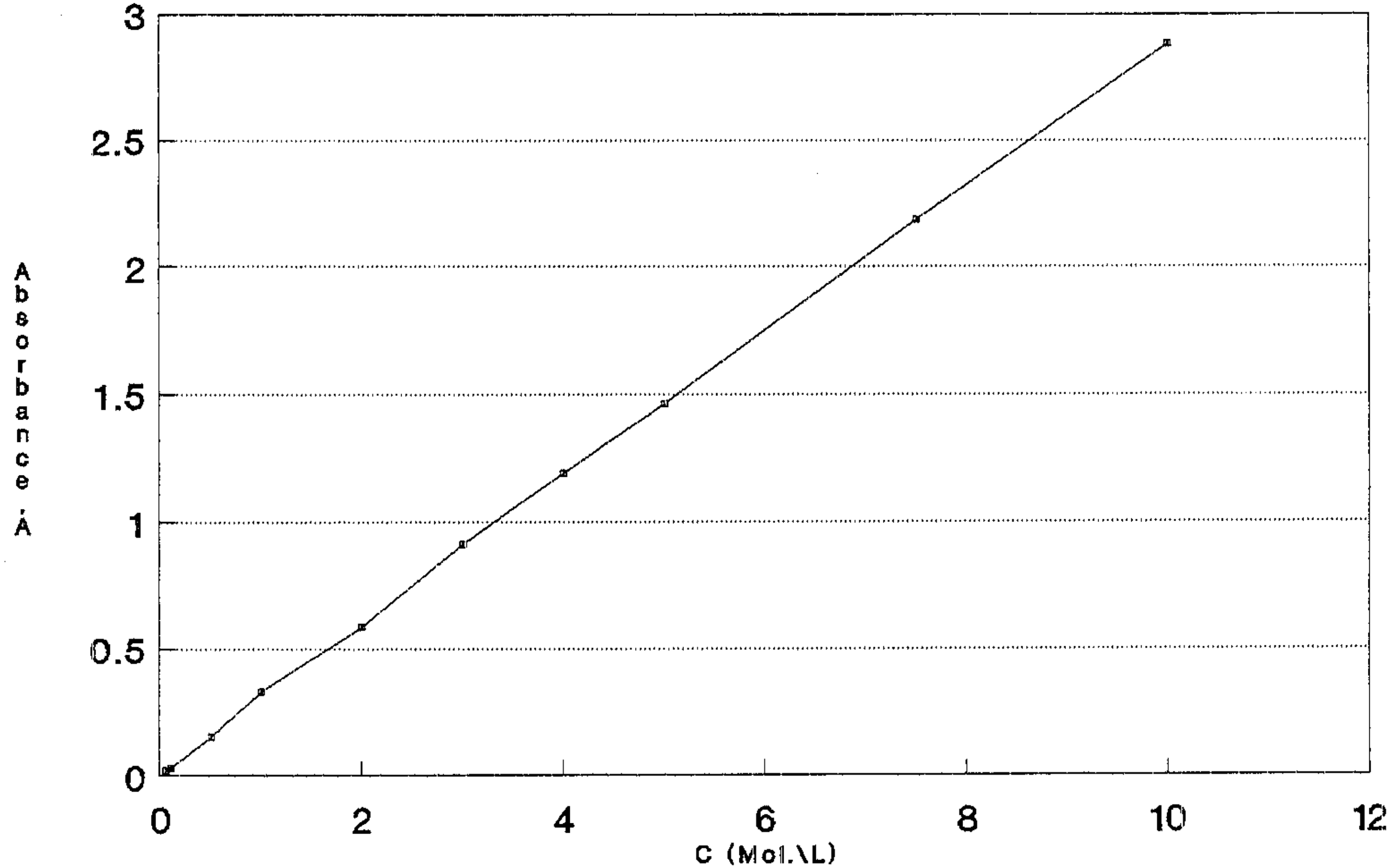


Fig.5 DB absorbance, A vs Concn.C (Mol.\L) at 567 nm.

4.3.1.2 Effect of pH

The spectra of 3.6×10^{-5} M ABS and 5.2×10^{-4} M DB were measured in buffer solutions in the pH range 2.1 - 11.7 (Tables 2 and 3). The solution (3.6×10^{-5} M) shows slight change in the magnitude of absorption with pH at λ_{max}630nm, while the magnitude of absorption of DB at λ_{max}567 nm decreases to a minimum at pH 9.6 and then increases with increasing the pH. A noticeable bathochromic shift is observed at pH 12 from 567 nm to 573 nm.

Table 2. 3.6 x 10^{-5} M ABS A vs pH at λ_{max} 630nm.

Sample No.	pH	Absorbance,A
1	2.5	0.2840
2	3.3	0.2880
3	4.3	0.2880
4	5.7	0.2920
5	6.3	0.2960
6	7.4	0.2840
7	8.5	0.2960
8	9.7	0.2880
9	11.9	0.2920

Table 3. 5.22×10^{-4}M DB variation of absorbance, A with pH at λ_{max} 567 nm.

Sample No.	pH	A
1	2.85	1.5000
2	3.36	1.5150
3	6.05	1.5450
4	6.90	1.5900
5	7.30	1.6200
6	8.90	1.6650
7	9.60	1.4400
8	10.05	1.5900
9	10.35	1.6050
10	11.10	1.6200
11	11.60	1.7100
12	12.00 12.00	1.8300 1.8450

4.3.2 THE STOICHIOMETRY OF COMPLEXES

To study the stoichiometry of the complexing species in solution, the absorbances of ABS metal ions complexes were measured at λ_{Max}630nm, at constant concentration of the metal ion (2×10^{-6}M). The concentration of the ligand was varied from $6 \times 10^{-7} - 4 \times 10^{-6}$ M. The absorbances of the DB metal ion complexes were measured at λ_{Max}567nm, where the concentration of DB was kept constant at 1×10^{-6} M and the concentration of the metal ion varied from $1 \times 10^{-7} - 4 \times 10^{-6}$ M. The absorbances of ABS complexes versus the ratio, [ABS]/[M] were plotted , where M = Zn(II), Cd(II), Hg(II) Ti(IV), Zr(IV) or Pd(II). The molar ratios were determined from Figs.6-11. The absorbances of DB metal ion complexes were plotted against the concentration ratio [M]/[DB] and the stoichiometries were also determined from (Figs.12-17). The metal/ligand ratio for ABS complexes amounted to 1:1 except for Pd(II) complex which gave 2:1. (M/L) Metal DB ratio amounted to 1:2 for all complexes except for Pd(II) which gave 2:3 and 1:1 for Zr(IV).

4.3.3 THE EFFECT OF pH ON COMPLEXES

The spectrum of the different metal ions with the studied ligands of a known stoichiometry were measured in the pH range 2.5-11.7. For ABS complexes the absorbances were taken at λ_{max}630 nm, while for DB at λ_{max}567 nm. The results are given in Tables 4 and 5 , where A vs pH curves were constructed and the pH values suitable for complex formation were determined.

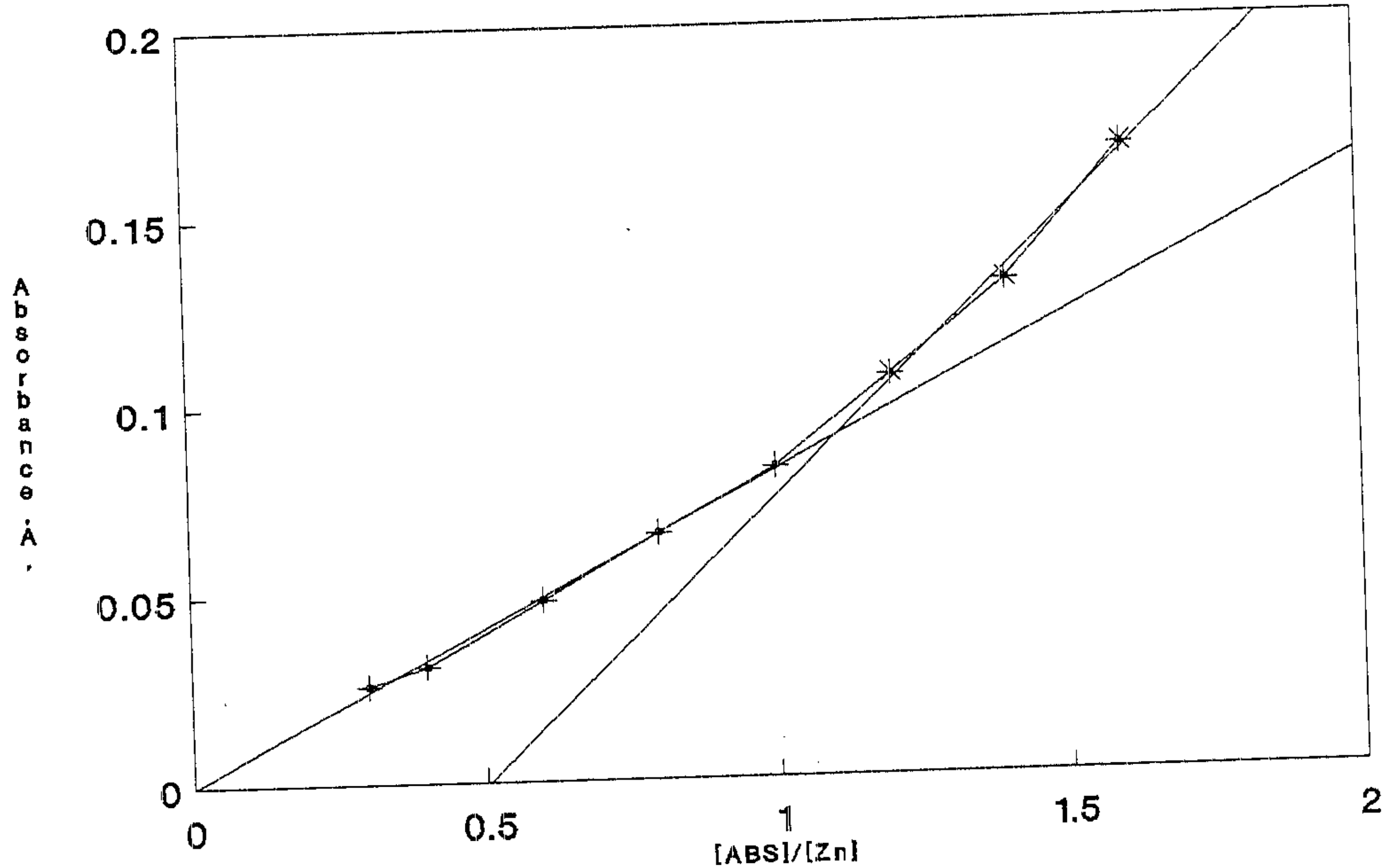


Fig. 6 Mole ratio curve for ZnABS complex [Zn] = 0.000002M at 630 nm.

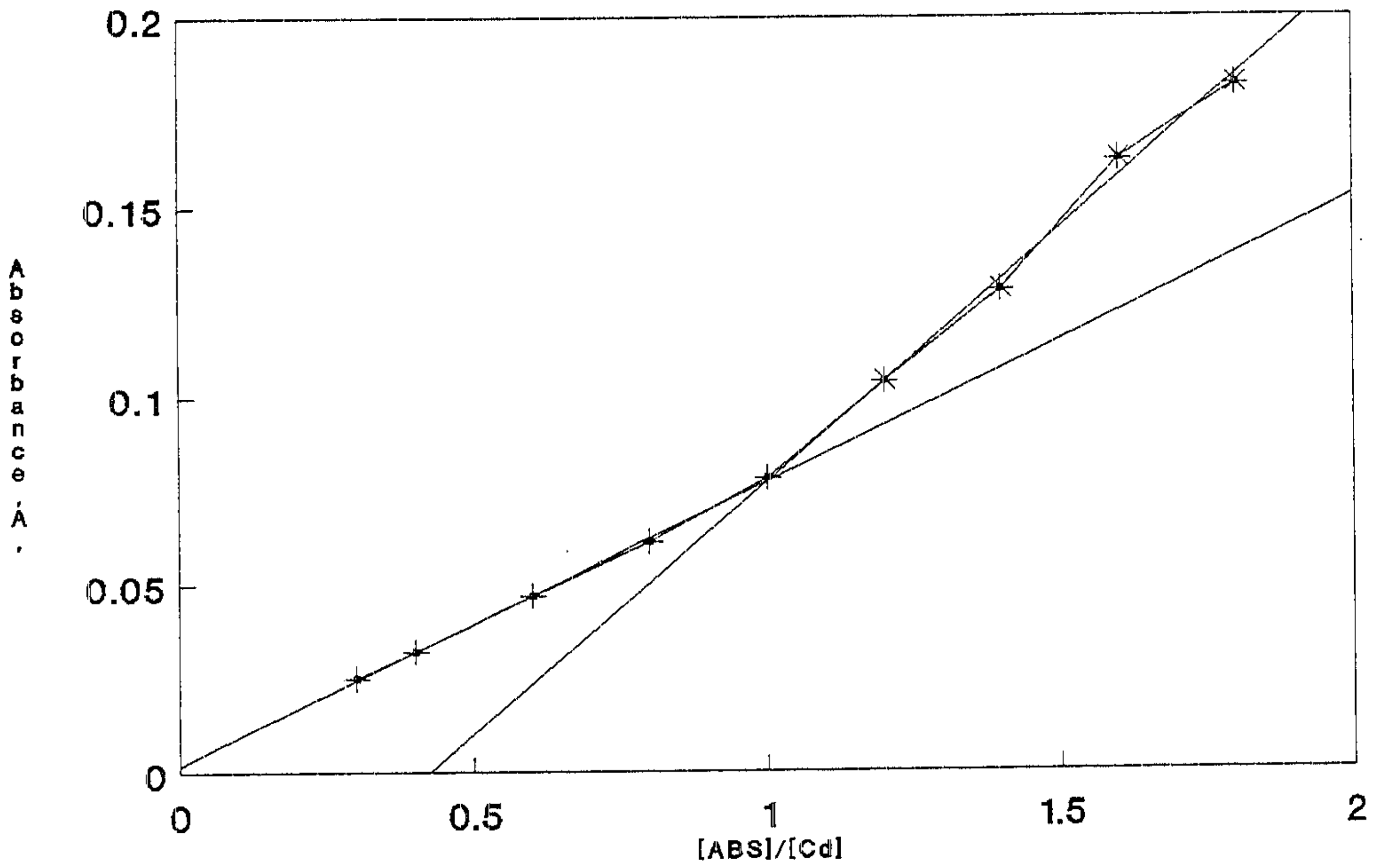


Fig.7 Mole ratio curve for CdABS complex [Cd] = 0.000002M at 630nm

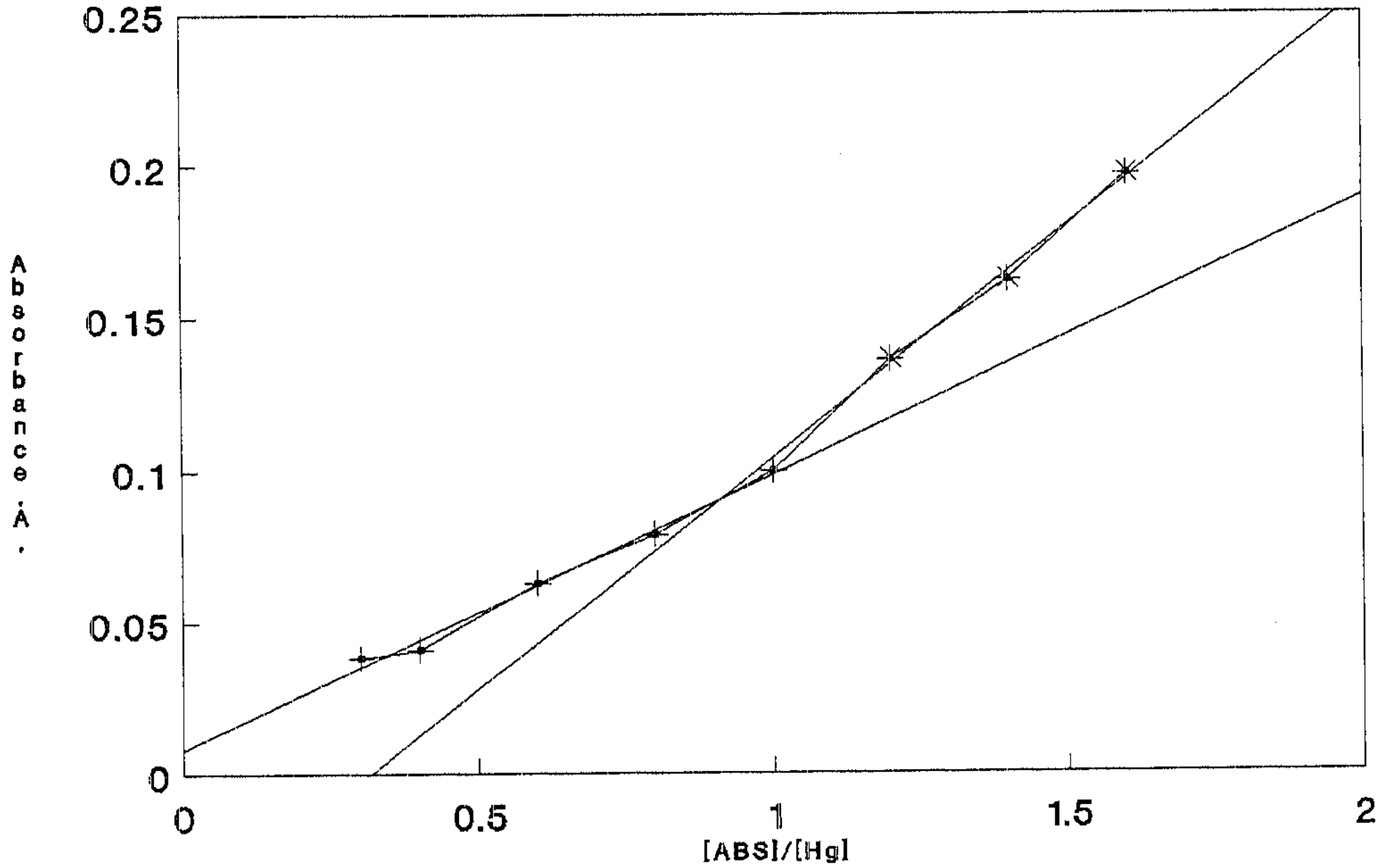


Fig. 8 Mole ratio curve for HgABS complex [Hg]=0.000002M,at630nm.

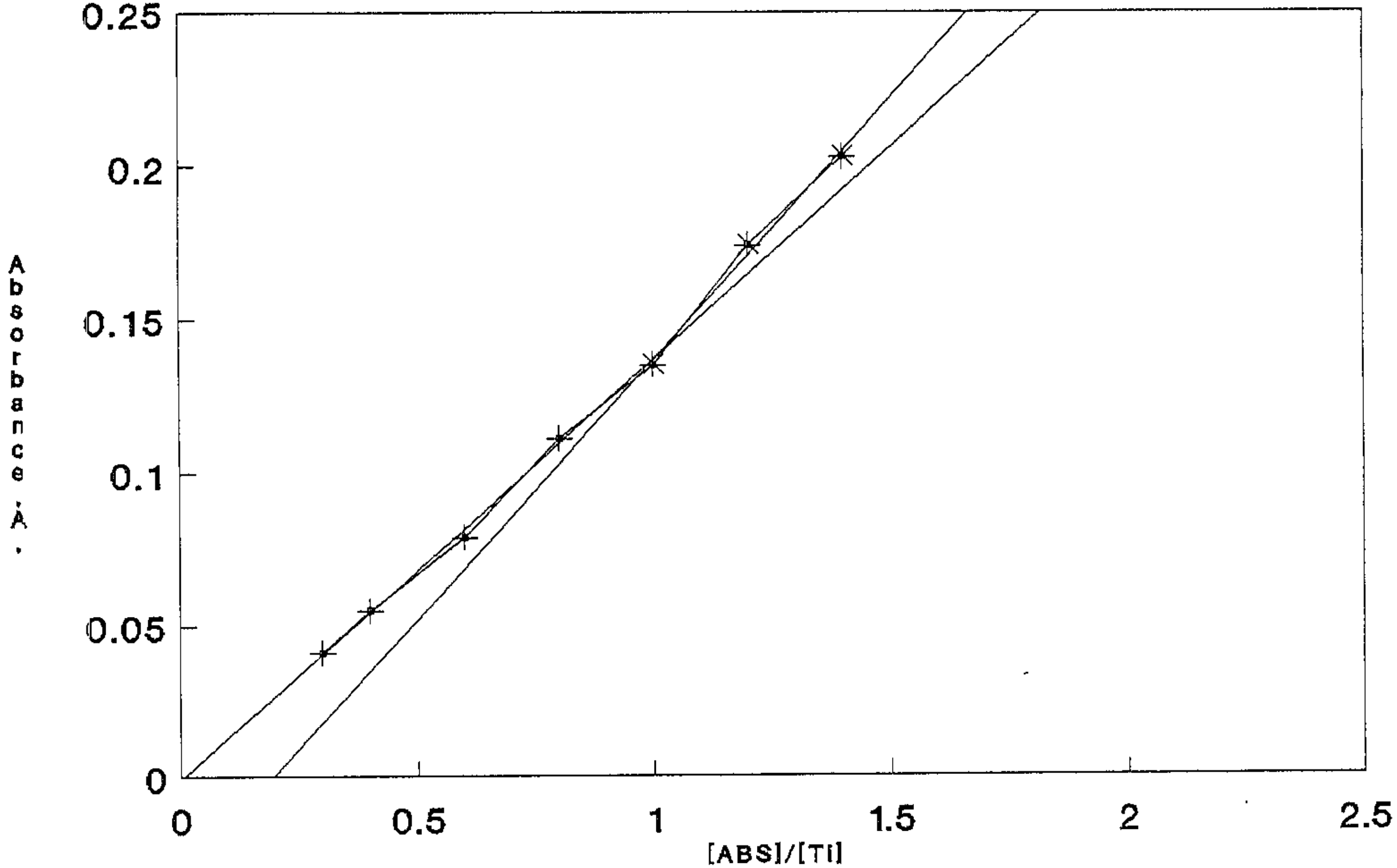


Fig.9 Mole ratio curve for TiABS complex
[Ti]=0.000002M,at630nm.

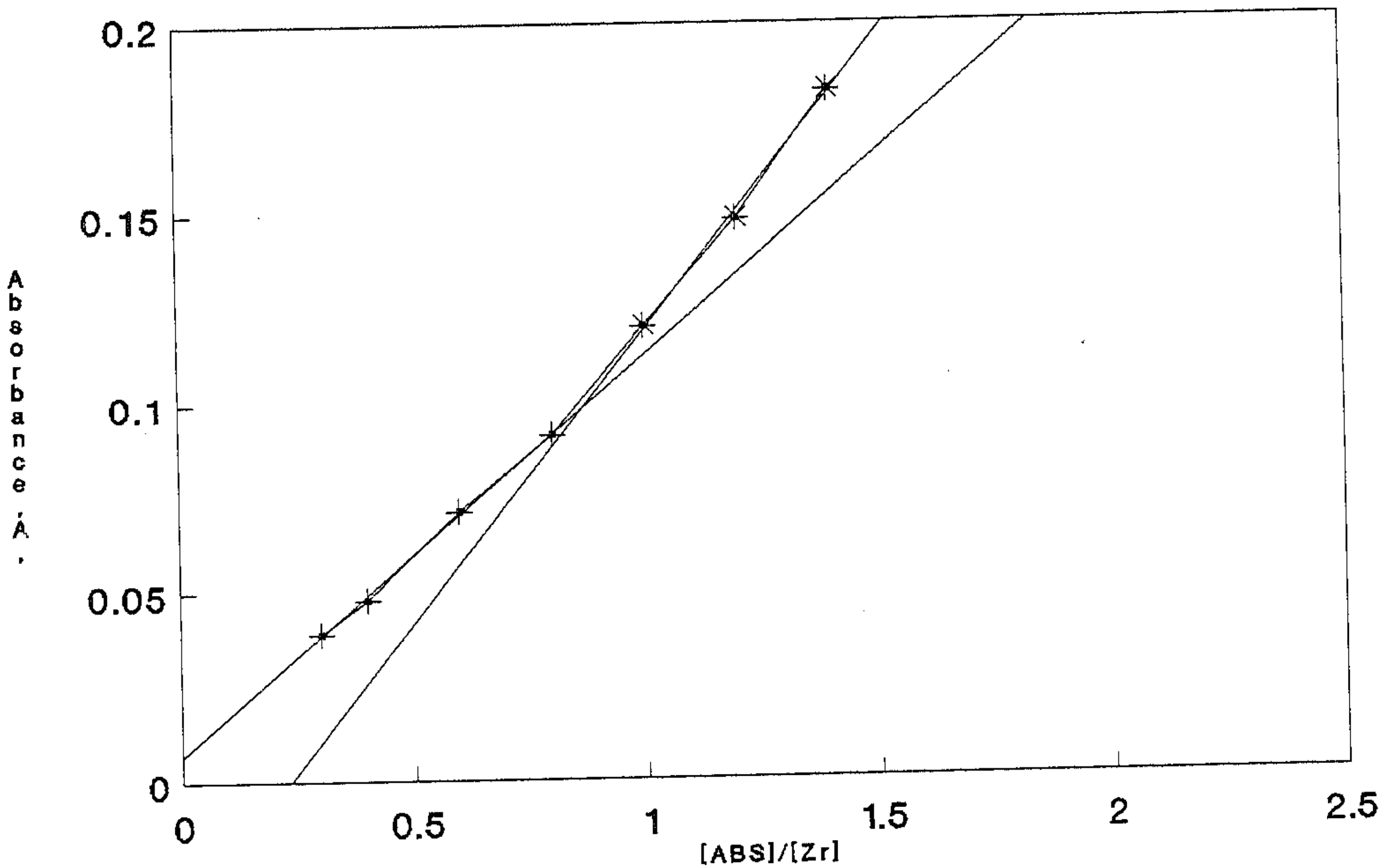


Fig.10 Mole ratio curve, ZrABS complex
[Zr]= 0.000002M at 630nm.

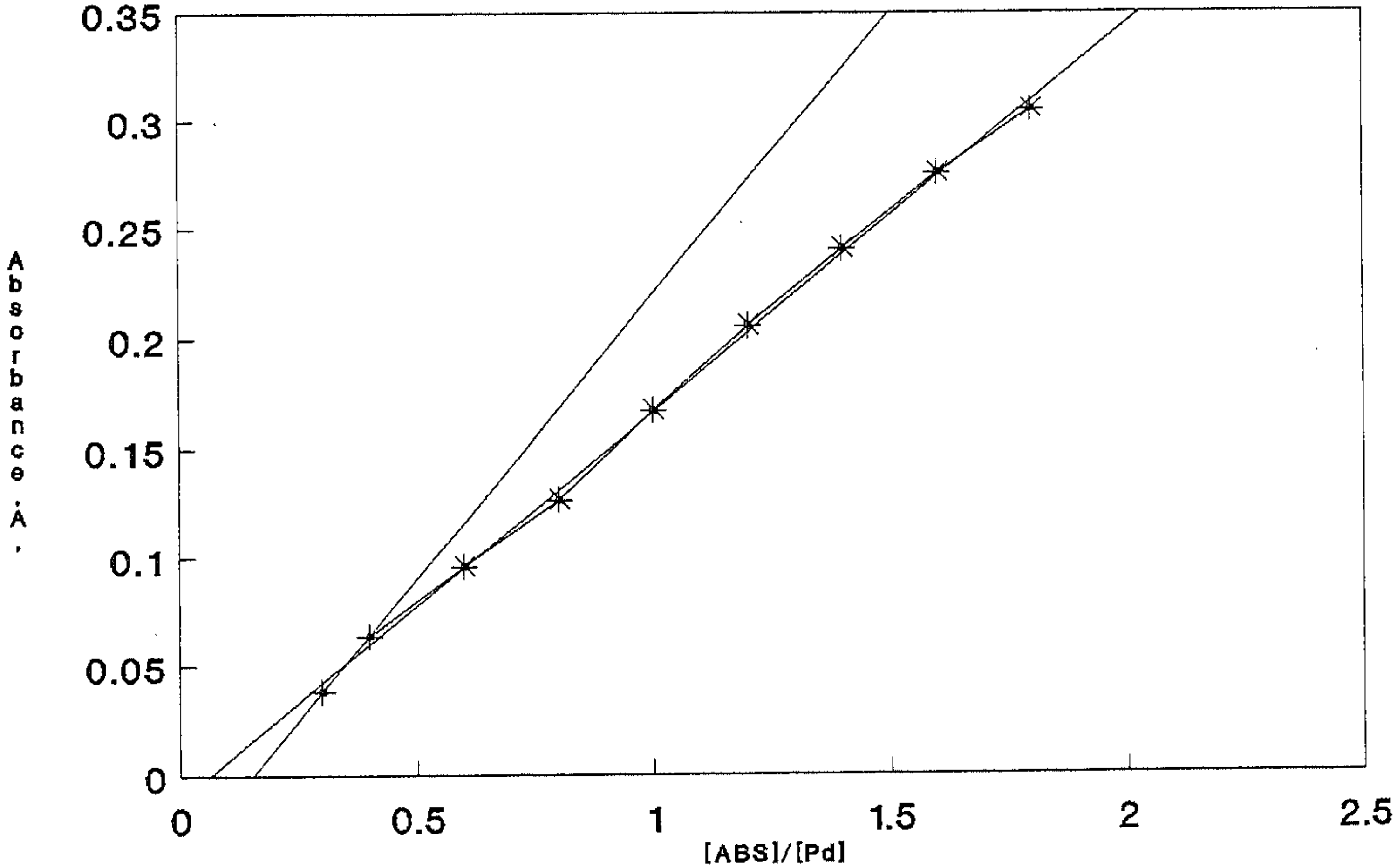


Fig.11 Mole ratio curve PdABS complex
[Pd]= 0.000002M at 630nm.

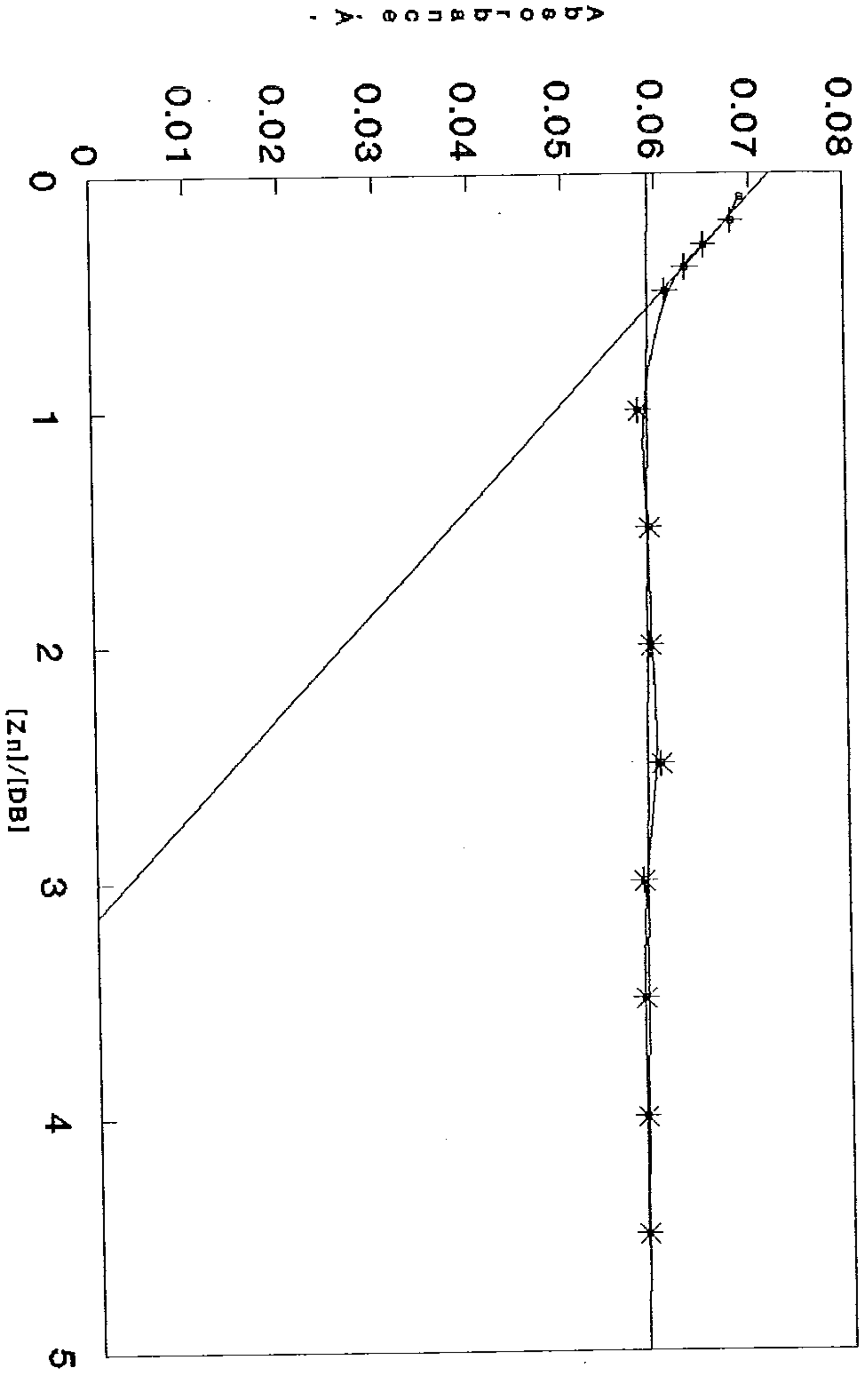


Fig.12.Mole ratio curve , ZnDB
complex,[DB]= 0.000001M,at567nm

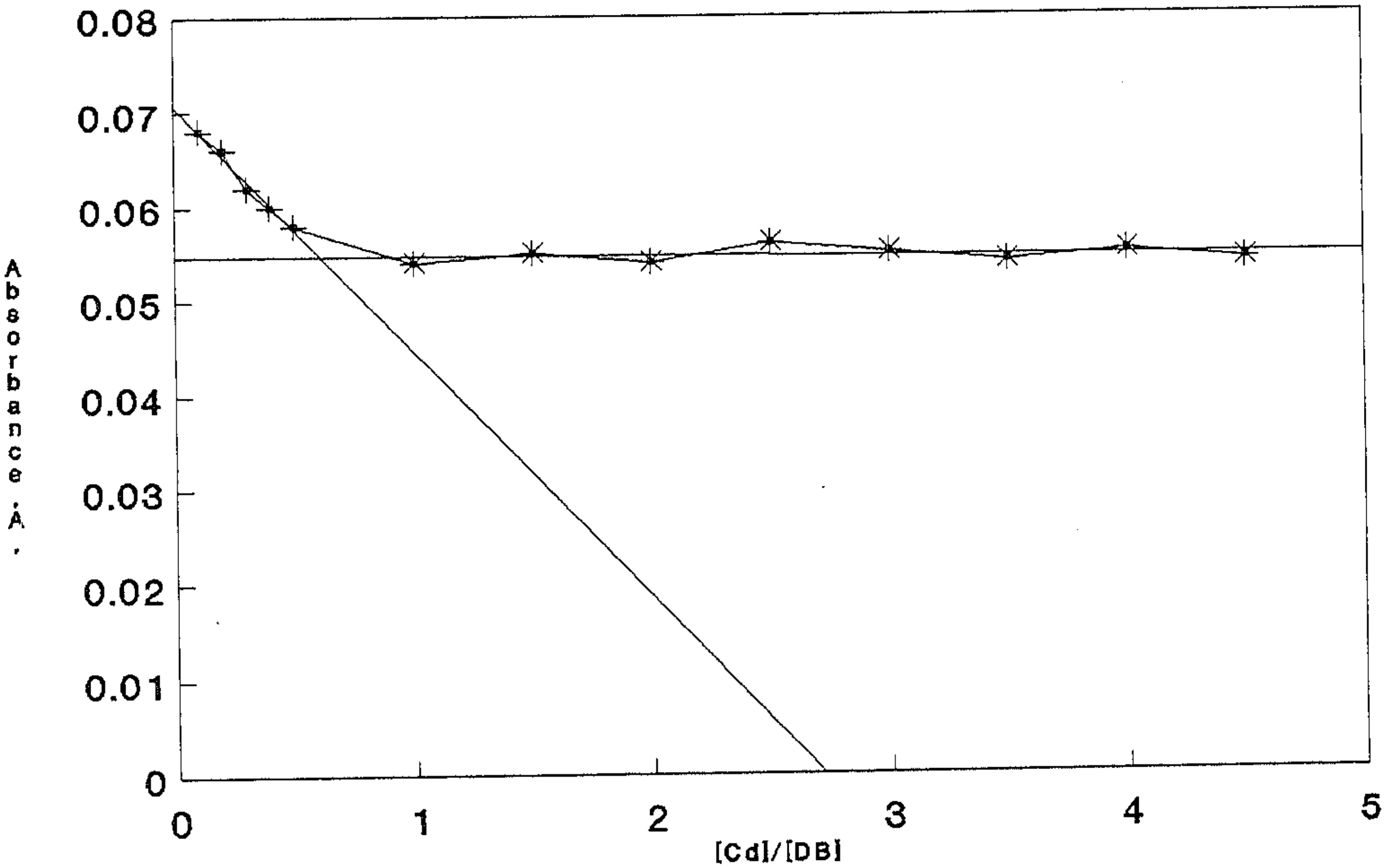


Fig.13 Mole ratio curve for CdDB complex,[DB]=0.000001M,at567nm.

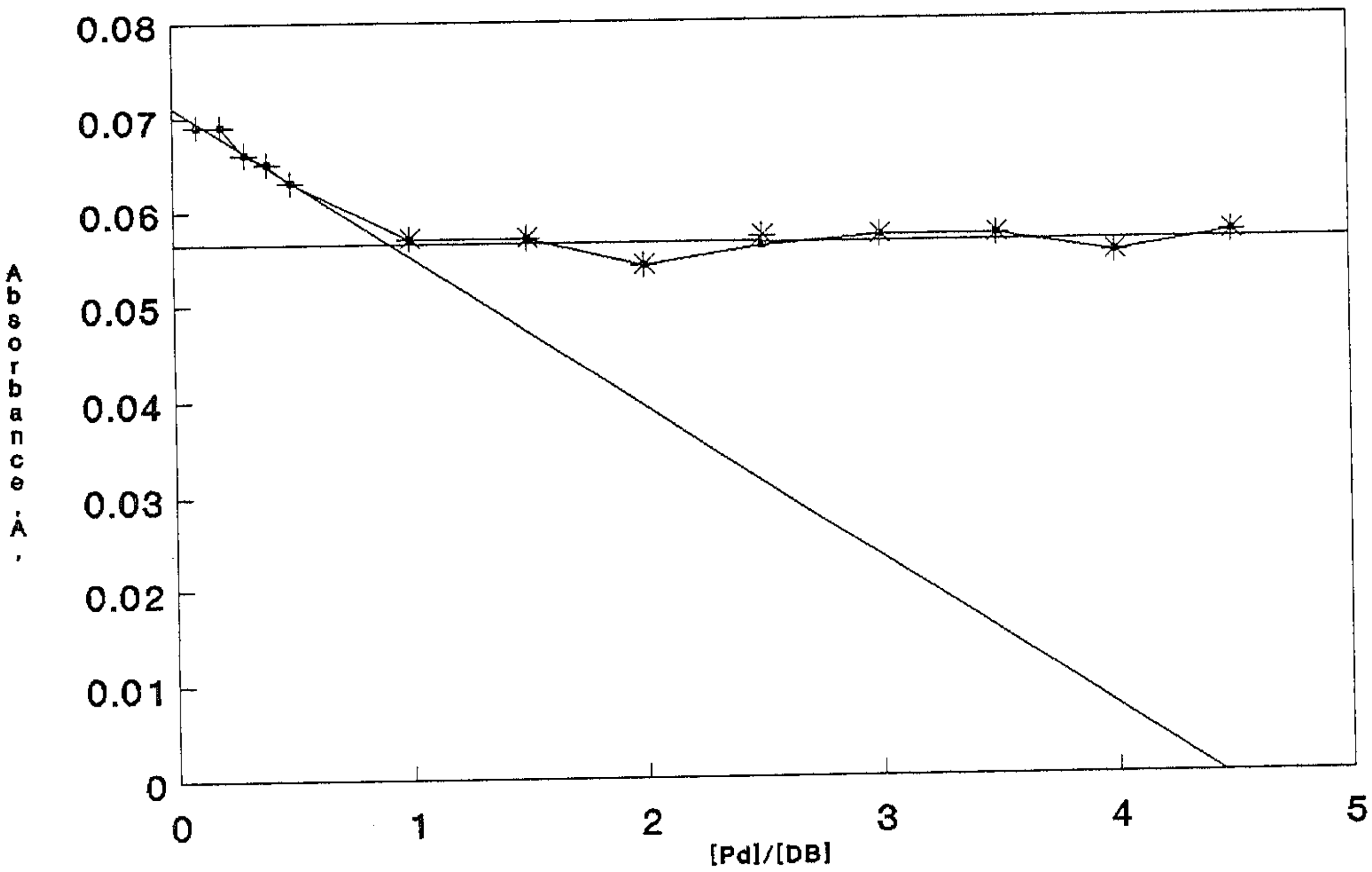


Fig.17 Mole ratio curve,PdDBcomplex
[DB]=0.000001M,at567nm.

Table. 4. Variation of Absorbance, A at 360nm, with pH for ABS metal ion complexes (2 ml of each Zn, Cd, Hg, Ti or Zr[$1x10^{-3}$M], added to 2 ml each of ABS [$1x10^{-3}$M], or 1 ml Pd [$1x10^{-3}$M] into a 50 ml measuring flask)

ZnABS		CdABS		HgABS	
pH	A	pH	A	pH	A
2.50	0.042	3.00	0.040	2.35	0.060
4.40	0.040	4.80	0.039	5.70	0.063
6.00	0.042	5.60	0.040	6.80	0.062
7.20	0.041	6.80	0.041	8.60	0.056
8.80	0.042	7.75	0.040	9.25	0.058
9.70	0.040	8.90	0.039	11.70	0.061
10.40	0.042	10.00	0.041		
11.70	0.043	11.60	0.040		

TiABS		ZrABS		PdABS	
pH	A	pH	A	pH	A
2.20	0.065	2.35	0.073	3.20	0.130
3.90	0.065	3.36	0.070	4.00	0.133
5.50	0.067	4.20	0.061	5.20	0.130
6.80	0.069	5.10	0.054	6.60	0.136
7.60	0.066	5.70	0.053	8.00	0.136
8.20	0.062	6.90	0.058	9.20	0.138
9.25	0.059	7.85	0.057	10.00	0.144
10.65	0.060	8.70	0.056	10.80	0.154
11.60	0.068	10.30	0.058	11.70	0.177

Table.5 Variation of Absorbance,A at 567nm, with pH for DB metal ion complexes ([M]=[DB]=$1x10^{-3}$M, made in a 25ml measuring flask-ml of M=1, ml of DB=2 ml for Zn, Cd, Hg and Ti, 2 ml each for Zr and 2 ml of Pd to 3 ml of DB)

ZnDB		CdDB		HgDB	
pH	A	pH	A	pH	A
2.40	0.090	2.30	0.089	2.50	0.106
5.60	0.088	5.70	0.087	5.80	0.103
6.80	0.085	6.75	0.084	7.00	0.110
8.40	0.079	7.90	0.078	8.10	0.119
9.40	0.084	9.30	0.086	9.10	0.117
10.50	0.093	10.40	0.087	10.60	0.110
11.70	0.096	11.50	0.083	11.55	0.105

TiDB		ZrDB		PdDB	
pH	A	pH	A	pH	A
2.60	0.113	2.25	0.113	2.3	0.106
5.30	0.112	4.00	0.116	5.4	0.112
6.80	0.085	6.75	0.084	6.5	0.111
8.40	0.079	7.90	0.078	7.8	0.107
9.40	0.084	9.30	0.086	9.3	0.108
10.50	0.093	10.40	0.087	10.3	0.114
11.70	0.096	11.50	0.083	11.6	0.110

4.4 ISOLATION OF THE SOLID COMPLEXES

In general the concentration of the metal ion was kept constant while that of the ligand varies according to the stoichiometry at the pH of complexation. The suitable conditions for complexation were then selected. It had been noticed that the complexes are insensitive to light and stable to air oxidation.

The metal ions concentration in the isolated complexes as, Zinc [67], Cadmium [68] and Mercury [69] were determined using EDTA in the presence of Erio Chrome Black T or Xylenol orange as an indicator. Palladium [70] was determined gravimetrically with dimethyglyoxime. Zirconium [71] and titanium [72] were determined colorimetrically with alizarin red S and hydrogen peroxide respectively. The results of metal ions determination together with the elemental analysis are summarised in Table 6.

Table 6. elemental analysis of ABS and DB and their metal complexes: [calcd.]

Compound	%M	%C	%H	%N
ABS	-	48.98 [49.9]	2.71 [2.77]	3.88 [5.54]
DB	-	56.01 [55.17]	3.10 [2.96]	- [9.20]
ZnABS	11.11 [11.40]	44.14 [44.33]	2.11 [2.11]	4.03 [4.93]
CdABS	18.10 [18.20]			
HgABS	27.40 [28.50]			
TiABS.2OH	7.85 [8.14]			
$ZrOABS.2H_2O$	16.20 [16.50]	38.35 [38.95]	2.90 [2.47]	3.47 [4.33]
$Pd_2ABS.4H_2O$	26.30 [26.90]			
$Zn(DB)_2$	9.40 [9.70]			
$Cd(DB)_2$	15.10 [15.60]			
$Hg(DB)_2$	24.40 [24.90]			
$Ti(DB)_2.2OH$	6.70 [6.90]			
$ZrODB.2H_2O$	23.60 [23.96]			
$Pd_2(DB)_3$	18.10 [18.90]			

4.4.1 PREPARATION OF ZnABS COMPLEX

$Zn(NO_3)_2$ $6H_2O$, 0.9916 g (3.3 mmoles) was dissolved in 200 ml of warm distilled water . To this a hot solution containing 1.6850 g (3.3 mmoles) ABS in 400 ml distilled water was added. The mixture was shaken vigorously. An immediate precipitate was formed. The content was then heated for a short time (20 min.) and stirred, then cooled to room temperature. The precipitate was collected by centrifugation and washed several times with distilled water until the washing was colourless,then washed with a little portion of acetone and dried in a desiccator over anhydrous calcium chloride. Dark grey solid was obtained; yield, 0.07213 g. The solid is slightly soluble in ethanol, DMF and DMSO but insoluble in water, chloroform, n-hexane and 1,4-dioxan. m.p.: does not melt below 300°C; FT-IR data: 3448, new bands, 410s, 428w, 431, 669 and 1370m cm^{-1};elemental analysis: %M = 11.11 [Calcd.11.4], %C = 44.14 [44.33], %N =4.03 [4.93], %H = 2.11 [2.11].

4.4.2 PREPARATION OF CdABS COMPLEX

Method 4.4.1 was used. Dark grey solid was obtained. Yield 0.7700 g (from 1.0282 g, 3.3 mmoles, $Cd(NO_3)_2 4H_2O$ in 200 ml distilled water and 1.6850 g, 3.3 mmoles, ABS in 400 ml distilled water). The solid is slightly soluble in ethanol, DMF and DMSO but insoluble in water, acetone, chloroform, n-hexane and 1.4-dioxan. m.p.: does not melt below 300°C; FT-IR data: 3446 (w), 1611, new bands, 403, 412, 453, 678 (vs), 877 (w), 923 (w) and 1379 (s) cm^{-1}; elemental analysis : % M = 18.10

[Calcd. 18.20].

4.4.3 PREPARATION OF HgABS COMPLEX

$Hg(NO_3)_2.H_2O$, 1.1420 g (3.3 mmoles) was dissolved in 200 ml distilled water. To this, 1.6850 g (3.3 mmoles) ABS dissolved in 400 ml distilled water was added. The mixture was shaken vigorously and allowed to stand for a short time at room temperature. The precipitate formed was collected by centrifugation and washed several times with distilled water until the washing was colourless. It was finally washed with acetone and air dried. Dark-blue solid was obtained; yield 0.6921 g. The solid is slightly soluble in ethanol, DMF and DMSO, sparingly soluble in 1.4-dioxan but insoluble in water, acetone, n-hexane and chloroform. m.p.: does not melt below 300°C but changes occurs above 255°C; FT-IR: 3442, 1612, new bands, 404w, 414w, 609 and 1383 cm^{-1}; elemental analysis: %M = 27.4 [Calcd. 28.5].

4.4.4 PREPARATION OF TiABS COMPLEX

TiO_2, 0.1333 g (1.65 mmoles) was dissolved in a mixture of 20 ml concentrated sulphuric acid and 8 g ammonium sulphate, the clear solution was filtered and diluted to 250 ml with distilled water after adjustment of the pH to 11.4. To this a hot solution containing 0.8341 g (1.65 mmoles) ABS in 250 ml distilled water was added. The volume of the reaction mixture was reduced to one-third by evaporation on a heating plate. An oily red coloured precipitate was formed. The precipitate was filtered and washed several times with distilled water until the washing was colourless. Finally, washed with acetone and air dried. Black crystals were obtained, yield 0.0537 g. The crystals are sparingly soluble in ethanol, DMF and DMSO but insoluble in water, acetone and chloroform; m.p.: do not melt below 300°C; FT-IR: 3383, new bands, 407s, 1035, 1227, 1492, and 1399 cm^{-1}; elemental analysis: %M = 7.85 [Calcd. 8.14].

4.4.5 PREPARATION OF ZrABS COMPLEX

$ZrOCl_2.8H_2O$, 0.1391 g (1.3 mmoles) was dissolved in a 250 ml of warm distilled water. To this a hot solution containing 0.6319 g (1.3 mmoles) ABS in 250 ml distilled water was added. The mixture was shaken vigorously heated for a short time with stirring and cooled to room temperature. The precipitate formed, was collected by the centrifugation washed several times with distilled water, until the washing was colourless; then with a little portion of ethanol, followed by acetone and air dried. Grey fine solid was obtained; yield 0.0911 g. The solid is insoluble in most common organic solvents; m.p.: does not melt below 300°C; FT-IR: 3384, 1611, 1578, new bands, 412w, 405s and 1460 cm^{-1}; elemental analysis [Calcd.]: %M = 16.2 [16.5], %C = 38.35 [38.98], %N = 3.47 [4.33], %H = 2.9 [2.47].

4.4.6 PREPARATION OF PdABS COMPLEX

Method 4.4.4 was used except that the heating time was extended to four hours and that the precipitate was not oily.

Black light crystals were obtained, yield 0.1860 g (from 0.3546 g, 2.0 mmoles, $PdCl_2$ in 250 ml distilled water and 0.2022 g, 0.4 mmoles- ABS in 250 ml distilled water). The crystals are slightly soluble in ethanol, DMF and DMSO, but insoluble in water, acetone, n-hexane, chloroform and 1.4-dioxan. m.p.: do not melt below 300°C; FT-IR: 3388, new bands, 410, 404s, 1326 and 1500 cm^{-1} ; elemental analysis: %M = 26.3 [Calcd. 26.9].

4.4.7 PREPARATION OF ZnDB COMPLEX

Method 4.4.1 was used except that the precipitate was collected by centrifugation. Dark brown crystals were obtained; yield 0.1071 g (from 0.1488 g, 0.5 mmoles, $Zn(NO_3)_2.6H_2O$ and 0.2284m g, 0.75 mmoles, DB each in 100 ml distilled water).

The crystals are slightly soluble in ethanol, 1.4-dioxan, DMF and DMSO but insoluble in water, chloroform and n-hexane . m.p.: do not melt below 300°C; FT-IR data: 3438, 3299, 1310, new bands, 406s, 411s, 443s, 440s and 1194 cm^{-1}; elemental analysis: %M = 9.4 [Calcd. 9.7].

4.4.8 PREPARATION OF CdDB COMPLEX

Method 4.4.2 was used. Grey solid was obtained; yield 0.1615 g (from 0.1542 g ,0.5 mmoles, $Cd(NO_3)_2.H_2O$ and 0.2284 g ,0.75 mmoles, DB). The solid is slightly soluble in ethanol, acetone, DMF and DMSO but insoluble in water and n-hexane; m.p.: does not melt below 300°C; FT-IR data: 3440, 3301, new bands, 617, 1104 and 1384 cm^{-1}; elemental analysis: %M = 15.1 [Calcd. 15.6].

4.4.9 PREPARATION OF HgDB COMPLEX

Method 4.4.3 was used. Dark brown solid was obtained; yield 0.6720 g (from 0.1542 g ,0.5 mmoles, $Hg(NO_3)_2.H_2O$ in 150 ml distilled water and 1.1418 g ,3.75 mmoles,DB in 250 ml distilled water). The solid is slightly soluble in acetone, DMF and DMSO but insoluble in water, ethanol and n-hexane. m.p.: does not melt below 300°C; FT-IR data: 3440, 3308, new bands, 452s, 432s, 567w, 1217 and 1384s cm^{-1}; elemental analysis %M = 24.4 [Calcd. 24.9].

4.4.10 PREPARATION OF TiDB COMPLEX

Method 4.4.4 was used, except that the precipitate was collected by centrifugation. Bluish-grey crystals were obtained. Yield 0.0513 g (from 0.0352 g ,0.44 mmoles, TiO_2 and 0.2710 g ,0.89 mmoles, DB each in 250 ml distilled water). The crystals are sparingly soluble in ethanol, acetone, DMF and DMSO but insoluble in water and n-hexane; m.p.: do not melt below 300°C. FT-IR data: 3430, 3290, 1309, new bands, 406vs, 423vs, 432s, 475w, 557w, 668s and 1221 cm^{-1}; elemental analysis: %M = 6.7 [Calcd. 6.9].

4.4.11 PREPARATION OF ZrDB COMPLEX

Methods 4.4.5 was used. Grey fine solid was obtained; yield 0.0812 g (from 1.0742 g ,3.3 mmoles, $ZrOCl_2.8H_2O$ and 1.0049 g ,3.3 mmoles, DB each in 250 ml distilled water). The solid is slightly soluble in ethanol, acetone, DMF and DMSO but insoluble in water and chloroform; m.p. does not melt below 300°C; FT-IR data: 3426, 3308, 1598, 1311, new bands, 412s, 435vs, 461s and 1228 cm^{-1}; elemental analysis [Calcd.]: %M = 23.6 [23.46], %C = [39.94[37.63], %N = 4.26 [6.27], %H = 3.36 [3.58].

4.4.12 PREPARATION OF PdDB COMPLEX

Method 4.4.6 was used. Black solid was obtained; yield 0.0850 g (from 0.3546 g, 2 mmoles, $PdCl_2$ and 0.1218 g, 0.4 mmoles, DB each in 200 ml distilled water). The solid is sparingly soluble in DMF and DMSO but insoluble in water, chloroform, acetone and ethanol; m.p.: do not melt below 300°C; FT-IR data: 3418, 3296, new bands, 402m, 414m, 433s, 465w, 745w and 1420 cm^{-1}; elemental analysis: %M = 18.1 [Calcd. 18.9].

5 RESULTS AND DISCUSSION

In general, all the isolated complexes are of low solubility in most common organic solvent, do not melt below 300°C and are free from anions.

5.1 IR SPECTRA

The FT-IR data of ABS (Fig.18) and its metal complexes are summarized in Table 7. In Zn, Cd and Hg, ABS complexes (Figs. 19, 20, and 21 respectively) the strong peak corresponding to νN-H (for both NH and NH_2 at 3446 cm^{-1}) was weakened and shifted to lower frequency. This suggests coordination through the nitrogen of the ligand. The band at 1360 cm^{-1} νC-N str. in ABS was shifted to higher frequency (Δν= 10, 19 and 23 for Zn, Cd and Hg complexes respectively). This gives further evidence for N-coordination. The band at 1630 cm^{-1} (νC=O) is shifted to a lower frequency (Δν = 19) in Zn, Cd and Hg complexes. This suggest coordination through the C=O group. New bands appear at: 428 cm^{-1} in ZnABS complex; 434 cm^{-1} in CdABS complex and 425 cm^{-1} in HgABS complex supporting the formation of M-O bonds (lit. M-O appears in the region 400-510 cm^{-1}). In the spectra of Ti, Zr and Pd complexes of ABS (Figs. 22, 23 and 24 respectively), the N-H str. frequencies at 3446 cm^{-1} in ABS are greatly shifted in the three complexes (Δν= 60 cm^{-1}) to lower frequencies and were broadened. This suggests coordination through both the amino groups (NH_2 and NH). The broadening suggests the presence of coordinated water molecules in Zr and Pd complexes. This is supported by the disappearance ofνN-H stretching frequency is shifted by 23 cm^{-1} and 5 cm^{-1}. This suggests the presence of coordinated water molecules in Zr complex. The phenolic OH def.is shifted from 1309 cm^{-1} to 1221 cm^{-1} in TiDB and 1228 cm^{-1} ZrDB, which supports coordination through the phenolic (OH). No evidence can be deduced for NH_2 coordination since the νC-N stretching at 1167 cm^{-1} and 1169 cm^{-1} are present. The νC=O str. at 1600 cm^{-1} appears as a shoulder indicating the uncoordinated C=O group. The presence of M-O bonds are supported by new bands at: 415 cm^{-1} in TiDB; 461 (s) cm^{-1} in ZrDB complex. The PdDB FT-IR spectrum (Fig.31) shows that both νN-H str. and νO-H str. are lowered ($\Delta\nu$ = 24 and 17 cm^{-1} respectively). The carbonyl frequency at 1600 cm^{-1} is shifted to a lower values suggests C=O co-ordination. The presence of M-O bond is supported by the presence of band at 465 cm^{-1}.

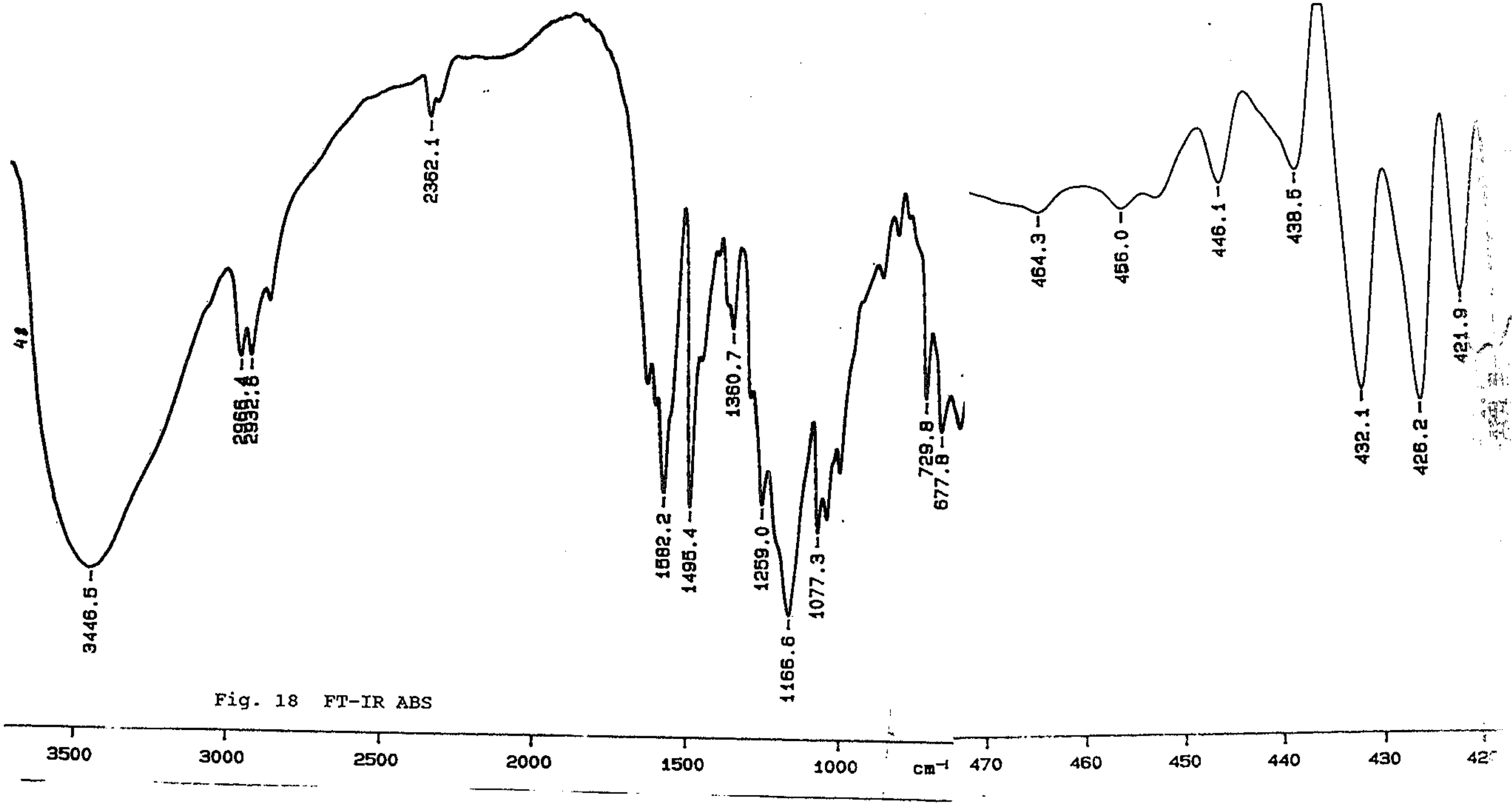


Fig. 18 FT-IR ABS

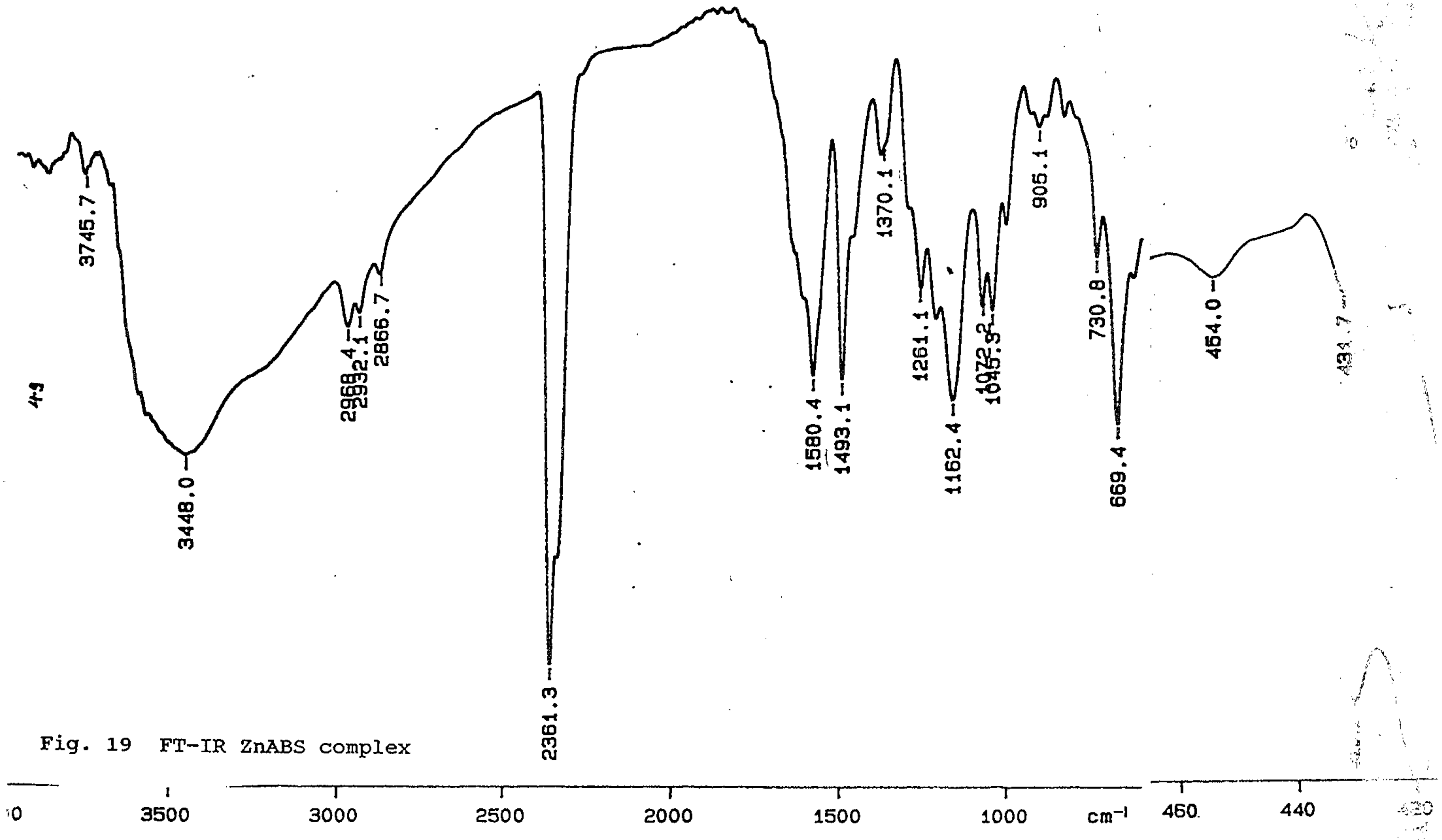


Fig. 19 FT-IR ZnABS complex

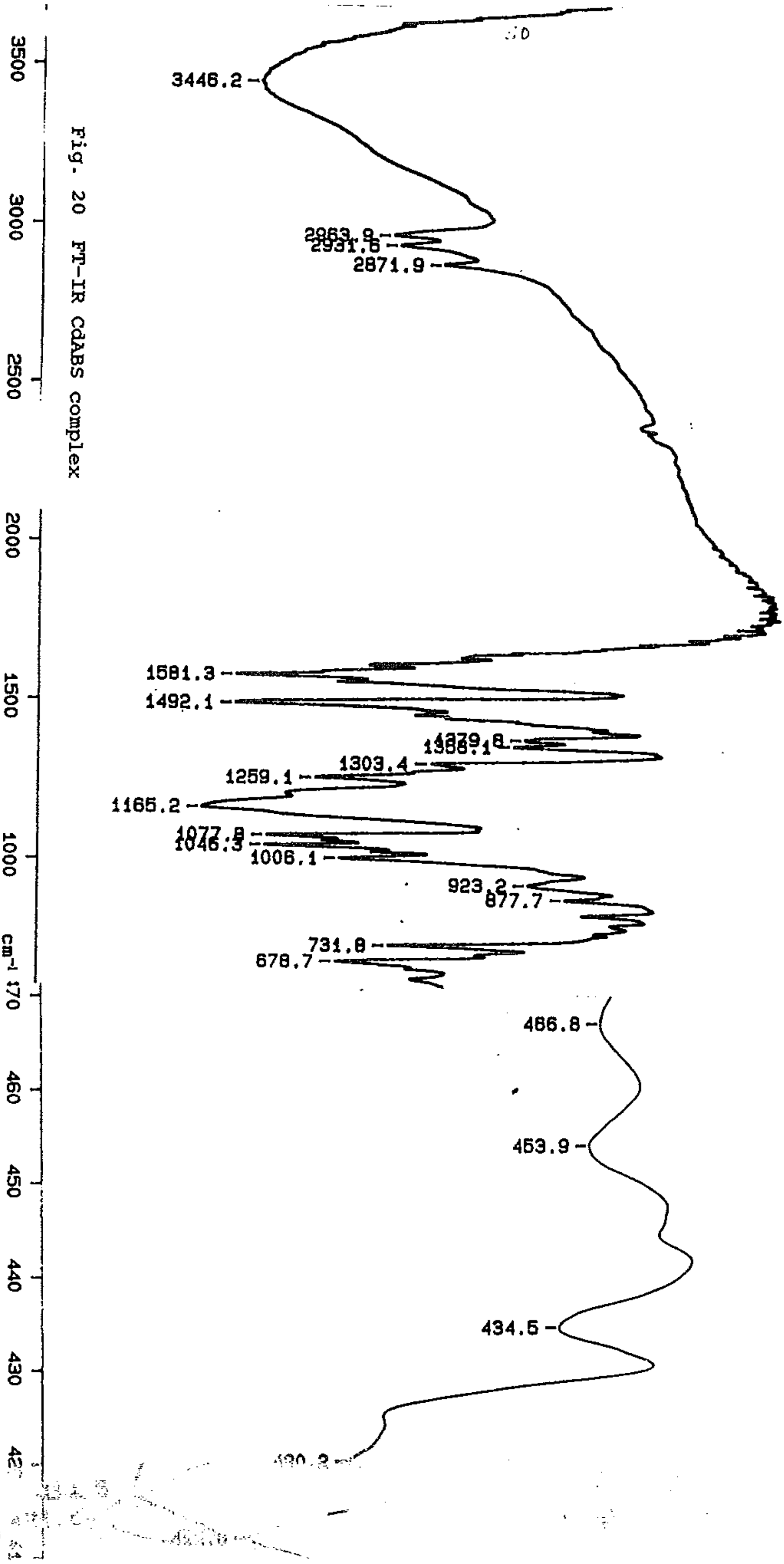


Fig. 20 FT-IR CdABS complex

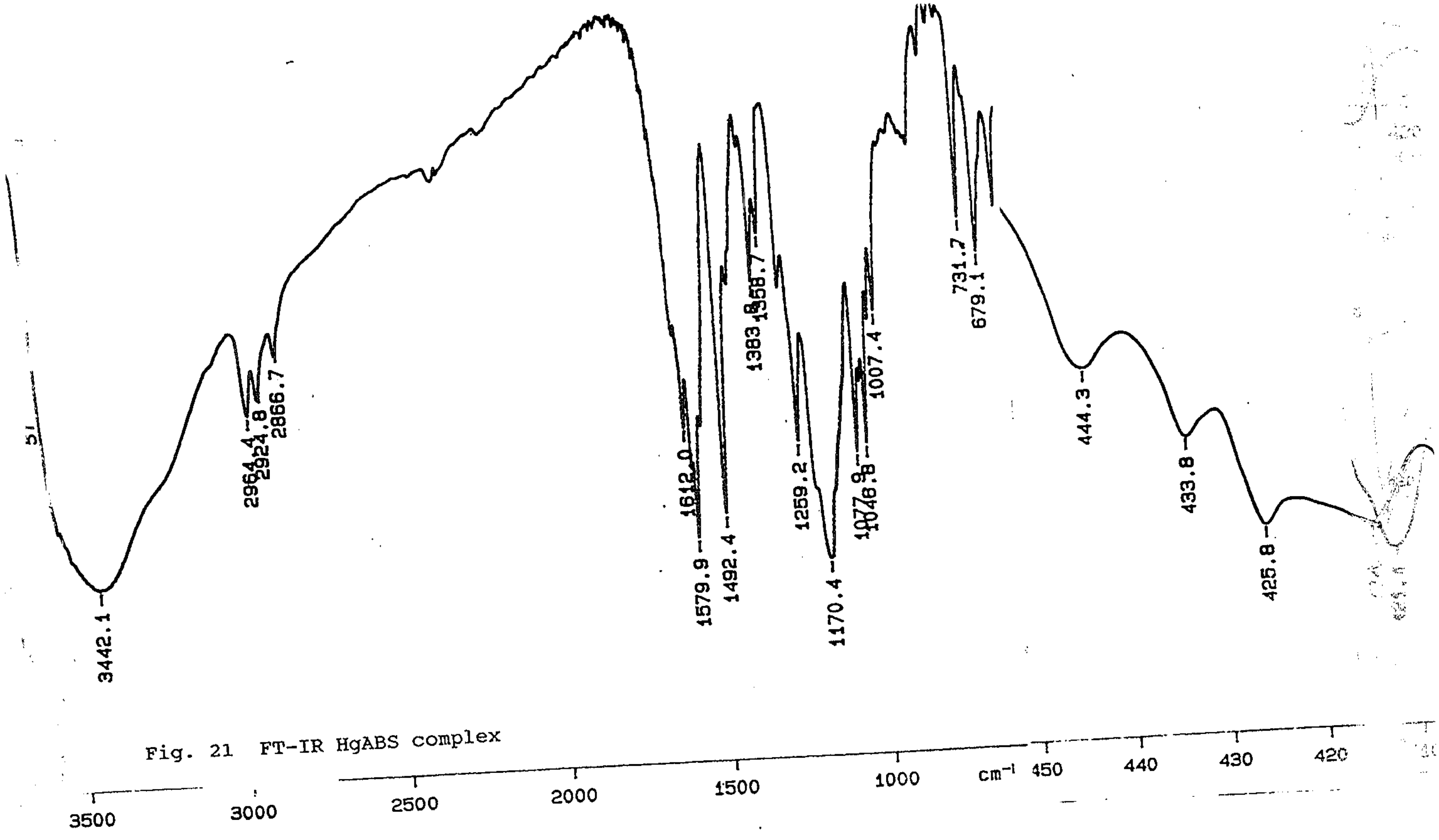


Fig. 21 FT-IR HgABS complex

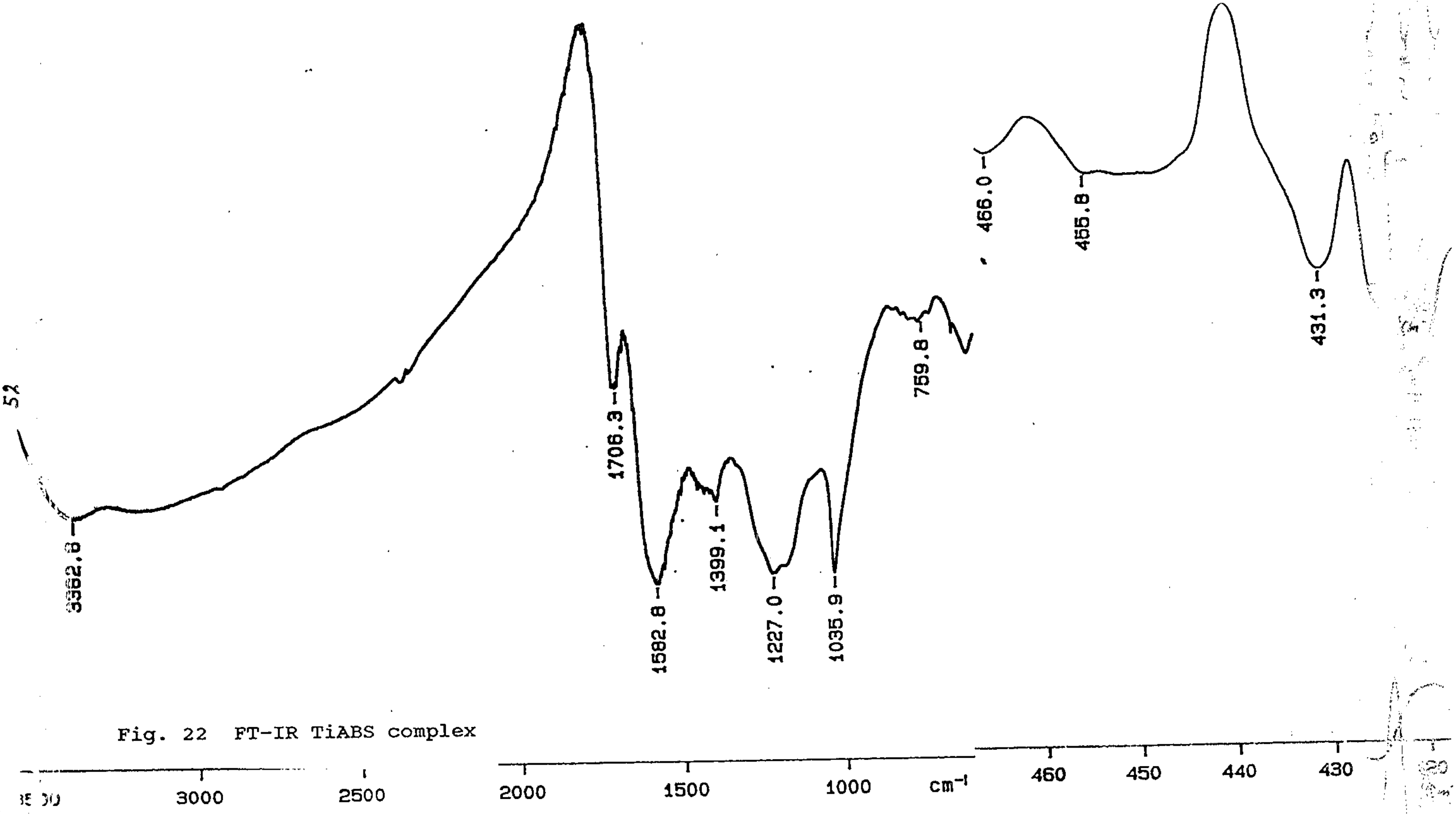


Fig. 22 FT-IR TiABS complex

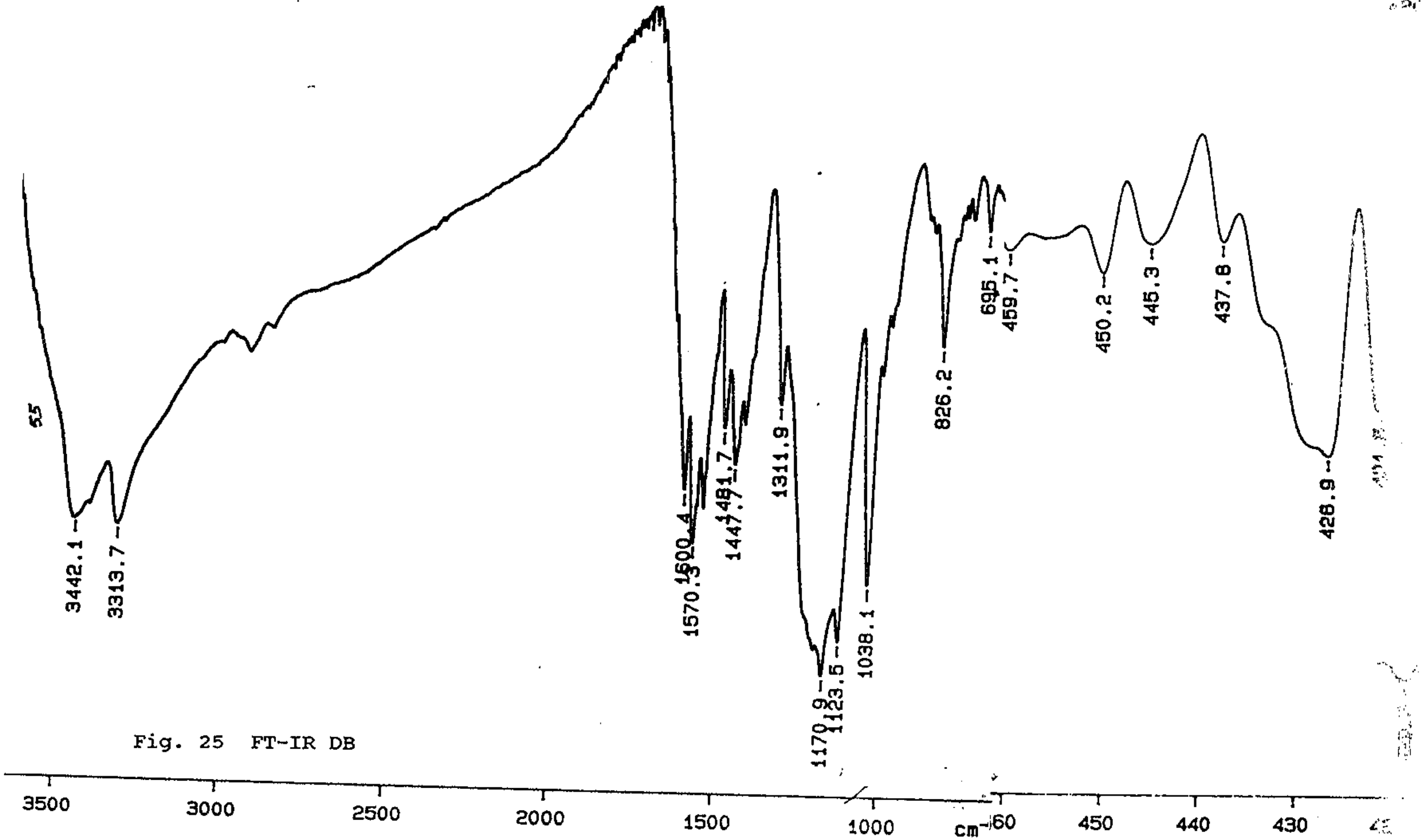


Fig. 25 FT-IR DB

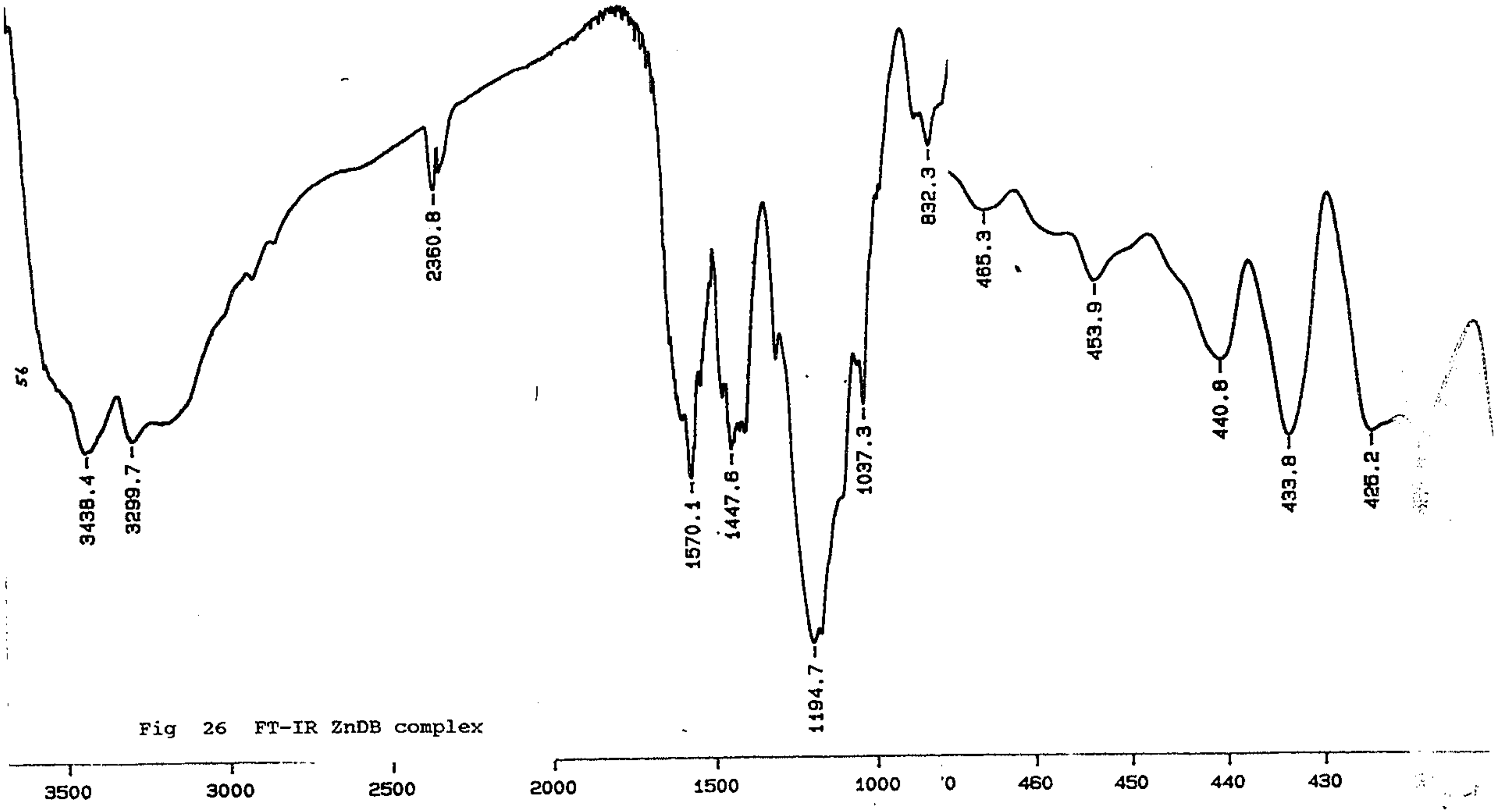


Fig 26 FT-IR ZnDB complex

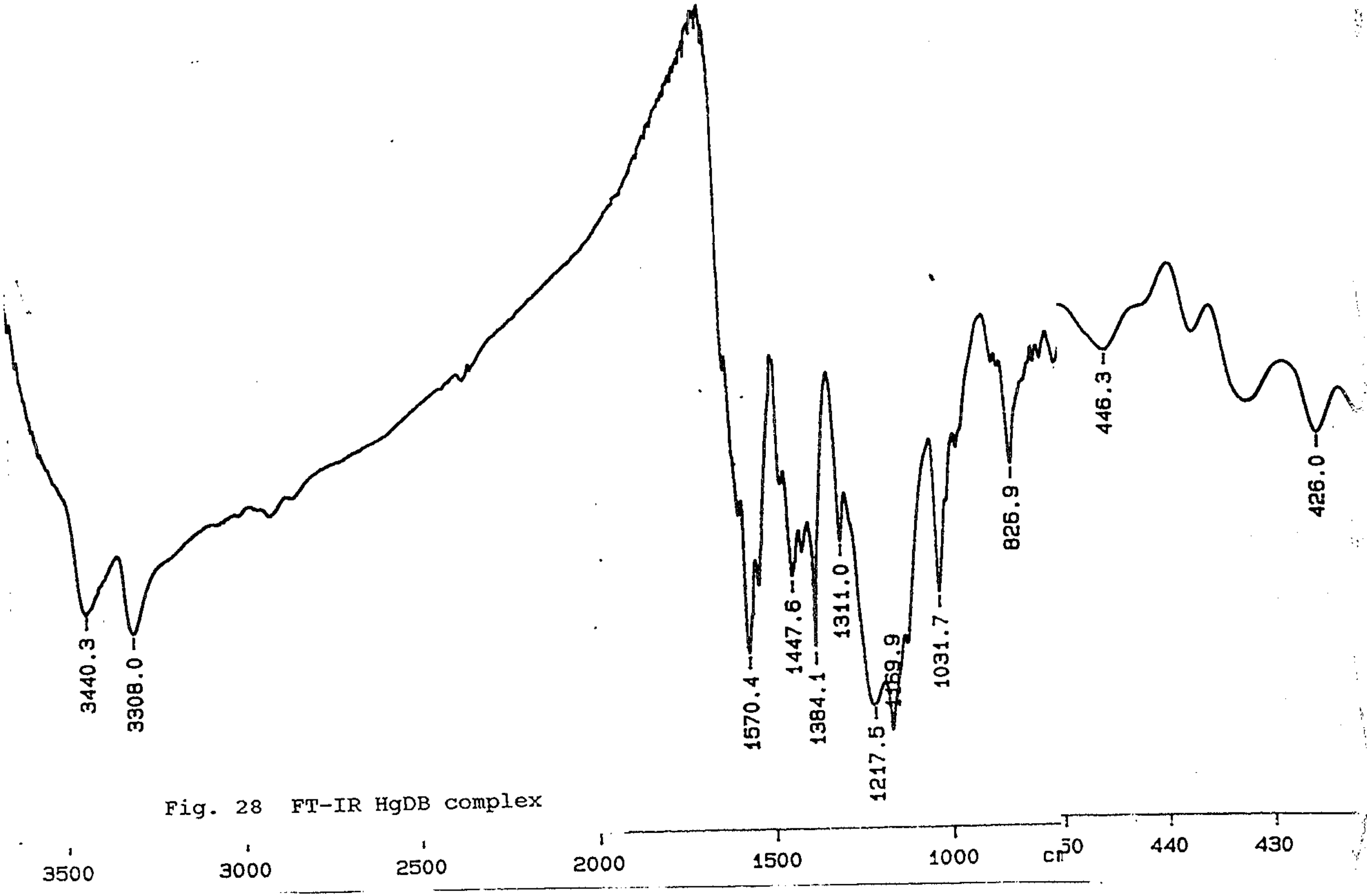


Fig. 28 FT-IR HgDB complex

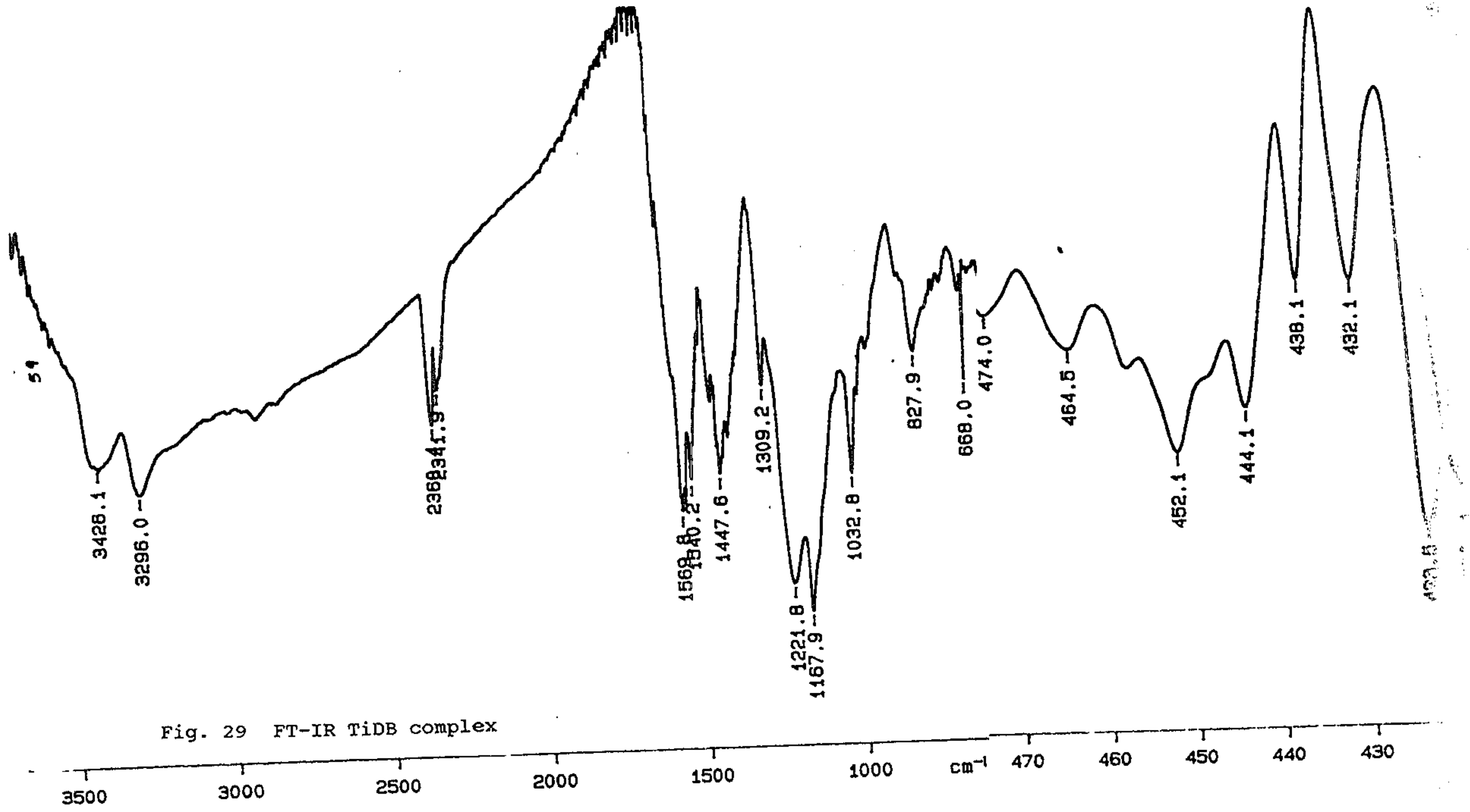


Fig. 29 FT-IR TiDB complex

Table 7. FT-IR data for ABS and ABS-metal complexes:

band (Cm^{-1})	assignment
3446s	N-H str {$N-H_2$}
2966m	C-H str
1631m	C=O str
1582s	C-C str
1495s	N-H def
1360w	=C-N str
1259w	SO_2,S=O str
1166s	=C-N str
1077s	S=O str
729	C-H str
677	C-Cl str
474	
464	
456	
446	
438	
432	
426	
421	
417	
410	
406	

ZnABS	CdABS	HgABS	TiABS	ZrABS	PdABS
3448w	3442w	34421	3382w,b	3384	3388b
2963	2964	1706n	1636n	1585	
2968w	1611	2924	1582	1611	1500n
2932	1581	1612	1399n	1578	1326n
1580	1492	1579	1227n	1460n	1246
1493	1379n	1492	407s,n	1361	1166
1370n	1358	1383		1259	1050
1261	1259	1358		1163s	404s,n
1162	1165	1259		1077	410s
1072	1077	1170		730	
730	923w,n	1077		405sn	
669n	877w,n	731		412wn	
431	731	679			
428w	678s	609n			
410s	453n	414n			
	412n	404n			

The thermal analysis data for DB (Fig.32) and CdDB (Fig.33) are summarized in Table 9. As a support to the melting point determinations none of them melt below 300°C, and no water of crystallization in the case of CdDB. The coordination of Cd leads to increased stability of the complex CdDB compared to DB in the temperature range 270-460°C. The data also suggest that Cd transforms as CdO from $Cd(DB)_2$ complex, from 500-600°C in the range studied.

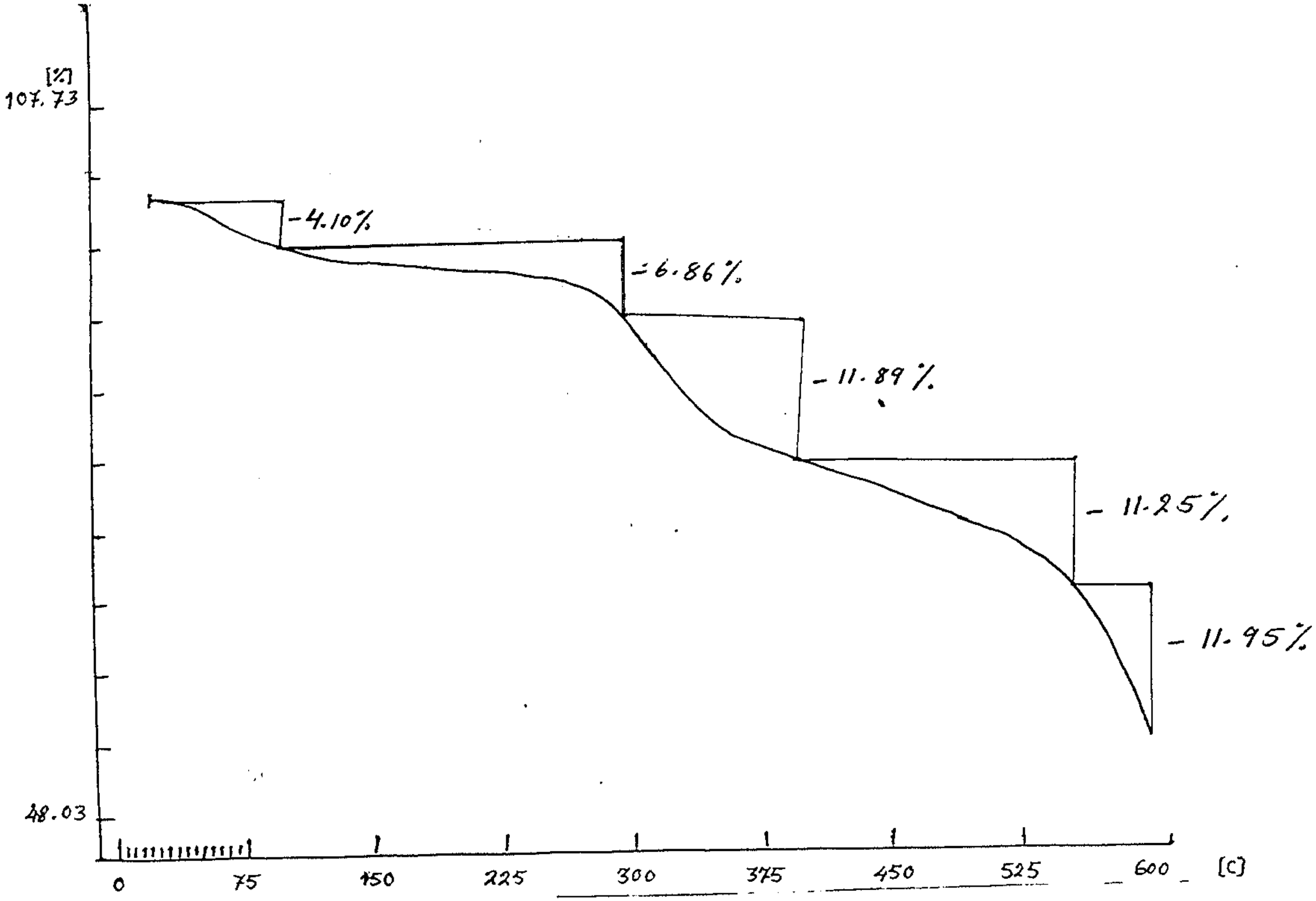
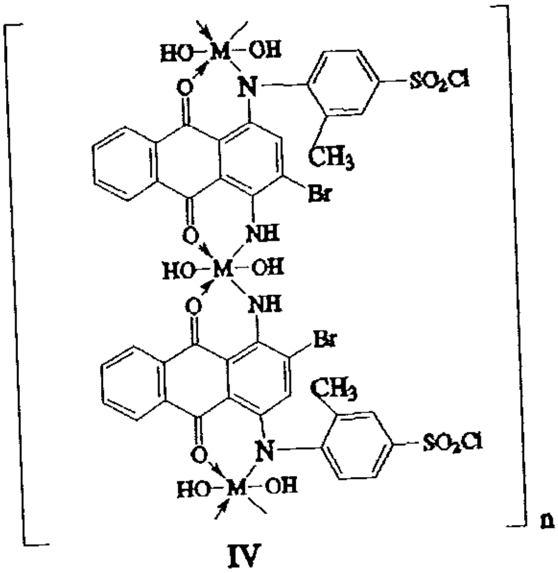
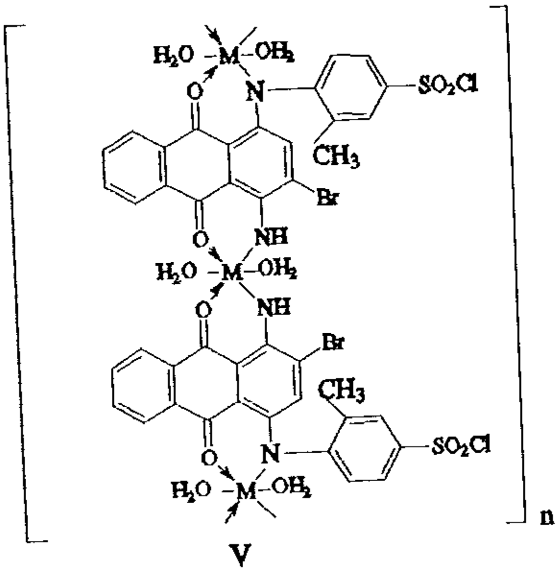


Fig. 32 Thermal analysis curve for DB.



IV

Ti (IV)ABS complex



V

ABS complexes (M = ZrO(II) or Pd(II))

Babco, A. k. Bull. Sci. Rec. Chim., No.3, 49-67 (1937) [Chem. Abs., 33, (1939) 2432-2435].

14. Krasorskii, A. A. Org. Chem. Ind., (USSR), 5, 597-604 (1938) [Chem. Abs., 33, (1939), 5389].

15. Beech, W. F. and Drew, H. D. K. J. Chem. Soc., 603-7 (1940) [Chem. Abs., 34, (1940) 5400].

16. Haller, R. Chim. Acta, 21, 844-43, (1938) [Chem. Abs., 32, (1938), 6869].

17. Neogi, P. and Mandal, K. L. J. Indian. Chem. Soc., 19, 501-2 (1942) [Chem. Abs., 37, (1943), 5670].

18. Wilson, C. J. Am. Chem. Soc., 67, 2003 (1945).

19. Herman, A. J. Am. Chem. Soc., 69, 136-4 (1947).

20. Herman, A. J. Am. Chem. Soc., 60, 1776-84 (1938).

21. Flagg, J. F. J. Am. Chem. Soc., 71, 3630-2 (1949).

22. Pobiner, H. Anal. Chem., 33, 790-3 (1961); Green, D. E. Anal. Chem., 20, 370 (1948).

23. Charlot, G. Anal. Chim. Acta, 1, 218-84 (1947) [Chem. Abs., 42, (1948) 7192h].

24. Nommik, H. Acta. Polytech., Chem. Met. Ser., 3, 7-121 (1953) [Chem. Abs., 48, (1954), 4364d].

25. Keiichiro, F. Japan Analyst, 3, 98-104 (1954) [Chem. Abs., 48, (1954), 9864j].

26. Guentin, K. E. and Indinger, J.Forsch, 110, 249-60 (1959) [Chem. Abs., 53, (1959), 21384e].

27. Babko, A. K. and Markova, L. V. Zavodkskaya Lab., 24, 524-8 (1958) [Chem.Abs. 54 (1960) 10632a].

28. Babko, A. K.and Markova, L. V. Anal. Chem., 11, 309-22 (1960) [Chem. Abs., 55 (1961) 8176f].

29. Huei-Sung, W. Fenhsihuahuahsueh, 7 (6), 488 (ch.) (1979)

[Chem. Abs., 95, (1981) 231099s].

41. Ceba, M. R. and Gutierrez, F. An Quim, ser. B, 76 (3), 442-6 (19600 (Spain) [Chem. Abs., 94, (1981) 149551d].

42. Robenko, N. L., Tashuta, G. N. and Blokhmvedeve, Z. V. J. Anal. Chem., 45, 702 (1990).

43. Pilipenko. A. T., Shorokhod, E. G. and Sarranskii, L. I. Khim. Khim. Tekhnol., 24 (10), 1227-91 (1981) (Russ.) [Chem. Abs., 96, (1982) 13299m].

44. Pilipenko. A. T. and Maksimyuk, E. G. Ukr. Khim. Zh. (Russ. Ed.), 48 (5), 500-2 (1982) (Russ.) [Chem. Abs., 97, (1982) 48905d].

45. Pilipenko. A. T., Shorokhod, E. G. and Sarranskii, L. I. Geo. Khim. Biol. Nauki., (8), 41-2 (1982) (Russ.) [Chem. Abs., 97, (1982) 211873c].

46. Gopalakrishna, V. and Rad, B. S. V. R. Anal. Chim. Acta, 19, 161-5, (1958) [Chem. Abs., 54, (1960) 155a].

47. Pilipenko. A. T., Shorokhod, E. G. and Sarranskii, L. I. Geo. Khim. Biol. Nauki.,(11), 53-7 (1982) (Ukrain) [Chem. Abs., 98, (1983) 82750e].

48. Issa, R. M., El-Hefnawey, G. B. and Ahmed, Y. Z. Egypt. J. Chem., 25(2), 53-8(1982) [Chem. Abs., 99, (1983) 111590f].

49. Boltei, R. S. and Lusardi, D. A. Thermochim. Acta, 43 (3), 355-63, (1981) [Chem.Abs., 94, (1981) 166848y].

50. Abu-Elwafasamy, M., Raafat, M. I. and Fatma, M. E. Egypt. J. Chem., 27 (5),665-74 (1985) [Chem. Abs., 105, (1986) 42174b].

51. Kantouri, M. L. and Christianopoulou, B. Thermochim. Acta., 104, 39-60, (1986) [Chem. Abs., 105, (1986) 217900q].

65. Jincai, Z. and Mingxing, S. Yexin Fenxi, 11,(6), 53,-5 (1991) (Ch.) [Chem. Abs., 117, (1992) 123600n]

66. Ju, 1. "Handbook of analytical chemistry", Mir Publishers, Moscow, p. 263, (1975).

67. Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis", 3rd ed., Longmans, Green and Co. Ltd, London p. 443 (1961).

68. Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis", 3rd ed., Longmans, Green and Co. Ltd, London p. 444 (1961).

69. Kolthoff, I. M., Elving, P. J and Sandell, E. B. "Treatise on Analytical Chemistry, Part II, Vol.3, Interscience, New York, p. 231 (1961).

70. Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis", 3rd ed., Longmans, Green and Co. Ltd, London p. 511 (1961).

71. Kolthoff, I. M., Elving, P. J and Sandell, E. B. "Treatise on Analytical Chemistry", Part II, Vol.5, Interscience, New York, p. 61 (1961).

72. Kolthoff, I. M., Elving, P. J and Sandell, E. B. "Treatise on Analytical Chemistry", Part II, Vol.5, Interscience, New York, p. 1 (1961).

73. Rao, C. N. R. "Chemical Applications of I. R Spectroscopy" Academic Press, London, 1963.

74. Bilger and Pechmeze, J. Chem. Abs., 53, 1959, 15097e.

75. Pannu, B. S. and Chopra, S. L. Indian J. Chem., 13, 732 (1975).

76. Shraa, Z. Z. M. Sc. Thesis, Alazhar University, 1983.

77. Babenko, N. L., Tashuta, G. N. and Medvedeva, Z. V. Anal. Chem., The USSR, 45(5), 702 (1990).

78. Kümmerl, L., Wolfrumand, H. and Haarer, D. J. Phys. Chem., 96, 10688-10693 (1992).