

STUDIES IN THE EXTRACTION OF METALS
WITH SOME CHELATING LIGANDS

Roma Lahiri

Thesis submitted to

INDIAN INSTITUTE OF TECHNOLOGY

NEW DELHI

for the award of the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

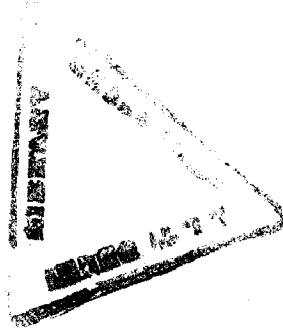
Indian Institute of Technology

New Delhi - 110016

December 27, 1984

TH
541-572
LAH-S

TH-12M-~~3~~



C E R T I F I C A T E

This is to certify that the thesis entitled "STUDIES IN THE EXTRACTION OF METALS WITH SOME CHELATING LIGANDS" by Roma Lahiri is a record of original bonafide research carried out under my supervision and has not been submitted elsewhere for a degree.



December 27, 1984

(G.N. Rao)

Associate Professor
Department of Chemistry
Indian Institute of Technology
New Delhi-110016.

A C K N O W L E D G E M E N T

I wish to express my deep sense of gratitude to Prof. G.N. Rao, Department of Chemistry, Indian Institute of Technology, for his unceasing encouragement and constant supervision throughout my research work.

I am grateful to Prof. N.K. Jha, Head of the Chemistry Department for providing me with all the facilities and to Prof. J.C. Ahluwalia for allowing me to use the calorimeter.

I am thankful to the technical staff of the instrument laboratory for providing me with the carbonhydrogen analysis data, IR and NMR spectra.

I am deeply indebted to my husband Bhaskar for his untiring help in every stage of this work.

Thanks are due to Maitrayee for her constant companionship, affection and well wishes that have kept me up.

I am also very thankful to V. Ramesh, C.S.R. Murthy and Viksita for their constant cooperation and assistance.

I am thankful to Dr. P.K. Banerjee, Deptt. of Textile Technology for helping me in understanding papers in German.

The financial assistance given by C.S.I.R. and I.I.T. Delhi is gratefully acknowledged.

Finally I am thankful to Mr. T.S.R. Iyer, for his excellent typing work.

ABSTRACT

Extraction of metals with chelating ligands is an excellent separation and preconcentration technique in analytical chemistry. Practically all the spectrophotometric and fluorimetric methods for the determination of metals depend on solvent extraction procedures.

This thesis contains,

- (a) investigation of the utility of some ligands binding through sulphur in the extraction and preconcentration work.
- (b) detailed study of the extraction of Cd(II) and Pd(II) with selected chelating ligands.
- (c) synergistic extraction studies in Cd(II)- β -diketone systems.
- (d) calorimetric studies related to extraction.

The utility of thionalide (HTN), 2-(2-pyridyl)-benzothiazoline (HPBT), 3-methyl-1-phenyl-4-thiobenzoyl-5-pyrazolone (HSBMPP) and a mixture of toluene 3,4-dithiol (H₂TD) and 1,10-phenanthroline (Phen) in the extraction of some metals was investigated. For most of the metals extracted here, these ligands showed better extraction characteristics than their oxygen analogues

or ligands having similar donor arrangements unless the metal had a definite tendency to form stronger complexes with oxygen donors.

Preconcentration of Co(II), Cd(II), Cu(II), Zn(II), Ni(II) and Pd(II) was carried out using a mixture of H₂TD and Phen. Tenfold concentration was achieved for the first four metals but concentration was less in the case of Ni(II) and Pd(II), probably due to incomplete back extraction. Preconcentration of Cd(II), Ni(II), Co(II), Fe(II), Pb(II) and Zn(II) gave almost tenfold concentration for all metals except Co(II).

The ligands studied for the extraction of Cd(II) were HTN, HSBMPP, HPBT, o,o' - diethylphosphorodithioic acid (HDEDTP), Salicylideneaminothiophenol (H₂SATP), thenoyltrifluoroacetone (HTTA), benzoyltrifluoroacetone (HBTA) and 1,2-butanedionemonoxime (HBDMO). The chelates were found to have a metal to ligand ratio of 1:2 on the basis of experimental results. It was generally observed that the K_{ex} values obtained with the ligands binding the metal through sulphur were higher than those binding through oxygen (except oxine and dichlorooxine). Out of all the ligands considered here HDEDTP, HSBMPP, dithizone, sodiumdiethyldithiocarbamate (HDEDTC) were found to be most

effective for the extraction of Cd(II); HDEDTP by virtue of its higher stability in acidic solutions as compared to HDEDTC and the higher solubility of its complex in the organic phase could be considered as a better ligand than HDEDTC. It can be said on the basis of separation factors that benzoylacetone, HTN and HBMPP (oxygen analogue of HSBMPP) will be more effective for the separation of Cd(II) from Zn(II), which coexists very often with Cd(II) in many natural substances, as compared to the rest of the reagents considered here.

The ligands taken for the extraction of Pd(II) were Schiff bases prepared by the condensation of benzil, 4-aminophenazone, 2-hydroxyacetophenone or salicylaldehyde with 2-aminobenzenethiol. Extraction of Pd(II) with HTN, HSBMPP, HSBTA (thiobenzoyltrifluoroacetone) and ion association systems involving aliquat-336 and nitroso-Rsalt or sulphosalicylic acid was also studied. The stoichiometry of the chelates formed with HTN, HSBMPP, HSBTA and the Schiff bases was found to be 1:2 (metal : ligand) on the basis of experimental results. Except for HSBMPP the K_{ex} values obtained for these ligands were higher than those reported with β -diketones. They were comparable to that for the Pd(II)-oxine system but lower than either Pd(II)-dithizone or Pd(II)-HDEDTC systems. The Schiff base

DEDICATED
TO
MY PARENTS

(vii.)

ligands and HTN can be conveniently used to separate Pd(II) from Ni(II) as Ni(II) does not get extracted under similar conditions.

Synergistic extraction of Cd(II) with HTTA and HBTA was studied in the presence of pyridine (PY), 3-methylpyridine (3MP), 4-methylpyridine(4MP), pyridine N-oxide(PO), 2-methylpyridine N-oxide(2MPO), 4-methylpyridine N-oxide(4MPO) tributylphosphate(TBP) and trioctylphosphine oxide(TOPO) as auxiliary ligands in benzene. Adduct formation constants (K_s) for the heterocyclic bases decreased in the following order,

4MP, 3MP, PY, 4MPO, 2MPO, PO .

This order is in accordance with the order of basicities of these ligands; TOPO was found to be the most effective of all the ligands and TBP more effective than pyridine N-oxides but less effective than pyridines. The pyridines, TOPO and TBP formed 1:2 adducts while the pyridine N-oxides formed 1:1 adducts. Interesting and useful information on the extracted species was obtained by isolating the solid adducts and examining them with IR and NMR techniques.

Thermodynamic functions and equilibrium constants(K) of adduct formation between $\text{Cu}(\text{TTA})_2$ or $\text{Cu}(\text{BTA})_2$ with PY, 4MPO, TOPO, TBP, dibenzylsulphoxide (DBSO), Phen and

2, 2 - bipyridyl (BiPY) were determined. The enthalpy changes (ΔH) were highly exothermic and entropy changes (ΔS) were unfavourable for all the systems studied. The values of ΔH and K were correlated with the nature of the ligands (i.e. Basicity, structure etc.) wherever possible.

CONTENTS

ACKNOWLEDGEMENT	iii
ABSTRACT	iv
LIST OF FIGURES	xiv
CHAPTER I	
INTRODUCTION	1
1.1 Classification of Extraction Systems	1
1.1.1 Systems Involving Uncharged Electrovalent Species	2
1.1.2 Systems Involving Uncharged Covalent Species	5
1.2 Extraction of Chelate Compounds	6
1.3 Synergistic Extraction	17
1.4 Scope of the Present Work	30
1.5 References	33
CHAPTER II	
EXTRACTION OF METALS WITH SOME SULPHUR LIGANDS	37
2.0 Introduction	37
2.1 Experimental Procedure	39
2.1.1 Apparatus and Reagents	39
2.1.2 Preparation of the Ligands	41
2.1.3 Extraction Procedure	42

2.2	Results and Discussion	44
2.2.1	Metal-Thionalide Systems	48
2.2.2	Metal-HPBT Systems	58
2.2.3	Metal-HSBMPP Systems	63
2.2.4	Metal-H ₂ TD-Phen Systems	63
2.2.5	Extraction Potential of Sulphur Ligands in Comparison with Similar Ligands	68
2.3	Preconcentration and Group Extraction of Metals with H ₂ TD-Phen System	71
2.3.1	Procedure for Group Extraction	72
2.3.2	Results	72
2.4	Preconcentration and Group Extraction of Metals with HSBMPP	74
2.4.1	Procedure for Extraction	74
2.4.2	Results	75
2.5	References	77
CHAPTER III		
STUDIES IN THE EXTRACTION OF CADMIUM(II)		78
3.0	Introduction	78
3.1	Experimental Procedure	80

3.2	Results	80
3.2.1	Cd(II) - HPBT System	81
3.2.2	Cd(II) - HTN System	81
3.2.3	Cd(II) - HSBMPP System	84
3.2.4	Cd(II) - H ₂ SATP System	86
3.2.5	Cd(II) - HDEDTP System	86
3.2.6	Cd(II) - HBDMO System	88
3.2.7	Cd(II) - HTTA System	88
3.2.8	Cd(II) - HBTA System	89
3.3	Discussion	89
3.4	References	101

CHAPTER IV

STUDIES IN THE EXTRACTION OF PALLADIUM(II) WITH SOME CHELATING LIGANDS		102
4.0	Introduction	102
4.1	Experimental Procedure	104
4.1.1	Preparation of Ligands	105
4.1.2	Procedure for Extraction	106

4.2	Results	106
4.2.1	Pd(II) - HSBMPP System	107
4.2.2	Pd(II) - HSBTA System	111
4.2.3	Pd(II) - HTN System	112
4.2.4	Pd(II) - H ₂ HAATP System	112
4.2.5	Pd(II) - H ₂ APATP System	115
4.2.6	Pd(II) - HBATP System	116
4.2.7	Pd(II) - H ₂ SATP System	116
4.2.8	Pd(II) - Nitroso-R Salt, Aliquat-336 System	118
4.2.9	Pd(II) - Sulphosalicylic acid-Aliquat-336 System	121
4.3	Discussion	121
4.4	References	128

CHAPTER V

STUDIES IN THE SYNERGISTIC EXTRACTION OF CADMIUM(II)	129	
5.0	Introduction	129
5.1	Experimental Procedure	131
5.1.1	Preparation of the Adducts	131
5.1.2	Analysis	133
5.1.3	Infrared Spectra	133
5.1.4	Proton Magnetic Resonance Spectra	133