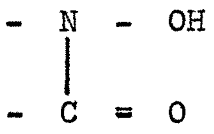
INTRODUCTION

Few branches of Chemistry have attracted the attention of scientists, as much as Coordination Chemistry. Ever since Alfred Werner, the recipient of Nobel prize in 1913 gave his well defined Coordination Theory (1), his postulates have been a guiding principle in the field of Inorganic Chemistry. The theory was further explained and modified by Lewis (2), Sidgwick and Lowry (3), to be followed by a series of theories on the metal-ligand bond formation, as the Valence Bond Theory, the Crystal Field Theory, the Ligand Field Theory and the Molecular Orbital Theory.

During the past twenty five years the development of the field of Coordination Chemistry gave through several general yet discernible phases. After the classic beginning based largely on descriptive and stereochemical studies a more physical approach developed in which quantitative studies led to the understanding of thermodynamics of complex formation in solutions. Subsequently the development of the ligand field theory and bonding concepts made possible successful correlation between electronic and magnetic spectra and the constitution and properties of coordination compounds. Presently, improvements in X-ray crystallographic techniques are providing a large body of structure property correlations and producing a new level of understanding of coordination chemistry. Also synthesis of new types of chelating agents and their metal complexes has opened new vistas in coordination chemistry. Hydroxamic acids possessing the bidentate functional grouping (I), provide a stimulating field for such study.

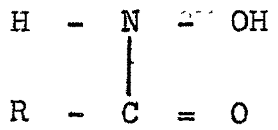


$$\begin{array}{l} -\mathrm{N}-\mathrm{OH} \\ \ \ | \\ -\mathrm{C}=\mathrm{O} \end{array}$$

(I)

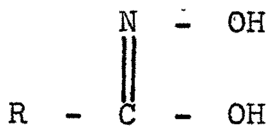
HYDROXAMIC ACIDS

Hydroxamic acids (II, III) may be regarded as N-acyl derivatives of hydroxylamine (4).



$$\begin{array}{l} \mathrm{H}-\mathrm{N}-\mathrm{OH} \\ \quad\ \ | \\ \mathrm{R}-\mathrm{C}=\mathrm{O} \end{array}$$

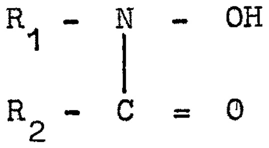
(II)



$$\begin{array}{r} \mathrm{N}-\mathrm{OH} \\ \| \quad\ \ \\ \mathrm{R}-\mathrm{C}-\mathrm{OH} \end{array}$$

(III)

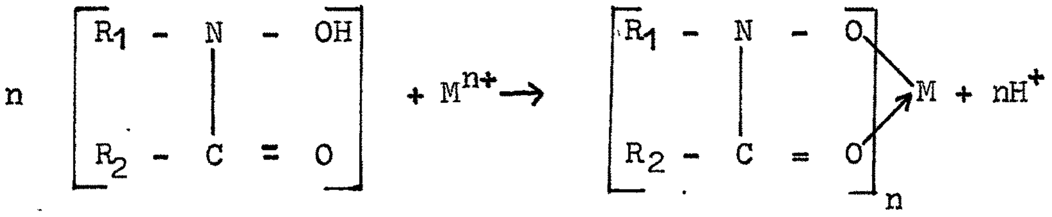
These compounds are capable of undergoing keto-enol tautomerism (5) ; the keto form is generally distinguished from the enol form by naming the former hydroxamic (II) and the latter as hydroximic acids (III) although in certain publications (6-8) both forms are termed as hydroxamic acids. Substitution of hydrogen atom attached to the nitrogen atom in (II) by alkyl, aryl or either group gives N-substituted hydroxamic acids (IV).



$$\begin{array}{ccccc} R_1 & - & N & - & OH \\ & & | & & \\ R_2 & - & C & = & O \end{array}$$

(IV)

These acids are capable of forming complexes with metal ions which are generally inner complex compounds. Complex formation is believed to take place by replacement of the hydroxylamino hydrogen by the cation and ring closure through the carbonyl oxygen.



Due to their non-ionic nature, these inner complexes can be extracted from aqueous or suspensions with water immiscible solvents such as chloroform, carbon tetrachloride, o-dichlorobenzene, and higher alcohols and thus form the basis of separation processes employing solvent extraction. In case the extracts are coloured and sufficiently stable, these can be employed for developing colorimetric methods for the determination of metal ions. Further, if the inner complexes are sufficiently water insoluble, thermally stable and of constant composition, they can be used for evolving gravimetric procedure.

A detailed survey of literature on hydroxamic acids is deliberately avoided because various aspects of their chemistry namely their methods of preparation, properties, molecular arrangements, structures and applications in diverse field have been reviewed exhaustively (5, 9-12). Likewise a general review on the 'Metal Complexes' is intentionally avoided because this subject is excellently covered by a number of speciallised monographs (13-29), review articles (30-37) and text books (38-42). As the present work is essentially concerned with the metal complexes of hydroxamic acids and their stability constants, a brief review of the same is being presented here.

REVIEW OF THE PREVIOUS WORK

A literature survey of the research papers on hydroxamic acids shows that they are versatile analytical reagents and used in organic and inorganic analysis (43-51). These analytical reagents are used in gravimetry and separation (52-66), metal extraction in two phase system and photometry (67-131), determination of metals (132-137), potentiometry

(138-141), amperometry (142, 143), chromatography (144-146), etc.

The chemistry of the hydroxamic acids was also revealed by the growing interest of scientists in the subject. Several reviews (147,5,148,149) have been written on the chemistry of hydroxamic acids. The first ever attempt to explain the physical and chemical properties of an iron(III)-acetohydroxamate complex prepared by earlier workers (150) was made by Werner in 1908 (151). He proposed the coordination of the hydroxamic acid via ionization of the hydroxyl hydrogen and subsequent chelation to metal ion through the carbonyl oxygen and the hydroxyl oxygen. There is strong X-ray crystallographic evidence (152,153-156) that this is the correct model for the chelation of a hydroxamic acid to a metal ion, where in replacement of hydroxylamine hydrogen by the metal ion and ring closure through carbonyl oxygen takes place.

The metal complexes of several transition metals and other metal ions with hydroxamic acids are reported (157-201). Rare earths, which though available in abundant quantities in nature, e.g. in monazite sand, rocks etc., pose a problem in their isolation in pure form. Due to the close physical and chemical nature of the rare earths metals, it is difficult to isolate them from each other and that too in extra pure quality. Ever since their potentiality as good nuclear fluents has been realised, there is a growing demand of the rare earths in the Nuclear Energy Programme of our country. To assist this vast project of the country, various methods are being attempted at with different reagents for the separation and estimation of rare earths. A review of the literature available on the metal ligand stability constants of rare earths with hydroxamic acids and their application are summarised in Tables 1-2.

AIMS AND SIGNIFICANCE

A thorough investigation of literature concerning the hydroxamic acids led to the following considerations.

- Hydroxamic acids are capable to form very stable complexes with several metal ions.
- A series of hydroxamic acids could be synthesised and their physico-chemical properties could be determined.
- The capability of complex formation with rare earths.

Considering the above points the present investigation has been carried out by keeping the following broad objects.

- Synthesis of the series of (substituted) hydroxamic acids.
- Determination of the physico-chemical properties of the synthesised hydroxamic acids and their correlation.

TABLE 1

METAL-LIGAND STABILITY CONSTANTS OF RARE EARTHS WITH HYDROXAMIC ACIDS

Hydroxamic acid	Conditions	k	Rare Earths											Ref
			La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb	Y	
Aceto-	pH, 0.1,-,20	k_1	5.16	5.45	-	-	5.96	-	6.10	6.52	-	6.61	-	202
		k_2	9.33	9.79	-	-	10.73	-	10.86	11.91	-	12.20	-	
		k_3	11.88	12.80	-	-	14.41	-	13.93	15.95	-	16.49	-	
Benzo-	pH, T, 50d,35	k_1	9.25	9.50	9.65	9.80	9.95	-	10.00	-	-	-	-	203
		k_2	7.75	8.01	8.15	8.31	8.46	-	8.50	-	-	-	-	
		k_3	6.73	7.00	7.13	7.30	7.46	-	7.49	-	-	-	-	
	pH,0.1,-,25	k_1	7.28	-	7.70	7.88	8.28	8.45	5.36	8.60	8.75	9.17	8.00	204
		k_2	5.76	-	6.20	6.30	6.35	6.42	6.32	6.70	6.70	6.95	6.32	
Decano-	dis,0.1,-,-.	β_3	-	-	-	-	-	25.4±0.1	-	-	-	-	-	205
N-m-tolyl-m-nitrobenzo-	pH,T,50d,35	k_1	8.50	8.75	8.91	9.00	9.21	-	9.35	-	-	-	-	203
		k_2	7.00	7.23	7.40	7.55	7.71	-	7.85	-	-	-	-	
		k_3	5.99	6.20	6.39	6.54	6.70	-	6.85	-	-	-	-	
N-o-tolyl-m-nitrobenzo-	pH,T,50d,35	k_1	8.37	8.60	8.72	8.85	8.97	-	9.10	-	-	-	-	203
		k_2	6.86	7.10	7.21	7.34	7.45	-	7.60	-	-	-	-	
		k_3	5.34	6.08	6.20	6.33	6.44	-	6.60	-	-	-	-	

Contd..

TABLE 1 Contd.

Hydroxamic acid	Conditions	k	Rare Earths											Ref
			La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb	Y	
N-p-chlorophenyl-m-nitrobenzo-	pH,T,50d,25	k_1	7.01	7.24	7.41	7.56	7.72	-	7.87	-	-	-	-	203
		k_2	5.50	5.74	5.91	6.07	6.23	-	6.32	-	-	-	-	
		k_3	4.46	4.69	4.89	5.04	5.21	-	5.29	-	-	-	-	
N-phenyl-benzo-	gl,0.1,75a,25	k_1	7.28	-	7.70	7.88	8.28	8.45	8.36	8.60	8.75	9.17	8.00	206
		k_2	5.76	-	6.20	6.30	6.35	6.42	6.32	6.50	6.70	6.95	6.32	
		k_3	4.74	-	5.00	5.03	5.15	-	-	5.50	5.90	6.15	-	
	gl,0.25,50d,25	k_1	6.15	-	-	-	-	-	-	-	-	-	7.73	207
	pH,T,70d,35	k_1	10.30	10.49	10.61	10.80	11.15	-	11.43	-	-	-	-	203
		k_2	8.80	9.00	9.11	9.31	9.65	-	9.94	-	-	-	-	
		k_3	7.76	7.96	8.08	8.29	8.63	-	8.91	-	-	-	-	
N-p-tolyl-m-nitrobenzo-	pH,T,50d,25	k_1	8.25	9.01	9.16	9.31	9.46	-	9.60	-	-	-	-	203
		k_2	7.25	7.51	7.65	7.81	7.96	-	8.10	-	-	-	-	
		k_3	6.62	6.81	6.62	6.79	6.95	-	7.11	-	-	-	-	

Contd..

TABLE 1 Contd.

Hydroxamic acid	Conditions	k	Rare Earths La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb	Y	Ref
Salicylo-	gl,0.1,75a, 25	k_1	6.30	-	6.94	7.03	7.20	7.40	7.35	7.72	7.82	8.13	7.24	208
		k_2	5.96	-	6.50	6.64	6.77	6.84	6.80	7.00	7.03	7.25	6.50	
		k_3	4.90	-	4.98	5.10	5.01	5.04	4.60	5.06	5.10	-	-	

Abbreviations used : pH = potentiometric titration method; dis = distribution method; gl = potentiometric method using a glass electrode; a = acetone; d = dioxan (50 denotes a 50% dioxan solution); T = thermodynamic const; k_1 = log K_1 = logarithm of stability constant; "-" data not presented in given study. The horizontal rows present the following data : method, ionic strength/thermodynamic constant, medium, temperature, stability constants, reference.

TABLE 2

ANALYTICAL APPLICATIONS OF HYDROXAMIC ACIDS FOR RARE EARTHS

Hydroxamic acid 1	Method 2	pH 3	Medium, temp. 4	λmax nm 5	ϵ 1 mol^{-1} cm^{-1} 6	Beer's law ppm 7	Interference 8	Ref 9
<u>Lanthanum</u>								
N-m-tolyl-m-nitrobenzo-	Gr	7.5-8.5	60°	-	-	-	Ag,Mn, Ni, Zn, Cd, Hg, Pb,Pd,Be,Ga,Sb,Bi,Ti,Zr, Al,Sn,Ce,Pr,Nd,Th,V,Mo, U,As,Cu.	209
	Gr	7.5-8.5	60°	-	-	-	-	210
N-p-chlorophenyl-m-nitrobenzo-	Gr	6.2-7.0	Aqueous-dioxan	-	-	-	Common metals,rare-earths	211
	Gr	7.3-8.8	-	-	-	-	Ag,Mn,Cu,Zn,Ni,Cd,Hg, Ga,Pd,Pb,Sn,Sb,Bi,Ti, Al,V,Mo.	212
N-p-chlorophenyl-m-nitrocinnamo-	Amp	5.5-8.5	-	-	-	-	-	213
N-p-nitrobenzo-	Gr	7.5-8.5	Ethanol-dioxan	-	-	-	-	214
N-p-tolyl-	Gr	7.5-8.5	Ethanol	-	-	-	-	214

Contd.

TABLE 2 Contd.

1	2	3	4	5	6	7	8	9
N-phenylbenzo-	Ppt	10.0	Aqueous-ethanol, 60°	-	-	-	-	215
	Gr	2-10	Aqueous-ethanol, 60°	-	-	-	Ni,Cu,Zn,Fe,Ce,U,Al,Ga, In,Sc,Zr,Th,Mn,Ti,Mo,W,	216
	Gr	6.4-7.2	-	-	-	-	V,Ta,Nb,Tartrate, Carbonate	217
N-phenyl-cinnamo-	Amp	5.5-8.5	-	-	-	-	-	213,218
N-phenyl-m-nitrocinnamo-	Amp	5.5-8.5	-	-	-	-	-	213
Cerium								
N-m-tolyl-m-nitrobenzo-	Gr	3.8-4.1	60°	-	-	-	Ag,Pd,Mn,Ni,Zn,Cu,Hg, Ca,Sb,As,Bi,Ti,Zr,Mo,Al.	219
	Gr	3.8-4.1	60°	-	-	-	Common metals,La,Pr,Nd, Sm,Gd.	210
	Gr	6.0-6.8	60°	-	-	-	-	209
	Sp	8.0	Chloroform	465	$4.0x10^3$	-	-	220

Contd..

TABLE 2 Contd.

1	2	3	4	5	6	7	8	9
N-p-chlorophenyl-m-nitrobenzo-	Gr	7.2-8.0	Aqueous-dioxan, 60°	-	-	-	Common metals,rare earths	211
N-p-chlorophenyl-p-methoxybenzo-	Sp	8-10	Chloroform	450	-	2 - 22	Cu,Ni,Co,Fe,Pb,Al,Ti,Zr, Th,U,La,Pr,Sm,Dy,Nd,Gd.	221
N-phenylbenzo-	Ppt	2.2	Ethanol	-	-	-	-	215
	Gr	2-10	Aqueous-ethanol, 60°	-	-	-	-	216
	Gr	6.5-7.5	-	-	-	-	Th	222
N-p-tolylbenzo-	Sp	8.4-9.8	Chloroform	465	4.6×10^3	0.03-40	-	223
N-p-tolyl-2-furo-	Sp	7.8-9.8	Chloroform	465	-	0.05-40	-	224
N-p-tolyl-0-methoxy-benzo-	Sp	7.9-8.2	Chloroform	460	3.25×10^3	2.47-39.46	-	225
Praseodymium								
N-m-tolyl-m-nitro-benzo-	Gr	8.6-9.2	60°	-	-	-	Common metals,Th,U,Ce,Nd, La,Sm,Gd.	209
	Gr	8.6-9.2	Aqueous-ethanol, 60°	-	-	-	Ag,Mn,Zn,Cd,Hg,Cu,Mg,Fe, Ga,Pb,Pd,Be,Sb,Sn,Bi,Zr, Ti,Al,V,Mo,U,Th,Ce,La,Sm,Nd.	226

Contd..

TABLE 2 Contd..

1	2	3	4	5	6	7	8	9
N-p-chlorophenyl-m-nitrobenzo-	Gr	8.5-9.0	Aqueous-dioxan, 60°	-	-	-	Ag,Mn,Zn,Cd,Hg,Cu,Ga,Pb, Pd,Be,Sb,Sm,Bi,Zr,Ti,Al, V,Mo,Ce,La,Gd.	211
N-p-nitrobenzo-	Gr	8.6-9.2	Ethanol	-	-	-	-	214
N-p-tolyl-	Gr	8.6-9.2	Ethanol	-	-	-	-	214
N-phenylbenzo-	Ppt	6.5	Aqueous-ethanol, 60°	-	-	-	-	215
	Gr	2-10	Aqueous-ethanol, 60°	-	-	-	-	216
<u>Neodymium</u>								
N-m-tolyl-m-nitro-benzo-	Gr	8.8-9.5	60°	-	-	-	Common metals,Th,U,Ce,La, Pr,Nd,Gd.	209
	Gr	8.8-9.5	Aqueous-ethanol	-	-	-	Ag,Mn,Zn,Cd,Hg,Cu,Mg,Fe, Ga,Pb,Pd,Be,Sb,Sn,Bi,Ti, Al,V,Mo,Ce,Th,U,La,Sm,Pr,Zr.	226
N-p-chlorophenyl-m-nitrobenzo-	Gr	8.7-9.3	Aqueous-dioxan, 60°	-	-	-	Common metals,rare earths	211

Contd..

TABLE 2 Contd.

1	2	3	4	5	6	7	8	9
N-p-nitrobenzo-	Gr	8.8-9.5	Ethanol	-	-	-	-	214
N-p-tolyl-	Gr	8.8-9.5	Ethanol	-	-	-	-	214
N-phenylbenzo-	Gr	6.3	Aqueous-ethanol, 60°	-	-	-	-	215
	Gr	2-10	Aqueous-ethanol, 60°	-	-	-	-	216
Samarium								
N-m-tolyl-m-nitrobenzo-	Gr	9.6-10.2	Aqueous-ethanol, 60°	-	-	-	Common metals,Th,U,Ce, La,Pr,Nd,Gd.	209
	Gr	9.6-10.2	60°	-	-	-	Fe,Cd,Mg,Cu,Pb,Pd,Zn,Al, Ag,Mn,Hg,Ga,Be,Sb,Sn,Bi, Zr,Ti,V,Mo,U,Th,Ce,La,Pr,Nd.	227
N-p-chlorophenyl-m-nitrobenzo-	Gr	9.5-10.0	Aqueous-dioxan, 60°	-	-	-	Common metals,rare earths.	211
N-p-nitro-	Gr	9.6-10.2	Ethanol	-	-	-	-	214

Contd..

TABLE 2 Contd.

1	2	3	4	5	6	7	8	9
N-phenyl-m-nitro-cinnamo-	Amp	5.5-8.5	-	-	-	-	-	213
<u>Terbium</u>								
N-m-tolyl-m-nitrobenzo-	Gr	9.0-9.5	Aqueous-ethanol	-	-	-	Ag,Mn,Zn,Cd,Hg,Cu,Mg,Fe,Ga,Pb,Pd,Sb,Sn,Bi,Zr,Th,Mo,U,La,Ce,Sm,Be.	229
N-phenyl-N-benzo-(I) + quinalizarin (II)	Sp	6.7-7.0	iso-Butanol	458	-	-	-	230
<u>Dysprosium</u>								
N-m-tolyl-m-nitrobenzo-	Gr	9.2-9.6	Aqueous-ethanol, 60°	-	-	-	Ag,Mn,Zn,Cd,Hg,Cu,Mg,Fe,Ga,Pb,Pd,Sb,Sn,Bi,Zr,Ti,Mo,Th,U,Sm,La,Ce,Al,V,Be.	229
<u>Erbium</u>								
N-m-tolyl-m-nitrobenzo-	Gr	9.5-10.0	Aqueous-ethanol, 60°	-	-	-	-	229

Contd...

TABLE 2 Contd.

1	2	3	4	5	6	7	8	9
N-p-tolyl-	Gr	9.6-10.2	Ethanol	-	-	-	-	214
N-phenylbenzo-	Ppt	6.4	Aqueous-ethanol, 60°	-	-	-	-	215
	Gr	2-10	Aqueous-ethanol, 60°	-	-	-	-	216
<u>Gadolinium</u>								
N-m-tolyl-m-nitrobenzo-	Gr	10.3-10.5	Aqueous-ethanol,	-	-	-	Ce,La,Pr,Nd,Sm,Cd,Hg,Cu, Mg,Fe,Ga,Ag,Mn,Zn,rare-earths.	228
	Gr	10.3-10.5	60°	-	-	-	-	209
N-p-chlorophenyl-m-nitrobenzo-	Gr	10.5-10.8	Aqueous-dioxan, 60°	-	-	-	Common metals,rare-earths.	211
N-p-chlorpphenyl-m-nitrocinnamo-	Amp	5.5- 8.5	-	-	-	-	-	213
N-p-nitrobenzo-	Gr	10.3-10.5	Ethanol	-	-	-	-	214
N-p-tolyl-	Gr	10.3-10.5	Ethanol	-	-	-	-	214
N-phenyl-cinnamo-	Amp	5.5- 8.5	-	-	-	-	-	213

Contd..

TABLE 2 Contd.

1	2	3	4	5	6	7	8	9
Yttrium								
N-m-tolyl-m-nitrobenzo-	Gr	5.7-6.5	-	-	-	-	-	231
	Gr	5.5-6.5	Aqueous-ethanol,	-	-	-	Ag,Mn,Zn,Cd,Hg,Cu,Mg,Fe,Ga,Pb,Pd,Sb,Sn,Bi,Zr,Ti,Al,V,Mo,Th,U,La,Ce,Sm,Be.	229
N-p-chlorophenyl-m-nitrocinnamo-	Amp	5.5-8.5	-	-	-	-	-	213
N-phenyl-cinnamo-	Amp	5.5-8.5	-	-	-	-	-	213
N-phenyl-m-nitro-cinnamo-	Amp	5.5-8.5	-	-	-	-	-	213

Abbreviations used for methods : Amp = amperometry; Gr = gravimetry;Ppt = precipitation; Sp = spectrophotometry.

- Study of the complexing ability of the synthesised hydroxamic acids.
- Study of the complex equilibria with rare earths.

PRESENT INVESTIGATION

The present investigation is a part of the broad project of our laboratory dealing with several aspects of the chemistry of 'HYDROXAMIC ACID'.

This thesis describes the preparation and properties of eight N-p-chlorophenyl-m-substituted benzohydroxamic acids, out of them two are the new compounds, have been described. The acids were prepared by reacting hydroxylamine with acid chloride in diethyl ether medium rendered alkaline by aqueous suspension of sodium bicarbonate at lower temperature (0°C or below).

These acids were characterized by m.p., elemental analysis, ultraviolet and infrared spectra. The alkaline hydrolysis constants are reported.

The thermodynamic proton-ligand stability constants, pK_a, of the N-p-chlorophenyl-m-substituted benzohydroxamic acids have been determined in dioxan-water media [50-70% (v/v)] at 25±0.1°C. Empirical correction to pH meter readings in mixed aqueous media have been applied. The pK_a varies linearly with mole fraction of dioxan. Numerical equations expressing this linear relationship have been obtained using the method of least squares. The Hammett correlation function and the effect of substituents on ionization constants of hydroxamic acids is discussed.

The thermodynamic metal ligand stability constants of rare earths, La, Pr, Nd, Sm, Eu, Gd, Tb, with N-p-chlorophenyl-m-substituted benzohydroxamic acids in different dioxan-water media (60-70%) at 25±0.1°C, have been determined by potentiometric method. The effect of basicity of the ligand, central metal ion, order of the stability constants are discussed.

The solid complexes of La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) with N-p-chlorophenyl-m-substituted benzohydroxamic acid (MBHA) have been prepared by precipitation. The optimum conditions of precipitation of these rare earths have been established. These solid complexes were characterised by elemental analyses and infrared spectra.

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