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DONOR PROPERTIES OF HYDROXAMIC ACIDS

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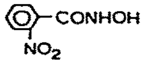
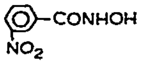
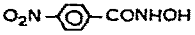
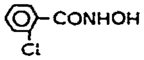
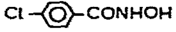
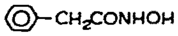
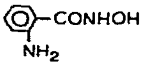
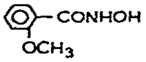
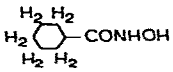
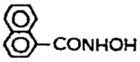
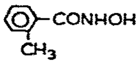
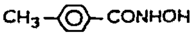
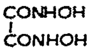
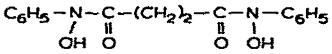
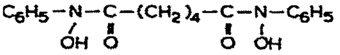
CONTENTS

ABBREVIATIONS

Benzohydroxamic acid $C_6H_5CONHOH$	BH_2
Salicylhydroxamic acid 	SH_2
o-Nitrobenzohydroxamic acid 	*o*-nitroBH_2

m-Nitrobenzohydroxamic acid 	*m*-nitroBH$_2$
p-Nitrobenzohydroxamic acid 	*p*-nitroBH$_2$
o-Chlorobenzohydroxamic acid 	*o*-chloroBH$_2$
p-Chlorobenzohydroxamic acid 	*p*-chloroBH$_2$
Phenylacetohydroxamic acid 	PhH$_2$
Anthranilhydroxamic acid 	AnH$_2$
o-Methoxybenzohydroxamic acid 	*o*-methoxyBH$_2$
p-Methoxybenzohydroxamic acid 	*p*-AH$_2$
Nicotinehydroxamic acid 	NicH$_2$
Cyclohexanehydroxamic acid 	CH$_2$
Quinoline 8-hydroxamic acid 	QH$_2$
o-Methylbenzohydroxamic acid 	*o*-MeBH$_2$
p-Methylbenzohydroxamic acid 	*p*-MeBH$_2$
Cinnamylhydroxamic acid $C_6H_5CH{=}CHCONHOH$	CnH$_2$
Oxaldihydroxamic acid  $\begin{array}{l}CONHOH\\ \vert\\ CONHOH\end{array}$	OxalH$_2$
Succinyl-bis-N-phenylhydroxamic acid  $C_6H_5-\underset{OH}{N}-\underset{O}{\overset{}{C}}-(CH_2)_2-\underset{O}{C}-\underset{OH}{N}-C_6H_5$	SuH$_2$

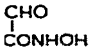
Adipyl-bis-N-phenylhydroxamic acid



$C_6H_5-N(OH)-C(=O)-(CH_2)_4-C(=O)-N(OH)-C_6H_5$

AdH_2

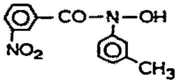
Glyoxalhydroxamic acid



$CHO-CONHOH$

GH_2

N-*m*-Tolyl-*m*-nitrobenzohydroxamic acid

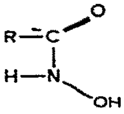


N-*m*-T-*m*-NBHA

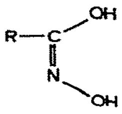
A. INTRODUCTION

Hydroxamic acids were used as colorimetric reagents [1—5] many years ago; in recent times there has been an increasing interest in the acids and a large number of them have been described in the literature. Besides their being used as colorimetric reagents and gravimetric reagents [6,7,44,45] attempts have been made to isolate stable, crystalline transition metal complexes [8—16]. The present review covers most of the recent studies of co-ordination complexes of hydroxamic acids.

Hydroxamic acid exists in two tautomeric forms

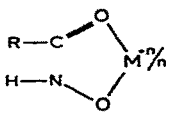


1



2

Structure **1** has one replaceable hydrogen atom and would behave as a monobasic acid while structure **2** has two replaceable hydrogens. Such keto—enol tautomerism provides a number of sites for chelation. The keto form predominates in acid medium and the enol form in alkaline medium [17]. This has been proved by extracting vanadiumbenzohydroxamic acid complexes using organic solvents [18]. The complex formed in alkaline medium cannot be extracted by such solvents. That the hydroxamic acid forms metal complexes through the hydroxamide functional group **1** and not through the hydroxyoxime structure **2** is proved by IR [9,12,19] and UV [20] spectral studies. It is thus probable that most hydroxamic acid metal complexes have the following structure **3**



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B. THE LIGANDS, HYDROXAMIC ACIDS

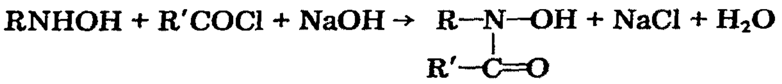
(i) Syntheses and general properties

Hydroxamic acids, in general, have been synthesised by adopting Blatt's procedure [21]. In this method, an alkyl or aryl ester (RCO_2Et) reacts with hydroxylamine in the presence of alkali and the free acid is obtained by the addition of acid (HX) in the appropriate quantity in cold solution

$$RCO_2Et + NH_2OH + KOH \rightarrow RCONHOK + EtOH + H_2O$$

$$RCONHOK + HX \rightarrow RCONHOH + KX$$

Dutta [2] has synthesised quinaldinehydroxamic acid and nicotinehydroxamic acid using sodium ethoxide instead of potassium hydroxide. On the basis of the Schotten—Baumann reaction, Tandon and co-workers [22,23] have also prepared several N-arylhydroxamic acids where N-phenylhydroxylamine (RNHOH) reacts with acetylchloride or its derivative (R'COCl) in the presence of dilute alkali



$$RNHOH + R'COCl + NaOH \rightarrow \begin{array}{c} R{-}N{-}OH \\ | \\ R'{-}C{=}O \end{array} + NaCl + H_2O$$

Wise and Brandt [24] adopted a quite different technique for the syntheses of hydroxamic acids in which the pure acid was recovered by passing a methanol solution of potassium benzohydroxamate (prepared by Blatt's method) through the hydrogen form of a cation exchanger (R'—H) and removing the excess solvent

$$RCONHOK + R'{-}H \rightarrow RCONHOH + R'{-}K$$

These workers claimed that, since the conditions of the reaction are mild, decomposition of the desired compound is very small.

Based on the hydroxamide structure the carbonyl oxygen will serve as a donor centre in the metal chelate. As a consequence, there will be electron withdrawal from the carbonyl group which, in turn, will increase the electron density in the C—N bond. Therefore, a lowering of the carbonyl frequency and an increase of the C—N frequency are expected. The carbonyl frequency in the free reagent at 1660 cm^{-1} is shifted to 1595 cm^{-1} in oxo-vanadium(IV) complexes [9] and to 1600 cm^{-1} in oxo-molybdenum(VI) complexes [12]. The C—N bond frequency at 1320 cm^{-1} in the free reagent changes to 1346 cm^{-1} in the vanadium complex and to 1360 cm^{-1} in the molybdenum chelates. The N—H frequency at 3300 cm^{-1} and the C—H stretch at 3070 cm^{-1} shift to 3095 cm^{-1} in the vanadium complex and to 3080 cm^{-1} in the molybdenum complex (Table 1). Thus the nature of attachment of ligand to vanadium(IV) and molybdenum(VI) is basically the same. The same generalization may be drawn for the oxo-molybdenum(V) [16] and chromium(III) chelates [16].

TABLE 1

IR data (cm^{-1}) for benzohydroxamic acid, oxo-vanadium(IV) and oxo-molybdenum(VI) complexes

Ligand/complex	IR data	Ref.
BH_2	710, 805, 910, 1030, 1052 1170, 1320, 1450, 1500, 1580, 1660 2810, 3070, 3300	9
$VO(BH)_2$	699, 790, 916, 974, 993, 1023 1150, 1346, 1444, 1479, 1513 1595, 3095	9
$MoO_2(BH)_2$	700, 800, 900, 940, 1040, 1070 1170, 1360, 1460, 1500, 1540 1600, 3080	12

(ii) Dissociation constants

The *pK* values of some hydroxamic acids have been determined by several workers following pH, potentiometric and spectrophotometric techniques. The values, tabulated in Table 2, indicate that hydroxamic acids are, in general, weak donors. N-arylhydroxamic acids are, in turn, even weaker donors than simple aromatic hydroxamic acids, due to intramolecular hydrogen bonding. It has also been found that unsaturated N-arylhydroxamic acids are stronger donors than the corresponding saturated compounds.

The *pK* values of the hydroxamic acids vary from 7.05 for *o*-nitrobenzohydroxamic acid to 11.33 for N-phenyl-n-butyrohydroxamic acid and the values influenced mainly by (i) introduction of groups having negative and positive inductive effect, (ii) substituents on the N-phenyl ring and (iii) various conjugated systems attached to the functional carbonyl group. Substituents like the nitro group, fluorine or chlorine, having a negative inductive effect, decrease the *pK* values. Whereas substituents like the methyl group, having a positive inductive effect, increase the *pK* values of the hydroxamic acids. It has been observed from the *pK* values of the hydroxamic acids (Table 2) that the unsaturated N-aryl hydroxamic acids are stronger acids than the corresponding saturated compound. This trend may be explained on the basis of the *pK* value of the corresponding carboxylic acids. In crotonic acid the α-carbon atom is in a state of sp^2 hybridisation as compared to sp^3 hybridisation for the α-carbon atom in butyric acid. It is more electronegative because its bonding orbitals have more *s* character. The double-bonded carbon atom brings about a decrease in the electron density on the oxygen thereby causing an easy rupture of the O—H bond. However, when two double bonds are present, as in sorbohydroxamic acid, the double bond character of the conjugated system decreases owing to resonance. Hence the electron density on the oxygen atom is affected very little. The *pK* values of

TABLE 2

Dissociation constants of hydroxamic acids

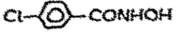
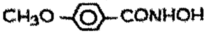
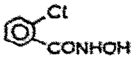
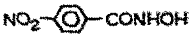
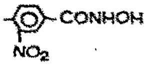
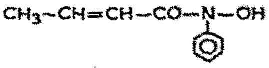
Hydroxamic acids	*pK*	Ref.
Aceto- $CH_3CONHOH$	7.397	24
Benzo- $C_6H_5CONHOH$	8.886 8.805 8.97 ± 0.03	24,27 23 5
n-Butyro- $CH_3CH_2CH_2CONHOH$	7.48	24
p-Chlorobenzo- 	8.585 8.62	24 10
p-Methoxybenzo- 	9.00	24,10
Phenylaceto- 	7.18	24
Propiano- $CH_3CH_2CONHOH$	7.455	24
Salicyclo- 	7.376 7.56	24 25
o-Nitrobenzo- 	7.05	10
o-Chlorobenzo- 	7.85	10
o-Fluorobenzo- 	8.00	10
p-Nitrobenzo- 	8.35	10
m-Nitrobenzo- 	8.40	10
o-Toluic- 	8.55	10
N-Phenylcrotono- $CH_3{-}CH{=}CH{-}CO{-}\underset{C_6H_5}{N}{-}OH$	10.94	26

TABLE 2 (continued)

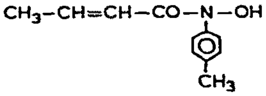
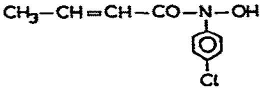
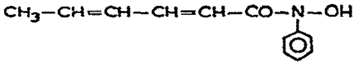
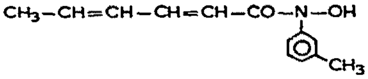
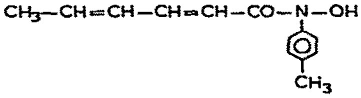
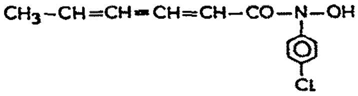
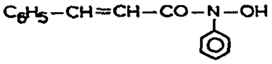
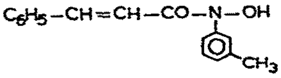
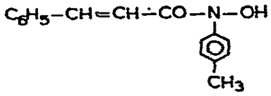
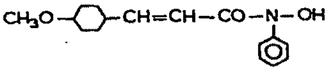
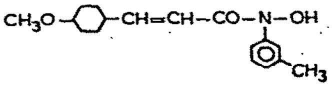
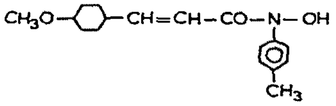
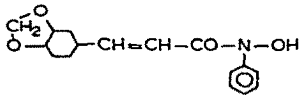
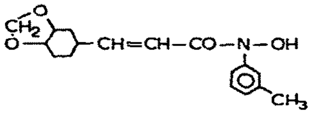
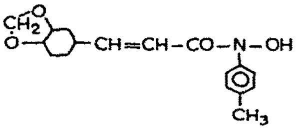
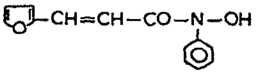
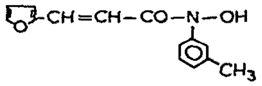
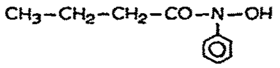
Hydroxamic acids	*pK*	Ref.
N-*p*-Tolylcrotono-  $CH_3-CH=CH-CO-N-OH$	10.94	26
N-*p*-Chlorophenylcrotono-  $CH_3-CH=CH-CO-N-OH$	10.80	26
N-Phenylsorbo-  $CH_3-CH=CH-CH=CH-CO-N-OH$	10.85	26
N-*m*-Tolylsorbo-  $CH_3-CH=CH-CH=CH-CO-N-OH$	11.18	26
N-*p*-Tolylsorbo-  $CH_3-CH=CH-CH=CH-CO-N-OH$	10.97	26
N-*p*-Chlorophenylsorbo-  $CH_3-CH=CH-CH=CH-CO-N-OH$	10.86	26
N-Phenylcinnamo-  $C_6H_5-CH=CH-CO-N-OH$	10.87	26
N-*m*-Tolylcinnamo-  $C_6H_5-CH=CH-CO-N-OH$	11.04	26
N-*p*-Tolylcinnamo-  $C_6H_5-CH=CH-CO-N-OH$	10.87	26
N-Phenyl-*p*-methoxycinnamo-  $CH_3O-C_6H_4-CH=CH-CO-N-OH$	10.97	26
N-*m*-Tolyl-*p*-methoxycinnamo-  $CH_3O-C_6H_4-CH=CH-CO-N-OH$	11.13	26

TABLE 2 (continued)

Hydroxamic acids	*pK*	Ref.
N-*p*-Tolyl-*p*-methoxycinnamo- 	11.09	26
N-Phenyl-3,4-methylene dioxycinnamo- 	10.90	26
N-*m*-Tolyl-3,4-methylene dioxycinnamo- 	11.13	26
N-*p*-Tolyl-3,4-methylene dioxycinnamo- 	11.03	26
N-Phenyl-2-furan acrylo- 	10.74	26
N-*m*-Tolyl-2-furan acrylo- 	11.03	26
N-Phenyl-n-butyro- 	11.33	26

sorbohydroxamic acids are, therefore, either similar to crotonohydroxamic acids or even slightly less. The strength of the acids are also found to decrease in the order of the terminal furan, phenyl or methyl group attached to the functional carbonyl group through the ethylenic linkage. Substituents having a negative inductive effect, such as a methoxy or a methylenedioxy group in the C-phenyl ring of cinnamohydroxamic acid, decrease the acid strength.

(iii) Stability constants

The overall stability constants of several metals have been evaluated by many workers who used Bjerrum's technique, pH titration, distribution method and potentiometric method. It has been pointed out by Mellor and Maley [28] and also by Irving and Williams [29] that the stability of chelate of bivalent transition metals increases regularly from Mn^{2+} to Cu^{2+} irrespective of the nature of the ligand used and there is a systematic decrease in stability from Cu^{2+} to Zn^{2+}. The stability constants of bivalent, trivalent, quadrivalent and hexavalent transition metals are tabulated in Tables 3 and 3a. The values were, in most cases, recorded at 25°C unless otherwise stated.

C. METAL COMPLEXES

(i) Titanium(IV) and zirconium(IV) complexes

Titanium(IV) chloride reacts with benzohydroxamic acid to yield oxo-bis-(benzohydroxamato)Ti(IV) [37]. The zirconium(IV) ion also forms oxo-bis-(benzohydroxamato)Zr(IV) [38].

Salicylhydroxamic acid also forms oxo compounds with Ti(IV) and Zr(IV) which are similar to the benzohydroxamic acid complexes in composition and in properties [8]. Ti(IV) and Zr(IV) complexes with phenylacetohydroxamic acid have been described by Majumdar and Pal [38a].

(ii) Oxo-vanadium(IV) and (V) complexes

A large number of hydroxamic acids have been used by Dutta and co-workers [9,10] to synthesise oxo-vanadium(IV) complexes. Most of the hydroxamic acids, with the exception of benzo-, *m*- and *p*-nitrobenzo-, *p*-methylbenzo- and *p*-methoxybenzo hydroxamic acid, yielded oxo-vanadium(V) complexes, due to oxidation of oxo-vanadium(IV) to oxo-vanadium(V) under the conditions used for the preparation of the complexes.

Aqueous solutions of vanadyl sulphate and the potassium salt of hydroxamic acid interact at around pH 3—4 to furnish coloured complexes having the general composition, $[VO(RH)_2]$, where RH_2 represents a molecule of hydroxamic acid. The complexes are quite stable in air, but when dissolved in ethanol and allowed to stand for an hour, oxidise to oxo-vanadium(V) complexes. This change has been confirmed by spectral measurements.

Of the hydroxamic acids which stabilise oxo-vanadium(IV), the *p*-nitrobenzohydroxamate complex is the most interesting since it exhibits *cis* (violet) and *trans* (green) isomerism. This has been confirmed by IR measurements [9]. The violet variety reacts more quickly with ethanol than the green variety.

The oxo-vanadium(V) complexes are also interesting as those containing a hydroxamic acid having a strong electron withdrawing group as a substituent in the aromatic nucleus, give an oxo-alkoxo derivative when refluxed with alcohols. The physical characteristics of oxo-vanadium(IV) and (V) complexes are presented in Table 4.

TABLE 3

Stability constants of metal complexes of hydroxamic acids

Ligand	Co(II)		Fe(III)		Cu(II)		Zn(II)	
	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2
Benzohydroxamic			12.18					
acid					9.95 [a]	8.12 [a]	7.57 [a]	5.62 [a]
N-phenyl benzo-					19.14		14.14	
hydroxamic acid					10.36	8.78	7.51	6.63
N-phenyl-*o*-tolyl-					10.51	8.85	8.19	6.71
benzohydroxamic					10.45 [b]	8.90 [b]	8.16[b]	6.70
acid								
N-phenyl-*o*-methoxy-	7.96	6.60			10.35	8.68	8.63	6.65
benzohydroxamic								
acid								
N-phenyl-*m*-tolyl-					10.51	8.86	Insoluble	
benzohydroxamic					11.68[c]	9.80 [c]	9.25[c]	7.77 [c]
acid					11.57 [d]	9.70 [d]	9.26 [d]	7.70 [d]
N-phenyl-*p*-tolyl-					10.66	8.79	Insoluble	
benzohydroxamic								
acid								
N-phenyl-*n*-butyro-					10.64	8.87	7.72	6.39
benzohydroxamic								
acid								

[a] At 35°C.
[b] At 30°C.
[c] Mean values at 25°C in 70% (v/v) dioxane—water.
[d] Mean values at 35°C in 70% (v/v) dioxane—water.

TABLE 3a

Stability constants of metal complexes of N-aryl *o*-substituted phenylhydroxamine acids [a]

o-substituted group	Cu(II)		Zn(II)		Ni(II)		Mn(II)		Ref.
	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2	
$-CH_3$	10.25	8.56	7.86	6.21	7.82	7.77	6.46	4.77	36
$-OCH_3$	10.35	8.68	8.63	6.65	5.86	5.68	6.80	5.67	36
—F	10.03	8.08	7.10	5.69	7.36	5.54	6.70	4.88	36
—Cl	9.96	8.04	7.52	5.92	7.23	5.45	6.40	4.93	36
—Br	9.90	7.97	7.49	5.87	7.21	5.33	6.07	4.76	36
—I	9.96	8.12	7.40	6.64	7.23	5.30	6.02	4.68	36
$-NO_2$	9.45	7.49	7.12	5.44	7.07	5.04	5.74	4.38	36
—H	10.29	8.73	7.71	6.63	7.20	—	—	—	36

[a] At 35°C in 50% (v/v) dioxane—water.

i(II)		Mn(II)		Be(II)		Zr(IV)		U(VI)		Ref.
g k_1	log k_2	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2	
						12.43	11.65	8.72	6.05	5
7.18 [a]	5.14 [a]	5.97 [a]	4.52							30
2.91		15.83								31
7.0	5.91	6.02	5.15							32
7.64	6.06	6.39	5.62							32
7.52 [b]	6.01 [b]	6.33 [b]	5.59 [b]							33
7.77	5.68	6.80	5.67							34
nsoluble		Insoluble								32
8.53 [c]	6.86 [c]	7.39 [c]	6.62 [c]							35
8.43 [d]	6.79 [d]	7.29 [d]	6.53 [d]							
nsoluble		Insoluble								32
7.61	5.69	6.23	4.53							32

Using succinyl-bis-N-phenylhydroxamic acid and adipyl-bis-N-phenylhydroxamic acid as donors, Ghosh and Sarkar [11] have isolated oxo-hydroxo-bis(hydroxamato)vanadium(V) complexes.

(iii) Chromium(III) complexes

A series of hydroxamic acid complexes of chromium(III), $Cr(RH)_2$ (RH_2 = molecule of hydroxamic acid) has been prepared by Chatterjee [16]. The aromatic hydroxamic acids studied include benzo-, salicyl-, *p*-chlorobenzo-, *p*-anisyl-, *p*-nitrobenzo-, nicotine-, phenylaceto- and cyclohexane hydroxamic acid. In general, it was observed that an aqueous solution of chrome alum (one mole) reacts with any of these hydroxamic acids (three moles) to provide green complexes. These have been identified as tris(hydroxamato)-chromium(III) on the basis of molar conductance, magnetic and spectral measurements. Magnetic moment measurements show three unpaired elec-

TABLE 4
Physical characteristics of oxo-vanadium (IV) and (V) complexes

Complex	Colour	Mag. moment (BM) at 300 K	$\lambda_{\text{max.}}$ (nm) ϵ(l mol cm^{-1})	Molar conductances (ohm^{-1} cm^2 mol^{-1} in 10^{-3} *M methanol*)	Ref.
$\mathrm{VO(BH)_2}$	Rose—red	1.72	—	—	9
$\mathrm{VO}(p\text{-nitroBH})_2$	Violet.	1.78	—	—	9
$\mathrm{VO}(p\text{-nitroBH})_2$	Green	1.74	—	—	9
$\mathrm{VO}(m\text{-nitroBH})_2$	Rose—red	1.61	—	—	9
$\mathrm{VO}(p\text{-methoxyBH})_2$	Rose—violet	1.63	—	—	9
$\mathrm{VO}(p\text{-meBH})_2$	Dark grey—violet	1.63	—	—	9
$\mathrm{VO(OH)}(o\text{-chloroBH})_2$	Dark violet	Diamagnetic	420(1540) [a]	2.8	10
$\mathrm{VO(OC_2H_5)}(o\text{-chloroBH})_2$	Orange—red	Diamagnetic	420(1536)	2.4	10
$\mathrm{VO(OH)}(p\text{-chloroBH})_2$	Violet	Diamagnetic	440(1956)	2.5	10
$\mathrm{VO(OC_2H_5)}(p\text{-chloroBH})_2$	Red	Diamagnetic	440(1956)	2.2	10
$\mathrm{VO(OH)}(o\text{-fluoroBH})_2$	Dark violet	Diamagnetic	440(1940)	2.7	10
$\mathrm{CO(OC_2H_5)}(o\text{-fluoroBH})_2$	Dark red	Diamagnetic	430(1960)	—	10
$\mathrm{VO(OH)}(o\text{-nitroBH})_2$	Violet	Diamagnetic	470—480(1100)	3.0	10
$\mathrm{VO(OH)}(o\text{-nitroBH})_2$	Blue	Diamagnetic	—	—	
$\mathrm{VO(OC_2H_5)}(o\text{-nitroBH})_2$	Deep red	Diamagnetic	480(1092)	—	10
$\mathrm{VO(OH)}(p\text{-iodoBH})_2$	Dark violet	Diamagnetic	430(2040)	2.2	10
$\mathrm{VO(OH)}(o\text{-meBH})_2$	Light violet	Diamagnetic	440—450(1762)	2.40	10
$\mathrm{V(OCH_3)}(o\text{-chloroBH})_2$	Orange—red	Diamagnetic	—	2.5	10
$\mathrm{V(OCH_3)}(p\text{-chloroBH})_2$	Deep red	Diamagnetic	—	2.2	10
$\mathrm{V(OCH_3)}(o\text{-nitroBH})_2$	Maroon—red	Diamagnetic	—	2.70	10
$\mathrm{V(OCH_3)}(o\text{-fluoroBH})_2$	Brick—red	Diamagnetic	—	2.5	10
$\mathrm{VO(OH)(PhH)_2}$	Blue Violet	Diamagnetic	420—430(1080) 420—430(1110)		9
$\mathrm{VO(OC_2H_5)(PhH)_2}$	Ruby—red	Diamagnetic	430(880)	—	9
$\mathrm{VO(OCH_3)(PhH)_2}$ ·	Ruby—red	Diamagnetic	—	—	9
$\mathrm{VO(OH)(CnH)_2}$	Violet—black	Diamagnetic	450(2040)	—	9
$\mathrm{VO(OH)(AnH)_2}$	Dark—violet	Diamagnetic	470(1900)	—	9
$\mathrm{VO(OH)(SH)_2}$	Blue—violet	Diamagnetic	620(3560)	—	9
$\mathrm{VO(OH)}(p\text{-nitroBH})_2$	Violet	Diamagnetic	430(1800)	—	9
$\mathrm{VO(OCH_3)}(p\text{-nitroBH})_2$	Brick—red	Diamagnetic	430(1900)	—	9
$\mathrm{VO(OH)}(m\text{-nitroBH})_2$	Violet	Diamagnetic	430(1300)	—	9

[a] The values in parenthesis indicate molar extinction coefficients (ϵ).

TABLE 5

Physical characteristics of chromium(III) complexes

Complex	Colour	Mag. moment (BM)	Absorption bands, $\lambda_{max.}$ (nm)	Molar conductance (ohm^{-1} cm^2 mol^{-1}) in 10^{-3} M methanol	Ref.
$Cr(BH)_3$	Green	3.75	—	14.1	16
$Cr(SH)_3$	Green	3.80	—	8.3	16
$Cr(NiCH)_3$	Green	3.80	430—450 600—620	Insoluble	16
$Cr(p\text{-nitroBH})_3$	Green	3.70	430 620	Insoluble	16
$Cr(p\text{-chloroBH})_3$	Green	3.80	—	Insoluble	16
$Cr(PhH)_3$	Green	3.80	420—430 610	Insoluble	16
$Cr(CH)_3$	Green	3.75	430—440 610	Insoluble	16
$Cr(p\text{-AH})_3$	Green	3.80	—	Insoluble	16

trons per chromium for each complex. The electronic absorption spectra reveal the usual two bands of octahedral chromium(III) complexes around 16 000 and 22 500 cm^{-1} representing transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ respectively (Table 5).

(iv) Iron(III) complexes

The bright orange—red, hydroxo-bis(succinyl-bis-N-phenylhydroxamato)-Fe(III), Fe(OH)(SuH), was prepared [11] by stirring an ethanol solution of the ligand with dilute ferric chloride solution in the mole ratio 2 : 1 and diluting the red solution to adjust the pH to 1.5. The orange—red, tris(adipyl-bis-N-phenylhydroxamato)di-iron dihydrate, $[Fe_2(Ad)_3] \cdot 2\,H_2O$ has been similarly synthesised [11]. A molecule of water was expelled by heating the complexes for 2 h at 120°C. These complexes are high-spin, having magnetic moments around 5.87—5.88 BM.

The red—brown, tris(benzohydroxamato)Fe(III) [8] is sparingly soluble in aqueous medium but soluble in acids, alkalies and most of the common organic solvents. Salicylhydroxamic acid, like benzohydroxamic acid, gave the orange—red tris chelate [8] with Fe(III) ion, $Fe(SH)_3$.

A series of tris(hydroxamato)Fe(III) complexes has been described by Ray [39]. These tris chelates have been prepared from benzo-, *p*-methylbenzo-, *o*-methylbenzo-, *p*-nitrobenzo-, *o*-nitrobenzo-, *p*-chlorobenzo-, *o*-chlorobenzo-, *p*-methoxybenzo- and *o*-methoxybenzohydroxamic acid. In synthesising these complexes one mole of an aqueous solution of hydrated ferric chloride reacts with either an aqueous or acetone solution of the ligand

TABLE 6

Physical characteristics of iron(III) complexes

Complex	Colour	Mag. moment (BM) at 300 K	$\lambda_{max.}$ (nm) in methanol	Molar conductance (ohm^{-1} cm^2 mol^{-1}) in 2×10^{-4} benzene	Ref.
Fe(OH)(SuH)$_2$	Orange—red	5.89	—	—	11
[Fe$_2$(Ad)$_3$] · 2H$_2$O	Orange—red	5.88	—	—	11
[Fe(BH)$_3$] · H$_2$O	Deep brown	5.91	440	—	36
[Fe(*p*-MeBH)$_3$] · H$_2$O	Deep brown	5.88	440	—	36
[Fe(*o*-MeBH)$_3$] · H$_2$O	Red	5.85	430	—	36
[Fe(*p*-nitroBH)$_3$] · 1.5H$_2$O	Deep chocolate	5.90	450 sh	—	36
[Fe(*o*-nitroBH)$_3$] · H$_2$O		5.86	—	—	36
[Fe(*p*-chloroBH)$_3$] · 0.5H$_2$O	Dull red	5.99	430	—	36
Fe(*o*-chloroBH)$_3$	Chocolate	5.91	420	—	36
[Fe(*p*-methoxyBH)$_3$] · 1.5H$_2$O	Deep chocolate	5.94	430	—	36
[Fe(*o*-methoxyBH)$_3$] · H$_2$O	Red	5.83	430	—	36
[Fe(BH)$_2$Cl] · 0.5H$_2$O		5.92 [b]	430	79.9	36
Fe(*p*-MeBH)$_2$Cl		5.95 [b]	430 sh	69.5 [a]	36
[Fe(*o*-MeBH)$_2$Cl] · 0.5H$_2$O		5.80 [b]	430 sh	67.4	36
[Fe(*p*-chloroBH)$_2$]Cl · 0.5H$_2$O		5.85	440	71.6	36
Fe(*o*-methoxyBH)$_2$Cl		5.82	430	70.9	36

[a] Concentration 1×10^{-4} (benzene)

[b] At 303 K.

and the pH of the solution is adjusted to about 5.0 with sodium acetate solution whereupon coloured complexes precipitate (Table 6). All these complexes have been prepared by following the above general procedure with the exception of the *o*-methoxy derivative which has been prepared by reacting ferric chloride and the ligand in situ and adjusting the pH to 5.0.

The chloro-bis(hydroxamato)Fe(III) complexes have been prepared by reacting tris(hydroxamato)Fe(III) with a calculated amount of ferric chloride in methanol. Among the complexes with *para* substituted acids, the tris(*p*-nitrobenzohydroxamato)Fe(III) complex did not produce the desired product.

The magnetic moments of the tris(hydroxamato) and chloro-bis(hydroxamato)Fe(III) complexes have been measured at room temperature. It has been observed that in the tris(hydroxamato) series, the *o*-nitro-, *o*-methyl- and *o*-methoxy complexes show slightly lower than normal spin-only values. In the case of the chloro-bis(hydroxamato) complexes, only the benzohydroxamato and the *p*-methylbenzohydroxamato complexes show normal magnetic moments (5.92—6.93 BM). The other complexes of this series also show slightly lower values.

Many of the ion complexes exhibit a strong band near 440 nm which is likely to be charge transfer in origin (Table 4). The molar extinction coefficients of the complexes have been determined. The highest value of ϵ_{max} is obtained when the —OCH_3 group is present in the *para* position of the phenyl ring and the value decreases with decreasing conjugation. Inclusion of a methoxy, chloro or methyl group at the *ortho* position in the phenyl ring further lowers the ϵ_{max} values, probably owing to steric hindrance. In the case of chloro-bis(hydroxamato) the same reasoning may be applied.

Comparison of the IR data of the halo complexes with those of the parent tris chelate shows a marked difference in their bands. Among the important differences is a 1606 cm^{-1} band, observed in chloro-bis(benzohydroxamato)-Fe(III) hemihydrate which has not been found in tris(benzohydroxamato)-Fe(III). It has been stated that changes in positions or disappearance of some bands and appearance of new bands on the formation of chloro-bis(hydroxamato)Fe(III) complexes may be due to an oxygen bridged structure. Chloro-bis(hydroxamato)Fe(III) complexes, having no substitution on the nitrogen, have an oxygen bridging structure while those with N-phenyl substitution are chloro bridged.

(v) Cobalt(II) and (III) complexes

The light pink bis(hydroxamato)Co(II) has been prepared [8] by interacting Co(II) salts with benzo-, salicyl-, cinnamyl-, dihydrocinnamyl- and methoxybenzohydroxamic acid at pH 3—6. These chelates have been oxidised to the anionic Co(III) complexes in alkaline medium. Glycinehydroxamic acid on the other hand, gave two isomeric (*cis* and *trans*?) dark red tris(glycinehydroxamato)Co(III) complexes in neutral medium [8]. With unsubstituted hydroxamic acid, no tris chelate of cobalt(III) has, so far, been obtained, because of their instability in neutral or acid medium. The cobalt(II) complexes give magnetic moment values of 4.0—4.20 BM which are rather low whereas cobalt(III) compounds have all been found to be diamagnetic.

(vi) Nickel(II) complexes

A few complexes of Ni(II) have been synthesised with hydroxamic acids [8]; the greenish-yellow bis(hydroxamato)Ni(II), NiR_2, has been prepared by heating benzo-, salicyl-, cinnamyl- and methoxybenzohydroxamic acid with a nickel(II) salt on a steam bath at pH 6.0. With glycine and α-alanine hydroxamic acids red or orange complexes have been obtained by adopting the same procedure in neutral medium.

The red and orange complexes are diamagnetic and presumably square planar whereas the greenish-yellow nickel(II) complexes are paramagnetic having magnetic values of 2.78—3.15 BM and are presumably associated octahedral.

(vii) Copper(II) complexes

Chakraburty [8] has described a series of copper(II) complexes with hydroxamic acid. When the acid has no additional functional group the copper(II) ion gives a bright green monochelate, $[R{\cdot}Cu(OH)H_2O] \cdot x\ H_2O$ and a bluish-green bis complex, CuR_2. The mono complexes have been isolated using simple aliphatic hydroxamic acids such as acethydroxamic and propionhydroxamic acids; on the other hand benzo- and salicylhydroxamide acids gave a bis chelate. Similarly, hydroxamic acids with additional functional groups such as $-NH_2$, $-OH$, $-SH$ etc. also produce a bright green mono chelate and a dark red or red—violet bis complex.

The red and violet complexes of copper(II) are paramagnetic having magnetic moments of 1.6—1.75 BM. All other compounds have magnetic moments between 1.72 and 1.92 BM.

A greenish-yellow complex salt of composition $H_2Cu_8Su_9$ has been described by Ghosh and Sarkar [11]. This is formed when an acetone solution of excess copper(II) acetate reacts with an ethanolic solution of succinyl-

TABLE 7

Physical characteristics of copper(II) complexes

Complex	Colour	Mag. moment (BM)	M.P. (°C)	Ref.
$H_2Cu_8(Su)_9$	Greenish yellow	1.88	—	11
Cu(Ad)	Green	1.87	211 [a]	11

[a] Decomposed.

bis-N-phenylhydroxamic acid, whereas the adipyl-bis-N-phenylhydroxamic acid and copper(II) acetate at pH around 4.5 provide a green complex of composition Cu(Ad)$_2$. The magnetic moments of the above complexes lie around 1.87 BM (Table 7).

Jones and Hurd [40] have reported the formation of grass green copper(II) complexes with triphenylacethydroxamic, pyromucylhydroxamic and thenoylhydroxamic acids.

(viii) Niobium(V) and tantalum(V) complexes

A few niobium(V) and tantalum(V) complexes of benzo- [41], phenylaceto- [43], salicyl- [8], and cinnamylhydroxamic acid [42] of general composition MO(RH)$_3$ (where M = Nb or Ta; RH$_2$ = a molecule of hydroxamic acid) have been described.

Tantalum(V) precipitates completely with benzohydroxamic acid [41] at pH 4.0—6.4 from oxalate solution while niobium(V) precipitates completely with cinnamylhydroxamic acid [42] from 5% H_2SO_4 solution to a solution of pH 6.5. This oxo-bis(cinnamylhydroxamato)Nb(V) complex is stable up to 225°C and may be used for gravimetric estimation.

(ix) Oxo-molybdenum(V) and (VI)

A few green or orange oxo-molybdenum(V) complexes with aromatic hydroxamic acids have been prepared [16] by the interaction of aqueous solutions of oxo-pentachloromolybdate ion and hydroxamic acids in a carbon dioxide atmosphere (Table 8). All these complexes are diamagnetic. The diamagnetism may be due to polymerisation of the complexes with consequent interaction of electron spins on the neighbouring molybdenum atoms which removes paramagnetism.

An attempt to isolate oxo-alkoxo-bis(hydroxomato)molybdenum(V) with anhydrous alcohol failed. This is due to facile oxidation of molybdenum(V) to molybdenum(VI).

TABLE 8

Physical characteristics of Mo(V) complexes

Complex	Colour	Electronic spectra (nm)			Ref.
		Band I	Band II	Band III	
MoO(OH)(BH)$_2$	Green	—	600—620	776—850	16
MoO(OH)(o-chloroBH)$_2$	Green	—	650—670	720—770	16
MoO(OH)(*p*-chloroBH)$_2$	Green	—	620—640	850—900	16
MoO(OH)(*p*-AH)$_2$	Green	—	—	750	16
MoO(OH)(Q')	Green	—	660—680	775—800	16
MoO(OH)(CH)$_2$	Orange	440—460	—	750	16

The reflectance spectra of these insoluble molybdenum(V) complexes were recorded but are not well defined. The bands (Table 8) are so broad that no correct assignment can be made without further analysis.

Molybdates and hydroxamic acids have been shown [12] to react in aqueous medium at around pH 3.0 to furnish yellow dioxo-bis(hydroxamato)-molybdenum(VI) as a sparingly soluble product. The complexes have been recrystallised unchanged from higher alcohols thus indicating no esterification of ligand units. These complexes have been shown to be diamagnetic and nonconducting.

(x) Silver(I) complexes

Jones and Hurd [40] have prepared silver(I) complexes with diphenylacethydroxamic acid, triphenylacethydroxamic acid, pyromucylhydroxamic acid and thenoylhydroxamic acid. In isolating silver(I) complexes, the potassium salts of the hydroxamic acids were used because in some cases the sodium salt undergoes hydrolysis. The silver(I) complexes, in general, have been isolated by mixing an ether—alcohol solution of the potassium salt with aqueous silver nitrate. In the case of triphenylacethydroxamic acid, the white complex turned, in a short time, to a canary yellow product. Sometimes, however, as in the case of the pyromucyl hydroxamic acid complex of silver(I), a lower temperature is required to inhibit hydrolysis.

(xi) Ruthenium(III), rhodium(III), iridium(II) and (III), and palladium(II) complexes

A series of ruthenium(II), rhodium(III), iridium(II) and (III) and palladium(II) hydroxamato complexes has been described by Misra [15].

Ruthenium forms a tris chelate with benzohydroxamic acid. On the other hand, two isomeric tris(oxaldihydroxamato)dirhodium(III) complexes have been isolated. In addition three anionic complexes have been reported with benzohydroxamic acid, salicylhydroxamic acid and anthranilhydroxamic acid.

In the bipositive state, iridium gives bis(glyoxalhydroxamato)nitrosyl iridate(II) with benzohydroxamic acid and also anionic monochloro-bis-(hydroxamato)nitrosyl iridate(II) with benzohydroxamic acid and salicylhydroxamic acid respectively. In addition to bipositive complexes, it forms dichloro-bis(anthranilhydroxamato)iridate(III).

Palladium provides bipositive complexes of benzohydroxamic acid, oxaldihydroxamic acid and glyoxal hydroxamic acid respectively. The physical characteristics of all the complexes are tabulated in Table 9.

(xii) Uranium(VI) complexes

The uranyl ion forms two different compounds with adipyl-bis-N-phenylhydroxamic acid under different conditions [11]; the red mono compound,

TABLE 9

Physical characteristics of Rh, Ir and Pd complexes

Complex	Colour	Physical prcperty
$Ru(BH)_2$	Dark red—brown	Sparingly soluble in water but soluble in alcohol, benzene, toluene etc.
$Rh_2(oxal)_3$	Brown and red—violet	The brown form is insoluble in alcohol, acetone, ethylacetate etc. but the red—violet variety is soluble in methanol, toluene etc.
$[Rh(BH)_2Cl_2]^- \cdot 5H_2O$	Light chocolate	Loses all water at 126° but the compound is fairly stable up to 326° without melting. Insoluble in water, benzene, ether—acetone and ethylacetate but is sparingly soluble in methanol and hot water when freshly prepared.
$[Rh(SH)_2Cl_2]^-$	Light brown	Soluble in methanol and ethanol.
$[Rh(AnH)_2Cl_2]^- \cdot 3H_2O$	Pale yellow—red	Loses all water at 128° and changes to black.
$[Ir(GH)_2] \cdot 3H_2O$	Green—brown—violet	Insoluble in water, alcohol and ether and loses all water at 108°.
$[Ir(BH)_2Cl(NO)]^-$	Brown—black	Is soluble in water but insoluble in alcohol, ether etc.
$[Ir(SH)_2Cl(NO)]^-$	Blue—black	Is soluble in water, insoluble in alcohol, ether etc. Gives blue fluorescence in dilute nitric acid.
$[Ir(AnH)_2Cl_2]^-$	Violet—brown	Is insoluble in water but soluble in ethanol, methanol etc.
$[Pd(BH)_2] \cdot H_2O$	Pale yellow—green	Insoluble in water, benzene, acetone, chloroform but sparingly soluble in ethanol. Loses water completely at 110°.
$Pd(OxalH)_2$	Dull buff	Is unstable in moist air but becomes stable in presence of carbon dioxide, ether vapour, silica gel etc.
$[Pd(GH)_2] \cdot 2H_2O$	Violet—brown	Insoluble in ethanol, methanol, acetone, carbon-tetrachloride etc. but sparingly soluble in water, ether.

dioxo-mono(adipyl-bis-N-phenylhydroxamato)uranium(VI) dihydrate, $[UO_2(Ad)] \cdot 2\ H_2O$ has been prepared by adding a saturated aqueous ethanolic solution of the ligand to uranylacetate in aqueous ethanol with continuous stirring. The compound loses all the water molecules at 110°C.

The light brown bis compound, dioxo-bis(adipyl-bis-N-phenylhydroxamato)-uranium(VI) pentahydrate, $[UO_2(AdH)_2] \cdot 5\ H_2O$ has been synthesised by mixing an aqueous ethanolic solution (1 : 1) of uranylacetate with an ethanolic solution of excess reagent of pH adjusted to 5.0. On complete dehydration at 115°C, the light brown compound changed to deep orange.

Following a similar procedure [11] and adjusting the pH to 5.0, succinyl-bis-N-phenyl hydroxamide acid furnished a brown compound of composition $UO_2(Su)(SuH)$.

(xiii) Rare earths

Phenylhydroxamic acid has been used by Agrawal and co-workers [44,45] to synthesise complexes of La, Ce, Pr, Nd, Sm, Zr and Th. An aqueous solution of the metal nitrate and an ethanolic solution of ligand interacts to give colourless crystals of general composition, MR_n (n = 4 for Zr, Th; 3 for others).

The complexes are fairly soluble in ethanol but sparingly soluble in other organic solvents. The IR study of the complexes registered no band around 3250 cm^{-1} indicating the absence of an OH group in the complex molecule and the $\nu(C{=}O)$ stretch which occurs at around 1650 cm^{-1} in the uncomplexed ligand is shifted to 1590 cm^{-1} (Table 10).

The electronic absorption spectra reveal the usual band around 36 000 cm^{-1} which is typical of octahedral La(III) complexes (Table 10).

By reacting aqueous $M(III)(NO_3)_3$ (M = Pr or Nd) with an ethanolic solution of N-*m*-tolyl-*m*-benzohydroxamide acid, Agrawal and Kapoor [46] have synthesised light green $Pr(N\text{-}m\text{-}T\text{-}m\text{-}NBHA)_3$ and light grey $Nd(N\text{-}m\text{-}T\text{-}m\text{-}NBHA)_3$ complexes.

The IR study of the complexes indicates that the coordination of the ligand is through carbonyl oxygen and nitrogen. The complexes can be used for gravimetric determination of Pr and Nd after drying at 110°C.

Using the same ligand and yttrium(III) nitrate hexahydrate Verma and co-workers [47] have synthesised a tris complex by following a similar procedure. The complex is stable at 120°C and has been used for gravimetric determinations of yttrium.

TABLE 10

IR and UV spectra of rare earth complexes

Complex	$\nu(C{=}O)$ (cm^{-1})	$\lambda_{max.}$ (cm^{-1})	Ref.
ZhR_4	1597	36 270	45
ThR_4	1598	35 080	45
LaR_3	1592	36 360	45
CeR_3	1598	31 250	45
PrR_3	1595	37 930	45
NdR_3	1599	35 080	45
SmR_3	1596	35 080	45

(xiv) Aluminium(III) and barium(II)

Aluminium(III) sulphate or nitrate and adipyl-bis-N-phenyl-hydroxamic acid [11] or a succinyl derivative [11] gave white crystalline compounds of composition $[Al_2(Ad)(AdH)_2(OH)_2] \cdot 4.5\ H_2O$ and $[Al(Su)(SuH)_2(OH)_2] \cdot 4.5\ H_2O$ respectively at pH 4.5—5.0.

Under similar conditions and at pH 2.5—3.0, Agrawal and co-workers [46] have synthesised bis(N-*m*-tolyl-*m*-nitrobenzohydroxamato)Ba(II) by interacting barium chloride and ligand. The complex can be utilised for the gravimetric determination of barium after drying at 110° C.

D. HETEROCHELATES

In recent years an attempt has been made by Ray [39] to synthesise heterochelates by reacting tris(hydroxamato)Fe(III) with copper(II) salts. The results are not encouraging. However, the best products are obtained when the tris chelates of iron(III) and anhydrous copper(II) perchlorate react in the mole ratio of 1.0 and 1.1 in pure and dry solvents. The analytical results of the heterochelates with FeL_3 ($LH_2 = BH_2$ and p-$MeBH_2$) are consistent with the theoretical values calculated for $FeL_3.Cu(ClO_4)_2$.

Magnetic susceptibilities of the heterochelates have been determined and compared with their theoretical values obtained by considering μ_{eff} (BM) for the iron(III) and copper(II) atoms respectively. The large lowering of molar susceptibility values indicates magnetic exchange interaction within the hetero metal atoms in the system $Fe{\diagup}^{Cu}{\diagdown}Fe$.

Infrared spectral studies of the heterochelates and tris chelates of iron(III) indicate that the latter retained their characteristics in the heterochelates. Thus the heterochelates may have the formula $(FeL_3)_n.CuX_2$ ($n = 1$ or 2; $X = ClO_4$) instead of being a mixture of FeL_2X and $CuLX$.

E. THERMAL DECOMPOSITION

There is only one report [48] on the thermal properties of metal hydroxamates. Dealing with tris(hydroxamato)chromium(III) complexes, this study includes the complexes of chromium(III) ion with salicyl-, benzo- and phenylacethydroxamic acids, and shows that the complex is thermally stable up to 70—80° C and then loses two-third ligand molecule around 220° C, ultimately producing Cr_2O_3 as a residue. The dissociation sequence appears to be

$$Cr(RH)_3 \rightarrow Cr(RH) + 2\ RH_2$$

$$Cr(RH) \rightarrow Cr_2O_3 + \text{other decomposition products}$$

F. CONCLUSION

The studies, so far reported, have established the close similarity of hydroxamic acids with the substituted phenylhydroxylamines in their transition metal chemistry. It is to be expected that future extensive studies will establish the donor properties of hydroxamic acids to a greater extent.

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