

Synthesis and characterization of normal and N-substituted octanohydroxamic acid complexes

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ABSTRACT

The synthesis of organic ligands L1H ($C_8H_{17}NO_2$), L2H ($C_9H_{19}NO_2$), and L3H ($C_{14}H_{20}NO_2Cl$) octanohydroxamic acids have been reported. The chelation of the ligands with some metals (ZrO^{2+} , Ce^{4+} , La^{3+} , Th^{4+} and UO_2^{2+}) under pH control have been synthesized. The ratios of 1:1, 1:2 and 1:3 metals to ligands have been recognized by the aid of elemental analysis, 1H NMR and IR spectroscopy.

Keywords: Synthesis, Octanohydroxamate, IR, pH control and metal complexes

INTRODUCTION

The chemistry of hydroxamic acids were began in 1869 when Lossen isolated oxalohydroxamic acids [1]. These acids are weak organic acids and have awide range variety of applications. One of the characteristics of hydroxamic acids are their ability to form stable and highly colored complexes with metal ions leading to their uses as analytical reagents, for example the hydroxamates ligand shows a high selectivity for iron(III) [2-3]. The synthesis and the biological activities of oxidovanadium (IV) hydroxamates have been considered [4-5]. The solvation energies of intramolecular proton transfer processes in thioformohydroxamic acid and thermodynamic and kinetic analysis of silathioformohydroxamic acid have been investigated [6-7].The properties and the metal complexes of many hydroxamic acids have been reviewed previously[8-9].In the present study the preparation and characterization of octanohydroxamates ligands and their metal complexes are investigated.

MATERIALS AND METHODS

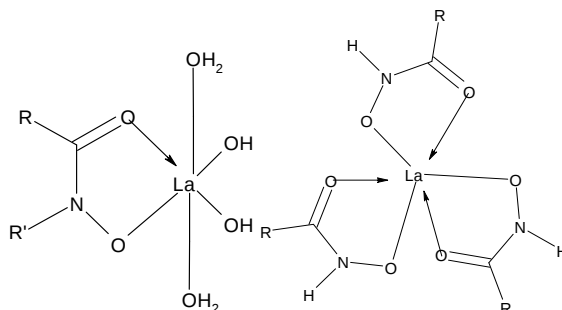
All materials used for synthesis of N-substituted hydroxamic acids and complexes are of analytical reagent. Adigital Philips PW9404 pH-meter was calibrated by means of standard buffer solutions (BDH).The IR spectra of studied complexes were recorded by Perkin-Elmer 580 spectrophotometer using KBr discs at micro analytical center, Cairo University Giza, Egypt. Microanalysis of C, H and N were recorded by Perkin-ElmerModel2400 elemental analyzer at micro analytical center, Cairo University Giza, Egypt. 1H NMR spectra were run on JEOL JNL-GX-90 FTNMR spectrometer using $CDCl_3$ as solvent and TMS as the reference standard at RasLanufOil Company(RASCO) Libya.

The preparation of ligandsand their complexes

Octanoylchloride (15.9g, 0.1mol) was added drop wise with stirring to an ice cooled methanol mixture of KOH (11.2g, 0.2mol) and hydroxylamine hydrochloride, the resulting mixture was stirred for 5hours. After the removal of potassium chloride and potassium carbonate by filtration, the reaction mixture was extracted with ether and the ethereal layer was evaporated under reduced pressure. The octanohydroxamic acid is obtained in the form of shiny white crystals, which recrystallized from chloroform.

N-methyloctanohydroxamic acid was prepared by adding (15.9g, 0.1mol) octanoylchloride to an ice mixture of Na_2CO_3 (21.2g, 0.2mol) and N-methylhydrochloride (8.35g, 0.1mol) in methanol, according to the same procedure described above, the product was in the form of apale yellow oil.

The p-chlorophenylhydroxyl amine was prepared by adding (2:1) molar ratio of Zn dust to nitrobenzene according to Brink and Crumbliss method [10]. The product was in the form of yellow needle crystals. N-(P-chlorophenyl)octanohydroxamic acid was prepared by similar method and a crude product was collected.



(Where R=heptyl and R'= CH_3 or $\text{C}_6\text{H}_4\text{Cl}$)

$\text{ZrO}[(\text{L}1)_2] \cdot \text{H}_2\text{O}$ was prepared by adding (3.22g, 0.01mol) of Zirconylchloride 8-hydrate to (3.18g, 0.02mol) of octanohydroxamic acid, the mixture was stirred for 30 minutes, the pH was raised to 9.45. A white precipitation was obtained.

$\text{Ce}[(\text{L}3)_2 \cdot 2\text{OH}] \cdot 4\text{H}_2\text{O}$ the complex was prepared by adding (4.04g, 0.01mol) of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in (75ml) double distilled water to (5.39g, 0.02mol) of N-(p-chlorophenyl) octanohydroxamic acid in warm ethanol, the pH raised to 2.19 the brown precipitate obtained was allowed to cool in refrigerator overnight.

$\text{La}[(\text{L}1)_3] \cdot 6\text{H}_2\text{O}$ complex was prepared by the addition of (3.18g, 0.02mol) of octanohydroxamic acid in (50ml) ethanol to stirring ethanolic solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.33g, 0.01mol), the pH was adjusted between 2.27 to 5.68 using 10% sodium hydroxide solution, white precipitate was allowed to cool then filtered off under nitrogen and dried over calcium chloride. $\text{La}[(\text{L}2) \cdot 2\text{OH}] \cdot 3.5\text{H}_2\text{O}$ complex is prepared as discussed above, the pH had adjusted to 6.67.

$\text{La}[(\text{L}3) \cdot 2\text{OH}] \cdot 6\text{H}_2\text{O}$, (5.39g, 0.02mol) of N-(p-chlorophenyl) octanohydroxamic acid was added to (4.33g, 0.01mol) of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in (50ml) ethanol, then the mixture was stirred for one hour. The pH is adjusted to 9.33 a dark yellow precipitate was obtained.

$\text{Th}[(\text{L}1)_2 \cdot 2\text{OH}] \cdot 6\text{H}_2\text{O}$, the complex was prepared by adding (3.18g, 0.02mol) of octanohydroxamic acid in (50ml) ethanol to (4.33g, 0.01mol) of $\text{Th}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in (50ml) ethanol, the pH was adjusted to 6.30, a white precipitate was obtained.

$\text{Th}[(\text{L}2) \cdot 3\text{OH}] \cdot \text{H}_2\text{O}$ complex was prepared as discussed before, where the pH had been adjusted to 5.21, a white precipitate was obtained.

$\text{Th}[(\text{L}3) \cdot 3\text{OH}] \cdot 6\text{H}_2\text{O}$ complex is prepared by the same procedure where the pH had been adjusted to 6.36, a white precipitate was obtained.

$\text{UO}_2[(\text{L}1)_2] \cdot 16\text{H}_2\text{O}$ complex was prepared by dissolving of (5.02g, 0.01mol) Uranyl nitrate in (50ml) ethanol and add to (3.18g, 0.02mol) of octanohydroxamic acid. This resulted in a color change to red-brown. The mixture was stirred for 30 minutes and 10% solution of sodium hydroxide was add drop wise to the mixture until a change of color occurred then the pH raised to 6.55, the solution became cloudy and the color changed to orange. The reaction mixture was left to cool overnight; the obtained solid product was filtered and dried.

$\text{UO}_2[(\text{L}3)_2] \cdot 6\text{H}_2\text{O}$ complex was prepared by adding (5.02g, 0.01mol) of Uranyl nitrate to (5.39g, 0.02mol) of N-(p-chlorophenyl) octanohydroxamic acid, according to the same procedure described above, the pH raised to 8.57, the obtained solid product was filtered and dried.

RESULTS AND DISCUSSION

The elemental analysis

The elemental analysis of C, H and N of the complexes are listed in Table 1. The results of C, H and N percentage are in accord with the composition suggested for the ligands and their complexes.

Table 1: Elemental analysis and some physical properties of the ligands and their complexes

Compound	Elemental analysis found (calc.)					
	%C		%H		%N	
L1H	61.05	(60.38)	10.77	(10.69)	7.52	(8.81)
L2H	56.60	(56.17)	3.40	(10.64)	5.50	(5.96)
L3H	60.10	(59.90)	4.60	(7.65)	6.90	(4.66)
ZrO(L1) ₂ .H ₂ O	36.10	(36.14)	5.10	(8.28)	4.40	(5.27)
Ce((L3)2.2OH).4H ₂ O	38.00	(38.01)	3.70	(5.43)	6.54	(4.75)
La(L1) ₃ .6H ₂ O	39.40	(39.95)	5.00	(8.32)	12.10	(5.83)
La((L2).2OH)3.5H ₂ O	26.30	(26.48)	4.40	(6.62)	5.80	(3.43)
La((L3).2OH).6H ₂ O	30.20	(30.19)	4.80	(6.11)	4.70	(2.52)
Th((L1) ₂ .2OH).6H ₂ O	27.20	(27.83)	4.80	(6.67)	6.30	(4.06)
Th((L2).3OH).H ₂ O	22.20	(2.83)	4.20	(4.86)	3.10	(2.96)
Th(L3).3OH).6H ₂ O	25.70	(26.88)	4.70	(5.60)	1.30	(2.24)
UO ₂ (L1) ₂ .16H ₂ O	22.50	(21.97)	4.50	(7.32)	4.20	(3.20)
UO ₂ (L3) ₂ .6H ₂ O	36.00	(36.72)	4.10	(5.46)	9.90	(3.06)

¹HNMR analysis

The ¹HNMR spectra of octanohydroxamic acid (L1H) in CDCl₃ Table 2, shows the following signals. A triplet at 0.9 ppm (J=8.0 Hz) corresponding to three protons of CH₃. Multiplet at 1.4 ppm equivalent to eight protons of four methylene groups (γCH₂ groups). Multiplet at 1.7 ppm assigned to βCH₂ and triplet at 2.2 ppm (J=5.6 Hz) is attributed to αCH₂ group. The disappearance of NH and OH protons may be due to the existence of intramolecular hydrogen bonds. The ¹HNMR spectra of N-methyloctanohydroxamic acid (L2H) in CDCl₃ Table 2, shows a triplet at 0.87 ppm integrating for a three protons is assigned to of CH₃ protons. Multiplet at 1.24 ppm equivalent to eight protons of four methylene groups (γCH₂ groups). A quintet at 1.60 and 1.24 ppm assigned to βCH₂ and αCH₂ protons respectively. The N-methyl group is represented by a singlet at 3.44 ppm integrating for three protons. The ¹HNMR spectra of N-(p-chlorophenyl)octanohydroxamic acid (L3H) in CDCl₃, shows a triplet at 0.9 ppm (J=7.2 Hz) corresponding to three protons of CH₃. Multiplet at 1.2 ppm equivalent to eight protons of four methylene groups (γCH₂ groups). A triplet at 2.55 ppm (J=9.0 Hz) is attributed to αCH₂ group. Two doublets are exhibited at 7.2 and 7.45 ppm (J= 7.9 Hz) corresponding to four protons of p-substituted phenyl group (A2B2 system). The disappearance of OH proton may be attributed to intramolecular hydrogen bond.

Table 2. ¹HNMR spectra of unsubstituted and N-methyloctanohydroxamic acid in CDCl₃ at 25C

Ligand	CH ₃	γCH ₂	βCH ₂	αCH ₂	N-CH ₃
L1H	0.90 (t)	1.40 (m)	1.70 (m)	2.20 (t)	-
L2H	0.87 (t)	1.24 (m)	1.60 (m)	2.40 (t)	3.44 (s)
L3H	0.90 (t)	1.20 (m)	-	2.45 (t)	-

The IR spectra

The most important vibrational frequencies for the ligands and their complexes are given in Table 3. The IR spectra of octanohydroxamic ligands show a sharp bands in the 1655-1615cm⁻¹ region which is attributed to the amide carbonyl vibrational frequency, the shift of this band is due to intramolecular hydrogen bonding, on complexation, this band undergoes a shift of about 40-60 wave numbers, which is consistent with chelation by carbonyl oxygen atom. This frequency shift is due to a reduction of C=O bond order caused by the interaction with metal. A broad band at 3566-3377cm⁻¹ in the spectra of the free ligands was assigned to free (OH) group. The free hydroxamic acids are bidentate and the bonding occurs through the two oxygen atoms[11].

In the region below 950 cm⁻¹ most bands are sensitive to the nature of the metal ion and the substituent. The IR spectra of octanohydroxamic acid showed a strong band at 1423-1467 cm⁻¹ is assigned to C-N stretching frequency and N-H deformation band. The carbonyl frequency is appeared at 1655 cm⁻¹. A strong band at 1182-1116 cm⁻¹ is assigned to N-O stretching frequency. The O-H bonded appears at 2957 cm⁻¹ while OH free at 3566 and 3054 cm⁻¹. The C-H of N-CH₃ stretching appears at 2868-2412 cm⁻¹. The frequencies are in agreement with the previously reported results [12-13].

Table 3. The Infrared spectra of ligands and their complexes (cm⁻¹)

Compound	$\nu(\text{C-O})$	$\nu(\text{C-N})$	$\nu(\text{O-H})$	$\nu(\text{M-O})$	$\nu(\text{M=O})$
L1H	1655	1423	3566	-	-
L2H	1615	1432	3372	-	-
L3H	1629	1463	3422	-	-
ZrO(L1) ₂ .H ₂ O	1603	1462	3675	409	997
Ce((L3) ₂ .2OH).4H ₂ O	1626	1483	3304	428	-
La(L1) ₃ .6H ₂ O	1601	1465	-	472	-
La((L2).2OH).3.5H ₂ O	1599	1483	-	482	-
La((L3).2OH).6H ₂ O	1564	1489	-	462	-
Th((L1) ₂ .2OH).6H ₂ O	1599	1483	3422	413	-
Th((L2).3OH).H ₂ O	1599	1482	3422	414	-
Th(L3).3OH).6H ₂ O	1600	1483	3277	403	-
UO ₂ (L1) ₂ .16H ₂ O	1594	1463	3285	423	915
UO ₂ (L3) ₂ .6H ₂ O	1554	1463	3269	433	830

Zirconyl form complexes with octanohydroxamic (L1H) only and it gave ZrO(L1)₂.H₂O complex. The complex exhibited a strong absorption band at 1603cm⁻¹ which is due to C=O stretching frequency. The band observed at 1462 cm⁻¹ is assigned to C-N stretching frequency. An intense absorption band at 997 cm⁻¹ is assigned to Zr=O frequency. Finally Zr-O stretching frequency is noted at 409 cm⁻¹.

Cerium(IV) formed a complex with N-(p-chlorophenyl)ocatanohydroxamic acid in a molar ratio 1:2 M:L. The Ce(L3)₂.4H₂O complex exhibited a strong absorption band at 1626cm⁻¹ which is due to C=O stretching frequency. The band observed at 1483 cm⁻¹ is assigned to C-N stretching frequency. The appearance of a new medium band at 830 cm⁻¹ is attributed to the rocking modes of coordinated water. Strong bands at 2917 and 2852 cm⁻¹ are due to C-H stretching frequency of CH₃ and CH₂ respectively. At lower frequency there is a band observed at 428 cm⁻¹ which is attributed to Ce-O interaction. Finally, the band at 3300 cm⁻¹ is due to O-H frequency of the coordinated water molecules. The thorium and lanthanum complexes showed similar bands as the cerium complex. The uranyl complexes showed the following frequencies, the carbonyl absorption bands which occurred at 1955 and 1629 cm⁻¹ in the free ligands are shifted to lower frequencies (1594 and 1554 cm⁻¹) on complexation. The vibrational frequency of C-N increased which indicates the hydroxamates group acts as a bidentate ligand by the chelation through the carbonyl oxygen and deprotonated hydroxyl oxygen to the uranyl ion. The band observed at 1463 cm⁻¹ is assigned to C-N stretching frequency in both complexes, other strong bands at 1122 and 1156 cm⁻¹ are assigned to the N-O stretching frequencies in both complexes. The bands at 3285 and 3269 cm⁻¹ are attributed to the O-H of coordinated water molecules in UO₂(L1).16H₂O and UO₂(L3).6H₂O respectively. Two strong absorption bands at 915 and 830 cm⁻¹ these are attributed to the U=O frequencies in UO₂(L1).16H₂O and UO₂(L3).6H₂O respectively.

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