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Contribution to the Study of Some Hydroxamic Acid Derivatives and Their Use in Gravimetric Determination

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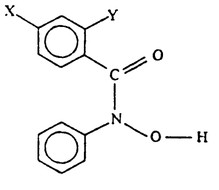
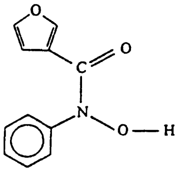
N-Benzoylphenylhydroxylamine (N-BPHA), four of its derivatives and N-furoyl-N-phenylhydroxylamine have been studied and used successfully for the gravimetric determination of Fe(III), V(V), Ni(II) and Cu(II). The study revealed that the ligands behave as monobasic bidentate ligands. The elements under investigation are successfully determined in the ranges 0.037–0.013 g for Fe, 0.0283–0.0189 g for V, 0.0284–0.0250 g for Cu and 0.0283–0.0189 g for Ni. The recovery was very high (99.7%) with low standard deviation (0.000208) which reflects the accuracy of this method. The solubility product (K_{sp}) was small enough (1.25×10^{-9}–1×10^{-11}); so the metal can be determined by weighing the precipitate directly.

INTRODUCTION

N-Benzoyl-N-phenylhydroxylamine (N-BPHA) has already been used as a reagent for the gravimetric determination of titanium[1], thorium and cerium[2], cobalt[3], beryllium[4], gallium and indium[5] and iron and copper[6]. In the present investigation N-BPHA was studied and employed in the gravimetric estimation of V(V), Cu(II) and Ni(II). Also four of its derivatives and N-furoyl-N-phenylhydroxylamine which have the following formula were studied and used for the gravimetric determination of the same metal ions.



X	Y	
H	H	1a
Cl	H	1b
Cl	Cl	1c
NO_2	H	1d
OCH_3	H	1e



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EXPERIMENTAL

The reagents (hydroxamic acid derivatives) were prepared as previously reported[7] through the condensation of the acid chloride with phenylhydroxylamine that was prepared by reduction of nitrobenzene by zinc powder[8].

Metals to be determined: standard solutions (10^{-2} M) of $FeCl_3$, NH_4VO_3, $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ were prepared separately by the usual methods[9].

Aqueous solutions (10^{-2} M) of the organic reagents were used for the precipitation of the iron and vanadium ions.

Alcoholic solutions (10^{-2} M) of the organic reagents were used for the precipitation of copper and nickel ions.

pH adjustment: The pH of the solutions was usually adjusted by adding the requisite quantities of 10% solution of sodium acetate and 1.08 N sulphuric acid in case of Fe, V, Cu chelates and ammonia solution in case of Ni chelates.

Determination of Fe, V, Cu and Ni

Procedure: Known quantity of either Fe(III), V(V), Cu(II) or Ni(II) solution containing about 0.013–0.037 g of Fe, 0.0189–0.0283 g of V, 0.025–0.0284 g of Cu and 0.016–0.022 g of Ni was taken and 5 mL of 1.08 N sulphuric acid solution was added in case of Fe, V and Cu ions. The solution was diluted with distilled water to about 400 mL and heated to boiling. The reagent (excess enough to ensure complete precipitation) was dissolved in 50 mL of hot water in case of Fe and V and in 10 mL alcohol in case of Cu and Ni; the solution was warmed and added to the metal solution. Sodium acetate solution (10%) was added to raise the pH of the solution to 4.5–5.2 in case of Fe, 2.3–3.5 in case of V and 2.3–3.5 in case of Cu. In the determination of Ni few drops of ammonia solution were added to raise the pH to 8.0. The precipitate formed was stirred for 1–2 h (1 h for Cu precipitate and 2 h for Fe, V and Ni precipitates). The precipitate was filtered on a G4 sintered glass crucible, and then washed thoroughly with hot water and dried at 110°C to constant weight.

Remarks:

(a) Iron precipitate tends to form hard lumps when precipitated above 70°C and hence precipitation was carried out at about 65°C. There should be good stirring whereupon the flocculent precipitate is changed to the granular form by heating on a water bath.

(b) During precipitation of the metal chelates, the ligand solution was not allowed to fall on the sides of the beaker; otherwise the organic reagent would be deposited on the sides owing to the evaporation of alcohol and necessitates the use of a large volume of wash-water.

The resulting organic reagents and their chelates were subjected to elemental analysis for C, H, N, Cl and metal in case of the chelates (Table-1), in the microanalytical centre of Cairo University. The IR spectra of the free ligands and solid chelates were recorded as KBr discs and in CCl_4 using Fourier Transform infrared spectrophotometer. The NMR spectra of the investigated ligands (1a–1f) are performed in deuterochloroform ($CDCl_3$) using tetramethylsilane (TMS) as internal standard. The spectra of some V(V) complexes were performed in dimethylsulphoxide (DMSO) solution using Varian Gimini 200 NMR spectrometer.

TABLE-1: ELEMENTAL ANALYSIS OF Fe(III), V(V), Cu(II) AND Ni(II) CHELATES WITH PREPARED LIGANDS

Complex	% Analyses, Calcd. (Found)				
	C	H	N	Cl	Metal
Complexes with Fe(III)					
1a	65.92 (66.31)	4.51 (4.09)	5.92 (6.02)	—	8.87 (8.61)
1b	57.64 (58.01)	3.57 (3.27)	5.17 (5.31)	12.93 (13.11)	6.90 (6.71)
1c	51.04 (52.11)	2.84 (2.49)	4.58 (4.11)	23.23 (23.31)	6.11 (6.01)
1d	55.38 (55.01)	3.43 (3.11)	9.94 (9.49)	—	6.63 (6.72)
1e	63.00 (63.12)	4.75 (4.82)	5.25 (5.01)	—	7.00 (7.05)
1f	58.24 (58.90)	3.82 (4.09)	6.18 (6.32)	—	8.24 (8.32)
Complexes with V(V)					
1a	64.90 (62.93)	4.43 (4.03)	5.82 (5.92)	—	7.07 (7.13)
1b	56.79 (55.21)	3.51 (3.72)	5.09 (4.97)	12.92 (12.83)	6.18 (6.01)
1c	50.43 (47.91)	2.80 (3.21)	4.52 (4.31)	22.95 (22.71)	5.49 (5.39)
1d	54.67 (52.13)	3.38 (3.01)	9.81 (9.71)	—	5.95 (6.01)
1e	62.14 (60.03)	4.68 (4.51)	5.17 (5.50)	—	6.28 (6.31)
1f	57.30 (55.31)	3.76 (3.81)	6.07 (5.72)	—	7.38 (7.11)
Complexes with Cu(II)					
1a	61.78 (60.01)	4.36 (4.01)	5.54 (5.63)	—	12.48 (12.30)
1b	54.35 (52.95)	3.48 (2.98)	4.88 (5.21)	12.37 (12.12)	10.98 (10.99)
1c	48.52 (47.01)	2.79 (2.19)	4.35 (4.01)	22.08 (21.91)	9.80 (9.72)
1d	52.44 (51.23)	3.36 (2.98)	9.41 (8.71)	—	10.59 (10.23)
1e	59.47 (57.91)	4.60 (3.15)	4.96 (5.10)	—	11.15 (11.03)
1f	54.43 (52.02)	3.71 (3.21)	5.77 (5.91)	—	12.99 (12.72)
Complexes with Ni(II)					
1a	62.77 (60.23)	4.42 (4.01)	5.63 (5.70)	—	11.06 (10.91)
1b	55.12 (53.11)	3.53 (3.11)	4.94 (4.61)	12.54 (12.13)	9.71 (9.59)
1c	49.13 (46.91)	2.83 (2.23)	4.40 (4.01)	22.36 (22.00)	8.66 (8.35)
1d	53.15 (50.93)	3.40 (3.20)	9.54 (9.00)	—	9.36 (9.31)
1e	60.32 (58.11)	4.66 (4.17)	5.02 (4.99)	—	9.87 (9.71)
1f	55.34 (52.21)	3.77 (3.13)	5.87 (5.33)	—	11.53 (11.31)

RESULTS AND DISCUSSION

The results for the gravimetric determination of Fe, V, Cu and Ni are shown in Tables 2–5. They indicate that these metal ions can be determined by weighing their complexes directly.

TABLE-2: GRAVIMETRIC DETERMINATION OF Fe(III) WITH PREPARED LIGANDS

Metal taken (g)	Wt. of ppt. (g)	Metal found (g)	Error (g)	Recovery (%)	Statistical results			
					Slope	St. deviation	Corr. coefficient	Intercept
Results using reagent 1a (pH 4.8)								
0.0370	0.4591	0.0369	–0.0001	99.72				
0.0252	0.3131	0.0256	+0.0004	101.58	1.008	0.00048	0.999	–0.0002
0.0130	0.1610	0.0127	–0.0003	97.69				
Results using reagent 1b (pH 5.2)								
0.0370	0.5264	0.0369	–0.0001	99.72				
0.0252	0.3593	0.0249	–0.0003	98.80	0.987	0.00028	0.999	0.0002
0.0130	0.1852	0.0132	+0.0002	101.53				
Results using reagent 1c (pH 5.0)								
0.0370	0.5961	0.0371	+0.0001	100.27				
0.0252	0.4056	0.0249	–0.0003	98.90	0.983	0.00040	0.999	0.00045
0.0130	0.2097	0.0134	–0.0003	103.70				
Results using reagent 1d (pH 5.2)								
0.0370	0.5481	0.0368	–0.0002	99.45				
0.0252	0.3731	0.0248	–0.0004	98.41	0.950	8.165 E-6	0.999	0.00085
0.0130	0.1928	0.0132	+0.0002	101.53				
Results using reagent 1e (pH 5.2)								
0.0370	0.5184	0.0367	–0.0003	99.18				
0.0252	0.3530	0.0250	–0.0002	99.20	1.000	8.165 E-5	0.999	–0.00026
0.0130	0.1819	0.0127	–0.0003	97.69				
Results using reagent 1f (pH 5.0)								
0.0370	0.4395	0.0372	+0.0002	100.54				
0.0252	0.2988	0.0248	–0.0004	98.41	1.020	0.00021	0.999	–0.00065
0.0130	0.1540	0.0127	–0.0003	97.69				

TABLE-3: GRAVIMETRIC DETERMINATION OF V(V) WITH PREPARED LIGANDS

Metal taken (g)	Wt. of ppt. (g)	Metal found (g)	Error (g)	Recovery (%)	Statistical results			
					Slope	St. deviation	Corr. coefficient	Intercept
Results using reagent 1a (pH 2.3)								
0.0283	0.3826	0.0281	–0.0002	99.29				
0.0255	0.3453	0.0258	+0.0003	101.17	1.013	0.00039	0.999	–0.00036
0.0189	0.0255	0.0187	–0.0002	98.94				

Metal taken (g)	Wt. of ppt. (g)	Metal found (g)	Error (g)	Recovery (%)	Statistical results			
					Slope	St. deviation	Corr. coefficient	Intercept
Results using reagent 1b (pH 2.3)								
0.0283	0.4395	0.0284	+0.0001	100.35				
0.0255	0.3961	0.0256	+0.0001	100.39	1.000	5.809 E-18	0.999	0.00010
0.0189	0.2936	0.0190	+0.0001	100.52				
Results using reagent 1c (pH 2.3)								
0.0283	0.4986	0.0286	+0.0003	101.06				
0.0255	0.4489	0.0259	+0.0004	101.56	1.082	0.00024	0.999	–0.00190
0.0189	0.3320	0.0185	–0.0004	97.88				
Results using reagent 1d (pH 2.3)								
0.0283	0.4580	0.0286	+0.0003	101.06				
0.0255	0.4129	0.0259	+0.0004	101.56	1.071	0.00022	0.999	–0.00160
0.0189	0.3054	0.0186	–0.0003	98.41				
Results using reagent 1e (pH 2.3)								
0.0283	0.4325	0.0280	–0.0003	98.93				
0.0255	0.3961	0.0256	+0.0001	100.39	0.942	0.00017	0.999	0.00140
0.0189	0.2994	0.0192	+0.0003	101.58				
Results using reagent 1f (pH 2.3)								
0.0283	0.3660	0.0281	–0.0002	99.29				
0.0255	0.3340	0.0259	+0.0004	101.56	1.051	0.0005	0.997	–0.00130
0.0189	0.2440	0.0184	–0.0005	97.35				

TABLE-4: GRAVIMETRIC DETERMINATION OF Cu(II) WITH PREPARED LIGANDS

Metal taken (g)	Wt. of ppt. (g)	Metal found (g)	Error (g)	Recovery (%)	Statistical results			
					Slope	St. deviation	Corr. coefficient	Intercept
Results using reagent 1a (pH 2.3)								
0.0284	0.2201	0.0281	–0.0003	98.94				
0.0271	0.2101	0.0269	–0.0002	99.26	0.973	4.997 E-5	0.999	0.00048
0.0250	0.1938	0.028	–0.0002	94.20				
Results using reagent 1b (pH 3.5)								
0.0284	0.2512	0.0286	+0.0002	100.70				
0.0271	0.2393	0.0269	–0.0002	99.26	0.981	0.00032	0.991	0.00055
0.0250	0.2212	0.0252	+0.0003	100.80				
Results using reagent 1c (pH 3.0)								
0.0284	0.2822	0.0280	–0.0004	98.59				
0.0271	0.2694	0.0268	–0.0003	98.89	1.035	0.00011	0.999	–0.0013
0.0250	0.2483	0.0245	–0.0005	98.00				

Metal taken (g)	Wt. of ppt. (g)	Metal found (g)	Error (g)	Recovery (%)	Statistical results			
					Slope	St. deviation	Corr. coefficient	Intercept
Results using reagent 1d (pH 3.0)								
0.0284	0.2608	0.0282	–0.0002	99.29	0.940	0.00016	0.997	–2.356 E-5
0.0271	0.2485	0.0267	–0.0004	98.52				
0.0250	0.2295	0.0248	–0.0002	99.20				
Results using reagent 1e (pH 2.3)								
0.0284	0.2475	0.0285	+0.0001	100.35	0.959	0.00019	0.996	0.0011
0.0271	0.2360	0.0270	–0.0001	99.63				
0.0250	0.2180	0.0252	+0.0002	100.80				
Results using reagent 1f (pH 2.3)								
0.0284	0.2113	0.0283	–0.0001	99.64	0.986	0.00024	0.994	0.00016
0.0271	0.2013	0.0267	–0.0004	98.52				
0.0250	0.1860	0.0249	–0.0001	99.60				

TABLE-5: GRAVIMETRIC DETERMINATION OF Ni(II) WITH PREPARED LIGANDS

Metal taken (g)	Wt. of ppt. (g)	Metal found (g)	Error (g)	Recovery (%)	Statistical results			
					Slope	St. deviation	Corr. coefficient	Intercept
Results using reagent 1a (pH 8.0)								
0.0283	0.2359	0.0281	–0.0002	99.29	0.995	0.00040	0.998	7.202 E-5
0.0230	0.1922	0.0233	+0.0003	101.30				
0.0189	0.1575	0.0187	–0.0002	98.94				
Results using reagent 1b (pH 8.0)								
0.0283	0.2691	0.0284	+0.0001	99.65	1.002	0.00024	0.999	–6.321 E-5
0.0230	0.2186	0.0228	–0.0002	99.13				
0.0189	0.1799	0.0190	+0.0001	100.52				
Results using reagent 1c (pH 8.0)								
0.0283	0.3037	0.0286	+0.0003	101.06	1.074	4.331 E-6	0.999	–0.0018
0.0230	0.2465	0.0229	–0.0001	99.56				
0.0189	0.2022	0.0185	–0.0004	97.88				
Results using reagent 1d (pH 8.0)								
0.0283	0.2803	0.0286	+0.0003	101.06	1.065	0.00013	0.999	–0.0015
0.0230	0.2274	0.0228	–0.0002	99.13				
0.0189	0.1867	0.0186	–0.0003	98.41				
Results using reagent 1e (pH 8.0)								
0.0283	0.2652	0.0281	–0.0002	99.29	0.949	0.00023	0.999	0.0011
0.0230	0.2155	0.0282	–0.0002	99.13				
0.0189	0.1775	0.0192	+0.0003	101.58				

Results using reagent 1f (pH 8.0)								
0.0283	0.2260	0.0279	–0.0004	98.58				
0.0230	0.1838	0.0228	–0.0002	99.13	1.008	0.00021	0.999	–0.00056
0.0189	0.1507	0.0184	–0.0005	97.35				

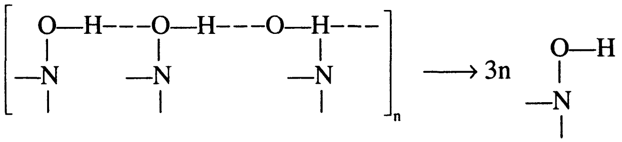
Effect of pH on the determination of the investigated metals

The precipitation of Fe, V, Cu and Ni metal ion complexes was quantitative between pH values 4.5–5.5, 2.3–5.0, 2.3–4.0 and 8.0 respectively. The chelates were not precipitated completely when the pH of the solution was lower than these ranges; meanwhile, higher pH values lead to slightly higher results in case of Fe, V, Cu and lower results were obtained in case of Ni .

In order to comment on the structure of the solid chelates using IR spectra, first the IR spectra of the free ligands must be discussed to assign the important bands in their spectra.

Infrared spectra of the free ligands and their metal chelates

The IR spectra of the free ligands show a weak broad intramolecular hydrogen bonding (R—O—H ← :X$^-$) in the 3520–3450 cm^{-1} range with medium frequency shifts from the non-bonded value, close to 3625 cm^{-1}. Another stronger broad band which can be attributed to the intermolecular hydrogen bonding appears at lower frequencies within the 3191–3111 cm^{-1} range. To differentiate between the two bands, the spectrum of N-BPHA in CCl_4 was examined. Results obtained show the diminishing of the ν(OH) band at 3111 cm^{-1} while the other band at 3459 cm^{-1} remains at nearly the same intensity. Accordingly, we can conclude that two types of hydrogen bondings are present:



Strong bands for (C=O) stretching vibration appear within the range 1640–1616 cm^{-1}. In the ligands prepared the acidic hydrogen, *i.e.*, that of the OH group is sufficiently close to a basic centre, which is the (C=O) in the same molecule, for the formation of the intramolecular hydrogen bonds to be energetically favourable. As in the case of the OH stretching frequency, the (C=O) stretching vibrations are shifted to lower values compared with normal ketone band near 1680 cm^{-1}.

The IR spectra of the metal chelates showed that the 3150 ± 40 cm^{-1} bands are either weakened or disappear completely indicating the deprotonation of the OH group and their participation in chelation.

^{1}H-NMR spectra of the free ligands and some metal chelates

The ^{1}H-NMR spectra of all ligands exhibit a singlet at 8.6–9.8 ppm which is assigned to the OH proton[10]. The signals observed at 6.8–8 ppm are assigned to the CH protons of the aromatic ring and those observed at 6.6–7.8 ppm are assigned to the C—H protons of the furoyl ring in ligand 1f. The three methyl protons in case of ligand V show their shift at 4 ppm.

^{1}H-NMR spectra of vanadium complexes with some of the investigated ligands

The ^{1}H-NMR spectra of some vanadium complexes are performed in dimethylsulphoxide (DMSO) solutions. All spectra exhibit a singlet at 2.5 ppm assigned to the CH_3 protons of the solvent. Water of crystallization appears at 3.4 ppm. All other signals appear generally within the same ranges as the corresponding ligands. An unexpected observation is that the ligand OH signals at 8.2–9.4 ppm are still represented as relatively weak signals at 10.1–10.6 ppm. This may be due to covalent bond formation between the vanadium ions and the oxygen atoms of the OH groups of organic reagents.

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