

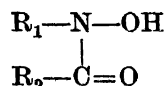
## Studies on Hydroxamic Acids. Part VII. Infrared Spectra of Their Metal Complexes

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The infrared spectra of several metal complexes of *N*-phenylbenzohydroxamic acid and its analogues *N*-phenyl-2-furohydroxamic acid and *N*-*p*-tolylbenzohydroxamic acid are presented.

The hydroxamic acids form chelates, by the replacement of hydrogen of the hydroxylamino group by metal ion and ring closure through coordination from oxygen of the carbonyl group. The bands due to O-H group in free ligand disappear, while bands due to N-O and C=O groups shift on complex formation.

*N*-Phenylbenzohydroxamic acid (abbreviated PBHA) I, is an organic analytical reagent for the colorimetric and gravimetric determination of several metal ions<sup>1,2,3</sup>. In the present investigation, the infrared spectra of several metal complexes of PBHA and its analogues *N*-Phenyl-2-furohydroxamic acid (abbreviated PFHA)II, and *N*-*p*-Tolylbenzohydroxamic acid (abbreviated *p*-TBHA)III, are presented.



- I,  $R_1 = R_2 = \text{phenyl}$ ,  
 II,  $R_1 = \text{phenyl}$ ,  $R_2 = 2\text{-furoyl}$ ,  
 III,  $R_1 = p\text{-tolyl}$ ,  $R_2 = \text{phenyl}$ .

### EXPERIMENTAL

*Hydroxamic Acids*: These were prepared and purified by the procedure reported previously<sup>4</sup>, m.p., PBHA 121°, PFHA 135°, *p*-TBHA 111°.

*Preparation of Metal Complexes*: For preparing the complexes of bivalent metal ions such as manganese (II), cobalt (II), nickel (II), copper (II) and zinc (II), the following procedure was followed.

An aqueous solution (1 litre) of the desired metal sulphate (0.005 mole) was heated to boiling. To this solution, a hot ethanolic solution of the hydroxamic acid (0.01 mole in 25 ml), followed by a dilute solution of ammonium hydroxide were added dropwise and with constant stirring. A granular precipitate was formed and the pH of the reaction

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mixture was always maintained below-6. The reaction mixture was digested for 2 hr over a steam bath and the granular precipitate was filtered off on a sintered crucible, washed thoroughly with hot water and finally with 1 : 1 ethanol ( $3 \times 10$  ml.). The metal complex so obtained was dried at  $110^\circ$ . The colour of the complexes are as follows : Mn(II), yellow; Co(II), pink; Ni(II) and Cu(II), green; Zn(II), white.

In the preparation of iron (III) complex, the mole ratio of the metal to ligand was 1 : 3. In this case the reaction was carried out at  $65^\circ$  only. Above this temperature sticky red lumps were formed. The complexes are red in colour.

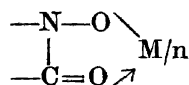
*Analyses* : The metal complexes were decomposed with a mixture of concentrated perchloric sulphuric and nitric acids and in the resulting solution the metals were determined by standard volumetric methods using EDTA and appropriate indicators such as murexide, eriochrome black T and salicylic acid<sup>5</sup>.

*Spectra* : The infrared spectra were recorded on Perkin-Elmer Model 137B spectrophotometer equipped with sodium chloride optics. The metal complexes were examined as mulls in nujol.

#### RESULTS AND DISCUSSION

The data obtained on the characterisation of the metal complexes are given in Table-I.

The hydroxamic acids react with the metal ions and form chelates of the type :



*O-H Vibrations* : The free O-H stretching vibrations in alcohols are usually found between  $3650\text{--}3500\text{ cm}^{-1}$ . The bands at  $3106\text{ cm}^{-1}$  in PBHA,  $3125\text{ cm}^{-1}$  in *p*-TBHA and  $3145\text{ cm}^{-1}$  in PFHA for O-H stretching vibration show that there is strong hydrogen bonding in these ligands. As is anticipated this band disappears in the spectra of all metal complexes.

*C=O Vibration* : The strong band at  $1631\text{ cm}^{-1}$  in PBHA and *p*-TBHA, at  $1603\text{ cm}^{-1}$  in PFHA were assigned to carbonyl stretching vibrations<sup>6</sup>. The band due to C=O stretching vibration in free ligand is displaced towards lower frequencies on complex formation and is superimposed on one of the bands due to C=C vibrations. This indicates the formation of a C=O ... M coordinate bond.

*N-O Vibration* : The bands at  $917\text{ cm}^{-1}$  in PBHA and *p*-TBHA, at  $920\text{ cm}^{-1}$  in PFHA are assigned to N-O stretching vibration<sup>6,7,8</sup>. This band is observed in the range  $945\text{--}920\text{ cm}^{-1}$  in metal complexes and the intensity is greater than for free ligands.

5. F. W. Welcher, "The analytical uses of Ethylene-Diamine tetra acetic acid", D. Van Nostrand Co. Inc., New York, 1958.
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TABLE I

*Data on metal complexes of N-arylohydroxamic acids*

Metal Complex No.	Molecular Formula	M.p. °C	Nitrogen%		Metal %		$\nu\text{C}=\text{O}\dots\text{M}$ $\text{cm}^{-1}$	$\nu\text{N}-\text{O}$ $\text{cm}^{-1}$
			Found	Calcd.	Found	Calcd.		
A: <i>PBHA Complexes</i> :								
I	(C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>2</sub> Mn	238 <sup>a</sup>	5.48	5.84	—	11.46	1582 s	927 m
II	(C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>3</sub> Fe	195 <sup>b</sup>	5.19	6.07	7.89	8.06	1575 m	929 vs
III	(C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>2</sub> Co	233 <sup>c</sup>	6.40	5.80	12.07	12.19	1582 s	927 m
IV	(C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>2</sub> Ni	280 <sup>d</sup>	5.50	5.80	12.19	12.15	1587 vs	934 vs
V	(C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>2</sub> Cu	203 <sup>e</sup>	5.77	5.74	12.96	13.03	1587 s	943 vs
VI	(C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub> ) <sub>2</sub> Zn	262 <sup>f</sup>	5.97	5.72	—	13.34	1587 s	935 m
B. <i>p-TBHA Complexes</i> :								
VII	(C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> ) <sub>4</sub> Mn	253	5.31	5.52	—	10.83	1592 vs	938 s
VIII	(C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> ) <sub>3</sub> Fe	137	5.24	5.71	—	7.60	1592 m	945 vs
IX	(C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> ) <sub>2</sub> Co	219	5.14	5.48	11.29	11.52	1590 vs	940 s
X	(C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> ) <sub>2</sub> Ni	263	5.60	5.48	11.93	11.48	1592 vs	936 s
XI	(C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> ) <sub>2</sub> Cu	193	5.51	5.43	12.26	12.31	1587 s	945 s
XII	(C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> ) <sub>2</sub> Zn	269	4.68	5.41	—	12.62	1587 vs	935 vs
C. <i>PFHA Complexes</i> :								
XIII	(C <sub>11</sub> H <sub>8</sub> NO <sub>3</sub> ) <sub>2</sub> Mn	223	5.77	6.10	—	11.96	1592 m	920 w
XIV	(C <sub>11</sub> H <sub>8</sub> NO <sub>3</sub> ) <sub>2</sub> Co	213	5.94	6.05	11.23	12.73	1592 vs	927 m
XV	(C <sub>11</sub> H <sub>8</sub> NO <sub>3</sub> ) <sub>2</sub> Ni	292	5.91	6.05	—	12.69	1592 vs	926 m
XVI	(C <sub>11</sub> H <sub>8</sub> NO <sub>3</sub> ) <sub>2</sub> Cu	203	5.43	5.99	13.53	13.58	1585 s	926 w
XVII	(C <sub>11</sub> H <sub>8</sub> NO <sub>3</sub> ) <sub>2</sub> Zn	251	5.95	5.96	—	13.91	1592 vs	926 w

M.p. reported a : 237.5–8.5<sup>10</sup>, 185 Dec.<sup>9</sup>;b : 192–2.5<sup>10</sup>, 183–4<sup>9</sup> ;c : 199<sup>9</sup> ;d : > 280<sup>9</sup> ;e : 212<sup>10</sup>, 200.5–1.0<sup>9</sup> ;f : 238.5–9<sup>9</sup>.

Bands due to aromatic ring, furan ring and *p*-disubstituted benzene ring are unaffected by the metal complex formation.

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