

## The Preparation and Characterization of Transition Metal Complexes of Cyclic Hydroxamic Acids

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Several cyclic hydroxamic acid complexes with first row transition metals have been synthesized. The coordination properties of the ligands 1-hydroxy-2-indolinone (HI) and 3-amino-3,4-dihydro-1-hydroxycarbostyryl (HADC) have been investigated using spectral, magnetic, and X-ray powder diffraction measurements. The results indicate that oligomeric species are formed by both ligands with Co(II), Ni(II), and Cu(II). Structures are proposed for these complexes with both ligands and for Fe(III) and Zn(II) with HI.

### Introduction

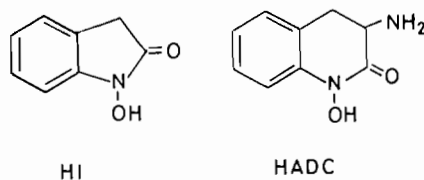
Hydroxamic acids play important and diverse roles in both chemistry and biology. Compounds with the functional group  $-\text{CON}(\text{OH})-$  have found extensive use as colorimetric and gravimetric reagents in analytical chemistry [1] and have been shown to be potent growth factors, antibiotics, antibiotic antagonists, tumor inhibitors, and cell division factors in natural products [2]. Complexation with transition metal ions is a vital part of the chemistry in both of these areas.

Most investigations of the coordination chemistry of hydroxamic acids have involved non-cyclic species [3]. In cyclic hydroxamic acids, where the hydroxamate group is part of a ring system, the flexibility of the coordinating atoms is limited, leading to different structural stabilities and properties of the coordination compounds.

Here we have investigated transition metal ions coordinated to two cyclic monohydroxamic acid compounds, 1-hydroxy-2-indolinone (HI), and 3-amino-3,4-dihydro-1-hydroxycarbostyryl (HADC), in

order to characterize their structural types. Both compounds have the hydroxamate group as part of a saturated ring system which is stabilized by a benzene ring. The two compounds differ in that the HADC has an amino group adjacent to the hydroxamate function, which offers a third site for coordination to metal ions. HADC exhibits a potent bacteriostatic effect against *Escherichia coli* and *Lactobacillus plantarum* not found in HI [4].

Compounds containing hydroxamates usually chelate by losing a proton and coordinating via the hydroxamate oxygen atoms. Previous studies have suggested that non-cyclic hydroxamate-containing ligands coordinate 1) to a central atom through both oxygen atoms, or 2) to form an oxygen-chelated oxygen-bridged polymeric complex. Complexes



analogous to the non-cyclic complexes of the first type have been isolated with HADC and HI. The second arrangement, which is like the  $[\text{M}(\text{acac})_2]_n$  formulation, is improbable for the cyclic hydroxamates because of the smaller chelate ring size and the flexibility limitations imposed by the hydroxamate group being part of a ring. In addition, the location of the amine group in HADC forces its coordination to be a different metal ion than those held by the hydroxamate oxygens. In the present study complexes of HI have been prepared with the ions  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  and complexes of HADC have been prepared with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$ . Elemental analysis, molecular

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weight measurements, magnetic susceptibility and ir spectroscopy have been employed in proposing structures for the new complexes.

## Experimental

### Preparation of Ligands

#### 1-Hydroxy-2-indoline (HI)

*o*-Nitrophenylacetic acid (Aldrich) was recrystallized from hot water after decolorization with Darco G-60. Recrystallized *o*-nitrophenylacetic acid (10.0 g) was dissolved in methanol (6 ml). Concentrated hydrochloric acid (1 ml) was added to 1 g of 5% Pt on C (Engelhard). The methanol solution was added to the wet catalyst because methanol vapor inflames in the presence of dry catalyst. The resulting mixture was hydrogenated for thirty minutes from an initial pressure of 50 p.s.i.g. The catalyst was removed by filtration in a sintered crucible, and the filtrate was cooled to 5 °C and the volume reduced in a flash evaporator, when HI crystallized (47%). The crude product may be used at once to prepare complexes or, if it is to be stored without decomposition, recrystallized from water and dried *in vacuo* over calcium chloride.

3-Amino-3,4-dihydro-1-hydroxycarbostyryl (HADC) was prepared by a known method [4].

### Preparation of Metal Chelates of HI

#### Fe(III)(HI)<sub>3</sub>

4 mmol (596 mg) of HI was dissolved in 0.5 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O (50 ml) on a steam cone. 4/3 mmol (216.3 mg) of FeCl<sub>3</sub> in hot water (minimum amount) was added, forming a purple precipitate of Fe(III) chelate. The precipitate was filtered hot with suction, washed three times with hot water and dried overnight *in vacuo* over calcium chloride. Yield 74%.

#### Cu(II)(HI)<sub>2</sub> green form

4 mmol (596 mg) of HI was dissolved in 0.5 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O (50 ml) on a steam cone. 6 mmol (1198 mg) of Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O in hot water (minimum amount) was added, forming an olive green precipitate of Cu(II) chelate. The precipitate was filtered hot with suction, washed three times with hot water, and dried overnight *in vacuo* over calcium chloride. Yield 85%.

#### Cu(II)(HI)<sub>2</sub> brown form

Approximately 0.01 mol (1.70 g) of CuCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in a minimum amount of water and added to a hot solution of 0.01 mol (1.48 g) of HI and 0.01 mol (1.36 g) of NaOAc·2H<sub>2</sub>O in a minimum amount of water (about 150 ml). The solution became brown. On addition of 4.6 g more

NaOAc·3H<sub>2</sub>O, the solution color darkened and became green. A second 0.01 mol of HI was added and the solution heated to simmering without effect. The volume was doubled with distilled water and the solution was boiled vigorously for five minutes, when a brown precipitate formed. The precipitate was suction filtered, washed seven times with hot water and once with acetone, and dried overnight *in vacuo* over Drierite. Yield 2.22 g or 62% based on the total mass of HI used.

#### Co(II)(HI)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

Approximately 4 mmol (596 mg) of HI was dissolved in 0.5 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·H<sub>2</sub>O (50 ml) on a steam cone. Addition of 2 mmol (496.2 mg) of Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O in a minimum amount of hot water resulted in the formation of a pink precipitate. The solution was digested for 4 min, filtered hot with suction, washed three times with hot water, and dried overnight *in vacuo*. Yield 96%.

#### Ni(II)(HI)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

Approximately 4 mmol (596 mg) of HI and 2 mmol (475.4 mg) of NiCl<sub>2</sub>·6H<sub>2</sub>O were reacted by the method used with Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O to form a light green precipitate. Yield 84%.

#### Zn(II)(HI)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

Approximately 4 mmol (596 mg) of HI and 2 mmol of Zn(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O (439 mg) were reacted by the method used with Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O to form a white precipitate. Yield 81%.

#### Isotopic copper complexes of HI

0.273 (22.1 mg) of <sup>63</sup>CuO were placed in a desiccator and heated with a heat lamp to remove excess HCl and H<sub>2</sub>O, resulting in a sample of 0.0363 g of CuCl<sub>2</sub>. The CuCl<sub>2</sub> was dissolved in a minimum amount of H<sub>2</sub>O and heated on a steam cone. A mass of 0.0796 g of 1-hydroxy-2-indolinone was dissolved in a minimum amount of 0.5 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and heated on a steam cone. On mixing and digestion on a steam cone, the solution gave a green precipitate, which was isolated by vacuum filtration through a sintered glass frit and dried overnight over CaCl<sub>2</sub>. Yield 0.0722 g (59% based on CuO).

### Preparation of Metal Chelates of HADC

#### Co(II)(HADC)<sub>2</sub>

HADC (0.100 g) and Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> (0.0351 g) were refluxed for 18 hours in acetone (20 ml), and a yellow precipitate which formed was recovered on a glass filter and dried. Yield 87% based on Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>.

#### Ni(II)(HADC)<sub>2</sub>

HADC and Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.600 g) were refluxed 48 hr in acetone (100 ml) and a precipitate

TABLE I. Analytical Data, Colors, and  $\mu_{\text{eff}}$  at Room Temperature.

Complex	C% found (reqd)	H% found (reqd)	N% found (reqd)	Color	$\mu_{\text{eff}}$ , B.M. (300 K)
1. Fe(HI) <sub>3</sub>	52.59 (53.38)	3.96 (4.11)	7.49 (7.84)	purple	5.82
2. Co(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	48.58 (49.12)	4.29 (4.11)	6.95 (7.05)	pink	4.22
3. Ni(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	48.62 (49.15)	4.16 (4.13)	7.15 (7.17)	light green	3.39
4. Cu(HI) <sub>2</sub>	53.49 (53.41)	3.47 (3.32)	7.52 (7.69)	olive green	2.18
5. Cu(HI) <sub>2</sub>	53.43 (53.41)	3.80 (3.32)	8.84 (7.69)	brown	2.05
6. Zn(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	47.88 (48.32)	4.13 (3.99)	6.55 (6.93)	white	diamagnetic
7. Co(HADC) <sub>2</sub>	52.17 (52.30)	4.36 (4.36)	13.46 (13.56)	yellow	4.01
8. Ni(HADC) <sub>2</sub>	51.81 (52.30)	4.07 (4.36)	13.16 (13.56)	light green	3.07
9. Cu(HADC) <sub>2</sub>	52.37 (51.67)	3.56 (4.31)	13.20 (13.40)	green	2.14
10. Cu(HADC) <sub>2</sub>	50.98 (51.67)	4.90 (4.31)	12.54 (13.40)	brown	2.01

which formed was recovered on a glass filter and dried. Yield 91% based on Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O.

#### *Cu(II)(HADC)<sub>2</sub> green form*

HADC (0.151 g) was dissolved in 50% dioxane over steam. A solution of CuCl<sub>2</sub> (0.072 g) in H<sub>2</sub>O (2 ml) was added, and the combined solution turned clear emerald green forming a green precipitate, which was filtered and dried. Yield 76% based on CuCl<sub>2</sub>.

#### *Cu(II)(HADC)<sub>2</sub> brown form*

HADC (0.100 g) in 50% dioxane (10 ml) was heated on a steam cone. Addition of Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O (0.0280 g) resulted in formation of a drab olive brown precipitate during the course of stirring for 12 hr. The precipitate was filtered and dried. Yield 84% based on Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O.

#### *Physical Measurements*

Elemental analyses for C, H, and N were done by M-H-W Laboratories, Phoenix, Arizona. Infrared spectra were measured on the Beckman IR-12 or IR-4240 spectrophotometers. Far-infrared spectra were measured on the Beckman IR-12 at Marquette University and the Hitachi FIS-3 at Texas A & M University. The spectra reported in the 4000–200 cm<sup>-1</sup> region were measured as Nujol or florolube mulls, while the spectra in the 2000–250 cm<sup>-1</sup> range were measured as KBr pellets or Nujol mulls.

Magnetic susceptibility measurements were made by the Faraday method using a Cahn Electrobalance, Model RM-02 and a Houston Instruments Omnigraphic Recorder. The reference compound employed was mercury(II) tetrathiocyanatocobaltate(II). Diamagnetic corrections used the empirical data for the susceptibility of the ligands and the value for water given by Figgis and Lewis [7]. All compounds were assumed to obey the Curie Law except the standard. Molecular weights of the copper complex in DMF were measured by Galbraith Laboratories, Inc., of Knoxville, Tennessee 37921. The corresponding measurements in chloroform were made by Huffman Laboratories, Inc., of Wheatridge, Colorado 80033. X-ray powder diffraction patterns for sodium chloride and for a mixture of sodium chloride and Ni(HI)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> as well as a mixture of sodium chloride and Ni(HADC)<sub>2</sub> were run on a Norelco X-ray Diffraction Unit, Type 1701 1200 with a nickel screen at 35 kV and 25 mA for a 4 hr exposure. In both cases only sodium chloride lines were observed; no additional lines were observed from the mixtures.

#### **Results and Discussion**

Analytical data and some physical properties of HI and HADC and their chelates are listed in Table I. The chelates are stable in air and essentially

TABLE II. Infrared Frequencies Associated with the Chelation of HI Frequencies ( $\text{cm}^{-1}$ ).

Formhydroxamic, HI Acid [8]	HI	Co(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Ni(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Cu(HI) <sub>2</sub>		Zn(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Assignment
				green	brown		
3123	3100s	—	—	—	—	—	O—H (intermolecular)
—	2710m	—	—	—	—	—	O—H (intramolecular)
—	—	3368s (2530)	3402s (2535)	—	—	3049s (2540)	H <sub>2</sub> O (asymmetric) (D <sub>2</sub> O)
—	—	3067m (2325)	3020m (2305)	—	—	3134m (2320)	H <sub>2</sub> O (symmetric) (D <sub>2</sub> O)
1653	1612s	1599s	1593s	1578s	1578s	1590s	$\nu(\text{C}=\text{O})$
1425	1403m	—	—	—	—	—	$\delta(\text{OH})$
985	991w	995m	995m	1000m	1001m	998m	$\nu(\text{N}-\text{O})$
828 or 837	828w	828w	823m	820m	820m	825w	$\gamma(\text{CNO})$
719	710m	—	—	—	—	—	$\gamma(\text{OH})$

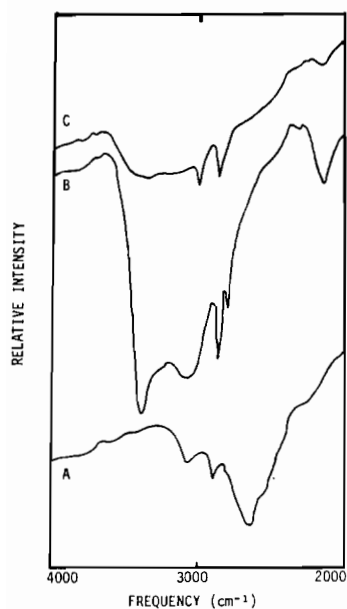


Fig. 1. Perfluorokerosene mull infrared spectra of A) 1-hydroxy-2-indolinone, B)  $\text{Co(II)(1-hydroxy-2-indolinone)}_2 \cdot (\text{H}_2\text{O})_2$ , and C)  $\text{Cu(II)(1-hydroxy-2-indolinone)}_2$ —brown.

insoluble in noncoordinating solvents, with the exception of  $\text{Fe(III)(HI)}_3$ , which is soluble in non-polar and moderately polar solvents. The green  $\text{Cu(HI)}_2$  complex is sufficiently soluble in DMF and chloroform for measurement of its molecular weight in solution. X-ray powder diffraction of the  $\text{Ni(HI)}_2(\text{H}_2\text{O})_2$  and  $\text{Ni(HADC)}_2$  gave no lines. Capillary melting point measurements on all chelates produced charring before even sintering could be observed, consistent with a possible polymeric structure and covalently bound water.

### IR Spectra (400 to 600 $\text{cm}^{-1}$ )

#### HI and its complexes

The spectra are shown in Fig. 1 and listed in Table II. Although HI contains only one O—H bond, two bands at 3100 and 2710  $\text{cm}^{-1}$  shift to lower energy at 2265 and 2090  $\text{cm}^{-1}$  upon deuteration. The OH moiety in solid HI therefore exists in two different forms of hydrogen bonding: intramolecular and intermolecular [5]. The OH stretching bands disappear when the hydrogen is replaced by a metal upon complexation.

$\text{Fe(III)(HI)}_3$  and  $\text{Cu(HI)}_2$  spectra show no OH stretching bands. The spectra of  $\text{M(II)(HI)}_2(\text{H}_2\text{O})_2$ , where M is Co, Ni, and Zn, show two bands, a sharp absorption at 3500  $\text{cm}^{-1}$  and a broad band just above 3000  $\text{cm}^{-1}$  which are affected by deuteration. These appear in the deuterated complexes near 2530 and 2320  $\text{cm}^{-1}$ , respectively, and are due to OH or OD stretching modes from the water molecules indicated in the elemental analysis.

The bending vibrations for the coordinated water molecules in the  $\text{Co(II)}$ ,  $\text{Ni(II)}$ , and  $\text{Zn(II)}$  chelates of HI occur at 1632, 1630, and 1633  $\text{cm}^{-1}$ , respectively. Upon complexation the frequency of the ligand carbonyl stretching mode at 1612  $\text{cm}^{-1}$  decreases as shown in Table II. These shifts follow the Irving—Williams order for the M—O bond strengths.

The other hydroxamate bands observed include the in-plane deformation of the hydroxyl group,  $\delta(\text{OH})$ , the out-of-plane deformation of the hydroxyl group,  $\gamma(\text{OH})$ , the nitrogen—oxygen stretching frequency,  $\nu(\text{NO})$ , and the carbon—nitrogen—oxygen in-plane deformation frequency,  $\delta(\text{CNO})$ . The assignments of these bands in HI and its complexes (Table II) are based on band assignments of formhydroxamic

TABLE III. Infrared Frequencies Associated with the Chelation of HADC.

HADC	Co(HADC) <sub>2</sub>	Ni(HADC) <sub>2</sub>	Cu(HADC) <sub>2</sub>		Possible Assignment
			green	brown	
3375w	3310sh	3310sh	3425m	3425m	$\nu$ N–H(asym) free
–	3275m	3290m	–	–	$\nu$ N–H(asym) H-bonded
3300w	3250m	3250m	3345m	3345m	$\nu$ N–H(sym) free
–	3180m	3180m	–	–	$\nu$ N–H(sym) H-bonded
2830w	–	–	–	–	$\nu$ O–H(inter-molecular)
2630w	–	–	–	–	$\nu$ O–H(intra-molecular)
1682	–	–	–	–	$\nu$ (C=O) <sub>1</sub>
1620s	1560s	1560s	1529s	1524s	$\nu$ (C=O) <sub>2</sub>
1410w	–	–	–	–	$\delta$ (OH)
1050m	980m	980m	978m	979m	$\nu$ (NO)
830w	870w	835w	834m	837m	$\gamma$ (CNO)
720m	–	–	–	–	$\gamma$ (OH)
1620s	1602m	1618m	1640m	1630m	$\delta$ (NH <sub>2</sub> )
970w	960w	980m	998m	977m	$\rho$ (NH <sub>2</sub> )
720m	700s	692w	668w	670w	$\rho$ (NH <sub>2</sub> )

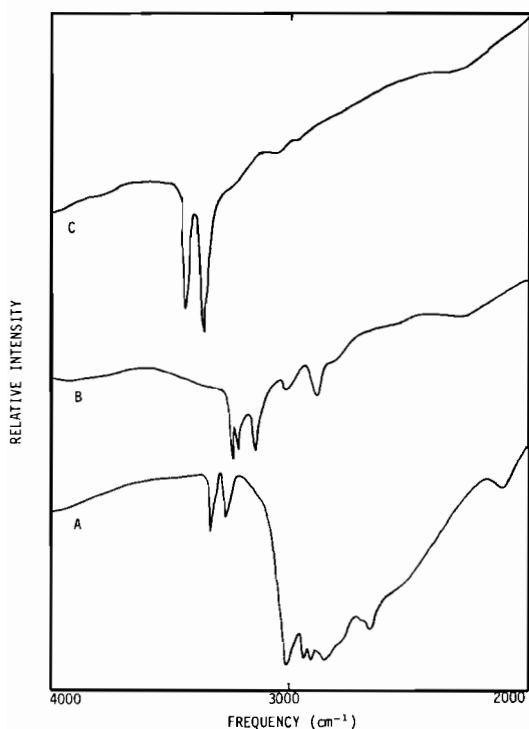


Fig. 2. Perfluorokerosene mull infrared spectra of A) 3-amino-3,4-dihydro-1-hydroxycarbostyryl, B) Ni(II)(3-amino-3,4-dihydro-1-hydroxycarbostyryl)<sub>2</sub>, C) Cu(II)(3-amino-3,4-dihydro-1-hydroxycarbostyryl)<sub>2</sub>.

acid by Orville–Thomas and Parsons, using a normal coordinate analysis [8].

#### HADC and its complexes

The spectra are shown in Fig. 2 and listed in Table III. HADC has both OH and NH stretching motions. The OH stretching bands which occur at 2830 and 2630 cm<sup>-1</sup> in HADC disappear upon complexation in Co, Ni and Cu(HADC)<sub>2</sub> (Table III). Water molecules are not associated with these complexes as indicated by the spectral data and the elemental analysis. HADC has asymmetric and symmetric NH stretching absorptions at 3375 and 3300 cm<sup>-1</sup>, respectively. The position and broadness of these bands suggest hydrogen bonding of the N–H moiety.

For the Ni(II)(HADC)<sub>2</sub> complex, four NH stretching bands at 3310(sh), 3290, 3250, and 3180 cm<sup>-1</sup> appear at lower frequency than the HADC NH stretching bands. Coordination of an amine group generally results in a NH stretching frequency decrease of 100 to 150 cm<sup>-1</sup> [9]. According to Bellamy [8] the symmetric ( $\nu_{\text{sym}}$ ) and asymmetric ( $\nu_{\text{asym}}$ ) stretching frequencies for the free amine group are related by the equation  $\nu_{\text{sym}} = 345.53 + 0.876 (\nu_{\text{asym}})$  with an observed standard deviation of 4.8 cm<sup>-1</sup>. When only one of the two amino hydrogen atoms is hydrogen bonded, the equation is not followed. In the Ni(HADC)<sub>2</sub> spectra the shoulder at 3310 cm<sup>-1</sup> may be assigned as an NH<sub>2</sub> asymmetric stretch. The equation then predicts  $\nu_{\text{sym}}$  at 3245 cm<sup>-1</sup>. The two bands at 3290 and 3180 cm<sup>-1</sup> represent  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  of an amine group in a different environment which allows more effective hydrogen bonding to one of the amine hydrogens than the other.

TABLE IV. Far-infrared Bands of HI and M(HI)<sub>2</sub> Complexes (600–250 cm<sup>-1</sup>).

HI	Co(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Ni(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Cu(HI) <sub>2</sub>		Zn(HI) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>
			green	brown	
	603m	603m			603m
595m	589m	588w	589m	589m	598m
576s	575w	556w			558w
544s	546w	543w	532s	531s	
514s	520m	518w			520m
494s	499m	500m	504s	504s	
488s	485w	480w			485w
	455m	455m			457m
			429sh	429sh	
407w	416s	417s	418s	418s	417s
384s	375m				
				386w	
370s	<i>363s</i> <sup>b</sup>	<i>369s(2.5)</i> <sup>a</sup>		369w	
	352m				351s
	328s	335s	331m	331m	
	304w	303m	<i>318m(3.5)</i>	317m	316w
		296s			
	282s	287m(4–6)	282w	280w	284m

<sup>a</sup>Parentheses indicate metal-isotope shifts. <sup>b</sup>Italicized bands indicate M–O stretching bands.

By contrast, the Cu(HADC)<sub>2</sub> spectrum shows only two NH stretching bands. They occur at higher energy than those in the Ni(HADC)<sub>2</sub> or free HADC spectra. The Cu(HADC)<sub>2</sub> bands which appear at 3425 and 3345 cm<sup>-1</sup> signify the absence of hydrogen bonding or metal complexation since they are comparable to the NH stretching bands in the methylamine vapor spectrum at 3427 and 3361 cm<sup>-1</sup> [11].

The carbonyl frequencies for Co(HADC)<sub>2</sub>, Ni(HADC)<sub>2</sub>, and Cu(HADC)<sub>2</sub> (Table III) occur 60, 60, 95 cm<sup>-1</sup> lower than in free HADC. These values follow the Irving–Williams order except that the cobalt shift is equal to, not less than, the nickel shift.

The C–N stretch and the deformation modes of the NH<sub>2</sub> group also produce bands in this region. The expected frequencies for these modes occur at 1650–1590 cm<sup>-1</sup> for the NH<sub>2</sub> bend and 840–760 cm<sup>-1</sup> for the NH<sub>2</sub> wag, ~977 cm<sup>-1</sup> for the NH<sub>2</sub> twist, and 1040 ± 3 cm<sup>-1</sup> for the C–N stretch of a primary amine with a secondary α-carbon atom, such as HADC [10, 11]. Some of the amine bands have been assigned in Table III, whereas others fall in areas where other absorptions are expected. The ambiguous cases are the NH<sub>2</sub> wag, which occurs in the region where the CNO in-plane deformation is expected, and the C–N stretch, which is expected in the same area as the in-plane deformations of the benzenoid hydrogens between 1080 and 1000 cm<sup>-1</sup>.

#### Far-Infrared Spectra (600–250 cm<sup>-1</sup>)

Absorptions which occur in this spectral region may be due to motions of the ligand atoms, metal–

TABLE V. Far-Infrared Frequencies of HADC and M(HADC)<sub>2</sub> Complexes (600–250 cm<sup>-1</sup>).

HADC	Co(HADC) <sub>2</sub>	Ni(HADC) <sub>2</sub>	Cu(HADC) <sub>2</sub>	
			green	brown
604s	607s			
	600s	600s	595m	598m
		580sh		
555s		555s	558w	556m
532m	540m			
		528m		520m
495sh		490sh		
458s	460s	460s	463m	468m
				445w
430s	430s	427s	430w	
	405w			
387w		388w	379m	
	377w			
366w	367w	365w		
340w			336m	336m
305w	315w	303m		
290w			246m	

ligand atoms, metal–ligand stretching or bending modes, or lattice modes. The richness of bands in this region (Tables IV and V) makes assignments challenging. The results of metal-isotope substitution are used below to begin to understand this spectral region.

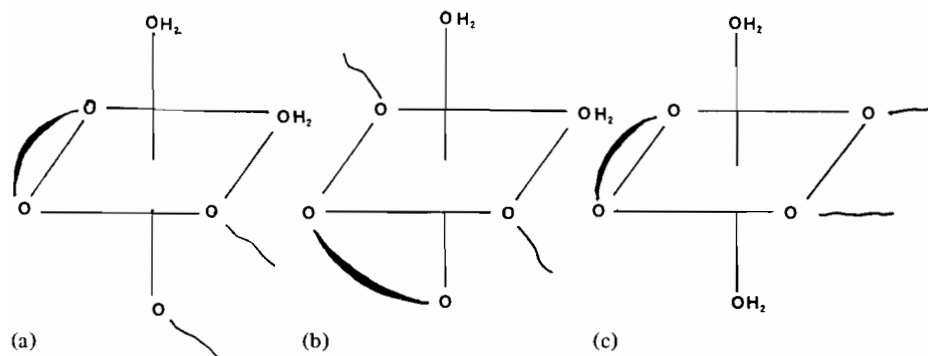


Fig. 3. Possible polymeric formulations of  $M(HI)_2(H_2O)_2$  stoichiometry.

### HI and its complexes

The far-ir spectra of Co, Ni, and  $Zn(HI)_2(H_2O)_2$  are similar in this region. Comparison of the  $^{58}Ni(HI)_2(H_2O)_2$  with  $^{62}Ni(HI)_2(H_2O)_2$  spectra show that two absorptions are isotopically dependent. A band at  $369.0\text{ cm}^{-1}$  in the  $^{58}Ni$  complex shifts to  $366.5\text{ cm}^{-1}$  in the corresponding  $^{62}Ni$ . The second shift occurs at  $921\text{ cm}^{-1}$ . The overlap of this band with a ligand absorption in the  $^{62}Ni$  complex spectrum is resolved in the  $^{58}Ni$  spectrum. The isotopic shift is estimated to be between 4 and  $6\text{ cm}^{-1}$ . Both these bands are assigned as Ni–O (hydroxamate) stretching bands since they show an appropriate metal-isotopic shift and fall in the range previously assigned to similar complexes containing Ni–O stretching bands [11, 12]. Ni–OH<sub>2</sub> stretching bands have been assigned [13] below  $220\text{ cm}^{-1}$  and are not observed in the range of the instrument employed. Other bands in this region show no metal-isotopic dependence and are assigned as primarily ligand bands. Because of the relative position of the carbonyl stretching frequencies and the assignment of M–O stretching bands in  $M(8\text{-hydroxyquinoline})_2(H_2O)_2$ , where M is also Co, Ni and Zn, it is probable that the bands at  $363$  and  $282\text{ cm}^{-1}$  in the  $Co(HI)_2(H_2O)_2$  spectra are Co–O stretching and the bands at  $350$  and  $256\text{ cm}^{-1}$  are the Zn–O stretching bands in the  $Zn(HI)_2(H_2O)_2$  spectra.

Metal-isotopic substitution of green  $Cu(HI)_2$  shifts the absorption at  $318.0\text{ cm}^{-1}$  for  $^{63}Cu(HI)_2$  to  $314.5\text{ cm}^{-1}$  in the corresponding  $^{65}Cu$  complex. This band is assigned as a Cu–O stretching mode and the assignment is in good agreement with that of the Cu–O stretching band in the planar  $Cu(8\text{-hydroxyquinoline})_2$ . The brown  $Cu(HI)_2$  complex shows a similar spectrum in the far-ir as the green complex with the addition of two weak bands at  $369$  and  $386\text{ cm}^{-1}$ .

### HADC and its complexes

These spectra are tabulated in Table V. Although metal-isotopic substitution was utilized in the study

of the  $Ni(HADC)_2$  complexes, no bands in the region studied showed isotopic shifts larger than  $1.0\text{ cm}^{-1}$ . Consequently, the bands observed are assigned as primarily ligand motions. The addition and coordination of the amino group may have weakened the M–O bonds and therefore lowered their frequency below the range of the instrument employed. The spectra of the green and brown copper complexes are similar in this region and differ from the spectra of the Ni complexes in the presence of a strong band at  $336\text{ cm}^{-1}$ . The band at  $336\text{ cm}^{-1}$  is tentatively assigned as a Cu–O stretching band, based on its similarity to the assignment in  $Cu(HI)_2$  and  $Cu(8\text{-hydroxyquinoline})_2$ .

### Molecular Structure

#### HI complexes

The complexes of HI fall into three groups, the Fe(III) complex, the complexes of Co(II), Ni(II), and Zn(II), and the green and brown Cu(II) complexes.

$Fe(HI)_3$  has a 1:3 metal:ligand ratio based on elemental analysis, and its magnetic susceptibility is consistent with octahedral coordination. The high solubility precludes a polymeric arrangement. The structure is a tris-bidentate, pseudo-octahedral iron complex, consistent with X-ray results by Lindner and Goettlicher for iron(III)benzohydroxamate [15].

The Co, Ni and Zn complexes of HI are considered to be amorphous polymers because of their low solubility in all types of solvents and their lack of X-ray diffraction patterns. Several covalently-bonded types of polymerization are conceivable. In one case, an oxygen atom of the hydroxamate moiety could be shared between two metal ions in the manner demonstrated by Cotton for anhydrous acetylacetonate complexes [16]. Formation of a polymer in this manner would give an empirical formula which would not allow for coordinated water molecules.

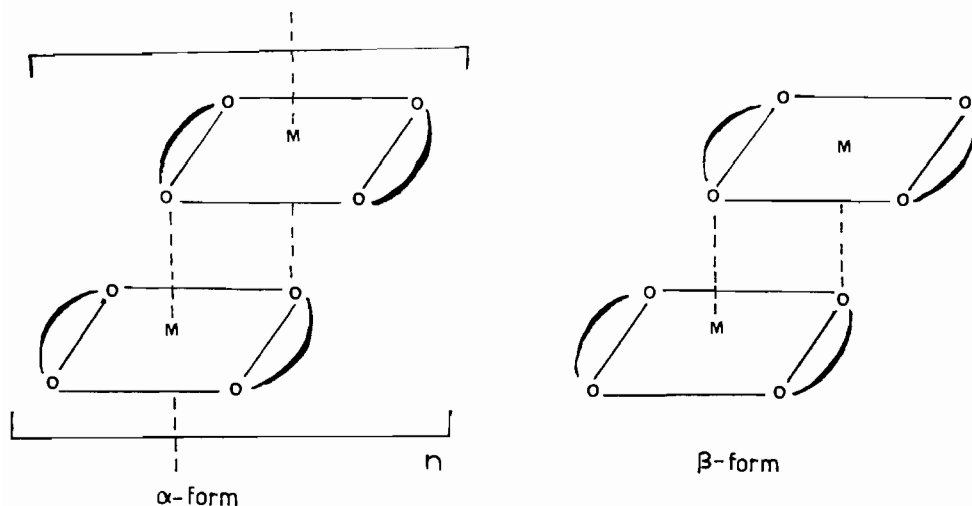


Fig. 4. The  $\alpha$  and  $\beta$  forms of the copper isomers of  $\text{Cu}(\text{HI})_2$  and  $\text{Cu}(\text{HADC})_2$ .

Two types of polymerization can lead to the experimentally determined empirical formula. Both involve ligand bridging in which the two oxygen atoms of a hydroxamate group are coordinated to separate metal ions. There are three possible ways to formulate the  $\text{M}(\text{HI})_2(\text{H}_2\text{O})_2$  for the case in which one ligand is chelating and the other bridging (Fig. 3). Framework molecular models show only one of these, Case a, is sterically allowed. Here the water molecules are *cis* and the chelated ligand is not coplanar with them. The relatively free rotation around the bonds within the bridging ligand would allow the polymeric chain to twist. This is consistent with the lack of an X-ray diffraction pattern found for the Ni complex.

It is interesting to compare the proposed structural arrangement for HI with complexes formed from similar ligands. Brown, McKeith, and Glass have reported complexes with non-cyclic hydroxamate containing ligands. Both anhydrous and one water-per-metal ion complexes were isolated, but none were reported with two water molecules per metal ion. The structures proposed for these non-cyclic hydroxamate complexes are similar to the bis-acetylacetonate Co and Ni complexes [14]. Oxygen bridging in the manner of these complexes is improbable for cyclic hydroxamates because of limited flexibility of the chelating moiety.

The tropolone ligand forms a five-member chelate ring system in which the chelating oxygen atoms are in a planar configuration but in which chelating and bridging occur together in the same plane. Structures with oxygen shared between two metals have been observed for some tropolone chelates [17]. It should be noted that these structures differ from those of the bis-acetylacetonates in that the chelate ring is

planar in the tropolone complexes. In this case, the structural differences from chelates of cyclic hydroxamates may be related to the relative electronegativity of the N atom in the hydroxamates compared to the corresponding C atom in the tropolonate. The hydroxamate ion has less electron density and is less likely to be in such a bridging arrangement; rather, the metal coordinates two water molecules which complete the coordination sphere.

The far-infrared assignments for the  $\text{M}(\text{HI})_2(\text{H}_2\text{O})_2$  complexes are consistent with the symmetry surrounding the metal ions, which would predict two infrared active metal-oxygen (hydroxamate) stretching modes.

Two experimental results indicate that the brown and green forms of  $\text{Cu}(\text{HI})_2$  are analogous to the well-studied  $\text{Cu}(\text{8-hydroxyquinoline})_2[\text{Cu}(\text{Q})_2]$  system [13]. First, two isomeric forms of the  $\text{Cu}(\text{HI})_2$  can be isolated. Second, molecular weights in chloroform indicate some association. X-ray crystal studies of  $\text{Cu}(\text{Q})_2$  isomers have shown that both the  $\alpha$  and  $\beta$  forms are in a *trans*-planar arrangement in which the  $\alpha$  form polymerizes to achieve six-coordination, with four shorter  $\text{Cu}-\text{O}$  bonds and two longer  $\text{Cu}-\text{O}$  bonds, while the  $\beta$  form dimerizes to achieve 5-coordination, Fig. 2 [18]. By analogy the green and brown forms of  $\text{Cu}(\text{HI})_2$  correspond to the structures below (Fig. 4).

#### *HADC complexes*

The complexes of HADC examined here fall into two groups, the complexes of Co(II) and Ni(II) and the complexes of Cu(II) in the green and brown forms.

The similarity of the spectra of the Co and Ni complexes established similarity of the structures of



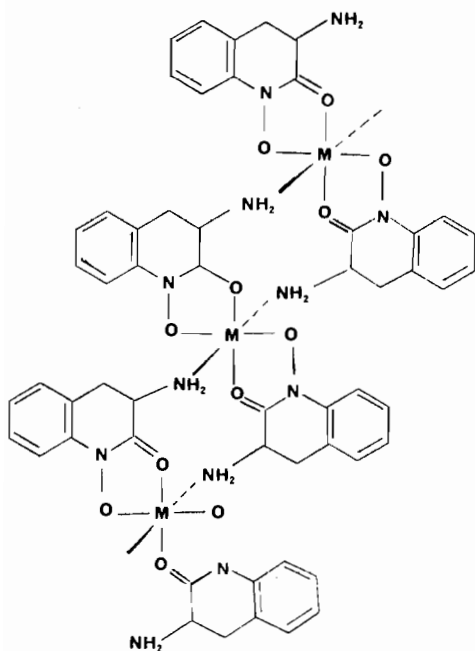


Fig. 5. The stair-step structure proposed for  $\text{Ni}(\text{HADC})_2$  and  $\text{Co}(\text{HADC})_2$ .

these complexes. The infrared spectra reflect the coordination of the amine and hydroxamate groups, but the stereochemistry of HADC is such that its amine nitrogen cannot be coordinated to the same metal ion as its hydroxamate group. The absence of water molecules in the elemental analyses necessitates coordination by the amine donor if the arrangement is six-coordinate.

Such coordination can be achieved in the form of a stair-step structure, shown in Fig. 5. This arrangement involves only the *trans*-coplanar orientation of the HADC molecules, and requires that the absolute configuration of the chiral carbons bearing the amine group change from R to S with each step of the ladder structure. Dudek and Snow [19] have proposed a similar structure for the metal complexes of 2-carbamoyldimmedone.

A different structure can be proposed in which the amine groups are *cis* to one another (Fig. 6). In this case hydrogen bonding from one nitrogen of a coordinated amine to the unused  $\text{sp}^2$  lobe of a chelating carbonyl oxygen may arise. Such a configuration provides an explanation for the multiple bands in the amine region. These bands appear to arise because the amine group exists in two different environments, one of which favors the formation of a hydrogen bond from one of the hydrogen atoms of the amine group but not from the other.

It should be noted that the presence of a third donor atom in the HADC molecule allows the formation of insoluble polymers in two ways without the

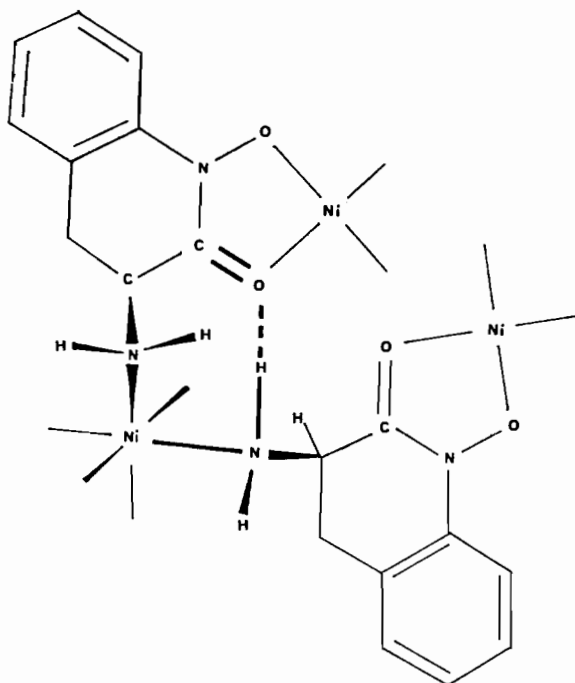


Fig. 6. A proposed structure for  $\text{Ni}(\text{HADC})_2$  and  $\text{Co}(\text{HADC})_2$  with the amine group in two different environments.

necessity for the kind of ligand bridging found in HI complexes. A mixture of these forms of polymerization is also consistent with the X-ray powder pattern and spectral results.

In the  $\text{Cu}(\text{HADC})_2$  systems, the amine group is not coordinated. Complexation of the hydroxamate moiety is indicated by the disappearance of the hydroxyl absorptions in the hydrogen region. Since a green and brown form of the  $\text{Cu}(\text{HADC})_2$  are isolated, we propose the structures are similar to those of the  $\text{Cu}(\text{HI})_2$  complexes.

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