constant for $[Ni(AO)(MeAO)\text{-}H]^+$ is large compared to $[Ni(MeAO)_2\text{-}H]^+$, showing that steric hindrance due to methyl group interaction is extremely important.

Steric hindrance to approach the 5 and 6 positions of planar Ni(II) complexes gives complexes of extreme stability to reaction with EDTA. This may be used to advantage in the analytical determination of Ni(II) in the presence of other transition ions.

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Contribution from the Wm. A. Noyes Laboratory,
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Spectrochemical Studies of a Series of Amides as Ligands with Nickel(II) and Chromium(III)

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The syntheses and spectra of some amide complexes of nickel(II) perchlorate and chromium(III) perchlorate are described. The ligand field parameters *Dq* and β are calculated for the octahedral complexes. Evidence is presented to support the presence of a steric effect in the interaction of some of these amides with the metal ions. The spectrochemical parameters *Dq* and β are compared with those reported for other ligands. These parameters also are compared with data which measure the donor properties of the amides toward phenol.

Introduction

Research[2] in the area of non-aqueous solvents has led us to believe that, instead of solvent autoionization, basicity and dielectric constant are the essential properties for understanding the behavior of solutes in many non-aqueous solvents. As a result, we have been concerned with the evaluation of the free energy of adduct formation between the acids iodine[3,4] and phenol[5] with several Lewis bases which may be employed as non-aqueous solvents. To gain information about the nature of the interaction of various solvents and Lewis bases with metal ions, we have evaluated the position of several of these ligands in the spectrochemical and nephelauxetic series.[6] We have described earlier[6] the spectral properties, *Dq*, and β values for cobalt(II), nickel(II), and chromium(III) complexes of dimethyl sulfoxide, tetramethylene sulfoxide, and pyridine N-oxide. In this article we report spectral data for the nickel and chromium complexes of a series of amides. The relative positions of these amides in the spectrochemical and nephelauxetic series have been determined. The *Dq* values are compared with enthalpy results for the interaction of the amides with phenol. The data can be rationalized from a consideration of inductive and steric effects.

Experimental

The metal amide complexes were prepared by the following procedure. The aquated metal perchlorate was dehydrated with a 40% excess of 2,2-dimethoxypropane[7] by stirring for 2 hr. at room temperature. The resulting solution then was treated with a sevenfold mole ratio of the amide. The volatile material then was removed by pumping at 1 mm. pressure until a viscous oil was obtained. The N,N-dimethylformamide (DMF) and N-methylformamide (NMF) complexes of nickel(II) and the acetamide and N,N-dimethylacetamide (DMA) complexes of chromium(III) were isolated as solids by extracting the respective oil with ether and ethanol. Oils of the other amide complexes did not solidify upon treatment with several solvents.

Anal. Calcd. for $[Ni(NMF)_6](ClO_4)_2$: C, 23.55; H, 4.91; N, 13.73. Found: C, 23.17; H, 5.27; N, 13.10.

Anal. Calcd. for $[Ni(DMF)_6](ClO_4)_2$: C, 31.05; H, 6.08; N, 12.07. Found: C, 30.97; H, 6.09; N, 11.76.

Anal. Calcd. for $[Cr(acetamide)_6](ClO_4)_3$: C, 20.45; H, 4.29; N, 11.92. Found: C, 21.63; H, 4.64; N, 12.09.

Anal. Calcd. for $[Cr(DMA)_6](ClO_4)_3$: C, 33.03; H, 6.23; N, 9.64. Found: C, 32.39; H, 6.43; N, 9.07.

Spectrophotometric Measurements.—Near-infrared and visible absorption spectra were obtained with a recording Cary spectrophotometer, Model 14M. The spectra of the solutions were measured in 1.0-cm. matched quartz cells with the solvent as the reference.

Solutions of the amide complexes were prepared by dissolving the oil or solid in the respective amide as a solvent. For solid amides, methylene chloride or nitromethane was used to dissolve the complex and excess amide was added to the solution. Spectral evidence is presented later to indicate that these conditions produce octahedral species in solution of the type $[M(amide)_6]^{+n}$. The solutions of the formamide and acetamide complexes exhibited distinctive light green and yellowish green solutions' respectively. The formamide derivatives, as a group, and acetamide form the light green solutions and have higher values of *Dq* than the other acetamide derivatives, which give yellowish green solutions. Typical spectra for the two series of ligands are illustrated in Fig. 1.

The O–H frequency shifts for the phenol-amide adducts were obtained by the method described previously.[8] Infrared spectra were obtained with a Beckman Model IR-7 spectrophotometer,

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(1) Abstracted in part from the Ph.D. thesis of M. Joesten, University of Illinois, Urbana, Illinois.

(2) D. W. Meek and R. S. Drago, *J. Am. Chem. Soc.*, **83**, 4322 (1961).

(3) R. S. Drago and D. A. Wenz, *ibid.*, **84**, 526 (1962).

(4) R. S. Drago, D. A. Wenz, and R. L. Carlson, *ibid.*, **84**, 1106 (1962).

(5) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2037, 2696 (1962).

(6) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(7) K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

(8) M. D. Joesten and R. S. Drago, submitted for publication.

using sodium chloride cells of 0.2 mm. thickness. The slit width at 3100 cm.$^{-1}$ was 0.37 mm.

Calculations.—A description of the procedure which was followed in making band assignments and calculating ligand field parameters is given in a previous paper.[6]

Results

The spectral data for the complexes are summarized in Table I. These abbreviations have been employed for the various amides: NMF for N-methylformamide, DMF for N,N-dimethylformamide, DEF for N,N-diethylformamide, NMA for N-methylacetamide, DMA for N,N-dimethylacetamide, and DMBu for N,N-dimethylbutyramide. For the Ni(II) complexes, the calculated and experimental values for λ_{max} of the second band are given in Table II.

TABLE I

SPECTRAL BANDS FOR Ni(II) AND Cr(III) COMPLEXES OF THE AMIDES

Compound	Solvent	ν_{max} (cm.$^{-1}$)	ϵ_{max}[a]	Band assignment[b]
$[Ni(NMF)_6](ClO_4)_2$	NMF	8,380		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		13,660 }[d]		$\rightarrow {}^3T_{1g}(F)$
		14,700 }		
		25,000		$\rightarrow {}^3T_{1g}(P)$
$[Ni(DMF)_6](ClO_4)_2$	DMF	8,500	6.35	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		13,600 }	5.35	$\rightarrow {}^3T_{1g}(F)$
		14,900 }	5.68	
		25,000	15.35	$\rightarrow {}^3T_{1g}(P)$
$[Ni(DEF)_6](ClO_4)_2$	DEF	8,400		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		13,700 }		$\rightarrow {}^3T_{1g}(F)$
		14,950 }		
		25,130		$\rightarrow {}^3T_{1g}(P)$
$[Ni(CH_3CONH_2)_6]$-$(ClO_4)_2$	Acetone	8,240		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		13,370		$\rightarrow {}^3T_{1g}(F)$
		(14,700)[c]		
		24,510		$\rightarrow {}^3T_{1g}(P)$
$[Ni(NMA)_6](ClO_4)_2$	NMA	7,520		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		12,660		$\rightarrow {}^3T_{1g}(F)$
		(14,580)		
		23,700		$\rightarrow {}^3T_{1g}(P)$
$[Ni(DMA)_6](ClO_4)_2$	CH_2Cl_2	7,580		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		12,740		$\rightarrow {}^3T_{1g}(F)$
		(14,700)		
		23,810		$\rightarrow {}^3T_{1g}(P)$
$[Ni(DMA)_6](ClO_4)_2$	DMA	7,690		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		12,900		$\rightarrow {}^3T_{1g}(F)$
		(14,700)		
		23,920		$\rightarrow {}^3T_{1g}(P)$
$[Ni(DMBu)_6](ClO_4)_2$	DMBu	7,490		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		12,020		$\rightarrow {}^3T_{1g}(F)$
		(14,550)		
		23,810		$\rightarrow {}^3T_{1g}(P)$
$[Cr(CH_3CONH_2)_6]$-$(ClO_4)_3$	CH_3NO_2	16,450	53.0	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
		22,940	41.3	$\rightarrow {}^4T_{1g}(F)$
$[Cr(DMA)_6](ClO_4)_3$	CH_3NO_2	14,880 }	59.8	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
		15,310 }	61.2	
		21,550	46.7	$\rightarrow {}^4T_{1g}(F)$

[a] ϵ is given in l. mole^{-1} cm.$^{-1}$ from the equation $A = \epsilon cl$. [b] The spectra of Ni(II) and Cr(III) complexes of these ligands are very similar to the spectra of the corresponding hexaaquo complexes except for the wave length of λ_{max}. [c] The parentheses designate a shoulder on a main peak of the spectrum. These are of very low intensity for all complexes except the acetamide complex. [d] The bracket indicates a doublet.

The values for Dq and for the P–F term splitting for the complexes are indicated in Table III. The quantity β is defined as the percentage lowering of the P–F term splitting in the complex compared to the value of the gaseous ion with no crystalline field.

The O–H frequency shifts for the phenol–amide adducts are summarized in Table IV.

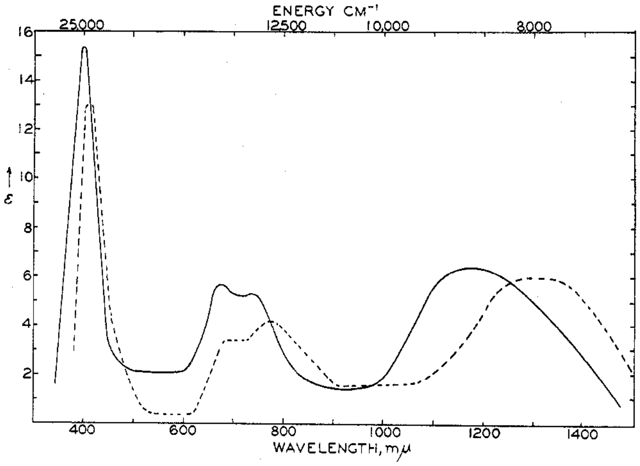

Fig. 1.—The spectra of nickel complexes of DMF and DMA. The solid line is for $[Ni(DMF)_6](ClO_4)_2$ in DMF and the dashed line is for $[Ni(DMA)_6](ClO_4)_2$ in DMA. The ϵ scale is arbitrary for the DMA complex; however the peak heights are shown in true relative scale.

TABLE II

CALCULATED AND EXPERIMENTAL FREQUENCIES OF THE SECOND BAND OF Ni(II) COMPLEXES

Compound	Solvent	Position of $\nu_2[^3T_{1g}(F)]$ Predicted, cm.$^{-1}$	Observed, cm.$^{-1}$
$[Ni(NMF)_6](ClO_4)_2$	NMF	13,950	14,180[a]
$[Ni(DMF)_6](ClO_4)_2$	DMF	14,108	14,250[a]
$[Ni(DEF)_6](ClO_4)_2$	DEF	13,991	14,320[a]
$[Ni(CH_3CONH_2)_6](ClO_4)_2$	Acetone	13,582	13,370
$[Ni(NMA)_6](ClO_4)_2$	NMA	12,645	12,660
$[Ni(DMA)_6](ClO_4)_2$	CH_2Cl_2	12,739	12,740
$[Ni(DMA)_6](ClO_4)_2$	DMA	12,903	12,900
$[Ni(DMBu)_6](ClO_4)_2$	DMBu	12,613	12,020

[a] The value reported here is an average of the two maxima in the doublet. This is in accord with the conclusion of Liehr and Ballhausen [*Ann. Phys.*, **6**, 134 (1959)] that the second peak is not the $^3A_{2g} \rightarrow {}^1E_g$ transition.

TABLE III

SUMMARY OF THE CALCULATED LIGAND FIELD PARAMETERS

Compound	Solvent	$E(P) - E(F)$, cm.$^{-1}$	Dq,[a] cm.$^{-1}$	β[b]
$[Ni(NMF)_6](ClO_4)_2$	NMF	13,811	838	12.8%
$[Ni(DMF)_6](ClO_4)_2$	DMF	13,608	850	14.1%
$[Ni(DEF)_6](ClO_4)_2$	DEF	13,917	840	12.1%
$[Ni(CH_3CONH_2)_6]$-$(ClO_4)_2$	Acetone	13,498	824	14.8%
$[Ni(NMA)_6](ClO_4)_2$	NMA	13,781	752	13.0%
$[Ni(DMA)_6](ClO_4)_2$	CH_2Cl_2	13,809	758	12.8%
$[Ni(DMA)_6](ClO_4)_2$	DMA	13,756	769	13.2%
$[Ni(DMBu)_6](ClO_4)_2$	DMBu	13,952	749	11.9%
$[Cr(CH_3CONH_2)_6]$-$(ClO_4)_3$	CH_3NO_2	9,683	1645	29.7%
$[Cr(DMA)_6](ClO_4)_3$	CH_3NO_2	11,113	1517	19.3%

[a] The error limits of Dq are ±5 cm.$^{-1}$ for Ni(II) complexes and ±10 cm.$^{-1}$ for Cr(III) complexes; error arises in determining ν_{max}. [b] The error limits of β are ±1.2% for Ni(II) complexes and ±2.4% for Cr(III) complexes.

Discussion

The preparation and elemental analyses are reported for metal ion complexes of NMF, DMF, DMA, and

TABLE IV

FREQUENCY SHIFTS FOR PHENOL–AMIDE ADDUCTS

Base	Solvent	$\Delta\nu_{O-H}$,^{a} cm.$^{-1}$
Acetamide	$Cl_2C{=}CCl_2$	270 ± 10
NMA	$Cl_2C{=}CCl_2$	292 ± 10
DMA	CCl_4	345 ± 3
DMF	CCl_4	294 ± 4
DEF	CCl_4	302 ± 5
NMF	CCl_4	261 ± 10
DMBu	CCl_4	325 ± 4

[a] ν_{O-H} = 3609 cm.$^{-1}$

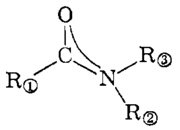

Fig. 2.—General structural formula for the amides studied.

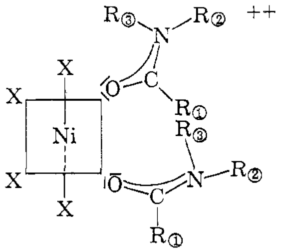

Fig. 3.—Interaction of neighboring amide groups in an octahedral complex.[14]

acetamide. Infrared spectra of Nujol mulls indicate[9] that the carbonyl oxygen is the donor in all of these complexes. Visible and near-infrared spectra as well as elemental analyses indicate that the complexes are six-coördinate, octahedral species. In those instances where intractable oils were obtained by our procedure, these oils were redissolved in the ligand as solvent and the spectra examined. The constancy of the intensity ratio of the $^3A_2(F) \rightarrow {}^3T_1(P)$ to $^3A_2(F) \rightarrow {}^3T_1(F)$ is taken as evidence[10,11] for the existence of octahedral nickel(II). The assignment of octahedral configuration to the Ni(II) complexes in solution also is substantiated by the good agreement between the calculated and experimental values for λ_{max} of the second band (Table II).

The basicity of the amides can be estimated from their interaction with phenol. The difference in the frequency of the O-H stretching vibration of phenol in an adduct compared to free phenol is reported[8] to be linearly related to the enthalpy of adduct formation when phenol complexes with a large number of oxygen and nitrogen donors.[12] The series of increasing donor strength toward phenol derived from the data reported in Table IV is: NMF $\sim$ acetamide $<$ NMA $\sim$ DMF $<$ DEF $<$ DMBu $<$ DMA. Except for DMBu, this is the series predicted on the basis of inductive effects. Successive replacement of hydrogens by methyl groups on the amide skeleton increases the basicity of the carbonyl oxygen atom.

The *Dq* values (in cm.$^{-1}$) calculated for the octahedral complexes of nickel(II) do not follow the inductive order but produce the series: DMF (850) $>$ NMF (838) $\sim$ DEF (840) $>$ acetamide (824) $\gg$ DMA (769) $>$ NMA (752) $\sim$ DMBu (749). Two main categories are discernible which are separated by a discontinuity of about 55 cm.$^{-1}$. The two groups consist of those amides in which R_1 and R_3 are both alkyl and those in which either R_1 or both R_2 and R_3 are hydrogen. The latter category gives rise to a higher *Dq* value even though inductive considerations and enthalpies of adduct formation with phenol indicate that these amides are weaker bases than DMA. An explanation can be tentatively proposed by considering the steric requirements of the alkyl groups. It is proposed that when R_1 is an alkyl group and when one of the groups on the nitrogen is alkyl, the rotamer in which R_3 is alkyl (*i.e.*, the *trans* structure) will be favored because of steric interaction between R_1 and R_2 when they are both alkyl. Dipole moment data[13] also have been interpreted to support a *trans* structure for a series of N-methyl benzamides. When the amides are coördinated to metal ions, a steric repulsion arises between coördinated ligands if R_1 and R_3 are both alkyl. Figure 3 illustrates the nature of this effect. Only two groups are illustrated and the concept is simplified to describe the effect. When R_1 is H as in DMF, DEF, or NMF, there is a pronounced decrease in steric repulsion, a strong interaction of the metal ion with the ligand results, and *Dq* is large compared to the case where R_1 is an alkyl group. The steric effect also is reduced in acetamide where both R_2 and R_3 are hydrogen. An appreciable steric effect is encountered in NMA, where R_1 and R_3 are methyl, and also in DMA and DMBu, where all R groups are alkyl. This explanation accounts for the difference in the *Dq* values for acetamide and NMA as well as the similarity of NMA and DMA.[14] Within a given main category, slight inductive effects can be detected as evidenced by the order DMF $>$ NMF and the order DMA $>$ NMA. A similar steric effect is operative in the chromium complexes.

It is difficult to interpret the β values obtained for the nickel complexes. The differences are so small as to be within the error limits of the calculated and predicted ν_2 bands (Table II). There appears to be a real difference between the β values for the chromium and nickel complexes of acetamide and DMA. In contrast to the halide ions and in accord with predictions from steric considerations the trend in *Dq* and β is in the same direction for these two amides.

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[9] C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

[10] C. K. Jørgenson, *Acta Chem. Scand.*, **9**, 1362 (1955).

[11] W. Low, *Phys. Rev.*, **109**, 247 (1958).

[12] The correlation was obtained for non-hydrogen bonded bases. Therefore, the heats predicted for the above series would be those for the non-hydrogen bonded donors interacting with phenol, *i.e.*, the measured heat of the amide-phenol interaction plus the heat of self-hydrogen bonding.

[13] J. E. Worsham and M. E. Hobbs, *J. Am. Chem. Soc.*, **76**, 206 (1954).

[14] Figure 3 is a simplified drawing to make clear the nature of the steric effect we are proposing. Actually the amide may be rotated slightly about the metal oxygen bond to minimize steric effects and interaction of each amide with all four of its neighbors is involved when a steric effect is operative.

It is of interest to place these amides in the spectrochemical series with other ligands. Toward Ni(II) these results are obtained: NH_3 (1060) > H_2O (860) > DMF (850) > C_5H_5NO (840) ~ DEF (840) ~ NMF (838) > acetamide (824) > TMSO (775) ~ $(CH_3)_2SO$ (773) ~ DMA (769) > NMA (752) ~ DMBu (749).

Toward Cr(III) this series is found: NH_3 (2160) > H_2O (1740) > acetamide (1645) > urea (1600) > TMSO (1575) ~ $(CH_3)_2SO$ (1577) > C_5H_5NO (1539) > DMA (1517).

Except for the ligand pyridine N-oxide, the Dq value toward chromium is approximately twice that of the corresponding nickel complex. This fact, plus the low β values for the pyridine N-oxide complexes,[6] indicates that the interactions of metal ions with this ligand are less covalent than with the amides and sulfoxides.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation and Photodecomposition of the Complex Acid, Hydrogen Aquoethylenediaminetetraacetatoferrate(III)

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The diprotic complex acid, hydrogen aquoethylenediaminetetraacetatoferrate(III), was characterized and its photodecomposition by irradiation in the charge-transfer region studied. A first-order production of both iron(II) by electron transfer and carbon dioxide by decarboxylation of the ligand was observed. Infrared studies indicate the presence of one uncoördinated carboxylate group in the unirradiated chelate and that the decarboxylation occurs in a coördinated carboxylate group.

Jones and Long[2] commented briefly on the photosensitivity of the ethylenediamine tetraacetatoferrate(III) anion, FeY^-, in their study of the iron(III) and iron(II) chelates of that ligand, and proposed the mechanism

$$FeY^- + h\nu \longrightarrow FeY^{-2} + \text{decomp. prod. of Y}$$

$$FeY^{-2} + {}^1/_2H_2O + {}^1/_4H_2O \longrightarrow FeY^- + OH^-$$

$$\text{(repeated photoreduction–reoxidation)} \longrightarrow Fe(OH)_3\downarrow$$

Hill-Cottingham[3] has contended that this reaction sequence is not correct, as he found no decomposition of the ligand taking place.

In our study of the photochemical reduction of the complex acid, $HFeYH_2O$, by irradiation in the charge-transfer region, carbon dioxide was observed to be one of the end products. The ligand undergoes the loss of one chelating carboxylate group, presumably *via* a free radical mechanism.

Experimental

Preparation and Properties of the Complex Acid.—The method of preparation was similar to that of Brintzinger, *et al.*,[4] except that a slight excess of H_4Y over the stoichiometric amount was used. Forty g. of reagent grade iron(III) nitrate, $Fe(NO_3)_3\cdot 9H_2O$, was dissolved in 100 ml. of water and the solution filtered. This solution then was added dropwise to a solution of 50 ml. of concentrated ammonium hydroxide (28–30%) and 50 ml. of water. The precipitated iron(III) hydroxide was washed five times by centrifugation and then added to a suspension of 35 g. of ethylenediaminetetraacetic acid (Fisher Certified grade, 99.2% purity by titration) in 100 ml. of water. The mixture was heated on a steam cone with stirring for approximately 1 hr. until no residue remained. Any uncomplexed free acid that precipitated when the solution cooled to room temperature was filtered from solution. Approximately 50 ml. of acetone was added and the solution heated on the steam bath until boiling ceased. This was repeated twice more with 50-ml. additions of acetone, by which time crystals of the complex acid began to form. Another 50 ml. of acetone was added and the solution set aside to cool to room temperature. The crystals of the complex acid then were collected, dissolved in a minimum quantity of water at room temperature, and reprecipitated by adding a large quantity of acetone. The yield was about 20 g. of bright yellow crystals.

Anal. Calcd. for $C_{10}H_{15}N_2O_9Fe$: C, 33.08; H, 4.16; N, 7.72; Fe, 15.38. Found: C, 33.02; H, 4.28; N, 7.66; Fe (as Fe_2O_3 from ash), 15.11.

The neutralization curve of the complex acid shows two inflections, one at pH 4.7 and the other at pH 9.7, indicating a diprotic acid whose pK_a values are approximately 2.2 and 7.6. The formula weight determined from the first inflection point was 363 (the theoretical for $HFeYH_2O$).

When excess iron(III) hydroxide was used to prepare the complex acid, a brown compound was obtained. Infrared spectra indicated the absence of a free carboxylic acid group by the absence of bands at 5.7 and 8.3 μ. Analysis showed 28.02% carbon, 4.28% hydrogen, 6.47% nitrogen, and 18.92% iron (from ignition to the ash), which indicated a ratio of Fe:Y:H_2O of 4:3:10.

If in the recrystallization of the complex acid only enough acetone was added to form a suspension of the solid, heating of the solution caused a dark red, oily liquid to form on the sides

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[1] Based upon a thesis submitted by Charles E. Godsey in partial fulfillment of the requirements for the degree of Master of Science, Kansas State University.

[2] S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).

[3] D. G. Hill-Cottingham, *Nature*, **175**, 347 (1955).

[4] V. H. Brintzinger, H. Thiele, and U. Müller, *Z. anorg. Chem.*, **251**, 289 (1943).