Iron(III) and Cobalt(III) Complexes of Some N-Salicylideneamino Acids[1a]

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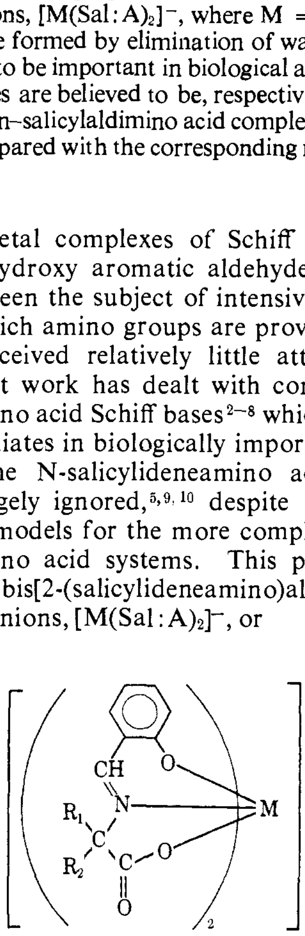
Abstract: The preparation and characterization of a series of bis[2-(saliyclideneamino)alkanoato(2−)]metalate(III) anions, $[M(Sal:A)_2]^-$, where M = Fe or Co, are described. The ligands are bivalent, terdentate Schiff bases which are formed by elimination of water between salicylaldehyde and an α-amino acid and which are of the type believed to be important in biological amination processes. Dark red and orange modifications of some of the iron complexes are believed to be, respectively, the 1,2,6 and the 1,2,3 geometrical isomers. Certain physical properties of the iron–salicylaldimino acid complexes prepared with either *d*- or *l*-alanine or with *l*-valine are very different from those prepared with the corresponding racemic amino acids.

Although metal complexes of Schiff bases derived from *o*-hydroxy aromatic aldehydes and various amines have been the subject of intensive research, the chelates in which amino groups are provided by amino acids have received relatively little attention. Most of the relevant work has dealt with complexes of the pyridoxal–amino acid Schiff bases[2–8] which are believed to be intermediates in biologically important amination processes. The N-salicylideneamino acid complexes have been largely ignored,[5,9,10] despite their apparent usefulness as models for the more complicated N-pyridoxylideneamino acid systems. This paper describes a number of bis[2-(salicylideneamino)alkanoato(2−)]-metalate(III) anions, $[M(Sal:A)_2]^-$, or



I

where R_1 and R_2 are hydrogen or alkyl or aryl groups, and *M* is iron or cobalt. Simple mnemonic abbreviations for the amino acid replace the symbol A in the condensed formula where reference is made to specific compounds.

Results and Discussion

Preparations. The ligands employed in this study were usually prepared *in situ* from salicylaldehyde and the appropriate amino acid. Although this procedure avoided the difficulties involved in working with either the free N-salicylideneamino acids[11–13] or their salts,[14–16] it also admitted the possibility of forming the various bidentate and mixed complexes. That only the Schiff-base products were actually obtained emphasizes the stability of the fused chelate ring system. Quantitative yields of the iron complexes were obtained by adding iron(III) nitrate to alcoholic solutions of stoichiometric amounts of salicylaldehyde, the amino acid, and potassium hydroxide. Although the reaction of iron(III) hydroxide with a mixture of the ligand components gave only poor yields, the corresponding reaction with cobalt(III) hydroxide proved to be an excellent synthetic procedure. The more usual sources of cobalt(III) complexes, *viz.*, sodium triscarbonatocobaltate(III) trihydrate and hexaamminecobalt(III) chloride, gave the desired products, but side reactions and incomplete substitution, respectively, made their use inconvenient. The cobalt complexes were also formed when a mixture of salicylaldehyde, the amino acid, sodium hydroxide, and a cobalt(II) salt was oxidized with air or hydrogen peroxide. Although this method was not used for this study, it may be more useful with oxidizable ligands than is generally supposed.

Composition. Microanalyses of the compounds prepared are shown in Table I. Other evidence supporting their compositions is given in the Experimental Section. The analyses reported correspond to compounds which contain varying amounts of water. Some of the materials are hygroscopic and retain moisture even if heated for long periods or treated with water-scavenging agents such as dimethoxypropane. The tenacity with which this water is held suggests that it may be a constitutional part of the complexes. Although the addition of water to coordinated Schiff bases to give coordinated amino alcohols is known,[17,18]

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Table I. Analytical Data for N-Salicylideneamino Acid Complexes

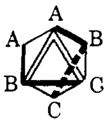
Compound[a,b]	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
K[Fe(Sal:gly)$_2$]·0.5H$_2$O	47.18	47.46	3.30	3.44	6.11	5.97
K[Fe(Sal:*dl*-alan)$_2$]·H$_2$O	48.50	48.47	4.07	3.86	5.65	5.47
K[Fe(Sal:*d*-alan)$_2$]·H$_2$O	48.50	48.63	4.07	3.86	5.65	5.33
K[Fe(Sal:*l*-alan)$_2$]·H$_2$O	48.50	48.84	4.07	4.13	5.65	5.57
K[Fe(Sal:β-alan)$_2$]·0.5H$_2$O	49.39	48.94	3.94	4.06	5.76	5.98
K[Fe(Sal:*dl*-but)$_2$]	52.29	51.83	4.39	4.52	5.54	5.22
K[Fe(Sal:*dl*-but)$_2$]·H$_2$O[c]	50.49	50.05	4.62	4.42	5.35	5.55
K[Fe(Sal:isobut)$_2$]·0.5H$_2$O	51.37	51.36	4.51	4.61	5.44	5.63
K[Fe(Sal:isobut)$_2$][c]	52.29	52.26	4.39	4.82	5.54	5.69
K[Fe(Sal:*dl*-norval)$_2$]	54.04	54.37	4.91	5.36	5.25	5.39
K[Fe(Sal:*dl*-norval)$_2$][c]	54.04	53.64	4.91	5.19	5.25	5.38
K[Fe(Sal:*dl*-val)$_2$]1·5H$_2$O	51.43	51.51	5.22	5.03	5.00	5.25
K[Fe(Sal:*l*-val)$_2$]·0.5H$_2$O	53.14	53.04	5.02	5.29	5.16	5.08
K[Fe(Sal:*dl*-isoval)$_2$]·0.5H$_2$O	53.14	52.96	5.02	5.43	5.16	5.14
K[Fe(Sal:*dl*-isoval)$_2$]·2H$_2$O[c]	50.62	50.86	5.31	5.25	4.92	5.34
K[Fe(Sal:*dl*-norleuc)$_2$]·H$_2$O	53.89	54.16	5.57	5.31	4.83	5.16
K[Fe(Sal:*dl*-leuc)$_2$]·0.5H$_2$O	54.74	54.58	5.48	5.55	4.91	5.22
K[Fe(Sal:*dl*-isoleuc)$_2$][c]	55.62	55.25	5.39	5.52	4.99	4.91
K[Fe(Sal:*dl*-isoleuc)$_2$]·0.5H$_2$O	54.74	54.31	5.48	5.17	4.91	4.89
K[Fe(Sal:*dl*-oct)$_2$]	57.51	57.48	6.27	6.42	4.47	4.38
K[Fe(Sal:Phgly)$_2$]·H$_2$O	58.17	58.23	3.91	3.86	4.52	4.57
K[Fe(Sal:Phalan)$_2$]	61.05	61.10	4.16	4.43	4.45	4.48
K[Fe(Sal:tyr)$_2$]·H$_2$O	56.56	56.75	4.15	4.16	4.12	4.28
H[Fe(Sal:Phgly)$_2$]	63.96	64.13	4.11	4.09	4.97	4.78
Na[Fe(Sal:Phgly)$_2$]·1.5H$_2$O	58.84	59.03	4.11	4.22	4.57	4.75
H[Fe(Sal:gly)$_2$]	52.58	46.85	3.68	3.57	6.81	6.78
Na[Fe(Sal:gly)$_2$]·2H$_2$O	46.08	45.98	3.87	3.60	5.97	6.19
Ba[Fe(Sal:gly)$_2$]$_2$·H$_2$O	44.32	44.10	3.10	3.21	5.74	5.66
HStry[Fe(Sal:gly)$_2$]·1.5 H$_2$O	60.63	60.64	5.22	5.34	7.25	7.40
Na[Co(Sal:gly)$_2$]·2H$_2$O	45.78	45.52	3.84	3.75	5.93	6.52
Na[Co(Sal:*dl*-alan)$_2$]·1.5H$_2$O	48.89	48.46	4.31	3.87	5.70	5.69
Na[Co(Sal:*dl*-but)$_2$]·H$_2$O	51.78	51.54	4.74	4.67	5.51	5.60
Na[Co(Sal:*dl*-norval)$_2$]·H$_2$O	53.54	53.88	5.24	5.28	5.20	5.48
Na[Co(Sal:*l*-val)$_2$]·0.5H$_2$O	54.45	54.81	5.14	5.22	5.29	5.35
Na[Co(Sal:*dl*-norleuc)$_2$]·H$_2$O	55.13	55.04	5.70	5.45	4.94	5.02
Na[Co(Sal:*dl*-oct)$_2$]	57.05	57.01	6.54	6.34	4.43	4.83

[a] The amino acid moieties are represented as follows: gly = glycine, alan = alanine, but = α-aminobutanoic acid, isobut = 2-methylalanine, norval = norvaline, val = valine, isoval = isovaline, norleuc = norleucine, leuc = leucine, isoleuc = isoleucine, oct = α-amino-octanoic acid, Phgly = phenylglycine, Phalan = β-phenylalanine, tyr = tyrosine; Stry = 1-strychnine. [b] Except where otherwise noted [Fe(Sal:A)$_2$]$^-$ is the red isomer. [c] Orange isomer.

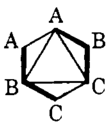
the infrared spectra and the inconstant amounts of water indicate that this reaction did not occur with these compounds.

The complexes are anionic as demonstrated by their quantitative and tenacious absorption by anion-exchange resins. This behavior also confirmed the absence of the uncharged bidentate complexes with the amino acids [MA$_3$], and with salicylaldehyde [MSal$_3$], and permitted estimation of equivalent weights. The iron(III), d^5, complexes exhibited the expected magnetic moments corresponding to the presence of five unpaired electrons; the cobalt(III), d^6, complexes were diamagnetic.

Isomerism. In coordination compounds of the type M(ABC)$_2$ eleven potential isomers exist: an optically active 1,2,6 form (II) and a set of five 1,2,3 forms (III), all but one of which are optically active. If, in addition, the ligands are themselves optically active, any of the three combinations, *dd*, *ll*, and *dl*, may theoretically occur with each form of the complex.



II



III

Previous workers have usually assigned the 1,2,3 structure to bis(terdentate) complexes in which the central nitrogen atom of the ligand is saturated, as in 1,2,3-triaminopropane[19] and aminodiacetic acid,[20] and the 1,2,6 structure to those in which it is unsaturated or aromatic, as in 1,8-bis(salicylideneamino)-3,6-dithiooctane,[21,22] 1,8-bis(salicylideneamino)-3,6-diazaoctane,[23] and terpyridyl.[24-26] Although Dwyer and Lions[27] have assigned the 1,2,3 structure to one isolable form of the cobalt complex of the sexadentate ligand (IV), which is in many respects similar to our terdentate ligands (I), it is much less stable than the form corresponding to the 1,2,6 structure. Molecular models

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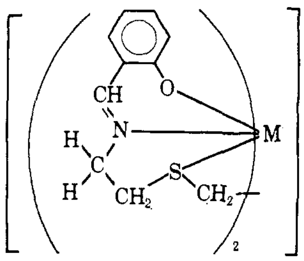
also strongly suggest that the 1,2,6 form of the octahedral complexes of the N-salicylideneamino acids should be much more stable than any of the 1,2,3 forms.



IV

Although no experimental evidence was obtained for isomerism in the $[Co(Sal:A)_2]^-$ compounds, many of the $[Fe(Sal:A)_2]^-$ complexes gave two distinctly different forms. As normally prepared, the iron complexes were dark red powders, but in some cases, when concentrated solutions of these products were allowed to stand or were warmed slightly, a bright orange flocculent precipitate separated. All of these orange compounds were much less soluble in nonpolar solvents than the corresponding red forms. Upon contact with the polar solvents in which they were soluble, they turned dark red before dissolving to give solutions which had the same electronic spectra as the solutions prepared directly from the red forms. If these solutions were then evaporated to dryness or precipitated with a nonsolvent, they gave solids which were identical in all respects with the corresponding red forms. The two modifications are apparently unrelated to optical activity in the ligand since nonactive 2-methyl-2-(salicylideneamino)propanoic acid, Sal:isobut, gave both orange and red forms as readily as did the asymmetric ligands. We assign the 1,2,6 structure to the typical dark red forms and the 1,2,3 structure to the orange forms which appear to retain their identity only in the solid state.

Another phenomenon observed with some of the iron complexes is the physical difference between red isomers prepared from optically active amino acids and those prepared from the corresponding racemic mixtures.[28] The complexes of N-salicylidenealanine with racemic and with either *d*- or *l*-alanine shows remarkably different solubilities although prepared by identical procedures. For example, whereas methylene chloride, chloroform, and nitrobenzene are good solvents for $K[Fe(Sal:d\text{-alan})_2]$ and for $K[Fe(Sal:l\text{-alan})_2]$, $K[Fe(Sal:dl\text{-alan})_2]$ is almost totally insoluble in these solvents. A corollary of this behavior is the gradual and complete precipitation of a product identical with that prepared from the racemic ligand when equal amounts of chloroform solutions of $K[Fe(Sal:d\text{-alan})_2]$ and $K[Fe(Sal:l\text{-alan})_2]$ are mixed and allowed to stand at room temperature. These and other striking solubility differences will be described elsewhere.

The electronic spectra of these N-salicylidenealanine complexes are essentially the same, but there are differences in the X-ray diffraction photographs and in the infrared spectra. The X-ray patterns of the complexes prepared from *d*- and *l*-alanine gave only diffuse halos indicative of an amorphous structure, whereas that of the complex from racemic alanine was rich and sharp. Identical infrared spectra were obtained for $K[Fe(Sal:d\text{-alan})_2]$ and $K[Fe(Sal:l\text{-alan})_2]$, but these differed slightly from the one for $K[Fe(Sal:dl\text{-alan})_2]$ (Table II). These discrepancies were observed repeatedly with different samples and different instruments.

Table II.[a] Differences in the Infrared Spectra of $K[Fe(Sal:alan)_2]$ Isomers

$K[Fe(Sal:$ *dl*-alan$)_2]$	$K[Fe(Sal:$ *d*-alan$)_2]$	$K[Fe(Sal:$ *l*-alan$)_2]$
1075 w	. . .	. . .
1150 m 1142 m	1145 m	1145 m
1268 w	. . .	. . .
1292 s 1308 s	1302 s	1302 s

[a] Band maxima (cm^{-1}); s = strong, m = medium, w = weak.

Marked solubility differences between $K[Fe(Sal:dl\text{-val})_2]$ and $K[Fe(Sal:l\text{-val})_2]$ suggest that formation of physically different complexes with racemic and optically active ligands may be a general phenomenon in this system. This idea is corroborated by some literature reports. In studying the crystal structure of the manganese(II) complex of N-pyridoxalidenevaline, Willstadter, Hamor, and Hoard[8] were forced to use a sample prepared from the racemic amino acid because crystals of the compound from *l*-valine were too disordered for this purpose. Willstadter, *et al.*, noted especially that $[Fe(Pyr:l\text{-val})_2]^-$ "displayed an astonishing internal disorder"; this agrees with our observation that the iron complexes both from N-salicylidene-*dl*-alanine and from N-salicylidene-*dl*-valine are much more crystalline than those prepared from the optically active ligands.

There are at least two possible explanations for the physically different products with racemic and optically active ligands. With racemic salicylideneamino acids either racemic coordination compounds, such as [D*dd*–L*ll*], or mixed ligand complexes, such as D*dl* and L*ld*, could form, whereas such entities are not possible with optically active ligands. We favor the latter alternative because racemic compound formation implies stereospecificity which is unlikely for these complexes[29] and because the formation of the racemic product from a mixture of D(L)-*dd* and L(D)-*ll* occurs slowly as if by ligand exchange.

Electronic Spectra. The visible and ultraviolet absorption spectra of the complexes of the same metal are essentially the same; they are summarized in Table III.

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[28] Physical differences between crystals of some racemic and optically active organic compounds are well known. The phenomenon has also been described for some coordination compounds: F. Basolo, "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p 340; J. Iball and C. H. Morgan, *Nature*, 202, 689 (1964); R. D. Gillard, H. M. Irving, R. Parkins, N. C. Payne, and L. P. Pettit, *Chem. Commun.*, 81 (1965).

[29] Puckering of the chelate rings, which is absent in these compounds, is probably required for stereospecificity: E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959). Molecular models also indicate very little difference in the steric requirements for D*ll* and L*ll*.

Table III. Electronic Spectra of N-Salicyclideneamino Acid Complexes[a]

$[Fe(Sal:A)_2]^-$		$[Co(Sal:A)_2]^-$	
λ_{max}, mμ	Log ϵ_{max}	λ_{max}, mμ	Log ϵ_{max}
470[b]	3.50	*Ca.* 665	1.95
420	3.48	505[d]	2.77
Ca. 310[c]	*Ca.* 3.95	378	3.71
290	4.00	*Ca.* 290[c]	*Ca.* 3.90
260	4.35	*Ca.* 255[c]	*Ca.* 4.65
235	4.60	248	4.72
220	4.55	225	4.66

[a] Ethanol solvent; approximately independent of amino acid except where noted. [b] 480 in bis(N-salicylideneglycinato)ferrate. [c] Shoulder. [d] 480 in bis(N-salicylideneglycinato)cobaltate in 50% aqueous ethanol.

The low solubility of the bis(N-salicylideneglycinato)-cobaltate complex in ethanol necessitated use of a mixed alcohol-water solvent. The only noticeable difference between this spectrum and those given in the table is that the second visible band appears at higher energy, near 480 mμ. The iron-N-salicylideneglycine complex also shows one band slightly shifted from that of its homologs; the normal 470-mμ peak appears at 480 mμ for $[Fe(Sal:gly)_2]^-$. Since the spectra of all of the iron complexes were measured on ethanol solutions, this peculiar effect cannot be a solvent shift but is apparently due to the special nature of the N-salicylideneglycine structure.

The spectrum of $K[Fe(Sal:gly)_2]$ is the same in methanol, ethanol, and 2-propanol, but in aqueous solutions the normal 420-mμ peak appears near 410 mμ as a shoulder on the adjacent ultraviolet band. This solvent shift is general in that aqueous solutions of all of the iron complexes examined display the 410-mμ shoulder, whereas the band uniformly appears as a peak at 420 mμ in any nonaqueous solvent. This, however, is the only band in any of the electronic spectra which appears to be appreciably influenced by these changes in solvent.

Solutions of the iron complexes which are protected from direct light are surprisingly stable. Upon aging in the dark, a 10^{-4} *M* aqueous solution of $K[Fe(Sal:gly)_2]$ slowly deposits a yellow, iron-containing solid, but there is no change in the position and only a slight change in the intensity of the electronic absorption bands (Table IV). No evidence for decomposition of this complex in various alcohols was observed after the solutions had aged in the dark for 3 weeks. After only 24 hr in the ordinary light of the laboratory, an aqueous solution of $K[Fe(Sal:gly)_2]$ deposits a large amount of yellow solid, and the electronic spectrum undergoes the changes indicated in Table IV.

Infrared Spectra. Water of hydration is indicated by a broad band centered near 3400 cm^{-1}. In a few cases spectra were obtained in which the 3400-cm^{-1} band was missing although the spectra were similar in other respects to the characteristic patterns. This result substantiates our belief that water is not an essential component of the complexes. The amine N-H stretching frequency and the hydroxyl O-H stretching frequency, where not covered by the water absorption, were shown to be absent from the spectra.

Table IV. Stability of Aqueous Solutions of $K[Fe(Sal:gly)_2]$

Fresh		3 weeks (dark)		24 hr (light)	
λ_{max}, mμ	Log ϵ_{max}	λ_{max}, mμ	Log ϵ_{max}	λ_{max}, mμ	Log ϵ_{max}
480	(3.45)	480	(3.38)	487	(3.25)
410	(3.38)	405	(3.36)	405	(3.25)
Ca. 320	(3.93)	*Ca.* 320	(3.91)	*Ca.* 320	(3.90)
295	(3.93)	295	(3.89)	295	(3.85)
260	(4.36)	260	(4.37)	260	(4.38)
232	(4.56)	232	(4.46)	. . .	
220	(4.49)	220	(4.49)	205	(4.64)

The low-intensity aromatic and conjugated azomethine C-H stretching bands in the potassium bromide and the hexachlorobutadiene spectra appear near 3050 cm^{-1}; they are not separately distinguishable. The aliphatic C-H stretching vibration of the amino acid moiety is seen in the potassium bromide spectra near 2950 cm^{-1}.

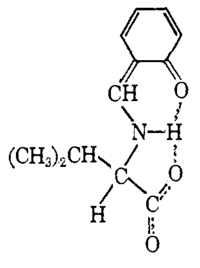
Table V presents the bands which appear in the functional group and fingerprint regions of the infrared spectra of the iron complexes. The red and orange isomers of the same ligand differ slightly, but no relevant conclusions were drawn from these observations. Those vibrations which are characteristic of specific ligands are not reported. Bands of interest in the spectra of glycinate, salicylaldehydate, and N-salicylideneglycinate(2−) are shown for comparison.

Table V. Infrared Spectra[a]

Assignment[b]	$[Fe(Sal:A)_2]^-$	$Sal:gly^{2-}$	Sal^-	Gly^-
			1660 s	
			1648 s	
C=N, str	1620–1630 s	1630 s		
Ring	1598–1630 s	1598 s	1600 s	
Antisym CO_2, str[c,d]	1575–1590 s	1580 s		1575 s
			1528 m	
Ring	1535–1550 m	1535 m	1515 m	
CH, def	1465–1470 m	1470 m		1480 m
Ring	1445–1450 s		1450 s	
Sym CO_2, str[c]	1395–1420 m	1405 m		1410 m
CH, def	1350–1365 s		1350 m	
C—O, str	1335–1340 s	1335 s	1325 m	1335 s
?	1295–1310 s	1300s		1300 s
			1200 w	
Ar-H in-plane, def	1195–1205 m		1165 m	
	1145–1150 m	1145 s	1148 s	
	1125–1135 w	1118 m	1118 m	
	1025–1030 w	1030 m	1032 w	
C—C skeletal	895–910 m	895 m	891 m	892 m
=CH out-of-plane, def	845–840 w	850 w	855 w	
?	795–805 m			
Ar—H out-of-plane, def	750–765 m	760 m	763 s	
	730–740 w	730 w	732 s	

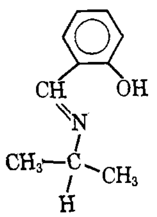
[a] Band positions are given in reciprocal centimeters: s = strong, m = medium, w = weak. [b] Assignments are derived from ref 30 except as noted. [c] Reference 13. [d] Frequently incompletely developed.

Rather disparate infrared assignments have been assigned to compounds of the type discussed. Heinert and Martell[13] have suggested an amide vinylog structure for N-salicylidenevalinate(1−)



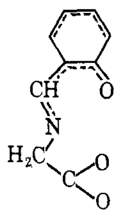
V

whereas Teyssie and Charette[30] assigned the more conventional phenol–imine structure to the seemingly analogous 2-(N-salicylideneamino)propane



VI

The highest frequency band in the functional group region for both of these compounds (1634 cm^{-1}) is assigned by the two sets of authors to the C=O stretch and to the C=N stretch, respectively. The corresponding band for N-salicylideneglycinate(2−)



VII

in which there can be no tautomerism, is only slightly lower (1630 cm^{-1}). The monobasic Schiff base V has a medium intensity band at 1513 cm^{-1}; this was attributed by Heinert and Martell to the exocyclic C=C stretch; in the dibasic compounds (VII) there is a similar band at 1540 cm^{-1}. If the resonance suggested in VII lowers the frequency of the carbonyl double bond of V when the proton is removed, it seems unlikely that it would also increase the frequency of the ethylenic double bond.

Teyssie and Charette, on the other hand, have considered the 1540-cm^{-1} band which appears in the spectra of their bivalent, tetracoordinate chelates of VI to be due to a 1584-cm^{-1} ring-stretching mode in the ligand which has been shifted to a lower frequency as the aromatic ring is loosened by cross-resonance between the aromatic and the chelate rings. The band assignments given in Table V are derived primarily from the Teyssie–Charette paper which we consider to be more compatible with the results of the present study.

The cobalt complexes give the same number of infrared bands as the corresponding iron compounds. Whereas most of these bands occur near the same frequencies and with the same intensities for both metals, there are a few consistent differences which are shown in Table VI. With the exception of the [M(Sal:gly)$_2$]$^-$ compounds, the C=N stretching frequency near 1625 cm^{-1} in [Fe(Sal:A)$_2$]$^-$ shifts to about 1640 cm^{-1} in [Co(Sal:A)$_2$]$^-$; a similar shift, from 1630 to 1643 cm^{-1}, has been observed[31] from the iron(III) and cobalt(III) complexes of 1,8-salicylideneamino-3,6-diazaoctane. Less marked but still significant shifts to higher energies also occur in the aromatic ring–phenolic oxygen stretching mode and in a band near 800 cm^{-1} which may be due to a chelate ring vibration since it does not appear in the free ligand. These effects seem to imply that a general tightening of the salicylaldimine chelate ring takes place when iron is replaced by the strongly π-bonding cobalt ion. The failure of the N-salicylideneglycine complexes to display the same infrared shifts as their homologs is not understood.

Table VI. Comparison of Selected Infrared Absorptions in [M(Sal:A)$_2$]$^-$ Complexes

Ligand	M	— Band positions, cm^{-1} —		
Sal:gly	Fe	1625	1340	802
	Co	1625	1352	798
Sal:*dl*-alan	Fe	1623	1335	800
	Co	1635	1345	805
Sal:*dl*-but	Fe	1628	1340	805
	Co	1642	1355	815
Sal:*dl*-norval	Fe	1620	1338	795
	Co	1642	1350	810
Sal:*dl*-val	Fe	1620	1335	801
	Co	1640	1348	807
Sal:*dl*-norleuc	Fe	1625	1340	800
	Co	1638	1350	810
Sal:*dl*-oct	Fe	1625	1338	800
	Co	1642	1350	811

Experimental Section

Preparations. A. Iron Complexes. The same general procedure was followed for all amino acids. An ethanolic solution of salicylaldehyde (vacuum distilled under nitrogen) (1.22 g, 10 mmoles) was cooled in an ice bath and stirred under an atmosphere of nitrogen. Addition of a solution of the amino acid (10 mmoles) and potassium hydroxide (1.32 g of 85% KOH, 20 mmoles) in absolute ethanol gave a bright yellow solution of the ligand. To this, an ethanolic solution of iron(III) nitrate enneahydrate (2.02 g, 5 mmoles) was added over about 15 min. A quantitative amount (1.52 g, 1.5 mmoles) of potassium nitrate was recovered as solid by-product; the complex was isolated from the dark red solution by concentrating it until crystallization occurred or by adding a nonsolvent. When the solution was evaporated to dryness, slightly more than a quantitative yield (*ca.* 105%) of the product was usually

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[30] P. Teyssie and J. J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963).

[31] B. Das Sarma, K. R. Ray, R. E. Sievers, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **86**, 14 (1964).

obtained, doubtlessly due to the presence of retained moisture. The complexes were dried under vacuum at 110°. Products prepared in this manner were deep red-brown in color. Aqueous solutions of these complexes hydrolyzed only slowly in 0.5 *N* KOH, but were immediately attacked by excess 0.1 *N* HNO_3 which released salicylaldehyde and converted the characteristic red color to purple.

A bright orange form of some of the potassium salts of the iron complexes precipitated from solutions of the dark red form in certain solvents. These products were usually prepared by stirring an excess of the red form with the selected solvent, quickly filtering the mixture, and allowing the intensely colored filtrate to stand until the orange solid separated. After precipitation was complete, the supernatant liquids were very nearly colorless. These transformations took place even if the solvent had been carefully dried and if the red solutions were stored in the dark under nitrogen. The time required for the precipitation to take place varied a great deal, depending on the structure of the ligand and on the solvent chosen. In some cases mere contact of the solid red form with the solvent effected isomerization. The orange products and the solvents from which they were obtained are as follows: $K[Fe(Sal{:}but)_2]$ (2-propanol); $K[Fe(Sal{:}isobut)_2]$ (acetone); $K[Fe(Sal{:}norval)_2]$ (acetone); $K[Fe(Sal{:}isoval)_2]$ (chloroform); and $K[Fe(Sal{:}isoleuc)_2]$ (benzene). These products were washed first with the solvent from which they precipitated and then with ethyl ether. The orange products were dried under air which had been dehumidified with molecular sieves and then at 110° under vacuum. Prolonged contact with humid air caused reversion to the dark red forms.

Other salts of the iron anions were prepared either by use of the appropriate hydroxide or through cation exchange. In the latter case a column of Dowex 50W-X8 in the acid form was treated with an excess of the appropriate base in methanol and washed with methanol until the effluent was neutral. A methanol solution containing much less than the amount of $K[Fe(Sal{:}gly)_2]$ required to saturate the resin was then passed through the column. Complete exchange was indicated by a negative flame test for potassium in the effluent, from which the complex was obtained by evaporation. For the preparation of $H[Fe(Sal{:}gly)_2]$, Dowex 50W-X8 was used directly in the acid form. This compound was also prepared by concentration of an ethanol solution containing the potassium salt and exactly 1 equiv of 0.10 *N* nitric acid. The complex $H[Fe(Sal{:}Phgly)_2]$ precipitated in a pure form from an aqueous solution of the corresponding potassium salt on careful addition of 0.10 *N* nitric acid. Addition of an aqueous barium chloride solution to a saturated aqueous solution of $K[Fe(Sal{:}gly)_2]$ precipitated $Ba[Fe(Sal{:}gly)_2]_2$. *l*-Strychnine hydrosulfate pentahydrate, $(HStry)_2SO_4 \cdot 5H_2O$, was intimately mixed in a solid state with an equivalent amount of $Ba[Fe(Sal{:}gly)_2]_2$ and the mixture extracted with methylene chloride. Addition of ether to this extract precipitated *l*-HStry-DL-$[Fe(Sal{:}gly)_2]$ in quantitative yield.[32]

B. **Cobalt Complex.** (1) **Cobalt(III) Hydroxide Method.** Hydrous cobalt(III) hydroxide was prepared by adding an excess of solid sodium peroxide cautiously to an aqueous solution of cobalt(II) nitrate hexahydrate (1.75 g, 5 mmoles + 20% excess), centrifuging, and washing the gelatinous precipitate until the wash water was neutral. This product was slurried under nitrogen with an aqueous or alcoholic solution of salicylaldehyde (1.22 g, 10 mmoles), the amino acid (10 mmoles), and sodium hydroxide (0.21 g of 97% NaOH, 5 mmoles) at 50–60° with water or at reflux with methanol or ethanol. After several hours, any undissolved cobalt(III) hydroxide was filtered from the deep brown solution; the product was obtained in 85–90% yield by addition of a nonsolvent or by complete evaporation.

(2) **Sodium Triscarbonatocobaltate(III) Method.** A mixture of sodium triscarbonatocobaltate(III) trihydrate[33] (1.81 g, 5 mmoles) and salicylaldehyde (1.22 g, 10 mmoles) was stirred in alcohol under nitrogen at room temperature while a solution of the amino acid (10 mmoles) in 10 ml of 1.00 *N* nitric acid (10 mmoles) was added slowly. If the red-brown color did not form after complete addition of the acid, the reaction mixture was heated on a stream bath for 10–15 min. The filtrate from this mixture was evaporated to dryness, the residue dissolved in an alcohol, and the solution separated from the sodium nitrate. The complex was obtained by precipitation with a nonsolvent or by evaporation to dryness. A relatively large amount of a yellow-orange by-product frequently formed in this reaction.

(3) **Hexaamminecobalt(III) Chloride Method.** A mixture of hexaamminecobalt(III) chloride (1.34 g, 5 mmoles), salicylaldehyde (1.22 g, 10 mmoles), the amino acid (10 mmoles), and sodium hydroxide (0.82 g of 97% NaOH, 20 mmoles) in water or alcohol was heated to 50–60°. As the reaction proceeded, ammonia was evolved and the mixture became dark brown. After at least 8 hr with water as the solvent or after several days with methanol or ethanol, the reaction mixture was filtered and the filtrate treated as in method 1. In some cases several recrystallizations were necessary to give compounds for which a N–H stretching vibration in the infrared spectrum did not appear.

(4) **Oxidation Method.** A clear, ice-cold solution of cobalt(II) nitrate hexahydrate (1.45 g, 5 mmoles) in aqueous alcohol yielded a light yellow-orange suspension when treated with an alcoholic solution of salicylaldehyde (1.22 g, 10 mmoles), the amino acid (10 mmoles), and sodium hydroxide (0.21 g of 97% NaOH, 5 mmoles). While this mixture was being stirred, 10 ml of 30% hydrogen peroxide was carefully added. When the mixture was allowed to warm slowly to room temperature, the deep red color characteristic of the desired complex developed within a few minutes. The liquid was filtered and treated as in method 1 to recover the complex in a fair yield (50–75%).

After purification, all of the $Na[Co(Sal{:}A)_2]$ complexes were air dried and then treated under vacuum at 110° for at least 8 hr. They were not attacked by cold, concentrated alkali or by moderately concentrated acids.

Analyses. Microanalytical C, H, N data are reported in Table I. In a few cases the transition metal was also analyzed. Iron was determined by dichromate titration and spectrophotometrically as the iron(II)–1,10-phenanthroline complex.[34] *Anal.* Calcd for $K[Fe(Sal{:}Phalan)_2]$: Fe, 8.87. Found: Fe, 9.31. Calcd for $K[Fe(Sal{:}gly)_2]\cdot 0.5H_2O$: Fe, 12.20. Found: Fe, 12.28. Cobalt was determined spectrophotometrically in 50% acetone by the thiocyanate procedure.[35] *Anal.* Calcd for $Na[Co(Sal{:}but)_2]\cdot H_2O$: Co, 11.55. Found: Co, 11.50.

The equivalent weight of $K[Fe(Sal{:}gly)_2]$ was evaluated by titrating with silver nitrate[34] the amount of chloride discharged when the complex was passed through a column containing an excess of the chloride form of Dowex 2-X8. *Anal.* Calcd for $K[Fe(Sal{:}gly)_2]$: equiv wt, 444. Found: equiv wt, 449. Attempts to determine equivalent weights using the hydroxide form of the anion-exchange resin and simple acid titration of the effluent gave high equivalent weights with the iron samples, apparently because the strong base generated by the reaction tended to hydrolyze the complexes on the column.

Magnetic Susceptibilities. Magnetic susceptibilities were determined by the Guoy method[36] using mercury(II) tetrakis(thiocyano)-cobaltate(II) ($\chi = 16.44 \times 10^{-6}$ emu) as the calibration standard: calculated for $K[Fe(Sal{:}gly)_2]$, $\mu = 5.99$ BM (spin only); found 5.95 BM. Samples of the cobalt complexes prepared from cobalt(III) hydroxide were diamagnetic. The small, variable paramagnetism in the samples prepared from the carbonato complex is in agreement with other work[37] and suggests the presence of cobalt(II) in this intermediate.

X-Ray Diffraction Patterns. X-Ray diffraction patterns were obtained by the Debye–Scherrer method[38] using an iron target with a MnO_2 filter. In general, only qualitative visual comparison of the developed films was made, but in a few cases the distances between corresponding lines in the patterns were measured and the relative intensities of lines visually estimated.

Electronic Spectra. A Cary Model 14 M recording spectrophotometer was used to obtain the quantitative ultraviolet, visible, and near-infrared spectra of solutions in 1- or 10-cm quartz cells. These well-defined spectra were constant for all compounds of the same transition metal and in all of the solvents tested except as noted previously. The spectra are described as they appeared; resolution analysis of the individual bonds was not attempted.

Infrared Spectra. The infrared spectra were obtained on Nujol and hexachlorobutadiene mulls or in potassium bromide disks. Perkin-Elmer infrared spectrophotometers, Models 21 and 521,

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and Beckman IR-7 and IR-5A infrared spectrophotometers were employed. In general, the band positions cited are considered to be accurate within 5 cm^{-1}.

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