the strengthening of the metal–olefin bonds by additional retrodative bonding to the coordinated olefins. This is a consequence of greater electron density on the metal atom arising from the presence of fewer strongly π-accepting (*i.e.*, electron-withdrawing) carbonyl groups.

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Chelates of Iron(III), Cobalt(III), Copper(II), and Zinc(II) with 2-(Trifluoroacetyl)picolinate Ion and Copper(II) with 2-(Acetyl)picolinate Ion

BY CHARLES A. ROOT, JAY E. ROWE, JR., AND HANS VEENING

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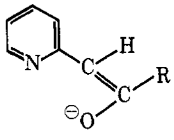
The Co(III), Fe(III), Zn(II), and Cu(II) complexes of trifluoroacetylpicolinate ion, TFAP, and the Cu(II) complex of acetylpicolinate ion, AP, are prepared and characterized. All the complexes are monomeric and neutral. Molecular weights, magnetic moments, electronic spectra, and ^1H and ^{19}F magnetic resonance data are reported. Particular attention is given to the structure of $Co(TFAP)_3$. Chemical shift differences of the three olefinic chelate ring proton resonances and of the three uniquely oriented CF_3 groups and analysis of the electronic spectrum indicate the synthesis of $Co(TFAP)_3$ to be highly specific for the meridional isomer.

Chelates of anions derived from 2-(trifluoroacetyl)picoline[1] and 2-(acetyl)picoline were first reported by McGrath and Levine[2] and by Beckett, Kerridge, Clark, and Smith.[3] McGrath and Levine developed a new synthesis of perfluoroacetylpicolines and found that these compounds react with copper(II) to give brown precipitates, mp 219.5–220°. They assumed that these compounds were copper chelates of the newly synthesized ligand. Beckett, Kerridge, Clark, and Smith studied the antibacterial activity of 2-phenacylpyridine and related compounds and found that it reacted with copper(II), iron(II), iron(III), and cobalt(II).[3] The resulting complexes were not characterized.

We report here the synthesis and characterization of Zn(II), Fe(III), Co(III), and Cu(II) complexes of the enolate derived from 2-(trifluoroacetyl)picoline, TFAP, and the copper(II) complex of 2-(acetyl)picolinate ion (AP). A discussion of the isomeric forms of $Co(TFAP)_3$ is included.



AP, R = CH_3
TFAP, R = CF_3

Experimental Section

Preparation of the Ligands.—2-(Trifluoroacetyl)picoline was synthesized according to the method described by McGrath and Levine,[2] and 2-(acetyl)picoline was prepared by the procedure of Burger and Allyot.[4]

Preparation of the Chelates. Tris(trifluoroacetylpicolinato)iron(III).—To 0.27 g (0.0010 mol) of ferric chloride, dissolved in water, was added 0.57 g (0.0030 mol) of trifluoroacetylpicoline dissolved in 25 ml of 95% ethanol. The mixture immediately turned purple and more water was added to decrease the solubility of the complex. The fine purple precipitate was filtered and recrystallized from a 1:4 benzene–petroleum ether mixture; mp 205°; yield 34%. *Anal.* Calcd for $C_{24}H_{15}O_3N_3F_9Fe$: C, 46.48; H, 2.44; N, 6.77; F, 27.57; Fe, 9.00. Found: C, 46.46; H, 2.54; N, 6.67; F, 27.42; Fe, 9.53.

Tris(trifluoroacetylpicolinato)cobalt(III).—An aqueous solution containing 0.24 g (0.0010 mol) of cobaltous chloride was added to 0.57 g (0.0030 mol) of trifluoroacetylpicoline dissolved in 25 ml of 95% ethanol. The mixture was heated to 50° while being stirred. Oxidation was effected by the addition of 1.2 ml of 10% hydrogen peroxide solution. The pink solution turned green and a brownish green precipitate formed quickly. The mixture was cooled and filtered and the resulting product was recrystallized several times from 1:1 benzene–petroleum ether; mp 205–208° dec; yield 64%. *Anal.* Calcd for $C_{24}H_{15}O_3N_3F_9Co$: C, 46.25; H, 2.43; N, 6.74; F, 27.43; Co, 9.45. Found: C, 45.66; H, 2.41; N, 6.52; F, 27.15; Co, 9.44.

Bis(trifluoroacetylpicolinato)copper(II).—Twenty-five milliliters of an absolute ethanol solution containing 0.20 g (0.0010 mol) of copper(II) acetate was treated with 0.38 g of trifluoroacetylpicoline (0.0020 mol) dissolved in 10 ml of absolute ethanol. The mixture was heated, and a dark brown precipitate formed immediately. After cooling, the solution was filtered and the brown crystals were recrystallized twice from ethanol; yield 85%; mp 218–220°. *Anal.* Calcd for $C_{16}H_{10}O_2N_2F_6Cu$: C, 43.70; H, 2.29; N, 6.37; F, 25.92; Cu, 14.45. Found: C, 43.83; H, 2.40; N, 6.32; F, 26.09; Cu, 14.58.

Bis(trifluoroacetylpicolinato)zinc(II).—A solution containing 0.38 g (0.0020 mol) of trifluoroacetylpicoline, dissolved in 95% ethanol, was added to a warm aqueous solution containing 0.29 g (0.0010 mol) of zinc(II) sulfate. The mixture was stirred and heated a few minutes on a hot plate. Upon cooling, white needles were formed and these were filtered and recrystallized from ethanol or chloroform; yield 55%; mp 215°. *Anal.* Calcd for $C_{16}H_{10}O_2N_2F_6Zn$: C, 43.51; H, 2.28; N, 6.34; F, 25.81; Zn, 14.80. Found: C, 43.59; H, 2.30; N, 6.18; F, 25.59; Zn, 14.64.

Bis(acetylpicolinato)copper(II).—Twenty-five milliliters of a 95% ethanol solution containing 0.27 g (0.0020 mol) of acetylpicoline was heated and mixed with 15 ml of an ethanolic solution containing 0.20 g (0.0010 mol) of copper(II) acetate. Complexation occurred immediately with the formation of a dark brown

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[1] The anionic ligands derived by enolization of 2-(trifluoroacetyl)picoline and 2-(acetyl)picoline are abbreviated TFAP and AP, respectively, in this paper.

[2] T. F. McGrath and R. Levine, *J. Amer. Chem. Soc.*, **77**, 3656 (1955).

[3] A. H. Beckett, K. A. Kerridge, P. M. Clark, and W. G. Smith, *J. Pharm. Pharmacol.*, **7**, 717 (1955).

[4] A. Burger and G. E. Allyot, *J. Org. Chem.*, **12**, 345 (1947).

solid. After filtration and recrystallization from 95% ethanol, greenish brown crystals of the chelate were obtained; mp 158°. *Anal.* Calcd for $C_{16}H_{16}O_2N_2Cu$: C, 57.91; H, 4.86; N, 8.44; Cu, 19.14. Found: C, 57.34; H, 4.87; N, 8.19; Cu, 19.23.

The carbon, hydrogen, nitrogen, iron, cobalt, and zinc analyses given for these compounds were performed by M. H. W. Laboratories, Garden City, Mich., and Galbraith Laboratories, Inc., Knoxville, Tenn. Copper analyses were carried out by dissolving a weighed amount of the copper complex in 10 ml of concentrated nitric acid, evaporating the solution to a small volume, and diluting the resulting solution to 50 ml. Excess potassium iodide was added to the solution and the resulting iodine was back-titrated with standard thiosulfate.

Molecular Weights.—Molecular weights for all compounds were determined by vapor pressure osmometry. A Mechrolab vapor pressure osmometer, Model 301A, calibrated with benzil was used.

Magnetic Susceptibilities and Spectral Measurements.—Magnetic susceptibilities were measured by the Gouy method using $Hg[Co(NCS)_4]$ as a standard. Ligand corrections were made using Pascal's constants. A Cary Model 14 recording spectrophotometer was used to determine electronic spectra. For solution spectra of the compounds, 1,2-dichloroethane was used as the solvent and 1.00-cm cells were used. For solid-state spectra, Nujol mulls of the solid complexes were prepared and suspended on filter paper.

Proton magnetic resonance spectra were measured with a Varian A-60A nmr spectrometer using acetone-d_6 as solvent. Benzene was used as the solvent for obtaining the ^{19}F spectrum.

Results and Discussion

The molecular weights of all new compounds reported here have been determined in solution and correspond to monomeric structures for each species; see Table I. In Table II, the magnetic data for the new compounds are given showing normal magnetic moments for each complex. The absorption maxima in the visible–ultraviolet region of the spectrum are given in Table III. Both solution and solid transmittance spectra are reported.

TABLE I

MOLECULAR WEIGHTS[a]

Chelate	Theoret	Found	Chelate	Theoret	Found
$Fe(TFAP)_3$	620	615	$Zn(TFAP)_2$	442	440
$Co(TFAP)_3$	623	615	$Cu(AP)_2$	332	334
$Cu(TFAP)_2$	440	465			

[a] Measurements were made in benzene except for $Zn(TFAP)_2$, for which acetone was used.

TABLE II

MAGNETIC DATA[a]

Compd	$10^6\chi_M$, cgsu	Temp, °C	μ_{eff}, BM
$Cu(AP)_2$	1,600	22	2.02
$Fe(TFAP)_3$	14,400	26	5.92
$Co(TFAP)_3$	−85	24	0.63
$Cu(TFAP)_2$	1,270	19	1.85

[a] μ_{eff} was calculated from susceptibilities corrected for ligand diamagnetism assuming Curie law behavior. The ligand corrections were -73×10^{-6} cgsu for 2-(acetyl)picolinate and -83×10^{-6} cgsu for 2-(trifluoroacetyl)picolinate based on Pascal's constants.

Structurally, the cobalt(III) complex lends itself most readily to further study. There have been several cobalt(III) systems involving unsymmetric bidentate ligands for which fac and mer isomeric structures have been deduced recently from electronic[5-10] and nuclear magnetic resonance[6,10-16] spectral data. The condition that the bidentate ligand contain donor atoms of appreciably different ligand field strength is a necessity for electronic spectroscopy to be of diagnostic value in determining geometric isomerism. This contention is illustrated by the work of those who have studied the spectra of substituted β-diketonate complexes. When unsymmetric ligands such as amino acids[5,7,9,10] and salicylaldimines[8] are used, the rhombic symmetry of the ligand field in the mer isomer (N–N, N–O, and O–O axes) perturbs the energy levels derived for six-coordination of the metal sufficiently to cause splitting of the first spin-allowed d–d transition whereas the fac isomer with three N–O axes yields only the two unsplit ligand field transitions expected for cubic symmetry.

TABLE III

SPECTRAL DATA

Compd	Solvent	$\tilde{\nu}_{max}$,[a] cm^{-1}	ε
$Zn(TFAP)_2$	1,2-Dichloroethane	~25,600 sh	
		29,600	19,000
		35,500	19,300
	Nujol	28,600 br	
		34,200	
$Co(TFAP)_3$	1,2-Dichloroethane	16,400	307
		~22,600 sh	1,080
		27,200	12,200
		~34,500 sh	22,100
	Nujol	~16,500 sh	
		~23,000 sh	
		~26,900	
$Fe(TFAP)_3$	1,2-Dichloroethane	18,500	2,270
		~27,800 sh	9,020
		32,500	20,400
		37,700	25,100
	Nujol	18,200	
		~24,400	
		~30,300	
		~33,900	
		38,000	
$Cu(TFAP)_2$	1,2-Dichloroethane	~16,700 sh	
		~22,200 sh	
		29,800	18,900
		35,100	24,200
$Cu(AP)_2$	1,2-Dichloroethane	~21,300 sh	439
		27,700	9,600
		33,700	16,700
		37,200	12,200
		38,300	45,300
		39,200	76,200
		40,300 sh	124,000
	Nujol	~16,000 sh	
		~21,700 sh	
		26,000 sh	
		27,400	
		33,200	
		33,600	
		42,600 sh	

[a] Abbreviations: sh, shoulder; br, broad.

In this study we have used a bidentate ligand with donors of different ligand field strength and it is expected that splitting of the lowest energy excited state ($^1T_{1g}$ in O_h symmetry) should be observed for the mer isomer. We assign the bands at 16,400 and ~22,600 cm^{-1} in $Co(TFAP)_3$ to transitions from the ground state to the two components of the $^1T_{1g}$ excited

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state expected for the mer isomer. The band at 27,200 cm^{-1} is assigned to the unsplit $^1A_{1g} \rightarrow {}^1T_{2g}$ transition of O_h symmetry. The visible spectrum includes intense ligand and charge-transfer absorption "tails" in the near-ultraviolet–visible region of the spectrum which raises the value of the apparent molar absorptivities above values expected for d–d transitions. The energy difference between the two components of the $^1T_{1g}$ state is quite large (~6200 cm^{-1}) but is comparable to the analogous splitting found for *trans*-Co(en)$_2$Cl$_2^+$ (~6400 cm^{-1}).[6] The assignment of the 27,200-cm^{-1} band is supported by the spectra of other complexes containing oxygen and nitrogen donors in which ligand transitions do not interfere with the crystal field transitions. For example, the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is seen at 27,600 cm^{-1} in *trans*-(*O*),*cis*(*N*)-[Co(gly)$_2$(*l*-pn)]Cl·6H$_2$O[10] and *trans*-Co(en)$_2$F$_2^+$[6] and at 27,000 cm^{-1} in *mer*-Co(β-ala)$_3$.[9]

The ^{1}H and ^{19}F nuclear magnetic resonance spectra of Co(TFAP)$_3$ in acetone-d_6 and benzene, respectively, provide support for the contention that the synthesis provides the mer isomer in vast predominance. The proton resonance spectrum shows a complex pattern typical of 2-substituted pyridines centered at −7.5 ppm from TMS. There are three peaks of equal intensity at −5.89, −6.07, and −6.26 ppm from TMS which are assigned to the –CH=C< protons in the three unique environments of the mer isomeric structure of the six-coordinate complex. The ^{19}F spectrum confirms this assignment showing three peaks of equal intensity at 72.50, 72.55, and 72.66 ppm upfield from CFCl$_3$. Also, in support of these assignments, the ^{1}H spectrum of the zinc(II) complex, assumed to have pseudotetrahedral coordination, affirms the simple spectrum expected for the ligand when all ligands are geometrically equivalent. In acetone-d_6 there is a multiplet at about −7.7 ppm of intensity 4 times that of a singlet at −5.85 ppm from TMS.

There is some evidence that the stereospecificity of the reaction is not complete. Thin layer chromatograms of the product on silica gel H show two components, one present in very small quantity relative to the other. Toluene elutes only the major product whereas absolute ethanol moves both products at slightly different rates. Also, the ^{1}H spectra of some batches of Co(TFAP)$_3$ show absorption above noise level at −6.13 ppm downfield from TMS. These observations suggest that small amounts of the fac isomer are produced.

Although initial studies using high-speed liquid chromatography with uv detection produced only one major elution peak for Co(TFAP)$_3$ and Fe(TFAP)$_3$ using Carbowax-400–Porasil-C as the column packing and 2,2,4-trimethylpentane as the mobile phase; it is planned to examine the liquid chromatographic behavior of these compounds on other column materials in order to facilitate the quantitative measurement of isomer distribution.

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Circular Dichroism of Copper(II) and Palladium(II) Complexes of *N*-Methyl-L-amino Acids and Dipeptides[1]

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Four spin-allowed ligand field bands are identified in the solution circular dichroism of the 2:1 *N*-methyl-L-alanine complexes of Cu(II) and Pd(II). For the Cu(II) complex the CD extrema appear at 510, 560, 656, and 784 nm. Two spin-forbidden transitions are also observed in the Pd(II) complex. A persistent net negative sign is noted for the magnetic dipole allowed transitions of several transition metal ion complexes of L-amino acids and (*S*)-1,2-diaminopropane. A possible role is suggested for π-electron interactions in transmitting asymmetry in amino acid or peptide ligands so that optical activity appears in the ligand field bands of transition metal ion complexes. Both vicinal effects of substituents and chelate ring conformation contribute to the optical activity in the ligand field bands of complexes of *N*-methylamino acids.

From extensive investigations of the optical activity generated in the ligand field bands of tetragonal Ni(II),[2] Pd(II),[3] and Cu(II)[4] complexes by amino acid and small peptide ligands, a hexadecant rule appears to provide the simplest general description of the results. Octant or quadrant rules are unsatisfactory for these complexes. The single main feature leading to the hexadecant sector rule is the consistent negative sign and additivity of CD magnitudes observed for complexes of di- and tripeptides composed of L-amino acid residues.[2-5] Hexadecants may be constructed by dividing the coordination plane including the transition metal ion perpendicularly into eight wedge-shaped sectors with nodal planes along the metal ion–ligand bonds

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[1] This research was supported by a grant from the National Science Foundation.

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