

Base Adducts of β -Ketoenolates. III. Complexes of Cobalt(II) and Nickel(II)¹

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The bis pyridine adduct of nickel(II) acetylacetonate has been studied using single crystal precession X-ray photographs. The complex crystallizes as monoclinic needles: $a = 8.28$, $b = 9.67$, $c = 14.65$ Å., $\beta = 116^\circ 50'$ with two molecules per unit cell. The uniquely determined space group of $P2_1/c$ requires the centrosymmetric trans arrangement. The isomorphous cobalt(II) complex also is reported. Primary amine adducts of several nickel(II) and cobalt(II) β -ketoenolates have been prepared and are found to be stable to Schiff base "rearrangement." Visible and infrared spectra are reported.

Introduction

Certain bivalent metal salicylaldehydes are known to react with primary amines to form Schiff base complexes,² the metal presumably stabilizing the ketamine formed. Several workers³ have demonstrated that certain metal ions may play an important role in stabilizing Schiff base products.

The reaction between a β -ketoenolate complex of a bivalent metal (except beryllium) and an organic base can involve the initial formation of a base adduct (A) followed either by intramolecular rearrangement or by nucleophilic attack by excess base on the coordinated ligand to produce the Schiff base complex (B) of the



metal. While base adducts of primary amines with metal salicylaldehydes do not appear to have been isolated, base adducts of cobalt(II) and nickel(II) acetylacetonate with ammonia, pyridine, and aniline have been known since 1904.⁴ Recently base adducts of several other bivalent transition metal acetylacetonates have been reported.^{1b,5-11}

(1) (a) Abstracted from the M. S. Thesis of J. T. H. This work was presented, in part, at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964. (b) Part II: J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963).

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Two things prompted us to prepare the series of base adducts reported in this study. First, while several recent papers have discussed the properties of bis pyridine adducts of cobalt(II) and nickel(II) acetylacetonate,^{1b,7,9} the structure of the adduct (*i.e.*, whether the complexes are *cis* or *trans*) has not been determined. Secondly, while bis(salicylaldehydato)nickel(II) readily reacts with primary amines to form the Schiff base complex,² no evidence is reported in the literature for a similar reaction between metal acetylacetonates and primary amine bases even though nickel(II) and other metal ions are known to form stable complexes with Schiff bases derived from acetylacetonate.¹²

Experimental

Preparations. The base adducts of nickel(II) and cobalt(II) acetylacetonate listed in Table I were prepared by the following methods.

Method A. To approximately 0.005 mole of Ni(AA)₂ or Co(AA)₂·2H₂O, approximately 0.01 mole of base was added. Methanol (~150 ml.) was added and the mixture heated and evaporated (to ~75 ml.) until all the solid dissolved. The solution was allowed to stand about 2 hr. open to the air. The crystalline product which formed was collected by suction filtration.

Method B. The procedure used was identical with the one reported by Bertrand, *et al.*,⁸ for Co(AA)₂(cy)₂.

Method C. The solid β -ketoenolate complex was dissolved in excess base and the solution evaporated to remove unreacted base.

Except as noted, ligands were obtained commercially or were prepared by standard techniques.^{13,14} The metal β -ketoenolate complexes in general were formed by established procedures.¹⁵

Bis(1-phenyl-1,3-propanediono)nickel(II), Ni(ϕ -Ac)₂. Approximately 20 g. (0.12 mole) of sodium benzoyl-acetaldehyde was dissolved in 250 ml. of water. This solution was filtered and added to a solution of 10 g. (0.04 mole) of Ni(OAc)₂·6H₂O in 600 ml. of water. The light green precipitate which formed was washed with water, ethanol, and ether and air dried; yield

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Table I. Base Adducts of Cobalt(II) and Nickel(II) β -Diketones

Complex ^a	Method	Yield, %	M.p., °C.	Color	Analyses, % ^b		
					C	H	M
Ni(AA) ₂ (py) ₂	A	77	183–184	Blue	57.5 (57.3)	5.8 (5.7)	6.6 (6.7)
Ni(AA) ₂ (cy) ₂	A	83	208–210	Blue	57.9 (57.7)	8.8 (8.8)	6.1 (6.1)
Ni(AA) ₂ (<i>i</i> -p) ₂	A	86	159–160	Blue	51.2 (51.2)	8.5 (8.8)	7.4 (7.4)
Ni(AA) ₂ (<i>n</i> -p) ₂	A	64	167–168	Blue	51.0 (51.2)	8.4 (8.5)	7.3 (7.4)
Ni(AA) ₂ (<i>n</i> -b) ₂	A	72	166–167	Blue	53.5 (53.6)	8.9 (8.9)	6.7 (6.9)
Ni(AA) ₂ bipy	<i>c</i>	87	235 dec.	Green	58.3 (58.2)	5.3 (5.3)	6.8 (6.8)
Ni(ϕ AA) ₂ (py) ₂	B	85	151–153	Green	66.6 (66.8)	5.2 (5.2)	4.9 (5.2)
Ni(ϕ AA) ₂ (cy) ₂	A	89	199–200	Green	66.2 (66.3)	7.4 (7.6)	4.7 (4.0)
Ni(F ₃ AA) ₂ (cy) ₂	B	86	179–180	Blue-green	46.9 (46.9)	5.9 (6.0)	4.8 (5.0)
Ni(ϕ -Ac) ₂ (py) ₂	A	..	173–174	Brownish green	65.6 (65.8)	4.9 (4.7)	5.2 (5.5)
Ni(ϕ -Ac) ₂ (<i>n</i> -b) ₂	C	~100	128–130	Green	61.1 (62.5)	7.2 (7.2)	5.7 (5.6)
Ni(ϕ -Ac) ₂ (<i>n</i> -p) ₂	C	~100	164	Green	62.2 (61.1)	7.0 (6.8)	6.0 (5.9)
Co(AA) ₂ (py) ₂	A	87	150–151	Orange	57.7 (57.5)	5.9 (5.8)	6.5 (6.7)
Co(AA) ₂ (cy) ₂	B	75	168	Orange	57.9 (58.0)	8.9 (8.8)	6.0 (6.1)
Co(AA) ₂ (<i>n</i> -p) ₂	B	75	148–149	Orange	50.9 (51.5)	8.5 (8.5)	7.2 (7.5)
Co(AA) ₂ (<i>n</i> -b) ₂	B	79	147–148	Orange	53.4 (53.5)	8.8 (8.9)	6.7 (6.9)
Co(AA) ₂ bipy	<i>c</i>	80	250–252	Dark orange	58.0 (58.1)	5.3 (5.3)	6.5 (6.5)
Fe(AA) ₂ (py) ₂	<i>d</i>	..	140	Brown-red	57.5 (57.9)	6.1 (5.8)	6.4 (6.8)

^a Abbreviations: AA, acetylacetonate; ϕ AA, benzoylacetonate; F₃AA, 1,1,1-trifluoroacetylacetonate; ϕ -Ac, benzoylacetaldehyde; py, pyridine; *i*-p, isopropylamine; *n*-b, *n*-butylamine; bipy, 1,10-bipyridine; cy, cyclohexylamine. ^b Calculated values in parentheses. ^c See ref. 11. ^d See ref. 6.

~100%, m.p. >325°. *Anal.* Calcd. for NiC₁₈H₁₄O₄: C, 61.2; H, 3.96. Found: C, 61.0; H, 3.88.

Bis(1,3-butanediono)copper(II). While this compound is reported in the literature and is prepared from the sodium salt of acetoacetaldehyde,¹⁶ the convenient preparation reported here gives considerably better yields.

To 5.3 g. (~0.04 mole) of 4,4-dimethoxy-2-butanone (Distillation Products), 10 ml. of 6 *N* HCl was added. The solution turned yellow in about 1 min. After 3–5 min. (no longer) the above solution was added to a copper acetate solution, 4 g. of Cu(OAc)₂·H₂O in 50 ml. of water. Immediately thereafter, 13.6 g. of sodium acetate was added to neutralize the excess acid. The desired complex was extracted into dichloromethane. After drying the CH₂Cl₂ solution with Na₂SO₄, dark blue crystals were obtained upon evaporation. Sublimation at 120° (1 μ) gave a 43% yield, m.p. 153–154° (lit.¹⁶ 153–154°). *Anal.* Calcd. for CuC₈H₁₀O₄: C, 41.2; H, 4.32. Found: C, 41.4; H, 4.28.

Bis(4-amino-3-penten-2-ono)nickel(II). The following procedure represents an alternative way to prepare the recently reported material.¹⁷ “4-Isopropylaminopenten-2-one” was prepared by mixing isopropylamine with acetylacetone¹⁸ at 0° and recrystallizing the white solid from ether. Upon standing at room temperature 2–3 days, a light yellow liquid was formed from the solid. This may be an isomeric form of the Schiff base similar to the compound reported by Dudek and Volpp.¹⁹ This liquid was used in the subsequent preparation of the nickel(II) complex.

To 50 ml. of a 1:1 water and 95% ethanol solution, 2.5 g. (0.01 mole) of Ni(OAc)₂·6H₂O was added. This mixture was made basic (pH 12 with pH indicator paper) by addition of ammonium hydroxide. A 3.2-g. (0.02 mole) sample of “4-isopropylaminopenten-2-one” was dissolved in 10 ml. of 95% ethanol and added to the nickel acetate solution. The mixture was al-

lowed to stand uncovered in the hood for 48 hr. while being kept at pH 12. The red-brown precipitate was collected and recrystallized by dissolving the product in 95% ethanol and precipitating with water. The yield of the crude nickel(II) complex was 1.8 g., or 70% based on the amount of nickel(II) acetate used. The melting point of the recrystallized material was 246–247° (lit.¹⁷ m.p. 246°). *Anal.* Calcd. for NiC₂₀H₁₆O₂N₂: C, 46.7; H, 6.29; N, 10.98. Found: C, 46.7; H, 6.48; N, 10.51.

Spectral Measurements. The near-infrared and visible solution spectra of the complexes in benzene were recorded on a Cary Model 14 spectrophotometer. Reflectance spectra were observed with a standard diffuse reflectance attachment for a Beckman Model DK-2 spectrophotometer. Infrared spectra in Nujol melts were recorded with Beckman Model IR-8 and IR-5A (CsBr) spectrophotometers.

Thermogravimetric Analyses. Thermogravimetric analysis of Ni(AA)₂(py)₂ on a Stanton thermobalance indicated that pyridine was lost essentially continuously from room temperature up, with barely perceptible breaks occurring at loss of ~1 and ~1.8 pyridines. At ~275°, after the two pyridine moieties had been removed, the compound appeared to partially decompose with rapid loss of ~15% of the original weight. Above 335° the weight loss appeared to be continuous.

X-Ray Measurements. Powder patterns of Co(AA)₂(py)₂ and Ni(AA)₂(py)₂ showed these materials to be isomorphous. Powder photographs of Fe(AA)₂(py)₂ and Ni(AA)bipy also were observed using a Debye-Scherrer camera with copper radiation. The *d*-spacings observed for the powders are given in Table II.

Single crystal precession data were obtained on a crystal of Ni(AA)₂(py)₂ mounted in a thin capillary. A trial-and-error procedure was used to find the principal crystal axes.

Molecular Weights. Molecular weights on appropriate compounds were obtained using a Mechrolab Inc. Model 301A vapor pressure osmometer at 37°. The solvent used was benzene.

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Table II. *d*-Spacings of X-Ray Powder Patterns

Co(AA) ₂ (py) ₂		Ni(AA) ₂ (py) ₂		Fe(AA) ₂ (py) ₂		Ni(AA) ₂ bipy	
<i>d</i> , Å.	I ^a	<i>d</i> , Å.	I ^a	<i>d</i> , Å.	I ^a	<i>d</i> , Å.	I ^a
7.86	vs	7.86	vs	8.46	s	12.14	vs
7.44	m	7.42	m	7.72	m	9.09	m
6.56	s	6.58	s	6.60	s	8.04	s
6.34	m	6.30	m	6.08	m	6.89	m
5.46	w	5.44	w	5.03	w	6.63	w
4.86	w	4.86	w			5.97	s
4.35	mw	4.34	mw	4.39	w	5.11	w
4.19	m	4.17	m	4.19	mw	4.52	w
4.07	mw	4.08	mw	4.09	mw	4.21	w
3.93	s	3.91	s	3.95	s	4.19	w
3.48	ms	3.47	ms	3.66	ms	3.99	ms

^a Key: I, intensity; vs, very strong; s, strong; m, medium; w, weak.

Table III. Visible Spectra of Nickel(II) β -Ketoenolates

Complex	Frequency, $\bar{\nu} \times 10^{-3} \text{ cm.}^{-1}$
Ni(AA) ₂ (py) ₂	9.75(6.8), ^a 13.1(vw), 16.65(8.0)
Ni(AA) ₂ (bipy)	10.1 (10.6), 13.0(vw), 16.95(11.6)
Ni(AA) ₂ (cy) ₂	9.35(6.2), 13.2(vw), 16.2(7.0)
Ni(AA) ₂ (<i>i</i> -p) ₂	9.45(7.0), 13.2(vw), 16.0(8.1)
Ni(AA) ₂ (<i>n</i> -p) ₂	9.50(6.0), 13.2(vw), 16.15(6.9)
Ni(AA) ₂ (<i>n</i> -b) ₂	9.75(6.0), 13.15(vw), 16.1(6.9)
Ni(F ₂ AA) ₂ (cy) ₂	9.70(7.6), 13.2(vw), 16.45(8.1)
Ni(ϕ AA) ₂ (py) ₂	9.65(9.0), 13.1(vw), 16.65(9.0)
Ni(ϕ AA) ₂ (cy) ₂	9.65(5.9), 13.2(vw), 16.25(6.9)

^a Molar absorbance in parentheses, vw = very weak.

Table IV. Infrared Spectra of M(AA)₂(py)₂^a

Complex	Selected bands frequency, $\bar{\nu}$, cm. ⁻¹
Ni(AA) ₂ (py) ₂	433, 437, 571, 625
Co(AA) ₂ (py) ₂	422, 430, 556, 620
Fe(AA) ₂ (py) ₂	416, 425, 548, 619

^a M = Fe(II), Co(II), and Ni(II).

Structural Results

The Structure of Bis(2,4-pentanedione)bis(pyridine)-nickel(II). Precession photographs showed the crystal of Ni(AA)₂(py)₂ to be monoclinic, $a = 8.28$, $b = 9.67$, and $c = 14.65 \text{ \AA.}$; $\beta = 116^\circ 50'$; density calculated (based on two molecules per unit cell), 1.32 g. cm.^{-3} (found, $1.3 \pm 0.1 \text{ g. cm.}^{-3}$). Systematic absences were found for $0k0$, k odd, and $h0l$, l odd. Upper level photographs of $h1l$ and $h2l$ showed no systematic absences. From the systematic absences, the space group is uniquely determined as $P2_1/c$. With two molecules in the unit cell, the presence of a center of symmetry in Ni(AA)₂(py)₂ is required. Thus a *trans* arrangement of the pyridine ligands exists in the complex.

Since Co(AA)₂(py)₂ is isomorphous with Ni(AA)₂(py)₂, a *trans* structure also is implied. The lack of a 1:1 correspondence between the X-ray powder photographs of Fe(AA)₂(py)₂ and the cobalt(II) and nickel(II) complexes makes a conclusive decision regarding a *cis* or *trans* arrangement in this molecule impossible. While there are many similar features in the X-ray powder photographs, the absence of the 100 reflection expected near 7.4 \AA. and the 111 reflection near 6.3 \AA. along with the presence of lines at 8.46 and 6.08 \AA. shows the complexes are not isomorphous.

The required *cis* arrangement of the β -diketone units in Ni(AA)₂bipy precludes any possibility of isomorphism with the *trans* Co(AA)₂(py)₂ and Ni(AA)₂(py)₂ species.

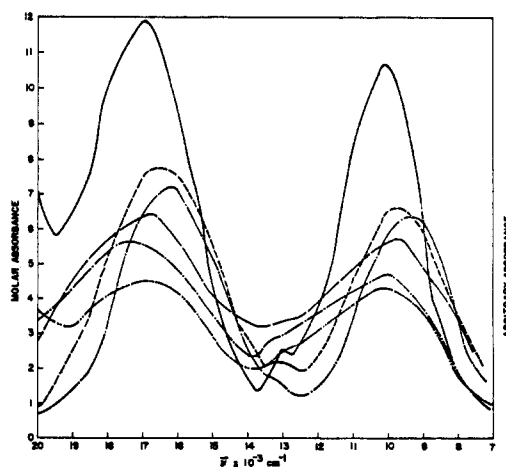


Figure 1. Solution and reflectance spectra of some base adducts of nickel(II) β -ketoenolates: —, Ni(AA)₂bipy (sol); ---, Ni(AA)₂(py)₂ (sol); - · - ·, Ni(AA)₂(cy)₂ (sol); — — —, Ni(AA)₂(cy)₂ (ref); - · - · - ·, Ni(AA)₂(py)₂ (ref); - · - · - ·, Ni(AA)₂bipy (ref).

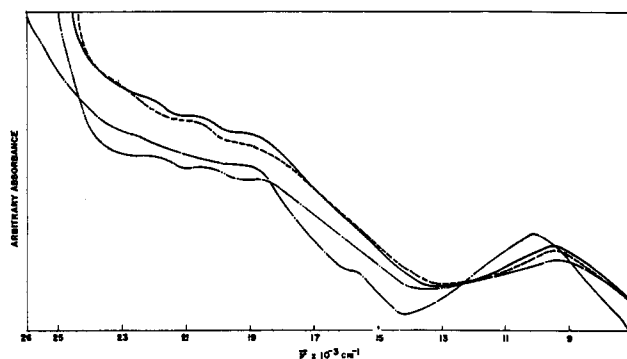


Figure 2. Reflectance spectra of some base adducts of cobalt(II) β -ketoenolates: —, Co(AA)₂(*n*-p)₂; ---, Co(AA)₂(*n*-b)₂; - · - ·, Co(AA)₂(py)₂; - · - · - ·, Co(AA)₂(cy)₂.

Attempts to determine the structure of Ni(AA)₂(py)₂ in benzene solution by comparing its dipole moment with that of Ni(AA)₂bipy failed owing to low solubilities and the equilibrium dissociation of Ni(AA)₂(py)₂. Molecular weight data for Ni(AA)₂bipy in benzene at $\sim 0.05 M$ suggested this material is not greatly dissociated. The value found was 421 while the calculated figure is 413. For a $\sim 0.05 M$ solution of Ni(AA)₂(py)₂, a molecular weight of 394 was found (calculated, 415).

Spectral Results

The solution spectra in benzene of Ni(AA)₂(py)₂ and Ni(AA)₂bipy from 7000 to $20,000 \text{ cm.}^{-1}$ show (Figure 1) two principal bands, at $\sim 17,000$ and $\sim 10,000 \text{ cm.}^{-1}$, of weak intensity with a very weak band near $\sim 13,000 \text{ cm.}^{-1}$. Similar bands (Table III) are observed with the other base adducts of nickel β -ketoenolates.

The solution spectra in benzene of the base adducts of cobalt(II) acetylacetonate are similar to the spectrum of Co(AA)₂(cy)₂ presented by Bertrand, *et al.*⁸ Reflectance spectra of several of the base adducts are given in Figure 2.

Infrared Spectra

The infrared spectra of M(AA)₂(py)₂ where M = Fe(II), Co(II), or Ni(II), are quite similar. The most notable feature appears to be the progressive shift of bands at ~ 625 , ~ 560 , ~ 460 , and $\sim 420 \text{ cm.}^{-1}$ to lower energy in the order Ni > Co > Fe (Table IV).

Infrared spectra of other base adduct complexes also were observed. No uncoordinated carbonyl frequencies were noticed for any of these complexes.

Discussion

Spectra of $\text{Ni}(\text{AA})_2\text{bipy}$ and $\text{Ni}(\text{AA})_2(\text{py})_2$ (with excess pyridine to prevent disproportionation⁹ to $[\text{Ni}(\text{AA})_2]_2\text{py}$ and py) suggested that the intensity of the d-d absorption bands in $\text{Ni}(\text{AA})_2(\text{py})_2$ might be lower than in the $\text{Ni}(\text{AA})_2\text{bipy}$ species (Figure 1) owing to a centrosymmetric (*trans*) configuration for the former compound while, of course, the bipyridine adduct must have a *cis* (noncentrosymmetric) configuration. Removing the center of symmetry in a complex allows mixing of functions which cannot mix in the centrosymmetric field, thereby supposedly increasing the intensity of d-d transitions. Unfortunately, the extent to which the intensity will increase cannot be estimated reliably since the intensity mechanism for the bands in centrosymmetric complexes is not yet well understood.²⁰ Presumably d-d transitions in centrosymmetric complexes are observed in the first place only because of vibrational or magnetic dipole interaction effects which are not readily calculated in molecules as complex as the ones studied here. Thus while the ${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$ (in O_h), $\sim 10,000 \text{ cm}^{-1}$, and ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$, $\sim 16,500 \text{ cm}^{-1}$, transitions apparently have a higher intensity in $\text{Ni}(\text{AA})_2\text{bipy}$ than in $\text{Ni}(\text{AA})_2(\text{py})_2$, the data are consistent with but do not require a *trans* arrangement in the latter complex. Since the position of the d-d bands in these complexes is the same in solution as in the diffuse reflectance spectra, it is reasonable to suggest, however, that the arrangement of the pyridines in $\text{Ni}(\text{AA})_2(\text{py})_2$ is for the most part the same in benzene as in the solid.

Single crystal X-ray data for $\text{Ni}(\text{AA})_2(\text{py})_2$ definitely show the complex²¹ to have a *trans* arrangement of pyridines. A similar configuration is required for the isomorphous crystalline $\text{Co}(\text{AA})_2(\text{py})_2$ and is likely for

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(21) It is noted that H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **7**, 1481 (1964), recently reported $\text{Ni}(\text{AA})_2(\text{H}_2\text{O})_2$ to have a *trans* configuration.

$\text{Fe}(\text{AA})_2(\text{py})_2$ from the similarity of the infrared spectra and the X-ray powder patterns, even though the latter compound is not strictly isomorphous with the others.

The solution spectra of all base adducts of the nickel(II) complexes studied in this work show a lower intensity (Table III) for the principal d-d transitions than is found in $\text{Ni}(\text{AA})_2\text{bipy}$. While a noncentrosymmetric arrangement of the six ligand atoms surrounding the nickel(II) is not definitely excluded, it is consistent to formulate these complexes also as being *trans*.

All attempts to cause the primary amine adducts of the nickel(II) β -ketoenolates studied to undergo a Schiff base rearrangement in nonpolar solvents were unsuccessful. Since a Schiff base rearrangement readily occurs in carbon tetrachloride between a metal salicylaldehyde and a primary amine, the possibility was considered that β -ketoenolato complexes do not react owing to steric protection of the ketonic carbon²² by the methyl groups. However, the inability of the adducts of $\text{Ni}(\phi\text{-Ac})_2$ to undergo a Schiff base rearrangement, even after 24 hr. of reflux, precludes steric inhibition as the cause for failure.

Since valence bond "resonance" structures are possible with metal salicylaldehydato complexes which are not permissible with β -ketoenolates, electronic differences may explain why base adducts of the latter compounds are stable to Schiff base "rearrangement" while adducts with the former materials are not. Studies currently in progress are designed to test this possibility with suitably substituted β -ketoenolato complexes.

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Silicon-Fluorine Chemistry. I. Silicon Difluoride and the Perfluorosilanes¹

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Silicon difluoride gas has been formed from silicon tetrafluoride and silicon at 1150° and low pressures. It has a lifetime at least 100 times greater than that of most carbenes. Condensation of the gas at low temperatures gives a plastic polymer $(\text{SiF}_2)_n$ which on heating generates all perfluorosilanes from SiF_4 through $\text{Si}_{14}\text{F}_{30}$. The new compounds Si_3F_8 and Si_4F_{10} have been isolated from the

distillate and characterized. The $(\text{SiF}_2)_n$ polymer reacts with aqueous HF to give 25-40% yields of silanes from SiH_4 through Si_8H_{14} .

Relatively little is known about silicon-fluorine compounds compared with other silicon halides or the silicon hydrides, probably because of the lack of convenient routes to the fluoro compounds. For ex-

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